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Absorption of Sound in Fluids*

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THE object of this paper is to review the absorption of sound in fluids. We shall be more interested in basic principles and concepts rather than detailed calculations which are both complicated and in many cases highly tentative. No attempt has been made to include all the complications in this field; rather we have tried to lay the foundation for a basic understanding of the underlying principles governing this field of physics.

The first two chapters give the basic theory. We have, here, reviewed the older, as well as the more recent theories. This is done to show the connection between the developments of the last century and present day developments. In doing this, the authors hope to show the unity of this field. In the later chapters a review of the data is made. All the data are not listed, but only those which appear to be reliable. On the whole, we have limited the data to the simpler phenomena.[1]

Chapter I. The Equation of State and Its Relation to Acoustic Propagation

1. INTRODUCTION—HYDRODYNAMIC EQUATIONS

Three equations are needed to study the propagation of an elastic disturbance in a fluid medium. Two of these, i.e., the equation of motion and the equation of continuity, are generally accepted in the classical form given by Euler. The third equation is the equation of state or the relation between stress and strain in the medium. It is vital for the study of the dissipative absorption of the disturbance. The variations in the theories of absorption can indeed be traced back to the equation of state used, though this is not always apparent. The equation of state which we shall talk about is not the general thermodynamic one but is along a specific path. Further, time appears in this equation. We shall call the relation between the excess pressure and the excess density the acoustical equation of state, sometimes omitting the word acoustical.

It will therefore be desirable to devote some time to developing various acoustical equations of state and examining their consequences. It should be emphasized at the outset that we must consider more than the static situation which presents no major difficulties but which leads to no absorption. The dynamic state equation, involving first and second time derivatives of the pressure and density, leads to the heart of the problem. Burgers (B36)[2] discusses various state equations for fluids, and we shall base some of our ideas on his development. However, his interest is confined to shearing while we shall introduce more general distortions. Though the expressions for velocity and absorption coefficients deduced by the following analysis are not for the most part new, we have attempted to present a more unified treatment.

A general infinitesimal distortion in a material medium, fluid or solid, can be described in terms of six strain components, which are defined as follows: (J3; p. 152)

$$e_{xx}=\frac{\partial q_x}{\partial x},\quad e_{yz}=e_{zy}=\frac{\partial q_y}{\partial z}+\frac{\partial q_z}{\partial y},\quad e_{yy}=\frac{\partial q_y}{\partial y},\quad e_{zx}=e_{xz}=\frac{\partial q_z}{\partial x}+\frac{\partial q_x}{\partial z},\quad e_{zz}=\frac{\partial q_z}{\partial z},\quad e_{xy}=e_{yx}=\frac{\partial q_x}{\partial y}+\frac{\partial q_y}{\partial x}\tag{1.1}$$[3]

where $\mathbf{q}=\mathbf{i}q_x+\mathbf{j}q_y+\mathbf{k}q_z$ is the displacement vector in the medium. The stress components are P_{xx}, P_{yy}, P_{zz}, $P_{xy}=P_{yx}$, $P_{xz}=P_{zx}$, $P_{yz}=P_{zy}$ which have their usual meaning. For isotropic bodies, to which we confine our attention, the general linear static relations between the stresses and the strains reduce to

$$\begin{aligned}P_{jj}&=\lambda_s\,\mathrm{div}\mathbf{q}+2\theta_s e_{jj},\\ P_{jk}&=\theta_s e_{jk},\end{aligned}\tag{1.2}$$

where λ_s and θ_s are the usual Lamé constants. λ_s and θ_s depend on the thermodynamic path taken by the e's The subscript implies that it is isentropic. If volume and total pressure are denoted by V and p, respectively, the bulk modulus, $-V(\partial p/\partial V)_s=K_s$, is related to λ_s and θ_s as follows:

$$K_s=\lambda_s+2\theta_s/3.\tag{1.3}$$

It should be emphasized that Eq. (1.2) implies static equilibrium and makes no allowance for the dynamical features of deformation. For this review we shall be interested only in those fluids which cannot support a shear; we therefore have $\theta_s=0$, leading finally to

$$P_{jj}=-p_e=K_s\,\mathrm{div}\,\mathbf{q}=-K_s s,\tag{1.4}$$

where p_e is the excess pressure and s is the condensation.

Joos shows that

$$s=-\mathrm{div}\,\mathbf{q}=-\delta V/V=\delta\rho/\rho,\tag{1.5}$$

where ρ is the density. We have indeed utilized the further fact that

$$P_{jj}=-p_e\quad\text{for}\quad j=1,2,3.$$[4]

In what follows p_e and ρ_e will always denote excess pressure and excess density in contrast to the total pressure p and the total density ρ. p_0 and ρ_0 are the equilibrium pressure and the equilibrium density.

Equation (1.4) is the conventional equation of state used in acoustics, and the first-order theory of elastic

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[1] Throughout this review, considerable use has been made of the compilations of data and references made by L. Bergmann (B15), C. Kittel (K8), H. O. Kneser (K11), W. T. Richards (R4), and D. Sette (S5). The authors wish to acknowledge the assistance provided by these writings in the preparation of the present paper.

[2] See bibliography at end of article.

[3] A list of symbols is given in Appendix I.

[4] $P_{jj}=-p_e$ follows from the theorem that states (L1; p. 1) "If the stress exerted across any small area situated at a point is wholly ormal, the pressure is the same in all directions." The sign appears because in the theory of elasticity a tension is positive while for fluids, a tension is considered as a negative pressure.

waves in fluids is based on it. However, it cannot account for the absorption of sound, and modification is necessary. This can be done in a large variety of ways, and indeed the successful modification seems to depend on the type of fluid in question, so that successful generalization has up to now eluded search.

We shall now consider certain changes that have been made in Eq. (1.4) to include processes which are affected by rates of change, i.e., the first and higher derivatives of the pressure or the volume with respect to time. The two principal types of modifications of historical interest are due to Maxwell and Stokes, respectively. In view of the confusion which seems to exist in published literature it will be worthwhile to review the early work before passing on to more recent developments.

2. MAXWELL'S EQUATION OF STATE

Maxwell (M5) modified Eq. (1.4) by incorporating a term depending on the integral $\int_0^t P_{ji} dt$. If we confine our attention once more to the case in which P_{jj} reduces to $-p_e$, his equation takes the form

$$\frac{\rho_e}{\rho_0}=\frac{1}{K_s}p_e+\frac{\gamma_s}{K_s}\int_0^t p_e dt, \tag{2.1}$$

where γ_s is a constant depending on the medium.

In differential form (2.1) becomes

$$\frac{dp_e}{dt}+\gamma_s p_e=K_s\frac{1}{\rho_0}\frac{d\rho_e}{dt}. \tag{2.2}$$

To understand its physical significance let us consider a special case. If ρ_e is held constant, i.e., constant strain, the equation reduces to

$$dp_e/dt=-\gamma_s p_e, \tag{2.3}$$

with a solution in the form

$$p_e=p_{e0}\exp[-\gamma_s t], \tag{2.4}$$

if p_{e0} is the initial excess pressure. If γ_s is positive, p_e decreases with time and in time $1/\gamma_s$ is reduced to $1/e$th of its initial value. The excess pressure is said to relax and to have a "relaxation time" of $1/\gamma_s$. The general equation (2.2) of which (2.3) is a special case appears in the paper of Maxwell (M5) in 1867 on the dynamical theory of gases. It is usually referred to as Maxwell's relaxation equation. A model whose behavior follows this equation has been suggested by J. M. Burgers (B36). It is illustrated in Fig. I-1a. The top element is a perfect spring obeying Hooke's law, whereas the lower element is a piston in a tank full of viscous liquid.[5] The two elements are here combined in series in the sense that the same force F acts on both. In the spring it produces a displacement x_1 directly proportional to the force, while in the piston it produces a velocity dx_2/dt directly proportional to the force. Since the total elongation of the spring is $x=x_1+x_2$, it follows that the differential equation for x is

$$\frac{dF}{dt}+(a/b)F=a\frac{dx}{dt}, \tag{2.5}$$

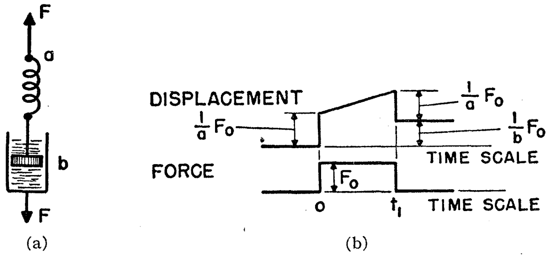
where $x_1=F/a$, $dx_2/dt=F/b$. This has the same mathematical form as Maxwell's equation (2.2) and becomes identical with it if we let $F=p_e$ and $x=\rho_e/\rho_0$. Then a becomes the bulk modulus K_s and $\gamma_s=a/b$.

The physical significance of (2.5) becomes apparent if F is a constant force which acts only for a finite time interval, i.e., if F is a *force pulse*. Thus we assume that

$$\begin{aligned} F&=0, && t<0\\ F&=F_0, && 0\leq t\leq t_1\\ F&=0, && t_1<t, \end{aligned} \tag{2.6}$$

a state of affairs illustrated in Fig. I-1b. We can integrate (2.5) in formal fashion to

$$x=F/a+1/b\cdot\int_0^t F dt. \tag{2.7}$$



(a) (b)

FIG. I-1 (a, b). Mechanical model corresponding to Maxwell's equation (after Burgers).

When $F=0$, $x=0$. At the instant F becomes F_0, x immediately rises to F_0/a. As t runs from 0 to t_1, x increases at the constant rate F_0/b and hence at any time t between 0 and t_1

$$x=F_0/a+(F_0/b)\cdot t. \tag{2.8}$$

When F is reduced to zero at $t=t_1$, the spring at once contracts to its original length but the piston retains the displacement it has gained and hence for $t>t_1$

$$x=(F_0/b)\cdot t_1.$$

The course of x as a function of t is also shown in Fig. I-1b.

Suppose now we shift our attention to the behavior of F with the passage of time as x changes in some presupposed fashion. A simple case is when the spring is initially displaced x_0 and x is maintained constant at this value. The solution of Eq. (2.5) is then

$$F=F_0\exp[-(a/b)\cdot t], \tag{2.9}$$

where F_0 is the initial value of F, i.e., $x_0 a$. We see that the force relaxes to zero in infinite time. The time it takes it to decrease to $1/e$th of the initial value can be

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[5] The reader will readily recognize the electrical circuit analog in which a capacitance C is arranged in parallel with a resistance R across a common electromotive force E.

described as a relaxation time, b/a. It is important to note that the relaxation described by Eqs. (2.2) or (2.5) is one of force (or excess pressure in the acoustical case) and not one of displacement (or condensation).

It will now be of interest to note the effect of assuming the Maxwell relaxational equation of state (2.2) on the propagation of a plane compressional wave in a fluid. For simplicity we confine our attention to harmonic propagation in the x direction with frequency $\omega/2\pi$ and write the equation of motion and the equation of continuity respectively in the form

$$\rho_0 \dot{u}_x = -\partial p_e/\partial x \tag{2.10}$$

$$\rho_0(\partial u_x/\partial x) = -\dot{\rho}_e, \tag{2.11}$$

where u_x is the particle velocity in the x direction. Here we shall use the dot to mean differentiation with respect to time. For this chapter it is not necessary to distinguish between the total and the partial time derivatives. The difference leads to higher order terms which become important only when second-order effects are considered. Usually in the equation of state the dot means total (hydrodynamic) derivatives. Actually, however, it is not an easy problem to distinguish between total and partial time derivatives in this case. In some sections it will be convenient to use partials and in others totals. When obtaining expressions for the velocity and the absorption only the partial time derivative is needed.

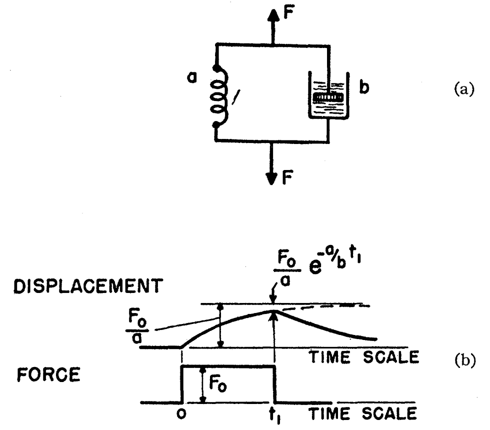

FIG. I-2 (a, b). Mechanical model corresponding to Stokes's equations (after Burgers).

It is now assumed that p_e, ρ_e, and u_x are propagated in accordance with the expressions

$$p_e = P_e \exp[i(\omega t - kx)], \tag{2.12}$$

$$u_x = U_x \exp[i(\omega t - kx)], \tag{2.13}$$

$$\rho_e = R_e \exp[i(\omega t - kx)], \tag{2.14}$$

where P_e, U_x, R_e are respectively complex amplitudes and k is a complex propagation parameter, i.e.,

$$\begin{aligned} k &= k_r + ik_i \\ &= k_r - i\alpha. \end{aligned} \tag{2.15}$$

α is the linear amplitude absorption coefficient of the wave. Substitution into Eqs. (2.2), (2.10), and (2.11) yields the relations

$$P_e(1 - i\gamma_s/\omega) - K_s R_e/\rho_0 = 0, \tag{2.16}$$

$$kP_e - \omega\rho_0 U_x = 0, \tag{2.17}$$

$$\omega R_e - k\rho_0 U_x = 0. \tag{2.18}$$

In order that these may have a nonvanishing solution, the determinant of the coefficients must vanish, yielding the equation

$$\omega^2(1 - i\gamma_s/\omega) = k^2 K_s/\rho_0. \tag{2.19}$$

In the majority of cases it is satisfactory to assume $|k_i| \ll |k_r|$. Equation (2.19) then yields at once for the velocity of propagation

$$c = \omega/k_r = (K_s/\rho_0)^{\frac{1}{2}}, \tag{2.20}$$

and for the absorption coefficient

$$\alpha = +\gamma_s/2c. \tag{2.21}$$

For ordinary fluids under standard conditions the dispersion of sound is very small, and hence the dependence of c on the frequency may probably be ignored in Eq. (2.21). If γ_s is a genuine constant of the medium, α will not depend on frequency. On this basis the sound absorption coefficient for a fluid resulting from Maxwell's equation is frequency independent. Since this contradicts experience we are tempted to conclude that this particular equation does not play a role in sound absorption in fluids. Actually this conclusion must be accepted as purely tentative since it is conceivable that a mechanism may be developed in which γ_s may turn out to be a function of frequency. So far it does not appear that this has been realized.

3. STOKES'S VISCOSITY EQUATION

An alternative modification of Eq. (1.4) is obtained by adding a term proportional to the rate of change of strain, giving for the linear case

$$p_e = \rho_e \frac{K_s}{\rho_0} + \frac{\zeta}{\rho_0}\dot{\rho}_e. \tag{3.1}$$

The association of ζ with viscosity of the medium is rather suggestive (see Sec. 14). We shall examine this with greater care later.

We have simplified the problem slightly by replacing a tensor by a scalar. Actually p_e is the pressure on a surface at right angles to the axis of wave propagation. This is the only pressure which enters into Eq. (2.10).

For the moment let us consider Burgers, (B36) model of this equation, shown in Fig. I-2a. Here the elements of the system in Fig. I-1 are combined in parallel. The forces on spring and piston are now respectively

$$F_1 = ax \quad \text{and} \quad F_2 = b\dot{x}, \tag{3.2}$$

since the displacement is the same for both elements.

The resultant force F is the sum of F_1 and F_2, the equation for the system becoming

$$F=ax+b\dot{x}, \tag{3.3}$$

which is identical with (3.1) if x becomes ρ_e/ρ_0, F becomes p_e, $K_s=a$, and $\zeta=b$.

To contrast (3.3) with (2.5) we consider once more the square force pulse (2.6). The general solution of (3.3) satisfying the boundary condition $x=x_0$ for $t=0$ is (S12; p. 284)

$$x=\frac{1}{b}e^{-(a/b)t}\int_0^t F(t')e^{(a/b)t'}dt'+x_0e^{-(a/b)t}. \tag{3.4}$$

If for simplicity we set $x_0=0$, the solutions fitting the square pulse become

$$\begin{aligned} x&=\frac{1}{a}F_0[1-e^{-a/b\cdot t}], \quad 0\leqq t\leqq t_1,\\ x&=\frac{1}{a}F_0[1-e^{-a/b\cdot t_1}]\cdot e^{-a/b\cdot(t-t_1)}, \quad t_1\leqq t. \end{aligned} \tag{3.5}$$

The time b/a is called the retardation time by Burgers. It may in fact be considered a kind of relaxation time. The behavior of x as a function of t is shown graphically in Fig. I-2b.

We next examine the use of Stokes's equation for a plane harmonic compressional wave. We again employ the expressions (2.12), (2.13), and (2.14) and substitute into (3.1), (2.10), and (2.11), respectively. Equations (2.17) and (2.18) remain unchanged but (2.16) is now replaced by

$$p_e=(R_e/\rho_0)(K_s+i\omega\zeta). \tag{3.6}$$

Application of the standard condition on the secular determinant yields the relation

$$\omega^2=(k^2/\rho_0)(K_s+i\omega\zeta). \tag{3.7}$$

We call K_s/ζ the angular frequency ω_v and then have

$$k^2=\frac{\rho_0\omega^2}{\zeta}\cdot\frac{\omega_v-i\omega}{\omega_v^2+\omega^2}. \tag{3.8}$$

Utilizing (2.15) and separating into real and imaginary parts results in

$$\begin{aligned} k_r^2-k_i^2&=\frac{\rho_0}{\zeta}\frac{\omega^2\omega_v}{\omega_v^2+\omega^2},\\ 2k_rk_i&=-\frac{\rho_0}{\zeta}\frac{\omega^3}{\omega_v^2+\omega^2}. \end{aligned} \tag{3.9}$$

The solutions are:

$$k_r^2=\frac{1}{2}\frac{\rho_0}{\zeta}\frac{\omega^2}{\omega_v^2+\omega^2}\omega_v\left\{1\pm\left(1+\frac{\omega^2}{\omega_v^2}\right)^{\frac{1}{2}}\right\} \tag{3.10}$$

$$k_i^2=-\frac{1}{2}\frac{\rho_0}{\zeta}\frac{\omega^2}{\omega_v^2+\omega^2}\omega_v\left\{1\mp\left(1+\frac{\omega^2}{\omega_v^2}\right)^{\frac{1}{2}}\right\}. \tag{3.11}$$

The signs are selected so that the original two equations are satisfied. Since it is desirable that the k's be real, we select the upper signs. If the lower signs are selected, k_i and k_r merely reverse their roles. The phase velocity in general is given by

$$c^2=\frac{\omega^2}{k_r^2}=\frac{2\zeta}{\rho_0\omega_v}(\omega_v^2+\omega^2)\frac{1}{1+(1+\omega^2/\omega_v^2)^{\frac{1}{2}}}. \tag{3.12}$$

The solutions can also be put in the following forms, (L14)

$$k_r=\frac{\omega^2/\omega_v}{(2\zeta\omega_v/\rho_0)^{\frac{1}{2}}}\{(1+\omega^2/\omega_v^2)[(1+\omega^2/\omega_v^2)^{\frac{1}{2}}-1]\}^{-\frac{1}{2}}, \tag{3.13}$$

$$\alpha=\left(\frac{\rho_0}{2\zeta\omega_v}\right)^{\frac{1}{2}}\omega\left[\frac{(1+\omega^2/\omega_v^2)^{\frac{1}{2}}-1}{(1+\omega^2/\omega_v^2)}\right]^{\frac{1}{2}}. \tag{3.14}$$

All the above expressions are exact. If we are interested in low frequencies for which $\omega\ll\omega_v$, the expressions for velocity and absorption reduce respectively to the following approximations:

$$c=\left(\frac{K_s}{\rho_0}\right)^{\frac{1}{2}}\cdot(1+\tfrac{3}{8}\omega^2/\omega_v^2), \tag{3.15}$$

$$\alpha=\frac{\omega^2\zeta}{2\rho_0c_0^3}\cdot(1-\tfrac{5}{8}\omega^2/\omega_v^2), \tag{3.16}$$

where $c_0=(K_s/\rho_0)^{\frac{1}{2}}$ and is approximately equal to c. In this range the absorption coefficient is very nearly proportional to the square of the frequency, and to the same approximation the phase velocity is constant and equal to c_0. If $\zeta=4\eta/3$ Eq. (3.16) takes the usual form for the viscous absorption. η is the shear viscosity coefficient.

On the other hand if $\omega\gg\omega_v$, the expressions (3.11) and (3.12) yield

$$c=c_0(2\omega/\omega_v)^{\frac{1}{2}}, \tag{3.17}$$

$$\alpha=\frac{1}{c_0}\left(\frac{\omega\omega_v}{2}\right)^{\frac{1}{2}}=\left(\frac{\rho_0}{2\zeta}\omega\right)^{\frac{1}{2}}. \tag{3.18}$$

Note that here $k_r=-k_i$. Both velocity and absorption coefficient vary with the square root of the frequency.

Experience indicates that in most fluid media, neither the Maxwell equation (2.1) nor the Stokes equation (3.1) is sufficient by itself to account for acoustic absorption. A combination of the two might be expected to be more successful. This has been shown to be true in the case of water by the theory of L. H. Hall (H1). A derivation of Hall's combined Maxwell-Stokes equation (assumed by him but not derived) will be presented in Sec. 7 where a more general viewpoint will be discussed. Moreover, we must not neglect a review of heat conduction as an origin of sound absorption.

4. EQUATION OF STATE FOR HEAT CONDUCTION

It was pointed out by Kirchhoff (K3) in 1868 that it is not proper to consider the effect of viscosity of a fluid on sound absorption without also accounting for the comparable effect of heat conduction. Applying the first law of thermodynamics we have for the rate at which heat enters the fluid

$$\frac{\partial Q}{\partial t}=\frac{\partial U}{\partial t}+p\frac{\partial V}{\partial t}, \tag{4.1}$$

where U is the total internal energy, Q is the heat, and V is the molar volume.

In this and the following sections we shall be forced to use a considerable number of thermodynamic equations. For the convenience of the reader, we have listed them in Appendix II. All the relations can be proven in an elementary manner as shown in many texts of thermodynamics, e.g., Slater (S8). We shall assume that the process is quasistatic so that thermodynamics can be used. For the one-dimensional case, using Eq. (A-10) of Appendix II, we can write Eq. (4.1) for one mole as

$$\frac{M\kappa}{\rho_0}\frac{\partial^2 T}{\partial x^2}=\frac{C_v}{K\beta}\cdot\frac{\partial p}{\partial t}+\frac{C_p}{V\beta}\cdot\frac{\partial V}{\partial t}, \tag{4.2}$$

in which K is the isothermal bulk modulus, κ the coefficient of thermal conductivity, β the coefficient of volume expansion at constant pressure, and C_p and C_v the usual molar heats. M is the molecular weight. Equation (4.2) thus serves as an equivalent equation of state or equation for time rate of change of state under the influence of heat conduction. We may rewrite (4.2) in the form

$$\frac{\partial p}{\partial t}-\frac{K_s}{\rho_0}\frac{\partial \rho}{\partial t}=\frac{M\kappa}{\rho_0}\cdot\frac{\beta K}{C_v}\cdot\frac{\partial^2 T}{\partial x^2}, \tag{4.3}$$

where $K_s=(C_p/C_v)K=\gamma K$. We eliminate T with the help of (A-8), and obtain,

$$\frac{\partial p}{\partial t}-\frac{K_s}{\rho_0}\cdot\frac{\partial \rho}{\partial t}=\frac{M\kappa}{\rho_0}\left[\frac{1}{C_v}\cdot\frac{\partial^2 p}{\partial x^2}-\frac{K}{\rho_0 C_v}\cdot\frac{\partial^2 \rho}{\partial x^2}\right]. \tag{4.4}$$

On the right-hand side we have thrown away the nonlinear term involving $(\partial\rho/\partial x)^2$ since the changes in p and ρ involved in the passage of the sound wave are very small. In Eq. (4.4) we may replace p and ρ by p_e and ρ_e respectively in order to make comparison with the earlier Eqs. (2.2) and (3.1).

We now examine the use of (4.4) for a plane wave of the form (2.12) to (2.14). Equations (2.17) and (2.18) remain unchanged but (2.16) becomes

$$\left(i\omega+\frac{M\kappa k^2}{\rho_0 C_v}\right)P_e-\left(\frac{i\omega K_s}{\rho_0}+\frac{M\kappa K k^2}{\rho_0^2 C_v}\right)R_e=0. \tag{4.5}$$

Combined with (2.17) and (2.18) this yields

$$k^2\left(\frac{i\omega K_s}{\rho_0}+\frac{M\kappa}{\rho_0^2}\frac{Kk^2}{C_v}\right)-\left(i\omega+\frac{M\kappa k^2}{\rho_0 C_v}\right)\omega^2=0. \tag{4.6}$$

This may be rewritten in the form

$$k^2=\omega^2\frac{\rho_0}{K}\cdot\frac{C_v-iWk^2}{C_p-iWk^2}, \tag{4.7}$$

where $W=M\kappa/\rho_0\omega$. This leads to a quadratic for the complex k^2. Fortunately, inspection shows that $k_r\gg k_i$. It will be sufficient, therefore, to replace k^2 in the term Wk^2 by $k_r^2=\omega^2/c^2$. Moreover on the left-hand side of (4.7) k^2 becomes to a good approximation $k_r^2+2ik_rk_i$. This is true as long as we neglect viscosity; when considering viscosity and heat conduction are combined, this approximation is questionable. Hence by equating real and imaginary parts of (4.7) we arrive at

$$\alpha=-k_i=\frac{1}{2}\frac{c}{c_0^2}(\gamma-1)\frac{\omega_c}{\omega_c^2+\omega^2}\omega^2 \tag{4.8a}$$

for the absorption coefficient. We have here set

$$\omega_c^2=\frac{C_p^2\rho_0^2c^4}{M^2\kappa^2} \tag{4.9}$$

which appears as the square of a kind of relaxation frequency, itself a function of frequency through c.

For comparison with other mechanisms we write (4.8a) as

$$\alpha=\frac{1}{2}\frac{c}{c_0^2}\frac{K_s^0-K_s^\infty}{K_s^\infty}\frac{\omega_c}{\omega_c^2+\omega^2}\omega^2, \tag{4.8b}$$

where in the case of heat conduction

$$K_s^0=\frac{C_p}{C_v}K$$

$$K_s^\infty=K.$$

Similarly to the indicated approximation, the phase velocity is

$$c^2=\frac{1}{\rho_0}\frac{\omega_c^2+\omega^2}{(\omega_c^2/K_s^0)+(\omega^2/K_s^\infty)}. \tag{4.10}$$

The fundamental difference between this mechanism and those described in subsequent sections should be clearly noted, even though the frequency dependence of k_r and α turns out to be approximately the same. The space gradient appears here while in the later equations of state only derivatives with respect to time appear.

5. EQUATION OF STATE FOR HEAT RADIATION

For the sake of completeness we present a review of the effect of heat radiation on sound transmission, following the general method of the preceding sections. We again use the first law in the form (4.1), but now

$$\frac{\partial Q}{\partial t}=-qC_v(T-T_0), \tag{5.1}$$

where we are following Stokes (S18) in using effectively Newton's law of cooling for the rate of radiation from the region traversed by the sound where the temperature is T to the surrounding fluid at temperature T_0.

If we put $V=M/\rho$, Eq. (4.2) now assumes the form, after differentiation with respect to the time

$$\frac{C_v}{K\beta}\frac{\partial^2 p}{\partial t^2}-\frac{MC_p}{\beta V\rho_0^2}\frac{\partial^2\rho}{\partial t^2}=-qC_v\frac{\partial T}{\partial t}. \tag{5.2}$$

Once more we write, using (A-8)

$$\dot{T}=\frac{1}{K\beta}\dot{p}-\frac{M}{\beta V\rho_0^2}\dot{\rho}, \tag{5.3}$$

and find for (5.2) after some reduction

$$\frac{\partial^2 p}{\partial t^2}+q\frac{\partial p}{\partial t}-\frac{K_s}{\rho_0}\frac{\partial^2\rho}{\partial t^2}-\frac{qK}{\rho_0}\frac{\partial\rho}{\partial t}=0. \tag{5.4}$$

Integrating with respect to the time, setting the constant of integration equal to zero and using excess pressure and density p_e and ρ_e, respectively, we arrive at

$$\frac{\dot{\rho}_e}{\rho_0}-\frac{1}{K_s^\infty}\dot{p}_e+\omega_r\left(\frac{\rho_e}{\rho_0}-\frac{1}{K_s^0}p_e\right)=0. \tag{5.5}$$

where $K_s^\infty=\gamma K$, $K_s^0=K$, and $\omega_r=q/\gamma$. The K's defined here do not agree with those defined in the last section. They really denote the bulk moduli for a slow or a fast process. In the case of radiation, the fast bulk modulus is adiabatic while in heat conduction, the fast bulk modulus is isothermal. In the case of thermal or structural relaxation, we have a fast and a slow adiabatic bulk modulus, and this is the reason for the notation of K_s^0 and K_s^∞. The model for this acoustical equation of state will be considered in the next section.

For a plane wave of the form (2.12) to (2.14) we obtain in place of (2.16) and (4.5)

$$(\omega-i\omega_r)\frac{R_e}{\rho_0}-\left(\frac{\omega}{K_s^\infty}-\frac{i\omega_r}{K_s^0}\right)P_e=0. \tag{5.6}$$

The secular equation connecting ω and k now becomes

$$\omega^2\rho_0\left(\frac{\omega}{K_s^\infty}-\frac{i\omega_r}{K_s^0}\right)=k^2(\omega-i\omega_r). \tag{5.7}$$

On the presumption that $|k_r|\gg|k_i|$ we can solve for k_r and k_i and get for the absorption coefficient

$$\alpha=\frac{1}{2}\frac{c}{c_0^2}\frac{\omega^2\omega_r}{\omega^2+\omega_r^2}\frac{K_s^\infty-K_s^0}{K_s^\infty}, \tag{5.8}$$

while the phase velocity (and associated dispersion law) is given by

$$c^2=\frac{1}{\rho_0}\frac{\omega^2+\omega_r^2}{(\omega^2/K_s^\infty)+(\omega_r^2/K_s^0)}. \tag{5.9}$$

At low frequency

$$c_0^2=K_s^0/\rho_0, \tag{5.10a}$$

while at high frequency

$$c_\infty^2=K_s^\infty/\rho_0. \tag{5.10b}$$

Stokes and Rayleigh made only empirical estimates of the magnitude of q, but it would seem possible to study it independently by applying radiation theory. One attempt is made here as a suggestion. Further work in evaluating q is certainly required. From the Stefan-Boltzmann law applied to a sphere of surface area A, with the temperature difference $T-T_0$ between the surface and the surrounding environment, we have

$$4A\sigma T_0^3(T-T_0)=qC_v(T-T_0), \tag{5.11}$$

where σ is the Stefan-Boltzmann constant. Let us apply this to a sphere of diameter $\lambda/2$, which we assume to be at the same temperature. Then

$$q=\frac{48T_0^3\sigma,}{\rho_0 c_v\lambda} \tag{5.12}$$

where c_v is the specific heat capacity per gram. From radiation measurements

$$\sigma=5.673\times10^{-5}\text{ erg/sec cm}^2\ {}^\circ\text{A}^4. \tag{5.13}$$

An estimate of q may readily be obtained, for example, argon, where

$$\rho_0=1.784\times10^{-3}\text{ g/cm}^3\quad\text{at}\quad T_0=273^\circ\text{A},$$
$$c_v=0.075\text{ cal/g }^\circ\text{A}\quad\text{and}\quad c=3.08\times10^4\text{ cm/sec}.$$

The result is $q=1.34\times10^{10}$ sec^{-1}, at 1 mc. The value of q in (5.12) is directly proportional to frequency, whereas Rayleigh (referred to by Rocard (R9)) estimated it would be independent of frequency. At low frequencies the value given by (5.12) is not far out of line with Rocard's estimate. It is not intended that our result should be taken seriously, but it does reinforce the conclusion that radiation absorption plays little role in gases, except possibly at very low pressures or very high temperatures.

6. EQUATION OF STATE FOR THERMAL RELAXATION

A. The Method of Irreversible Thermodynamics

In the analysis of Herzfeld and Rice (H10) sound absorption in a fluid is attributed to the lag in the adjustment between external and internal degrees of freedom of the constituent molecules during the passage of the sound wave. These authors apply thermodynamics to a nonequilibrium problem. The nonequilibrium effects are so important that one cannot even approximate them by equilibrium thermodynamics. In essence, their treatment is one of the first treatments of irreversible thermodynamics. The summarization presented here is in a form permitting close comparison with the analysis of the preceding sections.

The total energy U per mole is divided into a part U^e referring to the translational energy of the molecules as a whole and a part U^i characterizing the relative motions of the constituent parts of the molecules. For convenience two corresponding temperatures T^e and T^i are associated with these energies, respectively. These temperatures assume partial equilibrium of the internal and external energies. These postulates undoubtedly need further investigation. U^i is a function of T^i only. It is assumed that the only way in which U^i may change is through a change in the temperature T^e. We may express the above assumption analytically in the form

$$\dot{T}^i=(T^e-T^i)/\tau. \tag{6.1}$$

The quantity τ plays the role of a relaxation time.

The process by which the energy of the system is changed is assumed to be adiabatic. Under these conditions the first principle of thermodynamics takes the form

$$dU^e+dU^i+pdV=0, \tag{6.2}$$

where we are dealing with fluids in which it is possible to assign unambiguous meaning to p and V. Now from the definition of specific heat at constant volume

$$dU^i=C_v{}^i dT^i, \tag{6.3}$$

where $C_v{}^i$ is the internal molar heat at constant volume. Moreover, from Appendix II (Eq. A-11) we can write at once, so far as the external energy is concerned,

$$dU^e+pdV=C_v{}^e dT^e+T^eK\beta dV=0. \tag{6.4}$$

The use of this equation assumes that conventional thermodynamics holds for the relations among U^e, T^e, V, and p, i.e., for a given U^e and T^e, p and V are known. Equation (6.2) then becomes, if we apply time variation,

$$C_v{}^i\dot{T}^i+C_v{}^e\dot{T}^e+T^eK\beta\dot{V}=0. \tag{6.5}$$

To eliminate T^i from (6.5) we transform it to the form

$$C_v{}^i\left(\frac{d^2T^i}{dt^2}+\frac{1}{\tau}\frac{dT^i}{dt}\right)+C_v{}^e\left(\frac{d^2T^e}{dt^2}+\frac{1}{\tau}\frac{dT^e}{dt}\right)$$
$$+T^e\beta K\left(\frac{d^2V}{dt^2}+\frac{1}{\tau}\frac{dV}{dt}\right)+\beta K\frac{dT^e}{dt}\frac{dV}{dt}=0. \tag{6.6}$$

By using (6.1) and (6.5), we obtain

$$C_v{}^e\frac{d^2T^e}{dt^2}+K\beta T^e\frac{d^2V}{dt^2}+\frac{1}{\tau}(C_v{}^i+C_v{}^e)\frac{dT^e}{dt}$$
$$+K\beta\frac{dV}{dt}\left(\frac{dT^e}{dt}+\frac{1}{\tau}T^e\right)=0. \tag{6.7}$$

To compare this equation of state with those for viscosity, heat conduction, and heat radiation, we must express it in terms of the changes in p and V. For this purpose we must use the thermodynamic Eq. (A-8) of Appendix II and write

$$\dot{T}^e=\dot{p}/K\beta+\dot{V}/V\beta, \tag{6.8}$$

$$\frac{d^2T^e}{dt^2}=\frac{1}{K\beta}\frac{d^2p}{dt^2}+\frac{1}{V\beta}\frac{d^2V}{dt^2}-\frac{1}{V^2\beta}\left(\frac{dV}{dt}\right)^2. \tag{6.9}$$

On substitution back into (6.7) there results

$$(C_v{}^e/K\beta)\frac{d^2p}{dt^2}+[(C_v{}^i+C_v{}^e)/\tau K\beta]\frac{dp}{dt}+\left(\frac{dp}{dt}\right)\left(\frac{dV}{dt}\right)$$
$$+(C_v{}^e/\beta V+T^eK\beta)\frac{d^2V}{dt^2}+\left(\frac{K}{V}-\frac{C_v{}^e}{\beta V^2}\right)\left(\frac{dV}{dt}\right)^2$$
$$+[(C_v{}^e+C_v{}^i)/\tau\beta V+T^e\beta K/\tau]\frac{dV}{dt}=0. \tag{6.10}$$

Writing $\dot{V}=-M/\rho_0{}^2.\ \dot{\rho}_e$, etc. and neglecting the nonlinear terms as small compared with the rest, we finally secure the equation of state in the form (with $\dot{p}=\dot{p}_e$, as before)

$$C_v{}^e\frac{dp_e{}^2}{dt^2}+\frac{C_v{}^t}{\tau}\frac{dp_e}{dt}-\frac{K}{\rho_0}(C_v{}^e+T^e\beta^2KV)\frac{d^2\rho_e}{dt^2}$$
$$-\left(\frac{K}{\rho_0\tau}\right)(C_v{}^t+T^e\beta^2KV)\frac{d\rho_e}{dt}=0. \tag{6.11}$$

We have here set $C_v{}^t=C_v{}^e+C_v{}^i$ the total specific heat at constant volume for a slow process where $T^e=T^i$. Examination of the order of magnitude of the various terms in (6.10) for harmonic time dependence with angular frequency ω indicates the validity of the neglect of the nonlinear terms. We now find it convenient to make the following definitions:

$$K_s{}^0=K(1+T^e\beta^2KV/C_v{}^t), \tag{6.12}$$

and

$$K_s{}^\infty=K(1+T^e\beta^2KV/C_v{}^e). \tag{6.13}$$

A very fast process does not affect U^i and hence $C_v{}^e$ is the net specific heat. Thus (6.13) comes naturally from the general definition of the adiabatic bulk modulus (A-14)(Z2; p. 229). For a slow process $T^i=T^e$ and the net specific heat is $C_v{}^t$, hence again (6.12). This transforms (6.11)

$$\frac{\dot{\rho}_e}{\rho_0}-\frac{\dot{p}_e}{K_s{}^\infty}+\omega_0\left(\frac{\rho_e}{\rho_0}-\frac{p_e}{K_s{}^0}\right)=0. \tag{6.14}$$

We have also defined

$$\omega_0=\frac{1}{\tau}(C_p{}^t/C_p{}^e). \tag{6.15}$$

A comparison with Eq. (5.5) shows that the acoustical equation of state for thermal relaxation is identical in form with the one for heat radiation.

