REVIEWS OF MODERN PHYSICS VOLUME 31, NUMBER 4 OCTOBER, 1959

Ultrasonic Absorption Due to Chemical Relaxation in Electrolytes*

G. S. VERMA

Department of Physics, University of Allahabad, Allahabad, India

TABLE OF CONTENTS

I. Introduction
II. Theory
  (a) Excess Sound Absorption
  (b) Activation Energy for the Rate Process
  (c) Different Mechanisms
III. Methods for Measuring the Absorption
  (a) Methods Based upon Progressive Wave Technique
    (1) Mechanical Methods
    (2) Optical Method
    (3) Electrical Methods
  (b) Methods Based Upon Standing Wave Technique
    (1) Resonance Method
    (2) Reverberation Method
IV. Results and Discussions
  (a) Values of Absorption and Relaxation Frequencies
  (b) Effect of Concentration on Absorption
  (c) Effect of Concentration on Relaxation Frequency
  (d) Effect of Dielectric Constant
  (e) Effect of Temperature
  (f) Effect of Heavy Water When Used as Solvent
  (g) Effect of Pressure

I. INTRODUCTION

STUDY of ultrasonic absorption due to chemical relaxation in electrolytes has recently had considerable development.† As a result of the comprehensive work done by Professor Tamm and his associates at the University of Göttingen and Professor Leonard and his associates at the University of California in Los Angeles, this aspect of sound absorption is understood somewhat better compared to the thermal or structural relaxation in fluids. Recently Litovitz and his associates have contributed much to the understanding of the basic mechanisms responsible for the sound absorption in chemical solutions.

Einstein[1] was the first to point out that chemical processes can account for sound absorption in partially dissociated gases. He made a theoretical estimate of its contribution in nitrogen tetroxide.[2] According to him, the excess sound absorption in partially dissociated gases such as nitrogen tetroxide is due to dissociation.

Liebermann[3] in 1949 considered sound absorption in a chemically active fluid. According to him, chemically active media may exhibit unusual physical properties such as dynamic compressibility whose value depends upon the compression rate in contrast to the conventional static value. The case is similar for dynamic specific heat, which depends upon the rate of change of temperature. These distinctions between static and dynamic values become prominent when high-frequency sound waves pass through the medium which is in chemical equilibrium, provided the equilibrium is pressure and temperature dependent. Such chemical reactions occurring in liquids are expected to affect the propagation of sound waves too.

Acetic acid is the first liquid in which the chemical process was found to be responsible for excess sound absorption. Spakowski[4] and Richards[2] suggested that the absorption of ultrasonic waves arises from the perturbation of the equilibrium between the dimer and monomer forms of acetic acid. Pinkerton[5] in 1948 confirmed experimentally the existence of the relaxation phenomenon in acetic acid and, with Lamb,[6] studied the absorption and dispersion of ultrasonic waves in acetic acid in great detail. They showed that a dispersion and maximum in the value of absorption per wavelength occur and that a relaxation process which arises from the perturbation of the chemical equilibrium due to passage of sound waves does exist. Recent measurements of Piercy and Lamb[7] at low concentrations of acetic acid indicate the presence of a second relaxation region with a characteristic frequency an order of magnitude higher than that for the pure acid. This second relaxation is ascribed to the monomer-dimer reaction, whereas the first relaxation in pure acid is still unexplained. Litovitz and Carnevale[8] have studied effects of pressure on ultrasonic relaxation in pure acid and their results, however, are in agreement with monomer-dimer theory.

---

* Part of this work was carried out while the author was at Ultrasonics Research Laboratory, Western Reserve University, Cleveland, Ohio.

† Additional references, other than those cited in the text of this article, are listed at the end of the article on p. 1068.

[1] A. Einstein, Preuss. Akad. Wiss. Berlin Ber. 19, 380 (1920).

[2] W. T. Richards, Revs. Modern Phys. 11, 36 (1939).

[3] L. Liebermann, Phys. Rev. 76, 1520 (1949).

[4] B. Spakowski, Compt. rend. acad. sci. U.R.S.S. 18, 169 (1938).

[5] J. M. M. Pinkerton, Nature 162, 106 (1948).

[6] J. Lamb and J. M. M. Pinkerton, Proc. Roy. Soc. (London) A199, 114 (1949).

[7] J. E. Piercy and J. Lamb, Trans. Faraday Soc. 52, 930 (1956).

[8] T. A. Litovitz and E. H. Carnevale, J. Acoust. Soc. Am. 30, 134 (1958).

Another indication of the existence of such perturbation effects of sound waves on chemical equilibrium resulting in sound absorption is provided by measurements of the ultrasonic absorption in sea water and its comparison with fresh water below one megacycle per second by several workers.[9–14] Leonard discovered that the cause of excess sound absorption in sea water is the presence of $MgSO_4$. Above 1 Mc the absorption is similar to that of fresh water. Below 1 Mc the value of α/ν^2, where α is the absorption coefficient and ν the frequency, is found to increase with decrease in frequency. The absorption coefficient is governed by an empirical relation of the type

$$2\alpha = A_1[K\omega^2/(\omega^2+K^2)]+A_2\omega^2,$$

where ω is the angular frequency and K's and A's are constants. The first term has the form characteristic of a relaxation phenomenon, and this led to the suggestion that chemical relaxation is the process responsible for the excess sound absorption. Wilson[15] later reported that the relaxation frequency does exist near 130 kc. According to Liebermann,[3] the relaxation term arises from a pressure-dependent equilibrium of a chemical reaction within the liquid, and the cause of the excess sound absorption in $MgSO_4$ solutions lies in the dissociation reaction $AB \rightleftarrows A+B$ involving magnesium-sulfate molecules or ions. He developed a theory of sound propagation in chemically active media, but its application to $MgSO_4$ suffered from some errors with regard to concentration dependence; for example, he suggested that the absorption is proportional to the square root of the concentration. Wilson and Tamm and Kurtze[16a] have shown independently that absorption is linearly proportional to concentration. This led to the explanation that the process is unimolecular, $A \rightleftarrows B$, with a relaxing transition between two energy states of the ion pairs. Barthel[17] later discussed the concentration behavior and concluded that if the activity coefficients for ionic reactants are taken into consideration the experimental results of Wilson which suggest unimolecular reaction will fit equally well with the dissociation reaction. Bies[18] also considered the dependence of the activities of the ions with the passage of sound waves. He studied the effect of the dielectric constant of the solvent on the absorption and concluded in favor of a dissociation mechanism as responsible for the excess sound absorption.

Tamm and Kurtze[19] assume the existence of the complex MeR, H_2O, where Me = metal and R = radical. For this complex two different possibilities of dissociation are assumed in order to explain the presence of two relaxation frequencies. The other possibilities which may cause the anomalous sound absorption, according to Tamm, are ion association or a complicated combination of molecular dissociation and hydrolysis. Thermal relaxation is ruled out, simply because there is no appreciable change in the absorption near 4°C where isothermal propagation is expected to take place. The assumption of ion association, i.e., the association of anion and cation to form an ion pair (ion pair $\rightleftarrows$ anion and cation) gives a similar dependence of absorption and relaxation on frequency as in the case of the dissociation process. But this assumption explains only one relaxation mechanism. It does not explain the second increase in the product of absorption cross section and wavelength, which is observed in the case of 2–2-valent electrolytes.

Litovitz and Smithson[20] suggest that all observed data can be explained on the basis of the assumption that the reaction is between two dipole molecules. They rule out the reaction between two ions of unlike sign as the rate-determining step in the primary relaxation process. Their results also indicate that the hydrogen ion is not involved in the rate-determining reaction causing the observed relaxational effects.

II. THEORY

(a) Excess Sound Absorption

A plane acoustic wave in an absorbing medium can be represented in the form

$$\xi_x = \xi_0 \exp[i\omega(t-x/V_0)-\alpha x], \qquad (1)$$

where ξ_x is the amplitude at a distance x and α is the amplitude absorption coefficient. This expression can be written in the form

$$\xi_x = \xi_0 \exp[i\omega(t-x/V)], \qquad (2)$$

where

$$1/V = (1/V_0)-(i\alpha/\omega). \qquad (3)$$

If it is assumed that the chemical equilibrium is pressure dependent, then a change in the pressure will cause a shift in the equilibrium. Such a medium has a complex compressibility. The isothermal compressibility of a solution may be assumed to be equal to the isothermal compressibility of the solvent (assumed real) plus a complex factor due to the perturbed chemical equilibrium. Thus

$$\beta = \beta_0+\beta'. \qquad (4)$$

---

[9] F. A. Everest and O. H. O Neill, J. Acoust. Soc. Am. 19, 255 (1946).

[10] D. A. Wilson and L. N. Liebermann, J. Acoust. Soc. Am. 19, 286 (1947).

[11] R. W. Leonard, J. Acoust. Soc. Am. 20, 254 (1948).

[12] L. Liebermann, J. Acoust. Soc. Am. 20, 868 (1948).

[13] Leonard, Combs, and Skidmore, J. Acoust. Soc. Am. 21, 63 (1949).

[14] R. W. Leonard, Tech. Rept. No. 1, Physics Department, University of California, Los Angeles, California (1950).

[15] O. B. Wilson, Jr., Tech. Rept. No. 4, Physics Department, University of California, Los Angeles, California (1951).

[16] (a) K. Tamm and G. Kurtze, Acustica 3, 33 (1953); (b) *ibid.*, p. 42; (c) *ibid.*, p. 41.

[17] R. Barthel, J. Acoust. Soc. Am. 24, 313 (1952).

[18] D. A. Bies, Tech. Rept. No. 6, Physics Department, University of California, Los Angeles, California (1953).

[19] K. Tamm and G. Kurtze, Acustica 4, 380 (1954).

[20] S. R. Smithson and T. A. Litovitz, J. Acoust. Soc. Am. 28, 462 (1956).

The contribution to the intensity attenuation coefficient per wavelength of the complex compressibility is given by

$$2\alpha\lambda = -2\pi\,\mathrm{Im}(\beta'/\beta_0). \tag{5}$$

Consider the case of a two-state equilibrium reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B.$$

If N represents the molal fraction in the excited state, then at equilibrium

$$dN/dt = k_1 - (k_1 + k_2)N = 0. \tag{6}$$

Similarly in the case of a dissociation reaction

$$AB \underset{k_2}{\overset{k_1}{\rightleftarrows}} A + B$$

at equilibrium,

$$dN/dt = k_1(1-N) - k_2N^2. \tag{7}$$

If the equilibrium of the reaction is perturbed only slightly by the change of acoustic pressure, the rate of return towards equilibrium is, to a first-order approximation,

$$d(\Delta N)/dt = K(\Delta N - \Delta N_0), \tag{8}$$

where ΔN_0 represents the magnitude of small perturbation and K is defined as the equilibrium reaction rate. In the case where ΔN_0 is a constant the solution is given by

$$\Delta N = \Delta N_0[1 - \exp(-Kt)], \tag{9}$$

where $1/K$ is called the time constant or relaxation time τ of the reaction in the vicinity of equilibrium. However, if the perturbing force is the acoustic wave, the perturbation varies periodically with time, for example, as $\exp i\omega t$, then the solution is given by

$$\Delta N = \Delta N_0/(1 + i\omega/K). \tag{10}$$

Liebermann[3] showed that the dynamic partial isothermal compressibility β' is given by

$$\beta' = \beta_0'/(1 + i\omega/K), \tag{11}$$

where β_0' is the portion of the static isothermal compressibility which arises from the supposed chemical reaction.

Neglecting the small specific heat term, the contribution to the sound absorption coefficient arising from the chemical reaction is given by

$$2\alpha = \frac{\beta_0'}{\beta_0}\,\frac{\omega^2 K}{(\omega^2 + K^2)C_0}, \tag{12}$$

where β_0 is the total static isothermal compressibility, K is the rate constant for return to equilibrium after a slight perturbation, C_0 is the phase velocity of sound at very low frequencies, and ω is the angular frequency.

Leonard's measurements indicated $\beta'/\beta_0 = 0.5\times 10^{-4}$ and $K = 0.9\times 10^{-4}$ sec^{-1} in 0.02 M $MgSO_4$ at 25°C.

Liebermann considered two possibilities of the chemical reaction—unimolecular and dissociation type. Corresponding to these types Liebermann derives the following equations for β_0'. For a reaction of the type $A \rightleftarrows B$,

$$\beta_0' = (V/RT)[\Delta V/V]^2 N(1-N), \tag{13}$$

where V is the volume of solution containing 1 M of solute, R is the gas constant, T is the absolute temperature, N is the fraction of molecules in state B at equilibrium, and ΔV is dV/dN. For a reaction of the type $AB \rightleftarrows A + B$,

$$\beta_0' = (V/RT)[\Delta V/V]^2[N(1-N)/(2-N)]. \tag{14}$$

Here N is the fraction of AB dissociated.

Liebermann concluded that anomalous absorption in $MgSO_4$ had its origin in a dissociation reaction and stated that for this reaction K is proportional to m while β_0' would vary as $m^{3/2}$, where m is the molar concentration.

According to Barthel[17] the concentration behavior of β_0' and K is represented as follows. For a reaction of the type,

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B,$$

$$K = k_1 + k_2 \tag{15}$$

and

$$\beta_0' \propto k_1 k_2 (k_1 + k_2)^{-2} m; \tag{16}$$

and for

$$AB \underset{k_2}{\overset{k_1}{\rightleftarrows}} A + B,$$

mostly dissociated,

$$K \simeq k_1 \tag{17}$$

$$\beta_0' \propto [(k_2/k_1)\nu_A\nu_B m]m; \tag{18}$$

and for

$$AB \underset{k_2}{\overset{k_1}{\rightleftarrows}} A + B,$$

only slightly dissociated,

$$K \simeq 2(k_1 k_2 \nu_A \nu_B m)^{\frac{1}{2}} \tag{19}$$

$$\beta_0' \propto [(k_2/k_1)\nu_A\nu_B m]^{-\frac{1}{2}} m, \tag{20}$$

where m represents the molar concentration, k_1 is the rate constant for the forward reaction, k_2 is the rate constant for the reverse reaction, and ν's are activity coefficients. Activity coefficients for ionic reactants generally decrease rapidly with increase of concentration. If $MgSO_4 \rightleftarrows Mg^{++} + SO_4^{--}$ is taken as the mechanism corresponding to the case $AB \rightleftarrows A + B$, mostly dissociated, the data of Harned and Owen[21] show that

---

[21] H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions* (Reinhold Publishing Corporation, New York, 1950).

the mean activity coefficient for the magnesium and sulfate ions varies as $m^{\frac{1}{2}}$ with the result that the concentration dependence approximately cancel out of the factor $\nu_A\nu_Bm$ making β_0' proportional to m and K, independent of m even in the dissociation case, similar to unimolecular reaction.

