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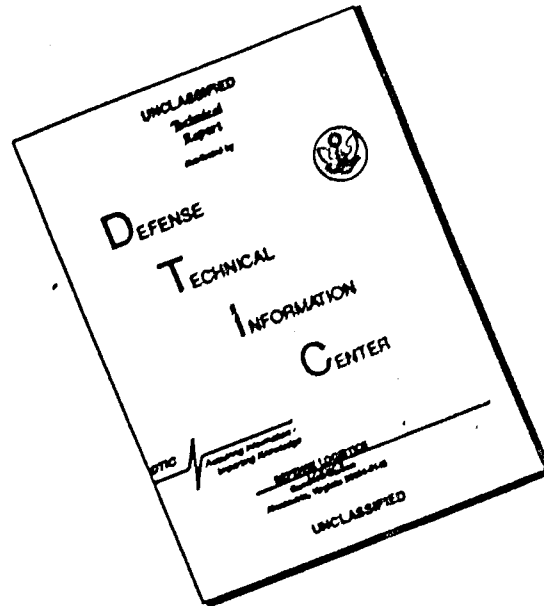
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ULTRASONICS RESEARCH LABORATORY

Department of Chemistry
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Cleveland, Ohio

TECHNICAL REPORT 25

ULTRASONIC RELAXATION IN ELECTROLYTIC
SOLUTIONS: I. A REVIEW

by

John Stuehr and Ernest Yeager

1 July 1962

Office of Naval Research
Contract No. Nonr 1439(04)
Project No. NR 384-305

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TABLE OF CONTENTS

	PAGE
LIST OF TABLES	iv
LIST OF FIGURES	v
ABSTRACT	vi
PREFACE	vii
LIST OF SYMBOLS	viii
I. THEORY OF CHEMICAL RELAXATION	1
A. General Considerations	1
B. Relation of Sound Absorption and Velocity Dispersion to the Relaxational Compressibility .	5
C. Relaxation Effects Involving the Ionic Atmosphere	10
D. Chemical Relaxation in Electrolytic Solutions .	14
1. Unimolecular Reactions	15
2. The Dissociation Reaction	21
3. Generalized Relaxation Analysis	26
E. Activation Energy	30
II. EXPERIMENTAL METHODS FOR THE STUDY OF RELAXATION IN LIQUIDS	33
A. Ultrasonic Absorption	33
B. Step Function Techniques for Relaxation Studies in Liquids	34
1. Pressure Step Function	36
2. Temperature Step-Function	37
3. Wien Effect II	38

TABLE OF CONTENTS (continued)

	PAGE
III. PRESENT STATE OF RELAXATION PROCESSES IN ELECTROLYTES	40
A. Measurements	40
B. Mechanisms	69
1. 2-2 Electrolytes	69
2. Protolytic Reactions	101
APPENDIX: EXPERIMENTAL METHODS FOR THE MEASUREMENT OF ULTRASONIC ABSORPTION IN LIQUIDS	113
A. Progressive Wave Methods	113
1. Pulse Methods	113
2. Radiation Pressure	115
3. Optical Method	117
B. Standing Wave Methods	118
C. Reverberation Methods	118
1. Resonance method (spherical resonator)	119
2. Statistical reverberation	121
D. Direct Methods	121
1. Acoustic streaming	121
2. Thermal and calorimetric methods	123
DISTRIBUTION LIST	125

LIST OF TABLES

	PAGE
Table 1 - Calculated relaxation parameters for ionic relaxation in NaCl and MgSO ₄ solutions	14
Table 2 - Methods for the measurement of ultrasonic absorption	33
Table 3 - Pressure dependence of the NH ₃ ·H ₂ O relaxation	43
Table 4 - Effect of dielectric constant and ionic strength upon the rate of reaction	51
Table 5 - Effect of dielectric constant and concentration on the primary relaxation frequency in MgSO ₄ at 25°C	54
Table 6 - Effect of dielectric constant and pressure on the primary relaxation frequency in 0.5 M MgSO ₄ at 25°C	55
Table 7 - Effect of dielectric constant and concentration on the primary relaxation process in MnSO ₄ at 25°C	63
Table 8 - Velocity dispersion in 2-2 electrolytes	66
Table 9 - Relaxation frequencies in aqueous solutions at 20°C	68
Table 10 - Rate constants for 2-2 electrolytes	76
Table 11 - Effects of charges and sizes on rates of reaction	96
Table 12 - Relation of the rate constants to the crystal field stabilization energy and enthalpy of hydration of cations	100
Table 13 - Rate constants for protolytic reactions	103

LIST OF FIGURES

	PAGE
Figure 1 - Volume variations following a pressure jump or drop	3
a. Pressure jump	3
b. Pressure drop	3
Figure 2 - Absorption per wavelength for a relaxation process	4
Figure 3 - Variation of α/r^2 with frequency for a relaxation process	9
Figure 4 - Sound dispersion according to relaxation theory	9
Figure 5 - A 2-state free energy diagram	31
Figure 6 - Effect of an abrupt impulse upon the degree of dissociation	35
Figure 7 - Absorption in sea water (from Markham, Beyer, and Lindsay)	48
Figure 8 - Absorption in $MgSO_4$ according to Kurtze and Tamm	50
Figure A-1 - Pulse-echo apparatus	114
Figure A-2 - Diagram of apparatus for absorption measurement by radiation pressure	116
Figure A-3 - Spherical resonator apparatus	120
Figure A-4 - Apparatus for measurement of ultrasonic absorption from acoustic streaming	122

ULTRASONIC RELAXATION IN ELECTROLYTIC

SOLUTIONS: I. A REVIEW

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-Abstract of Report-

Ultrasonic absorption measurements provide a means for studying the kinetic parameters of processes which occur too rapidly to be studied by conventional techniques. Considerable progress has been made, especially in the past decade, in the study and interpretation of relaxational acoustic absorption in aqueous solutions of electrolytes. The purpose of this technical report is to review and critically evaluate the available relaxation data for electrolytes.

Ultrasonic relaxation theory is reviewed with particular reference to solutions of electrolytes. Specific processes include the relaxation of the ionic atmosphere surrounding ions in solution, and unimolecular and dissociation reactions. The theoretical treatment of the multiple relaxation effects associated with consecutive equilibria is reviewed.

Eigen (1958-61) has shown that the observed acoustic absorption data in divalent sulfates can be explained on the basis of the step-wise loss of hydration water from between the partners of cation-anion ion pairs. This mechanism is used to examine critically the ultrasonic absorption data in solutions of divalent sulfates, thiosulfates, and chromates.

A number of proton-transfer reactions (e.g. hydrolysis or acid-base dissociation) have been studied by several relaxational techniques. Rate constants for reactions between ions in aqueous solution approach the theoretical limiting values anticipated for primarily diffusion-controlled processes. Representative values are collected and discussed in relation to the mechanisms responsible for the relaxation effects.

A brief survey of experimental methods for measuring ultrasonic absorption is given in an appendix.

--Preface--

During the past decade considerable progress has been made in interpreting ultrasonic relaxation in electrolytic solutions. Despite this progress, very few chemical physicists have made use of this very important tool for studying the kinetics of fast reactions in electrolytic solutions.

The purpose of this technical report is to present a review of the progress which has been made in the interpretation of ultrasonic relaxation in electrolytic solutions, principally during the past decade. Such a review has not appeared in a readily-available journal or text in recent years. Since it is hoped that this review will be useful to chemical physicists not familiar with general aspects of acoustical relaxation, the mathematical aspects of acoustical relaxation have been reviewed in more detail than might otherwise be necessary.

Later reports in this series will be concerned with experimental studies of ultrasonic relaxation in specific electrolytic systems.