A mechanical model governed by an equation of the form (6.14) has been suggested by Frenkel (F5; p. 208) and is shown schematically in Fig. I-3a (compare Figs. I-1a and I-2a).

Since (6.14) is identical in form with (5.5) the equations for the velocity and the absorption in this case are the same as before, i.e., (5.9) and (5.8) with ω_0 replacing ω_r. The meaning of the K's have changed. The equation for α is given by

$$\begin{aligned}\alpha&=\frac{1}{2}\frac{c}{c_0^2}\omega^2\frac{\omega_0}{\omega^2+\omega_0^2}\frac{K_s^\infty-K_s^0}{K_s^\infty}\\&=\frac{1}{2}\frac{c}{c_0^2}\omega^2\frac{\omega_0}{\omega^2+\omega_0^2}\left(\frac{C_p^t-C_v^t}{C_v^tC_p^e}\right)C^i.\end{aligned}\tag{6.16}$$

To obtain the last form we have used Eqs. (A-12) and (A-13) as well as the fact that on this model β and K are independent of frequency.

7. EQUATION OF STATE FOR A GENERAL INTERNAL LAG

A. The Method of Statistical Thermodynamics

In this section we shall employ a statistical model to derive an equation of state for a fluid for use in sound transmission calculations. This method has been used by Kneser (K11) and others but will be presented here in somewhat more general form, applicable to both gases and liquids (M2). We assume that the pressure changes associated with dilatations of the fluid are connected with changes in the energy states of the constituent molecules. Transitions between the various states are governed by finite probabilities, leading to finite relaxation times and hence to absorption and dispersion of acoustical radiation as suggested by the earlier parts of this review.

To make the model more concrete, several cases will now be examined in detail. First, consider gaseous hydrogen (F1; p. 84), which is complicated by the fact that two types exist, *ortho* and *para*. We shall, for simplicity, confine our attention to only one type, say *para*. A vibrational excitation requires high energy, so that below several thousand degrees, the average fraction of molecules in the excited vibrational state is very small. A useful concept is the characteristic temperature θ, i.e., $\Delta\epsilon/k'$, where $\Delta\epsilon$ is the energy difference of the transition, while k' is Boltzmann's constant. The characteristic temperature of vibration for hydrogen is about 6100°A.

The rotational levels are therefore the ones of interest here. The energy levels are given approximately by (H8).

$$Bc_lh(J+1)J,$$

where B is a constant which can be determined optically, c_l is the velocity of light and h is Planck's constant. In general, $J=0$, 1, 2, 3. However, for *para*hydrogen, the values of J are 0, 2, 4. The statistical weight of the levels is $2J+1$. Since $B=61\ \text{cm}^{-1}$ for H_2, we find that the fraction of molecules in state $J=0$ is 0.28, in state $J=2$ is 0.58 and in state $J=4$ is 0.13 for $T=600$°A. Therefore, in this case one must consider at least the three lower states. The two-state model to be developed in this section is not completely adequate for H_2. Rhodes (R3) has considered a more elaborate model which applies here.

In other molecules θ_{rot} is much lower than in hydrogen. One may assume that it is possible to assign a statistical weight to each vibrational level. Using the above information as to the weight of the rotational level and the energy distribution, the statistical weight of a vibrational level[6] is

$$\sum(2J+1)\exp[-Bc_lhJ(J+1)/k'T].$$

B has only a slight dependence on the vibrational state. There is no reason to believe that a high rotational level of a lower vibrational level has less energy than a lower rotational level of an excited vibrational band. In general, as a matter of fact, this is not the case (H8; p. 107). By the proper definition of a vibrational statistical weight given above, however, we may consider the vibrational molecule as having evenly spaced energy levels. The characteristic temperatures for vibration range from about 6100°A for H_2 to 310°A for I_2 (S8; p. 142). For I_2 at 620°A, the fraction of molecules in the ground state, 1st, 2nd, 3rd, and 4th excited states are 0.39, 0.24, 0.14, 0.09, and 0.05; and we cannot expect a two-state model to apply in this case. θ_v for Cl_2 is 810°A so that at 300°A the fractions of states in the lowest and first excited state are 0.94 and 0.06. This gas can therefore be approximated by a two-state model. For vibrational states, Landau and Teller have been able to work out a model for an n-state gas (L3).

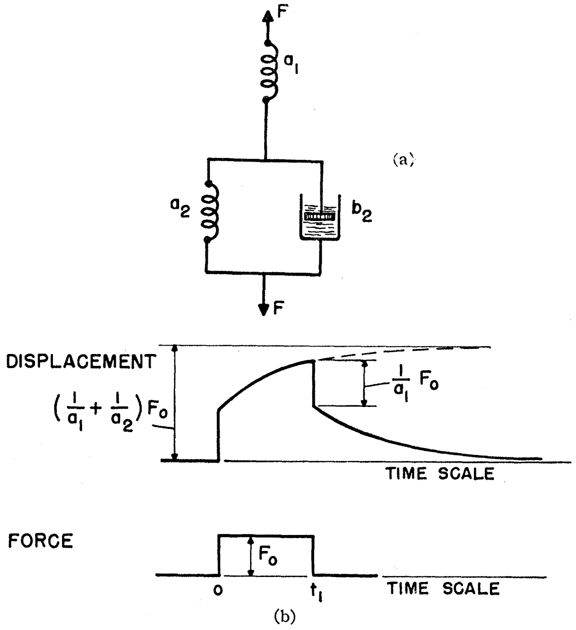

FIG. I-3 (a, b). Mechanical model corresponding to the relaxational equation (after Frenkel).

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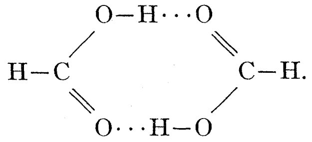
[6] For simplicity, we shall not define the summation over J. This depends on the type of molecules considered.

The lumping of the rotational levels into one is permissible only as long as there is a rapid readjustment of these levels. One might expect that as one goes up in frequency the readjustment in the vibrational levels will lag and produce an absorption region. Later, at higher frequency, another region of absorption will appear due to lags caused by readjustments of the rotational levels. Such effects have recently been observed by Zmuda[7] in N_2 at room temperature.

One may also consider the problem of dissociation of a diatomic gas for which there exists two states. One would expect that the general theory to be presented here can be adapted to this case, though the details have not been carried through. Another method has been used by Einstein (E4) and by Luck (L18) to solve this problem. (See also the paper of Kneser and Gauler (K10).)

At present we are unable to give as complete a physical theory of a liquid as of a gas or of a crystalline solid. For our purposes it will be necessary to distinguish between a normal liquid and an associated liquid. A normal liquid is a monomer. The basic unit is the individual atom; crudely speaking, the liquid is a dense imperfect gas. One would expect that the internal vibrations of normal liquids would be nearly the same as in the gaseous phase (we ignore the possibility of lower frequency interlattice modes), and such is the case for many fluids.

The associated liquid (H9; p. 534) on the other hand, has a group of molecules which bond together to form multi-molecular groups, or polymers. Formic acid in the liquid state shows a vibrational bond at 3080 cm^{-1}, whereas at high temperatures in the gaseous phase, the characteristic vibration is at 3570 cm^{-1} due to a vibration between H and O atoms. This has been interpreted by assuming that at lower temperatures molecular groups appear, such as



The new bond arises because of links characterized by H···O. Such binding is known as a hydrogen bond because it usually requires a hydrogen atom. The actual binding may take the form of rings or chains. It is to be stressed that the idea of the association is not based on the simple physical illustration but is required from basic chemical considerations. Associated liquids appear when there are hydroxyl (OH) and amino (NH_2) units (W4; p. 46).

A dilatation may cause two effects on the fluid. It may in the normal fluid cause transitions within the molecules, or in the associated liquid it may cause changes in the association. Both Hall (H1) and Ghosh (G2) assume that part of the absorption in water is due to the rearrangements of the polymer structure. In ice, each molecule has four nearest neighbors. In water, the number of nearest neighbors ranges from three to two. Hall postulates two states, of which the lower is more ice-like, while in the upper state the molecules are more random. We cannot, at present, make the picture more specific nor show that there are just two states, nor define just what the unit, which will be loosely called a molecule, is. Even the detailed Hall and Ghosh calculations do not answer these important questions.

In acetic acid, Lamb and Pinkerton (L2) suggested that part of the absorption is due to the breaking down of a dimer to a monomer. A difficulty of the concept is that there is no independent way of finding out just what the process is. It takes 16 kcal/mole at 25°C to dissociate the double molecule in the gaseous phase, but the acoustical processes suggest a much smaller value. We are, therefore, forced to conclude that here, as in the case of water, the exact model of what is broken up remains unclear. Equally uncertain is the model suggested by Liebermann (L12) for the absorption in sea water. This model is connected with the dissociation of $MgSO_4$ and will be discussed further in Sec. 30 below.

Liebermann has been able to get a numerical check of some of the *para*meters, but his method appears to be semi-empirical. For instance, Liebermann (L10) previously had been able to explain the absorption in sea water ignoring the presence of $MgSO_4$ altogether. This suggests that a more fundamental investigation of the problem should be made.

In spite of the many limitations of the two-state model, we shall develop it, since it shows the nature of the problem and is the most general model (known to the authors) using statistical thermodynamics, which would apply to gases and liquids.

For the sake of simplicity we suppose the two states of each molecule are alike: an unexcited state has an energy E_1 (per mole) and an excited state has an energy E_2 (per mole). It is assumed that the process of excitation alters the intermolecular forces so as to distort the molecular structure and change the average volume per molecule. The average volumes per molecule in the unexcited and excited states are denoted by v_1 and v_2, respectively, and the corresponding values per mole for V_1 and V_2. The change in volume V_2-V_1 may be expected to play a greater role in liquids than in gases.[8]

The instantaneous numbers of molecules per mole in the unexcited and excited states are N_1, and N_2, respectively, and $N_1+N_2=N$, where N is the total number of molecules per mole. It is assumed that for equilibrium the distribution is canonical and therefore at temperature T the average number of molecules in

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[7] A. J. Zmuda, private communication and (Z3).

[8] The association of v_1 and v_2 with states may seem artificial. Actually we shall only be interested in V_2-V_1 associated with the increase or decrease of the population in state 2.

state 1 is

$$N_1^0=Cw_1\exp[-E_1/RT],\qquad(7.1)$$

where w_1 is a weighting factor, C is a constant, and $R=k'N$, where k' is Boltzmann's constant. Similarly

$$N_2^0=Cw_2\exp[-E_2/RT].\qquad(7.2)$$

We find it convenient to assume $w_1=w_2$. Let A_{12} be the transition probability from state 1 to state 2 (i.e., the average number of transitions per second per molecule) and A_{21} the corresponding probability from state 2 to state 1. The fundamental equation governing transitions between the two states is

$$\dot{N}_1=N_2A_{21}-N_1A_{12}.\qquad(7.3)$$

For equilibrium, $\dot{N}_1=0$, and therefore

$$A_{12}^0/A_{21}^0=N_2^0/N_1^0=\exp[\Delta E/RT],\qquad(7.4)$$

where $\Delta E=E_1-E_2$.

Now the dilatation produces a disturbance which alters N_1, N_2, A_{21}, A_{12} as well as $\dot{N}_1$. Using ΔN_1, etc., to denote the change in value, by neglecting higher order terms we have from (7.3)

$$\Delta\dot{N}_1=N_2^0\Delta A_{21}+A_{21}^0\Delta N_2-N_1^0\Delta A_{12}-A_{12}^0\Delta N_1.\qquad(7.5)$$

From (7.4) and the fact that $\Delta N_1=-\Delta N_2$, it finally follows that

$$\Delta\dot{N}_1=-(A_{12}^0+A_{21}^0)\Delta N_1-N_2^0A_{21}^0\Delta W\qquad(7.6)$$

with

$$W=\Delta E/RT.\qquad(7.7)$$

We now set for convenience

$$A_{12}^0+A_{21}^0=1/\tau,\qquad(7.8)$$

where τ has the dimensions of time and indeed will be referred to as the relaxation time for the particular mechanism. W is treated as a function of the independent macroscopic variables p and T. We select T and p as the macroscopic independent variables—T, because of its unique position in statistics and p because it seems related to the external forces on a molecule. This selection is not unique and it might be advisable to use T and V as has been done by Mandelstam and Leontovich (M1). Since the process we are dealing with is irreversible, the selection of independent variables has an important effect on the detailed development of the theory. However, the final results should be independent of the choice of macroscopic variables. The existence of macroscopic variables assumes an intermolecular equilibrium.

We can now write (7.6) in the form

$$\Delta\dot{N}_1=-\Delta N_1/\tau-N_2^0A_{21}^0\left[\frac{\partial(W)}{\partial p}\Delta p+\frac{\partial(W)}{\partial T}\Delta T\right].\qquad(7.9)$$

Next we employ (7.4) again to replace $N_2^0A_{21}^0$ with a more convenient expression and obtain for (7.9)[9]

$$\Delta\dot{N}_1=-\Delta N_1/\tau-(N/\tau)(2+A_{21}^0/A_{12}^0+A_{12}^0/A_{21}^0)^{-1}\times\left[\frac{\partial(W)}{\partial p}\Delta p+\frac{\partial(W)}{\partial T}\Delta T\right].\qquad(7.10)$$

Finally it will be convenient to set

$$N_1=N_1^0+n,\quad N_2=N_2^0-n,\qquad(7.11)$$

so that

$$\dot{N}_1=\dot{n},\text{ etc.,}$$

and to write

$$2+A_{21}^0/A_{12}^0+A_{12}^0/A_{21}^0=2(1+\cosh W).\qquad(7.12)$$

Equation (7.10) can then be given the form of the differential equation

$$\tau\frac{d^2n}{dt^2}+\frac{dn}{dt}=B_p\frac{dp}{dt}+B_T\frac{dT}{dt},\qquad(7.13)$$

if we set

$$B_p=-\frac{N}{2(1+\cosh W)}\cdot\frac{\partial W}{\partial p},\qquad B_T=-\frac{N}{2(1+\cosh W)}\cdot\frac{\partial W}{\partial T}.\qquad(7.14)$$

It is necessary to introduce thermodynamical considerations, in particular the first law. For an adiabatic process this will now appear in the form

$$\Delta U^e+\Delta U^i+p\Delta V^e+p\Delta V^i=0.\qquad(7.15)$$

The total energy of the system is

$$U=U^e+U^i,\qquad(7.16)$$

where U^e is the "external" energy or that associated with the motion of the molecules as a whole, while U^i is "internal" energy or that associated with intramolecular energy states, such as those referred to at the beginning of this section. It is necessary to introduce two types of volume, V^e relating to the *macroscopic* volume per mole, and ΔV^i denoting effective change in volume per mole associated with the transition from state 1 to state 2 or vice versa. Thus

$$\Delta V^i=(v_1-v_2)n=\Delta v\cdot n,\qquad(7.17)$$

and

$$\Delta U^i=(\epsilon_1-\epsilon_2)n=\Delta\epsilon\cdot n,\qquad(7.18)$$

where $\epsilon_1=E_1/N$ and $\epsilon_2=E_2/N$. Introducing time derivatives and continuing to treat T and p as the independent variables, we can express the content of the

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[9] Equation (7.10) follows from (7.9) since

$$\frac{N_2^0A_{21}^0}{A_{12}^0+A_{21}^0}=\frac{N_1^0A_{12}^0}{A_{12}^0+A_{21}^0}=\frac{N_1^0A_{21}^0}{A_{21}^0+(A_{21}^0)^2/A_{12}^0}$$

$$=\frac{N_1^0A_{21}^0+N_2^0A_{21}^0}{A_{12}^0+A_{21}^0+A_{21}^0+(A_{21}^0)^2/A_{12}^0}=\frac{N}{2+(A_{21}^0/A_{12}^0)+(A_{12}^0/A_{21}^0)}.$$

first law for an adiabatic process in the form

$$\left[\left(\frac{\partial U^e}{\partial T}\right)_p+p\left(\frac{\partial V^e}{\partial T}\right)_p\right]\dot{T}$$

$$+\left[\left(\frac{\partial U^e}{\partial p}\right)_T+p\left(\frac{\partial V^e}{\partial p}\right)_T\right]\dot{p}+\dot{n}(\Delta\epsilon+p\Delta v)=0. \quad (7.19)$$

For the sake of simplicity we shall write $V^e=V$ in what follows, since V^i enters only through the term in Δv. From the principles of thermodynamics we have

$$(\partial U^e/\partial T)_p+p(\partial V/\partial T)_p=C_p{}^e, \quad (7.20)$$

the external molar heat capacity at constant pressure. The usual (reversible) relations are assumed to hold between U^e, T, and p. dU^e does not include effects due to changes in population. The use of the second law Eq. (A-9) yields

$$dU^e=[C_p{}^e-pV\beta^e]dT-[TV\beta^e-pV/K^e]dp, \quad (7.21)$$

so that

$$\left(\frac{\partial U^e}{\partial p}\right)_T=-T\beta^eV+pV/K^e, \quad (7.22)$$

and from Eq. (A-2),

$$p(\partial V/\partial p)_T=-pV/K^e. \quad (7.23)$$

In Eqs. (7.22) and (7.23)

$$K^e=-\frac{1}{(1/V)(\partial V/\partial p)_T}, \quad (7.24)$$

which is the external isothermal bulk modulus, and

$$\beta^e=(1/V)(\partial V/\partial T)_p, \quad (7.25)$$

which is the external coefficient of expansion at constant pressure.

If we use (7.20), (7.22), and (7.23) we can put (7.19) in the form

$$C_p{}^e\dot{T}-T\beta^eV\dot{p}+\dot{n}[\Delta\epsilon+p\Delta v]=0. \quad (7.26)$$

For convenience later we differentiate (7.26) with respect to time, neglecting nonlinear terms like $\dot{p}\dot{T}$ and $\dot{p}\dot{n}$ as small compared with $(d^2p/dt^2)T$, etc., multiply by τ and add to (7.26). The somewhat artificial result is

$$C_p{}^e\left[\frac{dT}{dt}+\tau\frac{d^2T}{dt^2}\right]-T\beta^eV\left[\frac{dp}{dt}+\tau\frac{d^2p}{dt^2}\right]$$

$$+[\Delta\epsilon+p\Delta v]\left[\frac{dn}{dt}+\tau\frac{d^2n}{dt^2}\right]=0. \quad (7.27)$$

This immediately enables us to use (7.13) and hence to write (7.27) in the form

$$C_p{}^e\frac{d^2T}{dt^2}-T\beta^eV\frac{d^2p}{dt^2}$$

$$+\frac{1}{\tau}\left\{[C_p{}^e+B_T\Delta\epsilon+B_Tp\Delta v]\frac{dT}{dt}\right.$$

$$\left.-[T\beta^eV-B_p\Delta\epsilon-B_pp\Delta v]\frac{dp}{dt}\right\}=0. \quad (7.28)$$

We may simplify (7.28) by making the following definitions:

$$C_p{}^i=\Delta\epsilon B_T+B_Tp\Delta v, \quad (7.29)$$

$$\beta^i=-(1/TV)(\Delta\epsilon B_p+p\Delta vB_p), \quad (7.30)$$

$$1/K^i=-(1/V)\Delta vB_p. \quad (7.31)$$

These definitions require justification.

For a slow process, the first two terms of (7.28) will be very small. If the process is slow enough, we may also assume that the process is quasistatic. This means that the right-hand side of (7.3) is always very small. Such a process can be considered reversible as well as adiabatic and, therefore, from thermodynamic arguments it follows that

$$C_p{}^t\dot{T}-T\beta^tV\dot{p}=0. \quad (7.32)$$

The superscript refers to the total, or static, values of C_p and β. Definitions (7.29) and (7.30) assure that

$$C_p{}^t=C_p{}^i+C_p{}^e \quad (7.33)$$

and

$$\beta^t=\beta^e+\beta^i. \quad (7.34)$$

We see from (7.32), (7.33), and (7.34) that $C_p{}^i$ is the additional molar heat and β^i is the additional thermal coefficient of expansion. This justifies definitions (7.29) and (7.30).

Another way to satisfy ourselves about these definitions is to return to (7.10) and consider equilibrium states, i.e., $\dot{n}=0$. Then, with the help of (7.10) and (7.14), we have

$$n=B_p\Delta p+B_t\Delta T, \quad (7.35)$$

where by (7.11) n is the change in population. The specific heat at constant pressure is defined as

$$C_p=(\partial U/\partial T)_p+p(\partial V/\partial T)_p. \quad (7.36)$$

By (7.35) it follows that the shift in the populations per unit temperature at constant pressure is B_T; hence, the first term on the right of Eq. (7.29) corresponds to the first term on the right of Eq. (7.36). Likewise the same holds for the second term.

We can also justify this by referring to the customary definition of a complex specific heat. This definition is (K11, R4, and E6).

$$C^{\text{eff}}=C^i/(1+i\omega\tau), \quad (7.37)$$

based on the assumption that the disturbance is harmonic. C^{eff} is the effective value of the specific heat of vibration (or rotation) at frequency $\omega/2\pi$. From (7.13) it follows that

$$(\partial n/\partial T)_p = B_T/(1+i\omega\tau). \tag{7.38}$$

The complex number in (7.37) and (7.38) implies a phase lag between changes of T and n. The effective internal specific heat is

$$\begin{aligned} C_p^{\text{eff}} &= (\Delta\epsilon + p\Delta v)(\partial n/\partial T)_p \\ &= \{\Delta\epsilon B_T + p\Delta v B_T\}/(1+i\omega\tau). \end{aligned} \tag{7.39}$$

Comparison of (7.37) and (7.39) provides justification of (7.29). Similar justification can be made for (7.30) and (7.31). The usual theory does not distinguish between C_p^i and C_v^i. Our system is more general, and these quantities are not equivalent. C_p^i is the more basic (to our theory) because our independent variables are p and T.

An alternative definition of β^i is possible. Following (7.39) we may write that

$$\beta^{\text{eff}} = (\Delta v/V)(\partial n/\partial T)_p = \Delta v B_T/[V(1+i\omega\tau)], \tag{7.40}$$

or

$$\beta^i = \Delta v B_T/V. \tag{7.41}$$

One can also obtain (7.41) by arguments similar to those connected with Eqs. (7.35) and (7.36). Comparing (7.41) and (7.30), one must conclude that

$$\frac{\Delta v}{V} B_T = -\frac{1}{TV}(\Delta\epsilon B_p + p\Delta v B_p). \tag{7.42}$$

It seems that this requirement must be imposed on this model if it is to obey reversible thermodynamics at frequencies far below and far above $1/\tau$.

Using the definitions just made, we can simplify (7.28) to the form

$$C_p^e \frac{d^2T}{dt^2} - T\beta^e V \frac{dp^2}{dt^2} + \frac{1}{\tau}\left\{ C_p^t \frac{dT}{dt} - TV\beta^t \frac{dp}{dt} \right\} = 0. \tag{7.43}$$

This is the adiabatic equation of state for our model. To compare it with the previous equations of state we must eliminate T. Further, we have four variables—u_x, ρ_e, p_e, and T—but only three equations, (2.10), (2.11), and (7.43). The density is not an independent variable in the usual sense, and V is not a function of T and p alone, but also depends on time. To find dV which will depend on dp and dT as well as on the change in volume produced by changes in the population, we use (7.17), (7.24), and (7.25). The result is

$$dV = -(V/K^e)dp + V\beta^e dT + \Delta v \cdot n. \tag{7.44}$$

If we obtain $\dot{V}$ and d^2V/dt^2 from (7.44), divide the former by τ and add to the latter, we obtain (neglecting as usual terms like $\dot{V}\dot{p}/K^e$, etc.)

$$\begin{aligned} \frac{d^2V}{dt^2} + \frac{1}{\tau}\frac{dV}{dt} &= -\frac{V}{K^e}\left(\frac{d^2p}{dt^2} + \frac{1}{\tau}\frac{dp}{dt}\right) \\ &\quad + V\beta^e\left(\frac{d^2T}{dt^2} + \frac{1}{\tau}\frac{dT}{dt}\right) + \frac{1}{\tau}\Delta v\left(B_p\frac{dp}{dt} + B_T\frac{dT}{dt}\right), \end{aligned} \tag{7.45}$$

in which (7.13) accounts for the last term on the right. Utilizing (7.31) and (7.41), and transposing a few terms, we can rewrite (7.45) as

$$\begin{aligned} &\beta^e\frac{d^2T}{dt^2} + \beta^t\frac{1}{\tau}\frac{dT}{dt} \\ &\quad = \frac{1}{K^e}\frac{d^2p}{dt^2} + \frac{1}{\tau K^t}\frac{dp}{dt} + \frac{1}{V}\left(\frac{d^2V}{dt^2} + \frac{1}{\tau}\frac{dV}{dt}\right), \end{aligned} \tag{7.46}$$

where

$$1/K^t = 1/K^e + 1/K^i. \tag{7.47}$$

We now differentiate with respect to time, keeping only first-order terms, and multiply through by β^e. We then multiply (7.43) by β^t/τ and add the two. The result is:

$$\begin{aligned} &C_p^e\left(\beta^e\frac{d^3T}{dt^3} + \frac{1}{\tau}\beta^t\frac{d^2T}{dt^2}\right) - T\beta^e V\left(\beta^e\frac{d^3p}{dt^3} + \frac{1}{\tau}\beta^t\frac{d^2p}{dt^2}\right) \\ &\qquad + \frac{1}{\tau}C_p^t\left(\beta^e\frac{d^2T}{dt^2} + \frac{1}{\tau}\beta^t\frac{dT}{dt}\right) \\ &\qquad\qquad - \frac{TV\beta^t}{\tau}\left(\beta^e\frac{d^2p}{dt^2} + \frac{1}{\tau}\beta^t\frac{dp}{dt}\right) = 0. \end{aligned} \tag{7.48}$$

Changing $\dot{v}/v$ to $-\dot{\rho}_e/\rho_0$ and using (7.46), the general acoustical equation of state is obtained:

$$\begin{aligned} &\frac{C_v^e}{K^e}\frac{d^2p_e}{dt^2} - \frac{C_p^e}{\rho_0}\frac{d^2\rho_e}{dt^2} + \frac{1}{\tau}\left\{\frac{C_p^e}{K^t} + \frac{C_p^t}{K^e} - 2TV\beta^e\beta^t\right\}\frac{dp_e}{dt} \\ &\quad - \frac{1}{\tau}(C_p^e + C_p^t)\frac{1}{\rho_0}\frac{d\rho_e}{dt} + \frac{1}{\tau^2}\frac{C_v^t}{K^t}p_e - \frac{1}{\tau^2}C_p^t\frac{\rho_e}{\rho_0} = 0.^{10} \end{aligned} \tag{7.49}$$

We have used Eq. (A-13) to define C_v^e and C_v^t:

$$C_v^t = C_p^t - TV(\beta^t)^2K^t \tag{7.50}$$

$$C_v^e = C_p^e - TV(\beta^e)^2K^e. \tag{7.51}$$

Further, the definition is made

$$C_v^i = C_v^t - C_v^e. \tag{7.52}$$

We shall not attempt to examine the acoustical behavior of this equation of state in this general form. Three simplifying assumptions will now be made and discussed. They are:

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[10] On integrating, we assume an appropriate constant, so that $\rho_e = \rho - \rho_0$ and $p_e = p - p_0$ appear.

(a) Thermal Relaxation:

$$B_T \neq 0,$$
$$\Delta\epsilon \neq 0,$$

but

$$B_p = \Delta v = 0.$$

(b) Structural Relaxation:

$$B_p \neq 0,$$
$$\Delta v \neq 0,$$

but

$$B_T = 0.$$

(c) General Linear Case:

Here the assumption is made that the products of any of the terms defined by (7.29), (7.30), and (7.31) are negligible.[11]

(a) *Thermal Relaxation*

This case applies to gases one would expect $\Delta\epsilon$ to be independent of temperature, and W is a function of T only. Since we neglect Δv, $\beta^i = 0$, and $\beta^e = \beta^t$. Further, $K^e = K^t = K$. From these relations and (A-13), it follows that $C_p^t - C_p^e = C_v^t - C_v^e = C_p^i = C_v^i$. Consequently, in Eq. (7.49) the coefficient of $\dot{p}_e$ becomes

$$\frac{C_p^e}{K} + \frac{C_p^t}{K} - 2TV\beta^e\beta^t = \frac{C_v^e}{K} + \frac{C_v^t}{K}, \tag{7.53}$$

and we may write (7.49) in the following operational form:

$$\left(\frac{d}{dt} + \frac{1}{\tau}\right)\left\{\frac{C_v^e}{K}\dot{p}_e + \frac{C_v^t}{\tau K}p_e - C_p^e\frac{\dot{\rho}_e}{\rho_0} - \frac{C_p^t}{\tau}\frac{\rho_e}{\rho_0}\right\} = 0. \tag{7.54}$$

The operator on the left does not equal zero; hence

$$\frac{\dot{\rho}_e}{\rho_0} - \frac{1}{K_s^\infty}\dot{p}_e + \omega_0\left(\frac{\rho_e}{\rho_0} - \frac{1}{K_s^0}p_e\right) = 0. \qquad (7.55)^{12}$$

Here we have defined $\omega_0 = C_p^t/\tau C_p^e$, which is the relaxation frequency for this process. Since K is frequency independent for this case, K_s^0 and K_s^∞ are given (6.12) and (6.13). Equation (7.55) is equivalent to the acoustical equation of state obtained by the method of Herzfeld and Rice, i.e., Eq. (6.14).

(b) *Structural Relaxation*

Here, $B_T = 0$. Hence $C_p^i = 0$ and from (7.41) $\beta^i = 0$. Now from (7.30) we see that

$$\Delta\epsilon B_p + p\Delta v B_p = 0, \tag{7.56}$$

or

$$\Delta\epsilon + p\Delta v = 0. \tag{7.57}$$

Equation (7.57) looks like a statement of the first law for an adiabatic process and may not be an unreasonable requirement. Since $C_p^i = 0$, $C_p^e = C_p^t C_p$. From (7.52) we know that $C_v^i \neq 0$. Equation (7.49) takes the form

$$\left(\frac{d}{dt} + \frac{1}{\tau}\right)\left\{\frac{C_v^e}{K^e}\dot{p}_e - C_p\frac{\dot{\rho}_e}{\rho_0} + \frac{1}{\tau}\frac{C_v^t}{K^t}p_e - \frac{C_p}{\tau}\frac{\rho_e}{\rho_0}\right\} = 0. \tag{7.58}$$

Thus the acoustical equation of state for structural relaxation is

$$\frac{\dot{\rho}_e}{\rho_0} - \frac{1}{K_s^\infty}\dot{p}_e + \omega_0\left(\frac{1}{\rho_0}\rho_e - \frac{1}{K_s^0}p_e\right) = 0, \qquad (7.59)^{13}$$

where

$$K_s^\infty = K^e C_p / C_v^e \tag{7.60}$$

$$K_s^0 = K^t C_p / C_v^t \tag{7.61}$$

$$\omega_0 = 1/\tau. \tag{7.62}$$

Though Eq. (7.59) is formally similar to (7.55), K_s^0, K_s^∞, and ω_0 have different definitions.

As far as the authors know, Eqs. (7.55) and (7.59) first appear in a paper by Frenkel and Obraztsov (F4). The connection shown here between the equation of state and the statistical model, as well as the linear case, is more recent (M2). It was also derived in an independent manner by Hoff Lu (H13) (see Sec. 8). Equation (7.59) was used by Hall in his calculation of the absorption of sound in water. Since, in this case, C_p is nearly equal to C_v, and C^i is very small, Hall neglected the adiabatic correction. For many liquids $C_p - C_v$ is not small, and consideration of these corrections may be of value.

From Eq. (7.47) we note that $K^t < K^e$ and because of (7.50) and (7.51) $C_v^e < C_v^t$, and hence $K_s^e > K_s^t$, an assumption made by Hall. Since Eq. (7.59) is identical in form with (5.5) the absorption and velocity dispersion are given by (5.8) and (5.9) except that the K's and the ω_0 have different meaning.

(c) *General Linear Case*

We shall make the special assumption that quotients and products such as (C_p^i/K^i) and $C_p^i C_v^i$ are small. It is to be stressed that this is not generally true. Dutta (D4) has calculated C^i (he assumed thermal relaxation, where $C_p^i = C_v^i$) for several liquids. His calculations are based on Einstein's specific heat equation (S8; p. 142), the internal vibration of the molecules having been obtained from observed Raman spectra. Under the assumption that $(C_p^i)^2$, etc., are small, the third term on

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[11] One might assume a relaxation process where $B_T \neq 0$ and $\Delta v \neq 0$, but $\Delta\epsilon = B_p = 0$. Such a model leads to a contradiction because of (7.30) and (7.41). The same holds if one assumes that $B_p \neq 0$ and $\Delta\epsilon \neq 0$, but $B_T = \Delta v = 0$. These are thermodynamic limitations on the model.

[12] One may obtain (7.54) more simply by returning to (7.44) since, for this case, $V = V(p, T)$.

[13] This equation can also be obtained without a double differentiation by returning to (7.44).

the left of (7.49) can be transformed as follows:

$$\frac{C_p{}^e}{K^t}+\frac{C_p{}^t}{K^e}-2TV\beta^e\beta^t=\frac{C_p{}^e}{K^e}+\frac{C_p{}^t}{K^t}-TV(\beta^e)^2$$

$$-TV(\beta^t)^2=\frac{C_v{}^e}{K^e}+\frac{C_v{}^t}{K^t}, \quad (7.63)$$

which gives for the general linear equation of state

$$\frac{C_v{}^e}{K^e}\frac{d^2p_e}{dt^2}-\frac{C_p{}^e}{\rho_0}\frac{d^2\rho_e}{dt^2}$$

$$+\frac{1}{\tau}\left\{\left(\frac{C_v{}^e}{K^e}+\frac{C_v{}^t}{K^t}\right)\frac{dp_e}{dt}-(C_p{}^e+C_p{}^t)\frac{1}{\rho_0}\frac{d\rho_e}{dt}\right\}$$

$$+\frac{1}{\tau^2}\left\{\frac{C_v{}^t}{K^t}p_e-C_p{}^t\frac{\rho_e}{\rho_0}\right\}=0. \quad (7.64)$$

The difference between this case and the two previous cases for a harmonic disturbance is in the region where $\omega\sim 1/\tau$. At low frequencies there is a well-defined set of constants, $C_v{}^t$, K^t, and $C_p{}^t$ as there are at high frequency, $C_v{}^e$, K^e, and $C_p{}^e$.