Wilson[15] and Tamm and Kurtze[16a] have applied relaxation theory to chemical equilibrium and obtain the following expressions for the absorption coefficient per wavelength. For the unimolecular reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B,$$

the absorption per wavelength is

$$\alpha\lambda = \frac{\pi(\Delta V)^2}{\beta_0 RT}\frac{CK}{(1+K)^2}\frac{\omega\tau}{1+\omega^2\tau^2}, \tag{21}$$

with the angular frequency of relaxation

$$1/\tau = k_1 + k_2. \tag{22}$$

In these equations C is the total concentration of the solute, ΔV is the difference between the partial molar volumes, $K = C_B/C_A = k_1/k_2$ is the equilibrium constant, k_1 and k_2 are the forward and reverse reaction rates, respectively, β_0 is the static compressibility, ω is the angular frequency, and τ is the relaxation time.

For the dissociation reaction

$$AB \underset{k_2}{\overset{k_1}{\rightleftarrows}} A+B,$$

the results are

$$\alpha\lambda = \frac{\pi(\Delta V)^2}{\beta_0 RT}\frac{C\delta(1-\delta)}{(2-\delta)}\frac{\omega\tau}{1+\omega^2\tau^2} \tag{23}$$

and

$$\begin{aligned} 1/\tau &= k_1 + 2C\delta\Pi k_2 \\ &= k_1\{1+[2(1-\delta)/\delta]\}, \end{aligned} \tag{24}$$

where δ is the fractional dissociation and Π is the mean activity coefficient product.

Bies[18] considers a small unit cube in a homogeneous volume of solution. Supposing that no molecules of solvent nor of solute get in or out of the cube and that the dimensions of the cube, which is in a plane sound field, are small compared to wavelength, then the rate reaction for a dissociation reaction $AB \rightleftarrows A+B$ can be written in terms of the numbers of molecules and ions per unit volume as

$$dn_1/dt = k_1 n - k_2 f_\pm{}^2 n_1 n_2, \tag{25}$$

where $AB = C(1-\delta) = n/N$, $A = C\delta = n_1/N$, $B = C\delta = n_2/N$, and $f_\pm{}^2$ = mean squared activity coefficient provided C is the total concentration of A in either the molecular or the ionized state and δ, the fraction of A in ionized state.

At equilibrium

$$dn/dt = -dn_1/dt = -dn_2/dt = 0. \tag{27}$$

Here k_1 and k_2 are assumed to be independent of concentration while $f_\pm{}^2$ is assumed to be a function of concentration. All the parameters n, n_1, n_2, k_1, k_2, and $f_\pm{}^2$ are assumed to be pressure dependent and have a harmonic time dependence of the form $\exp i\omega t$ in a harmonic sound field. When sound waves pass through the medium, the concentration of the molecules and the ions varies because of the variation in their numbers and the volume. The contribution of the latter to absorption is, however, negligible.

Thus, the general irreversible rate equation may be represented by a Taylor series in terms of small variations in all of the parameters.

If we consider only linear terms,

$$\begin{aligned} i\omega\Delta n_1 = n\Delta k_1 - f_\pm{}^2 n_1 n_2 \Delta k_2 + k_1\Delta n \\ - k_2 f_\pm{}^2(n_1\Delta n_2 + n_2\Delta n_1) - k_2 n_1 n_2 \Delta f_\pm{}^2 \\ - (k_1 n - 2k_2 n_1 n_2 f_\pm{}^2)\Delta v. \end{aligned} \tag{28}$$

By using the mass action equilibrium law

$$K = k_1/k_2 = (f_\pm{}^2 n_1 n_2)/n, \tag{29}$$

we get

$$n\Delta k_1 - f_\pm{}^2 n_1 n_2 \Delta k_2 = k_2 f_\pm{}^2 n_1 n_2 (\Delta K/K). \tag{30}$$

From well-known thermodynamic relations

$$\partial(\Delta F_0)/\partial p = -\Delta V_0 \tag{31}$$

and

$$\Delta F_0 = -RT\ln K, \tag{32}$$

the following expression for ΔV_0 is obtained:

$$\Delta V_0 = (-RT/K)(\partial K/\partial n)(\partial n/\partial p)_T. \tag{33}$$

Here ΔV_0 is considered to be an empirical constant as the associated energy change ΔF_0 represents the free energy change when all the reactants are in their standard state.

The contribution β' to the isothermal compressibility due to a perturbation of the dissociation process is

$$\beta' = -(\partial v/\partial n)(\partial n/\partial p)_T. \tag{34}$$

We define

$$\Delta V = N(\partial v/\partial n)_T, \tag{35}$$

$$\beta' = -(\Delta V/N)(\partial n/\partial p)_T. \tag{36}$$

Hence,

$$\begin{aligned} \Delta V_0 &= (+RT/K)(\Delta K/\Delta n)(N\beta'/\Delta V) \\ \Delta K/K &= +[(\Delta V_0)(\Delta V)]\Delta n/(N\beta' RT) \end{aligned} \tag{37}$$

or

$$= (W\Delta n/N\beta' RT), \tag{38}$$

where $W = (\Delta V_0)(\Delta V)$. Thus

$$n\Delta k_1 - \Delta k_2 f_\pm{}^2 n_1 n_2 = (nk_1 W\Delta n/N\beta' RT). \tag{39}$$

To estimate the variation in the unit volume with the passage of sound waves we note that the net change in volume Δv must lag behind the acoustic pressure p

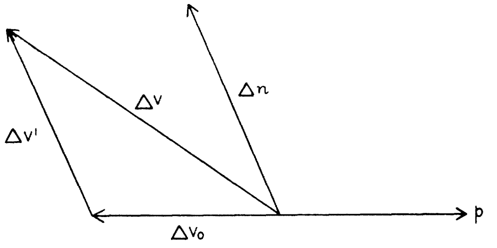


FIG. 1. Vectorial representation of the variations in volume, pressure, and number of molecules n, with the passage of a sound wave.

since this gives the work done on the system as positive. Δv_0 is the variation in volume of the solvent which is assumed dissipationless so that it lags behind the acoustic pressure by 180°. The variation in volume $\Delta v'$ due to a shift in the equilibrium is assumed to be in phase with the variation in the number of molecules Δn. The resultant change in the volume of the solution is Δv. A decrease in volume associated with the dissociation process has been assumed. The foregoing can be represented vectorially in Fig. 1.

From Fig. 1 it follows that

$$\Delta v = -(\beta_0 + \beta')\gamma p \tag{40}$$

$$\Delta v' = -\beta' \gamma p. \tag{41}$$

Since the process is assumed to be adiabatic, the ratio of the specific heats γ has been introduced.

Also it may be assumed that

$$\Delta v' = (\partial v / \partial n_2)\Delta n_2 = (\Delta V)\Delta n / N.$$

Eliminating $\Delta v'$ and γp between the last three expressions, we have

$$\Delta v = \Delta V(\beta_0 + \beta')\Delta n / N\beta'. \tag{42}$$

To estimate $\Delta f_\pm^2$, consider a function F defined such that

$$F = -(Z_1^2 + Z_2^2)d(\ln f_\pm^2)/d\Gamma, \tag{43}$$

where Γ is the ionic concentration and is given by

$$\Gamma = N^{-1} \sum_{i=1}^{i=4} n_i z_i^2. \tag{44}$$

Thus, it can be shown that

$$\Delta f_\pm^2 = -f_\pm^2 F(\Delta n / N - \Gamma' \Delta v), \tag{45}$$

where $\Gamma' = \Gamma / (Z_1^2 + Z_2^2)$.

After substituting Eqs. (39), (42), and (45) into Eq. (28) and canceling out Δn, the following expression for β' is obtained:

$$\beta' = k_1 n N^{-1} [W(RT)^{-1} - (\Delta V)\beta_0 (F\Gamma' - 1)][i\omega - K]^{-1},$$

where

$$K = k_1 [1 + n(n_1^{-1} + n_2^{-1}) + nN^{-1}(F + \Delta V - F\Gamma' \Delta V)]. \tag{46}$$

If we assume that (ΔV) is very small, such that $(\Delta V) \ll F$ and $(\Delta V) \ll (\Delta V_0)$, all the terms containing (ΔV) may be neglected. Thus,

$$\beta' = [k_1 n W / NRT(i\omega - K)],$$

where

$$K = k_1 [1 + n(n_1^{-1} + n_2^{-1} - FN^{-1})]. \tag{47}$$

β' has a maximum value at $\omega = K$ and thus K is the relaxation frequency.

The maximum value of $(2\alpha\lambda)$ is given by

$$(2\alpha\lambda)_{\max} = -2\pi_{\max} \operatorname{Im}(\beta'/\beta_0),$$

where

$$\beta' = n k_1 W / NRT(i\omega - K).$$

Thus, the maximum value is

$$(2\alpha\lambda)_{\max} = (\pi n k_1 W / NRTK\beta_0). \tag{48}$$

Expressing in terms of concentration and the degree of dissociation δ, the maximum value of the energy absorption per wavelength is given by

$$(2\alpha\lambda)_{\max} = \mu_{\max} = [\pi C(1-\delta) k_1 W / K\beta_0 RT] \tag{49}$$

and

$$K = k_1 [1 + (1-\delta)\delta^{-1}(2 - Fc\delta)]. \tag{50}$$

As the function F always appears as $Fc\delta$, it is better to consider the latter. The function F, as expressed earlier, is

$$F = -(Z_1^2 + Z_2^2)(d/d\Gamma)(\ln f_\pm^2) = -8(d/d\Gamma)(\ln f_\pm^2),$$

where $Z_1 = -Z_2 = 2$ and

$$\ln f_\pm^2 = -4.606 S\Gamma^{\frac{1}{2}}(1 + A\Gamma^{\frac{1}{2}})^{-1} \tag{51}$$

according to Debye-Hückel theory. If the ionic diameter is considered equal to 3.08 A, S and A are given by

$$S = 5.132 \times 10^6 (DT)^{-\frac{3}{2}}, \tag{52}$$

$$A = 109.6(DT)^{-\frac{1}{2}}, \tag{53}$$

where D is the dielectric constant, and T the temperature. Thus

$$Fc\delta = 18.424 Sc\delta \Gamma^{-\frac{1}{2}}(1 + A\Gamma^{\frac{1}{2}})^{-2}. \tag{54}$$

Eigen[22] has considered the general case which is characterized by a consecutive reaction of the form given below:

$$A^{++} + B^{--} \rightleftarrows (AB)_1 \rightleftarrows (AB)_2 \rightleftarrows \cdots \rightleftarrows (AB)_n.$$

According to him the recombination of oppositely charged ions is hindered by hydration layers and can not be treated as a one-step mechanism. It has to proceed stepwise. This system has a spectrum of relaxation times, in which the number of time constants corresponds to the number of independent steps. The relaxation times have to be calculated from the whole

---

[22] M. Eigen, Discussions Faraday Soc. **17**, 194 (1954); **24**, 25 (1957); *Chemische Relaxation* (Steinkopf, Darmstadt, 1958); Eigen, Kurtze, and Tamm, Z. Elektrochem. **57**, 103 (1953).

system of linearized rate equations. For example, in the case of a reaction consisting of two steps,

$$\underset{\text{I}}{A^{++}+B^{--}}\underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}}\underset{\text{II}}{AB'}\underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}}\underset{\text{III}}{AB}$$

with k_{12}, $k_{21} \gg k_{23}$, k_{32}, the linearized rate equations are

$$\begin{aligned}\dot{x}_1&=-k_{12}'x_1+k_{21}x_2\\ \dot{x}_2&=k_{12}'x_1-(k_{21}+k_{23})x_2+k_{32}x_3\\ \dot{x}_3&=k_{23}x_2-k_{32}x_3,\end{aligned}\tag{55}$$

where $\delta C_B=\delta C_A=x_1$, $\delta C_{AB'}=x_2$, $\delta C_{AB}=x_3$, and $k_{12}'=k_{12}(\bar{C}_A+\bar{C}_B)$, where the $\bar{C}$'s are the equilibrium concentrations.

The transformation to a new system, $\dot{y}_i=-y_i/\tau_i$, where y_i is a new set of concentration variables instead of the given variables x_i and τ_i, the corresponding relaxation time, may be written in the vectorial forms

$$\mathbf{y}=M\mathbf{x}$$

and

$$\mathbf{x}=M^{-1}\mathbf{y},\tag{56}$$

where the matrices M and M^{-1} are given by

$$M=\begin{vmatrix}1 & 1 & 1\\ \dfrac{1}{1+A} & \dfrac{1}{1+A} & \dfrac{-A}{1+A}\\ -\dfrac{k_{12}'}{k_{12}'+k_{21}} & \dfrac{k_{21}}{k_{12}'+k_{21}} & 0\end{vmatrix}$$

$$M^{-1}=\begin{vmatrix}\dfrac{k_{21}k_{32}}{k_{12}'k_{23}} & \dfrac{1}{1+A} & \dfrac{k_{21}}{k_{12}'+k_{21}} & -1\\ \dfrac{k_{32}}{k_{23}} & \dfrac{1}{1+A} & \dfrac{k_{12}'}{k_{12}'+k_{21}} & 1\\ \dfrac{1}{1+A} & & -1 & 0\end{vmatrix}$$

with

$$A=(k_{32}/k_{23})[1+(k_{21}/k_{12}')].$$

The relaxation times result as eigenvalues of the functional equation

$$\frac{1}{\tau_1}=0,\quad \frac{1}{\tau_2}=\frac{k_{12}'(k_{23}+k_{32})+k_{21}k_{32}}{k_{12}'+k_{21}},\quad \frac{1}{\tau_3}=k_{12}'+k_{21}.\tag{57}$$

The relaxing parts of the compressibility are given by

$$\beta_{0(2)}'=\frac{C_0\beta(1-\beta)}{2-\beta}\,\frac{1+(k_{12}'/k_{21})}{1+(k_{32}/k_{23})}\,\frac{(\Delta V_2)^2}{RT},$$

$$\Delta V_2=\Delta V_{\text{II–III}}+\Delta V_{\text{I–II}}\frac{k_{21}}{k_{12}'+k_{21}},$$

and

$$\beta_{0(3)}'=\frac{C_0\beta(1-\gamma)}{2-\gamma}\,\frac{(\Delta V_3)^2}{RT},\quad \Delta V_3=\Delta V_{\text{I–II}},\tag{58}$$

where $\Delta V_{\text{I–II}}=V_A+V_B-V_{AB'}$, $\Delta V_{\text{II–III}}=V_{AB'}-V_{AB}$. β and γ are degrees of dissociation; $\beta=C_A/C_0$, $(1-\beta)=(C_{AB'}+C_{AB})/C_0$, $\gamma=C_A/(C_0-C_{AB})$, $(1-\gamma)=C_{AB'}/(C_0-C_{AB})$.