LIST OF SYMBOLS

A	—	amplitude
a	—	effective reaction distance
C	—	molar concentration
C_p	—	heat capacity at constant pressure
C_v	—	heat capacity at constant volume
c	—	acoustic propagation velocity
D	—	dielectric constant
E	—	electrical field density
e	—	electronic charge
F	—	free energy
f	—	frequency, c/s
H	—	enthalpy
h	—	Planck's constant
I	—	sound intensity
J	—	Joule's mechanical equivalent of heat
K	—	equilibrium constant
K_r	—	relaxational bulk modulus
k	—	specific reaction rate constant; Boltzmann constant
<u>M</u>	—	moles/liter
N	—	Avogadro's number
n	—	number of moles of reactant
P	—	pressure
Q	—	absorption cross-section
R	—	perfect gas constant
r	—	distance of separation of ions
S	—	entropy
s	—	relative compression $\Delta V/V$
T	—	absolute temperature
t	—	time
V	—	volume
\bar{V}_i	—	partial molal volume of i^{th} component
ΔV°	—	standard state volume change
v	—	phase velocity
x	—	displacement, distance

LIST OF SYMBOLS (continued)

y_{\pm}	— mean molal stoichiometric ionic activity coefficient
z	— unit of ionic charge
α	— amplitude absorption coefficient
$\underline{\alpha}$	— degree of dissociation
β	— compressibility
β_s	— adiabatic compressibility
β_r	— relaxational compressibility
γ	— specific heat ratio
γ_{\pm}	— thermodynamic mean ionic activity coefficient
$\Delta()$	— finite increase in quantity ()
$\delta()$	— variation in quantity ()
η	— viscosity
κ	— reciprocal of average radius of the ionic atmosphere
Λ	— equivalent conductance of electrolyte
λ	— wavelength of acoustic waves
μ	— mobility; dipole moment
μ_r	— relaxational absorption per wavelength
ξ	— particle displacement
ρ	— density
ρ_i	— frictional coefficient of i^{th} ion
τ	— relaxation time
ω	— angular frequency

ULTRASONIC RELAXATION IN ELECTROLYTIC SOLUTIONS:

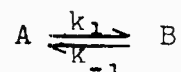
A REVIEW

I. THEORY OF CHEMICAL RELAXATION

A. General Considerations

The inability of a classical theory based on simple viscous loss and thermal conductivity to explain the excess sound absorption in liquids led to the postulation that other physical or chemical processes of a relaxational type were causing the excess absorption. Chemical relaxation will be discussed in this report.

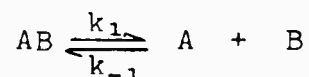
Consider a reversible chemical reaction at dynamic equilibrium. The reaction may be of the type



with an equilibrium constant

$$K = \frac{k_1}{k_{-1}} = \frac{C_B}{C_A} = \frac{\alpha}{1 - \alpha} \quad (1)$$

where k_1 and k_{-1} are the forward and reverse rate constants, respectively, α is the fraction of A converted to B, and C_A and C_B are the indicated concentrations. The reaction may also be one of dissociation



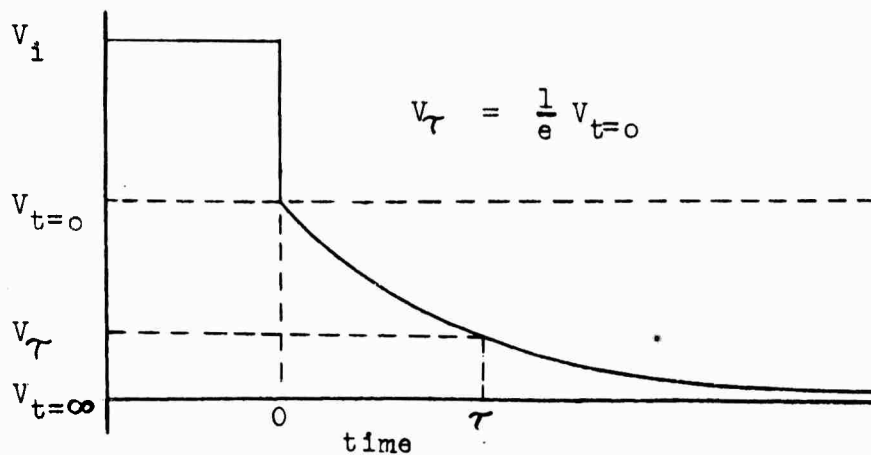
for which the equilibrium constant is

$$K = \frac{k_1}{k_{-1}} = \frac{\alpha^2 C}{1 - \alpha} \quad (2)$$

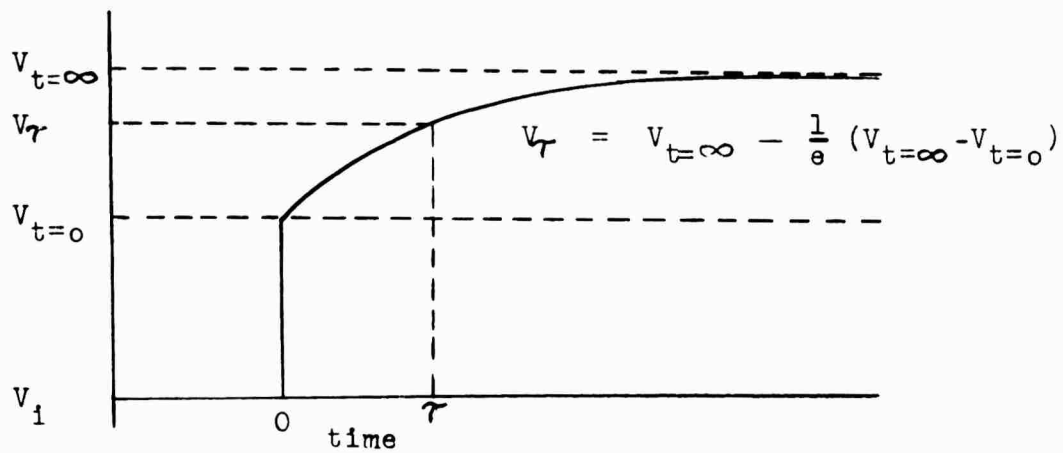
where α is the degree of dissociation and C is the molar concentration for AB if all of the chemical system were in the form of AB. Although these represent the types of chemical processes which have received the most thorough theoretical treatments, it should be understood that the reactions may be considerably more complicated. Activity coefficients have been assumed to be unity.

If the volume of the products and reactants differ, a pressure-sensitive chemical equilibrium results. Under these circumstances, a decrease in the specific volume associated with an instantaneous pressure increment in the system can be resolved into a virtually instantaneous portion plus a time-dependent portion which will asymptotically approach a new limiting value. The latter portion is associated with the shift of the chemical equilibrium with the pressure increment. For small displacements from equilibrium, the equilibrium will shift such that after a finite time τ the time-dependent portion of the specific volume will approach to within $1/e$ of its final value. If the pressure is restored to its original value, the specific volume will again undergo an instantaneous change followed by a time-dependent change such that the time-dependent portion approaches to $1/e$ of its final value within a time τ . The situation is represented graphically in Fig. 1.

If the pressure in the liquid is now periodically varied so slowly that the chemical equilibrium is continuously maintained, then the specific volume-pressure relation will be the normally measured static one. If, on the other hand, the pressure in the liquid is varied so rapidly that the chemical equilibrium cannot be appreciably altered during the pressure change, practically no chemical transposition takes place, and the medium will be less compressible than previously. The sound velocity thus will increase with an increase in frequency and will approach a limiting value. Since the system cannot immediately re-establish equilibrium with a pressure change, it follows that there is a phase lag between pressure and specific



a. Pressure jump



b. Pressure drop

Fig. 1. Volume variations following a pressure jump or drop

volume. This phase lag causes energy to be dissipated within each cycle. The integral $\oint PdV$ represents the energy lost per cycle. At low frequencies, the sound energy lost each cycle is small, since most of the potential energy stored in shifting the equilibrium can be regained by the acoustic wave. As the frequency rises from a low value, the shift in equilibrium will increasingly lag behind the pressure. The energy lost per cycle increases and attains a maximum value at an angular frequency $\omega_r = 1/\tau$. At higher frequencies, variations of acoustic pressure occur so rapidly that little shift in equilibrium occurs and the energy lost per cycle again becomes small. The excess absorption per wavelength is illustrated in Fig. 2.

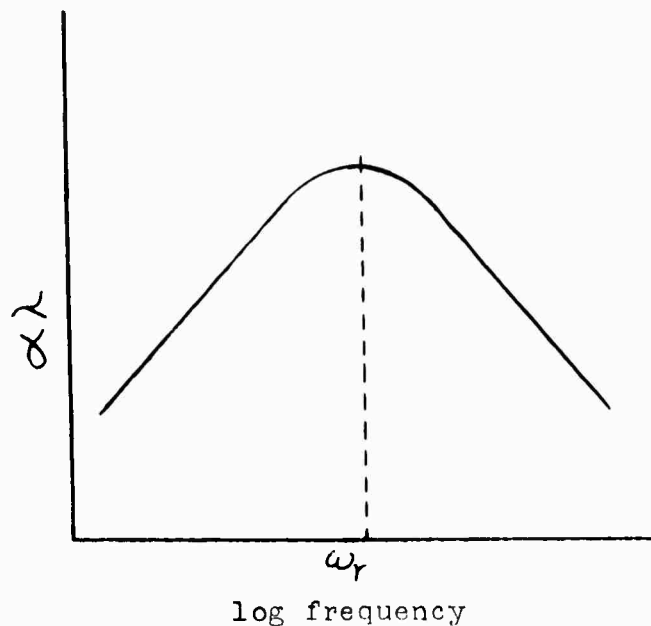


Figure 2: Absorption per wavelength for a relaxation process

The above discussion considered a system in which the perturbations from equilibrium conditions were brought about by pressure variations. It should be noted that temperature variations also present a method for perturbing the system from equilibrium. For liquids and solutions the ratio of specific heats is nearly unity, and therefore, the temperature variations associated with the propagation of sound waves are small. As a result, a relatively large entropy change is required before the equilibrium is shifted sufficiently because of temperature fluctuations to give significant coupling of the equilibrium process to the sound wave. The question of how large a volume change or entropy change is required for sufficient coupling of the process to the sound wave to show up as absorption will be discussed later.