There is no essential difference in the behavior of an acoustic wave in this case, however. Equations (2.17) and (2.18) still apply but (2.16) is replaced by

$$\left(i\omega+\frac{1}{\tau}\right)\left[i\omega\frac{C_v{}^e}{K^e}P_e+\frac{C_v{}^t}{\tau K^t}P_e-i\omega\frac{C_p{}^e}{\rho_0}R_e-\frac{1}{\tau}\frac{C_p{}^t}{\rho_0}R_e\right]=0. \quad (7.65)$$

To obtain (7.65) we have used (2.12) and (2.14). Since the expression in the first parenthesis does not effect the evaluation of k, (7.65) can be replaced by

$$\left(\frac{i\omega}{K_s{}^\infty}+\frac{\omega_0}{K_s{}^0}\right)P_e-(i\omega+\omega_0)\frac{R_e}{\rho_0}=0, \quad (7.66)$$

where in this case

$$K_s{}^\infty=K^e(C_p{}^e/C_v{}^e), \quad (7.67)$$

$$K_s{}^0=K^t(C_p{}^t/C_v{}^t) \quad (7.68)$$

and

$$\omega_0=C_p{}^t/\tau C_p{}^e. \quad (7.69)$$

These relations are generalizations of (6.12), (6.13), and (6.15) as well as (7.60) and (7.62). The absorption and dispersion are again given by (5.8) and (5.9) with appropriate interpretations of the constants. An alternative expression for α is

$$\alpha=\frac{1}{2}\frac{\omega^2\omega_0}{\omega^2+\omega_0{}^2}\frac{c}{c_0{}^2}\left[K^e\left(\frac{1}{K^t}-\frac{1}{K^e}\right)+\frac{C_v{}^i}{C_v{}^e}-\frac{C_p{}^i}{C_p{}^e}\right]. \quad (7.70)$$

One cannot but raise the question as to what happens if $K_s{}^\infty\leqslant K_s{}^0$. In this system, energy will be taken from the body and transformed into mechanical work, a clear violation of the second law. One must, therefore, conclude that $K_s{}^\infty\geqslant K_s{}^0$ from this argument. We shall not examine the definitions of K^i, $C_p{}^i$, and β^i to show this is true, and, as far as we know, it has not been attempted. It could be done but would require some thermostatistical arguments along the line followed by Hall.

B. Section 7 Appendix

One may object to Eq. (7.3) on the grounds that it is too specialized and that many possible reactions cannot be characterized that simply. Actually the form of (7.3) is not a fundamental assumption to the equations derived in this section. Let us examine a more complex case. Consider the reaction

$$2Y_1\rightleftarrows Y_2. \quad (7.71)$$

Let us assume that the backward reaction is of first order with respect to Y_2 while the forward reaction is of second order with respect to Y_1, i.e.,

$$\dot{n}_2=k_{12}n_1{}^2-k_{21}n_2, \quad (7.72)$$

where the n_i's are the numbers of particles per unit volume. We may rewrite (7.72) in the form

$$\dot{N}_2=A_{12}N_1{}^2-A_{21}N_2, \quad (7.73)$$

where

$$A_{21}=k_{21}, \quad (7.74a)$$

$$A_{12}=k_{12}/V. \quad (7.74b)$$

V is the volume which contains a mole of atoms some of which are associated and some of which are disassociated. V, of course, is a function of the equilibrium thermodynamic variables.

We introduce the Helmholtz free energy for a system which obeys classical statistics. It can be defined as follows (F1; p. 67)

$$F=-RT\{\ln f-\ln N+1\}. \quad (7.75)$$

Here,

$f=$ the partition function, namely

$=\sum_i \exp\{-E_i/RT\}$.

The free energy for a mole of associated molecules can be defined as

$$F_2=-RT\{\ln f_2-\ln N+1\}, \quad (7.76)$$

where for f_2 the sum extends only over the associated states. From (7.76) it follows that

$$f_2=\frac{N}{e}\exp(-F_2/RT). \quad (7.77)$$

Likewise for a mole of disassociated atoms

$$f_1=\frac{N}{e}\exp(-F_1/RT). \quad (7.78)$$

By standard statistics (F1; p. 158) we know that

$$N_1^2/N_2=f_1^2/f_2=\exp\{\Delta F/RT+\delta\} \tag{7.79}$$

where

$$\Delta F=F_2-2F_1,$$
$$e^\delta=N/e, \text{ a constant.}$$

Returning to (7.73), we consider a small perturbation from the equilibrium value

$$\Delta\dot{N}_2=(A_{12}{}^0+\Delta A_{12})(N_1{}^0+\Delta N_1)^2 -(A_{21}{}^0+\Delta A_{21})(N_2{}^0+\Delta N_2). \tag{7.80}$$

At equilibrium

$$\frac{(N_1{}^0)^2}{N_2{}^0}=\frac{A_{21}{}^0}{A_{12}{}^0}=\exp(\Delta F^0/RT+\delta) \tag{7.81}$$

and

$$\Delta A_{21}=\frac{(N_1{}^0)^2}{N_2{}^0}\Delta A_{12}+A^0{}_{12}\frac{(N_1{}^0)^2}{N_2{}^0}\Delta W, \tag{7.82}$$

where ΔW is the variation of $\Delta F/RT$. Since $\Delta N_2=-\frac{1}{2}\Delta N_1$ (7.80) gives, with the help of (7.81) and (7.82),

$$\begin{aligned}\Delta\dot{N}_2&=-(A_{21}{}^0+4A_{12}{}^0N_1{}^0)\Delta N_2-A_{21}{}^0N_2{}^0\Delta W\\&=-(1/\tau)\Delta N_2-A_{12}{}^0(N_1{}^0)^2\Delta W,\end{aligned} \tag{7.83}$$

where now

$$1/\tau=(A_{21}{}^0+4N_1{}^0A_{12}{}^0). \tag{7.84}$$

Consider two extreme cases. For a substance which is almost completely dissociated, i.e., $N_1 \gg N_2$,

$$A_{12}{}^0(N_1{}^0)^2=A_{21}{}^0N_2{}^0,$$

$$A_{12}{}^0N_1{}^0 \ll A_{21}{}^0 \tag{7.85}$$

and

$$1/\tau \approx A_{21}{}^0 \tag{7.86}$$

which means that $1/\tau$ is independent of concentration. If, however, $N_1 \ll N_2$—the substance is almost completely associated, then

$$A_{12}{}^0N_1{}^0 \gg A_{21}{}^0. \tag{7.87}$$

Here

$$1/\tau \approx 4A_{12}{}^0N_1{}^0=4k_{12}n_1{}^0. \tag{7.88}$$

That is $1/\tau$ is proportional to the concentration of nonassociated molecules. Equation (7.83) is identical in form with Eq. (7.6) if we consider (7.8). (7.84) suggests that $1/\tau$ may be a complicated function of the thermodynamic variables and may depend on the concentration. It would seem that the basic assumption made in going from (7.3) to (7.6) is that only linear terms are kept. One would expect, however, that the definition of τ and the coefficients of $(\partial W/\partial p)$ and $(\partial W/\partial T)$ in Eq. (7.14) would depend on (7.3). The general shape of the absorption curves is independent of the form of (7.3), but the detailed behavior may depend on it.

8. VARIOUS RELAXATION METHODS

In addition to the methods presented in Sections 6 and 7, many approaches to the relaxation problem, i.e., (6.14), (7.55), (7.59), and (7.69), are possible and have been made in the past 50 years. The occurrence of several distinct approaches to the same problem is, of course, nothing new. Classical mechanics has several different formulations—i.e., Newton's second law, D'Alembert's principle, Hamilton's principle, Lagrange's equations, etc. In such a case the various methods complement each other and lead to a deeper understanding of the field. The object of this section is to review briefly the various approaches that have been made to the relaxation problem. A complete analysis of all the theories is clearly beyond the scope of any one paper. We shall attempt only to classify the various approaches and, in some cases, describe the basic steps.

It seems useful to classify the various relaxation theories into four groups according to the methods on which the theories are based, namely: (a) kinetic theory, (b) irreversible thermodynamics, (c) statistical thermodynamics, and (d) phenomenological approach. The equivalence of these various approaches is not always demonstrated, although many papers assume that the methods are essentially equivalent. We have seen above, that for gases a formulation based on statistical thermodynamics leads to the same acoustical equation of state as one based on irreversible thermodynamics. In this section we shall show that the kinetic theory approach and the phenomenological approach lead to the same acoustical behavior.

(a) *The Method of Kinetic Theory*

There are at least three treatments of relaxation which use kinetic theory. The oldest one is that of Jeans (J2) who in 1904 considered a gas of rough nonsymmetric molecules. Here it takes time to establish equilibrium between rotational and translational energy. From his development it is possible to define a translational and a rotational temperature, indeed it is possible to arrive at an equation corresponding to (6.1). Later, Bourgin developed a general theory of absorption in gases. Another variation of this method has been given by Saxton, (S1a). Saxton's treatment includes heat conduction and viscosity.[14] Although Bourgin's theory (B26 to B32) is applicable to far more complicated cases, a simplified version will be presented here which applies to the two state gas. In the case of gases his treatment can be applied to very complicated systems.

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[14] An interesting point appears in Saxton's theory. At low frequency, i.e., below the relaxation maximum the contribution of viscosity to the amplitude absorption per wavelength is given by

$$\alpha\lambda=4\pi\omega\eta/3\rho_0c_\infty{}^2. \tag{8.1}$$

Here $c_\infty{}^2$ is the square of the velocity at high frequency (beyond the absorption maximum) which seems surprising since one might expect $c_0{}^2$ to appear as it does in Sec. 11, where we have treated a similar problem by a different method. For H_2 at room temperature $C_v{}^i$ is nearly equal to the gas constant (for further details see Sec. 22). At this temperature the vibration degrees of freedom do not enter in, and $C_v{}^i$ is due entirely to rotation. Hence

$$c_\infty{}^2/c_e{}^2=(C_p{}^\infty/C_v{}^\infty)(C_v{}^0/C_p{}^0)=25/21=1.19.$$

This means a decrease of 20 percent in the viscous absorption term if Saxton's result is correct.

We start by considering a gas with the internal states 1, 2, 3, $\cdots$. Let n_i be the number of molecules per unit volume in state i and $n=\sum_i n_i$, where n is the total number per unit volume. The n of this section is not related to the n of Sec. 7. The equations of continuity and of motion can be found in Jeans (J1; Eqs. (286), (290), and (298)). For the one-dimensional case, where second-order terms have been neglected, these are:

equation of continuity:

$$\partial n/\partial t=-\partial nv/\partial x; \tag{8.2}$$

equation of motion:

$$mn\partial v/\partial t=-\partial mn\langle u^2\rangle/\partial x=-(2/3)\partial(nE_k)/\partial x; \tag{8.3}$$

equation of the conservation of kinetic energy:

$$\partial(nE_k)/\partial t=-(5/3)\partial nE_kv/\partial x+\Delta E_k, \qquad (8.4)^{15}$$

where $v=$ the average particle velocity along the x axis, i.e., the drift velocity (particle velocity); $m=$ the mass of the molecule; $E_k=$ the kinetic energy of translation $=3/2k'T$; $\langle u^2\rangle=$ the square of the velocities along the x axis; and $k'=$ Boltzmann's constant. Kinetic theory shows that $\langle u^2\rangle$ equals $k'T/m$.

We require a fourth equation; this will describe the transition of the molecules from one state to another. By state we mean an energy grouping within which there is some kind of an equilibrium, i.e., the time to establish equilibrium within the state is short relative to the time to establish equilibrium between the states. We select an arbitrary particle in state i. The probability that this particle is transformed in unit time to state j due to a collision with another particle also in state i, is

$$\bar{f}_{ij}(n_i-1)\approx\bar{f}_{ij}n_i.$$

The above expression defines $\bar{f}_{ij}$. The net number of transitions from state i to j due to collisions with molecules in state i is

$$n_i^2\bar{f}_{ij}^2.$$

Similarly we have to consider collisions between molecules in state i and state j. The corresponding expression is

$$n_i(n-n_i)f_{ij}.$$

The net change of the number in the ith state, due to collision, is

$$\begin{aligned}\Delta n_i=-\textstyle\sum_j\{&[n_i^2(\bar{f}_{ij}-f_{ij})+nn_if_{ij}]\\&-[n_j^2(\bar{f}_{ji}-f_{ji})+nn_jf_{ji}]\}.\end{aligned} \tag{8.5}$$

The first terms in the square bracket give the number of particles that leave the ith state and the second bracket is for the number of particles that enter the ith state.

One now assumes that n_i can be calculated from an expansion about the equilibrium value. This results in

$$\begin{aligned}\Delta n_i=-\textstyle\sum_j\{&\delta n(n_if_{ij}-n_jf_{ji})\\&+\delta n_i[2n_i(\bar{f}_{ij}-f_{ij})+nf_{ij}]\\&-\delta n_j[2n_j(\bar{f}_{ji}-f_{ji})+nf_{ji}]\\&+[n_i^2\delta(\bar{f}_{ij}-f_{ij})+nn_i\delta f_{ij}\\&-n_j^2\delta(\bar{f}_{ji}-f_{ji})-nn_j\delta f_{ji}]\}.\end{aligned} \tag{8.6}$$

Bourgin, borrowing a concept from the thermodynamical development, here assumes that a change of the population in the ith state is given by

$$\delta n_i=\frac{n_i}{n}\delta n+\beta_in_i'\delta E_k \tag{8.7}$$

where $n_i'=(dn_i/dE_k)$.[16] Implicitly this equation assumes that the disturbance which makes $\Delta n_i\neq 0$ is harmonic. The first term of (8.7) arises because of a change in density. The second is caused by a change of the populations in each of the levels due to changes in temperature (since $E_k=3k'T/2$). β_i is a complex function of the frequency implicit in (8.7) and describes the phase lag between the translational energy and the energy in the ith state, as well as the fraction of the translational energy δE_k which affects this state.

For a slow process, where equilibrium is approached, $\beta_i\rightarrow 1$ and $\Delta n_i\rightarrow 0$. Substituting (8.7) into (8.6) and recalling (8.5), we get for a slow process,

$$\begin{aligned}\delta E_kn\textstyle\sum_j(n_i'R_{ij}-n_j'R_{ji})&\\=-\textstyle\sum_j[&n_i^2\delta(\bar{f}_{ij}-f_{ij})+nn_i\delta f_{ij}\\&-n_j^2\delta(\bar{f}_{ji}-f_{ji})-nn_j\delta f_{ji}],\end{aligned} \tag{8.8}$$

where

$$R_{ij}=(1/n)[2n_i(\bar{f}_{ij}-f_{ij})+nf_{ij}]. \tag{8.9}$$

Δn_i can be expressed in terms of δn, δE_k, and δf by using (8.6). Further, the terms multiplying δn equal zero because of (8.5). Eliminating the δf terms with the help of (8.8) we finally obtain for $\beta_i\neq 1$,

$$\Delta n_i=-n\delta E_k\textstyle\sum_j\{n_i'R_{ij}(\beta_i-1)-n_j'R_{ji}(\beta_j-1)\}. \tag{8.10}$$

Equations (8.2), (8.3), (8.4), and (8.10) are the basic equations of Bourgin's treatment. We consider the simplest case where all the β_i's are equal. That is, all the internal modes are in phase with each other. Our next problem is to eliminate ΔE_k from (8.4); for this purpose the equation of continuity for the n_ith state,

$$\partial n_i/\partial t=-(\partial/\partial x)(n_iv)+\Delta n_i, \tag{8.11}$$

is used. As previously, we assume that our solutions are of the form $\exp\{i(\omega t-kx)\}$, where k is complex. Specifically, for n_i we assume the solution

$$\delta n_i^0\exp\{i(\omega t-kx)\}.$$

δn_i^0, δv^0 etc. are the amplitudes. Substituting this type

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[15] Equation (8.4) follows from Jeans, Eq. (298), if we assume that the velocity of a molecule in the x direction is $[u_x+v(x)]$, while the other components are u_y and u_z.

[16] In Bourgin's 1929 paper, β_i is introduced only by the word "evidently," and we have been unable to find out Bourgin's exact interpretation of this step but believe that it can be justified as is done above. More details are given in his later papers.

of solution into (8.2) and (8.11) we express Δn_i in terms of δn^0 and δn_i^0. Now using (8.7), (8.10), and the assumption that the β_i's are equal, we obtain

$$\beta_i = nA_i/(A_i n + i\omega), \tag{8.12}$$

where

$$A_i = 1/n_i' \textstyle\sum_j (n_i' R_{ij} - n_j' R_{ji}). \tag{8.12a}$$

The last term of (8.4) arises because of a redistribution of the levels which increases or decreases the internal energy at the expense of the translational energy. We may evaluate it by first writing

$$\Delta E_k = -\textstyle\sum_i \epsilon_i \Delta n_i, \tag{8.13}$$

where ϵ_i is the energy of the ith state. It follows by means of (8.10) that

$$\begin{aligned}\Delta E_k &= \{\textstyle\sum_i \epsilon_i n(\beta_i - 1)\sum_j (n_i' R_{ij} - n_j' R_{ji})\}\delta E_k \\ &= \{(\beta_i - 1)nA_i \textstyle\sum_i \epsilon_i n_i'\}\delta E_k.\end{aligned}$$

Since β_i is independent of the state, A_i must be also, because of (8.12). Further,

$$\begin{aligned}\Delta E_k &= \left\{-\frac{i\omega A_i n}{nA_i + i\omega}\sum_i \epsilon_i \frac{\partial n_i}{\partial E_k}\right\}\delta E_k \\ &= -\frac{2}{3k'}\left\{\frac{i\omega A_i n}{nA_i + i\omega}\sum_i \epsilon_i \frac{\partial n_i}{\partial T}\right\}\delta E_k, \\ &= -\frac{2}{3k'}\left\{\frac{i\omega}{(nA_i + i\omega)} A_i n^2 c^i\right\}\delta E_k, \end{aligned} \tag{8.14}$$

where

$$\begin{aligned} c^i &= \frac{1}{n}\sum_j \epsilon_j \frac{dn_j}{dT} \\ &= \frac{1}{n}\left(\frac{3}{2}k'\right)\sum_j \epsilon_j n_j'. \end{aligned} \tag{8.15}$$

If we insert (8.14) into (8.4) and recall the type of solutions in which we are interested, we have

$$\begin{aligned} i\omega[n\delta E_k^0 + E_k \delta n^0] &= (5/3)iknE_k \delta v^0 \\ &\quad - \frac{2}{3k'}\left(\frac{i\omega}{nA_i + i\omega}\right)A_i n^2 c^i \delta E_k^0. \end{aligned} \tag{8.16}$$

The higher order terms have been omitted. Using (8.2), (8.3), and (8.16) the desired relation between k^2 and ω^2 is finally obtained:

$$\frac{\omega^2}{k^2} = \frac{2}{3}\frac{E_k}{m}\left[\frac{5k'/2 + c^i + i5k'\omega\tau/2}{3k'/2 + c^i + i3k'\omega\tau/2}\right], \tag{8.17}$$

where the relaxation time τ is now given by

$$1/\tau = A_i N. \tag{8.18}$$

If we make use of the fact that in kinetic theory the pressure equals $1/3mn\langle u^2\rangle = 2nE_k/3$ and employ the definitions

$$c_p^e = 5k'/2$$
$$c_v^e = 3k'/2$$

(8.17) can be transformed into

$$\frac{\omega^2}{k^2} = \frac{p}{\rho_0}\frac{(1/\tau)C_p^t + iC_p^e\omega}{(1/\tau)C_v^t + iC_v^e\omega}, \tag{8.19}$$

where the C's are the molar heats and $C_v^t = C_v^e + C^i$. Since $K = p$ for an ideal gas, (8.19) is equivalent to

$$\omega^2 \rho_0 \left(\frac{\omega}{K_s^\infty} - \frac{i\omega_0}{K_s^0}\right) = k^2(\omega - i\omega_0) \tag{8.20}$$

where

$$K_s^0 = KC_p^t/C_v^t = pC_p^t/C_v^t, \tag{8.21}$$

$$K_s^\infty = KC_p^e/C_v^e = pC_p^e/C_v^e, \tag{8.22}$$

and

$$\omega_0 = C_p^t/\tau C_p^e. \tag{8.23}$$

Equation (8.20) is equivalent to Eq. (5.7) and this shows the equivalence of the kinetic method to the other approaches to the subject.

(*b*) *The Method of Irreversible Thermodynamics*

The usual methods of thermodynamics consider only equilibrium processes. A treatment of absorption based on irreversible thermodynamics has been given by DeGroot (D2a; p. 51). Although the second law usually is stated as an inequality, use is rarely made of the fact that it is indeed an inequality. This occurs because we most often discuss only reversible processes. It is necessary now to go beyond this limitation and include processes which are irreversible. If we neglect heat conduction and heat radiation relaxation, then we are dealing with an adiabatic but a non-isentropic process. This means that a certain extension of conventional thermodynamics must be made. For an isolated system, a reversible process can be characterized by the statement $\Delta S = 0$, where S is the entropy. For an irreversible process S increases with time, and we require a statement of its rate of increase. In general, however, this equation need not contain the entropy explicitly. We shall call this relation, giving the rate of entropy increase, "the equation of irreversibility."

As we have already seen the method of Herzfeld and Rice states this equation in terms of two temperatures, the internal T^i and the external T^e—i.e.,

$$\dot{T}^i = (T^e - T^i)/\tau. \tag{8.24}$$

In the literature the equation of irreversibility takes many forms; only in recent years has it been related to more basic thermodynamic concepts. Some of the forms of the equation of irreversibility will be reviewed.

Several years after the paper of Herzfeld and Rice, Henry (H6) suggested a variation of (8.24). After making the following definitions: E_T = Total equilibrium energy, E_0 = Total energy without vibration (or rotation), and E_x = Actual energy of system at time t, he states the equation as

$$d(E_x - E_0)/dt = (E_T - E_x)/\tau. \tag{8.25}$$

From (8.25) one may obtain the same results as from (8.24).

Eucken and Becker (E6) use the concept of the internal specific heat in setting up the equation of irreversibility. If one defines C_t^i = the internal specific heat (vibrational) at instant t, and C^i = the internal specific heat for a static process, then

$$\dot{C}_t^i = (C^i - C^t)/\tau. \tag{8.26}$$

In liquids, the process is more complicated than in gases and the above concept must be generalized. One of the most direct means is that recently presented by Hoff Lu (H13) in which he used the volume directly.

By letting s_0 = the static value of $-\Delta V/V$, s_∞ = the value of $-\Delta V/V$ at very high frequencies, and s = the value of $-\Delta V/V$ at instant t, Hoff Lu's equation of irreversibility becomes:

$$d(s - s_\infty)/dt = (s_0 - s)/\tau. \tag{8.27}$$

Using (8.27) one can obtain the acoustical equation of state for a single relaxation process. The assumption is made that the equation holds for liquids and gases. In general, however, (8.27) depends on the thermodynamic path selected.

The approach of Mandelstam and Leontovich (M1) shows an advance in that they relate the problem more closely to thermodynamics.[17] Thermodynamics enters in Eqs. (8.24) to (8.27) only explicitly and these equations do not seem to give a deep insight into the problem. Mandelstam and Leontovich, on the other hand, consider a system with three (in the simplest case considered) independent variables. They select T, ρ, and ξ. ξ is not defined precisely. It may be related to the population of the states or to an internal temperature. Since T and ρ are being used, the thermodynamic function chosen is the Helmholtz free energy F.[18] F is a function of T, ρ, and ξ—i.e., $F(p, \rho, \xi)$. Conventional thermodynamics applies when

$$\partial F/\partial \xi = 0. \tag{8.28}$$

Since (8.28) does not always hold, our problem is to find a relation between F and ξ. The one chosen by Mandelstam and Leontovich, is

$$\dot{\xi} = K' \partial F/\partial \xi, \tag{8.29}$$

where K' is a constant. This leads to the usual expression for absorption and velocity. K' is related to τ of Herzfeld and Rice as follows:

$$1/\tau = K' \partial^2 F/\partial \xi^2. \tag{8.30}$$

The difference between this method and the ones previously mentioned is that the terms here can be defined with greater care, and, in principle, the development is not confined too closely to a particular problem or a specific experiment.

One would like to connect the equation of irreversibility with the recent developments of irreversible thermodynamics. At least three such attempts have been made, namely: Damköhler's (D1), Meixner's (M6), and Eckart's (E3a). We shall discuss only the paper of Eckart, which considers a simple case. In setting up the equation of irreversibility, he uses the concept of chemical potential (G8; p. 17) or (Z2; p. 322) (also known as partial potential).

Consider a reaction which can be characterized by the relation $Y_1 \rightleftarrows Y_2$. Eckart's equation of irreversibility is

$$\dot{N}_2 = -g(\mu_2 - \mu_1), \tag{8.31}$$

where g is a constant which can be related to the law of mass action. The quantity μ_1 is the chemical potential due to molecules in state 1, i.e., $(\partial F/\partial N_1)_{T,V,N_2}$, and μ_2 is the chemical potential corresponding to state 2. In this theory,

$$1/\tau = (g\partial/\partial N_2)(\mu_2 - \mu_1). \tag{8.32}$$

The importance of Eckart's paper is that Eq. (8.31) has not been set up *ad hoc* to explain the absorption of sound but is part of a more general theory of irreversible processes (E1). The problem of sound absorption in Eckart's formulation becomes just one phase of a more basic field—i.e., "thermodynamics" as contrasted with "thermostatics."[19]

We have listed some of the equations of irreversibility that have been used in the past. We may deduce (8.25) from (8.24) by assuming that E_0 is in equilibrium with the macroscopic variables; for a gas this is characterized by T^e. The nonvibrational part of E_x is E_0. The vibrational part of E_x will be characterized by an internal temperature T^i. It seems logical to expect the following relations to hold:

$$E_x - E_0 = a(T^i - \bar{T}) + b, \tag{8.33}$$

$$E_T - T_0 = a(T^e - \bar{T}) + b. \tag{8.34}$$

The parameters a, b, and $\bar{T}$ have the following meaning: $\bar{T}$ corresponds to some average temperature; b is the internal (vibrational) energy at $\bar{T}$; and a is the rate of change of the internal energy with temperature. By substituting into (8.25) we obtain

$$A\dot{T}^i = a(T^e - T^i)/\tau, \tag{8.35}$$

which is the same as (8.24). An argument such as this

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[17] J. Meixner recently presented a similar theory at the 1951 Ultrasonics Conference in Brussels.

[18] The use of the letter F to denote the Helmholtz free energy is not universal since students of G. N. Lewis' school denote the Gibbs free energy by F. Since the reaction rate theory has been developed to a large extent by American chemists, the use of F for the Gibbs function appears in a few papers referred to in this review. At times, the distinction between the Gibbs and the Helmholtz function is not made in these papers. We use F for the Helmholtz free energy, the notation followed by Guggenheim. (G8).

[19] There is a slight difference between Eckart's development as contrasted with the others. His theory defines $\omega_0 = K_s^0/\tau K_s^\infty$ instead of $C_p^e/\tau C_p$. This must be the result of the method used in proceeding from the equation of irreversibility. The definition of ω_0 in the paper of Mandelstam and Leontovich is the same as that of Herzfeld and Rice in the case of thermal relaxation. The authors would like to thank Dr. Eckart for the use of his notes.

can also be used to show that (8.26) is equivalent to (8.24).

By equating the ξ of Mandelstam and Leontovich to the N_2 of Eckert's development, one may show that they are equivalent. On the other hand, Mandelstam and Leontovich have defined an internal temperature by assuming that a given distribution of level population can be characterized by a given value of ξ. For this ξ and macroscopic temperature T^e,

$$\partial F\{T^e, \rho, \xi\}/\partial \xi \neq 0. \qquad (8.36)$$

But an internal temperature T^i can be defined such that

$$\partial F\{T^i, \rho, \xi\}/\partial \xi = 0. \qquad (8.37)$$

Using these equations, Mandelstamm and Leontovich have shown that

$$\dot{T}^i - A\dot{\rho} = (1/\tau)(T^e - T^i), \qquad (8.38)$$

where A is a complicated thermodynamic function. For a gas, the pressure is independent of the level population and $A=0$; hence, (8.38) is the equation of Herzfeld and Rice, with a more precise meaning of T^i.

(c) *The Method of Statistical Thermodynamics*

This method has already been given essentially in Sec. 7, and we shall not elaborate on it here. Two interesting modifications of the theory will be given here—the development of Landau and Teller (L3) for a many-state vibrational gas and a means of calculating collision efficiencies for gases.

Landau and Teller consider a gas with a single nondegenerate vibrational mode of frequency ν_M. The states of the gas can be listed as $l=0, 1, 2\cdots$. It is assumed that transitions occur because of binary collisions and that A_{ij} is the transition probability from the ith to the jth state. One assumes further that the effectiveness of a collision depends on the translational energy and not on the vibrational state of the hitting molecule. The following relations between the A's are assumed.

$$A_{01}:A_{12}:A_{23}\cdots = A_{10}:A_{21}:A_{32}\cdots = 1:2:3\cdots$$
$$A_{ij}=0 \quad \text{if} \quad i-j \neq \pm 1. \qquad (8.39)$$

These assumptions may be justified by considering quantum-mechanical definitions of the transition probability. The A's should depend on the square of the matrix element

$$\int \psi_i V_p \psi_j d\tau, \qquad (8.40)$$

where the ψ's are the wave functions of the states, and V_p is the perturbed part of the Hamiltonian. If one assumes that V_p is directly proportional to the normal vibrational coordinate of the molecule (D3 and R10; p. 343) then (8.40) results. From (8.40) we see that the temperature affects A_{01} in exactly the same way as it does A_{12}, etc.

Consider $\dot{N}_0$, which is given by

$$\dot{N}_0 = A_{10}N_1 - A_{01}N_0 \qquad (8.41)$$

or, at equilibrium, as before,

$$\frac{A_{01}}{A_{10}} = \frac{N_1{}^0}{N_0{}^0} = \exp(-h\nu_M/k'T) = e^{-x}, \qquad (8.42)$$

where h is Planck's constant and x is defined by (8.42). We now define

$$Z = \sum_l N_l l, \quad l = 0, 1, 2, \cdots, \qquad (8.43)$$

and it follows that

$$\dot{Z} = \sum_l [(l+1)N_l A_{l,\,l+1} - lN_l A_{l,\,l+1} - lN_l A_{l,\,l-1} + (l-1)N_l A_{l,\,l-1}] = \sum_l [N_l A_{l,\,l+1} - N_l A_{l,\,l-1}].^{20} \qquad (8.44)$$

Using (8.39) we obtain

$$\dot{Z} = A_{01}\sum_l (l+1)N_l - A_{10}\sum_l lN_l = A_{01}N - (A_{10}-A_{01})Z = A_{01}\{N - Z(e^x-1)\}. \qquad (8.45)$$

If we expand (8.45) about the equilibrium value and neglect higher order terms, we get

$$\dot{Z} = [A_{01} + \Delta A_{01}]\left[N - (Z^0 + \Delta Z)\left(e^x - 1 - \frac{x}{T}e^x \Delta T\right)\right].$$

Since at equilibrium $\dot{Z}=0$, we know that

$$N - Z^0(e^x - 1) = 0,$$

or

$$\dot{Z} = (A_{01} - A_{10})\Delta Z + A_{01}Z^0(x/T)e^x \Delta T. \qquad (8.46)$$

Here A_{01}, A_{10}, Z, and T are evaluated at the equilibrium value. If we assume that

$$\Delta Z = \Delta Z^0 e^{i\omega t},$$
$$\Delta T = \Delta T^0 e^{i\omega t},$$

then (8.46) gives

$$\Delta Z^0[i\omega + (A_{10} - A_{01})] = A_{01}(x/T)Z^0 e^x \Delta T^0 = B\Delta T^0. \qquad (8.47)$$

B is defined by (8.47). Returning to (8.43) we see that $h\nu_M \Delta Z$ is just the change of the oscillator's energy due to the shift in population caused by the temperature change ΔT. Following Landau and Teller, we define

$$C_t{}^i = C^i/(i\omega\tau + 1), \qquad (8.48)$$

where

$$C^i = h\nu_M B/(A_{10} - A_{01}), \qquad (8.49a)$$

$$\tau = 1/(A_{10} - A_{01}). \qquad (8.49b)$$

It should be noted that for a harmonic disturbance, the τ of (8.49b) is the same as the τ of (8.26). Equation (8.49b) shows that the relaxation frequency for a vibrating molecule is not proportional to $A_{10}+A_{01}$, as derived in Sec. 7, but to $A_{10}-A_{01}$. The result obtained in Sec. 7 holds only if $e^{-x} \ll 1$ and, under these conditions, the difference between the two results is very small.

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[20] For convenience $A_{0(-1)}$ is set equal to zero.

Equation (8.49), of course, does not apply to rotational modes or to liquids.

Before leaving this subject we would like to show the relation between the relaxation time τ and the ratio of collisions which cause transitions to the total number of collisions. Let us assume that for a gas the A's of Sec. 7 are due to binary collisions; then we may write

$$A_{10}=(1/V)k_{10}(N_0+N_1)\approx k_{10}N_0/V, \tag{8.50a}$$

$$A_{01}=(1/V)k_{01}(N_0+N_1)\approx k_{01}N_0/V, \tag{8.50b}$$

if one assumes that $N_0 \gg N_1$. Equations (8.50a) and (8.50b) define the k's. The volume V appears because N_i is the total number of molecules in state i. The actual number of collisions between N_1 and N_0 can be calculated from statistical mechanics (F1; p. 491, Eq. (1201, 18)) and is

$$Z_{ij}=\frac{2}{V}\frac{N_iN_j}{\sigma_{ij}}D_{ij}^2\left(2\pi\frac{k'T}{m}\right)^{\frac{1}{2}}. \tag{8.51}$$

Here D_{ij}= the average diameter of the jth and ith molecule (distance of nearest approach) and m= the reduced mass $m_im_j/(m_i+m_j)$.

$$\sigma\begin{cases}=2 \text{ if } i \text{ and } j \text{ are the same molecule.}\\ =1 \text{ if they are not the same molecule.}\end{cases}$$

Since $A_{10}N_1$ is the number of N_0 molecules that are produced by collisions per unit time, the fractional number of collisions which are effective is

$$P_{10}=\frac{A_{10}N_1}{Z_{10}}=\frac{k_{10}}{2D_{10}^2[4\pi(RT/M)]^{\frac{1}{2}}}, \tag{8.52}$$

where M is the molar mass. Because the masses in states 0 and 1 are equal, $m=M/2N$. Since $A_{01} \ll A_{10}$, for $N_1 \ll N_0$ the experimental value of ω_0 effectively gives A_{10}, and one may calculate P_{10}. Actually, a slight correction [known as the Sutherland correction (J1; p. 176)] should be applied to Eqs. (8.51) and (8.52).

Further modifications of the statistical model are needed for more complex gases such as CO_2 or COS. CO_2 is a linear molecule and has four internal degrees of vibration, one of which is doubly degenerate. The question now arises as to whether one can treat the molecules as ones having a single internal temperature corresponding to a single ω_0, or several, corresponding to the different degrees of freedom. Results seem to show, at least to first approximation, that one needs only a single internal temperature. The static value of the specific heat is due mainly to the three lower vibrational levels. Since C_p/C_v enters into the velocity, one may obtain C_v by acoustical means. Measurements of Eucken (E7) and his co-workers indicate that the various vibrations relax essentially at a single frequency [for CO_2 and COS]. Schafer (S2) has indicated how the data on COS can be interpreted in terms of a double relaxation process, but the evidence does not seem decisive.

More complicated vapors, however, may have more than one distinct relaxation process. One such example is given in the work of Alexander and Lambert (A1) on acetaldehyde (CH_3CHO). They have demonstrated the existence of three distinct relaxation times.

(*d*) *The Phenomenological Approach*

Each of the preceding approaches is based on some kind of molecular model. This is not necessary, as Stokes's treatment shows. Considering the macroscopic features, one may write down relations between the density and the pressure and then explore the acoustical consequences. An example of this type of approach is found in a paper of Frenkel and Obraztsov (F4). They examine two possible acoustical equations of state, *viz.*,

$$ap_e+b\dot{p}_e+d\rho_e+e\dot{\rho}_e=0, \tag{8.53}$$

and

$$ap_e+b\frac{dp_e}{dt}+c\frac{d^2p_e}{dt^2}+e\frac{d\rho_e}{dt}+f\frac{d^2\rho_e}{dt^2}=0. \tag{8.54}$$

Their theory is broad enough to describe a medium which can support a shearing stress. The great advantage of this method is that it is possible to explore many equations of state without constructing complicated molecular models. This has great usefulness, as for example, in treating glass-like substances. The main disadvantage is that the final equations are usually very complicated. Frenkel and Obraztsov unfortunately are able to give only a limited amount of experimental evidence to support their generalized theory.