The excess absorption per wavelength is given by

$$(\alpha\lambda)=\frac{\pi}{\beta_0}\left[\beta_{0(2)}'\frac{\omega\tau_2}{1+\omega^2\tau_2^2}+\beta_{0(3)}'\frac{\omega\tau_3}{1+\omega^2\tau_3^2}\right].\tag{59}$$

If k_{12}', $k_{21}\gg k_{23}$, k_{32}, the first step of the reaction is identical with the relaxation effect due to τ_3. For $C_{AB}\rightarrow 0(\gamma=\beta=\delta)$ it becomes identical with the binary one-step equilibrium treated by Bies. The other effect (τ_2) corresponds to the final equilibrium between the state AB and the two states A^{++}, B^{--} and AB'. The relaxation time τ_2 is almost independent of concentration, except in a small transition range at concentrations C_A for which $k_{12}'\approx k_{21}$. Such a treatment seems to describe the experimental facts in a more extended concentration range which Bies's theory fails to do. It could not explain the behavior for concentrations above 10^{-2} M, where the relaxation time as well as the absolute value of $(\alpha\lambda/C)$ becomes almost independent of concentration.

(b) Activation Energy for the Rate Process

The temperature dependence of the relaxation frequency may be utilized to determine an experimental activation energy for the rate process.

Consider the reaction $A\rightarrow M'\rightarrow B$ where M' represents the activated or transition state for the reaction.

According to Eyring's reaction rate theory, the specific rate for the forward reaction is given by

$$k=(k'T/h)(C'/C_A)=(k'T/h)K',\tag{60}$$

where K' is the equilibrium constant for the activation reaction, k' is Boltzmann's constant, h is Planck's constant, T is temperature, and C' and C_A are the concentrations of the indicated species. $k'T/h$ represents the rate at which molecules pass from the activated state. The true equilibrium constant for the activation reaction is

$$K_0'=K'\nu'/\nu_A,\tag{61}$$

where ν' and ν_A are the activity coefficients. Then the reaction rate is given by

$$\begin{aligned}k&=(k'T/h)(\nu_A/\nu')K_0'\\ &=(k'T/h)(\nu_A/\nu')\exp(-\Delta F^{0\prime}/RT),\end{aligned}\tag{62}$$

where $\Delta F^{0\prime}$ is standard free energy of activation.

Hence the specific rates for the forward reaction and

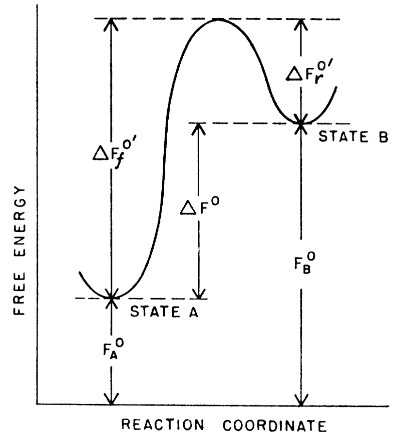


FIG. 2. A two-state potential-energy diagram.

the reverse reaction are

$$k_f=(k'T/h)\exp(-\Delta F_f{}^{0\prime}/RT) \qquad (63)$$

$$k_r=(k'T/h)\exp(-\Delta F_r{}^{0\prime}/RT) \qquad (64)$$

considering the activity coefficients as unity. Figure 2 illustrates the relation between the energies in the three states.

The relaxation time τ is given by

$$\tau=1/(k_f+k_r),$$

where

$$k_f+k_r=(k'T/h)[\exp(-\Delta F_f{}^{0\prime}/RT)+\exp(-\Delta F_r{}^{0\prime}/RT)].$$

If we assume that $k_f \ll k_r$,

$$\tau=1/k_r=(h/k'T)\exp(\Delta F_r{}^{0\prime}/RT). \qquad (65)$$

Hence the relaxation frequency f_m is given by

$$f_m=(k'T/2\pi h)\exp(-\Delta F_r{}^{0\prime}/RT). \qquad (66)$$

Assuming activation energy independent of the temperature

$$\log(f_m/T)=-(\Delta H_r'/RT)\log e+\text{constant}$$

$$\Delta F_r{}^{0\prime}=\Delta H_r'-T\Delta S_r, \qquad (67)$$

where $\Delta H_r'$ is the enthalpy and $\Delta S_r'$ is the entropy of activation.

The activation enthalpy can be obtained from the slope of the curve $\log(f_m/T)$ *vs* $1/T$. Since the pdV term is negligible, ΔH is approximately the activation energy.

(c) Different Mechanisms

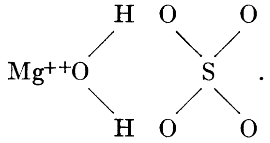
(a) The simplest dissociation reaction for the primary relaxation, which has been suggested by Liebermann,[3] and supported by Leonard, Bies,[18] and Verma and Kor[23] for a 2–2-valent metallic sulfate MSO_4 is

$$MSO_4\rightleftarrows M^{++}+SO_4{}^{--}. \qquad (68)$$

(b) Barthel[16] has suggested the following mechanism:

$$M^{++}+H_2O\rightleftarrows MOH^{+}+H^{+}. \qquad (69)$$

(c) Tamm and Kurtze[19] assume the existence of a complex of the form MeR, H_2O where Me = metal, R = radical. For example, in the case of $MgSO_4$ the complex is represented by



For this complex two different possibilities of dissociation are assumed.

(1) The formation of two univalent ions

$$(MgSO_4,H_2O)\rightarrow MgOH^{+}+HSO_4{}^{-} \qquad (70)$$

which each split up in a subsequent step

$$MgOH^{+}+HSO_4{}^{-}\rightarrow Mg^{++}+OH^{-}+H^{+}+SO_4{}^{--}. \qquad (71)$$

The first step is considered to be acoustically inefficient. The two dissociation processes are independent of each other and explain the two relaxation frequencies which are observed. For example, in $MgSO_4$ the dissociation of $MgOH^+$ explains the relaxation frequency at 130 kc and the dissociation of $HSO_4{}^-$ the second relaxation frequency at 200 Mc.

(2) Another possibility exists in the separation of either of the metal ion or of the radical ion from the complex in the form

$$\begin{aligned} MgSO_4,\ H_2O &\rightarrow Mg^{++}+H_2O\cdot SO_4{}^{--}\\ &\rightarrow Mg\cdot H_2O^{++}+SO_4{}^{--}. \qquad (72)\end{aligned}$$

(d) Smithson and Litovitz[20] assume the reaction to be between two dipole molecules, i.e., the reaction between the solute molecules (ion pairs) and the dipole solvent. The great excess of the solvent assures that this reaction is of first order. The reaction might be of the type

$$MnSO_4+H_2O\rightleftarrows Mn\cdot H_2O^{++}+SO_4{}^{--}. \qquad (73)$$

(e) According to Eigen,[22] the simplest possible mechanism allowing an explanation of all hitherto found results may be represented by the following scheme:

$$\underset{\text{I}}{A^{++}+B^{--}}\rightleftarrows\underset{\text{II}}{AB'}\rightleftarrows\underset{\text{III}}{AB''}\rightleftarrows\underset{\text{IV}}{AB'''}. \qquad (74)$$

The first equilibrium (I-II) corresponds to diffusion-controlled steps of interaction of the completely hydrated ions, which is present in all electrolytic solutions, especially in those which do not show any detectable absorption below 300 Mc. A relaxation effect due to this interaction should be expected at frequencies higher than 10^3 Mc. The relaxation effects found in 2–2-valent electrolytes are connected with further consecutive re-

---

[23] G. S. Verma and S. K. Kor, Proc. Phys. Soc. (London) 72, 81 (1958); J. Chem. Phys. 29, 9 (1958).

action steps in the above scheme (II-III,III-IV). The physical reality of such discrete steps is provided by the fact that the maxima, at least at lower frequencies, have the shape of monochromatic relaxation curves. However, there exists the possibility of more complicated mechanisms in which all the relaxation steps are not detectable.

(f) Recently Verma[24] has proposed a mechanism which shows that when H_2O is replaced by D_2O as the solvent, the primary relaxation frequency should not change, whereas the rate of process responsible for the secondary relaxation is altered considerably. The mechanism is as follows:

$$\mathrm{MSO_4},\ n\mathrm{H_2O} \rightleftarrows [\mathrm{M},\ (n-1)\mathrm{H_2O}]^{++} + [\mathrm{SO_4},\mathrm{H_2O}]^{--} \quad \text{(a)}$$

$$\mathrm{M^{++}} + 2\mathrm{H_2O} \rightleftarrows (\mathrm{MOH})^{+} + (\mathrm{H_3O})^{+} \quad \text{(b)}$$

$$\mathrm{SO_4^{--}} + (\mathrm{H_3O})^{+} \rightleftarrows (\mathrm{HSO_4})^{-} + \mathrm{H_2O} \quad \text{(c)}$$

$$\mathrm{MOH^{+}} + (\mathrm{HSO_4}) \rightleftarrows \mathrm{MSO_4} + \mathrm{H_2O}. \quad \text{(d)}$$

The process (a) with higher activation energy corresponds to the primary relaxation frequency and the process (d) with the lower activation energy to the secondary relaxation frequency. Processes (b) and (c) are acoustically inefficient.

III. METHODS FOR MEASURING THE ABSORPTION

The methods for measuring sound absorption can be classified into two groups depending upon the technique utilized, namely, (1) progressive wave technique and (2) standing wave technique. In the former, absorption is determined from the decrement in the intensity of the plane progressive sound waves governed by the relation

$$I_x = I_0 e^{-2\alpha x}, \tag{75}$$

where I_0 is the intensity at the source, I_x the intensity at a distance x from the source and α the attenuation constant. This is only applicable to measurements above 1 Mc as the absorption, being proportional to the square of the frequency, decreases to such an extent below 1 Mc that the measurements are not reliable. How low is the absorption in water at frequencies below 1 Mc is evident from the fact that the amplitude of a plane wave is reduced only by 10% in a distance of 1 km. Thus, in order to have accurate and reliable results there should be very large volumes of the liquid available in the laboratory, which is hardly possible on such a large scale. Moreover, in order to have the proper directivity of the sound beam, the transducer should be very large.

These difficulties are considerably reduced if absorption is measured by the standing wave technique. In this the absorption is determined from the decay with time of the energy E of a standing wave between the boundaries of the liquid. The decay is governed by the relation

$$E_t = E_0 e^{-2\delta t}, \tag{76}$$

where $\delta = \alpha c$, c being the velocity of propagation of sound waves. The difficulty here lies in the elimination of the boundary losses which influence the decay constant considerably. The decay constant can either be determined by the resonance method or the reverberation method. In the resonance method the decay constant is determined from the decay time of only a single mode of oscillation of the system consisting of the liquid plus the container, whereas in the reverberation method the system is excited to a large number of normal modes of oscillation.

(a) Methods Based upon Progressive Wave Technique

Methods which are based upon the progressive wave technique can be further classified into three main groups which are (1) mechanical methods, (2) optical methods, and (3) electrical methods.

(1) Mechanical Methods

The mechanical method, which is in frequent use, depends upon the measurement of sound radiation pressure. When sound waves meet an obstacle the pressure at the front differs from that at the back. The pressure behind the obstacle is assumed to be the pressure in the medium at rest, i.e., in the absence of the sound beam. According to Lord Rayleigh the difference of the pressure, which is known as radiation pressure, is given by

$$S = \tfrac{1}{2}(\gamma + 1)(I/C), \tag{77}$$

where γ is the ratio of specific heats, C the velocity, and I the intensity of sound waves. Thus if the radiation pressure is measured at different distances the absorption coefficient for the intensity is easily known from the variation with distance.

The actual radiation pressure, however, as encountered in an acoustic beam under ordinary experimental conditions is different from Rayleigh's pressure. Mean radiation pressure $\bar{P}$ per unit area of a plane compressional wave, however, is defined by

$$\bar{P} = \bar{p} + \langle \rho u^2 \rangle, \tag{78}$$

where p is the excess pressure of the acoustic waves, ρ the density of the medium, and u the velocity. As a generalization of Eq. (78), the mean radiation pressure upon an obstacle of arbitrary shape in an acoustic field can be written

$$\langle \mathbf{P} \rangle = \bar{p}\mathbf{n} + \langle \rho \mathbf{u}(\mathbf{u}\cdot\mathbf{n}) \rangle, \tag{79}$$

where $\mathbf{u}$ now stands for the vector of the velocity $\mathbf{u}(x,y,z)$ and $\mathbf{n}$ is the vector of the inner normal on the surface element under consideration. According to

---

[24] G. S. Verma, J. Chem. Phys. 29, 1186 (1958).

Borgnis,[25] the radiation pressure for a beam of finite width in any fluid and on any plane reflecting surface is given by

$$\bar{P}=2\langle\langle E\rangle\rangle_{\text{kin}}=\langle\langle E\rangle\rangle_{\text{total}}+(\langle\langle E\rangle\rangle_{\text{kin}}-\langle\langle E\rangle\rangle_{\text{pot}}). \tag{80}$$

At small amplitudes $\langle\langle E\rangle\rangle_{\text{pot}}=\langle\langle E\rangle\rangle_{\text{kin}}$ and, therefore,

$$2\langle\langle E\rangle\rangle_{\text{kin}}=\langle\langle E\rangle\rangle_{\text{total}}=\bar{E}_i(1+\beta^2), \tag{81}$$

where $\bar{E}_i$ is the mean energy density of the incident waves and β the reflection coefficient. Hence

$$\begin{aligned}\bar{P}=2\bar{E}_{\text{kin}}&=\bar{E}_i(1+\beta^2)\\&=\tfrac{1}{2}\rho_0\omega^2\xi_0^2(1+\beta^2)=(I/C)(1+\beta^2).\end{aligned} \tag{82}$$

The above expression is valid both in liquids and gases, when terms of third and higher order in $k\xi_0=(2\pi/\lambda)\xi_0$ are excluded.

There are various ways to measure the radiation pressure. One way uses a torsion balance, which carries on one side a plate or cone which is struck by sound waves, while on the other side weights can be placed to balance the upthrust upon the plate or cone. Sometimes the displacement of the plate or the bead at the end of a long wire when a sound beam traveling horizontally impinges upon it, is used as a measure of sound radiation pressure. Another convenient way to measure the intensity uses a movable vane forming one plate of the condenser, and variations in the capacitance of the system are noted. W. Rufer,[26] employing the above technique, successfully measured the absorption in a large number of electrolytes over a frequency range of 2.9–8.85 Mc for concentrations of 10% and 1 mole/liter.

Ultrasonic absorption in aqueous solutions of $MnSO_4$ has been studied by the pressure balance method in the frequency range (12–43 Mc) by Smith, Barret, and Beyer[27] with the purpose of examining the behavior of aqueous solutions at higher frequencies.

McNamara and Beyer[28] have suggested a variation of radiation pressure method which possesses an accuracy comparable to that of pulse and optical methods. It consists in modulating the transducer at an audio-frequency and detecting the consequent low-frequency variations in the radiation pressure with a condenser microphone.

According to Markham, Beyer, and Lindsay,[29] the measurements with this method below 3 Mc are not reliable since difficulties arise such as those due to retarding forces which might be comparable to the forces which are being measured, specular reflections from the walls of the container, hydrodynamic flow, failure of the detector to intercept the divergent sound beam at low frequencies, and cavitation at high intensities.