B. Relation of Sound Absorption and Velocity Dispersion to the Relaxational Compressibility

The adiabatic compressibility of a fluid, which is defined by

$$\beta_s = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S \quad (3)$$

may be written as consisting of two terms, one involving a relaxational compressibility β' , which is dependent upon the frequency of the compression, and a second term β_∞ , the compressibility at infinite frequency¹

$$\beta_s = \beta' + \beta_\infty \quad (4)$$

If one now uses the notation $s = (\beta_s)^* P = \frac{\Delta V}{V}$, where s is the relative compression, the presence of both instantaneous and relaxational compressibilities in a medium may be expressed by the dynamical stress-strain differential equation

$$\frac{d(s - s_\infty)}{dt} = \frac{s_0 - s}{\tau} \quad (5)$$

¹This treatment is substantially the same as that presented by L. Hall, Phys. Rev. 73, 775 (1948).

*For simplicity, β_s is taken as the negative of the value defined by eq. 3.

or

$$\dot{s} = \frac{s_0 - s}{\tau} + \dot{s}_\infty = \frac{\beta_0 P - \beta_s P}{\tau} + \beta_\infty \dot{P} \quad (6)$$

where β_∞ is the instantaneous compressibility (the compressibility as $\omega \rightarrow \infty$), β_0 is the total or static compressibility (as $\omega \rightarrow 0$), $\beta_0 P = s_0$ is the equilibrium value of the compression for an applied constant pressure, and the constant τ will be identified as the relaxation time. Eq. 5 and 6 are applicable only for small values of $s_0 - s$. For a sinusoidal pressure variation $P = P_0 e^{i\omega t}$, one may write

$$\dot{s} = i\omega s = \frac{s_0 - s}{\tau} + i\omega s_\infty, \quad (7)$$

the solution of which is

$$s = \frac{s_0 + s_\infty i\omega\tau}{1 + i\omega\tau} = \frac{s_0 - s_\infty}{1 + i\omega\tau} + s_\infty \quad (8)$$

which is equivalent to

$$\beta_s = \frac{\beta_r}{1 + i\omega\tau} + \beta_\infty \quad (9)$$

in which

$$\beta_r = \beta_0 - \beta_\infty \quad (10)$$

Comparison with eq. 4 shows that

$$\beta' = \frac{\beta_r}{1 + i\omega\tau} \quad (11)$$

At very low frequencies the compressibility becomes the ordinarily measured static one

$$\beta_0 = \beta_\infty + \beta_r \quad (12)$$

The compressibility is related to the velocity by

$$c^2 = \frac{1}{\rho\beta_s} \quad (13)$$

By combining eq. 9 and 13, the square of the velocity of a wave in a relaxational medium may be written in the complex form

$$c^2 = \frac{1}{\rho\left(\beta_\infty + \frac{\beta_r}{1 + i\omega\tau}\right)} \quad (14)$$

The relaxational compressibility may now be related to the plane wave absorption coefficient α which is defined by

$$I = I_0 e^{-2\alpha x} \quad (15)$$

where I_0 is the initial sound intensity, I is the intensity at a distance x , and α is the amplitude absorption coefficient². The equation describing the sinusoidal motion of a plane damped wave may be written in the form

$$\xi = A e^{i\omega(t-x/v)} e^{-\alpha x} \quad (16)$$

where ξ is particle displacement and v is phase velocity. Comparison of eq. 16 with the usual equation for ξ , i.e.,

$$\xi = A e^{i\omega(t-x/c)} \quad (17)$$

shows that

$$\frac{i\omega}{c} = \alpha + \frac{i\omega}{v} \quad (18)$$

which gives

$$\frac{1}{c^2} = \frac{1}{v^2} - \frac{\alpha^2}{\omega^2} - \frac{2i\alpha}{\omega v} \quad (19)$$

Equation 14 can be rearranged to the form

$$\frac{1}{c^2} = \rho \left(\frac{\beta_0 + \omega^2 \tau^2 \beta_\infty}{1 + \omega^2 \tau^2} - \frac{i\omega \tau \beta_r}{1 + \omega^2 \tau^2} \right) \quad (20)$$

If the imaginary parts of eq. 19 and 20 are equated and one solves for the relaxational absorption,

$$\alpha = \frac{\omega}{2c} \cdot \frac{\omega \tau \beta_r}{\beta_0 (1 + \omega^2 \tau^2)} \quad (21)$$

where ρ has been replaced by $1/(c^2 \beta_s) \cong 1/c^2 \beta_0$ and v has been replaced by c - reasonable assumptions, since $\frac{\omega}{v} \gg \alpha$. Furthermore,

$$\frac{\omega}{2c} = \frac{\pi}{\lambda} \quad (22)$$

²It should be noted that, particularly in the older literature, α sometimes also refers to the intensity absorption coefficient, which is twice the amplitude absorption coefficient.

where λ is the wavelength. Therefore, the excess or relaxational absorption per wavelength³ may be written as

$$(\alpha\lambda)_r = \mu_r = \frac{\pi\beta_r}{\beta_0} \cdot \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (23)$$

This equation has a maximum value at an angular frequency $\omega_r = 1/\tau$, at which frequency

$$(\alpha\lambda)_r = \frac{\pi\beta_r}{2\beta_0} \quad (24)$$

The excess absorption per wavelength may be expressed in terms of the related quantity α_r/f^2 :

$$\frac{\alpha_r}{f^2} = \frac{2\pi^2\tau\beta_r}{\beta_0 c} \cdot \frac{1}{1 + \omega^2\tau^2} \quad (25)$$

$$= 2\pi^2\tau\beta_r \rho c \cdot \frac{1}{1 + \omega^2\tau^2} \quad (26)$$

where $f = \omega/2\pi$ is the frequency expressed in cycles/second. One can write then³

$$\frac{\alpha}{f^2} = A \frac{1}{1 + \omega^2\tau^2} + B \quad (27)$$

where B represents the absorption when $\omega \gg 1/\tau$ and A is the constant factor in the relaxational absorption of eq. 25. The shape of this curve is shown in Fig. 3.

A complicating factor in the measurement of relaxational sound absorption associated with specific chemical processes is that it must be distinguished from absorption due to other processes, principally associated with the solvent. If the relaxation frequencies due to different processes are separated by at least decades, to a good approximation the effects of absorption processes are additive.

In addition to the maximum absorption per wavelength occurring at the relaxation frequency, there is also a dispersion of the sound velocity in the vicinity of the relaxation frequency. Calculation from theory⁴ gives for the velocity dispersion in the case of a single relaxation process

$$c^2 - c_0^2 = \frac{\beta_r}{\beta_0} c_0 c_{\infty} \cdot \frac{\omega^2\tau^2}{1 + \omega^2\tau^2} \quad (28)$$

³The symbols α_r and μ_r refer to the excess or relaxational absorption, whereas α generally is used to mean the total absorption.