9. SUMMARY OF RESULTS

Absorption occurs when the density gets out of phase with the pressure. This can be caused by two mechanisms. One is a frictional lag which we call viscosity (Sec. 3). The other is caused by a change in the bulk modulus which has one value for a slow process and another for a fast process. The second mechanism we call a relaxation process (L14). Reserving the term relaxation to the second process is not universal, for some authors speak of a viscous relaxational process. The change of the bulk modulus with frequency occurs when one considers heat radiation (Sec. 5), thermal relaxation (Secs. 6 and 7) structural relaxation (Sec. 7), a combination of thermal and structural relaxation (Sec. 7), and heat conduction (Sec. 4). In general, the dispersion and the absorption are different, depending on the mechanism. In Fig. I-4 we have plotted the sound velocity and the absorption per wavelength as a function of angular frequency for the two types of effects. At high frequency, where there is a lot of to and fro motion per unit length one would expect higher linear absorption simply because of the additional motion; for this reason we take the absorption per wavelength ($\alpha\lambda$).

If it is possible to obtain values of the absorption or velocity over a large range, then one may easily interpret the results and decide which mechanism is the underlying cause. If we have data only over the range where $\omega \ll \omega_0$, then it may be impossible to interpret the results fully. Nonacoustical information regarding the medium can, at times, help our interpretation.

The results of Secs. 3 to 8 may be summarized as follows:

(a) Viscosity Mechanism. (Stokes 1845)

Phase velocity

$$c^2=\frac{2\zeta}{\omega_v\rho_0}\frac{\omega_v^2+\omega^2}{\{1+[1+(\omega^2/\omega_v^2)]^{\frac{1}{2}}\}}, \qquad (9.1)$$

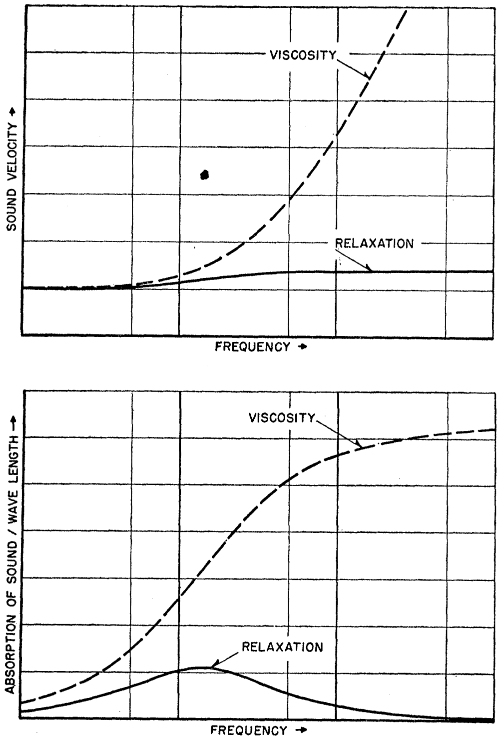

FIG. I-4 (a). Velocity *vs* frequency for a viscous mechanism and a relaxational mechanism (b). Amplitude absorption per wavelength *vs* frequency for a viscous mechanism and a relaxational mechanism.

where

$$\omega_v=K_s/\zeta.$$

For $\omega \ll \omega_v$,

$$c^2\approx\frac{K_s}{\rho_0}\left(1+\frac{3}{4}\frac{\omega^2}{\omega_v^2}\right); \qquad (9.2)$$

for $\omega \gg \omega_v$,

$$c^2\approx 2\zeta\omega/\rho_0\text{—viscous wave.} \qquad (9.3)$$

Absorption coefficient:

$$\alpha=\left(\frac{\rho_0\omega_v}{2\zeta}\right)^{\frac{1}{2}}\left\{\frac{\omega^2}{\omega^2+\omega_v^2}\left[\left(1+\frac{\omega^2}{\omega_v^2}\right)^{\frac{1}{2}}-1\right]\right\}^{\frac{1}{2}}. \qquad (9.4)$$

For $\omega \ll \omega_v$,

$$\alpha=\frac{1}{2}\frac{1}{c_0^3}\frac{\zeta}{\rho_0}\omega^2\left(1-\frac{5}{8}\frac{\omega^2}{\omega_v^2}\right)\approx\frac{1}{2}\frac{1}{c_0^3}\frac{\zeta}{\rho_0}\omega^2; \qquad (9.5)$$

for $\omega \gg \omega_v$,

$$\alpha\approx(\rho_0\omega/2\zeta)^{\frac{1}{2}}\text{—viscous wave.} \qquad (9.6)$$

Absorption per wavelength:

$$\alpha\lambda=2\pi\alpha c/\omega. \qquad (9.7)$$

For $\omega \ll \omega_v$,

$$\alpha\lambda=\pi\frac{\zeta}{\rho}\frac{\omega}{c_0^2}\left(1-\frac{1}{4}\frac{\omega^2}{\omega_v^2}\right); \qquad (9.8)$$

for $\omega \gg \omega_v$,

$$\alpha\lambda=2\pi. \qquad (9.9)$$

Setting $\zeta=4\eta/3$ we have,

for air $\omega_v=6000$ mc at normal pressure
for water $\omega_v=2\times10^6$ mc.

(b) Relaxation Mechanism

Phase velocity

$$c^2=\frac{1}{\rho_0}\frac{\omega^2+\omega_0^2}{[(\omega^2/K_s^\infty)+(\omega_0^2/K_s^0)]}. \qquad (9.10)$$

Absorption coefficient:

$$\alpha=\frac{c\omega_0}{2c_0^2}\frac{\Delta K_s}{K_s^\infty}\frac{\omega^2}{\omega_0^2+\omega^2}, \qquad (9.11)$$

where

$$\Delta K_s=K_s^\infty-K_s^0.$$

Absorption per wavelength,

$$\alpha\lambda=\pi\frac{\Delta K_s}{(K_s^\infty K_s^0)^{\frac{1}{2}}}\omega_m\frac{\omega}{\omega^2+\omega_m^2}. \qquad (9.12)$$

Here

$$\omega_m^2=\omega_0^2/K_s^\infty/K_s^0, \qquad (9.13)$$

for which $\alpha\lambda$ has its maximum value. At $\omega=\omega_m$ we obtain

$$\alpha\lambda=\frac{\pi}{2}\frac{\Delta K_s}{(K_s^\infty K_s^0)^{\frac{1}{2}}}. \qquad (9.14)$$

Types of relaxation

(i) Heat radiation[21] (Stokes 1851)

$$\omega_0=\omega_r=q/\gamma, \qquad (9.15)$$

$$\Delta K_s=(\gamma-1)K. \qquad (9.16)$$

For air $\omega_r=0.002$ cycle, based on a value of q estimated

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[21] We have tried to list the names of the authors who developed the theory. At places several authors are listed when each developed his own point of view. Several attempts to develop a generalization of (ii) and (iii) which are in process of being published are not listed.

roughly by Rocard (R9).[22] He assumes it is independent of frequency.

(ii) Thermal relaxation (Jeans 1904, Bourgin 1928, Herzfeld and Rice 1928, Kneser 1931).

$$\omega_0 = C_p{}^t / C_p{}^e \tau \tag{9.17}$$

$$\Delta K_s = TV\beta^2 K^2 (C^i / C_v{}^t C_v{}^e). \tag{9.18}$$

(iii) Structural relaxation (Hall 1948, B. B. Ghosh 1950).

$$\omega_0 = 1/\tau. \tag{9.19}$$

(iv) General case (Mandelstam and Leontovich 1937, Liebermann 1949, Markham 1950).

$$\omega_0 = C_p{}^t / \tau C_p{}^e. \tag{9.20}$$

The actual expression of ΔK_s in the text for (iii) and (iv) are not reproduced here.

(v) Thermal conduction. (Kirchhoff 1868).

$$\omega_c = C_p \rho_0 c^2 / M\kappa. \tag{9.21}$$

In this case,

$$\Delta K_s = K_s{}^0 - K_s{}^\infty = (\gamma - 1)K \tag{9.22}$$

for air $\omega_c = 6\times 10^9$ cycles, while for water $\omega_c = 10^{13}$ cycles. One might classify thermal conduction as a third mechanism because it is based on a different equation of state: ΔK_s is $K_s{}^0 - K_s{}^\infty$ instead of $K_s{}^\infty - K_s{}^0$. Here $K_s{}^0 > K_s{}^\infty$, and ω_c is a function of the frequency through c.

(*c*) *Temperature Dependence*

(i) Viscosity

For a gas, the viscosity coefficient depends on the mean velocity; hence, one would expect the coefficient to be a function of the square root of the absolute temperature (J1; p. 170)[23] ρ_0 at constant pressure depends inversely on the temperature, while K is independent of the temperature. Therefore, at low frequencies, the velocity is given by

$$c = \text{const } T^{\frac{1}{2}},$$

while at high frequencies

$$c = \text{const } T^{\frac{3}{4}}.$$

On the other hand at low frequencies the absorption is given by

$$\alpha = \text{constant, independent of temperature,}$$

while at high frequencies,

$$\alpha = \text{const } T^{-\frac{3}{4}}.$$

This means that in gases the absorption and velocity have only a small dependence on the temperature for the viscous case.

For many liquids, the viscosity coefficient depends exponentially on the reciprocal of the temperature—i.e., $\zeta = Ae^{B/T}$. The factor A may have a slight temperature dependence, which we shall ignore (G2a; p. 477). We shall ignore the temperature dependence of K and ρ since ζ depends so critically on T. Hence, for low frequencies one obtains

$$c = \text{const}$$
$$\alpha = \text{const } e^{B/T},$$

and, on the other hand, at high frequencies

$$c = \text{const } e^{\frac{1}{2}B/T}$$
$$\alpha = \text{const } e^{-\frac{1}{2}B/T}.$$

(ii) Relaxation

We shall limit our remarks to cases (ii), (iii), and (iv) of (*b*), and to the special condition where $N_2{}^0 \ll N_1{}^0$. First, we shall consider the absorption at low frequencies. For these cases $K_s{}^\infty - K_s{}^0$ depends on $N_2{}^0$, which[24] in turn depends on $\exp[-(E_2 - E_1)/RT]$. We may, therefore, write

$$K_s{}^\infty - K_s{}^0 = ae^{-b/T}. \tag{9.23}$$

The form of ω_0 depends on $A_{12}{}^0 + A_{21}{}^0$. Since $N_2{}^0 \ll N_1{}^0$, $A_{12}{}^0 \ll A_{21}{}^0$ and ω_0 are proportional to $A_{21}{}^0$ or the rate with which the molecules drop from state 2 to state 1, $A_{21}{}^0$ and ω_0 should have the same temperature dependence as do the reaction rate constants, namely

$$A_{21}{}^0 \sim \omega_0 \sim a' \exp(-b'/T). \tag{9.24}$$

For our estimates we shall ignore the temperature dependence of the a's. At low frequencies the temperature dependence of α should arise through ω_0 and ΔK, or

$$\alpha \approx \frac{1}{\omega_0}(K_s{}^\infty - K_s{}^0) \approx \exp[-(b-b')/T]. \tag{9.25}$$

α may decrease or increase with temperature depending on the values of the b's.

At high frequencies α depends on the temperature through $\Delta K\omega_0$ or

$$\alpha \approx \Delta K\omega_0 \approx \exp[-(b+b')/T]. \tag{9.26}$$

---

[22] Rocard (R9) has calculated α for air. He gets for the radiation part of α at 6 kc, 1.5×10^{-8}. Assuming that $\omega_r \ll \omega$ at this frequency one obtains $\alpha = c_\infty \Delta K \omega_r / 2c_0{}^2 K_s{}^\infty$, where c_∞ is the high frequency sound velocity i.e., the adiabatic value. The above equation gives $\omega_r = 2\alpha c_\infty / (\gamma - 1)$.

[23] Actually the temperature exponent is not exactly $\frac{1}{2}$. For He the viscosity varies as $T^{0.65}$.

[24] To justify this statement we return to Eq. (7.10) and show that

$$N\left(2 + \frac{A_{21}{}^0}{A_{12}{}^0} + \frac{A_{12}{}^0}{A_{21}{}^0}\right)^{-1} = \frac{N_1{}^0 N_2{}^0}{N} \approx N_2{}^0.$$

The last step holds if $N_1{}^0 \gg N_2{}^0$. If we use the equilibrium condition,

$$N_1{}^0 A_{12}{}^0 = N_2{}^0 A_{21}{}^0 = (N - N_1{}^0) A_{21}{}^0$$

or

$$\frac{A_{21}{}^0}{A_{21}{}^0 + A_{12}{}^0} = \frac{N_1{}^0}{N}.$$

Using this relation, Eq. (7.12) and the footnote after Eq. (7.9) it follows that

$$\frac{N}{2(1+\cosh W)} = \frac{N_2{}^0 A_{21}{}^0}{A_{12}{}^0 + A_{21}{}^0} = \frac{N_2{}^0 N_1{}^0}{N}.$$

Hence for $N_2{}^0 \ll N_1{}^0$, B_p, and B_T depend on $N_2{}^0$ or e^W.

Hence one would expect α to increase with temperature depending on the sizes of the b's.

The important point is that the temperature dependence does not depend on the type of relaxation, i.e., thermal, structural, or general. This is certainly true if $N_2^0 \ll N_1^0$. If N_2^0 is not much smaller than N_1^0, then the temperature dependence may be more complicated and, perhaps a difference between the various relaxation mechanisms may appear. This argument seems to indicate that one must be very careful in arriving at conclusions from the temperature dependence of absorption.

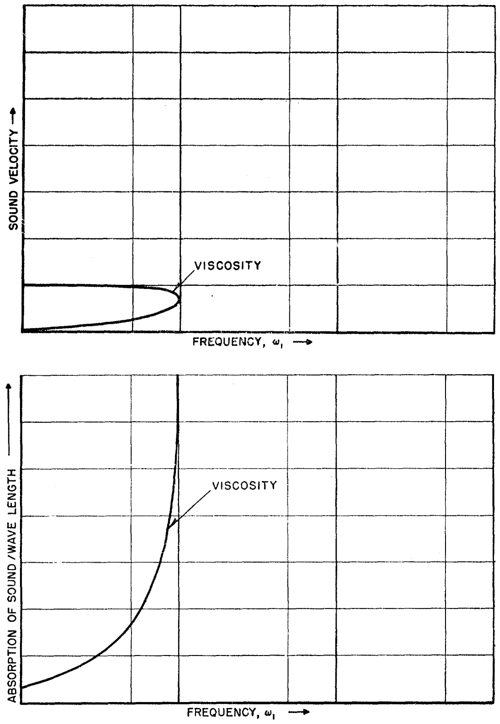


FIG. I-5 (a). Velocity *vs* frequency for a viscosity mechanism in the case of temporal absorption. (b). Amplitude absorption per wavelength *vs* frequency for a viscosity mechanism in the case of temporal absorption.

10. TEMPORAL ABSORPTION *VERSUS* SPATIAL ABSORPTION

We pause here, to introduce a consideration with respect to absorption and dispersion of sound not usually emphasized (L14a). Going back to Eq. (2.13), we note that if we set $k = k_r + ik_i$ we get

$$p_e = P_e \exp(k_i x) \exp[i(\omega t - k_r x)]. \tag{10.1}$$

Here $\alpha = -k_i$ appears as the coefficient measuring attenuation of the wave in space. We may call it the *spatial* absorption coefficient. It is of course the commonly used coefficient in ordinary progressive wave propagation studies. However, it is equally possible to set

$$\omega = \omega_1 + i\omega_2 \tag{10.2}$$

and obtain

$$p_e = P_e \exp(-\omega_2 t) \exp[i(\omega_1 t - kx)]. \tag{10.3}$$

Stokes (S17) in his early study of sound attenuation in viscous media used (10.3). Here ω_2 gives the coefficient which measures attenuation in time. We may call it the *temporal* absorption coefficient. It has been used extensively in studies of the attenuation of sound in finite solid rods. It is clear, that it applies appropriately to the temporal decay of a wave train or standing wave in a medium, whereas α applies more appropriately to a progressive wave due to a constant source. An interesting point is that the dispersion may be different in the two cases and indeed, for the case of viscous absorption the velocity corresponding to (10.1) is always greater than c_0, while that corresponding to (10.3) is always less than c_0.

The temporal absorption due to viscosity alone is interesting, since in the case of liquids, heat conduction plays a much smaller role. The relation between ω and k given by (3.7) yields the results,

$$c = \frac{\omega_1}{k} = c_0\left(1 - \frac{1}{4}\zeta^2 \frac{k^2}{\rho_0^2 c_0^2}\right)^{\frac{1}{2}} \tag{10.4}$$

and

$$\omega_2 = \frac{1}{2}\zeta \frac{k^2}{\rho_0}. \tag{10.5}$$

Equation (10.5) gives the temporal absorption coefficient precisely for a fluid in which viscosity provides the only attenuating mechanism. It, of course, agrees in form with Stokes's original calculation, if ζ is properly reinterpreted. The dispersion equation (10.4) is interesting because of its prediction of a frequency cutoff.

We have plotted c against ω_1 in Fig. I-5a. ω_2/c should correspond to α so that in Fig. I-5b, $2\pi\omega_2/kc$ is plotted against ω_1.

To explore temporal absorption in the case of a relaxation mechanism we return to Eq. (5.7) and use assumption (10.2). We write (5.7) in the form

$$\frac{\omega^2}{k^2} = \frac{1}{\rho_0} \frac{1}{[(\omega/K_s^\infty)^2 + (\omega_0/K_s^0)^2]} \times \left\{ \frac{\omega^2}{K_s^\infty} + \frac{\omega_0^2}{K_s^0} + i\omega_0\omega\left(\frac{1}{K_s^0} - \frac{1}{K_s^\infty}\right)\right\}, \tag{10.6}$$

where ω_0 has replaced ω_r, since we are interested in the general relaxational case. Assuming that $\omega_1 \gg \omega_2$ we have

$$\frac{\omega_1^2}{k^2} = \frac{1}{\rho_0} \frac{(\omega_1^2/K_s^\infty) + (\omega_0^2/K_s^0)}{[(\omega_1/K_s^\infty)^2 + (\omega_0/K_s^0)^2]} \tag{10.7}$$

and

$$2\frac{\omega_1\omega_2}{k^2} = \frac{1}{\rho_0} \frac{\omega_1\omega_0}{[(\omega_1/K_s^\infty)^2 + (\omega_0/K_s^0)^2]}\left(\frac{1}{K_s^\infty} - \frac{1}{K_s^0}\right). \tag{10.8}$$

Several approximations have been made in arriving at (10.7) and (10.8). They can be justified if $\omega_1 \gg \omega_2$, a condition which always seems to be true. Solving (10.8) for ω_2 we obtain,

$$\omega_2 = \frac{1}{2\rho_0} \frac{\omega_0}{[(\omega_1/K_s^\infty)^2 + (\omega_0/K_s^0)^2]} \frac{\omega_1^2}{c^2} \left(\frac{1}{K_s^\infty} - \frac{1}{K_s^0} \right). \tag{10.9}$$

The velocity given by (10.7) is slightly different from that given by (5.9). However, again at low frequencies,

$$c_0^2 = \frac{K_s^0}{\rho_0}, \tag{10.10}$$

and at high frequencies

$$c_\infty^2 = \frac{K_s^\infty}{\rho_0}. \tag{10.11}$$

One would expect that α might equal ω/c. This actually holds to a good approximation, since we may obtain from (10.9)

$$\alpha \approx \frac{\omega_2}{c} = \frac{1}{2\rho_0} \frac{\omega_t}{\omega^2 + \omega_t^2} \frac{\omega_1^2}{c^3} K_s^0 K_s^\infty \left(\frac{1}{K_s^\infty} - \frac{1}{K_s^0} \right), \tag{10.12}$$

where

$$\omega_t = \omega_0 \frac{K_s^\infty}{K_s^0}. \tag{10.13}$$

If we make a further slight approximation,

$$\alpha \approx \frac{1}{2c} \frac{\omega_t}{\omega_1^2 + \omega_t^2} \omega_1^2 \left(\frac{K_s^\infty - K_s^0}{K_s^\infty} \right). \tag{10.14}$$

This means that there is no essential difference in the expressions for c and α in the case of temporal and spatial absorption. As we have seen this is not the case when viscosity is considered. The reason for this difference seems to be that in the viscous case k_i is not always much smaller than k_r. Indeed at some frequencies they are almost equal. However, in the relaxation case where K_s^∞ is not much larger than K_s^0, k_i is always much smaller than k_r, a fact we have used all along and will now prove. If

$$k_r \gg k_i, \tag{10.15}$$

then

$$1 \gg \alpha\lambda/2\pi, \tag{10.16}$$

From Sec. 9 Eq. (9.14) we know that the maximum value of $\alpha\lambda$ for relaxation is given by

$$\frac{\pi}{2} \frac{\Delta K_s}{(K_s^\infty K_s^0)^{\frac{1}{2}}}.$$

By using (6.12), (6.13), (10.16), and (A-13) of Appendix II we may show that for gases our approximation (10.15) requires

$$1 \gg \frac{1}{4} \frac{C_v^i (C_p^0 - C_v^0)}{[C_p^\infty C_p^0 C_v^\infty C_v^0]^{\frac{1}{2}}}. \tag{10.17}$$

For gaseous hydrogen at room temperature where $C_v^i = R$ (see Sec. 22) $C_p^0 = 7R/2$, $C_p^\infty = 5R/2$, $C_v^0 = 5R/2$, and $C_v^\infty = 3R/2$, the right-hand side of (10.17) gives approximately 0.04. Actually in spatial absorption we assume that $k_r^2 \gg k_i^2$ which is certainly true for gases since the maximum correction is less than 0.1 percent.

We have to proceed slightly differently in the case of liquids. Let us assume that $\omega_0 \gg \omega$ and write (5.8) in the form

$$\alpha = B\nu^2, \tag{10.18}$$

where now B is an experimental constant and ν is the frequency, i.e., $\omega/2\pi$. Equation (10.16) takes the form

$$1 \gg (1/2\pi) B\nu c. \tag{10.19}$$

The most absorbing liquid known is CS_2 where $c = 1.2 \times 10^5$ cm/sec (B15 (1949 p. 279)) and B ranges from 6×10^{-14} sec^2/cm at 3 mc to 1.4×10^{-14} sec^2/cm at 75 mc (see Sec. 27). Since B and c are known we may calculate the frequency at which the right-hand side of (10.19) equals 0.1. This frequency is about 100 mc. Our treatment should hold at least to 100 mc in an extreme case. CS_2 however, relaxes above 70 mc so that at higher frequencies $\alpha\lambda/2\pi$ is smaller than the value calculated here; further it does not increase with frequency. We may thus conclude that for CS_2 our formulas hold and we should thus expect them to hold for all cases known at present. Since $\alpha \approx \omega_2/c$ and $k_\gamma = \omega_1/c$ the above arguments hold for temporal absorption as well.

For high values of α_λ the form of the solution, i.e., (10.1) and (10.3) affects the value of the absorption and velocity. Present experimental results seem to fit Eq. (10.1). The possibility is, however, that some future experiment may give results which agree with (10.3). In this review we have found solutions to a set of equations but we have *not* considered initial or boundary conditions. These conditions would dictate the form of the solution and may in some extreme cases influence the definition of the velocity and the absorption. Combinations of (10.1) and (10.3) are quite possible.

11. COMBINED EFFECTS

In any fluid, the problem of sound propagation is far more complicated than the treatment given so far, since one must correct for all the effects acting at the same time. We therefore, desire an equation which includes heat radiation, heat conduction, viscosity, and the various relaxational phenomena. One should even include effects of diffusion of various gases in gas mixtures, such as air.

During the last century, effects of both viscosity and thermal conductivity have been considered by Kirchhoff (K3) and his work is reproduced in Rayleigh

(R2; Vol. II, p. 319) and Lamb (L1; p. 648). He considered the propagation of a plane wave and a wave in a cylindrical tube. For the plane wave at low frequencies ($\omega \ll \omega_v$ or ω_e) the absorption due to heat conduction can simply be added to the absorption due to viscosity.

Herzfeld and Rice have considered the combined effects of heat conduction, viscosity, and thermal relaxation. If $\omega \ll \omega_c$, ω_v, and ω_0 then the net absorption is the sum of the individual effects. As mentioned in Sec. 8, Saxton has considered heat conduction, viscosity, and thermal relaxation. So has Sakadi (S1) in a more recent paper.

We shall now consider the combined effect of: heat conduction and viscosity; viscosity and relaxation; and two relaxation processes.

(*a*) *Heat Conduction and Viscosity*

The equation of state for the classical problem of Kirchhoff, combined effect of heat conduction and viscosity, can be obtained most simply by going back to Eq. (4.4) for heat conduction alone,

$$\dot{p}_e - \frac{K_s}{\rho_0}\dot{\rho}_e = \frac{M\kappa}{\rho_0}\left[\frac{1}{C_v}\cdot\frac{\partial^2 p_e}{\partial x^2} - \frac{K}{\rho_0 C_v}\frac{\partial^2 \rho_e}{\partial x^2}\right]. \tag{11.1}$$

Now the equation of state for viscosity alone is Eq. (3.1). Since we shall shortly apply this development to a monatomic gas we set $\zeta = 4\eta/3$. This step will be discussed more fully in Sec. 13. By differentiating the viscosity equation with respect to the time, we get

$$\frac{\partial p_e}{\partial t} = \frac{K_s}{\rho_0}\frac{\partial \rho_e}{\partial t} + \frac{4}{3}\frac{\eta}{\rho_0}\frac{\partial^2 \rho}{\partial t^2}. \tag{11.2}$$

One's intuition suggests, that one may modify (11.1) to include viscosity by adding to $K_s\dot{\rho}_e/\rho_0$ of the left-hand side, the term $(4\eta/3\rho_0)\partial^2\rho_e/\partial t$ and by adding to $K\rho_e/\rho_0$ of the right-hand side, the term $(4\eta/3)\dot{\rho}_e/\rho_0$. This leads to the equation

$$\frac{\partial p_e}{\partial t} - \frac{K_s}{\rho_0}\frac{\partial \rho_e}{\partial t} = \frac{4}{3}\frac{\eta}{\rho_0}\frac{\partial^2 \rho_e}{\partial t^2} + \frac{M\kappa}{\rho_0 C_v}\frac{\partial^2 p_e}{\partial x^2} - \frac{M\kappa}{\rho_0 C_v}\frac{\partial^2}{\partial x^2}\left[\frac{K\rho_e}{\rho_0} + \frac{4}{3}\frac{\eta}{\rho_0}\frac{\partial \rho_e}{\partial t}\right]. \tag{11.3}$$

(We use partial time derivatives here for convenience (see Sec. 2).) Equation (11.3) is really only one term of a tensor equation, as is Eq. (3.1), and applies only to a plane wave in this form. p_e is the negative of the stress at right angles to the wave vector.

We introduce the kinematic viscosity, namely,

$$\eta' = \eta/\rho_0, \tag{11.4}$$

and the thermometric conductivity which will be defined as

$$\kappa' = \frac{M}{\rho_0}\frac{\kappa}{C_v}. \tag{11.5}$$

Using solutions (2.12) and (2.14), (11.3) gives

$$P_e(i\omega + k^2\kappa') - R_e\left[ic_0^2\omega - \frac{4}{3}\eta'\omega^2 + k^2\kappa'\left(\frac{c_0^2}{\gamma} + \frac{4}{3}i\omega\eta'\right)\right] = 0. \tag{11.6}$$

Proceeding as usual with (2.17) and (2.18) we obtain ultimately,

$$\omega^3 - k^2\omega\left[c_0^2 + i\omega\left(\frac{4}{3}\eta' + \kappa'\right)\right] + ik^4\left(\frac{c_0^2}{\gamma} + i\omega\frac{4}{3}\eta'\right) = 0. \tag{11.7}$$

Equation (11.7) was first derived by Kirchhoff (K3) by another method; this justifies, in part, the use of (11.3).

We shall consider spatial absorption only here. For every value of ω there are two independent values of k. At low frequencies one k will give a very high value of α and is important, only near the source of sound. We shall call this solution k' to distinguish it from the usual acoustical solution. As Dr. H. Grad has pointed out, in a private communication, α increases with frequency and α' decreases so that in some region the primed solution may be important.

At present, the most interesting application of this theory is to rarefied monatomic gases. The most detailed experimental work has been done in helium by Greenspan (G3, G4) so that we shall specialize (11.7) to that gas. This reduces the constants in the equation.

The kinetic theory of transport phenomena in gases leads to the general relation

$$\kappa = \epsilon\eta c_v, \tag{11.8}$$

where c_v is the specific heat per unit mass at constant volume, and ϵ is a constant. The evaluation of ϵ, which depends on the assumed intermolecular force, has been summarized by Loeb (L16; p. 240). The most reliable value is that of Chapman and Enskog who used a repulsive force law of the form Gr^{-n} for effectively monatomic molecules, i.e., those in which the energy is translational only. Enskog showed that

$$\epsilon = \frac{5}{2}\cdot\frac{1+(n-5)^2/4(n-1)(11n-13)+\cdots}{1+3(n-5)^2/2(n-1)(101n-113)+\cdots}. \tag{11.9}$$

For $n=5$, $\epsilon = 5/2$. This is the celebrated result of Maxwell. Actually ϵ varies little with n. Thus for $n=2$, $\epsilon = 2.71$ and for $n \to \infty$, $\epsilon \to 2.52$. We therefore, choose the factor 5/2 for ϵ. Hence,

$$\kappa' = 5\eta'/2. \tag{11.10}$$

A word or two must be said about the limiting velocity, which depends on the adiabatic bulk modulus K_s. The latter in turn comes from the conventional thermodynamic (as distinct from the acoustical) equation of state, through the isothermal bulk modulus (Eq. (A-2) of Appendix II.) If we use the Holborn and

Otto equation for a real gas (see Zemansky (Z2; p. 94)) we may write

$$pV = A + Bp + Cp^2 + Dp^3 + \cdots, \tag{11.11}$$

where $A, B, C, D, \cdots$ are the virial coefficients, which are functions of the temperature and the mass of gas. Using (11.11) we obtain,

$$K = p[1 + (Bp/A)] \approx p. \tag{11.12}$$

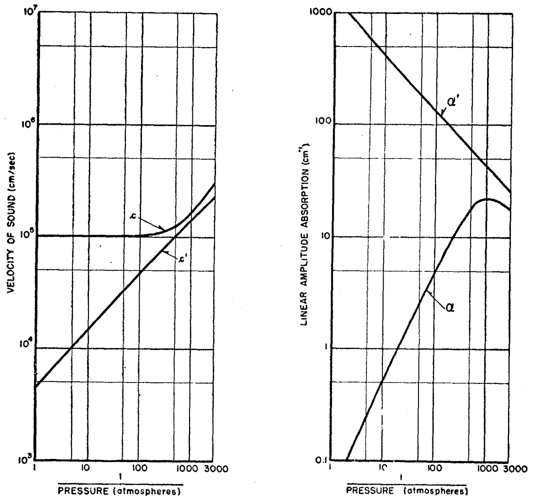
The term Bp/A is a correction term of the order of 0.05 percent under standard conditions for a gas like helium. We shall ignore this correction. We have thus reduced the constants in (11.7).

Instead of changing the frequency the experimeter usually varies the pressure and obtains curves (velocity and absorption), as a function of the pressure. The pressure enters into (11.7) through η' and κ'. Thus the imaginary parts of the coefficients of k^2 and ik^4 are proportional to ω/p_0. This suggests plotting the two velocities (ω/k_r and ω/k_r') and the two absorptions (α and α') against $1/p_0$, since $1/p_0$ plays a role similar to ω. This is done in Fig. I-6.[25] The graph figures indicate that even at 0.2 mm of Hg the "prime" wave is attenuated much faster. Some comparison of these curves with experiments will be made in Sec. 21.

General expressions which can be used for various frequencies and pressures have been developed by Greenspan (G4) and by Tsien and Schamberg (T4). For low enough frequencies and high enough pressures Wang Chang (W2) (see also Wang Chang and Uhlenbeck (W1)) has developed the following approximate expression for α

$$\alpha = \frac{7}{10}\frac{\omega}{c_0}\frac{\omega}{p}\eta\left[1 - 1.114\left(\frac{\omega\eta}{p}\right)^2\right], \tag{11.13}$$

which holds for monatomic gases since in this development they have assumed (11.8) with $\epsilon = 2.5$ and $\gamma = 5/3$.



(a) (b)

Fig. I-6 (a). Velocity *vs* 1/pressure for helium at room temperature. (b). Amplitude absorption *vs* 1/pressure for helium at room temperature.

(b) *Relaxation and Viscosity*

We shall now consider the combined effect of viscosity and relaxation. The equation of state for a simple relaxation process, Eq. (5.5), (6.14), or (7.59), is

$$\frac{\dot{\rho}_e}{\rho_0} - \frac{1}{K_s^\infty}\dot{p}_e + \omega_0\left(\frac{\rho_e}{\rho_0} - \frac{1}{K_s^0}p_e\right) = 0. \tag{11.14}$$

To add viscosity, which will give a term in $(1/\rho_0)\partial^2\rho/\partial t^2$ at high frequencies, and a term in $\dot{\rho}_e/\rho_0$ at low frequencies, we write

$$\frac{1}{\rho_0}\frac{\partial\rho_e}{\partial t} + \left(\frac{\zeta}{\rho_0 K_s^\infty}\right)\frac{\partial^2\rho_e}{\partial t^2} - \frac{1}{K_s^\infty}\frac{\partial p_e}{\partial t} + \omega_0\left[\frac{\rho_e}{\rho_0} + \left(\frac{\zeta}{\rho_0 K_s^0}\right)\frac{\partial\rho_e}{\partial t} - \frac{1}{K_s^0}p_e\right] = 0. \tag{11.15}$$

This equation is "written down by inspection" as was (11.2) and is a combination of (11.14) and (3.1). For simplicity, ζ is assumed to be independent of frequency. As we shall show in Sec. 14, one may derive Eq. (11.15) for a plane wave from Stokes's basic postulates of viscosity. Using (11.15) one may, by the method used before, obtain the following relations,

$$c^2 = \frac{1}{\rho_0}\frac{\omega_0^2 + \omega^2 + 2\omega^2\omega_0\zeta[(1/K_s^0) - (1/K_s^\infty)] + \omega^2\zeta^2[(\omega/K_s^\infty)^2 + (\omega_0/K_s^0)^2]}{(\omega_0^2/K_s^0) + (\omega^2/K_s^\infty)}, \tag{11.16}$$

and

$$\alpha = \frac{\frac{1}{2}\rho_0\omega^2 c\{\omega_0(1/K_s^0 - 1/K_s^\infty) + \zeta[(\omega/K_s^\infty)^2 + (\omega_0/K_s^0)^2]\}}{\omega_0^2 + \omega^2 + 2\omega^2\omega_0\zeta[(1/K_s^0) - (1/K_s^\infty)] + \omega^2\zeta^2[(\omega/K_s^\infty)^2 + (\omega_0/K_s^0)^2]}. \tag{11.17}$$

To simplify the above expressions we assume that the dispersion due to viscosity occurs at a frequency well beyond ω_0. Below the frequency where one gets viscous dispersion (we recall that $\omega_v = K_s/\zeta$, Sec. 3), the velocity is given by the usual expression

$$c^2 = \frac{1}{\rho_0}\frac{\omega_0^2 + \omega^2}{(\omega_0^2/K_s^0) + (\omega^2/K_s^\infty)} \quad \text{for} \quad \omega \ll \omega_v \quad \text{and} \quad \omega_0 \ll \omega_v, \tag{11.18}$$

---

[25] The following constants were used: $\omega = 2\pi \times 10^6$, $c_0 = 1.02 \times 10^5$ cm/sec, $\eta = 1.97 \times 10^{-4}$ poise, $\gamma = 5/3$, and $\rho_0 = 2.35 \times 10^{-7} p_0$ (in mm of Hg). These values correspond approximately to room temperature. If these values were extrapolated to exactly the same temperature, the difference between our curves and the corrected graphs would not show up in Fig. I-6.

while for the region well beyond ω_0, the velocity expression becomes

$$c^2=(K_s^{\infty}/\rho_0)[1+\omega^2(\zeta/K_s^{\infty})^2] \quad \text{for} \quad \omega_0 \ll \omega \ll \omega_v \tag{11.19}$$

and

$$\omega_0/\omega \ll \omega/\omega_v.$$

This equation is not identical with Eq. (3.15) because we have made a different approximation here: namely, we have set $k_r^2 \approx k_r^2-k_i^2$.