Another convenient and accurate method of measuring the absorption coefficient is provided by the velocity of acoustic streaming in a fluid. It is now a well-established fact that there exists a time-independent gradient of radiation pressure associated with the propagation of plane progressive waves of sound through an attenuating fluid medium. This constant gradient produces an acceleration of the fluid and hence streaming. Viscous forces arise which resist the streaming till the steady state condition is reached when these forces exactly balance the gradient of radiation pressure. According to Eckart[30] (1948), Liebermann[31] (1949), Karim and Rosenhead[32] (1952), and Karim[33] (1953), measurements of the streaming velocity provides an independent method of determining the ratio of the second coefficient of viscosity to coefficient of shear viscosity. On the other hand, Nyborg[34] (1953) and Piercy and Lamb[35] (1954) have established both by theory and experiments that the sound attenuation rather than the second viscosity is the factor responsible for streaming. This conclusion was originally pointed out by Fox and Herzfeld[36] (1950). Markham[37] (1952) too supported this view.

The experimental arrangement for measuring the sound absorption in liquids at frequencies around 1 Mc is shown in Fig. 3. The main tube is completely filled by the beam of progressive sound waves and the side tube provides the return path of the streaming where progressive sound waves do not extend.

According to Poiseuille, the flow velocity v_0 of a fluid along the axis of a tube of radius r and length l is given by

$$v_0=(\Delta p r^2/4\eta l), \tag{83}$$

where Δp is the difference in pressure between the ends of the side tube and η is the coefficient of shear viscosity of the fluid, provided the effect of the corners of the side

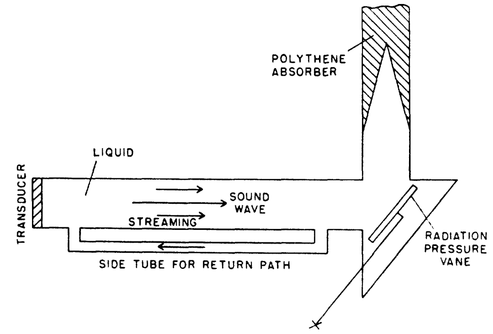


FIG. 3. Sound absorption measurement by acoustic streaming method.

---

[25] F. E. Borgnis, Revs. Modern Phys. **25**, 653 (1953).

[26] W. Rufer, Ann. Physik **41**, 301 (1942).

[27] Smith, Barret, and Beyer, J. Acoust. Soc. Am. **23**, 71 (1951).

[28] F. L. McNamara, and R. T. Beyer, J. Acoust. Soc. Am. **25**, 259 (1953).

[29] Markham, Beyer, and Lindsay, Revs. Modern Phys. **23**, 353 (1951).

[30] C. Eckart, Phys. Rev. **73**, 68 (1948).

[31] L. Liebermann, Phys. Rev. **75**, 1415; **76**, 440 (1949).

[32] S. M. Karim and L. Rosenhead, Revs. Modern Phys. **24**, 108 (1952).

[33] S. M. Karim, J. Acoust. Soc. Am. **25**, 997 (1953).

[34] W. L. Nyborg, J. Acoust. Soc. Am. **25**, 68 (1953).

[35] J. E. Piercy and J. Lamb, Proc. Roy. Soc. (London) **A226**, 43 (1954).

[36] F. E. Fox and K. F. Herzfeld, Phys. Rev. **78**, 156 (1950).

[37] J. J. Markham, Phys. Rev. **86**, 497 (1952).

tube on the flow is neglected, which is true for small velocities of streaming. The difference in pressure Δp arises because of the change in radiation pressure due to attenuation in sound waves over a length l in the main tube. Thus, the streaming velocity on the axis of the tube is given by

$$v_0=\frac{E_0r^2(1-e^{-2\alpha l})}{4\eta l}, \tag{84}$$

where E_0 is the acoustic energy density at the entrance to the side tube nearer the source, which is experimentally known by using the radiation pressure vane. Small aluminum particles are suspended in the liquid, and the velocity of flow is determined by noting their motion through a microscope and η is taken from published tables. According to Piercy, absorptions accurate within 5% can be measured. Recently Hall and Lamb[38] have extended the frequency range of this method down to 100 kc, with an accuracy of ±11% at 130 kc.

(2) *Optical Method*

The optical method is based on the Debye-Sears effect and was first of all developed by Bicquard.[39] Recently many improvements in the general technique have been made by Burton,[40] Willis,[41] and Sette.[42] Kurtze and Tamm used the optical method for the measurement of ultrasonic absorption in electrolytic solutions in the frequency range 3–200 Mc.

The experimental arrangement used by Tamm and Kurtze for the frequency range 3–15 Mc is shown in Fig. 4. Sound beam from the quartz crystal is crossed perpendicularly by a parallel beam of light which, by moving the mirrors can be shifted along it. The liquid tank is 1 m in length and has rubber wedges placed at its ends to avoid the formation of standing waves. The first order of the resulting diffraction pattern is given to a photoelectric cell which is followed by a multiplier. The output of this multiplier is connected to a logarithmic level recorder. The sound is modulated and the multiplier is also tuned to the modulation frequency. In the frequency range 20–100 Mc the principle of the method is the same except that the vessel itself is moved instead of a light beam.

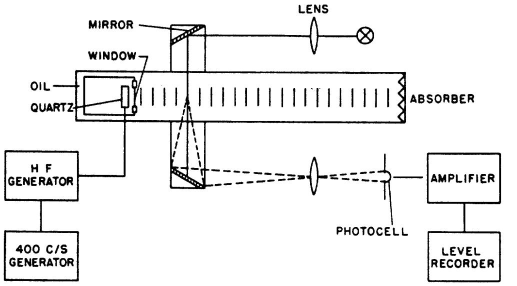


FIG. 4. Sound absorption measurement by the optical method.

(3) *Electrical Methods*

There are three general electrical methods for measurement of ultrasonic absorption in fluids based upon the progressive wave technique. They are (1) interferometric methods, (2) direct methods, and (3) pulse method.

The interferometric methods consist essentially of a plane quartz crystal which acts as a transducer and a reflector set parallel and opposite to the radiating face of the crystal. The distance between them can be varied either by moving the reflector or the transducer itself. Sound waves emanating from the crystal are reflected from the reflector, and stationary waves are formed in the space in between them. If the reflected waves reaching the radiating face are 180° out of phase with the signal just coming out, distrubance just at the radiating face will be reduced to zero and the plate current in the output stage of the driver oscillator will increase. As the reflector is moved towards or away from the source, plate current increases every time the reflector is moved away a half wavelength. According to Pielemeier,[43] the current reading in the output stage of the driving oscillator is proportional to excess pressure in the sound beam at the face of the crystal. Thus, if x represents the distance through which the reflector is moved, the increase in path length will be $2x$ and the pressure of the returning wave is decreased by $e^{-2\alpha x}$. Hence the absorption can be determined by noting the current at two maxima and its decrement with distance.

The whole picture is not so simple, for it has been shown by Hubbard[44] and others that the current is a complicated function of the absorption coefficient, the reflection coefficient of the reflecting surface, and the distance moved by the reflector. Hubbard used a buffer amplifier between the oscillator and the interferometer to reduce the effects of load variations on the frequency of the oscillator. Alleman[45] showed that lack of perfect alignment between the transducer and the reflector leads to erroneous results. Pumper[46] has discussed the departure of the sound beam from a plane wave. Some uncertainty regarding the reflection also remains, as it is alleged to be modified by heat conduction. This method has been used by several workers[47–49] including the author.[50]

In the *direct method* the excess pressure or the in-

---

[38] D. N. Hall and J. Lamb, Proc. Phys. Soc. (London) **73**, 354 (1959).

[39] P. Bicquard, Compt. rend. **196**, 257 (1933).

[40] C. J. Burton, J. Acoust. Soc. Am. **20**, 186 (1948).

[41] F. H. Willis, J. Acoust. Soc. Am. **19**, 242 (1947).

[42] D. Sette, Nuovo cimento **7**, 55 (1950); J. Chem. Phys. **18**, 1592 (1950).

[43] W. H. Pielemeier, Phys. Rev. **34**, 1184 (1929).

[44] J. C. Hubbard, Phys. Rev. **38**, 1011 (1931); **41**, 523 (1932).

[45] R. S. Alleman, Phys. Rev. **55**, 87 (1939).

[46] E. J. Pumper, J. Phys. U.S.S.R. **1**, 411 (1939).

[47] F. E. Fox, Phys. Rev. **52**, 973 (1937).

[48] J. L. Hunter, J. Acoust. Soc. Am. **13**, 36 (1941).

[49] J. L. Hunter and F. E. Fox, J. Acoust. Soc. Am. **22**, 238 (1950).

[50] G. S. Verma, J. Chem. Phys. **18**, 1352 (1950).

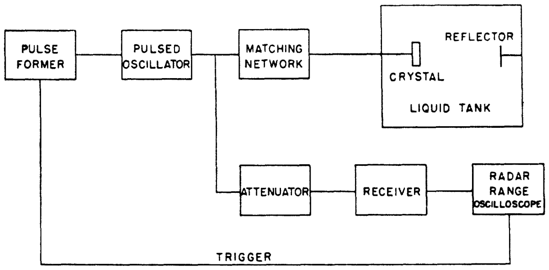


FIG. 5. Sound absorption measurement by the pulse method.

tensity is measured by the microphone which is placed along the axis of the sound beam. The method is not so simple as it appears to be, as many difficulties are associated with it. In the case of the transducer which is assumed to be a pistonlike source, Fraunhofer diffraction takes place within a distance of a^2/λ from the crystal, where a is the radius of the transducer and the typical Fresnel pattern is observed at much greater distances. King[51] and Born[52] have deduced approximate theoretical expressions for the radiation field which can be used for the determination of the absorption coefficient. Correction has to be made for the finite size of the microphone in case its dimensions are not small compared to the wavelength. Standing waves as usual offer a problem which can be reduced by tilting the microphone, so that the face of the microphone is not perpendicular to the axis of the beam.

The direct method has been successfully utilized by Smith, Barrett, and Beyer[27] on the determination of ultrasonic absorption in $MgSO_4$ in the neighborhood of 3 Mc. The detector consisted of a barium titanate crystal connected in parallel with a selenium detector. These two units are mounted in the edge of a probe and connected with a Rubicon galvanometer. The response of the rectifier as read on the galvanometer is proportional to the average intensity of the sound beam over crystal face.

Any method which utilizes continuous waves suffers from two defects. First, there always exists the possibility of stationary waves being formed, which leads to erroneous results of absorption, and secondly, local heating due to sound energy in the main beam may cause temperature waves from the center of the sound beam, which is at a higher temperature, towards the edges of the beam, which is comparatively at a lower temperature. Because of the change in temperature, the temperature recorded by the thermometer kept at a certain distance from the main beam is not the true temperature at which absorption is being measured. But these difficulties are removed in the pulse method.

The experimental arrangement used by Pellam and Galt[53] for the measurement of ultrasonic absorption in liquids is shown in Fig. 5. The arrangement consists of a quartz transducer and polished reflector set up parallel to each other. The pulsed radio-frequency voltage at 15 Mc with a repetition rate of the order of 1000 per sec and pulse width of 1 μsec was applied to the quartz crystal. Thus the average power is only 1/1000 that of a continuous signal at the same amplitude. The same crystal which acts as a transducer is used as a receiver. The distance between the crystal and the reflector can be arranged such that the reflected signal arrives at the instant when there is no transmission of pulse so that stationary waves are not formed. "The scheme is essentially to use the liquid sample as a storage medium for short sound pulses and to measure the time delay and the attenuation undergone by the sound in traversing a known path within the liquid. The acoustical pulses are generated from electrical pulses by means of a crystal transducer and are converted back to electrical form upon completing a transit through the liquid. The effect of changing the acoustic length can be compensated for electrically. Hence, the measured delay produced by the increase in path length gives a measure of the sound velocity; the attenuation which must be removed from the electrical circuit to balance the acoustical losses in additional distances provides a measure of the absorption. With the help of suitable electronic equipment the central and the reflected pulses are compared on an oscilloscope. The initial pulse is generally allowed to pass through a calibrated attenuator and the attenuation required to reduce the size of the initial pulse to match that of the reflected pulse measures the power loss in transmission plus losses due to reflection. When the reflector is moved through a distance x it will mean an increase in path length by $2x$. Thus, if the attenuation noted is plotted against the distance $2x$, the absorption coefficient can be determined from the graph."[53]

Litovitz and his associates have studied ultrasonic absorption in $MnSO_4$ and NH_4OH by the pulse method. Lamb and his associates have utilized pulse technique in studying the relaxation due to rotational isomerism in unsaturated aldehydes and ketones[54] and triethylamine.[55] Young and Petrauskas have also studied rotational isomers of methylbutanes[56] by the pulse method. Recently, the details of the pulse technique have been reviewed by Lamb and others.[57]

(b) Methods Based upon Standing Wave Technique

As stated earlier, there are two methods based upon standing wave technique—namely, the reverberation method and the resonance method. These are frequently

---

[51] L. V. King, Can. J. Research **11**, 135; **11**, 484 (1934).

[52] H. Born, Z. Physik. **120**, 383 (1943).

[53] J. R. Pellam and J. K. Galt, J. Chem. Phys. **14**, 608 (1946).

[54] M. S. de Groot, and J. Lamb, Trans. Faraday Soc. **51**, 1676 (1955).

[55] E. L. Heasell and J. Lamb, Proc. Roy. Soc. (London) **A237**, 233 (1956).

[56] J. M. Young and A. A. Petrauskas, J. Chem. Phys. **25**, 943 (1956).

[57] Andreae, Bass, Heasell, and Lamb, Acustica **8**, 131 (1958).

used for the measurement of ultrasonic absorption below 1 Mc. The reverberation technique has been used by Mulders,[58] Moen,[59] and Tamm and Kurtze.[16a] The resonance method has been used by Leonard, Bies, and Tamm and Kurtze.

(*1*) *Resonance Method*

The *resonance method* differs from the reverberation method in several aspects, the most important of which is the use of a single resonant mode of the spherical resonator. "A small piezo-electric crystal transducer attached to the wall of a liquid-filled spherical resonator is used to excite one of the natural modes of the resonator until the sound intensity reaches a sufficiently high level. The transducer is then switched from the exciting amplifier to a receiving amplifier. The sound energy level now in the resonator decays exponentially at a rate determined by the energy losses in the system. A high-speed power level recorder which plots the logarithm of the decaying receiver output voltage against time, yields a straight decay curve, the slope of which is easily measured. If the losses of the sound energy at the walls and supports of the resonator are negligible, the decrease in sound level results only from the absorption of sound in the contained liquid, and thus the decay rate is a measure of the sound absorption coefficient for the liquid. The decay rate in decibels per second divided by the sound velocity yields the plane wave absorption coefficient in decibels per unit of distance." The schematic diagram of the apparatus is shown in Fig. 6.