⁴J. Markham, R. Beyer, and R. Lindsay, Revs. Modern Phys. 23, 374 (1951)

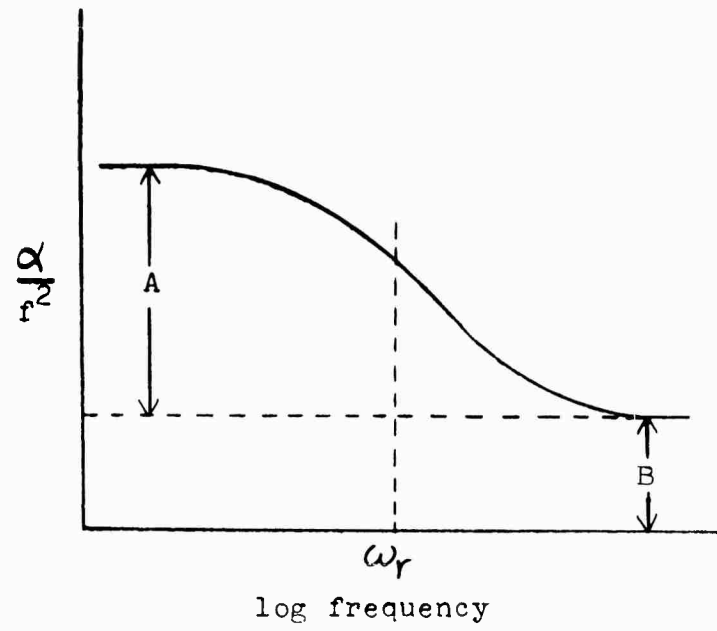


Figure 3: Variation of α/f^2 with frequency for a relaxation process

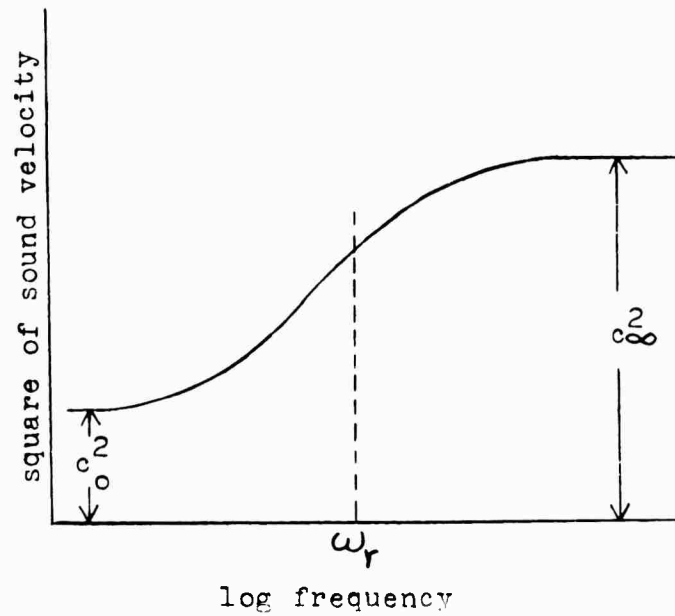


Figure 4: Sound dispersion according to relaxation theory

where c_0 and c_∞ are the limiting low and high values of the velocity. This is related to the maximum excess absorption per wavelength by

$$c^2 = c_0^2 + \frac{2}{\pi} (\alpha\lambda)_{\max} c_0 c_\infty \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \quad (29)$$

Furthermore, if $c = c_0 + \Delta c$, where $\Delta c \ll c_0$, eq. 29 becomes

$$\Delta c = \frac{(\alpha\lambda)_{\max}}{\pi} c_\infty \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \quad (30)$$

The shape of the sound dispersion curve from eq. 29 is illustrated in Fig. 4.

Equations 23 and 25 are general acoustic relaxation equations. It remains to evaluate the relaxational part of the compressibility (β_r), the form of which depends on the type of process under consideration.

C. Relaxation Effects Involving the Ionic Atmosphere

A complication in the study of chemical relaxation in electrolytic solutions is the possibility of simultaneous excess absorption due to relaxation effects involving the ionic atmosphere. For this reason, a brief discussion of ionic atmosphere relaxation will be presented.

According to the Debye-Hückel interionic theory⁵, any ion in a solution may be considered to be surrounded by an ionic atmosphere of predominantly opposite charge. Rearrangements of the ionic atmosphere associated with some type of disturbance may be characterized by a relaxation time. The relaxation of the ionic atmosphere has been treated theoretically by Hall⁶. The ionic atmosphere about a particular ion is time-average symmetrical as to charge, but there are continuous rearrangement and interchange of the ions in different

⁵P. Debye and E. Hückel, Phys. Z. 24, 185 (1923).

⁶L. Hall, J. Acoust. Soc. Am. 24, 704 (1952).

atmospheres. When the central ion moves, an asymmetry develops in the ionic atmosphere because of the finite time required for the re-establishment of an equilibrium distribution of the ionic atmosphere. The resulting charge asymmetry exerts a retarding force on the motion of the central ion.

Hall⁶ gives the following rate equation for the rearrangement of ions in a solution of a symmetrical electrolyte under the influence of an external electrical field or mechanical force:

$$\tau \frac{d(\delta C)}{dt} + \delta C - \frac{1}{\kappa^2} \frac{d^2(\delta C)}{dr^2} = \frac{\kappa^2}{8\pi C} e^{-\kappa r} \quad (31)$$

where δC is the deviation from the time-average concentration C , r is the distance of separation of ions, and τ is the relaxation time given by

$$\tau = \frac{1}{RT \kappa^2 (\overline{1/\rho})} \quad (32)$$

In this equation⁷, k is the Boltzmann constant, T is the absolute temperature, κ is the reciprocal of the effective radius of the ionic atmosphere, and $(\overline{1/\rho}) = \frac{1}{2} (\frac{1}{\rho_1} + \frac{1}{\rho_2})$ with ρ_1 and ρ_2 the friction coefficients for cations and anions.

For a harmonic sound field, the time dependence of all variables is assumed harmonic (first-order solution), and eq. 31

⁷Hall gives this equation with a factor of 2 in the denominator. The correct form is given by Harned and Owen, The Physical Chemistry of Electrolytic Solutions, Reinhold Publ. Corp., New York, 1950, p. 65.

leads to the relaxational bulk modulus⁸

$$K'_r = - \frac{kT \kappa^3}{24 \pi} \left(\frac{V \partial \ln \kappa^2}{\partial V} \right)_T \cdot \left(\frac{V \partial \ln \kappa^2}{\partial V} \right)_S \cdot \frac{2}{1 + (1 + i\omega\tau)^{1/2}} \quad (33)$$

or $K'_r = K_r \cdot f(\omega t)$. The term K_r is the maximum value of K'_r occurring at $\omega = 0$. The static ($\omega \rightarrow 0$) bulk modulus is

$$K_0 = K_\infty + K_r \quad (34)$$

where K_∞ is the modulus at high frequencies.

The excess absorption per wavelength is given by

$$(\alpha\lambda)_r = - \frac{\pi c K_r}{c_0 K_0} \cdot \frac{(\gamma^2 - 1)^{1/2}}{\gamma(\gamma + 1)} \quad (35)$$

where $\gamma = \left[\frac{(1 + \omega^2 \tau^2)^{1/2} + 1}{2} \right]^{1/2}$ and c_0 is the low-frequency value of the velocity c . The maximum in the absorption per wavelength occurs at $\omega\tau = 2(2 + \sqrt{5})^{1/2} \approx 4.1$ for which $\frac{(\gamma^2 - 1)^{1/2}}{\gamma(\gamma + 1)}$ is about 0.30. The maximum absorption per wavelength is then

⁸The adiabatic bulk modulus is defined, as $K = -V \left(\frac{\partial P}{\partial V} \right)_S = 1/\beta_S$. Like the compressibility, it may be written as the sum of two terms,

$$K = K_\infty + K'_r$$

where K_∞ is the instantaneous or high frequency modulus and K'_r is the frequency-dependent relaxational bulk modulus. It is negative because $K_\infty > K$ (i.e. at very high frequencies the system becomes less compressible). From these definitions, the various compressibilities and moduli are related as follows:

$$\beta_S = 1/K \quad ; \quad \beta_\infty = 1/K_\infty$$

but

$$\beta'_r = -K_r \beta \beta_\infty \neq 1/K'_r$$

$$(\alpha\lambda)_{\max} = -0.94 \frac{K_r c}{K_o c_o} \approx -\frac{K_r}{K_o} \quad (36)$$

since the velocity dispersion is small.

The maximum absorption per wavelength may be calculated from eq. 33 and 36 with the following approximation:

$$\left(\frac{v \partial \ln \kappa^2}{\partial v}\right)_T \cdot \left(\frac{v \partial \ln \kappa^2}{\partial v}\right)_r \approx \left(\frac{v \partial \ln \kappa^2}{\partial v}\right)_r^2 = \left(\frac{v \partial D}{D \partial v} + 1\right)^2 = \left(\frac{K \partial D}{D \partial P} - 1\right)^2 \quad (37)$$

where D is the dielectric constant.

The quantity $\frac{1}{D} \frac{\partial D}{\partial P}$ is taken⁹ as $59.4 \times 10^{-12} \text{ cm}^2 \text{ dyne}^{-1}$.

The relaxation time is calculated from eq. 32. A convenient expression for $(1/\rho)$ is

$$(1/\rho) = \frac{300}{96500\epsilon} \frac{\Lambda}{|z_1| + |z_2|} \quad (38)$$

where Λ is the equivalent conductance of the electrolyte, z_1 and z_2 are the ionic valences, and ϵ is the electronic charge.