If the absorption is small, so that one can neglect the terms in ζ^2 and $\zeta(1/K_s^{\infty}-1/K_s^0)$, one obtains in place of Eq. (11.17)

$$\alpha=\frac{1}{2}\frac{1}{c_0^2}c\frac{\omega^2}{\omega_0^2+\omega^2}\omega_0\frac{K_s^{\infty}-K_s^0}{K_s^{\infty}} +\frac{1}{2}\rho_0 c\zeta\frac{\omega^2}{\omega_0^2+\omega^2}\left[\left(\frac{\omega}{K_s^{\infty}}\right)^2+\left(\frac{\omega_0}{K_s^0}\right)^2\right]. \tag{11.20}$$

This can be simplified still more by assuming that for the correction in the second term $K_s^0=K_s^{\infty}$ and $c_0=c$, or

$$\alpha=\frac{1}{2}\frac{1}{c_0^2}c\omega_0\frac{\omega^2}{\omega_0^2+\omega^2}\frac{K_s^{\infty}-K_s^0}{K_s^{\infty}}+\frac{1}{2}\frac{\omega^2}{c^3}\zeta/\rho_0 \tag{11.21}$$

for $\omega \ll \omega_v$ and $\omega_0 \ll \omega_v$, i.e., a simple combination of (5.8) with ω_0 in place of ω_r and (3.16).

For a frequency well beyond ω_0, the absorption becomes

$$\alpha=\frac{1}{2}\rho_0 c(K_s^{\infty})^2(1/K_s^0-1/K_s^{\infty})\frac{\omega_0}{(K_s^{\infty})^2+\omega^2\zeta^2} +\frac{1}{2}\rho_0 c\zeta\frac{\omega^2}{(K_s^{\infty})^2+\zeta^2\omega^2} \tag{11.22}$$

for $\omega_0 \ll \omega \ll \omega_v$ and $\omega_0/\omega \ll \omega/\omega_v$. Equation (11.22) makes the basic assumption that $k_r \gg k_i$. If this is not true (11.19) and (11.22) are not valid. The method used in Sec. 3 has to be employed.

Our conclusion is that at most frequencies of interest in ordinary fluids one would expect the effects of relaxation and viscosity to be additive. The dispersive effect of viscosity can be disregarded below ω_0. This agrees with Herzfeld and Rice in the range considered.

(c) *Double Relaxation*

Let us consider a model with two internal energies $U^{(1)}$ and $U^{(2)}$. We postulate no direct interaction between the two internal parts. This may occur in a fluid with a complicated molecule, which has two means of getting excited. If the activation energy for a direct transition from one type of excitation to another is very large compared to the activation energy from the unexcited to the excited levels, we may assume two separate U^{i}'s which do not interact. Other models are possible.

A simple way to proceed is to expand the treatment of Herzfeld and Rice. Schafer (S2) has considered two ways of doing this. We adopt his first treatment to our method and write

$$C_v^{(1)}dT_1+C_v^{(2)}dT_2+C_v^e dT^e+T^e\beta K dV=0, \tag{11.23}$$

$$\dot{T}_1=\frac{1}{\tau_1}(T^e-T_1), \tag{11.24}$$

and

$$\dot{T}_2=\frac{1}{\tau_2}(T^e-T_2). \tag{11.25}$$

This set of equations corresponds to Eqs. (6.1), (6.2), (6.3), and (6.4) of Sec. 6. $C_v^{(1)}$ is related to $U^{(1)}$ and $C_v^{(2)}$ is related to $U^{(2)}$. By differentiation and some relatively simple algebra, we obtain

$$C_v^e\frac{d^3T^e}{dt^3}+T^e\beta K\frac{d^3V}{dt^3}+\frac{1}{\tau_2}\left\{C_{v2}^e\frac{d^2T^e}{dt^2}+T^e\beta K\frac{d^2V}{dt^2}\right\} +\frac{1}{\tau_1}\left\{C_{v1}^e\frac{d^2T^e}{dt^2}+T^e\beta K\frac{d^2V}{dt^2}\right\} +\frac{1}{\tau_1\tau_2}\left\{C_v^t\frac{dT^e}{dt}+T^e\beta K\frac{dV}{dt}\right\}=0, \tag{11.26}$$

where we have defined

$$C_{v1}^e=C_v^e+C_v^{(1)}, \tag{11.27}$$

$$C_{v2}^e=C_v^e+C_v^{(2)}, \tag{11.28}$$

and

$$C_v^t=C_v^e+C_v^{(1)}+C_v^{(2)}. \tag{11.29}$$

Making use of (A-8) and (A-13) of Appendix II the acoustical equation of state becomes

$$\frac{C_v^e}{K}\frac{d^3p_e}{dt^3}-\frac{C_p^e}{\rho_0}\frac{d^3\rho_e}{dt^3}+\frac{1}{\tau_2}\left\{\frac{C_{v2}^e}{K}\frac{d^2p_e}{dt^2}-\frac{C_{p2}^e}{\rho_0}\frac{d^2\rho_e}{dt^2}\right\} +\frac{1}{\tau_1}\left\{\frac{C_{v1}^e}{K}\frac{d^2p_e}{dt^2}-\frac{C_{p1}^e}{\rho_0}\frac{d^2\rho_e}{dt^2}\right\} +\frac{1}{\tau_1\tau_2}\left\{\frac{C_v^t}{K}\frac{dp_e}{dt}-\frac{C_p^t}{\rho_0}\frac{d\rho_e}{dt}\right\}=0, \tag{11.30}$$

where

$$C_{p1}^e=C_{v1}^e+T^eV\beta^2K, \text{ etc.} \tag{11.31}$$

This equation further reduces to

$$\frac{1}{K_s^{\infty}}\frac{d^3p}{dt^3}-\frac{1}{\rho_0}\frac{d^3\rho_e}{dt^3}+\omega_2\left(\frac{1}{K_s^{(2)}}\frac{d^2p_e}{dt^2}-\frac{1}{\rho_0}\frac{d^2\rho_e}{dt^2}\right) +\omega_1\left(\frac{1}{K_s^{(1)}}\frac{d^2p_e}{dt^2}-\frac{1}{\rho_0}\frac{d^2\rho_e}{dt^2}\right) +\omega_1\omega_2\left(\frac{1}{K_s^0}\frac{dp_e}{dt}-\frac{1}{\rho_0}\frac{d\rho_e}{dt}\right)=0, \tag{11.32}$$

where

$$\omega_1 = C_{p1}^e / \tau_1 C_p^t, \tag{11.33}$$

$$\omega_2 = C_{p2}^e / \tau_2 C_p^t, \tag{11.34}$$

$$K_s^0 = KC_p^0 / C_v^0, \tag{11.35}$$

$$K_s^{(1)} = KC_{p1}^e / C_{v1}^e, \tag{11.36}$$

$$K_s^{(2)} = KC_{p2}^e / C_{v2}^e, \tag{11.37}$$

$$K_s^\infty = KC_p^e / C_v^e. \tag{11.38}$$

To arrive at (11.32) we have assumed that $C_v^{(1)}$ and $C_v^{(2)}$ are small. We have, therefore, written

$$C_p^e C_p^t = C_{p1}^e C_{p2}^e, \tag{11.39}$$

which neglects the term $C_v^{(1)} C_v^{(2)}$. Using (2.17), (2.18), and (11.32), we arrive at the following expression for the velocity

$$c^2 = \frac{1}{\rho_0} \frac{\omega^4 + \omega^2(\omega_1^2 + \omega_2^2) + \omega_1^2\omega_2^2}{(\omega^4/K_s^\infty) + \omega^2[(\omega_1^2/K_s^{(1)}) + (\omega_2^2/K_s^{(2)})] + \omega_1^2\omega_2^2/K_s^0} \tag{11.40}$$

while for the absorption

$$\alpha = \frac{1}{2} \frac{c\rho_0\omega^2}{\omega^4 + \omega^2(\omega_1^2 + \omega_2^2) + \omega_1^2\omega_2^2} \times \left\{ \omega^2\omega_1\left(\frac{1}{K_s^{(1)}} - \frac{1}{K_s^\infty}\right) + \omega^2\omega_2\left(\frac{1}{K_s^{(2)}} - \frac{1}{K_s^\infty}\right) + \omega_1^2\omega_2\left(\frac{1}{K_s^0} - \frac{1}{K_s^{(1)}}\right) + \omega_2^2\omega_1\left(\frac{1}{K_s^0} - \frac{1}{K_s^{(2)}}\right) \right\}. \tag{11.41}$$

We have assumed that $C_v^{(1)}$ and $C_v^{(2)}$ are small compared to C_v^e.

For simplicity we shall consider only the case where $\omega_2 \gg \omega_1$. Then we see that there are two dispersive ranges. Let us first explore the region around ω_1. Since in this case ω approximates ω_1, we have the further inequality $\omega \ll \omega_2$. Equations (11.40) and (11.41) reduce to

$$c^2 = \frac{1}{\rho_0} \frac{\omega^2 + \omega_1^2}{(\omega^2/K_s^{(2)}) + (\omega_1^2/K_s^0)} \tag{11.42}$$

for $\omega \ll \omega_2$ and $\omega_1 \ll \omega_2$ and

$$\alpha = \frac{1}{2} c\rho_0\omega^2 \left\{ \frac{\omega_1}{\omega^2 + \omega_1^2}\left(\frac{1}{K_s^0} - \frac{1}{K_0^{(2)}}\right) + \frac{1}{\omega_2}\left(\frac{1}{K_s^{(2)}} - \frac{1}{K_s^\infty}\right) \right\} \tag{11.43}$$

for $\omega \ll \omega_2$ and $\omega_1 \ll \omega_2$. Again, we have assumed that $C_v^{(1)}$ and $C_v^{(2)}$ are small compared to C_v^0.

The second dispersive regions occur when ω is in the region of ω_2. Now $\omega \gg \omega_1$ and the equations reduce to

$$c^2 = \frac{1}{\rho_0} \frac{\omega^2 + \omega_2^2}{(\omega^2/K_s^\infty) + (\omega_2^2/K_s^{(2)})} \tag{11.44}$$

for $\omega_1 \ll \omega$ and ω_2, and

$$\alpha = \frac{1}{2} c\rho_0 \left\{ \frac{\omega^2}{\omega^2 + \omega_2^2}\omega_2\left(\frac{1}{K_s^{(2)}} - \frac{1}{K_s^\infty}\right) + \omega_1\left(\frac{1}{K_s^{(1)}} - \frac{1}{K_s^\infty}\right) \right\} \tag{11.45}$$

for $\omega_1 \ll \omega$ and ω_2.

Equations (11.42) to (11.45) are exactly what one might expect by simply adding two relaxation effects together. The method of derivation, of course, has a serious limitation in that we have made rather restricting assumptions. If the ω_i's are about equal then one cannot split up the effects and one is required to use (11.40) and (11.41). In such a case, the simple conclusions arrived at here do not hold.

Schafer has carried out some numerical calculations on this problem. He has also considered a variation of Eqs. (11.23), (11.24), and (11.25).

Some authors (Korn (K15), and Alfrey (A1a)) have suggested summing over a large number of relaxation effects and even integrating over a range of values of τ. Their method is slightly different from ours in that they simply divide the pressure into p_1, p_2, p_3, etc., the first p being related to ρ_e/ρ_0 by a static equation—i.e., Eq. (1.4)—while the p_i (for $i \neq 1$) are related to ρ_e/ρ_0 by means of a Maxwellian equation—i.e., Eq. (2.2). This second approach has the great advantage of mathematical simplicity. However, it seems to depart a great deal from the simple physical picture presented here. It is essentially like a mathematical way of expressing data which does not give much physical insight into the problem.

12. CONCLUSION

The summary of the individual effects is given in Sec. 9. Actually the theory presented in this chapter is rather formal in that it does not attempt to evaluate some of the basic parameters in the equations. In Sec. 3 we talk about ζ without attempting to evaluate it. If Stokes's relation is assumed, η still is not evaluated because we have to know the shear viscosity which is usually obtained from experiments. In Sec. 6 we have two unknowns τ and C_v^i. They appear as parameters in the theory. This is also true of the A's of Eq. (7.3) and the B's of Eq. (7.14). The theory also assumes partial equilibrium without considering the importance and consequences of this hypothesis. For instance, can one really write Eq. (7.3) in the form (7.9)? That is, is one allowed to assume that the A's are functions of the temperature and the pressure? These assumptions are certainly a weakness in the theory and offer an opportunity for further study. Attempts to evaluate τ of

Sec. 6 have been made in the past and work is continuing along this line. The evaluation of ζ and η is a problem in kinetic theory of gases and liquids. For gases, $C_v{}^i$ can be calculated from optical data and attempts to evaluate the B's of (7.14) are also in progress. We shall make no attempt to review these problems here. They are mentioned simply to point out that they do exist and imply that the theory of sound absorption is far from complete. One may hope, however, that the framework of the theory is correct and that the problem is to discover what combination of the various effects, viscosity, heat conduction, and relaxation accounts for the experimental results. Of course one cannot be sure of this until all the data have been analyzed and until better methods of computing the various parameters have been found.

From Sec. 11 we can conclude that the contribution of the various mechanisms can usually be added together. This has been proven, only for relatively simple models neglecting higher order terms. In many cases the specific heat need not be small, and higher order terms may well be considered. Consideration of more elaborate models than have been made here or by Schafer (S2) would be useful.

Chapter II. The Effects of Viscosity on Sound Absorption

Usually, the absorption of sound due to viscosity is treated very briefly, since it is generally believed to be well understood. This idea stems from the acceptance of Stokes's relation between the viscosity coefficients. The use of this relation has been questioned recently for liquids and polyatomic gases by Tisza (T3) as well as by Liebermann. Further, experiments of Liebermann (L11) indicate that Stokes's assumption may be incorrect for many liquids. If this interpretation is true, then relaxation (Sec. 6 and Sec. 7) may not play a role in some liquids.

In view of the renewed interest in viscosity, it seems advisable to return to the basic assumption made by Stokes over a century ago and consider the limitation of his proof, then bring the subject up to date by considering the special case of gases, the recent suggestions of Tisza, and discuss some of the problems of second-order acoustic fields. Some of the developments are found in standard texts, but we hope that by bringing all of them together the reader's attention may be focused on the basic problems in this field.

13. STOKES'S RELATION BETWEEN THE VISCOSITY COEFFICIENTS

We shall here follow closely the derivation of Stokes's relation given by Lamb (L1; p. 571). As pointed out in the first chapter, a general stress can be characterized by three stresses along the principal axes of stress, and a general strain is characterized by three strains along the principal axes of strain. A definition of an isotropic body is that the principal axes are in the same direction. By simple generalization, we replace the six components of strain (these reduce to three along the principal axes) by six components of the rate of change of strain. Analogous to Eq. (1.1) we write:

$$\begin{aligned} &\dot{e}_{xx}=\frac{\partial u_x}{\partial x}, \quad \dot{e}_{yz}=\dot{e}_{xy}=\frac{\partial u_y}{\partial z}+\frac{\partial u_z}{\partial y},\\ &\dot{e}_{yy}=\frac{\partial u_y}{\partial y}, \quad \dot{e}_{zz}=\dot{e}_{xz}=\frac{\partial u_z}{\partial x}+\frac{\partial u_x}{\partial z},\\ &\dot{e}_{zz}=\frac{\partial u_z}{\partial z} \quad \dot{e}_{xy}=\dot{e}_{yz}=\frac{\partial u_x}{\partial y}+\frac{\partial u_y}{\partial x}. \end{aligned} \tag{13.1}$$

The u's are the components of velocity along the x, y, and z, axes. By rotating the axes, one may reduce these quantities to three—i.e., $\dot{e}_1$, $\dot{e}_2$, and $\dot{e}_3$. Here $\dot{e}_1$ is defined as $\partial u_1/\partial x_1$, where u_1 is the component of velocity along the first principal axis.

Analogous to the static case, we define an isotropic viscous body as one in which the principal axes of rate of strain are in the same direction as the principal axes of stress. Therefore,

$$p_i=-p_0+\eta'\textstyle\sum_j\dot{e}_j+2\eta\dot{e}_i. \tag{13.2}$$

Here η and η' are the viscosity coefficients, η being the shear viscosity and $\eta'+\frac{2}{3}\eta$ the bulk viscosity. The reader will recall that in elasticity a tensor is positive, while pressure is negative. The p's with subscripts are components of the stress matrix, and the negative sign appears because of the difference between the ordinary pressure and tension. In the usual development p_0 is the static pressure.[26] Shortly we shall attempt the generalization of (13.2) and p_0 will be the nonviscous pressure which may not equal the static value.

By rotating the axes, one finds that for arbitrary Cartesian coordinates,

$$\begin{aligned} p_{jj}&=-p_0+\eta'\nabla\cdot\mathbf{u}+2\eta\dot{e}_{jj},\\ p_{ji}&=\eta\dot{e}_{ji} \quad \text{for} \quad i\neq j, \end{aligned} \tag{13.3}$$

where

$$\nabla\cdot\mathbf{u}=\dot{e}_{xx}+\dot{e}_{yy}+\dot{e}_{zz}. \tag{13.4}$$

If we have a static fluid or uniform motion, the e's are zero and

$$p_1=p_2=p_3=-p_0.$$

Let us now find the relations between $\sum_i p_{ii}$ along the principal axes and along any arbitrary Cartesian system. One may show from geometrical arguments that the pressure along the x axis is related as follows to the pressure along the principal axes:

$$p_{xx}=p_1l_1{}^2+p_2l_2{}^2+p_3l_3{}^2, \tag{13.5}$$

where the l's are the direction cosines. From similar ex-

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[26] In this section, as well as the next, p_0 is not the equilibrium pressure. In a fluid where both the e_j's and $\dot{e}_j$'s are not zero, p_0 will not equal the equilibrium value.

pressions for p_{yy} and p_{zz}, we obtain the equality

$$p_{xx}+p_{yy}+p_{zz}=p_1+p_2+p_3. \tag{13.6}$$

The x, y, z system is completely arbitrary, and Eq. (13.6) makes it sensible to define the average pressure, p_{av}, as

$$p_{\mathrm{av}}=-\tfrac{1}{3}(p_{xx}+p_{yy}+p_{zz})=-\tfrac{1}{3}(p_1+p_2+p_3). \tag{13.7}$$

For the static case, we see that

$$p_{\mathrm{av}}=p_0,$$

while for the dynamic case,

$$p_{\mathrm{av}}=-p_0+\tfrac{1}{3}(3\eta'+2\eta)\textstyle\sum_i \dot{e}_{ii}. \tag{13.8}$$

Equation (13.8) is the core of the lengthy argument regarding Stokes's viscosity relation. Is p_{av} equal to p_0, or are they not equal? Stokes's original proof in 1845 (S17) can hardly be considered rigorous. Stokes himself admits this in his original paper.

The original assumption is that

$$p_{\mathrm{av}}=p_0, \tag{13.9}$$

and

$$3\eta'+2\eta=0. \tag{13.10}$$

General thermodynamic arguments may be presented to show that the following equality or inequality must hold:

$$\eta'+2\eta/3\geqslant 0. \tag{13.11}$$

The proof of this relation may be found in an elegant paper by J. H. C. Thompson (T2a).

Basset (B3), in his treatment, derives Stokes's relation for gases by assuming that Eq. (13.9) holds. This he claims is a third assumption required to obtain Stokes's viscosity equations, i.e., Eqs. (13.3) and (13.10). He considers that liquids are incompressible and that $\rho_e=0$.

To find a more rigorous proof of Eq. (13.10) we must turn to models of the fluid used, and the subject separates itself into two parts—the gas and the liquid.

(a) *Stokes's Relation for a Gas*

At present, it seems fair to state that the general basis of the kinetic theory is accepted for real monatomic gases, (J1). From the rigorous development of the theory, one may show that Stokes's relationship holds. The only assumption as to the nature of the gas is that one has central forces between molecules. A further assumption is usually made that the process occurs at constant temperature. This, of course, is not true, and would lead to a term arising from thermal diffusion. The effect of thermal diffusion is a separate one which one would expect in the first-order approximation to be superimposed on viscosity. Polyatomic gases have additional degrees of freedom which are not considered in the usual development. Recently Grad (G2b and G2c) developed a new kinetic theory of gases. For monatomic gases Stokes's relation is not changed.

Wang Chang and Uhlenbeck (W2) (see also Wang Chang (W1)) recently developed equations for the absorption and velocity dispersion, using terms (nonlinear) beyond those which were considered by Stokes. These terms arise from an expansion of the kinetic theory. Assuming that ϵ of (11.8) equals 2.5, they find that α of (11.13) for the combined effect of heat conduction and viscosity should be replaced by

$$\alpha=\frac{7}{10}\frac{\omega}{c_0}\frac{\omega}{p}\eta\left[1-3.68\left(\frac{\omega\eta}{p}\right)^2\right]. \tag{13.12}$$

One would expect, therefore, that one is not allowed to expand Stokes's equation (for a gas) and obtain corrections to the conventional viscosity absorption term, i.e., Eq. (9.5).

Experimental work by Greenspan (given in Sec. 21 below) indicates, however, that Stokes's approximation gives better results for He gas than do "corrected" expressions. For absorption measurements, the agreement between Stokes's theory and experiment is very good; for velocity dispersion, both Stokes and higher approximations are off, the Stokes's form being slightly inferior.

One must therefore, conclude that at present our knowledge is too limited to do effective work using terms beyond those derived by Stokes. The work of Wang Chang and Uhlenbeck indicates that one should attempt to derive an expression for sound absorption and dispersion from a generalized transport equation rather than the cruder methods presented here. For sound absorption, the transport equation, however, does not seem to give reliable results at present. Further experimental and theoretical work in this field is very necessary. It is to be hoped that Grad's new development will give better results than the previous theories.

(b) *Stokes's Relation for a Liquid*

The kinetic theory of liquids is at present being developed by Born and Green (B24) and by Kirkwood (K5). A recent paper by Kirkwood, Buff, and Green (K6) indicates that the calculation of the viscosity coefficients is still in a primitive stage. Indeed, they rely on sound absorption measurements to estimate the value of the bulk viscosity coefficient. Turning to experimental data, we find (Sec. 24) an agreement between theory and experiment for several simple liquids. This indicates that Stokes's relation holds for some liquids.

On the basis of this discussion, we must conclude that Stokes's relation for liquids cannot at present be established on theoretical grounds. Since the burden of proof should be on the establishment of the relation, the Stokes's relation cannot be accepted unconditionally. As Basset has pointed out, the viscosity relation is a basic assumption made when setting up the viscosity equation for fluids. This procedure can be justified theoretically for real, dilute monatomic gases. Further, there is good experimental evidence to support this assumption in some gases and liquids, and this assumption leads to no contradiction at present.

14. VISCOSITY AND SOUND ABSORPTION

Let us return to Eq. (13.2) and consider its connection with an acoustical equation of state. First, consider the case where there is no relaxation. p_1, p_2, and p_3 are related to the force on an element of volume. These p's have to be used in the equation of motion (2.10). Also p_0 has to be related to the condensation by Eq. (1.4) or an equivalent relation. If the p_i's were related directly to the condensation, then the viscous term of Eq. (13.2) would not play a role. Using Eq. (1.4), i.e.,

$$(p_0)_e = K_s \rho_e / \rho_0 \tag{14.1}$$

and Eq. (13.3), we get

$$\begin{aligned}(p_{jj})_e &= -K\rho_e/\rho_0 + \eta' \nabla \cdot \mathbf{u} + 2\eta \dot{e}_{ii} \\ p_{ji} &= \eta \dot{e}_{ji}.\end{aligned} \tag{14.2}$$

Equation (14.2) is then the basic acoustical equation of state for a viscous medium. One should emphasize that it is a tensor relation and when substituting into the equation of motion, the term on the right must be replaced by terms involving tensors or dyads.

If we are interested in a plane wave traveling along the x axis, $\mathbf{q}$ becomes $q_x = f(x)$, and

$$p_e = (-p_{11})_e = K_s \frac{\rho_e}{\rho_0} + (2\eta + \eta') \frac{\partial}{\partial t} \frac{\rho_e}{\rho_0}, \tag{14.3}$$

where

$$\dot{\rho}_e / \rho_0 = -\partial u_x / \partial x$$

by Eq. (2.11). The use of (2.11) means that a slight approximation has been made in (14.3); it is the same type of approximation made when using (2.10) and (2.11). This is equivalent to Eq. (3.1). Here p_e is the excess pressure at right angles to the x axis, which does not equal the pressure in the other directions. By equating Eq. (14.3) to Eq. (3.1), we have

$$\zeta = \eta' + 2\eta. \tag{14.4}$$

Or, if Stokes's viscosity relation holds,

$$\eta' = -2\eta/3 \tag{14.5}$$

and

$$\zeta = 4\eta/3, \tag{14.6}$$

the standard classical expression.[27]

We should like to combine viscosity and relaxation, by assuming that (1.4) is not valid and considering effects within and between molecules. In general, one is not permitted to make this separation. However, for many substances, namely, gases, many liquids, and molecular solids, such a step may be useful. For substances made of complex molecules, the phase lag between pressure and density occurs because of intermolecular processes and processes within the molecules themselves. The intermolecular processes can be accounted for by means of viscosity, while the intramolecular processes can be accounted for by means of a relation between ρ_e and p_0'. When generalizing (14.2), we replaced p_0 by p_0' where p_0' includes both the static pressure and the pressure arising from the relaxation process. (It is necessary to interpret "within the molecules" quite broadly (Sec. 7).) The above approach is probably only a rough approximation to the truth, which holds for gases and probably for some liquids.

It is impossible to justify completely this last paragraph. Indeed, for some substances, this separation may be incorrect and useless, but there are some arguments to support this concept.

For Gases:—As mentioned above, the rigorous theory of real gases requires us to accept Stokes's relation, if intramolecular effects are ignored. The method of statistical thermodynamics gives us a model which associates the internal processes with a relation between ρ_e and p_0'. It seems, therefore, completely logical to make this separation for a gas. The general kinetic theory of gases is preserved, yet the absorption is explained. More elaborate kinetic theories may be able to arrive at a relation between p_e and ρ_e.

For Liquids:—Here we know very little at present. The calculation of Hall (H1) and the model of a general relaxation implies this separation, since relaxation is something that happens within a molecule or a small cluster of molecules. Further, data taken by Liebermann on ethyl formate can be easily explained by this hypothesis (M2a).

We, therefore, assume that p_0' is related to ρ_e by means of a relaxation equation (Eq. (6.14)). Here p_0' is no longer a static pressure. It is only the static pressure for processes slow relative to the internal equilibrium. The acoustic equation for viscosity and relaxation becomes

$$\frac{1}{\rho_0}\frac{\partial \rho_e}{\partial t} + \frac{1}{K_s^\infty}\frac{\zeta}{\rho_0}\frac{\partial^2 \rho_e}{\partial t^2} - \frac{1}{K_s^\infty}\frac{\partial p_e}{\partial t} + \omega_0\left(\frac{\rho_e}{\rho_0} + \frac{1}{K_s^0}\frac{\zeta}{\rho_0}\frac{\partial \rho_e}{\partial t} - \frac{1}{K_s^0} p_e\right) = 0. \tag{14.7}$$

This is identical to Eq. (11.15) and is the "derivation" mentioned.

Tisza (T3) has suggested that one should force all the effects into an equation similar to Eq. (14.3). η is the ordinary shear viscosity, but $3\eta' + 2\eta$ no longer has its traditional meaning. By making this sum complex and frequency dependent, one may obtain the experimental results for gases. In this case, the sum will be dependent on the type of process, i.e., isothermal or adiabatic. To evaluate the sum, Tisza uses the conventional theory of

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[27] The standard derivations (see Lamb (L1; p. 646); Rayleigh (R2; Vol. II, p. 315)) proceed in a slightly different manner. They use Eq. (13.3) and the equation of motion, then in a final step introduced the static equation of state (1.4). We have proceeded differently to try to bring out the equation of state for the viscous process to compare it with other processes.

thermal relaxation. This approach, while mathematically correct, seems less useful than the usual approach. If one uses Tisza's method and adopts it to other hydrodynamical problems, one must keep in mind that his evaluation of $3\eta'+2\eta$ is for an adiabatic process, and that it may be zero for an isothermal process.

Frenkel and Obraztsov (F4) have suggested that one may define a low frequency bulk viscosity by returning to (6.14), i.e.,

$$\frac{\dot{\rho}_e}{\rho_0}-\frac{1}{K_s^{\infty}}\dot{p}_e+\omega_0\left(\frac{\rho_e}{\rho_0}-\frac{1}{K_s^{0}}p_e\right)=0. \tag{14.8}$$

For a slow process $\dot{p}_e=(K_s^0/\rho^0)\dot{\rho}_e$, or we may write (14.8) in the form

$$p_e=\frac{K_s^0}{\rho_0}\rho_e+\frac{K_s^0}{\omega_0}\left(\frac{K_s^{\infty}-K_s^0}{K_s^{\infty}}\right)\frac{\dot{\rho}_e}{\rho_0}. \tag{14.9}$$

For low frequencies,

$$\eta''=\frac{K_s^0}{\omega_0}\left(\frac{K_s^{\infty}-K_s^0}{K_s^{\infty}}\right) \tag{14.10}$$

can be defined as a viscosity coefficient. To extend η'' to higher frequencies it has to be made complex and frequency dependent. While one can make the mathematical treatment of viscosity and relaxation similar by using Eq. (14.10), the physical difference shown in Fig. I-4 remains.

15. SECOND-ORDER EFFECTS

It is well known that the derivation of the standard acoustical wave equation is based on certain approximations involving the neglect of terms usually considered too small to be retained; e.g., terms like $\mathbf{u}V\cdot\mathbf{u}$ in the hydrodynamic equations of motion and $\mathbf{u}\cdot\nabla\rho$ in the equation of continuity. Such terms must be retained or accounted for in some way when higher order effects are considered. It is interesting to note the breakdown of the analogy between acoustic and electromagnetic radiation in this respect: no approximations are involved in the derivation of the electromagnetic wave equation, since it follows directly from the field equations. It is consequently not permissible to draw conclusions about second-order quantities in acoustics such as average energy and radiation pressure, from electromagnetic analogies.

Though much work on second-order acoustical effects has been published by Eckart (E3), Bergmann (B16), and Westervelt (W3) among others, the present authors believe that the field has not yet been sufficiently explored to justify a thorough review. This section therefore will be confined to a few general remarks.[28]

A convenient method of dealing with second-order effects has been used by Eckart. He expands the density, pressure and particle velocity in series of terms of successively decreasing order of magnitude as in standard perturbation technique. Thus

$$\begin{aligned} p&=p_0+p_1+p_2+\cdots,\\ \rho&=\rho_0+\rho_1+\rho_2+\cdots,\\ \mathbf{u}&=0\ +\mathbf{u}_1+\mathbf{u}_2+\cdots. \end{aligned} \tag{15.1}$$

Here p_0[29] and ρ_0 are the zero-order terms, i.e., equilibrium pressure and density. Terms like p_1, ρ_1, and $\mathbf{u}_1$ are first-order terms, etc. A product like $\rho_0\mathbf{u}_1$ is assumed to be of first order while $\rho_1\mathbf{u}_1$ is of second order, i.e., in this respect on a par with p_2, ρ_2, and $\mathbf{u}_2$.

The usual acoustic wave equation is satisfied by terms of the first order. Let us consider what can be done with a problem involving second-order terms, such as the energy density in a sound field (M3). The stored potential energy for compressing a mass of fluid Δm is

$$-\int p\,dV=\Delta m\int_{\rho_0}^{\rho_0+\rho_1+\rho_2}p\frac{d\rho}{\rho^2}$$

$$=\Delta m\int\frac{(p_0+p_1)}{(\rho_0+\rho_1)^2}d\rho. \tag{15.2}$$

For a nonabsorbing medium we can use the relation $p_1=c_0^2\rho_1$ and obtain for the stored energy

$$\begin{matrix} & \text{(a)} & \text{(b)} & \text{(c)} & \text{(d)} \end{matrix}$$

$$\frac{\Delta m}{\rho_0^2}\left\{p_0(\rho_1+\rho_2)+\left(\frac{c_0^2}{2}-\frac{p_0}{\rho_0}\right)\rho_1^2\right\}. \tag{15.3}$$

In Eq. (15.3), the terms have the following meaning: (a) is a harmonic term, (b) arises because of Eq. (15.1), (c) is the term which is commonly given. We shall call it the Rayleigh term, since it dates back to that period. (d) is a term which, as far as the authors know, has not been included previously. At least it does not appear in the "standard" treatments.

For a liquid where $c\approx 10^5$ cm/sec, $p_0\approx 10^6$ dynes/cm^2 and $\rho_0\sim 1$, the ratio of (c) to (d) is about 1 to 10^{-4}, and the omission of (d) is correct. One may likewise show that one can omit (b) for liquids. For a gas, $c\sim 3\times 10^4$, $\rho\sim 10^{-3}$, and (d) cannot be omitted. To obtain the average of (15.3) for a gas one needs more exact solutions than are usually used.

A very complicated problem exists in setting up the viscosity tensor in the equation of motion for a fluid. The viscosity coefficients are highly dependent on the temperature, and, since one is interested in an adiabatic process, the variation with temperature must be taken into account. Correcting the viscosity coefficient in the tensor, i.e., expanding η and η' in Eq. (13.3) in terms of ρ_1, leads to very complicated equations which have not been studied fully. Finally, it would seem advisable to include relaxation in any development of second-order acoustical effects.

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[28] Further details will be published elsewhere.

[29] p_0 is the equilibrium pressure and therefore has a different meaning in this section from p_0 of Secs. 13 and 14.

In conclusion we should like to mention Eckart's (E3) theory and Liebermann's experiments (L11). Using these data, one may conclude that Stokes's viscosity relation does not hold, and that its breakdown is sufficient to explain the absorption in liquids. While this theory and experiment are of major importance, they, by themselves, do not resolve the problem. The reason for this conclusion is that when one carries out Eckart's theory a little further, one can show that a relaxation effect combined with viscosity in a manner similar to (14.7) can equally well explain the results (M2a). The recent work of Nyborg (N2) on acoustic streaming adds weight to this conclusion. Further, the viscosity idea alone cannot explain Liebermann's experiment on ethyl formate, or the work of Lamb and Pinkerton (L2) on acetic acid. More work is required here, before one fully understands the phenomenon of streaming and its relation to absorption.

Chapter III. Experimental Methods of Sound Absorption Measurements

Sound absorption measurements can be classified roughly into three groups: (1) mechanical, (2) optical, and (3) electrical. Although some absorption measurements have been made on the basis of thermal effects, notably by Richardson (R5), their reliability is open to some question, and they will not be considered here.[30] We shall give here only a brief outline of the most frequently used methods, referring the reader to particular papers for the experimental details. We shall also endeavor to classify the methods by range of usefulness and accuracy. In this way we shall be better able to judge the validity of the experimental measurements.

16. MECHANICAL METHODS

The mechanical method which is most frequently used is based on radiation pressure. When a rigid wall confronts a sound beam, there is a difference between the pressure at the wall and the pressure in the same medium at rest, behind the wall (i.e., the pressure in the medium in the absence of the beam). This net pressure is known as the Langevin radiation pressure, and is approximately equal in magnitude to twice the energy density of the oncoming sound wave (B18, B34, H7). This net pressure can be employed to measure a quantity proportional to the sound intensity in several ways. For example, if the sound is allowed to rise vertically in a tank of liquid, a cone or plate may be suspended in the sound field, and its apparent weight measured both in the presence and absence of the sound beam (C4, H14). In a variation of this method, a horizontal sound beam may be used to displace a plate or bead, either on the end of a long wire (F3), or mounted as the vane of a torsion balance (A3). Finally, the movable vane has been made one plate of a condenser, and the intensity measured by the change in capacitance of the system (B38).

The successful use of these mechanical methods is confined almost exclusively to liquids. As a class, measurements of this type suffer from five general difficulties:

1. Surface tension or other retarding forces which act on the wire or detector may easily be of a magnitude comparable to that of the forces being measured (which usually are of the order of 10 dynes). These extraneous forces can be reduced in magnitude, but are never entirely eliminated. Their effect is to cause a "sticking" of the detector in the vicinity of its balance point, thus decreasing the accuracy with which the apparent weight changes can be measured.