The system is normally in the receiving condition as shown. Boundary losses which are an important factor can be eliminated by subtracting the decay constant corresponding to the case when the resonator is filled with a standard liquid. Thus the true absorption of the electrolyte is known from

$$\alpha_{\text{electrolyte}} = \alpha - \alpha_{\text{standard}} = (\delta - \delta_{\text{standard}})/C. \qquad (85)$$

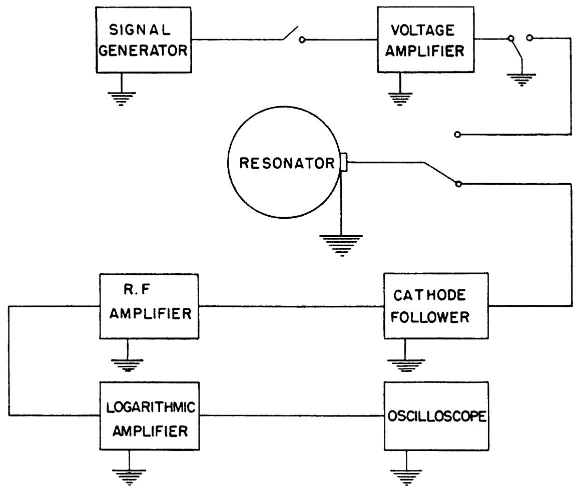


FIG. 6. Sound absorption measurement by the resonance method.

The advantages of having a spherical glass resonator are many. First, the deformation and wall frictional losses are minimized by making the walls extremely thin, which is possible in this stable shape. Secondly, there exist certain radial modes of vibrations of which boundary losses can be neglected. Thirdly, it is possible to estimate theoretically the boundary losses considering the deviations of the sound field in the case of an ideal spherical resonator. Bies used round-bottom twelve-liter Pyrex boiling flasks as resonators.

(*2*) *Reverberation Method*

In the reverberation method the vessel which is filled with the liquid is excited to a large number of normal modes of oscillations so that a diffuse sound field occurs. The absorption coefficient is determined from the rate of decay of the sound. The decay of sound energy is exponential provided the boundary losses affect all the normal modes of vibration nearly uniformly. The nature of the sound field does not matter so long as the sound field is almost uniform throughout the volume of the liquid. If the walls of the container are irregular or very symmetrical, standing wave patterns do not offer any serious problem. Scattering of the sound field, instead of leading to erroneous absorption, helps in achieving the diffuse sound field. The vessel used by Tamm and Kurtze is a seamless cylindrical 100-liter vessel (54 cm in diam and in height) made of pure anodized and varnished aluminum, 3.5 mm thick.

According to Mulders[58] the time constant of the decay of sound amplitude not only depends upon the absorption of ultrasonic waves in the liquids but also on other causes such as the radiation of sound energy into the air and the energy losses by the friction of sound waves along the walls. According to him the decay constant can be expressed as a function of the dimensions of the vessel. In the case of a cylindrical vessel of radius R and height H filled with a liquid of density ρ and shear viscosity coefficient η, the observed decay constant δ is given by

$$\delta = \alpha C + 1.18[(2/R) + (1/H)](f\eta/\rho)^{\frac{1}{2}} + (140/\rho H), \qquad (86)$$

neglecting the absorption in the attachment of the vessel and the microphone, etc. The second term represents corrections due to the friction of the walls. The third term represents the correction due to radiation into air from the liquid surface, a factor which is not very important. In the case of a cylindrical vessel filled with water, Mulders found at 25°C and 1010 kc $\delta = 58.5$ sec^{-1}, $1.18[(2/R)+(1/H)](f\eta/R)^{\frac{1}{2}} = 26$ sec^{-1}, $(140/\rho H) = 1.5$ using the constants $R = 0.14$ m, $H = 0.10$ m, $\rho = 1000$, $\eta = 0.89\times10^{-3}$, $C = 1500$ msec^{-1}. Thus αC comes out to be equal to 31.0 sec^{-1} and $(\alpha/\nu^2)\times10^{15}$ m^{-1}sec^2

---

[58] C. E. Mulders, Appl. Sci. Research **B1**, 149 (1949); **B1**, 341 (1950).

[59] C. J. Moen, J. Acoust. Soc. Am. **23**, 62 (1951).

TABLE I. Values of the absorption coefficient α in decibels per unit length as referred to 0.1-M/l solution at 20°C in the electrolytes investigated so far.

Electrolytes	10 kc/sec db/km	100 kc/sec db/km	1 Mc/sec db/m	10 Mc/sec db/cm	100 Mc/sec db/cm
H_2O	0.0217	2.17	0.217	0.217	21.7
$Al_2(SO_4)_3$	$\geqq 0.1$	10.0	1.0	1.0	57
$BeSO_4$	1.75	4.8	0.29	0.29	28
$CaCrO_4$		$\geqq 3.1$	0.31	0.31	29
$Ca(CH_3COO)_2$	$\geqq 0.036$	3.6	0.36	0.36	36
$CoSO_4$	1.77	162	2.3	0.39	31
$CuSO_4$	0.282	23	0.43	0.39	39
$MgCrO_4$	$\geqq 0.72$	54.7	0.48	0.29	29
$MgSO_4$	3.92	247	0.9	0.3	29
MgS_2O_3	1.42	90	0.57	0.28	23.8
$MnSO_4$	0.55	51	5.2	0.74	29
$NiSO_4$	31.0	86	0.48	0.39	29
$ZnSO_4$	$\geqq 0.05$	5	0.5	0.5	36
H_2SO_4			0.24	0.24	24
$AlCl_3$			0.223	0.223	22.3
K_2SO_4			0.227	0.227	22.7
K_2CrO_4			0.226	0.226	22.6
$La(NO_3)_3$				0.5	34
Li_2CO_3			0.238	0.238	23.8
Li_2SO_4			0.229	0.229	22.9
Na_2CO_3			0.24	0.24	24
Na_3PO_4		3.9	0.39	0.35	30.7
Na_2SO_4			0.25	0.25	25
$(NH_4)_2SO_4$			0.227	0.227	22.7

$= 20.5$ in agreement with measurements of other workers utilizing other methods. Thus, all that is necessary is one measurement of the reverberation time, and other corrections can be calculated from the dimensions of the vessel and the physical constants of the liquid, namely, the viscosity η and the density ρ.

The schematic arrangement of the apparatus is shown in Fig. 7. After the sound source has been stopped, the sound reverberates in the vessel. This can be observed by a crystal microphone and an amplifier. The time constant of decay of sound can be measured at the output of the amplifier. Tamm and Kurtze used the frequency band for excitation of width 20 kc. This is generated by pulsing a variable carrier frequency which is restricted to five definite values, i.e., 50, 100, 200, 500, and 1000 kc. The electric output of a piezoelectric receiver, which is a measure of the sound energy in the vessel (i.e., after amplification, frequency conversion, and filtering) is recorded by a Newman type high-speed level recorder or by a log amplifier combined with an oscilloscope.

Lamb and Sherwood[60] and Karpovich[61] used this technique in the study of relaxations due to rotational isomers in cyclohexane derivatives.

IV. RESULTS AND DISCUSSIONS

(a) Values of Absorption and Relaxation Frequencies

1–1-valent electrolytes, for example, NaCl, NaBr, and KBr, have very low absorption, i.e., the solutions of these electrolytes have almost the same absorption as that of the pure water. 2–1- and 3–1-valent electrolytes as well as 1–2-valent electrolytes behave almost in a similar way to 1–1-valent electrolytes below 10 Mc. Only above 10 Mc do they exhibit measurable absorption.

2–2-valent electrolytes, in general, possess a considerably high absorption in the whole frequency range which has been investigated. In view of the fact that sulfates of bivalent metals are soluble in water and are obtained in sufficient quantities with necessary degree of purity, mostly the sulfates have been investigated; for example, $BeSO_4$, $NiSO_4$, $MgSO_4$, $CoSO_4$, $MnSO_4$, $ZnSO_4$, $CuSO_4$, etc. Thiosulfates and chromates such MgS_2O_3, $MgCrO_4$, and $CaCrO_4$, which have been investigated, also possess high absorption. $Al_2(SO_4)_3$, which is a 3–2-valent electrolyte, has strikingly very large absorption.

The values of the absorption coefficient α in decibels per unit length as referred to 0.1-M/l solution at 20°C in the electrolytes investigated so far are given in Table I. Table II gives the values of the primary and secondary relaxation frequencies.

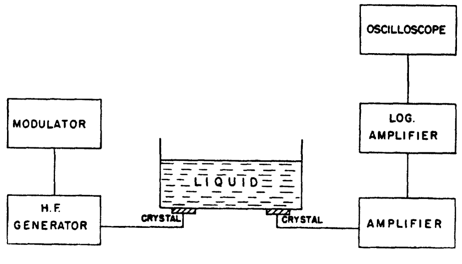


FIG. 7. Sound absorption measurement by the reverberation method.

---

[60] J. Lamb and J. Sherwood, Trans. Faraday Soc. **51**, 1674 (1955).

[61] J. Karpovich, J. Chem. Phys. **22**, 1767 (1954); J. Acoust. Soc. Am. **26**, 819 (1954).

Figure 8(a) represents a summary of all measured frequency curves by Tamm and Kurtze at 0.1 M/l. Figure 8(b) shows α/ν^2 for 0.1-M/l solutions plotted against frequency (Tamm and Kurtze[16b]).

(b) Effect of Concentration on Absorption

In nearly all of the 2–2-valent electrolytes investigated the absorption is approximately linearly dependent upon the concentration in the concentration range from 0.001 to 0.1M/l (Tamm and Kurtze). The absorption cross section Q is defined by

$$Q=2\alpha/nL, \tag{87}$$

where n is the concentration in moles per liter and L is the number of molecules per mole. This can be written as

$$Q[m^2]=1.66\times10^{-25}[2\alpha(\text{cm}^{-1})/n(\text{M/l})]. \tag{88}$$

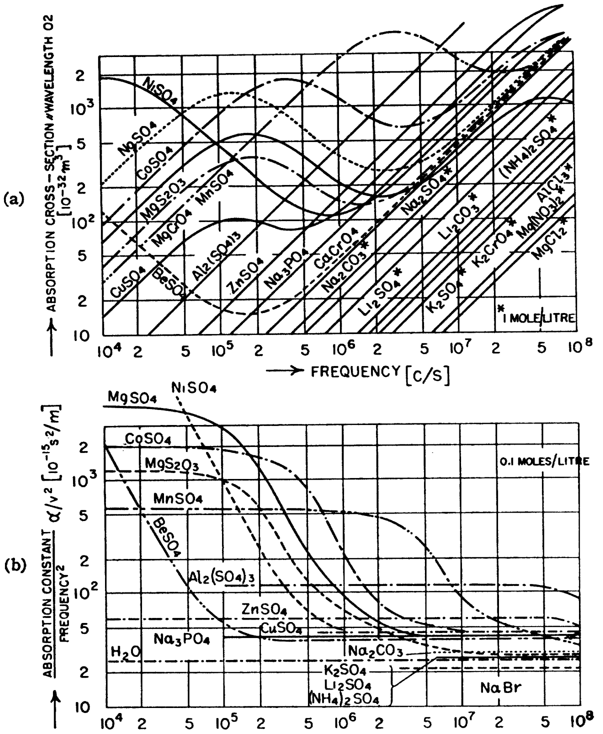


FIG. 8. (a) Sound absorption spectra of electrolytes in aqueous solutions at 20°C according to measurements of Tamm, Kurtze, and Kaiser (relative to water) for 10^{-2} to 10^{-1} M solutions. (b) α/ν^2 for 0.1-M/l solutions of some electrolytes plotted against frequency. [In Fig. 8(a) read $MgSO_4$ for $NgSO_4$ and replace "//" by "×" before and "02" by "$Q\lambda$" after wavelength.]

The absorption cross section is thus found to be constant in the range 0.001 to 0.1 M/l. Figure 9 shows the dependence of the absorption cross section Q of $MgSO_4$, $MnSO_4$, $ZnSO_4$, and $CuSO_4$ on concentration (Tamm and Kurtze[16c]). Wilson carried out the measurements on the concentration behavior of the excess sound absorption in $MgSO_4$ in the concentration range from 0.003 to 0.02M. According to him the relationship between the excess sound absorption and the concentration is nonlinear; in fact, the absorption cross section tends to zero as the concentration goes to zero. Table III gives the values of the maximum absorption per wavelength in $MgSO_4$ solutions at several concentrations, temperature being 23° to 25°C.

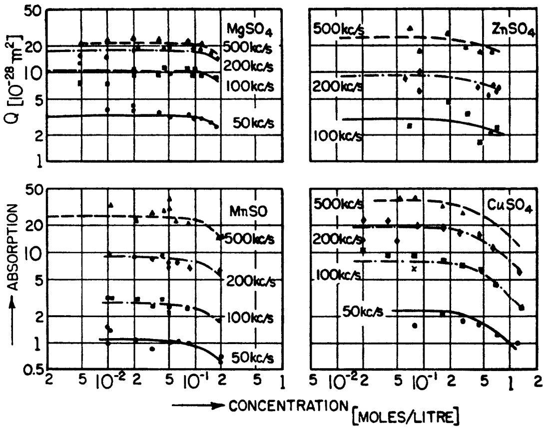


FIG. 9. Dependence of the absorption cross section (Q) of $MgSO_4$, $MnSO_4$, and $CuSO_4$ on concentration.

Kor and Verma[23] have studied the concentration behavior of $MnSO_4$ in great detail from 0.0025 to 1.0M. The relationship between the excess sound absorption and the concentration is found to be linear from 0.02 to 0.1M (Fig. 10), but becomes nonlinear both below 0.02M (Fig. 10) and above 0.1M (Fig. 11). The absorption cross section is constant over the range 0.02 to 0.1M and then diminishes as the concentration increases beyond 0.1M. As the concentration is lowered below 0.02M, the absorption cross section increases.

(c) Effect of Concentration on Relaxation Frequency

According to Wilson's measurements in $MgSO_4$, the relaxation frequency remains approximately constant in the range of concentration from 0.003 to 0.02M.

TABLE II. Values of primary and secondary relaxation frequencies in some of the electrolytes.

Electrolyte	Primary relaxation frequency	Secondary relaxation frequency
$BeSO_4$	10^3 cps	300 Mc
$NiSO_4$	10^4 cps	...
$MgSO_4$	130 kc	200 Mc
MgS_2O_3	180 kc	No relaxation in 100–300 Mc
$MgCrO_4$	180 kc	200 Mc
$CoSO_4$	400 kc	200 Mc
$MnSO_4$	3 Mc	30 Mc
$ZnSO_4$	200 Mc	...
$CuSO_4$	150 kc	>100 Mc
$Al_2(SO_4)_3$	20 Mc (very low conc.)	...
$La(NO_3)_2$	50 Mc	...

TABLE III. Values of maximum absorption per wavelength and relaxation frequency in $MgSO_4$ solutions at different concentrations at 23°–25°C.