The maximum excess absorption per wavelength and relaxation times have been calculated for a typical uni-univalent electrolyte (NaCl) and di-divalent electrolyte (MgSO_4). The results are given in Table 1. A comparison of the values of $(\alpha/f^2)_{\text{excess}}$ at the frequencies f_r with the value of 22×10^{-17} for α/f^2 for water at 25°C indicates that the excess absorption associated with relaxation of the ionic atmosphere is much too small to be measured by present-day techniques. Thus, relaxation effects in the ionic atmosphere should not result in any direct complications in the study of chemical relaxation in electrolytic solutions with ultrasonic absorption techniques. The ionic atmosphere cannot be neglected in such studies,

⁹C. Bachem. Z. Physik 101, 541 (1936).

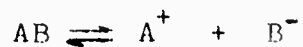
Table 1: Calculated relaxation parameters for ionic relaxation in NaCl and MgSO₄ solutions

NaCl	τ , sec. $\times 10^9$	f_r mc/s	$(\alpha\lambda)_{\max}$ $\times 10^9$	$(\alpha/f^2)\tau$ $\times 10^{17}$
0.001 <u>M</u>	112	5.9	2.7	0.0003
0.01	11.7	56	87	0.0010
0.1	1.29	510	2700	0.0035
<hr/>				
MgSO ₄				
0.001 <u>M</u>	3.1	21	20	0.00064
0.01	0.46	164	660	0.0027
0.1	0.096	683	21000	0.020

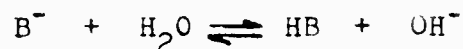
however, since the interactions associated with the ionic atmosphere concept have a major influence on the kinetics of the chemical processes.

D. Chemical Relaxation in Electrolytic Solutions

Several chemical processes are of particular interest in electrolytic solutions. If these are characterized by rate constants corresponding to relaxation times between 10^{-5} and 10^{-9} sec., these very fast processes may be studied by the relaxation techniques involving ultrasonic absorption measurements. Among these processes are the dissociation and hydrolysis reactions which are known to occur for many electrolytes. These include reactions of the type

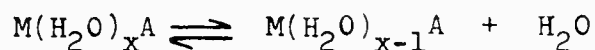


and



Specific examples for which relaxation processes have been characterized include the dissociation of weak electrolytes such as $NH_3 \cdot H_2O$ ¹⁰ and the hydrolysis of salts such as $La(NO_3)_3$ ¹⁰ and Na_3PO_4 ¹¹. These are effectively first-order second-order processes since water is in great excess.

Another type of relaxation which occurs in aqueous solutions of electrolytes is that found in di-divalent salts, particularly the sulfates,¹²⁻¹⁴ for which the reaction associated with the relaxation process is of the type



i.e. the removal of water of hydration from an ion pair. The mechanism for this process will be discussed more fully in a later section.

1. Unimolecular Reactions

For a reaction of the type



¹⁰K. Tamm, G. Kurtze, and R. Kaiser, *Acustica* 4, 380 (1954).

¹¹G. Kurtze and K. Tamm, *Acustica* 3, 33 (1953).

¹²L. Liebermann, *Phys. Rev.* 76, 1520 (1949).

¹³M. Eigen, G. Kurtze and K. Tamm, *Z. Elektrochem.* 57, 103 (1953).

¹⁴J. Smithson and T. Litovitz, *J. Acoust. Soc. Am.* 28, 1162 (1956).

let C_A be the concentration of A at any time, C_B the concentration of B, and C the total concentration such that $C = C_A + C_B$. For this reaction the forward and reverse rate constants will be designated as k_1 and k_{-1} , respectively. If the equilibrium is now perturbed from its equilibrium value by an external force, the rate of return of the system to equilibrium is governed by the rate law

$$\frac{dC_B}{dt} = - \frac{dC_A}{dt} = k_1 C_A - k_{-1} C_B \quad (39)$$

At equilibrium the net rate is 0, so that

$$k_1^{\circ} C_A^{\circ} = k_{-1}^{\circ} C_B^{\circ} \quad (40)$$

where the superscript is used to indicate the equilibrium value.

The mass action equilibrium constant for this reaction is

$$K = \frac{C_B^{\circ}}{C_A^{\circ}} = \frac{k_1^{\circ}}{k_{-1}^{\circ}} \quad (41)$$

If very small periodic perturbations are applied to the system, it may be assumed that the perturbed rate constants and concentrations differ only slightly from their equilibrium values. Equilibrium is then re-established with a time constant τ which is defined by

$$\frac{dC_i}{dt} = - \frac{C_i - C_i^{\circ}}{\tau} \quad (42)$$

where C_i and C_i° are the instantaneous and equilibrium values of the concentrations of the i^{th} species, respectively. One can write for the perturbed variables a series of relations such as

$$C_A = C_A^{\circ} + (\delta C_A) e^{i\omega t} \quad (43)$$

$$k_1 = k_1^{\circ} + (\delta k_1) e^{i\omega t} \quad (44)$$

and similar expressions for C_B and k_{-1} . The quantities δC_A and δk_1 represent the amplitudes of the small variations in C_A and k_1 associated with the sound field. If these equations are substituted into eq. 39, there results

$$\dot{C}_B = i\omega(\delta C_B)e^{i\omega t} = \left[C_A^\circ + (\delta C_A)e^{i\omega t} \right] \left[k_1^\circ + (\delta k_1)e^{i\omega t} \right] - \left[k_{-1}^\circ + (\delta k_{-1})e^{i\omega t} \right] \left[C_B^\circ + (\delta C_B)e^{i\omega t} \right] \quad (45)$$

If this is now expanded with all second order terms neglected and the resulting expression further simplified by using the relationships $k_1^\circ C_A^\circ = k_{-1}^\circ C_B^\circ$ and $\delta C_A = -\delta C_B$, one obtains

$$i\omega(\delta C_B) = C_A^\circ(\delta k_1) - k_1^\circ(\delta C_B) - k_{-1}^\circ(\delta C_B) - C_B^\circ(\delta k_{-1}) \quad (46)$$

Factoring terms involving δC_B results in

$$\delta C_B(k_1^\circ + k_{-1}^\circ + i\omega) = \frac{k_{-1}^\circ \delta k_1 - k_1^\circ \delta k_{-1}}{k_{-1}^\circ} C_A^\circ \quad (47)$$

Since the equilibrium constant $K = \frac{k_1}{k_{-1}}$,

$$k_{-1}^\circ \delta K = \frac{k_{-1}^\circ \delta k_1 - k_1^\circ \delta k_{-1}}{k_{-1}^\circ} \quad (48)$$

Substitution of this into eq. 47 yields

$$\delta C_B(k_1^\circ + k_{-1}^\circ + i\omega) = k_{-1}^\circ C_A^\circ (\delta K) \quad (49)$$

The variations in K in eq. 49 are produced by the pressure and temperature variations associated with the sound waves. We shall consider here the case where the pressure dependence of K is the predominant factor — as is usually the case for electrolytic solutions.

The thermodynamic dependence of the equilibrium constant on pressure is given by the equation

$$\left(\frac{\partial K}{\partial P}\right)_T \frac{1}{K} = - \frac{\Delta V^\circ}{RT} \quad (50)$$

where ΔV° is the standard volume change per mole of reaction. One can then write for a small change in K

$$\delta K \cong - \frac{(\Delta V^\circ)(\delta P)}{RT} K \quad (51)$$

Substitution of this into eq. 49 gives

$$\delta C_B = - \frac{k_{-1}^\circ C_A^\circ (\Delta V^\circ)(\delta P)}{RT(k_1^\circ + k_{-1}^\circ + i\omega)} K \quad (52)$$

From the relationships $C = C_A + C_B$ and $\frac{C_A + C_B}{C_B} = \frac{k_1 + k_{-1}}{k_1}$, it follows by algebraic manipulation that

$$\frac{\delta C_B}{\delta P} = - \frac{CK(\Delta V^\circ)}{RT(K^2 + 2K + 1) \left[1 + i\omega/(k_1 + k_{-1})\right]} \quad (53)$$

where the superscripts have been dropped since only the time-average values of the rate constants henceforth will be considered.

The time-average rate constants may now be related to the relaxation time for a first-order process. From eq. 39 with the notation $\delta x = C_B - C_B^\circ = -(C_A - C_A^\circ)$, one obtains

$$\frac{d(\delta x)}{dt} = -k_1 \delta x - k_{-1} \delta x \quad (54)$$

because $k_1 C_A^\circ - k_{-1} C_B^\circ = 0$. Integration yields

$$\ln(\delta x) = - (k_1 + k_{-1})t + Q \quad (55)$$

where Q is the integration constant defined by the conditions that at $t = 0$, δx must be its initial value $\delta x_0 = (C_B)_0 - C_B^\circ$.