2. Specular reflection from the walls of the container, if it is too narrow, or from the detector, will result in standing waves, and lead to grossly incorrect results. This was the case in some of the early work, particularly that of Sörensen (S11), and Hartmann and Focke (H5). A rather striking confirmation of this difficulty was given by Claeys, Errera, and Sack in the article previously cited (C4). These observers measured the apparent absorption with tanks of different diameters, and were able to get almost any desired (higher) value for the absorption coefficient by using a sufficiently narrow container. As the diameter of the container was increased, the apparent value of the absorption coefficient fell off to a constant value.

3. It would seem that the first error mentioned above could be minimized by increasing the sound intensity. However, high intensity can cause cavitation, in which case a larger fraction of the energy of the beam is lost than in simple propagation. Cavitation can be avoided if the instantaneous pressure in the medium is not permitted to fall below zero. The average energy density $\bar{E}$ in a plane wave is related to the maximum excess pressure p_e by

$$\bar{E}=p_e^2/2\rho_0c^2, \qquad (16.1)$$

where c is the velocity of propagation and ρ_0 is the mean density of the liquid. If the pressure in the medium is not to fall below zero, the excess pressure should not exceed the hydrostatic pressure.[31] If this latter is the atmospheric value, then for water, $\bar{E}\sim 20$ dynes/cm^2. Since the mean intensity $\bar{I}$ is given by $\bar{I}=\bar{E}c$, this limits us to intensities no higher than about 0.3 watt per sq cm.

4. As its frequency is lowered, a sound beam diverges more and more, so that a detector of fixed size will

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[30] A refinement of this technique, involving hot-wire interferometry, has recently been reported by Matta and Richardson (M4). This instrument is believed by its designers to give very accurate measurements of the absorption coefficients in gases.

[31] If a dissolved gas is present, the excess pressure should not exceed p_A-p_V where p_A and p_V are the atmospheric and vapor pressures respectively. This has been pointed out by Boyle and Taylor (B33).

eventually fail to intercept the entire beam. Consequently, the simple formula for plane waves

$$I=I_0e^{-2\alpha x} \qquad (16.2)$$

cannot correctly be employed. (Here I_0 is the sound intensity at the plane $x=0$ and I is the intensity at $x=x$.)

5. Hydrodynamic flow (a manifestation of quartz wind) can itself exert a net force on the detector, giving rise to an incorrect value of the radiation pressure. This can be reduced by placing a thin Cellophane screen (H14) directly in front of the detector. This serves to stop the liquid flow while it allows the sound to pass through with small loss.

These various difficulties limit the radiation pressure method to the use of moderate sound intensities at high frequencies. For most liquids, careful measurements with the radiation pressure method can be made with a probable error of ±5 or 10 percent at frequencies above 10 megacycles. In the region 3–10 megacycles, the measurements are less trustworthy, except in liquids of fairly high absorption. (In liquids of very high viscosity, the detector cannot move with sufficient freedom, so that an upper limit of usefulness also exists.) Few if any measurements made below 3 megacycles can be relied upon.[32]

17. OPTICAL METHODS

Most optical measurements of the absorption coefficient have been carried out by means of a method developed by Biquard (B20), based on the Debye-Sears (D2) effect. While the number of measurements made recently by this method is not large, it is still a useful method within certain ranges of frequency.[33]

In the Debye-Sears experiment, Fig. III-1, light from a narrow slit traverses a beam of sound which is at right angles to the light. The light is then focused on a screen. The successive compressions and rarefactions of the sound beam alter periodically the refractive index of the liquid. Thus the sound beam acts as a diffraction grating, and a series of parallel diffraction lines are produced on the screen. The greater the intensity of the sound beam, the more the light is diffracted away from the main beam (i.e., the central maximum). In the application of Biquard, the light in the main beam falls on a photocell, and a current is measured which is proportional to the sound intensity. If the intensity of the sound at a distance x cm from the crystal is $I_0e^{-2\alpha x}$, then the loss in intensity of the light beam at this point is proportional to this quantity, and hence if J_0 is the intensity of the transmitted light in the absence of sound, and J is the intensity in the presence of sound,

$$1-(J/J_0)=kI_0e^{-2\alpha x}. \qquad (17.1)$$[34]

The output θ of the photocell is directly proportional to the incident light intensity. Hence

$$1-(\theta/\theta_0)=kI_0e^{-2\alpha x}. \qquad (17.2)$$

In the measurement θ is measured as a function of x. If the equation is put in the form

$$\ln[1-(\theta/\theta_0)]=\ln kI_0-2\alpha x, \qquad (17.3)$$

then a graph of $\ln[1-(\theta/\theta_0)]$ *vs* x will have a slope of -2α, so that the absorption coefficient can be determined.

This measurement suffers from many of the same limitations as the mechanical method. Thus, it assumes a plane wave with constant intensity across the wave front. As the frequency decreases, the divergence of the beam increases, so that the method is not a practical one at low frequencies.

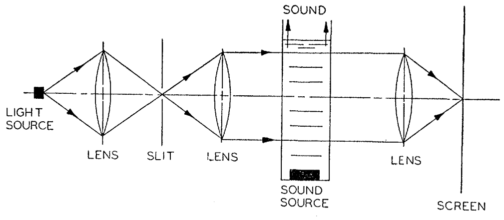

FIG. III-1. Sound absorption measurement by the optical method.

Multiple reflections and high intensity are responsible for the same type of errors here as in the mechanical method. In addition, high intensity will cause appreciable excitation of higher order images, in which case some light may be diffracted back into the main beam. More simply, the loss in light intensity in such a case is no longer directly proportional to the sound intensity. Finally, alignment problems are very important. The light beam must be narrow, and accurately perpendicular to the sound beam; the medium must be sufficiently transparent so that appreciable light can penetrate it.

More recent observers have made improvements in the general technique. Burton (B37) employs a monochromatic light source and an electron-multiplier tube so that much narrower light beams and lower acoustic intensities can be used.

The frequency range over which optical methods can be trusted is similar to that for mechanical methods. Where comparison by method is possible in a given liquid, good agreement is obtained by most observers using optical methods in comparison with other methods. Below 10 megacycles many of the measurements which are available are not in good agreement with those of other methods. Most of these lower fre-

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[32] Strictly speaking, any such classification of results must take the absorption into account, since as it increases, the errors due to (2) and (3) become proportionally less significant. As a general rule, measurements in which the values of the amplitude absorption coefficient are larger than 0.05 cm^{-1} are quite reliable when the tank is at least 10 cm in diameter; values in the range 0.01 cm^{-1} to 0.05 cm^{-1} are less satisfactory, and values below 0.01 cm^{-1} are usually invalid in a tank of this size.

[33] Within the past year, however, D. Sette (S6a) has published a considerable number of measurements obtained by an optical method. These results appear to be of high accuracy.

[34] k is an experimental constant not related to the previous k's.

quency measurements, such as those of Parthasarathy (P1), are older works, where the techniques were less satisfactorily developed. The recent works of Burton (B37), Willis (W7), and Sette (S6, S6a) indicate that agreement with accepted values in some liquids exists at frequencies as low as 4 mc.

Hydrodynamic flow is also a serious problem with the optical method, since it leads to a sizeable variation in the optical properties of the medium. As mentioned above, a Cellophane screen can be used to decrease the amount of this flow.

18. ELECTRICAL METHODS

In this section are grouped all methods in which a microphone, piezoelectric or otherwise, is used to receive sound signals. There are four general methods used to determine the absorption coefficient with such equipment and each of these will be discussed in turn.

(*a*) *Interferometric Methods*

In the basic interferometric method, a plane quartz crystal is used as a transducer. A plane reflector is set accurately parallel to the transducer at a distance which can be varied. If sound waves emanate from the transducer, they will be reflected from the reflecting surface. If the reflected wave returning to the crystal is 180° out of phase with the signal emanating from the crystal, the disturbance at the crystal will be reduced essentially to zero. This will produce a considerable rise in the plate current of the output stage of the driving oscillator (or in the plate current in the tube). Since the problem is essentially one of standing waves, it is clear that a maximum in the plate current will be produced every time the reflector is moved a half-wavelength.[35] The interferometer is therefore of fundamental importance in the measurement of the sound velocity.

The instrument has also been used to measure absorption. The variation in the current reading in the output stage of the driving oscillator was shown by Pielemeier (P5) to be proportional to the excess pressure in the sound beam at the face of the crystal. If now the reflector is moved through a distance x, the path length is increased by $2x$, so that the pressure of the returning wave will be decreased by the factor $e^{-2\alpha x}$. Hence, by registering the current at two maxima, the absorption coefficient can then be computed.

The work of Hubbard and his associates (A2, H15, H16, S14, S16) indicates that the current is a more complicated function of the absorption coefficient, the reflection coefficient of the reflecting surface, and the distance moved by the reflecting plate.

The interferometer has become a standard instrument for absorption measurements in gases. It has also had some use in liquids. Recently, Hunter and Fox (H18, H19) have developed an interferometer using the liquid-air interface as the reflecting surface.

The use of an interferometer is limited by the following difficulties:

1. Imperfect alignment of the crystal and the reflecting surface.
2. Departure of the sound beam from a plane wave. Pumper (P9) has shown that a correction can be made for deviation from plane waves, and that this correction is essentially a constant, experimentally measurable term (at a given frequency) which is to be subtracted from the measured absorption value to give the correct value.
3. Lack of adequate knowledge concerning the reflection coefficient. According to Herzfeld (H11) and Hubbard (H16) the reflection coefficient is modified by heat conduction, so that separate measurements must be made of this quantity.

As a general estimate, interference methods appear to be capable of measuring absorption coefficients accurately, provided that the values of α are greater than about 0.1 cm^{-1}. In general, older values are less reliable, especially in gases, because of deviations of the reflection coefficients from theoretical values, and because of the presence of impurities in the gases under measurement. This latter difficulty will be discussed more fully later (Sec. 22).

(*b*) *The Direct Method*

In the so-called direct method, a microphone is located on the axis of an ultrasonic beam, and excess pressure or intensity is measured along the axis. If the beam approximates a plane wave, the decay law $I=I_0e^{-2\alpha x}$ may be used to evaluate the absorption. If, at the other extreme, the waves are spherical, the law $I=(I_0/r^2)e^{-2\alpha r}$ can be employed.

While this method has been widely used in both liquids and gases, there are many difficulties attendant upon it, and frequently neither of the above formulas can be employed. For example, if the transducer is assumed to operate as a piston-like source, one can show that Fraunhofer diffraction takes place within a distance a^2/λ of the crystal (a = radius of transducer, λ = wavelength of sound) while the beam diverges, and a typical Fresnel pattern is obtained at much larger distances. King (K2) and H. Born (B23) have obtained approximate theoretical expressions for the radiation field and these formulas may be employed to determine the absorption. Corrections must also be included for the finite size of the microphone (W6), if the wavelengths are not very long compared with the dimensions of the microphone.

Standing waves are again a problem here (as they must be for all methods employing continuous waves). Where the beam is well defined, it is possible to tilt the microphone so that it is not quite perpendicular to the

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[35] A more rigorous treatment by Grossmann (G6) indicates this is not strictly true. Because of the curvature of the wave fronts, the distances between successive maxima near the crystal are slightly larger than $\lambda/2$. A correction term has been calculated by him.

axis of the beam. This will reduce standing waves from the front face of the microphone. To reduce reflection from walls, various absorbent materials have been used. The problem here is more serious in gases, where the reflection coefficients are larger than in liquids.

The frequency range over which successful measurements have been made is not very great, except in water. The method has been used from 1 mc down to 50 kc in measurements in water, where a medium of very great extent is available. In the laboratory, measurements have been made in the range 1 to 4 mc. Some of these measurements are rather inaccurate. The absorption is low and since α is computed as a log of a number which almost equals unity, it does not take a very large error of measurement to make the result meaningless.

In gases, the frequency range over which measurements are made is much lower due both to the higher absorption values in gases and to the shorter wavelengths. Measurements are made mainly in the region 20–150 kc.

A variation of this method has been employed by Knudsen and Fricke (K14). From the measurements of other observers [e.g., van Itterbeek and Thys (V3)] it appears that absorption in nitrogen is almost exactly classical. (See Sec. 22.) The absorption coefficient of nitrogen can then be used as a standard. The intensity of sound is first measured by a microphone with a nitrogen-filled chamber, and again with the chamber filled with the test gas. Corrections are made for wall absorption. While there is a small difference in the results obtained by Fricke (F6) by this method for CO_2 and those obtained by Leonard (L5) for the same gas, it is quite probable that the difference is due entirely to the presence of impurities.

(*c*) *Pulse Methods*

Two general objections may be raised against all methods involving continuous waves. In the first place, there is always the possibility of the creation of standing waves, which would then lead to incorrect values for 2α. In the second place, the amount of energy introduced into the medium may change the local temperature somewhat, leading to refractive effects, since the temperature in the center of the beam would be higher than on its edges. In addition, the changed temperature would also bring it about that measurements would actually be made at a higher temperature than that recorded by a thermometer located outside of the beam. Both of these difficulties are avoided by the use of pulses. In the arrangement of Pellam and Galt (P2) a quartz transducer and a polished reflector are set up, parallel to each other, as in the interferometer method. The high frequency voltage applied to the transducer is pulsed, with a repetition rate of the order of 1000 per second. The width of the pulse in this particular case was 1 microsecond, with a frequency of 15 mc. Thus the average power is only 1/1000 that of a continuous signal of the same amplitude.

The signal is reflected from the polished surface and is picked up by the quartz, now acting as a receiver. If the distance between the transducer and the reflector is appropriately chosen, (relative to the repetition rate), the reflected signal will arrive while there is no transmitted pulse so that standing waves are entirely avoided. By the use of suitable electronic equipment, the initial and the reflected pulse may be compared on an oscilloscope. The customary technique (P2) is to pass the initial pulse through a calibrated attenuator. The attenuation required to reduce the size of the initial pulse to that of the reflected one measures the power lost in transmission, plus reflection losses. If the reflector is now moved through a distance x, parallel to the axis of the beam, the path length is increased by $2x$. A graph of attenuation *vs* $2x$ will then permit a calculation of the absorption coefficient.

The theory of measurement at this point becomes identical to that of the direct method. Regions of Fraunhofer and Fresnel diffraction must be treated differently. An adequate treatment of this problem is given by Pinkerton (P8).

One problem raised by the pulse method is that the use of a narrow pulse increases the spread of frequencies in the Fourier spectrum of the pulse. A simple calculation (P3) shows however that for pulses containing at least 15 cycles (at a frequency of 15 mc), this error is no greater than 1 part in 250.

Inherently, the pulse method is the most accurate method of making absorption measurements—provided that the experimental procedures are sufficiently refined. While observers using pulse techniques estimate errors as being below 15 percent, and frequently of the order of 2–3 percent, large discrepancies have appeared in certain measurements, even though very similar apparatus and procedures have been used.[36]

So far, pulse techniques have been applied mainly to liquids and solids. In the latter field, they form in fact the principal method of measurement. The frequency range of pulse measurements extends from about 1 mc up to 200 mc and even beyond.

(*d*) *Reverberation Methods*

The methods discussed so far have been strongly limited in their application to frequencies of the order of a megacycle and higher in liquids, with a lower range possible in gases. The use of the reverberation method in liquids extends greatly the lower limit of frequencies which can be employed. This method was first employed by Knudsen (K13) for gases, and has been extended to liquids by Leonard (L6), Liebermann and Wilson (L9), Mulders (M10), and Moen (M8).

In principle, the method rests on the measurement of

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[36] An example of this is given by the values which have been obtained for ethyl alcohol. Measurements by four observers, all using the pulse technique, include the following values of $\alpha/\nu^2 \times 10^{17}$ cm^{-1} sec^2: Pellam and Galt (P2)23, Pinkerton (P8)52, Rapuano (R1)54, Teeter (T1)225. ν is the frequency.

TABLE III-I. Range of absorption measurements in liquids.

Method	Range of α in cm^{-1}	Corresponding frequency range in water (in mc)
Mechanical	0.001 (C3) to 1 (B17)	2 to 60
Optical	0.02 (B22) to 5 (B1)	7 to 140
Interferometric	0.05 (H17) to 4 (H17)	15 to 130
Pulse	0.05 (P3) to 310 (R1)	15 to 800
Reverberation	10^{-5} (L7) to 0.003 (M8)	0.15 to 3

the reverberation time in a given enclosure. In the application of Liebermann and Wilson, a brass sphere containing the liquid is excited in a radial mode of vibration by a crystal attached to the surface of the sphere. The transmitter is shut off and the same crystal is used as a detector. During this stage spherical waves are repeatedly reflected from the walls of the container, with the energy of the beam gradually being dissipated by the absorption in the medium and the walls. The rate at which the intensity falls off is then a function of these two quantities. If a radial mode is used, and if the brass sphere has a thickness of an odd number of quarter wavelengths, the energy transmitted through the walls is essentially negligible. Under these conditions, the absorption coefficient α will be given by

$$\alpha = (1/ct)\ \ln(I_0/I_t), \tag{18.1}$$

where I_0 is the initial sound intensity, I_t is the intensity t seconds later, c is the speed of sound. The theoretical analysis of this problem was given by C. F. Eyring (E9). This method or a slight variation of it has been successfully applied in measurements in the frequency range in liquids from 24 kc to 200 kc. The frequency limitations are the following. At very low frequencies, the absorption coefficients are so small that any error in calculating wall losses will be significant. At high frequency, resonant modes lie very close together so that it is difficult to excite a radial mode only. If nonradial modes are excited, wall transmission will become more complicated and in general its magnitude becomes greater. In addition, the decay time gets smaller and therefore more difficult to measure accurately.

The arrangement by Mulders makes possible measurements in liquids in the somewhat higher frequency range of 500 to 1500 kc. In this arrangement, a frequency modulated source is employed and as many as 10^4 modes of vibration are excited. Thus the sound becomes essentially diffuse. Many corrections must be employed, but the results for water are in substantial agreement with those of other methods. The method of Moen also enables an extension of the frequency range up to 1 megacycle.

The diffuseness of the sound was obtained by Knudsen in gases by employing a motor-driven paddle.

In all low frequency measurements, a particular problem is presented by the formation of bubbles. The presence of bubbles increases the absorption and also produces scattering so that the absorption coefficient which is measured may be considerably larger than that of the pure liquid. Since the value of α in water at 50 kc is of the order of 0.75×10^{-6} neper per centimeter, it does not take the presence of many bubbles to make the results wholly meaningless. Elaborate procedures are required to avoid any dissolved gases in the liquid. This leads to some uncertainty as to the validity of open water measurements at these same low frequencies, since such precautions cannot be taken.

19. SUMMARY OF METHODS

It is clear from the foregoing that no one method will give satisfactory results over the range of frequencies experimentally available. The following should serve as an approximate criterion for measurements.

(a) *Gases*

In general, it appears that systematic errors in the various methods employed today are small in comparison with the error caused by the presence of minute amounts of impurities. These will not only change the magnitude of the total absorption at a given frequency, but may also have a profound effect on the relaxation frequencies. Thus the presence of only 0.01 percent of H_2O in CO_2 *doubles* the relaxation frequency (K14) (see Sec. 22). In comparing experimental results by different observers, greatest credibility can be given in general to the one obtaining the lowest relaxation frequency. At low frequencies reverberation methods appear to be most satisfactory. From 20–200 kc, the direct method has been quite successful, while for measurements in the highest frequency ranges, interferometry is employed. It should be pointed out that in gases, increase in frequency or decrease in pressure are essentially equivalent. Using an interferometer at low pressures, Zartman (Z1) has obtained consistent results up to 85 mc/atmosphere. At atmospheric pressure, the highest frequency at which measurements have been made are those of Stewart (S14) in hydrogen (up to 6 mc). Both of these sets of measurements were made by interferometric methods.

(b) *Liquids*

Because the absorption in liquids varies more widely, from one substance to another, it is more convenient to express ranges of usefulness in terms of measured values of α, citing the frequency range in water at room temperature which corresponds to these values. This is done in Table III-I for the principal methods of measurement. It is to be noted that the absorption has not necessarily been measured in water over these frequencies. The values are listed merely for comparison purposes. In addition the range of frequencies measured in open water has been omitted, since this constitutes a rather special case which obviously cannot be repeated for any other liquid. It should be pointed out that *the standard criterion for the accuracy of a given method (in a liquid) is the obtaining of a value of α/ν^2 for water (above 1 megacycle) which agrees with the universally accepted value.*

Chapter IV. Experimental Results in Gases

20. INTRODUCTION

The absorption coefficient attributed to shear viscosity and heat conduction (the so-called classical absorption coefficient) as calculated by Stokes (S17) and Kirchhoff (K3) may be written

$$\frac{\alpha}{\nu^2}=\frac{2\pi^2}{\gamma p_0 c}\left[\frac{4}{3}\eta+\frac{\gamma-1}{c_p}\kappa\right], \tag{20.1}$$

where p_0 = mean pressure, γ = ratio of specific heats, η = coefficient of shear viscosity, κ = thermal conductivity, c_p = specific heat at constant pressure, and ν = frequency. Equation (20.1) is a combination of Eq. (3.16) and (4.8a) of Chapter I. Use has been made of the condition that $\zeta=4/3\eta$ and that $K=p$ (see Sec. 11a).

TABLE IV-I. Ratio of α heat conduction/α shear viscosity, computed at 20°C.

Gas	$\alpha/\nu^2\times10^{13}$ cm^{-1} sec^2 heat conduction	$\alpha/\nu^2\times10^{13}$ cm^{-1} sec^2 viscosity	$\alpha_{\text{hc}}/\alpha_{\text{vis}}$
Argon	0.77	1.08	0.71
Helium	0.216	0.309	0.70
Neon	0.75	0.07	0.70
Hydrogen	0.052	0.117	0.44
Oxygen	0.47	1.14	0.41
Nitrogen	0.39	0.96	0.41
Air	0.38	0.99	0.39
Sulfur dioxide	0.27	1.10	0.28
Ammonia	0.110	0.453	0.25
Carbon dioxide	0.31	1.09	0.24

In general, the viscosity term is somewhat larger than that due to heat conduction. The magnitudes of these two effects have been computed at atmospheric pressure for several gases from standard physical data (I1, L4), and the results are shown in Table IV-I.

In addition to viscosity and heat conduction, a number of other causes of absorption have been discussed in the past, and may be added to the "classical" group. Chief among these are the thermal radiation losses (see Sec. 5, above), and the losses due to diffusion in a gas mixture (C1, R8). The radiative absorption coefficient, as calculated by Rayleigh (R2, v. II, p. 24) and Stokes (S18), is frequency independent. In air the absorption due to the interdiffusion of the nitrogen and oxygen molecules must also be considered. The sizes of these four effects in air are listed in Table IV-II.

Thus, at a frequency of 6 kc, the absorption resulting from radiation is only about 0.5 percent of that which results from shear viscosity. The absorption caused by radiation is even less significant at higher frequencies and may therefore be neglected.

In making absorption measurements in gases, it is generally more convenient to employ a constant frequency of sound and vary the gas pressure, rather than vice versa. It is therefore more meaningful to give the experimental values of $\alpha p/\nu^2$ instead of α/ν^2. In this case, it is desirable to use ν/p as the abscissa of the graph of the absorption, rather than ν. (The reason for this choice will become clearer later when it is shown that for a relaxational effect, an increase in pressure has the same effect as a decrease in the frequency.)

In the case of a monatomic gas, we should expect $\alpha\cdot p/\nu^2$ to be independent of either p or ν, since no relaxational effects are present.

21. MONATOMIC GASES

A considerable number of measurements have been made in argon and helium over a wide range of frequencies and pressures. Here as elsewhere in gases, the presence of impurities, and a lack of accurate knowledge of the radiation field led to many errors in the results of the earlier investigators. Among the values which are quoted, the results of Van Itterbeek and Mariens (V5) for helium are probably in error due to the departure of the character of the sound beam from a plane wave.

(a) *Helium*

The results of the various experiments in helium have been put in the form of Eq. (20.1) and are plotted in Fig. IV-1.[37] These experimental values are recorded at temperatures in the ranges 15–25°C. No attempt has been made to adjust for this variation. The velocity of sound in helium was taken to be 1.01×10^5 cm/sec. The classical value of $\alpha p/\nu^2$ is computed from standard critical (I1) (L4) data at or near 15°C and equals 0.545×10^{-13} cm^{-1} sec^2 atmosphere.

It can be seen from the graph that the classical absorption value for helium is substantially verified in the

TABLE IV-II. Values of α/ν^2 for various types of classical absorption in air.

(20°C, atmospheric pressure)	$\alpha/\nu^2\times10^{15}$ cm^{-1} sec^2
Shear viscosity	99
Thermal conduction	38
Diffusion	7.4
Radiation	0.42 [at 6 kc (R9, p. 57)]

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[37] Copies of the numerical data on which this and other graphs in this paper are based, can be obtained from the authors.

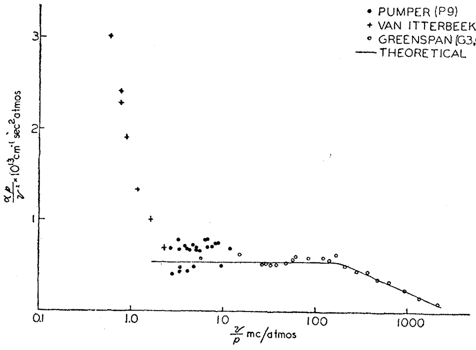

FIG. IV-1. $\alpha p/\nu^2$ *vs* ν/p for helium.

range above 2 mc/atmos. The rise in the values of $\alpha p/\nu^2$ at the lower end of the frequency scale is in all probability due to experimental errors.[38]

The falling off of the curve at high values of ν/p can also be explained on the basis of classical behavior (see Sec. 11). Greenspan has computed the effect of viscosity and heat conduction when higher order terms are considered. The solid line at the high values of ν/p represents the numerical solution of the hydrodynamic equation. The agreement with experiment is thus shown to be excellent. It should be emphasized that this is obtained from the classical equations, without altering the expression for viscosity. It therefore resembles the behavior found experimentally in highly viscous liquids (see Sec. 28).

(*b*) *Argon*

The $\alpha p/\nu^2$ data for argon are plotted in Fig. IV-2. The computed value of the classical $\alpha p/\nu^2=1.88\times 10^{-13}$ cm^{-1} sec^2 atmosphere at 20°C. While there is a considerable spread of values in the figure, they fluctuate about the classical value. The spread is occasioned, at least partly, by the spread in temperatures at which the measurements were recorded. The behavior of $\alpha p/\nu^2$ at large ν/p has been computed as in the helium case, and is plotted on the graph.

On the basis of these measurements one can conclude that the measured absorption in monatomic gases is entirely accounted for by the classical theory.[39]

22. DIATOMIC GASES

The absorption per wavelength for a thermal relaxation may be written approximately (see Secs. 6 and 7):

$$\mu=\alpha\lambda=A\omega_0\omega/(\omega_0^2+\omega^2), \tag{22.1}$$

where

$$A=\pi R C^i/C_v(R+C_v), \tag{22.2}$$

C^i = internal molar heat capacity, C_v = molar heat capacity at constant volume, R = molar gas constant, and ω_0 = angular relaxation frequency. We recall the more rigorous expression (6.16) which can be put in the form,

$$\alpha\lambda=\frac{1}{2}\frac{c^2}{c_0^2}\frac{2\pi\epsilon\omega\tau}{1+\omega^2\tau'^2}, \tag{22.3}$$

where

$$\frac{c^2}{c_0^2}=\frac{1+\omega^2(\tau')^2}{1+\omega^2(\tau')^2(1-\epsilon)}, \tag{22.4}$$

$$\frac{1}{\omega_0}=\tau'=\tau\frac{C_p^\infty}{C_p^0} \tag{22.5}$$

and

$$\epsilon=\frac{R}{C_v^0(C_v^\infty+R)}C^i. \tag{22.6}$$

C_v^0 is the low frequency value of C_v and C_v^∞ is the high frequency value. With the exception of hydrogen, the value $C^i=C_v^0-C_v^\infty$ is quite small, so that $\tau'\approx\tau$, $\epsilon\ll 1$, $C_v^\infty\approx C_v$, and

$$\alpha\lambda=\pi\epsilon\omega\tau/(1+\omega^2\tau^2). \tag{22.7}$$

It has been observed by van Itterbeek and Mariens (V2) and also by Keller (K1) that the relaxation time τ of Sec. 6 is inversely proportional to the pressure. This result is a consequence of the fact that the reaction rate $\omega_0\approx 1/\tau$ is directly proportional to the number of molecular collisions which occur per second, and this latter quantity is in turn directly proportional to the pressure (see Sec. 8c). We may therefore rewrite Eq. (22.1) in the form

$$\mu=\frac{A'(\nu/p)}{1+B(\nu/p)^2}. \tag{22.8}$$

Hence, both classical (Eq. (20.1)) and relaxational (Eq. (22.8)) effects can be plotted in a graph of μ *vs* ν/p. The expression for the velocity may be written in a similar form. We now consider specific cases.

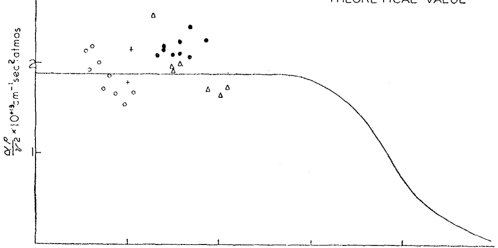

FIG. IV-2. $\alpha p/\nu^2$ *vs* ν/p for argon.

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[38] Discussions of these errors may be found in Halpern (H2) and Pumper (P9).

[39] A recent paper by E. Skudrzyk (S7) has advanced the hypothesis that Stokes's assumption (that the dilatational viscosity is equal to zero) fails even for ideal monatomic gases. On this basis he adds 50 percent to the viscosity term in the expression for the absorption coefficient (changing $4/3\eta$ to 2η). The experimental evidence collected here appears to be contrary to such a hypothesis.

(*a*) *Hydrogen*

The internal specific heat of hydrogen is due to the rotational degrees of freedom. The characteristic temperature for vibration of the hydrogen molecule is 6140°A, which is so high that the vibrational specific heat is entirely negligible at room temperature.[40] The characteristic temperature for rotation on the other hand is 171°A, so that many energy states are excited at room temperature. Epstein gives the molar heat capacity due to rotation as $0.97R$ at 293°A (R = molar gas constant). Therefore, using the exact relations Eq. (22.3) and Eq. (22.4), one should expect

$$c_\infty^2/c_0^2=1.19,\qquad \mu_{\text{max}}=(\alpha\lambda)_{\text{max}}=0.273. \tag{22.9}$$

These quantities should be virtually independent of temperature in the range above 0°C, although the relaxation frequency itself may be expected to depend upon the temperature. The principal results are shown in Fig. IV-3 and Fig. IV-4. In Fig. IV-3 the smooth curves have been drawn to give a best fit to the experimental data. The values plotted in Fig. IV-4 are for the excess absorption per unit wavelength, i.e., above the classical value. The results of Zartmann indicate conclusively that the velocity dispersion takes place over the frequency range predicted theoretically.[41] The temperature dependence is reflected only in the value of the relaxation frequency which is approximately 10.0 mc at 25°C Stewart (S14) and Rhodes (R3) and 13.6 mc at 36.5°C Zartmann (Z1).

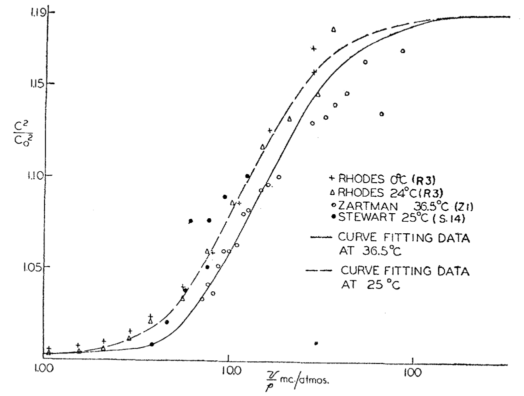

FIG. IV-3. Sound velocity in hydrogen.

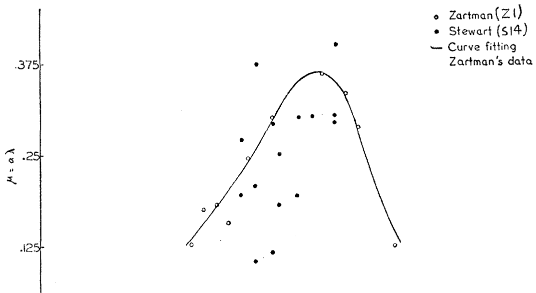

FIG. IV-4. $\alpha\lambda$ *vs* ν/p for hydrogen.

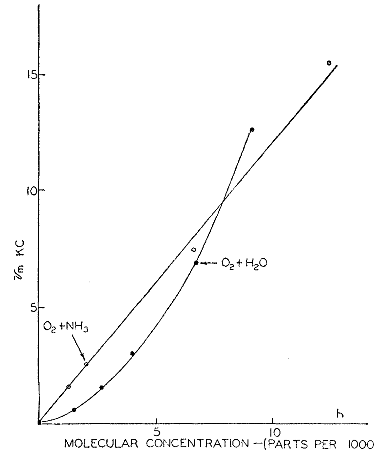

FIG. IV-5. Effect of impurities on sound absorption oxygen. (L. and H. Knötzel (K12).)

The values for the absorption coefficients shown in Fig. IV-4 are somewhat high (compared to the theoretical value) and have a greater spread. Nevertheless, the results, especially those of Zartmann, indicate a relaxation frequency of the order of 10–12 megacycles. Stewart attributes some of her high values to misalignment of the crystal in the interferometer. The data points are too widely scattered to form a definite conclusion on the maximum experimental value of μ.

In summation, the results in hydrogen give satisfactory support to the theory of a relaxation of the rotational degree of freedom.

(*b*) *Nitrogen, Oxygen*

The study of relaxation effects in diatomic gases is complicated by the very small values of the internal molar heat capacity C^i and the consequently small values of μ_{max}. In addition, the relaxation frequency is generally a very low one, so low in fact that it might be well below the frequency range in which sound absorption can be accurately studied. A useful technique however has been developed by Kneser and Knudsen (K9) to bring the maximum values of μ within the range of measurement. Their experiments have shown that the presence of an impurity in the gas increases the relaxational frequency ν_m *without affecting the value of* μ_{max}. The absorption is therefore measured at a number of different concentrations of the impurity and the curve

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[40] The texts of Slater (S8) and Epstein (E5) should be consulted for a more detailed discussion of this topic. The reader should also recall Sec. 7 of this review.

[41] None of the observers measured the velocity at low (dispersion free) frequencies. The curve is drawn with an assumed $V_0=1316$ m/sec at 25°C and 1341 m/sec at 36.5°C. An error here could shift the values of the relaxational frequencies somewhat.

Table IV-III.

		$\mu_{\max}$(thermal) $\times 10^4$			
Gas	T°C	Exper.	Theoret.	ν_m(exper.)	Observer
Nitrogen	20°	4	2.5		Schmidtmüller (S2a)
Oxygen	19°	52		50±10 cps	Knötzel (K12)
Oxygen	20°	54.5	51		Kneser and Knudsen (K9)
Oxygen	22°	54		170 cps	Oberst (O1)
Oxygen	55°	98	102		Kneser and Knudsen (K9)

for ν_m is extrapolated to zero concentration of the impurity. This method is somewhat inaccurate, since the relaxation frequency changes rapidly with concentration, but it does serve to give an upper bound to that frequency. An illustration of this behavior is shown in Fig. IV-5 which is taken from the results of H. and L. Knötzel (K12). Here the relaxation frequency ν_m for oxygen is plotted as a function of the ratio of molecules of impurity to the total number of molecules in parts per mil (h). Both ammonia and water vapor have been used as impurities. While the value of ν_m has been measured at $h=0$, it is somewhat more accurate to obtain a best-fit curve through the various points and solve for $h=0$. This gives $\nu_m=50\pm10$ cps in good agreement with the actual experimental values at $h=0$.

Since $\mu_{\max}$ is not affected by the impurity, this method can be used to find the value of $\mu_{\max}$. A sufficient impurity is introduced to get ν_m in the most convenient frequency range, and $\mu_{\max}$ can then be measured directly.

Table IV-III summarizes the results. The values of $\mu_{\max}$ are computed from Eq. (22.3) and Eq. (22.6), using the values of C^i computed from standard data.

The results in Table IV-III indicate substantial agreement between theory and experiment. In addition, the exceedingly low frequencies at which these $\mu_{\max}$ occur indicate that these gases may safely be used in the calibration of absorption measuring instruments at higher frequencies (where α/ν^2 due to this process may be entirely neglected. See Sec. 18 above).