Conc. M/l	$\mu_m \times 10^6$	ν_m (kc)
0.003	4.6	130
0.0053	15.5	140
0.008	25.5	140
0.01	35.5	130
0.014	48	138
0.02	80	150

Tamm and Kurtze also report that the relaxation frequency is approximately constant in the range from 0.01 to 0.1*M*. In $MnSO_4$ Smithson and Litovitz report no effect of the concentration on the secondary relaxation frequency with concentration but, according to them, there is indication of a small increase beyond 0.1*M*. According to Kor and Verma the relaxation frequency is independent of the concentration in the range 0.02 to 0.1*M* but increases with concentration in the range 0.0025 to 0.02*M*. It again increases with concentration above 0.1*M*.

Smithson and Litovitz argue that the specific reaction rate k_1 is concentration dependent too (which has been neglected in the past) and the effect of increasing the ionic strength by increasing the concentration is always to increase the reaction rate, whatever may be the nature of the reaction whether it is between two ions of same sign or opposite signs or between ions and neutral molecules. Hence very small concentration dependence of the reaction rate may favor the reaction between two dipoles. Dissociation of an ion pair also remains a possibility, but at present there is no theory for the effect of ionic strength on the dissociation of an ion pair.

(d) Effect of Dielectric Constant

According to Tamm and Kurtze the electrolytic dissociation is caused by the dipole forces of the molecules of the solute, a measure of this dissociation is the dielectric constant of the liquid. In liquids with smaller dielectric constant than water, the dissociation energy therefore is larger and the relaxation frequencies shifted to lower values. Tamm and Kurtze used water-alcohol mixtures to vary the dielectric constant of the solvent and report lowering of the relaxation frequency with the decrease in the dielectric constant of the solvent. However, the maximum absorption increases in magnitude, the reason for which, according to them, most probably lies in the increase in the percentage of the undissociated molecules.

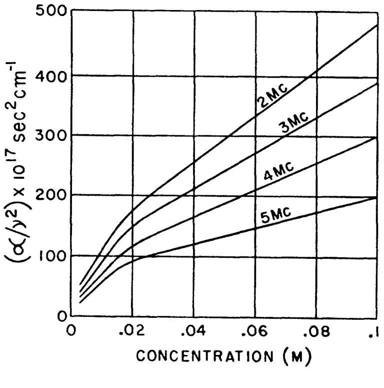


FIG. 10. Variation of the absorption coefficient (α/ν^2) with concentration (0.0025 to 0.1 *M*) at various frequencies in $MnSO_4$ at 25°C.

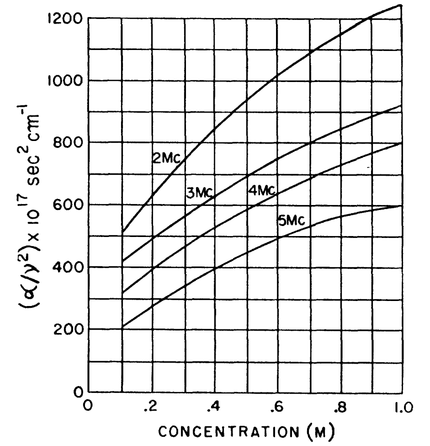


FIG. 11. Nonlinearity of the absorption coefficient with concentration at various frequencies above 0.1 *M* in $MnSO_4$ at 25°C.

Bies used dioxane-water mixtures as a solvent. According to his measurements there is small change in the relaxation frequency with concentration. By extrapolating it to zero concentration, he determined the forward reaction rate k_1 on the assumption that the mechanism responsible for the excess sound absorption is of the dissociation type $MgSO_4 \rightleftarrows Mg^{++} + SO_4^{--}$. He found that the reaction rate k_1 first went up and then down as the dielectric constant of the solvent was lowered. He calculated the reverse reaction rate k_2 utilizing the experimentally measured values of equilibrium constant *K* by conductivity bridge and the above extrapolated values of k_1. According to Laidler,[62] the rate of change of the specific rate of reaction of a pair of reacting ions of valence Z_1 and Z_2 with the reciprocal of the dielectric constant is given by the equation

$$[-d \ln k_2/d(1/D)] = (\epsilon^2 Z_1 Z_2/KTr), \qquad (89)$$

where $Z_1 = -Z_2 = 2$ in the above dissociation, r is equal to twice the mean ionic radius 3.08×10^{-8} cm, *K* the Boltzmann constant, and ϵ is the electrostatic unit of charge. Bies reported that the specific rate of association does increase with the reciprocal of the dielectric constant of the medium as it should if ions of opposite signs are involved, but apparently not in a linear fashion as expected from the above expression. However, Bies gave no explanation for his observation that the forward reaction rate went first up and then down

---

[62] K. Laidler, *Chemical Kinetics* (McGraw-Hill Book Company, Inc., 1950).

as the dielectric constant was lowered. At present there does not seem any explanation for this anomalous behavior of the reaction rate with respect to the dielectric constant. However, Kor and Verma report continuous increase in the reaction rate k_1 with the lowering of the dielectric constant in $MnSO_4$ solutions. They also used water-dioxane mixtures to vary the dielectric constant of the solvent.

Smithson and Litovitz used methanol-water mixtures for varying the dielectric constant. These mixtures have the advantage that water and methanol are similar and the absorption in such mixtures changes only slightly and almost linearly with percentage methanol (Burton),[63] but in this mixture both the molecules are polar and the interaction between the polar constituents of the mixtures may affect the absorption due to main dipole-dipole reaction if it is so. They find a decrease in the primary relaxation frequency by a small amount with decreasing dielectric constant. However, the secondary relaxation peak was observed to increase with decreasing dielectric constant. The magnitude of the absorption increased considerably as D was lowered.

The theory of the influence of the dielectric constant on the rates of reaction, which has experimental evidence in the case of slow reactions has been discussed in several books; see Amis,[64] Laidler,[62] or Glasstone, Laidler, and Eyring.[65] Table IV, presented by the latter authors, shows the effect of dielectric constant and ionic strength on the rates of a reaction. According to Smithson and Litovitz, the lowering of the primary relaxation frequency with the decrease in the dielectric constant suggests that the forward reaction is either between ions of like sign or between dipole molecules. Either of these reactions would be of the first order if one of the reactants were present in great excess and would behave like a dissociation process.

TABLE IV. Effect of dielectric constant and ionic strength on the rates of a reaction.

Reaction type	Effect of increasing dielectric constant	Effect of increasing ionic strength
1. Two dipole molecules	increase	no effect
2. Two ions		
(a) same sign	increase	increase
(b) opposite sign	decrease	increase
3. Ion and neutral molecule	decrease	increase

However, the reaction involving two charged ions of the same sign does not seem to satisfy the condition of large excess. Hence, they conclude in favor of a forward reaction between solute molecules (ion pairs) and the dipole solvent molecules, and the excess of the solvent assures that the reaction is of the first order.

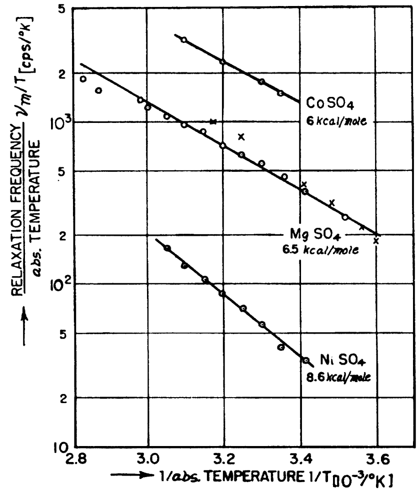


FIG. 12. Temperature dependence of the relaxation frequency: ν_m/T vs $1/T$ for $CoSO_4$, $MgSO_4$, and $NiSO_4$.

(e) Effect of Temperature

The relaxation frequency ν_m increases with increase in temperature, while the maximum excess absorption is not altered appreciably. A plot of $\log\nu_m/T$ vs $1/T$ gives a straight line, as found by Wilson for $MgSO_4$, by Tamm and Kurtze for $MgSO_4$, $CoSO_4$, and $NiSO_4$ (Fig.12), and by Smithson and Litovitz, and Kor and Verma for $MnSO_4$. The experimental activation energy for the relaxation process obtained from the slope of the above curve are about 6.5 kcal/M for $MgSO_4$, 8.6 kcal/M for $NiSO_4$, about 6 kcal/M for $CoSO_4$. In $MnSO_4$ Smithson and Litovitz found activation energy to be 8.68 kcal/M in the isodielectric solution. Isocomposition measurements were made with two different solvents, pure water and 29.52% methanol gave energies of 7.85 and 8.05 kcal/M, respectively, both of which are lower than isodielectric activation energy.

According to Amis and Jaffe[66] the activation energy ΔE for an ionic reaction consists of two parts, ΔE_1, which represents a contribution to activation energy due to electrostatic forces and ΔE_2, a contribution due to nonelectrostatic forces, $\Delta E=\Delta E_1+\Delta E_2$. According to Amis ΔE_1, in the case of a reaction between two bivalent ions, should be equal to 50% of the total activation energy. However, Smithson and Litovitz, using the methods outlined by Amis and utilizing their values of $d(k_1)/d(1/T)$ and $d(k_1)/d(1/D)$, find ΔE_1 to be just equal to 8% of the total activation energy. Such a low value of the activation energy for the electrostatic contribution, according to them, rules out ion-ion reaction as the rate determining step. However, such a low value may fit with the dipole-dipole reaction.

---

[63] C. J. Burton, J. Acoust. Soc. Am. **20**, 186 (1948).

[64] E. S. Amis, *Kinetics of Chemical Change in Solution* (The Macmillan Company, New York, 1949).

[65] Glasstone, Laidler, and Eyring, *Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

[66] E. S. Amis and G. Jaffe, J. Chem. Phys. **10**, 646 (1942).

(f) Effect of Heavy Water When Used as Solvent

When heavy water is used as a solvent in place of water, the rate of the reaction in the solution is expected to change if the rate-determining step involves making or breaking a bond between a hydrogen and an oxygen atom, apart from the pure solvent effect, which is very small, since the dielectric constant of heavy water differs only by less than 1% and the viscosity by about 20%. The half-quantum zero-point energy in the case of D_2O is smaller than that of H_2O since the heavier deuterium atom oscillates more slowly compared to the lighter protium atom. If the total energy required to make a molecule react is almost the same whether it is a deuterium or a protium compound, the critical increment is larger and hence the reaction rate smaller for a deuterium compound. Smithson and Litovitz, however, notice no measurable shift in the lower relaxation peak. This means that the rate determining step does not involve the OH bond. It rules out such possibilities as Eqs. (69) or (70). However, a secondary relaxation peak is not observed in D_2O solvent. This might be due to the OH bond which might have shifted out of the frequency range or that the relaxation which is normally observed at about 200 Mc in H_2O solution is shifted down so as to obscure the small peak.

(g) Effect of Pressure

Fisher[67] for the first time reported that acoustic absorption in $MgSO_4$ solutions shows a considerable decrease with elevated pressure. Absorption measurements were made near 100 kc by means of a resonant cylindrical steel cavity which could be pressurized. Observations at several frequencies in this region give the pressure dependence of the relaxation frequency. Carnevale and Litovitz[68] have also studied the effect of pressure on ultrasonic relaxation in manganous sulfate and ammonium hydroxide. Absorption data were obtained for $MnSO_4$ at frequencies from 9 to 75 Mc/sec up to pressures of 3930 kg/cm^2 and a temperature of 60°C. The relaxation frequency increased from 19.1 Mc/sec at atmospheric pressure to 30.7 Mc/sec at 3930 kg/cm^2. Absorption measurements in NH_4OH were obtained at frequencies from 15 to 75 Mc/sec up to pressures of 2030 kg/cm^2 and a temperature of 45°C. The relaxation frequency increased from 21.2 Mc/sec at atmospheric pressure to 52.0 Mc/sec at 2030 kg/cm^2. The results are explained on the basis of chemical dissociation.

ACKNOWLEDGMENTS

The author wishes to acknowledge with thanks the helpful discussions he has had with Professor Ernest Yeager. He is especially grateful to Professor K. Bannerji for his valuable suggestions. Special thanks are also due Professor Frank Hovorka for the grant which made possible his stay at Western Reserve University and for the facilities which enabled him to complete this article. Finally, the author also wishes to thank Mr. Jacob Schrope for his help in the preparation of the diagrams.

OTHER REFERENCES ON ULTRASONIC ABSORPTION IN LIQUIDS SINCE 1951

Earlier references found in *Reviews of Modern Physics* are

(a) W. T. Richards, "Supersonic phenomena," Revs. Modern Phys. **11**, 36 (1939);

(b) Markham, Beyer, and Lindsay, "Absorption of sound in fluids," Revs. Modern Phys. **23**, 353 (1951);

(c) S. M. Karim and L. Rosenhead, "The second coefficient of viscosity of liquids and gases," Revs. Modern Phys. **24**, 108 (1952);

and in the following textbooks:

(d) Ludwig Bergmann, *Der Ultraschall und Anwendung in Wissenschaft und Technik* (S. Hirzel Verlag, Stuttgart, 1954), sixth edition;

(e) E. G. Richardson, *Ultrasonic Physics* (Elsevier Publishing Company, London, 1952);

(f) P. Vigoureux, *Ultrasonics* (Chapman and Hall Ltd., London, 1950);

(g) E. G. Richardson, *Technical Aspects of Sound* (Elsevier Publishing Company, London, 1957), Vols. I and II;

(h) A. E. Crawford, *Ultrasonic Engineering* (Academic Press, Inc., New York, 1955);

(i) T. F. Heuter and R. H. Bolt, *Sonics* (John Wiley and Sons, Inc., New York, 1955);

(j) E. G. Richardson, *Relaxation Spectrometry* (Interscience Publishers, Inc., New York, 1957);

(k) K. F. Herzfeld and T. A. Litovitz, ***Absorption and Dispersion of Ultrasonic Waves*** (Academic Press, Inc., New York, to be published).

Further references include:

(1) T. A. Litovitz, "Ultrasonic absorption of glycerin in the liquid and vitreous state," J. Acoust. Soc. Am. **23**, 75 (1951).

(2) K. Tamm and G. Kurtze, "Absorption of sound in aqueous solutions of electrolytes," Nature **168**, 346 (1951).

(3) E. Freedman, "On the propagation of ultrasonic waves in acetic acid," J. Chem. Phys. **19**, 1318 (1951).

(4) A. G. Chynoweth and W. T. Schneider, "Ultrasonic propagation in binary liquid system near their critical solution temperature," J. Chem. Phys. **19**, 1566 (1951).

(5) R. E. Barrett and R. T. Beyer, "Anomalous effect in the ultrasonic absorption of an electrolytic solution," Phys. Rev. **84**, 1061 (1951).

(6) A. B. Pippard, "Ultrasonic propagation in liquid helium near lambda point," Phil. Mag. **42**, 1209 (1951).

(7) A. N. Hunter, "Ultrasonic absorption in supercooled liquids," Proc. Phys. Soc. (London) **B64**, 288 (1952).