Therefore,

$$C_B - C_B^{\circ} = [(C_B)_o - C_B^{\circ}] e^{-(k_1 + k_{-1})t} \quad (56)$$

Differentiation yields

$$\dot{C}_B = -(k_1 + k_{-1}) (C_B - C_B^{\circ}) \quad (57)$$

Comparison with eq. 42 defining the relaxation time τ shows that

$$\tau = \frac{1}{k_1 + k_{-1}} \quad (58)$$

for a unimolecular process. Substituting this and the relation $\Delta F^{\circ} = -RT \ln K$ into eq. 53 results in

$$\left(\frac{\partial C_B}{\partial P}\right)_T = - \frac{C \Delta V^{\circ}}{2RT [1 + \cosh(\Delta F^{\circ}/RT)]} \frac{1}{1 + i\omega\tau} \quad (59)$$

The excess adiabatic compressibility for this reaction is defined as

$$\beta'_s = - \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_s = - \frac{1}{\gamma V} \left(\frac{\partial V}{\partial P}\right)_T, \quad (60)$$

where γ is the ratio of heat capacities C_p/C_v . This may now be related to the change in concentration of component B with pressure at constant temperature. Before doing so, it would be well to examine the compressibility terms in some detail.

The relative compression of the system brought about by the sound pressure may be expressed (cf. eq. 4) as the sum of two terms, one the instantaneous compression and the other a frequency-dependent relaxational compression

$$v \beta_s = v(\beta_s)_{\infty} + v \beta'_s \quad (61)$$

The term $(\beta_s)_{\infty}$ is the adiabatic compressibility at very high frequencies and is expressed by

$$(\beta_s)\omega = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S, C_A, C_B} \quad (62)$$

The relaxational compressibility is that due to a change in the relative amounts of A and B, but at constant partial molal volumes for all components,

$$\beta'_s = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S, \bar{V}_A, \bar{V}_B, \bar{V}_1} \quad (63)$$

where \bar{V}_A , \bar{V}_B , and \bar{V}_1 are the partial molal volumes of components A, B, and the solvent, respectively.

Equation 60 can be written in the form

$$\beta'_s = -\frac{1}{\gamma V}\left(\frac{\partial V}{\partial C_B}\right)_T \left(\frac{\partial C_B}{\partial P}\right)_T = -\frac{1}{\gamma V}\left(\frac{\partial V}{\partial n_B}\right)_T \left(\frac{\partial C_B}{\partial P}\right)_T \quad (64)$$

The quantity $\left(\frac{\partial V}{\partial n_B}\right)_{T, P}$ is ΔV° , the partial molal volume change

for the chemical process at constant temperature and pressure.

In the present case, $\left(\frac{\partial V}{\partial n_B}\right)_T$ is not at constant pressure, but \bar{V}_A , \bar{V}_B , and \bar{V}_1 are constant. For practical purposes, however,

$$\left(\frac{\partial V}{\partial n_B}\right)_{T, \bar{V}_A, \bar{V}_B, \bar{V}_1} = \left(\frac{\partial V}{\partial n_B}\right)_{T, P} = \Delta V^\circ \quad (65)$$

Substituting the expressions for $\left(\frac{\partial V}{\partial n_B}\right)_T$ and $\left(\frac{\partial C_B}{\partial P}\right)_T$ from eq. 65 and 59, respectively, into eq. 64 results in

$$\beta'_s = \frac{1}{\gamma} \frac{C(\Delta V^\circ)^2}{2RT[1 + \cosh(\Delta F^\circ/RT)]} \cdot \frac{1}{1 + i\omega\tau} \quad (66)$$

Since β'_s is of the form $\beta'_s = \frac{\beta_r}{1 + i\omega\tau}$, it is now apparent that

$$\beta_r = \frac{1}{\gamma} \frac{C(\Delta V^\circ)^2}{2RT[1 + \cosh(\Delta F^\circ/RT)]} \quad (67)$$

This may now be substituted into eq. 23 to give

$$(\alpha\lambda)_r = \frac{1}{\gamma} \frac{\pi C (\Delta V^\circ)^2}{2\beta_0 RT [1 + \cosh \Delta F^\circ / RT]} \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (68)$$

For liquids and solutions, $\gamma \cong 1$. Furthermore,

$$1 + \cosh\left(\frac{\Delta F^\circ}{RT}\right) = \frac{(1 + K)^2}{2K} \quad (69)$$

The corresponding equation in terms of α_r/f^2 is

$$\left(\frac{\alpha}{f^2}\right)_r = \frac{\pi^2 \rho_c (\Delta V^\circ)^2 c}{\gamma RT [1 + \cosh(\frac{\Delta F^\circ}{RT})]} \frac{\tau}{1 + \omega^2 \tau^2} \quad (70)$$

It will be recalled that

$$\tau = \frac{1}{k_1 + k_{-1}}$$

i.e. the relaxation time is independent of the concentration of reacting species and the magnitude of the excess absorption is directly proportional to the concentration.

2. The Dissociation Reaction

The effect of acoustic pressure variations on the equilibrium



will be considered. As in the unimolecular reaction, k_1 and k_{-1} will represent the rate constants for the forward and reverse directions, and C_{AB} , C_A , and C_B the molar concentrations of components AB, A, and B. The rate of approach to equilibrium is given by

$$-\frac{dC_{AB}}{dt} = \frac{dC_A}{dt} = \frac{dC_B}{dt} = k_1 C_{AB} - k_{-1} C_A C_B \quad (71)$$

Letting α° designate the equilibrium value of the degree of dissociation, we have the relations $C_B = C_A = (\alpha^\circ)C$ and $C_{AB} = (1 - \alpha^\circ)C$, where C is the concentration if the entire system were in the form AB. The equilibrium constant for this

reaction is

$$K = \frac{C_A^{\circ} C_B^{\circ}}{C_{AB}^{\circ}} = \frac{C(\alpha^{\circ})^2}{1 - \alpha^{\circ}} = \frac{k_1^{\circ}}{k_{-1}^{\circ}} \quad (72)$$

if activity coefficients are assumed to be unity.

Again it is assumed that the periodic perturbations of the equilibrium are so small that the perturbed quantities can be represented in the form $C_A = C_A^{\circ} + C(\delta\alpha)e^{i\omega t}$ and so forth for the other functions. These are now substituted into eq. 71. Expansion as described for the unimolecular reaction, neglecting the second order terms, and use of the equilibrium conditions yields, after algebraic simplification

$$\delta\alpha = \frac{(1 - \alpha^{\circ})\delta k_1 - C(\alpha^{\circ})^2 \delta k_{-1}}{k_1^{\circ} + 2\alpha^{\circ} C k_{-1}^{\circ} + i\omega} \quad (73)$$

Differentiation of the equilibrium constant yields

$$\delta K \cong \frac{k_{-1}^{\circ} \delta k_1 - k_1^{\circ} \delta k_{-1}}{(k_{-1}^{\circ})^2} \quad (74)$$

which becomes after the application of the definition of the equilibrium constant

$$k_{-1}^{\circ} (1 - \alpha^{\circ}) \delta K = (1 - \alpha^{\circ}) \delta k_1 - C(\alpha^{\circ})^2 \delta k_{-1} \quad (75)$$

Substitution of this into eq. 73 gives for the change in the degree of dissociation

$$\delta\alpha = \frac{k_{-1}^{\circ} (1 - \alpha^{\circ}) \delta K}{k_1^{\circ} + 2\alpha^{\circ} C k_{-1}^{\circ} + i\omega} \quad (76)$$

Again from eq. 50 one can write

$$\delta K \cong - \frac{(\Delta V^{\circ})}{RT} \delta P \quad K \quad (77)$$

which, substituted into eq. 76, gives

$$\frac{\delta \alpha}{\delta P} = - \frac{k_{-1} (1 - \alpha^0) \Delta V^0}{RT (2 \alpha^0 C k_{-1} + k_1 + i \omega)} \quad (78)$$

The relaxational compressibility may be written in terms of the pressure dependence of the degree of dissociation

$$\beta'_s = - \frac{1}{\gamma V} \left(\frac{\partial V}{\partial \alpha} \right)_T \left(\frac{\partial \alpha}{\partial P} \right)_T \quad (79)$$

in which $\left(\frac{\partial V}{\partial \alpha} \right)_T$ must be evaluated. One may write for the total volume of the reacting species

$$V = n_A \bar{V}_A + n_B \bar{V}_B + n_{AB} \bar{V}_{AB} \quad (80)$$

where n and \bar{V} are the indicated number of moles and partial molal volumes. Differentiation with respect to α yields¹⁵

$$\frac{\partial V}{\partial \alpha} = \bar{V}_A \frac{\partial n_A}{\partial \alpha} + \bar{V}_B \frac{\partial n_B}{\partial \alpha} + \bar{V}_{AB} \frac{\partial n_{AB}}{\partial \alpha} \quad (81)$$