Some of the principal results obtained in diatomic gases at higher frequencies are shown in Table IV-IV.

The experimental values tabulated here are undoubtedly not more accurate than within ±10 percent, and are perhaps worse in some cases. One may say therefore that a reasonable agreement has been obtained between theory and experiment, although more extensive and more accurate data would be useful here.[42]

23. TRIATOMIC GASES

The relaxation effects in triatomic gases are more pronounced and the relaxational frequencies are considerably higher than for diatomic gases. Among these gases, carbon dixode has been thoroughly studied by a number of investigators. The chief results are plotted in Fig. IV-6.

If we take the results of Fricke (F6) as the more accurate,[43] a relaxation frequency of 20 kc is indicated. The approximate theoretical curves (based on this relaxation frequency) have been drawn in the figure. The combined relaxation-classical (viscosity-heat conduction) curve is seen to be in excellent agreement with the results of Fricke, van Itterbeek, and Zartmann over the entire frequency range (8 kc/atmos to 85 mc/atmos).

Table IV-IV.

			$\alpha p/\nu^2\times10^{13}$ cm^{-1} sec^2 atmosphere	
Observer	Range of ν/p in mc/atmosphere	T°C	Experimental	Classical
	Nitrogen			
Zartmann (Z1)	1–38.5	25.6	1.91	1.35
Keller (K1)	0.35–1.60	18	1.71	1.35
Schmidtmüller (S2a)	0.08–0.115	20	1.85	1.35
Van Itterbeek and Thys (V3)	0.61–1.97	20	1.35	1.35
	Oxygen			
Van Itterbeek and Thys (V4)	0.60–1.69	20	1.57	1.61
Van Itterbeek and Thys (V4)	0.60–1.55	50	2.22	1.70
	Nitric oxide (NO)			
Van Itterbeek and Thys (V4)	0.60–0.97	16.3	1.58	1.48

The chief results in the triatomic gases are summarized in Table IV-V. The data are mainly those of Fricke. The values of $\mu_{\max}$ were computed by him from thermal data.

Chapter V. Experimental Results in Liquids

24. MONATOMIC AND DIATOMIC LIQUIDS

It is to be expected that the values of the sound absorption coefficient in a monatomic liquid such as mercury should show good experimental agreement with the classical values since the usual types of internal degrees of freedom are lacking. The same should be true of liquefied monatomic or diatomic gases. In the latter case, the internal degrees of freedom of such molecules as O_2, N_2, and H_2 are "frozen" in their liquid state and therefore should not contribute to any relaxational process.

The experimental results for mercury are shown in

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[42] Several experimental investigations (P1a, T1b, Z3) have recently been reported on the relaxation of rotational degrees of freedom in both oxygen and nitrogen.

[43] Professor Leonard has informed the authors that the CO_2 used by Fricke was probably of somewhat higher purity than that used in his research. The graph suggests that the CO_2 used by Keller was of approximately the same purity as that used by Leonard.

TABLE IV-V.

Gas	T°C	Theoretical $\mu_{\max}$	ν_m(exp.) in kc
CO_2	23	0.115	20
COS	23	0.175	28
CS_2	23	0.203	370
N_2O	23	0.148	157
SO_2	23	0.0745	1040

Fig. V-1. The values of Ringo *et al.* (R7) are the most recent and indicate that the observed absorption lies within about 15 percent of the classical value. This is probably within the margin of experimental error. The case of mercury differs from most other liquids in that heat conduction is the primary source of ultrasonic absorption. It is also to be noticed that no frequency dependence of α/ν^2 has been observed in the range 20–1000 mc.

Pellam and Squire (P4) have measured the absorption coefficient in liquid helium, at 15 mc, as a function of temperature. Their results are reproduced in Fig. V-2, along with a curve showing the classical value of the absorption coefficient. From these data, one may conclude that ultrasonic absorption in liquid helium is a classical phenomenon above the λ-point (2.19°A). In the neighborhood of this point, and below it, there is no agreement between classical and experimental values. The fact is not surprising, in view of the complicated hydrodynamics associated with HeII.

Measurements have also been made by Galt (G1) on liquefied monatomic and diatomic gases. His results are shown in Table V-I. All measurements were made at 44.4 mc. The velocity measurements made by Galt have also been included.

The calculations of the theoretical absorption coefficients (B19) were based on viscosity and density data by van Itterbeek and van Paemel (V6) and Rudenko and L. W. Schubnikov (R11). Experimental values for the thermal conductivity for liquid oxygen and nitrogen are taken from Hamman (H3). Corresponding values for argon or hydrogen were not available, and an empirical formula of Borovik (B25) (which gives at least the order of magnitude) was used in these two cases.

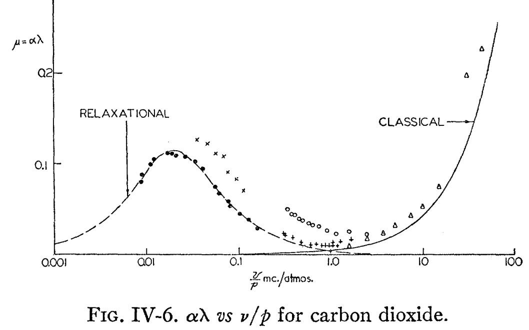

FIG. IV-6. $\alpha\lambda$ *vs* ν/p for carbon dioxide.

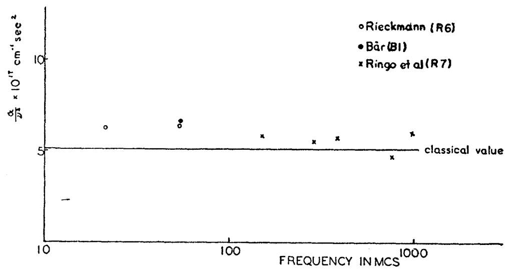

FIG. V-1. α/ν^2 *vs* frequency for mercury.

In their paper on the viscosity of liquids, Kirkwood, Buff, and Green (K6) made use of Galt's results to estimate an upper bound of $\frac{1}{3}$ for the ratio of bulk to shear viscosity in argon. When thermal conductivity is included, however, it is clear that such a ratio must be far smaller. The bulk viscosity of argon is essentially negligible, so far as ultrasonic absorption is concerned. The general agreement between the experimental and theoretical values in Table V-I warrants the conclusion that the absorption processes in monatomic and diatomic liquids (with the exception of helium below the λ-point) are well accounted for by classical theory.

25. WATER

Of all liquids water has been the one whose sound absorption properties have been studied most frequently (B5, B10, B12, B21, C4, F2, F3, H14, L7, L10, M10, P6, R1, S7, S9, V7). The principal results are shown in Fig. V-3.[44] The temperatures are all in the vicinity of 20°C, but a variation of several degrees for operating temperatures among the different observers increases somewhat the spread of values.

The results indicate a constant value of α/ν^2 at frequencies above 1.0 mc, a value which is about $3\frac{1}{2}$ times the classical value of Stokes. The spread of values below 1.0 mc (which is understandable because of the extremely small value of the absorption coefficient α in

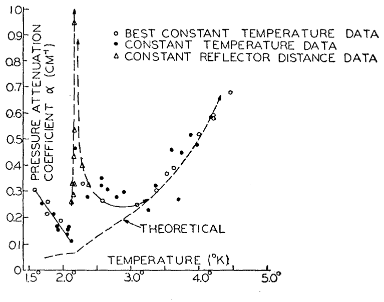

FIG. V-2. α *vs* absolute temperature for helium (after Pellam and Squire (P4)).

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[44] It is to be noted that the values of Sörensen (S11), Hartmann and Focke (H5), and others (B38, O2, R5, R12) are not plotted. These were early values, and have since been shown to have been unreliable (see Sec. 16). In this case, as in all others in this paper, the authors are attempting to plot only those values which are at present believed reliable.

TABLE V-I. Absorption coefficients of liquefied gases.

Liquid	T(°A)	Velocity cm/sec² $\times10^{-4}$	$\alpha/\nu^2\times10^{17}$ cm^{-1} sec^2 Shear viscosity	Thermal conductivty	Total theoretical	Experiment
Argon	85.2±0.2	8.53	7.9	2.6	10.5	10.1
Oxygen	87.0±0.2	9.52	5.5	1.8	7.3	8.6
	70 ±1	10.94	5.6	1.1	6.7	8.6
	60 ±5	11.19	7.3	1.0	8.3	8.6
Nitrogen	73.9±0.2	9.62	6.6	2.9	9.5	10.6
Hydrogen	17 ±1	11.87	3.7[a]	2.1	5.8	5.6

[a] This is considerably larger than the value computed by Galt. The discrepancy lies in his use of a density of liquid hydrogen, taken from Bergmann (B15), of 0.355 g/cm³. The value of 0.075 g/cm³ used here is that given by van Itterbeek and van Paemel (V6) and also appears in the *Handbook for Chemistry and Physics*, thirtieth edition, p. 1703.

this range) makes it difficult to decide whether or not there exists a low frequency relaxation process, but the evidence seems against it, at least at frequencies above 100 kc.[45] The absorption in water was at first thought to be due to a thermal relaxation (Dutta and Ghosh (D4), Herzfeld (H12)) but inconsistencies made this impossible. Thus, as Herzfeld pointed out, the constancy of α/ν^2 up to 200 mc requires, from the relation

$$\frac{\alpha_{\text{excess}}}{\nu^2}=\frac{A\tau}{1+\omega^2\tau^2}\approx 15\times10^{-17}\ \text{cm}^{-1}\ \text{sec}^2,$$

that $(2\pi\tau)\ll 1/(2\times10^8)$ or $\tau\ll 8\times10^{-10}$ second. One may calculate A from (6.16) from thermal data giving $A=2\times10^{-9}$ cm^{-1} sec. This figure was obtained from the value of C^i given by Dutta (D3a). The other parameters were taken from Herzfeld's paper (H12). The product $A\tau=15\times10^{-17}$ cm^{-1} sec^2 at low frequencies yields $\tau\sim 7\times10^{-8}$ sec which contradicts the above.

In addition to this difficulty, there is a second objection. The thermal term depends on the difference C_p-C_v which vanishes in water at 4°C (since C_p-C_v varies directly as the thermal expansion coefficient). However, the measurement of absorption in the vicinity of 4°C shows no dip at all in the excess absorption when it is plotted as a function of temperature (see Fig. V-4).

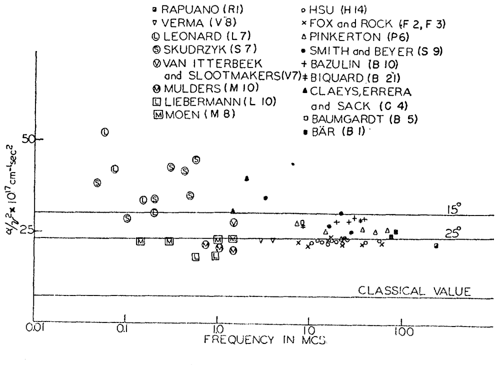

FIG. V-3. α/ν^2 *vs* frequency for water.

As was observed in Sec. 7, Hall (H1) has attributed the effect to a structural rearrangement in the water molecules: the impact of a sound beam on water first compresses the groups of molecules (which are assumed to possess some degree of order in an ice-like state). Then a structural compression sets in, in which the molecules break their structural bands and move into a close packed arrangement. Since there is a time lag, absorption will appear.

Hall has calculated a theoretical absorption coefficient on the basis of an instantaneous compressibility $\mu_T{}^\infty$. In his theory, this quantity, as well as the relaxation time for the process and the so-called *bulk viscosity* coefficient are evaluated in terms of independently known parameters. The results are shown in Fig. V-4 where Hall's theoretical curve for structural absorption is plotted in the temperature range 0–80°C. The excess absorption found by various investigators, is also plotted.

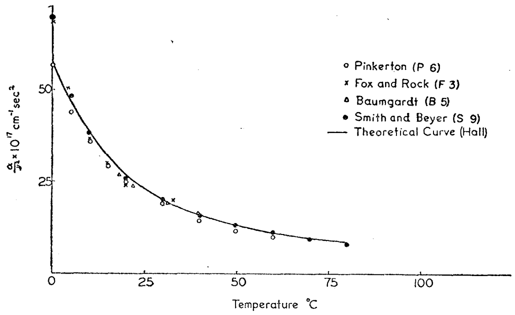

FIG. V-4. Temperature dependence of sound absorption coefficient in water.

While the agreement between Hall's theory and the experimental results is satisfactory, it must be pointed out that the constants from which the final theoretical curve is drawn are known only very approximately. In addition, the ratio of excess to classical absorption is (experimentally) very nearly independent of the temperature, so that any theory which deduces an excess absorption approximately proportional to the *shear viscosity* will take on the same temperature dependence as that shown. Before the theory can be more generally accepted, it should be applied to other associated liquids.

It should also be pointed out that Sette (S4) has recently reported a calculation for ethyl alcohol, based on the Hall theory. He found that the relative change in volume between the two structural arrangements was much smaller than in water, so that the resulting contribution to the absorption coefficient was inadequate to account for the excess above the classical value. Apparently the simple model of a two-state liquid is inadequate in such a case.

As shown in Chapter II a more macroscopic approach to this problem has been made by Liebermann (L11) on

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[45] Kneser (K11) has recently (1949) hypothesized the existence of a thermal relaxation in water with a relaxation frequency of about 3 megacycles. This hypothesis was made on the basis of the data obtained by Skudrzyk (S7). The more recent experimental work of Leonard (L7), Liebermann (L10), Mulders (M10), Moen (M8), and Verma (V8), however, indicate that this is not the case.

the basis of hypotheses set forth by Tisza (T3) and Eckart (E3). Tisza and others (E3, L17, M1) have pointed out that the original Stokes equation for sound propagation contained a term involving a bulk or dilatational viscosity, which Stokes set equal to zero. If one does not make this assumption, then the second viscosity coefficient can be adjusted so as to fit the experimental results.

What was needed was an independent determination of this second viscosity coefficient. An experimental method was first suggested by Eckart (E3) who developed the second-order equation for wave propagation in this case. This method involves the phenomenon of streaming of the fluid (quartz wind or hydrodynamic flow) in which the driving force is dependent on both viscosity coefficients (shear and bulk) but in which the retarding force is dependent only on shear viscosity. Hence the equilibrium velocity of streaming should depend on the ratio of the coefficients. Liebermann has measured the viscosity ratio by this method for a number of liquids at 5 megacycles. In the case of water, the ratio of absorption due to bulk viscosity to that due to shear viscosity was found by him to be 3.3 while the ratio of total absorption to classical absorption at the same temperature is 2.95.

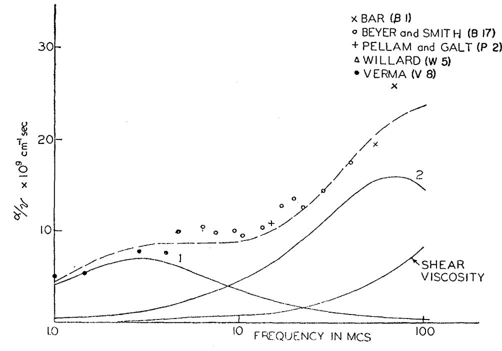

FIG. V-5. α/ν *vs* frequency for ethyl acetate.

As will be seen later (Table V-VII), rather satisfactory agreement exists between Liebermann's results and data obtained by direct experimental measurement of the absorption. It must be borne in mind however that this identification of excess absorption with a bulk viscosity does not indicate of itself any mechanism by which the second viscosity coefficient can be calculated. Thus Hall's treatment might be reconciled with Liebermann's, in which case the bulk viscosity would be attributed to a structural compression. Unfortunately, Hall and Liebermann have employed somewhat different equations of state, so that a direct equivalence is not immediately possible (see Sec. 15).

26. LIQUIDS WITH PRONOUNCED RELAXATIONAL EFFECTS

The stimulation for the development of a successful theory for sound absorption in gases was provided by the existence of relaxational processes whose relaxation frequencies generally lay within the range of experimental measurement. This is not the usual case for liquids, but some exceptions have been found to exist. It is the study of these exceptions which gives the greatest promise of progress toward understanding absorption mechanisms in liquids. The most important of these liquids are organic compounds containing the acetate (CH_3COO) and the formate ($HCOO$) radicals.

TABLE V-II. Relaxation frequencies in ethyl acetate.

Curve	ν_m (relaxation frequency) in megacycles	$(\alpha'/\nu)_{\max}$ (cm^{-1} sec)
I	2.9	7.0×10^{-9}
II	70	$16\ \times10^{-9}$

(a) *Acetates*

The experimental values of α/ν for ethyl acetate ($CH_3COOC_2H_5$) are plotted in Fig. V-5. Most of the values appear to lie in the transition region between two relaxation frequencies. This was first suggested by Kneser (K11). In line with his hypothesis, the curves I and II (along with the curve for shear viscosity absorption) have been fitted to the data. The sum of these three curves is represented by the dashed line. The constants obtained by the curve fitting are given in Table V-II.

While some data exist (B1, B22, C4, P2) for methyl acetate (CH_3COOCH_3) showing at least one relaxational effect, the results are too fragmentary to allow any conclusions to be drawn from them.

The data which are now available for acetic acid (CH_3COOH) (Lamb and Pinkerton (L2)), are quite extensive. It should be pointed out that ultrasonic absorption in this liquid was first studied by Bazulin (B7, B12) in 1936. He was the first to observe a relaxation process in a liquid. His data are largely omitted from what follows only because of the completeness of the work of Lamb and Pinkerton and because of the difficulty of making corrections for small temperature differences. Wherever the two sets can be compared, the experimental agreement is excellent.

Figure V-6 reproduces graphs of $\mu'=(\alpha\lambda)_{\mathrm{excess}}$ *vs* frequency, computed by Lamb and Pinkerton from their data at 20°C, 35°C, and 50°C, respectively. These results demonstrate clearly the existence of a relaxational effect, the characteristic frequency of which increases with temperature. The maximum of the absorption per unit wavelength increases in a similar manner.

The relation between the relaxation time and the temperature is indicated by Lamb and Pinkerton to be of the form

$$\nu_m = AT^n \exp(-\Delta E_a/RT), \qquad (26.1)$$

where ν_m is the relaxation frequency, A is a constant, n = a number in the range 0 to 1, and ΔE_a is the apparent

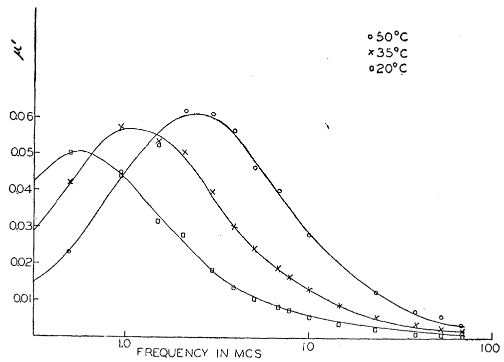

FIG. V-6. Excess absorption per unit wavelength *vs* frequency for acetic acid (after Lamb and Pinkerton (L2)).

energy of the backward reaction involved in the propagation process.

While A is not known, the form of Eq. (26.1) can be checked against the experimental results. Unfortunately, the experimental values of Lamb and Pinkerton fit the expression equally well for $n=0$ or $n=1$. The value of ΔE_a which is computed is nearly the same in each of these cases, being 8.86 kcal/mole for $n=0$ and 8.46 kcal/mole for $n=1$. It would be very desirable to compute ν_m directly from spectroscopic data, but this is not possible at the present time.

The plot of α/ν^2 *vs* frequency for acetic acid (see Fig. V-7) indicates that the high frequency value (132×10^{-17} sec^2 cm^{-1}) is still far above the classical viscosity value of 20×10^{-17} sec^2 cm^{-1}. Thus it seems probable that there is yet another relaxational process, not yet discernible at the highest frequency measured. Lamb and Pinkerton have advanced the hypothesis that there are two relaxation phenomena, each one connected with one of the hydrogen bonds that ordinarily hold the acetic acid in a double molecule.

The temperature dependence of the absorption coefficient can be used to gain considerable information about relaxational processes, as Kittel (K7) has pointed out. The absorption coefficient due to shear viscosity has a negative temperature coefficient. We now consider relaxation processes of the form $M'=\alpha'/\nu^2=A\tau/(1+\omega^2\tau^2)$.

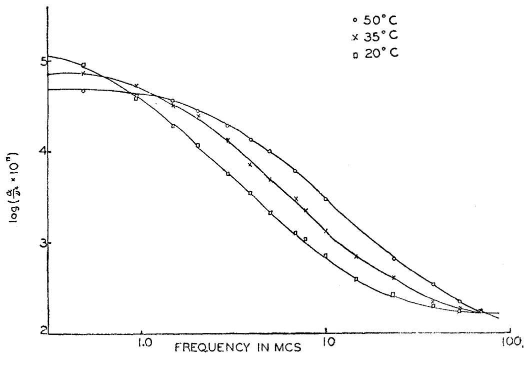

FIG. V-7. $\alpha/\nu 2$ *vs* frequency for acetic acid (after Lamb and Pinkerton (L2)).

It follows from Eq. (9.24) that τ has a negative temperature coefficient. Then the sign of the temperature coefficient of $M'[=(1/M')\partial M'/\partial T]$ depends on two factors: (i) whether ω is greater or less than $1/\tau$ (i.e., greater or less than $2\pi\nu_m$), and (ii) whether the product $A\tau$ has a positive or negative temperature coefficient. Thus, if $A\tau$ has a positive temperature coefficient, i.e., if A has a large positive coefficient, then $(1/M')\partial M'/\partial T$ will always be positive. On the other hand, if A has a smaller temperature coefficient than τ (be it positive or negative), then $(1/M')\partial M'/\partial T'$ will be negative at frequencies below ν_m and positive at frequencies above ν_m. (See also Sec. 9.)

The process of thermal relaxation may be shown to be one in which $(1/A)\partial A/\partial T$ is positive. The temperature behavior of structural relaxation is not so clear, but the work of Hall indicates a small negative value of $(1/A)\partial A/\partial T$ for water.

In general it appears that the relaxational frequency for a structural or bulk viscosity effect is so high that the resulting temperature coefficient of absorption will always be negative over the frequency range available to investigation. Where this is not the case, one can perhaps distinguish between bulk viscosity and thermal relaxation by the temperature dependence of A.

An example of this temperature dependence is given in Fig. V-7 for acetic acid. At frequencies below the relaxation range ($\sim$1 mc) the absorption coefficient decreases with increasing temperature. At frequencies above this range, the absorption coefficient increases with increasing temperature, at least up to 67.5 mc. Above this frequency, extrapolation seems to indicate that the absorption once more decreases with increasing temperature. However, this is the region in which a second relaxation effect appears to enter the picture. In addition, the relaxation frequency (see Fig. V-6) increases with temperature, while the peak of the $(\alpha\lambda)_{\text{excess}}$ curve (which is proportional to A) also increases.

(*b*) *Formates*

Work on absorption in formate compounds has so far been limited to some absorption values for formic acid (HCOOH) obtained by Bazulin (B10) and a few absorption values for ethyl formate ($HCOOC_2H_5$) obtained by Parthasarathy (P1). The measurements of the latter investigator, where they can be compared with accurate results by other investigators, tend to be high and also to have large fluctuations, and can be regarded only as very rough or even qualitative information.

Bazulin's results in formic acid indicate that a relaxation process exists with a frequency of the order of 5 megacycles. The values have been recorded over a temperature range of 4°C and for 87 percent concentration. These two limitations, plus the small number of points available, prevent any more detailed analysis of ultrasonic absorption in the liquid.

The main interest in ethyl formate lies in the fact that its second (or bulk) viscosity coefficient has been measured by Liebermann at four different frequencies. His results are given in Table V-III, together with ratio of excess to classical absorption obtained by Parthasarathy's experimental data.

The results of Liebermann indicate a relaxation frequency for the *bulk viscosity* of the order of 2 megacycles, which is at least partially borne out by the direct absorption measurements. A great deal more experimental data, especially in the range 1–10 megacycles, is needed to clarify the picture.

(*c*) *Toluene* ($C_6H_5CH_3$)

Recent measurements of Moen (M8) indicate strongly the presence of a relaxational process in toluene at relatively low frequencies. A relatively large number of experimental results exist for this liquid, mostly at higher frequencies. The most reliable of these are listed in Table V-IV. From these it can be observed that a substantially constant value of $\alpha/\nu^2(\approx 78\times 10^{-17}$ cm^{-1} sec^2) is obtained above 1 megacycle. If this value is subtracted from the low frequency data, and the graph constructed of (α'/ν) *vs* frequency, (where α'/ν^2 is the excess α/ν^2 above the high frequency value) the results are those given in Fig. V-8. The solid curve in the figure has been fitted to the first four points, since the values at the higher frequencies are more in doubt, due to the uncertainty in the value of the subtracted term. The results indicate a relaxation frequency of about 120 kc and a value of $(\alpha'/\nu)_{\max}$ of about 3×10^{-10} cm^{-1} sec. This compares with a calculated value of $(\alpha'/\nu)_{\max}$ for thermal relaxation of 250×10^{-8} cm^{-1} sec (K11). This low frequency effect would therefore appear to be due to a different phenomenon. On the other hand, the value of α'/ν (above the classical at the highest frequency measured, 75 mc) is 5×10^{-8} cm^{-1} sec. Apparently the relaxation frequency for the thermal effect here is of the order of several hundred megacycles.

Table V-III.

Freq. mc	$\frac{\alpha_{\text{excess}}}{\alpha_{\text{classical}}}$ (computed from viscosity measurements of Liebermann)	$\frac{\alpha_{\text{excess}}}{\alpha_{\text{classical}}}$ (computed from absorption measurements of Parthasarathy)
2	64	
3	24	17
4	17	
5	12	
7		1.8[a]
16		8.2

[a] In a number of liquids observed by Parthasarathy, the values of the absorption obtained at 7 megacycles are significantly lower than those at either 3 or 16 megacycles and are in disagreement with the results of other observers. This value is therefore open to serious question.

27. DISTINCTION IN BEHAVIOR BETWEEN ASSOCIATED AND NON-ASSOCIATED LIQUIDS

Both Hall (H1) and Pinkerton (P7) have pointed out that the absorption results in non-associated liquids exceed the classical value far more greatly than do the results in associated liquids. We have already discussed water in the associated group and toluene among the non-associated liquids. The other more important results follow.

Table V-IV.

Observer	T°C	Frequency in megacycles	$\alpha/\nu^2\times 10^{17}$ cm^{-1} sec^2
Moen (M8)	27	0.15	276
		0.20	210
		0.25	170
		0.4	111
		0.6	86
		0.8	80
		1.0	79
		1.2	78
Biquard (B22)	20	4.78	83
	19.5	7.96	83.5
Willard (W5)		10.34	90
Bazulin (B10)	19.2	10.69	83.1
	19.4	13.95	80.7
	19.6	17.23	84.2
	21.6	24.39	84.1
	21.3	37.37	79.5
Grobe (G7)	20	30	68
	20	43	74
	20	75	72.5
Verma (V8)	25	1.00	92
		1.46	91
		2.89	93
		4.00	94
Classical			7.8

(*a*) *Benzene* (C_6H_6)

Benzene has been studied by a very large number of observers over a frequency range from 150 kc to 165 mc. A graph of α/ν^2 *vs* frequency is shown in Fig. V-9. While these results are taken at various temperatures in the vicinity of 20°C, the spread of values is greater than that which could be attributed to the temperature effect. Moen (M8) points to the possibility that a small impurity could lower the absorption value appreciably. The best evidence of this is furnished by Bazulin (B8, B10) who performed the experiment with benzene of two grades of purity. For the purest sample he obtained a value of $\alpha/\nu^2=874\times 10^{-17}$ cm^{-1} sec^2 while for the less pure he obtained a value of 714×10^{-17} cm^{-1} sec^2.

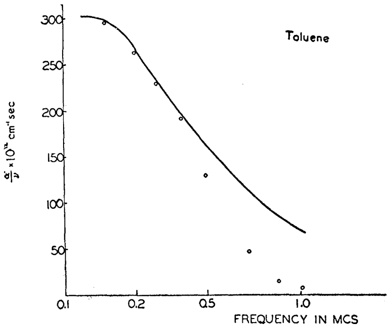

Fig. V-8. Excess absorption in toluene (data from Moen (M8)).

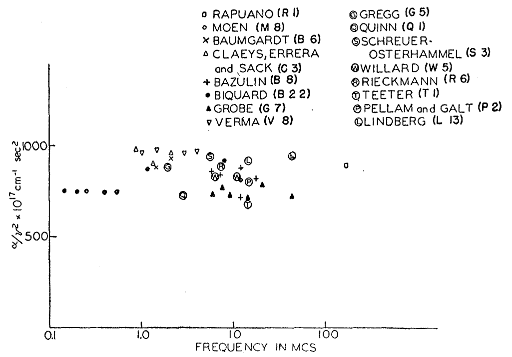

FIG. V-9. α/ν^2 *vs* frequency for benzene.

With this in mind, it is reasonable to assume that the best value of α/ν^2 is about 900×10^{-17} cm^{-1} sec^2.

The temperature coefficient of excess absorption in benzene is positive in the range 3–15 mc (B8, G5, P2). Since this frequency range is definitely below the relaxation frequency (α/ν^2 is still a constant) it appears from the discussion of the temperature coefficient that the excess absorption here is probably due to thermal relaxation.

(*b*) *Carbon Bisulfide* (CS_2)

The absorption values of CS_2 are very high. The most reliable results are shown in Fig. V-10. It is easily seen that the scattering of the points make it difficult to calculate any relaxation frequency. In a recent paper on the theory of sound absorption in unassociated liquids, Bauer (B4) suggested the presence of three vibrational relaxation processes. However, he fitted his calculations to the value of Claeys, Errera, and Sack at 0.87 mc, the value of Willard at 6.57 mc and the values of Rapuano near 100 mc. Since in general, Bazulin's results are more accurate in the range 1–10 mc than those of most other early observers, this selection of points does not appear too satisfactory. The more recent values of Moen (M8) and Verma (V8) make the picture even more uncertain. Because of the very high values of the absorption, it is possible that the results are easily affected by small impurities. It appears that a relaxation frequency exists in the range 8–70 mc, but a more definite appraisal must wait upon additional data.[46]

(*c*) *Carbon Tetrachloride* (CCl_4)

In CCl_4, there is no observable decrease in α/ν^2 as the frequency increases.[47] The mean value at room temperature is about 500×10^{-17} cm^{-1} sec^2. At the highest frequency measured, (105 mc (R1)) $\alpha/\nu=525\times10^{-9}$ cm^{-1} sec, as compared with a maximum value of 5050×10^{-9} cm^{-1} sec, computed on the basis of a thermal relaxation (K11). Evidently the maximum occurs at a much higher frequency.

(*d*) *Ethyl Alcohol* (C_2H_5OH) *and Methyl Alcohol* (CH_3OH)

The best available data for ethyl and methyl alcohol are shown in Fig. V-11. No relaxation frequencies are distinguishable in either set of data.

28. LIQUIDS OF HIGH VISCOSITY

One might expect in a general way that highly viscous liquids would come closer to the classical behavior than other liquids. We first recall the Stokes equations for absorption due to viscosity (R2, vol. II, p. 316), which appeared in Sec. 3:

$$k^2-\alpha^2=\frac{3\rho_0}{4\eta}\frac{\omega^2\omega_v}{\omega_v^2+\omega^2}, \tag{28.1}$$

$$2k\alpha=\frac{3\rho_0}{4\eta}\frac{\omega^3}{\omega_v^2+\omega^2}, \tag{28.2}$$

where ρ_0 = mean density, c_0 = low frequency value of sound velocity, η = shear viscosity coefficient, and $\omega_v=3\rho_0c_0^2/4\eta$. From these, one can solve explicitly for α^2 and c^2:

$$\alpha^2=\frac{3\rho_0}{8\eta}\frac{\omega^2\omega_v}{\omega_v^2+\omega^2}\left[\left(1+\frac{\omega^2}{\omega_v^2}\right)^{\frac{1}{2}}-1\right], \tag{28.3}$$

$$c^2=\frac{8\eta}{3\rho_0}\frac{\omega_v^2+\omega^2}{\omega_v}\frac{1}{\left(1+\dfrac{\omega^2}{\omega_v^2}\right)^{\frac{1}{2}}+1}. \tag{28.4}$$

The most interesting measurements in a highly viscous medium are those of Mikhailov and Gurevich (M7) on rosin. They measured the absorption at four fre-

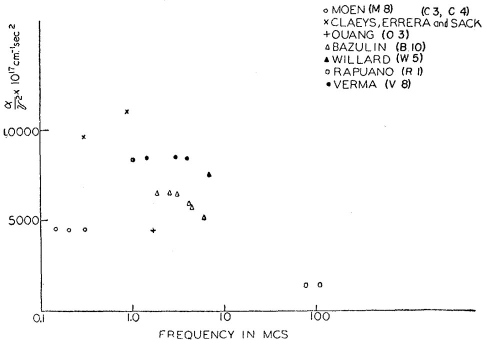

FIG. V-10. α/ν^2 *vs* frequency for carbon bisulfide.

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[46] Lamb and Andreae (L2a) have recently found this frequency to be 72 mc at 25°C.

[47] The values of Claeys, Errera, and Sack for CCl_4 have been omitted from consideration here. Their values of α/ν^2 are only about 1/20 of those of other observers. While no experimental reasons can be given for discarding these values (in general their other results are only about 20–30 percent above the commonly accepted values), the great divergence from the results of investigators whose other results are reliable, and who agree in these cases seems to offer sufficient justification. It is quite probable that small amounts of impurities can produce a great effect in these liquids of high absorption.

quencies between 0.5 mc and 5 mc for various temperatures. The shear viscosity was also measured in the same range. Their results indicate that at a fixed frequency the absorption increases with increasing viscosity only for low values of the viscosity. At high values of the viscosity, a maximum absorption coefficient is reached, and thereafter the absorption coefficient *decreases* as the viscosity increases. This is precisely the behavior predicted by Eq. (28.3). A complete check of the theoretical (classical) and experimental values is not possible since the values of the sound velocity in rosin are not available. However, it is possible to check the behavior at the highest values of the viscosity when, according to Eq. (28.3),

$$\alpha = \left(\frac{3\rho_0\omega}{8\eta}\right)^{\frac{1}{2}}, \quad \omega \gg \omega_v, \tag{28.5}$$

i.e., α is independent of the sound velocity at these frequencies. At 42°C the value of the viscosity of rosin is about 10^8 poise (M7). Assuming a density of 1.07 g/cm^3, we obtain the results shown in Table V-V.

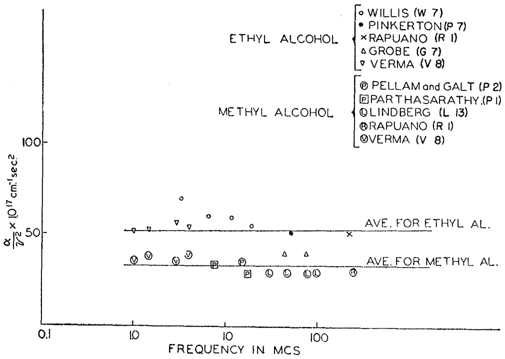

FIG. V-11. α/ν^2 *vs* frequency for ethyl alcohol and methyl alcohol.

This represents surprisingly good agreement when we recall that η is known only to an order of magnitude.

In the same paper, values of the absorption in methyl-metacrylate at two different frequencies are also reported. Here again, with $\eta > 10^{13}$ poise, the ratio of $\alpha/\nu^{\frac{1}{2}}$ is the same at the two frequencies.

Both of these results seem to point to a perfectly classical behavior for materials of very high viscosity. Unfortunately the only velocity data which are available (for methyl-metacrylate in the same frequency range) show that the velocity is essentially constant over the range 1 to 6.8 mc, whereas the limiting form of the velocity from Eq. (28.4) is

$$c = (8\eta\omega/3\rho_0)^{\frac{1}{2}}. \tag{28.6}$$

A second objection to this application has been raised by Bazulin and Leontovich (B14), who point out that some approximations had already been made by Stokes in setting up his original equation of motion, and that so long as these are neglected, it is misleading to employ an "exact" solution of the inexact equation.

TABLE V-V. Absorption in rosin.