(8) K. F. Herzfeld, "Origin of ultrasonic absorption in liquids," J. Chem. Phys. **20**, 288 (1952).

(9) D. Sette, "On the elastic relaxation in CS_2," Ricerca sci. **22**, 467 (1952).

(10) D. Sette, "Elastic relaxation and structure of liquids, Ricerca sci. **22**, 461 (1952).

(11) P. A. Hudson and M. Eisner, "Debye-Frenkel theory of ultrasonic absorption," Phys. Rev. **85**, 746 (1952).

(12) H. J. McSkimin, "Measurements of dynamic shear viscosity and stiffness of viscous liquids by means of traveling torsional waves," J. Acoust. Soc. Am. **24**, 355 (1952).

(13) Y. Wada and S. Shumbo, "Experimental investigation on the origin of anomalous absorption of ultrasonic waves in liquids," J. Acoust. Soc. Am. **24**, 199 (1952).

(14) L. H. Hall, "Attenuation of sound resulting from ionic relaxation," J. Acoust. Soc. Am. **24**, 704 (1952).

(15) J. Meixner, "General theory of sound absorption in gases and liquids with allowance of transport phenomena," Acustica **2**, 101 (1952).

---

[67] F. Fisher, J. Acoust. Soc. Am. **29**, 656 (1957); **30**, 442 (1958).

[68] E. H. Carnevale and T. A. Litovitz, J. Acoust. Soc. Am. **29**, 769 (1957); **30**, 610 (1958).

(16) I. M. Chalatnikov, "Thermal conductivity and sound absorption in helium II," J. Exptl. Theoret. Phys. **23**, 21 (1952).

(17) M. Manes, "On the relaxation time of equilibrium system as related to ultrasonic absorption and reaction kinetics," J. Chem. Phys. **20**, 1658 (1952).

(18) S. Parthasarthy, Chari, and Srinivasan, "Ultrasonic absorption in various organic liquids at 15 Mcs," Naturwissenschaften **39**, 483 (1952).

(19) Nomoto, Kishimoto, and Ikeda, "Ultrasonic absorption in castor oil," Bull. Kobayashi Inst. Phys. Research **2**, 72 (1952).

(20) T. A. Litovitz and D. Sette, "Dielectric and ultrasonic relaxation in glycerol," J. Chem. Phys. **21**, 17 (1953).

(21) T. Kishimoto and O. Nomoto, "Absorption of ultrasonic waves in CS_2," Bull. Kobayashi. Inst. Phys. Research **2**, 63 (1952).

(22) A. K. Dutta, "Ultrasonic absorption and relaxation mechanism," Indian J. Phys. **35**, 279 (1952).

(23) D. Sette, "Ultrasonic absorption in liquid mixtures and structural effects," J. Chem. Phys. **21**, 558 (1953).

(24) K. Tamm, "Sound absorption measurement in water and in aqueous solutions of electrolytes in the frequency range 5 kc to 1 Mc," Nachr. Akad. Wiss. Göttingen, Math.-physik. Kl. **80**, 110 (1952).

(25) Parthasarthy, Srinivasan, and Chari, "Absorption of ultrasonic waves in liquids at 5 Mc from thermal considerations," Nuovo cimento **10**, 264 (1953).

(26) Parthasarthy, Chari, and Mahendroo, "Calorimetric determination of the absorption coefficient in organic liquids," J. phys. radium **14**, 366 (1953).

(27) Parthasarthy, Chari, and Mahendroo," Determination of ultrasonic absorption coefficient in liquids by a new technique," Z. Naturforsch. **8a**, 272 (1953).

(28) C. E. Chase, "Ultrasonic measurements in liquid helium," Phys. Rev. **91**, 489 (1953).

(29) F. E. Fox and T. M. Marion, "Ultrasonic dispersion in water solutions of $MgSO_4$," J. Acoust. Soc. Am. **25**, 661 (1953).

(30) P. L. Connoly and F. E. Fox, "Ultrasonic absorption in $MgSO_4$ solutions," J. Acoust. Soc. Am. **25**, 658 (1953).

(31) M. Pancholy, "Temperature variation of velocity and absorption coefficient of ultrasonic waves in heavy water," J. Acoust. Soc. Am. **25**, 1003 (1953).

(32) S. Parthasarthy and A. F. Chapghar," Viscosity as a factor in the anomalous absorption of ultrasonic waves in liquids," Ann. Physik **12**, 316 (1953).

(33) I. G. Mikhailov, "Absorption of ultrasonic waves in certain viscous liquids," Doklady Akad. Nauk. S.S.S.R. **89**, 991 (1953).

(34) S. Parthasarthy and P. P. Mahendroo, "Absorption coefficient in some liquids determined by a new thermal technique," Nuovo cimento **10**, 1196 (1953).

(35) Parthasarthy, Chari, and Srinivasan," Variation of ultrasonic absorption with frequency in organic liquids," Acustica **3**, 363 (1953).

(36) I. G. Mikhailov and V. A. Soloviev, "Ultrasonic absorption in liquids and the molecular mechanism of bulk viscosity," Upsekhi Fiz. Nauk. **50**, 3 (1952).

(37) M. Manes, "Relationship between kinetics and acoustic phenomenon in equilibrium systems," J. Chem. Phys. **21**, 1791 (1953).

(38) E. Freedman, "On the use of ultrasonic absorption for the determination of very rapid reaction rates at equilibrium," J. Chem. Phys. **21**, 1784 (1953).

(39) G. F. Alprey and W. G. Schneider, "Ultrasonic absorption in binary liquid systems near the critical region of temperature," Discussions Faraday Soc. **15**, 218 (1953).

(40) A. W. Pryor and R. Roscoe, "The velocity and absorption of sound in aqueous sugar solutions," Proc. Phys. Soc. (London) **B67**, 70 (1954).

(41) Parthasarthy, Srinivasan, and Chari, "The thermal effects of ultrasonic waves in liquids and its relation to their absorption coefficient," Acustica **3**, 407 (1954).

(42) C. E. Chase, "Ultrasonic measurements in liquid helium," Proc. Roy. Soc. (London) **A220**, 116 (1953).

(43) J. F. Mifsud, "Absorption of ultrasonic waves in liquids under pressure," Phys. Rev. **94**, 812 (1954).

(44) Litovitz, Higgs, and Meista, "Ultrasonic propagation and its relation to molecular structure in the diols," J. Chem. Phys. **22**, 1281 (1954).

(45) Litovitz, Lyon, and Peselnick, "Ultrasonic relaxation and its relation to structure in viscous liquids," J. Acoust. Soc. Am. **26**, 566 (1954).

(46) Barret, Beyer, and McNamara, "Ultrasonic absorption in acetate solutions," J. Acoust. Soc. Am. **26**, 966 (1954).

(47) E. L. Carstensen, "Relaxational processes in aqueous solutions of $MnSO_4$ and $CoSO_4$," J. Acoust. Soc. Am. **26**, 862 (1954).

(48) W. J. Fry and R. B. Fry, "Determination of absolute sound levels and acoustic absorption coefficients by thermocouple probes—experiment and theory," J. Acoust. Soc. Am. **26**, 311 (1954); **26**, 294 (1954).

(49) F. E. Fox and W. A. Wallace, "Absorption of finite amplitude sound waves," J. Acoust. Soc. Am. **26**, 994 (1954).

(50) S. Parthasarthy, "Absorption and dispersion of ultrasonic waves in liquids," J. Acoust. Soc. Am. **26**, 611 (1954).

(51) I. G. Mikhailov and L. I. Savina, "The absorption of ultrasonic waves in binary mixtures of liquid with one relaxing component," Doklady Akad. Nauk. S.S.S.R. **96**, 1147 (1954).

(52) N. I. Koshkin and V. F. Nozdrev, "Investigation on the absorption of ultrasound in the series of hydrocarbons using the pulse method," Doklady Akad. Nauk. S.S.S.R. **92**, 793 (1953).

(53) T. Kishimoto and O. Nomoto, "Absorption of ultrasonic waves in organic liquids I. Liquids with positive temperature coefficient of absorption," J. Phys. Soc. Japan **9**, 620 (1954).

(54) N. S. Taskoprulu, "The laws for the excess absorption and the dispersion of sound in $MgSO_4$ solutions at frequencies about 3 Mc," Istanbul Üniv. Fen Fak. Mecmuasi **C19**, 10 (1954).

(55) E. Grossetti, "Determination of the ultrasonic absorption coefficient of benzol with thermal method," Nuovo cimento **1**, 525 (1955).

(56) D. Sette, "Ultrasonic absorption in water-methyl alcohol mixtures," Ricerca. sci. **25**, 576 (1955).

(57) D. Sette, "Ultrasonic absorption in aniline-ethyl alcohol mixtures," Acustica **5**, 195 (1955).

(58) S. Parthasarthy and A. P. Deshmukh, "Sound absorption in liquids in relation to light scattering data," Ann. Physik **15**, 417 (1955).

(59) T. A. Litovitz and E. H. Carnevale, "The effect of pressure on sound propagation in water," J. Appl. Phys. **26**, 816 (1955).

(60) C. E. Chase and M. A. Herlin, "Ultrasonic measurements in magnetically cooled liquid helium," Phys. Rev. **99**, 669 (1955).

(61) A. Cilesiz, "A new pulse method to measure absorption in transparent liquids," Istanbul Üniv. Fen Fak. Mecmuasi **C20**, 94 (1955).

(62) R. T. Beyer, "Ultrasonic absorption in toluene," J. Acoust. Soc. Am. **27**, 1 (1955).

(63) E. H. Carnevale and T. A. Litovitz, "Pressure dependence of sound propagation in the primary alcohols," J. Acoust. Soc. Am. **27**, 547 (1955).

(64) Fox, Culey, and Larson, "Phase velocity and absorption measurements in water containing air bubbles," J. Acoust. Soc. Am. **27**, 534 (1955).

(65) M. M. Kannuna, "Measurements of the absorption of ultrasonic waves in liquids by the method of isochromates," J. Acoust. Soc. Am. **27**, 5 (1955).

(66) Stakutis, Morse, Dill, and Beyer, "Attenuation of ultrasound in aqueous suspensions," J. Acoust. Soc. Am. **27**, 539 (1955).

(67) D. M. Towle and R. B. Lindsay, "Absorption and velocity of ultrasonic waves of finite amplitude in liquids," J. Acoust. Soc. Am. **27**, 530 (1955).

(68) E. G. Richardson, "Acoustic experiments relating to the coefficients of viscosity of various liquids," Proc. Roy. Soc. (London) **A226**, 16 (1954).

(69) Parthasarthy, Chari, and Srinivasan, "The dependence of intensity of sound at source on its absorption coefficient in liquids," J. Chem. Phys. **21**, 185 (1953); Physik. Ber. **34**, 2031 (1953).

(70) A. W. Pryor and E. G. Richardson, "Velocity and absorption of ultrasonics in liquid sulphur," J. Phys. Chem. **59**, 14 (1955).

(71) H. Krishnamuthi, "Relaxational effects in aqueous solutions of sulphur dioxide," Proc. Indian Acad. Sci. **41**, 125 (1955).

(72) S. Parthasarthy and M. Pancholy, "Ultrasonic absorption constants in liquids by an improved optical method," Z. Physik **138**, 635 (1954); Physik. Ber. 34, 2032 (1954).

(73) Parthasarthy, Tipnis, and Pancholy, "Relation between optically determined absorption of ultrasonic waves and specific heat," Z. Physik **140**, 504 (1955).

(74) V. Nozdrev and A. Sultanov, "On the establishment and study of two relaxation regions during the passage of ultrasonic waves in ethyl acetate," Doklady Akad. Nauk. S.S.S.R. **104**, 837 (1955).

(75) A. W. Nolle, "The effect of hydrostatic pressure in the two

state model of compressional relaxation in liquids," Phys. Rev. **94**, 812 (1954).

(76) S. Parthasarthy and D. S. Guruswamy, "Sound absorption in liquids in relation to their specific heats," Ann. Physik **16**, 31 (1955).

(77) I. Gabrielli and L. Verdini, "Velocity of propagation and absorption coefficient of ultrasonics in mesomorphic liquids," Nuovo cimento **2**, 426 (1955).

(78) T. Lyon and T. A. Litovitz, "Ultrasonic relaxation in normal propyl alcohol," J. Appl. Phys. **27**, 179 (1956).

(79) J. Lamb and D. H. A. Huddart, "The absorption of ultrasonic waves in propionic acid," Trans. Faraday Soc. **46**, 540 (1950); Physik. Ber. **34**, 5836 (1955).

(80) T. Kishimoto and O. Nomoto, "Absorption of ultrasonic waves in organic liquids II. Liquids with negative temperature coefficient of absorption," Bull. Kobayashi Inst. Phys. Research **4**, 175 (1954).

(81) A. Van Itterbeek, "Acoustische Relaxatieversch ynselen in fluida by lage temperaturen," Tijdschr. Natuurk. **21**, 349 (1955).

(82) K. Eppler, "Absorbion of ultrasonics in liquid mixtures," Z. Naturforsch. **10a**, 744 (1955).

(83) B. B. Deo, "Ultrasonic absorption in solutions," Indian J. Phys. **38**, 352 (1955).

(84) C. E. Chase, "Ultrasonic propagation in liquid helium," Am. J. Phys. **24**, 136 (1956).

(85) S. Parthasarthy and A. F. Chapghar, "Sound absorption in liquids in relation to their physical properties—viscosity and specific heats," Ann. Physik **16**, 297 (1955).

(86) S. Parthasarthy and D. S. Guruswamy, "Sound absorption in liquids in relation to their specific heats II," Ann. Physik **16**, 287 (1955).

(87) L. E. Lawley and R. D. C. Reed, "A reverberation method for the measurement of the absorption of ultrasonics in liquids," Acustica **5**, 316 (1955).

(88) T. Kishimoto and O. Nomoto, "Absorption of ultrasonic waves in organic liquids III., Liquids with negative temperature coefficient of sound absorption," J. Phys. Soc. Japan **10**, 933 (1955).

(89) C. R. Rao, "Sound absorption coefficients based on intensity measurements of diffraction orders," Proc. Indian Acad. Sci. **A42**, 331 (1955).

(90) Parthasarthy, Pancholy, and Tipnis, "A new thermal method for sound absorption in liquids," Nature **176**, 611 (1955).

(91) A. Mer and W. Maier, "Absorption of ultrasonics and association in solutions of phenol in CCl_4, C_6H_{12}, and C_6H_5Cl," Z. Naturforsch. **10a**, 997 (1955).

(92) I. G. Mikhailov and G. N. Fep-Fanaov, "Differential method of measuring ultrasonic absorption in fluids," Akust. Z. **2**, 194 (1956).

(93) E. Grossetti, "Determination of the ultrasonic absorption coefficient by thermal methods," Nuovo cimento **3**, 673 (1956).

(94) Bormosov, Nozdrev, Sobolev, and Sultanav, "Experimental investigation of relaxational processes arising in the passage of ultrasonic waves through fluids," Akust. Z. **2**, 118 (1956).