Since $n_A = n_B = \alpha CV$ and $n_{AB} = (1 - \alpha) CV$, this is equivalent to

$$\frac{\partial V}{\partial \alpha} = \bar{V}_A VC + \bar{V}_B VC - \bar{V}_{AB} VC = CV (\Delta V^0) \quad (82)$$

The insertion of this and the approximate value of $\left(\frac{\partial \alpha}{\partial P} \right)_T$ from eq. 78 into 79 gives

$$\beta'_s = \frac{1}{\gamma} \cdot \frac{k_{-1} K (\Delta V^0)^2 C (1 - \alpha)}{RT (k_1 + 2 \alpha C k_{-1} + i \omega)} \quad (83)$$

Treatment of the kinetics of a first-second order process in a manner analogous to that for the first-first order process gives

¹⁵It should be noted that $n_A d\bar{V}_A + n_B d\bar{V}_B + n_{AB} d\bar{V}_{AB} = 0$

$$\frac{d\delta x}{dt} = -(k_1 + 2k_{-1}C_B)\delta x \quad (84)$$

where $\delta x = C_B - C_B^0$. Comparison with eq. 42 shows that

$$\tau = \frac{1}{k_1 + 2C_B k_{-1}} = \frac{1}{k_1 + 2\alpha C k_{-1}} \quad (85)$$

in which the superscripts have been dropped, since only the equilibrium values are henceforth considered. Substituting this and the relation $K = \frac{\alpha^2 C}{1-\alpha}$ into eq. 83, one obtains

$$\beta' = \frac{1}{\gamma} \cdot \frac{(\Delta V^0)^2}{RT} \cdot \frac{\alpha C (1-\alpha)}{2-\alpha} \cdot \frac{1}{1+i\omega\tau} \quad (86)$$

From eq. 11, one can identify the relaxational part of the compressibility and substitute it into eq. 23 to obtain for the relaxational absorption per wavelength

$$(\alpha\lambda)_r = \frac{1}{\gamma} \cdot \frac{\pi (\Delta V^0)^2}{\beta_0 RT} \cdot \frac{\alpha C (1-\alpha)}{2-\alpha} \cdot \frac{\omega\tau}{1+\omega^2\tau^2} \quad (87)$$

If γ is assumed to be unity, the corresponding equation in terms of α_r/f^2 is

$$\left(\frac{\alpha}{f^2}\right)_r = \frac{2\pi^2 \rho C (\Delta V^0)^2}{RT} \cdot \frac{\alpha C (1-\alpha)}{2-\alpha} \cdot \frac{\tau}{1+\omega^2\tau^2} \quad (88)$$

where

$$\tau = \frac{1}{k_1 + 2\alpha C k_{-1}} = \frac{1}{k_1 \left[1 + \frac{2(1-\alpha)}{\alpha}\right]} \quad (89)$$

The rate expression for a dissociation reaction involving ions is more correctly expressed in terms of the activities of the reacting species. Thus,

$$\dot{C}_B = k_1 \frac{\gamma_{AB}}{\gamma^*} C_{AB} - k_{-1} \frac{\gamma_{\pm}^2}{\gamma^*} C_A C_B \quad (90)$$

where γ_{AB} is the concentration activity coefficient* of substance AB, γ_{\pm} is the mean activity coefficient of the ions A^+ and B^- , and γ^* is the activity coefficient of the activated complex. If one assumes the activity coefficients are not perturbed from their equilibrium values, treatment of the concentrations and rate constants as described in eq. 71 - 87 yields expressions for the relaxational absorption per wavelength and relaxation time for the dissociation of a molecule into its ions. Equation 87 for the absorption per wavelength remains unchanged, but the relaxation time becomes

$$\tau = \frac{\gamma^*}{\gamma_{AB} k_1 + 2\alpha C (\gamma_{\pm})^2 k_{-1}} \quad (91)$$

For practical purposes, both γ^* and γ_{AB} may be assumed to be unity, so that eq. 91 is the same expression for τ as that obtained by other authors.^{16,17} Wilson and Leonard¹⁶ arrived at this equation by introducing the activity coefficients into the equilibrium constant for the reaction. They did not, however, introduce the activity coefficients into the rate expression as required by eq. 90. As a result, their expression for $(\alpha\lambda)_r$ involves the activity coefficient γ_{\pm} , whereas eq. 87 does not. This difference will be discussed further in connection with the mechanism for the relaxation process in solutions of divalent sulfates.

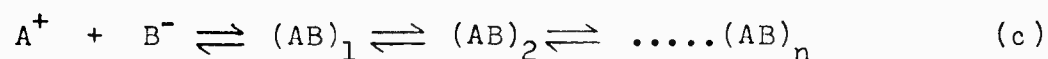
¹⁶O. Wilson and R. Leonard, Absorption of Ultrasonic Waves in Solutions of Magnesium Sulfate, Tech. Report No. 4 (Office of Naval Research Contract N6-onr-27507), Dept. of Phys., University of California, Los Angeles, Calif., June, 1951.

¹⁷K. Tamm, G. Kurtze, and R. Kaiser, Acustica 4, 380 (1954).

* See footnote 95, p. 81.

3. Generalized Relaxation Analysis

Normally the specific interaction cannot be treated as a one-step mechanism. The recombination of oppositely charged ions, for example, is hindered by hydration layers, which have to be removed stepwise. In the general case the specific interaction may be characterized by a consecutive reaction system which may take a form such as the following:



This system has a spectrum of relaxation times, in which the number of time constants corresponds to the number of independent steps. On the other hand, a particular relaxation time does not necessarily correspond to a particular step in the relaxation scheme. In practice, the application of relaxation theory to the generalized situation described by (c) leads to complicated expressions for the relaxational parameters τ and β_r . A mathematical analysis, however, of such systems may be made under certain assumptions.

The following simple system will illustrate the mathematical approach^{18,19}



Using the notation $X_1 = \delta C_A$, $X_2 = \delta C_B$ and $X_3 = \delta C_C$ and

¹⁸Double relaxation has also been treated by other authors, including R. Beyer - R. Beyer, J. Acoust. Soc. Am. 29, 243 (1957).

¹⁹This treatment of simultaneous coupled relaxation processes is similar to that presented by Eigen - M. Eigen, Disc. Faraday Soc. 24, 25 (1957). See also M. Eigen and L. De Maeyer in Techniques of Organic Chemistry, Vol. VIII, Part 2, Interscience Publ., New York (at press, 1962).

$\dot{X}_1 = \lambda_1 X_1$ where $\lambda_1 = -1/\tau_1$, one may write for the approach to equilibrium

$$\dot{X}_1 = -k_{12}X_1 + k_{21}X_2 \quad (92)$$

$$\dot{X}_2 = k_{12}X_1 - (k_{21} + k_{23})X_2 + k_{32}X_3 \quad (93)$$

$$\dot{X}_3 = k_{23}X_2 - k_{32}X_3 \quad (94)$$

These equations may be arranged to the form

$$-(k_{12} + \lambda)X_1 + k_{21}X_2 = 0 \quad (95)$$

$$k_{12}X_1 - (k_{21} + k_{23} + \lambda)X_2 + k_{32}X_3 = 0 \quad (96)$$

$$k_{23}X_2 - (k_{23} + \lambda)X_3 = 0 \quad (97)$$

These homogeneous linear equations then lead to the condition that the corresponding determinant of the coefficients be equal to zero; i.e.,

$$\begin{vmatrix} -(k_{12} + \lambda) & k_{21} & 0 \\ k_{12} & -(k_{21} + k_{23} + \lambda) & k_{32} \\ 0 & k_{23} & -(k_{23} + \lambda) \end{vmatrix} \equiv 0$$

where the specific values for λ are the eigenvalues of the functional equation. Expansion and cancellation of terms yields

$$\lambda^3 + (k_{12} + k_{21} + k_{23} + k_{32})\lambda^2 + (k_{12}k_{23} + k_{12}k_{32} + k_{21}k_{32})\lambda = 0 \quad (98)$$

It is immediately apparent that one root corresponds to $\tau_1 = \infty (\lambda_1 = 0)$ and that eq. 98 reduces to the quadratic

$$\lambda^2 + (k_{12} + k_{21} + k_{23} + k_{32})\lambda + (k_{12}k_{23} + k_{12}k_{32} + k_{21}k_{32}) = 0 \quad (99)$$