Frequency mc	α_{theor} cm^{-1}	$\alpha_{\exp}$(M7) cm^{-1}
0.66	0.13	0.15
1.52	0.20	0.20
3.04	0.28	0.31
4.67	0.40	0.47

Nevertheless it would seem that the excellent agreement between Eq. (28.5) and the experimental results should be more than merely fortuitous. The agreement between classical theory and experiment in helium gas at very low pressures, discussed in Sec. 21 also indicates that the assumptions involved in the Stokes's equation of motion remain valid at what is effectively a very high frequency (i.e., high value of the frequency-pressure ratio). It may be that further corrections affect the velocity equation appreciably, but not the absorption relation.

The results in highly viscous glycerin are also of considerable interest. The frequency dependence of α/ν^2 is shown in Fig. V-12, while the temperature dependence of the ratio $\alpha_{\text{observed}}/\alpha_{\text{classical}}$ is shown in Fig. V-12.

The run of measurements at room temperature agree reasonably well with the classical values. As the absorption coefficient changes rapidly with temperature, the small variation in operating temperature among the various observers makes this quite understandable.

The recent results of Litovitz (L15) shown in Fig. V-13 indicate the presence of an additional, nonclassical absorption process. In his case, two runs were made with slightly different water contents (and hence different viscosities). In both cases a peak absorption was obtained (−9.2°C, −6.2°C).

These results may be interpreted by assuming that there exists a compressional viscosity which has a characteristic frequency of the same order of magnitude as $\omega_v/2\pi$ in Eq. (28.3). The existence of a maximum absorption (as a function of viscosity) places glycerin in a class with rosin, since, in both cases, the absorption

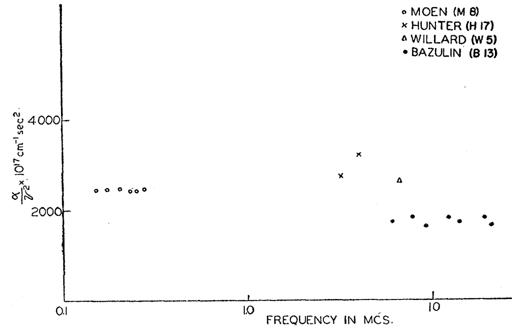

FIG. V-12. α/ν^2 *vs* frequency for glycerin.

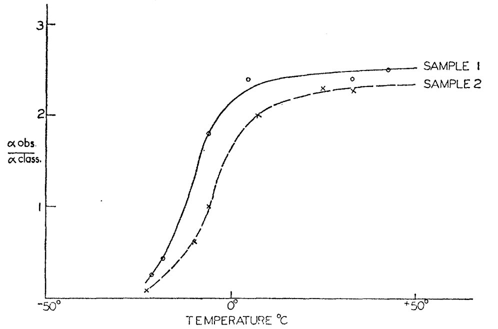

FIG. V-13. Temperature dependence of absorption in glycerin (data from Litovitz (L15)).

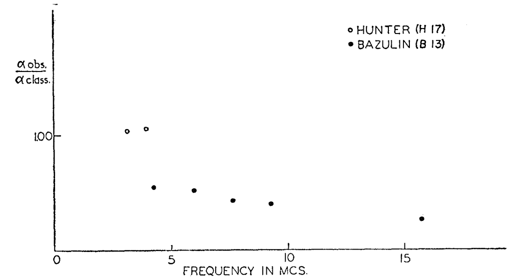

FIG. V-14. Sound absorption in castor oil.

decreases with increasing viscosity (at sufficiently high viscosity).

Another highly viscous liquid is castor oil, the chief experimental results (B13, H17) for which are shown in Fig. V-14.

These results indicate that the experimental value of α/ν^2 lies below the classical value at frequencies above 4 mc. In addition, α/ν^2 falls off with rising frequency. This would be in accord with Eq. (28.3) except that the computed value $\omega_v/2\pi$ for castor oil is about 300 mc, whereas the distribution of points in Fig. V-14 indicates a value of $\omega_v/2\pi$ of about 5 mc.

29. SUMMARY

Pinkerton (P7) has presented a rough classification of liquids according to values of the absorption coefficients. A modified form of this scheme is reproduced in Table V-VII. A detailed listing of specific examples is given in Table V-VIII. The ratio of α as calculated on the basis of Liebermann's experiments to the classical value is also given.

Chapter VI. Experimental Results in Solutions

30. SEA WATER

A great many experimental measurements have been made on the transmission of sound in sea water, especially at frequencies between 10 kc and 100 kc. Most of these measurements have been made in the ocean itself. As an experimental medium, however, the ocean presents many disadvantages. It is not a medium of constant velocity,[48] so that the sound rays are bent away from rectilinear propagation; it is not actually a medium of infinite extent; both surface and bottom reflection must be considered. In addition, there are slight changes in the chemical constitution of sea water from place to place, and finally, air bubbles, seaweed, fish, and similar scattering objects are often present.

Since there are many applications of underwater sound which are concerned with the sound transmitted from point to point, it is well to distinguish between the total attenuation, due to absorption, scattering, etc., and true absorption. It is probable that a failure to distinguish adequately between these quantities accounts for the relatively high "absorption" values sometimes reported at very low frequencies. Fortunately, the perfection of the reverberation tank method has

TABLE V-VII. Classification of liquids.

Classical	$\alpha_{\text{exp}}/\alpha_{\text{class}}$	Temperature coefficient of α	Type of liquid	Examples
AI anomalous	3–1500	Positive, $(\alpha_{\text{exp}}/\alpha_{\text{cl}})$ varies with temperature	unassociated, polyatomic	CS_2, C_6H_6, CCl_4
AII anomalous	1.5–3	Negative, $(\alpha_{\text{exp}}/\alpha_{\text{cl}})$ virtually independent of temperature	associated, polyatomic	water, alcohols
AIII anomalous	5–5000	Depends critically upon frequency	organic acids and esters	acetic and formic acid; ethyl acetate
NI normal	1	Positive	monatomic, diatomic	helium, mercury, liquid oxygen
NII normal	1	Negative, $(\alpha_{\text{exp}}/\alpha_{\text{cl}})$ varies with temperature and may even become <1	associated polyatomic	glycerin, castor oil, highly viscous liquids

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[48] For a general discussion of this problem, see *Physics of Sound in the Sea*, Part I. (N1). A brief, elementary survey has been given by Harnwell (H4).

TABLE V-VIII.

Class	Liquid	Formula	T°C	Frequency mc	$\alpha/\nu^2_{\text{exp}}$ $\times 10^{-17}$ cm^{-1} sec^2	α/ν^2_{Cl} $\times 10^{-17}$ cm^{-1} sec^2	$\frac{\alpha_{\text{exp}}}{\alpha_{\text{cl}}}$	$\left[\frac{\alpha_{\text{total}}}{\alpha_{\text{class}}}\right]$ (Liebermann)	$\frac{1}{\alpha}\frac{dT}{d\alpha}$	References
AI	Carbon bisulfide	CS_2	20	1–10	6000	5	1200	>150		B10, B22, C4, V8
			21	75–105	1400	5	280			R1
	Benzene	C_6H_6	20–25	1–165	900	8.7	103	82	0.006	B7, B8, G7 P7, Q1, V8
	Methyl iodide	CH_3I	25	1–4	820					V8
			20	15	316					P2
			2	15	247	10	24.7		0.010	P2
	Toluene	$C_6H_5CH_3$	27	0.15	205	7.8	26			M8
			20–25	1–75	80	7.8	10.3		0.013	B10, L17, V8
	Acetylene dichloride	$C_2H_2Cl_2$	25	1–10	420	7.7	55			P7, V8, W5
	Methyl bromide	CH_3Br	2	15	304					P2
	Chloroform	$CHCl_3$	20–25	1–10	400	10	40	20		B22, V8, W5
	Carbon tetrachloride	CCl_4	20	1–100	500	20	25	23	0.001	B1, P2, Q1, W5
	Chlorobenzene	C_6H_5Cl	25	1–4	124	8	15.5			V8
	n-butyl chloride	$CH_3(CH_2)_2CH_2Cl$	2	15	108	10	10.8			P2
	Acetone	$(CH_3)_2CO$	25	1–4	70	7	10			V8
			20	5–70	30	7	4.3	5.3		B21, B22
	m-xylene	$C_6H_4(CH_3)_2$	25	1–15	78	8.4	9.3	10		P7, V8, W5
	n-heptane	$CH_3(CH_2)_5CH_3$	22	15	80	10	8			P2
	n-hexane	$CH_3(CH_2)_4CH_3$	21	15	77	10	7.7			P2
	ethyl bromide	CH_3CH_2Br	2	15	61	10	6.1			P2, V8
	nitrobenzene	$C_6H_5NO_2$	25	1–15	80	14	5.7		0.005	P2, V8
	n-propyl chloride	$CH_3CH_2CH_2Cl$	2	15	42	8	5.3			P2
	n-propyl iodide	$CH_3CH_2CH_2I$	2	15	54	14	3.86			P2
	n-butyl bromide	$CH_3(CH_2)_2CH_2Br$	2	15	49	13	3.77			P2
	n-propyl bromide	$CH_3CH_2CH_2Br$	2	15	39	11	3.54			P2
	ethyl iodide	CH_3CH_2I	2	15	40	12	3.25			P2
	n-butyl iodide	$CH(CH_2)_2CH_2I$	2	15	48	17	2.82			P2
AII	water	H_2O	20	7–250	25	8.5	2.95	3.3	−0.031	P6, R1, S9
	methyl alcohol	CH_3OH	20–25	1–250	34	14.5	2.35	2.5	−0.010	P2, R1, V8
	ethyl alcohol	CH_3CH_2OH	20–25	1–220	54	22	2.45	4.4	−0.015	R1, V8
	n-propyl alcohol	$CH_3CH_2CH_2OH$	22–28	15–280	75	36	2.08		−0.008	P2, R1, V8
	n-butyl alcohol	$CH_3(CH_2)_2CH_2OH$	25	1–4	104	50	2.02			P2, R1, V8, W5
	m-amyl alcohol	$CH_3(CH_2)_3CH_2OH$	29	15	106	58	1.83		−0.014	P2
AIII	Acetic acid	CH_3COOH	18	0.5	90000	17	5300		[a]	L2
			18	67.5	158	17	10.8		−0.010	L2
	Formic acid	$HCOOH$	17.5	4.04	2270	5	454			B10
			20.5	9.83	1170	5	234			B10
	Methyl acetate	CH_2COOCH_3	25	1.00	468	6.8	69			V8
			22	69	34	6.8	5			B1
	Ethyl acetate	$CH_3COOCH_2CH_3$	25	1.00	516	8.3	62			V8
			22	69	37	8.3	4.5			B1
	Ethyl formate	$HCOOCH_2CH_3$	23–28	3	138	7.6	18.1	25		P1
			23–28	16	70	7.6	9.2	13 (at 5 mc)		P1
			T°A							
NI	Helium	He	4°A	15	231	204	1.12		0.6	P4
	Argon	A	85°A	44.4	10.1	10.5	0.97			G1
	Hydrogen	H_2	17°A	44.4	5.6	5.8	0.97			G1
	Nitrogen	N_2	73.9°A	44.4	10.6	9.5	1.12			G1
	Oxygen	O_2	87°A	44.4	8.6	7.3	1.18		0.0	G1
	Mercury	Hg	20–25°C	20–50	6	5.05	1.2			B1, R6, R7
			T°C							
NII	Castor oil		21.4	15.72	2100	7980	0.26			B13
			21.5	4.29	4500	7900	0.57			B13
			18.6	3.157	10900	9130	1.20		−0.075	H17
			21.6	3.95	8400	7820	1.17			H17
	Olive oil		21–25	1–4	1250	1100	1.14		−0.038	H17, V8
	Linseed oil		20.5	3.157	1470	1450	1.01		−0.032	H17
NII	Glycerin	$C_3H_8O_3$	20–27	0.15–4	2500				−0.069	M8, W5
			21–23	6–21	1700				−0.056	B13, H17
			32.8	30	1410	590	2.4			H17
			−18.8	30	12500	29100	0.43		0.036	H17

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[a] The value of $(1/\alpha)\partial\alpha/\partial T$ in this case depends critically on both frequency and temperature. It may be either positive or negative. See Lamb and Pinkerton, reference L2.

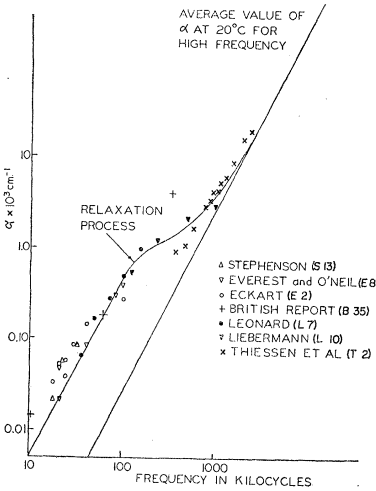

FIG. VI-1. Sound absorption in sea water.

made it possible to compare the open sea results with those obtained under the controlled conditions of the laboratory. A plot of available values of the absorption coefficient in sea water is shown in Fig. VI-1.

It is clear from the characteristic shape of the curve drawn through the experimental points that a relaxational phenomenon exists, with a relaxation frequency of about 145 kc.

The relaxational effect in sea water was at first attributed by Liebermann (L10) to a shift in the chemical equilibrium of ionized sodium chloride. The weight of experimental evidence, however, seems to be against this point of view (B10, B38, C3, R12, T2, V7) although one recent observer (V7) did obtain a large absorption in sodium chloride solution.[49] It is quite probable that these values may have been caused by impurities since their experimental methods used appear to be otherwise satisfactory.

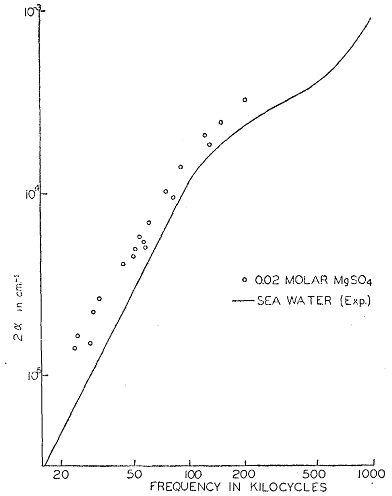

FIG. VI-2. Sound absorption in 0.02 molar magnesium sulfate solution (data from Leonard (L7)).

Recent experiments of Leonard (L7) and others indicate that the excess absorption in sea water can be explained by the presence of small amounts of $MgSO_4$. This is present in sea water in a concentration of slightly more than 0.02 molar. The available results are plotted in Fig. VI-2. The solid curve represents the best fit of sea water data. Thus the absorption in 0.02 molar $MgSO_4$ more than accounts for the excess absorption.

As was pointed out in Sec. 7 above, Liebermann has advanced a second theory of sound absorption by electrolytes in which the absorption is attributed to a shift in the ionization equilibrium by the passage of the sound wave. He defines a static isothermal partial compressibility

$$\mu_T{}^i = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \qquad (30.1)$$

and a static partial molar heat capacity C^i, and introduces the dynamic quantities $\mu_T{}^{\text{eff}}$, C^{eff}, defined by the relations

$$\mu_T{}^{\text{eff}} = \frac{\mu_T{}^i}{1+i\omega\tau}; \quad C^{\text{eff}} = \frac{C^i}{1+i\omega\tau}. \qquad (30.2)$$

TABLE VI-I. Values of A and τ for sea water.

	A	τ
Sea water (Liebermann, L10)	1.45×10^{-10} sec/cm	1.1×10^{-6} sec
$0.02M$ $MgSO_4$ (Leonard, L7)	2.3×10^{-10} sec/cm	1.3×10^{-6} sec
$0.02m$ $MgSO_4$ (Liebermann) theory, L10	6.5×10^{-10} sec/cm	...

From these relations, Liebermann obtained an approximate expression for the absorption:

$$\alpha = \frac{1}{2c}\left[\frac{C^i}{C^2}(C_p - C_v) + \frac{\mu_T{}^i}{\mu_T{}^0}\right]\frac{\omega^2\tau}{1+\omega^2\tau^2}, \qquad (30.3)$$

where C and $\mu_T{}^0$ are the limiting values (at low frequency) of C_p and μ_T respectively.

Liebermann's evaluation of the constants in Eq. (30.3) indicated that the thermal effect is very small in comparison with the compressibility effect. In addition, it appears that the compressibility term is sufficient to account for the absorption present, at least at frequencies below 1 megacycle.

If the total absorption in the solution is written in the form

$$\alpha = \frac{A\tau\omega^2}{1+\omega^2\tau^2} + \text{const}\,\omega^2, \qquad (30.4)$$

the values of A and τ obtained in sea water and $0.02m$ $MgSO_4$ and the value of A obtained by Liebermann's theory are given in Table VI-I.

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[49] Professor van Itterbeek has informed the authors that recently repeated measurements with sodium chloride of very high purity gave no excess absorption over the fresh water value.

From Table VI-I one may draw the following conclusions:

(1) The experimentally measured absorption in $MgSO_4$, as has already been pointed out, is larger than the total absorption in actual sea water. This indicates that a more complicated reaction among the various ions present in sea water must take place, so as to modify the results which exist for the simpler magnesium sulfate-water solution.[50]

(2) The theoretical value obtained by Liebermann is at least of the same order of magnitude as the experimental value. The discrepancy in numerical values is not surprising in view of the roughness of available data. Some criticism can be made in regard to the use of data for evaluating $\mu_T{}^i$ which were obtained by Bachem at 5 mc, at which frequency this absorption effect is no longer of consequence. One should also emphasize that Liebermann's treatment is not necessarily unique. The application of the method to other solutions or the direct calculation of the relaxation time of the process would be highly desirable.

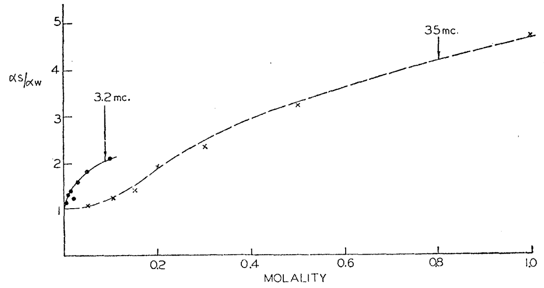

FIG. VI-3. Sound absorption in magnesium sulfate solution as a function of concentration (data from Smith, Barrett and Beyer (S10)).

The sound absorption in magnesium sulfate solutions has more recently been investigated at higher frequencies (S10), above those at which the process just described is significant. These results show that there is an additional absorption, not attributable to any of the classical effects or to the compressibility effect of the chemical reaction. In addition, the temperature dependence of the absorption in such solutions has been measured in the range 0°–30°, and no anomalous effect exists in the neighborhood of 4°C, thus ruling out the thermal relaxation (which being proportional to $C_p - C_v$ must vanish near 4°C).

The variation of absorption with concentration obtained in these experiments is shown in Fig. VI-3. The results indicate that at lower frequencies, absorption is proportional to the square root of the concentration, but that at higher frequencies, there is a more complicated dependence, particularly at low concentrations. In addition, Wilson and Leonard (W8) have recently reported that the relaxation frequency of an aqueous $MgSO_4$ solution is virtually a constant over the concentration range 0.003 to 0.02 molal. Thus there is still a great need of further experimental and theoretical developments.

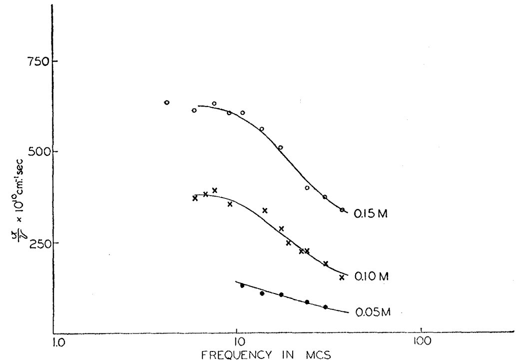

FIG. VI-4. Sound absorption in zinc acetate solution (data from Bazulin (B11)).

Mention should be made here of an earlier theory for absorption in strong electrolytes, due to Leontovich (L8). He has investigated the effect of the sound wave on the "ionic atmosphere" of the ions, from the point of view of the Debye theory of electrolytes. While his estimates of the magnitude of the absorption to be expected fall far short of what is obtained experimentally, it is of interest to note that the theory predicts that α should be proportional to the square root of the concentration at low frequencies and proportional to the square of the concentration at high frequencies, which is just the dependence shown in Fig. VI-3 (at low concentrations). A further study of this approach would be desirable.

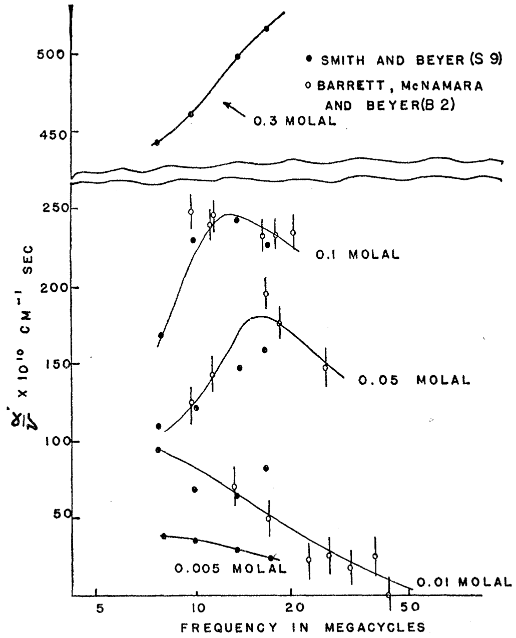

FIG. VI-5. Sound absorption in copper acetate solutions.

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[50] Tamm and Kurtze (O1a, T1a) have found that the excess absorption in a solution of $MgSO_4$ above the value for water can be virtually eliminated by the addition of large amounts of NaCl.

TABLE VI-II.

Concentration of copper acetate (molality)	Relaxation frequency in megacycles
0.005	$\ll 5$
0.01	~ 5
0.05	15
0.10	13
0.30	~ 22

It may well be that two or more general types of absorption processes exist in electrolytic solutions, namely, (1) that due to increased dissociation on the part of the solute in the presence of sound (Liebermann theory) and (2) that due to distortions produced in an ionic atmosphere of a wholly dissociated solute (Leontovich theory). Finally, the question may be raised[51] as to whether one is justified in assuming a simple additivity (total absorption = solute absorption + solvent absorption) for the various processes. The presence of solute ions in the neighborhood of water molecules certainly produces some change in the liquid structure, and may

TABLE VI-III.

Type	Solute	Mol. wt.	Observer	Ref.	Molarity	T°C	Freq. mc	α_s/α_w	α_s/α_w corrected to unit molarity
1–1	NaCl	58.5	Rüfer	R12	0.96	18	7.45	0.98	0.98
	$NaNO_3$	85.0	Bazulin	B9	1.00	20	30.5	0.97	0.97
	KCl	74.6	Bazulin	B9	1.00	24	20.1	0.97	0.97
	KNO_3	101.1	Bazulin	B9	1.00	17	30.5	0.97	0.97
	$AgNO_3$	169.9	Bazulin	B9	0.94	19–20.5	30.5	1.11	1.17
	NaBr	102.9	Rüfer	R12	1.63	18	7.45	1.02	1.01
			Rüfer		1.63	18	8.55	0.93	0.96
	KBr	119.0	Bazulin	B10	1.00	16–17	30.5	1.00	1.00
			Rüfer	R12	1.95	18	7.45	1.09	1.04
			Rüfer		1.95	18	8.55	1.00	1.00
	$NaClO_3$	106.5	Rüfer	R12	2.79	18	8.55	1.60	1.22
	$NaClO_4$	122.5	Rüfer	R12	2.06	18	7.45	2.04	1.51
			Rüfer		2.06	18	8.55	1.85	1.41
2–1	$MgCl_2$	95.2	Rüfer	R12	1.05	18	6.3	1.08	1.07
			Rüfer		1.05	18	8.55	1.39	1.37
	$SrCl_2$	158.5	Bazulin	B9	0.43	18	30.5	1.11	1.26
	$Cu(NO_3)_2$	187.6	Bazulin	B9	0.5	19–20	30.5	1.25	1.50
			Rüfer	R12	0.47	18	7.45	1.22	1.47
	$Cd(NO_3)_2$	236.4	Bazulin	B9	0.45	18–19	30.5	1.32	1.64
	$Pb(NO_3)_2$	331.2	Bazulin	B9	0.5	18–19	30.5	1.75	2.50
	$UO_2(NO_3)_2$	394.2	Rüfer	R12	0.32	18	8.55	1.77	
1–2	$(NH_4)_2SO_4$	80.1	Bazulin	B9	0.5	17.5	30.5	1.43	1.86
	Na_2SO_4	142.1	Bazulin	B9	0.5	17–18	30.5	1.50	2.00
	K_2SO_4	174.3	Bazulin	B9	0.5	17–17.5	30.5	1.89	2.78
2–2	$MgSO_4$	120.4	Bazulin	B9	0.974	22.5	20.64	4.48	4.6
			Rüfer	R12	0.99	18	6.3	5.10	5.1
			Smith, Beyer Barrett	S10	0.99	20	35.44	4.80	4.8
	$MnSO_4$	151.0	Bazulin	B9	0.05	21–24	30.5	1.39	8.8
			Bazulin		0.125	21–23	30.5	2.04	9.2
			Bazulin		0.250	21–24	30.5	2.93	8.7
	$NiSO_4$	154.8	Bazulin	B9	0.125	19–21	30.5	1.75	7.0
	$CuSO_4$	223.2	Bazulin	B9	0.125	20–22	30.5	2.04	9.3
			Rüfer	R12	0.56	18	6.3	4.28	6.9
	$CdSO_4$	208.5	Bazulin	B9	0.125	22–23.5	30.5	2.46	12.7
3–1	$La(NO_3)_3$	324.9	Bazulin	B9	0.1	16	12.45	4.6	37
			Bazulin		0.1	16	15.60	4.1	32
			Bazulin		0.1	17	17.35	3.9	30
			Bazulin		0.1	20	20.74	3.3	24
			Bazulin		0.1	20	30.56	2.8	19
			Bazulin		0.1	20–21	37.12	2.4	15
			Bazulin		0.25	17	9.24	10.7	40
			Bazulin		0.25	17	10.74	12.1	45
			Bazulin		0.25	17	12.40	12.0	44
			Bazulin		0.25	17.5	14	10.4	39
			Bazulin		0.25	18	20.64	9.9	37
			Bazulin		0.25	17–18	25.60	8.2	30
3–2	$Al_2(SO_4)_3$	342.12	Bazulin	B9	0.041	21–24	30.5	2.18	30
			Bazulin		0.084	21–24	30.5	3.14	27
			Bazulin		0.165	21–24	30.5	3.09	26
			Bazulin	B11	0.1	18	15.7	4.94	40
			Bazulin		0.1	17–18	17.35	4.87	40
			Bazulin		0.1	17–18	24	4.55	37
			Bazulin		0.1	20–21	30.5	3.54	26

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[51] This was suggested by Dr. E. B. Yeager. Some recent measurements (B2a) indicate that the presence of a solute may lower the absorption coefficient below that of pure water.

possibly decrease the absorption attributed to structural relaxation.

31. ACETATE AND FORMATE ELECTROLYTES

The anomalies present in acetate and formate liquids have prompted some investigation of aqueous solutions of salts containing these radicals. While the results are only fragmentary, they show some interesting trends, which merit further attention.

The most complete data available are for water solutions of zinc acetate (B11). In order to isolate the relaxation process, the values of α/ν for pure water have been subtracted from the experimentally determined values for the solution and the results have been plotted in Fig. VI-4. The corresponding results for solutions of copper acetate (B2, B17) have been similarly plotted in Fig. VI-5. (The vertical lines indicate the approximate uncertainty range in the more recent values.)

For zinc acetate the relaxation frequency at 0.10 and 0.15M has a value of about 8 megacycles. There is not sufficient evidence to indicate any relation between the concentration and the relaxation frequency. Liebermann's treatment of absorption in magnesium sulfate presumed that this frequency was directly proportional to the concentration.

Some rough information on the relation of the relaxation frequency to concentration may be obtained from the data on copper acetate solutions. The approximate relaxation frequencies are given as a function of concentration in Table VI-II.

It must be remembered that these numbers are based on only a very small number of points and are therefore a very rough estimate. Nevertheless they do point toward an increase in the relaxation frequency with increasing concentration, although not in a linear fashion.

32. VARIOUS ELECTROLYTES

The ratios of α_{solution} to α_{water} for aqueous solutions of various electrolytes are given in Table VI-III. The results are classified according to valence combinations. Molality values have been converted to molarity and a linear correction has been applied to give α_s/α_w for unit molarity in each case. Inasmuch as the actual dependence of α_s on concentration is not clearly known (compare discussion of $MgSO_4$ solutions above), this may be taken only as a rough guide, especially in those cases in which the experimental measurements have been made at very low concentrations.

The following conclusions may be drawn from the table:

(1) For 1–1 solutes, the excess absorption resulting from the solute is negligible, except in the cases of $NaClO_3$ and $NaClO_4$. In these two cases, there appears to be a small but real excess.

(2) In a general way, the ratio α_s/α_w increases with increase in valence of either ion.

(3) For a given negative radical, the absorption increases with the atomic weight of the positive ion. This is most clearly brought out in the series of nitrate compounds of the (2–1) type and to a lesser extent in the series of sulfate compounds of the (2–2) type.

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APPENDIX I. LIST OF SYMBOLS

Below are listed the most important symbols:

a—See Eq. (2.5), reciprocal of the compliance in Burgers's model.
b—See Eq. (2.5), fluid resistance in Burgers's model.
c—Sound velocity at frequency $(1/2\pi)\omega$.
c_0—Limiting velocity of sound at low frequencies.
c_∞—Limiting sound velocity for high frequencies.
f_{ij}—See Eq. (8.5)
k—See Eqs. (2.12) to (2.14).
k_r—Real part of k.
k_i—Imaginary part of k.
h—Planck's constant.
k'—Boltzmann's constant.
m—Mass of a molecule.
n—Sec. 7; see Eq. (7.11).
n—Sec. 8, number of molecules per unit volume.
n_i—Number of molecules per unit volume in state i.
p—Total pressure.
p_e—Excess pressure.
p_0—Equilibrium pressure (except in Sec. 13 and 14).
$\mathbf{q}$—Displacement vector.
t—Time.
$\mathbf{u}$—Particle velocity.
u_x—x component of the particle velocity.
v_1—Volume per molecule associated with state 1.
v_2—Volume per molecule associated with state 2.
A_i—See Eq. (8.12a).
A_{12}—Transition probability from state 1 to state 2.
A_{21}—Transition probability from state 2 to state 1.
A_{12}^0—Equilibrium value of the transition probability from state 1 to state 2.
A_{21}^0—Equilibrium value of the transition probability from state 2 to state 1.
B_p—See Eq. (7.14).
B_T—See Eq. (7.14).
C_v—Molar heat at constant volume.
C^{eff}—Dynamic partial molar heat capacity.
C^i—Internal molar heat capacity.
$C_p^e = C_p^\infty$—Molar heat at constant pressure related to intermolecular processes.
$C_v^e = C_v^\infty$—Molar heat at constant volume for intermolecular processes.

$C_p{}^i$—Molar heat at constant pressure for intramolecular processes.
$C_v{}^i$—Molar heat at constant volume for intramolecular processes.
$C_p{}^t = C_p{}^0$—$= C_p{}^e + C_p{}^i$, see Eq. (7.33).
$C_v{}^t = C_v{}^0$—$= C_v{}^i + C_v{}^e$.
E_1—Energy of an unexcited state (per mole).
E_2—Energy of an excited state (per mole).
E_k—See Eqs. (8.2) to (8.4), kinetic energy of translation.
F—Force in Burgers's model.
K—Isothermal bulk modulus.
K_s—Adiabatic bulk modulus.
K^e—Isothermal bulk modulus related to intermolecular effects.
$K^t = K^0$—Net isothermal bulk modulus.
$K_s{}^0 = K_s{}^t$—Low frequency adiabatic bulk modulus.
$K_s{}^\infty = K_s{}^e$—High frequency adiabatic bulk modulus.
M—Molecular weight.
N—Number of molecules in given volume usually taken as a mole.
N_1—Number of molecules in state 1.
N_2—Number of molecules in state 2.
$N_1{}^0$—Number of molecules in state 1 at equilibrium.
$N_2{}^0$—Number of molecules in state 2 at equilibrium.
P_e—See Eq. (2.12), pressure amplitude.
Q—Heat.
R—Gas constant.
R_e—See Eq. (2.14), excess density amplitude.
T^e—Temperature related to intermolecular equilibrium.
T^i—Temperature related to intramolecular equilibrium.
U_x—See Eq. (2.13), particle velocity amplitude.
U^e—Internal intermolecular energy.
U^i—Internal intramolecular energy.
V—Molar volume.
α—Amplitude absorption coefficient.
α_s—Amplitude absorption coefficient for solution.
α_w—Amplitude absorption coefficient for H_2O.
α'—Excess α.
β—Volume coefficient of thermal expansion.
β^e—Volume coefficient of thermal expansion related to the intermolecular forces.
β^i—See Eq. (7.30).
β^t—See Eq. (7.34).
γ—Ratio of specific heats.
γ_s—Parameter, related to Maxwell's equation.
ϵ_1—$= E_1/N$.
ϵ_2—$= E_2/N$.
ζ—See (Eq. (3.1)), viscosity coefficient.
η—Shear viscosity.
η'—See Eq. (13.2), viscosity coefficient.
θ_s—See Eq. (1.2), elastic constant.
κ—Coefficient of thermal conductivity.
λ—Sound wavelength.
λ_s—See Eq. (1.2), elastic parameter.
$\mu = \alpha\lambda$—Amplitude absorption coefficient per wavelength.
μ_i—Electrochemical potential.
μ'—Excess value of μ.
ρ—Total density.
ρ_e—Excess density.
ρ_0—Equilibrium density.
τ—See Eq. (6.1), relaxation time.
ν—Sound frequency.
ν_m—Relaxation frequency.
ω—Angular frequency.
ω_c—Angular relaxation frequency for heat conduction.
ω_m—See Eq. (9.13).
ω_0—Angular relaxation frequency.
ω_r—$= q/\gamma$, see Eq. (5.5).
ω_v—$= C_p\rho_0 c^2/M\kappa$, see Eq. (4.9).

APPENDIX II. SUMMARY OF SOME THERMODYNAMIC EQUATIONS

We are interested in irreversible processes, and we must, therefore, be careful in our use of thermodynamics. In general, we shall assume that there is a functional relation between the four variables, pressure p, volume V, temperature T, and the time t. Namely, the equation

$$\Delta V = \left(\frac{\partial V}{\partial p}\right)_{T,t} \Delta p + \left(\frac{\partial V}{\partial T}\right)_{p,t} \Delta T + \left(\frac{\partial V}{\partial t}\right)_{p,t} \Delta t$$

will always hold. For a system with energy dissipation, the second law becomes an inequality, and one is not allowed to apply the relationships based on the assumption that the law is an equality (Maxwell's thermodynamics relations) without carefully re-examining them. We shall not attempt this here, but simply note which equations were derived by taking the second law as an equality and avoid using them for irreversible processes. We assume that consistent units are used throughout. Thus the specific heat will be in ergs per moles in cgs units.

We list some useful definitions and some equations. The equations are either found in Slater (S8) or can be derived simply.

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{A-1}$$

$$\frac{1}{K} = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{A-2}$$

$$\frac{1}{K_s} = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S \tag{A-3}$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V \tag{A-4}$$

$$C_p = \left(\frac{\Delta Q}{\Delta T}\right)_p \tag{A-5}$$

$$dp = -\frac{K}{V}dV + \beta K dT \qquad \text{(A-6)}$$

$$dV = -(V/K)dp + V\beta dT \qquad \text{(A-7)}$$

$$dT = (1/K\beta)dp + \frac{1}{\beta}\frac{dV}{V} \qquad \text{(A-8)}$$

$$dU = (C_p - Vp\beta)dT - \left(T\beta - \frac{p}{K}\right)Vdp$$

(A-9) Using second law

$$= \frac{C_v}{K\beta}dp + \left(\frac{C_p}{V\beta} - p\right)dV \qquad \text{(A-10)}$$

$$= C_v dT + (T\beta K - p)dV \qquad \text{(A-11) Using second law}$$

$$K_s = K\frac{C_p}{C_v} \qquad \text{(A-12) Using second law}$$

$$C_p = C_v + TV\beta^2 K \qquad \text{(A-13) Using second law}$$

$$K_s = K\left(1 + \frac{TV\beta^2 K}{C_v}\right) \qquad \text{(A-14) Using second law}$$

$$\frac{C_p}{\beta K_s}\left(\frac{C_p}{C_v} - 1\right) = TV\beta \qquad \text{(A-15) Using second law}$$

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