(95) H. J. McSkimin, "Wave propagation and the measurement of the elastic properties of liquids and solids," J. Acoust. Soc. Am. **28**, 1288 (1956).

(96) J. F. Mifsud and A. W. Nolle," Velocity and absorption of ultrasonic waves in several nonassociated liquids under high pressure, J. Acoust. Soc. Am. **28**, 469 (1956).

(97) M. Mokhtar and M. Youssef, "Sensitive electrodynamic balance for measurement of absorption of ultrasonic waves in liquids," J. Acoust. Soc. Am. **28**, 651 (1956).

(98) L. Liebermann, "On the pressure dependence of sound absorption in liquids," J. Acoust. Soc. Am. **28**, 1253 (1956).

(99) V. Narsimhan and R. T. Beyer, "Attenuation of ultrasonic waves of finite amplitude in liquids," J. Acoust. Soc. Am. **28**, 1233 (1956).

(100) M. S. Cohen, "An ultrasonic spectrometer for measuring acoustic absorption," Proc. Natl. Electronics Conf. p. 490 (1956).

(101) S. Parthasarthy and S. S. Mathur, "Ultrasonic absorption in liquids from thermal steady states," Nature **178**, 378 (1956).

(102) S. Parthasarthy and M. Pancholy, "Sound absorption in liquids," Ann. Physik **17**, 417 (1956).

(103) R. Cerf and E. Meyer, "Absorption measurements in liquids by ultrasonic interferometry. Determination of the intrinsic absorption of a macromolecule in solution," Compt. rend. **243**, 148 (1956).

(104) M. S. de Groot and J. Lamb, "Ultrasonic relaxation in unsaturated aldehydes," Nature **177**, 1231 (1956).

(105) Zarembo, Krassilnikov, and Schklovskaya-Kordi, "Absorption of ultrasonic waves of finite amplitude in liquids," Doklady Akad. Nauk. S.S.S.R. **109**, 731 (1956).

(106) J. A. Newell and J. Wilks, "Absorption of sound in liquid helium below 1°K," Phil. Mag. **1**, 588 (1956).

(107) J. H. Andreae and J. Lamb, "Ultrasonic relaxation theory for liquids," Proc. Phys. Soc. (London) **B69**, 814 (1956).

(108) R. T. Beyer, "Ultrasonic absorption—theory of Gierer and Wirtz," J. Chem. Phys. **25**, 219 (1956).

(109)S. Parthasarthy, "Ultrasonic absorption in liquids in relation to their physical properties," Communs. congr. intern. traitments ultrasons, Marseille, p. 71 (May, 1956).

(110) Parthasarthy, Pancholy, and Mathur, "Sound absorption in liquids—thermal methods," Ann. Physik **18**, 220 (1956).

(111) V. F. Nozdrev and V. D. Sobolev, "Investigation of the ultrasonic properties of ethyl acetate in the critical region," Akust. Zhur. **2**, 379 (1956).

(112) O. Nomoto, "Theory of ultrasonic absorption in aqueous solutions I. Introduction and general theory," J. Phys. Soc. Japan **11**, 827 (1956).

(113) J. Lamb, "Ultrasonic relaxation phenomenon in organic liquids," Communs. congr. intern. traitments ultrasons, Marseilles, p. 61 (May, 1956).

(114) A. K. Dutta and K. Samal, "Real and apparent absorption coefficient of ultrasonic waves in liquids," Nature **179**, 95 (1957).

(115) A. N. Hunter, "Measurements of the velocity and absorption of high frequency ultrasonic waves in supercooled liquids," Proc. Phys. Soc. (London) **B69**, 965 (1956).

(116) E. L. Heasell and J. Lamb, "The absorption of ultrasonic waves in a number of pure liquids over the frequency range 100 to 200 Mc/sec," Proc. Phys. Soc. (London) **B69**, 869 (1956).

(117) L. Van Craeynest, "Absorption measurements of ultrasonic waves in water and electrolytic solutions," Verhandel. Koninkl. Vlaam. Acad. Wetenschap. **49** (1955).

(118) G. D. Mikhailov, "On the question of interaction of ultrasonic waves in fluids," Zhur. Eksptl. i Teoret. Fiz. **30**, 1142 (1956).

(119) Sarembo, Krasilinikov, and Skhlovskaya-Kordi, "On the propagation of ultrasonic large amplitude waves in liquids," Akust. Z. **3**, 29 (1957).

(120) R. T. Beyer, "Recent research in ultrasonics & physical acoustics in U.S.S.R.," Nuovo cimento **4**, 31 (1956).

(121) F. A. Levi, "On the measurement of ultrasonic intensities by means of a radiation pressure balance," Nuovo cimento **4**, 1073 (1956).

(122) S. Parthasarthy and P. P. Mahendroo, "Relation between efficiency of quartz transducers and ultrasonic absorption coefficients of liquids. I, II.," Z. Physik **147**, 573 (1957).

(123) S. Parthasarthy and S. S. Mathur, "Ultrasonic absorption by steady thermal methods," Ann. Physik **19**, 242 (1956).

(124) O. Nomoto, "Theory of the ultrasonic absorption in aqueous solutions II. Aqueous solutions of some alcohols," J. Phys. Soc. Japan **12**, 300 (1957).

(125) W. Maier and H. D. Rudolph, "Ultrasonic absorption measurements in dilute solutions for determining the rates of association and dissociation of benzoic acid in CCl_4," Z. physik. Chem. **10**, 83 (1957).

(126) T. A. Litovitz, "Theory of ultrasonic thermal relaxation in liquids," J. Chem. Phys. **26**, 469 (1957).

(127) Litovitz, Carnevale, and Kendall, "Effects of pressure on ultrasonic relaxation in liquids I," J. Chem. Phys. **26**, 465 (1957).

(128) J. H. Andreae, "Ultrasonic relaxation in methylene chloride," Proc. Phys. Soc. (London) **B70**, 71 (1957).

(129) R. Piccirelli and T. A. Litovitz, "Ultrasonic shear and compressional relaxation in liquid glycerol," J. Acoust. Soc. Am. **29**, 1009 (1957).

(130) H. J. McSkimin, "Ultrasonic pulse technique for measuring acoustic losses and velocities of propagation in liquids as a function of temperature and hydrostatic pressure," J. Acoust. Soc. Am. **29**, 1185 (1957).

(131) T. Tashimoto and Y. Kikuchi, "Ultrasonic propagation measurement in sea water up to 400 Kc," J. Acoust. Soc. Am. **29**, 702 (1957).

(132) T. A. Litovitz, "Relation of nuclear spin-lattice relaxa-

tion to ultrasonic viscous relaxation in liquids," J. Acoust. Soc. Am. **29**, 648 (1957).

(133) Krassilnikov, Shklovskayakordy, and Zarembo, "On the propagation of ultrasonic waves of finite amplitude in liquids," J. Acoust. Soc. Am. **29**, 642 (1957).

(134) K. F. Herzfeld, "On the origin of ultrasonic absorption in liquids," J. Acoust. Soc. Am. **29**, 1180 (1957).

(135) Schuele, Gutowski, and Carome, "Interferometric determination of ultrasonic absorption in castor oil," J. Acoust. Soc. Am. **29**, 1081 (1957).

(136) R. T. Beyer, "Double relaxation effects," J. Acoust. Soc. Am. **29**, 247 (1957).

(137) D. Tabuchi, "Dispersion and absorption of sound in liquids in general chemical equilibrium and its application to chemical kinetics," J. Chem. Phys. **26**, 993 (1957).

(138) L. K. Sarembo, "On the temperature dependence of high intensity sound absorption in viscous liquids," Akust. Zhur. **3**, 163 (1957).

(139) V. F. Nozdrev and V. D. Sobolev, "Measurement of ultrasonic wave absorption in ethyl acetate at the saturation line by a pulse method with a double fixed distance," Doklady Akad. Nauk. S.S.S.R. **III**, 808 (1956).

(140) R. E. Nettleton, "Theory of the equation of state and ultrasonic absorption in associated liquids at ordinary temperatures," Phys. Rev. **106**, 631 (1957).

(141) I. G. Mikhailov, "Ultrasonic absorption in viscous liquids," Akust. Zhur. **3**, 177 (1957).

(142) O. Nomoto, "Phenomenological theory of the molecular absorption and dispersion of sound in fluids and the relation between the relaxation time of the internal energy and the relaxation time of the internal specific heat," J. Phys. Soc. Japan **12**, 85 (1957).

(143) A. Carreli and F. S. Gaeta, "A new method for the determination of the acoustic absorption coefficient in liquids," Nuovo cimento **5**, 773 (1957).

(144) R. I. Tait, "An apparatus for the study of ultrasonic propagation in liquids under pressure," Acustica **7**, 193 (1957).

(145) E. G. Richardson and R. I. Tait, "Ratio of specific heat and high frequency viscosities in organic liquids under pressure derived from ultrasonic propagation," Phil. Mag. **2**, 441 (1957).

(146) "Molecular aspects of sound propagation in gases and liquids," Proc. Intern. Comm. Acoust. Congr. 2nd. Cambridge Massachusetts, 1956 (published 1957).

(147) R. O. Davies and J. Lamb, "Ultrasonic analysis of molecular relaxational processes," Chem. Soc. London Quart. Revs. **11**, 134 (1957).

(148) W. Craya, "Two fluid model and sound absorption in helium II," Helv. Phys. Acta **30**, 447 (1957).

(149) V. P. Glotov, "The theory of the relaxation absorption and dispersion of sound in strong electrolytes which are not fully dissociated," Soviet Phys. Acoustics **3**, 236 (1957).

(150) G. Laville, "Apparatus for measuring the absorption of ultrasound in liquids," Compt. rend. **245**, 1523 (1957).

(151) M. S. de Groot and J. Lamb, "Ultrasonic relaxation in the study of rotational isomers," Proc. Roy. Soc. (London) **A242**, 36 (1957).

(152) O. Nomoto, "Ultrasonic absorption and dispersion in liquids in relation to liquid structure II. Liquid mixtures and solutions," J. Acoust. Soc. Japan **13**, 156 (1957).

(153) R. S. Musa, "Two crystal interferometric method for measuring ultrasonic absorption coefficient in liquids," J. Acoust. Soc. Am. **30**, 215 (1958).

(154) T. A. Litovitz, "Origin of ultrasonic volume viscosity in associated liquids," J. Acoust. Soc. Am. **30**, 210 (1958).

(155) Dransfeld, Newell, and Wilks, "The absorption of sound in liquid helium II," Proc. Roy. Soc. (London) **A243**, 500 (1958).

(156) M. Mokhtar and H. Youssef, "Ultrasonic absorption in liquids I, J. Acoust. Soc. Am. **30**, 549 (1958).

(157) D. Tabuchi, "Dispersion and absorption of sound in ethyl formate and study of the rotational isomers," J. Chem. Phys. **28**, 1014 (1958).

(158) R. M. Mazo, "Absorption and dispersion of sound in chemically reacting fluid," J. Chem. Phys. **28**, 1223 (1958).

(159) N. Hirai and H. Eyring, "Bulk viscosity of liquids," J. Appl. Phys. **29**, 810 (1958).

(160) M. Cevolani and S. Petralia, "Ultrasonic absorption in aniline and in mixtures," Nuovo cimento **7**, 866 (1958).

(161) K. Herzfeld, "Bulk viscosity and shear viscosity in fluids according to the theory of irreversible processes," J. Chem. Phys. **28**, 595 (1958).

(162) S. Parthasarthy and M. Pancholy, "Ultrasonic velocity and absorption coefficient in a chemically reactive medium," Z. angew. Phys. **10**, 193 (1958).

(163) H. Singh, "Sound absorption in relation to free volume of liquids," Nuovo cimento **9**, 545 (1958).

(164) B. R. Ramachandra Rao and H. S. Rama Rao, "A method of studying the variation with temperature of ultrasonic absorption in liquids," Nature **182**, 1794 (1958).

(165) S. Parthasarthy and M. Pancholy, "Studies in ultrasonic propagation in mixtures of ethyl alcohol and water," Z. angew. Phys. **10**, 453 (1958).

(166) P. White and G. C. Benson, "Ultrasonic absorption in (pure) butyric acid," Can. J. Chem. **36**, 1135 (1958).

(167) Murphy, Ganison, and Potter, "Sound absorption at 50 to 500 kc from transmission measurements in the sea," J. Acoust. Soc. Am. **30**, 871 (1958).

(168) K. Barron and L. E. Lawley, "Absorption of sound in sediments of small particles in liquids," Proc. Phys. Soc. (London) **72**, 933 (1958).

(169) R. Bass and J. Lamb, "Ultrasonic relaxation of the vibrational specific heat of carbon dioxide, sulphur hexafluoride, nitrous oxide, cyclopropane and methyl chloride in the liquid state," Proc. Roy. Soc. (London) **A247**, 168 (1958).

(170) R. T. Beyer and V. Narsimhan, "On the absorption of ultrasonic waves of finite amplitude in liquids," Soviet Phys.-Acoust. **4**, 196 (1958).

(171) V. P. Glotov, "Reverberation tank method for the study of sound absorption in the sea," Soviet Phys.-Acoust. **4**, 243 (1958).

(172) B. I. Kal'ianov and V. F. Nozdrev, "Investigation of the frequency-temperature dependence of the ultrasonic absorption coefficient in the critical region of methyl acetate," Soviet Phys.-Acoust. **4**, 198 (1958).

(173) I. G. Mikhailov, "On the absorption of ultrasonic waves in ethyl acetate," Soviet Phys.-Acoust. **4**, 200 (1958).

(174) V. F. Nozdrev, "On the absorption of ultrasonic waves in ethyl acetate," Soviet Phys.-Acoust. **4**, 205 (1958).

(175) Parthasarthy, Pancholy, and Chapghar, "Ultrasonic absorption in some homologous series of organic liquids," Nuovo cimento **10**, 111 (1958).

(176) Y. Wada, "Attenuation of ultrasonic waves in suspensions of viscoelastic spheres," J. Phys. Soc. Japan **13**, 1390 (1958).

(177) R. E. Nettleton, "Compressional relaxation in liquids," J. Acoust. Soc. Am. **31**, 557 (1959).

(178) R. O. Davies, "Some equilibrium and non-equilibrium properties of an $(n+1)$-state ideal solution," Proc. Phys. Soc. (London) **73**, 25 (1959).

(179) R. O. Davies and J. Lamb, "On the derivation of reaction parameters from observations of ultrasonic relaxation," Proc. Phys. Soc. (London) **73**, 767 (1959).

(180) D. N. Hall and J. Lamb, "The effect of polar and nonpolar solvents on the isomeric reaction in ethyl formate demonstrated by ultrasonic measurements," Trans. Faraday Soc. **55**, 784 (1959).

(181) T. A. Litovitz, "Ultrasonic spectroscopy in liquids," J. Acoust. Soc. Am. **31**, 681 (1959).