Solving this yields

$$\lambda = \frac{-b \pm \sqrt{b^2 - 4c}}{2} \quad (100)$$

where $b = (k_{12} + k_{21} + k_{23} + k_{32})$ and $c = (k_{21}k_{23} + k_{12}k_{32} + k_{21}k_{32})$. Then with the assumption that $k_{12}, k_{21} \gg k_{23}, k_{32}$, eq. 100 yields for the eigenvalue λ_2

$$\lambda_2 \approx \frac{-b - \sqrt{b^2}}{2} = -b \quad (101)$$

or

$$\tau_2 = -\frac{1}{\lambda_2} \approx \frac{1}{k_{12} + k_{21}} \quad (102)$$

Expanding the square root term in the form $(1 - x)^{1/2} \approx 1 - \frac{1}{2}x$ yields

$$\lambda_3 = -\frac{c}{b} \quad \text{and} \quad (103)$$

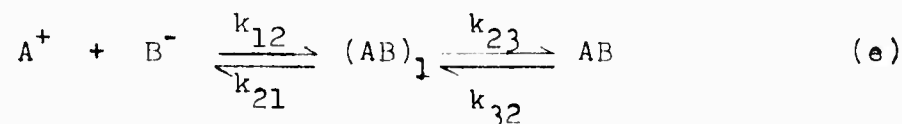
$$\tau_3 = \frac{k_{12} + k_{21}}{k_{12}(k_{23} + k_{32}) + k_{21}k_{32}} \quad (104)$$

or

$$\tau_3 = \frac{1}{k_{32} + k_{23} \frac{k_{12}}{k_{12} + k_{21}}} \quad (105)$$

For the special case $k_{12} \gg k_{21}$, this reduces to the ordinary relaxation time associated with the isolated process $B \rightleftharpoons C$.

The system



may be treated in an analogous manner with the exception that wherever k_{12} appears it is replaced by $[k_{12}(C_A^0 + C_B^0)]$. Thus, for this system

$$\tau_1 = \infty \quad (106)$$

$$\tau_2 = \frac{1}{k_{12}(C_A^0 + C_B^0) + k_{21}} \quad (107)$$

$$\tau_3 = \frac{k_{12}(C_A^0 + C_B^0) + k_{21}}{k_{12}(C_A^0 + C_B^0)(k_{23} + k_{32}) + k_{21}k_{32}} \quad (108)$$

The relaxational absorption per wavelength is given in general by

$$(\alpha\lambda)_r = \frac{\pi}{\beta_0} \left(\beta_2 \frac{\omega\tau_2}{1 + \omega^2\tau_2^2} + \beta_3 \frac{\omega\tau_3}{1 + \omega^2\tau_3^2} \right) \quad (109)$$

where β_2 and β_3 correspond to β_r for the double relaxation. The principle result of these calculations under the special assumption $k_{23}, k_{32} \ll k_{12}, k_{21}$ is that there are two absorption maxima due to two independent steps. These maxima, however, do not correspond uniquely to the specific steps in the relaxation scheme; i.e., a particular maximum may be a function of the kinetic parameters of both steps. Only when the rate constants are at least 10-fold different for the two steps (i.e., $k_{12}, k_{21} \gg k_{23}, k_{32}$) can a particular maximum in the $(\alpha\lambda)_r$ function be associated specifically with a given step.

Eigen has extended this treatment to more complicated cases.²⁰ In general it is then more convenient to handle the problem by means of matrix analysis. The relaxation times must

²⁰M. Eigen, Chemische Relaxation, Steinkopf, Darmstadt, 1961. as quoted by M. Eigen and L. De Maeyer in Techniques of Organic Chemistry, Vol. VIII, Part 2, Interscience Publ., New York (at press, 1962).

be calculated from the whole system of linearized rate equations. Mathematically this is a problem of "principle axis transformation" in which one has to find a new set of concentration variables (normal variables Y_i) instead of the given variables X_i ($= \delta C_A, \delta C_B, \delta C_{AB} \dots$). The new variables have to fulfill the condition

$$\dot{Y}_i = - Y_i / \tau_i \quad (110)$$

where $\dot{Y} = dy/dt$ and τ_i is the corresponding relaxation time. Eigen²¹ has applied this method to coupled reactions of the type considered above.

E. Activation Energy

For the reaction $A \rightleftharpoons M^* \rightleftharpoons B$, where M^* represents the activated or transition state for the reaction, Eyring's theory of absolute reaction rates gives the specific rate constant for the forward reaction as

$$k_r = \frac{kT}{h} \frac{C^*}{C_A} = \frac{kT}{h} K^* \quad (111)$$

where K^* is the equilibrium constant for the activation reaction, k is Boltzmann's constant, h is Planck's constant, T is the absolute temperature, and C^* and C_A are the concentrations of the indicated species. The term kT/h represents the frequency at which molecules pass through the activated state.

The true equilibrium constant for the activation is

$$K_o^* = \frac{\gamma^*}{\gamma_A} K^* \quad (112)$$

²¹M. Eigen, Disc. Faraday Soc. 24, 25 (1957).

where γ^* and γ_A are the activity coefficients. The reaction rate is then given by²²

$$k_r = \frac{kT}{h} \frac{\gamma_A}{\gamma^*} e^{-(\Delta F^\circ)^*/RT} \quad (113)$$

where $(\Delta F^\circ)^*$ = the standard free energy of activation.

The specific rate constants for the forward and reverse reactions can now be written as

$$k_1 = \frac{kT}{h} e^{-(\Delta F_1^\circ)^*/RT} ; \quad k_{-1} = \frac{kT}{h} e^{-(\Delta F_{-1}^\circ)^*/RT} \quad (114)$$

where the activity coefficients are assumed equal to unity.

The relationship between the various free energies in the three states is shown in Figure 5.

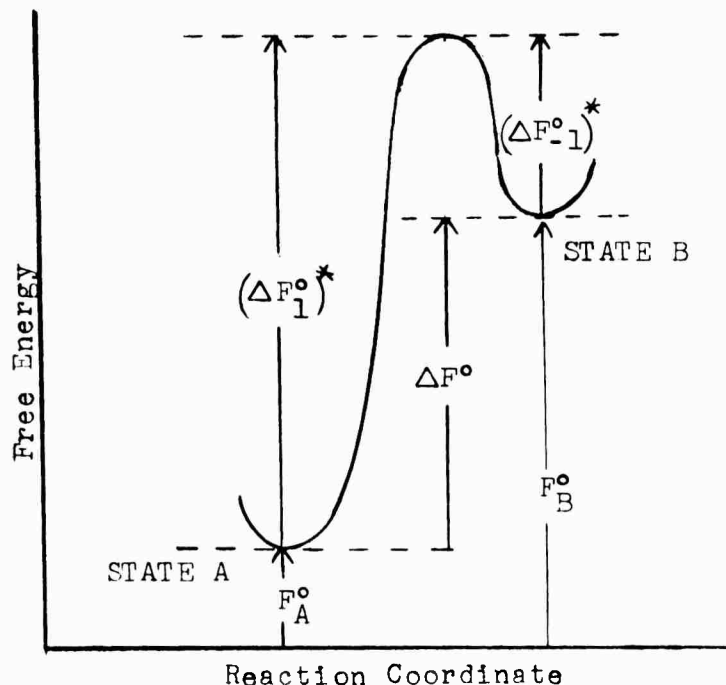


Figure 5: A 2-state free energy diagram

²²K. Laidler, Chemical Kinetics, McGraw-Hill, New York, 1950, p. 119.

In the case of sound absorption by a chemical reaction, the relaxation time is given by $1/\tau = k_1 + k_{-1}$ for a first-order process. If one assumes that $(\Delta F^\circ) = (\Delta F_1^\circ)^* - (\Delta F_{-1}^\circ)^*$, the reciprocal of the relaxation time can then be written

$$k_1 + k_{-1} = \frac{kT}{h} \cdot \frac{1 + e^{-(\Delta F^\circ)/RT}}{e^{(\Delta F_{-1}^\circ)^*/RT}} \quad (115)$$

If it is further assumed that one of the rate constants is negligibly small compared to the other, e.g. $k_1 \ll k_{-1}$, then

$$\frac{1}{\tau} = 2\pi f_r \cong k_{-1} = \frac{kT}{h} e^{-(\Delta F_{-1}^\circ)^*/RT} \quad (116)$$

Using the well known relation $\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ$, the variation of relaxation frequency with temperature may be used to obtain an experimental activation energy, which is assumed to be temperature independent,

$$\log \left(\frac{f_r}{T} \right) = - \frac{(\Delta H_{-1}^\circ)^*}{RT} \log e + \text{const.} \quad (117)$$

A plot of $\log f_r/T$ is made against $1/T$. The slope of the resultant straight line is then used to obtain $(\Delta H_{-1}^\circ)^*$. Since the $(p\Delta V)$ term in the case of liquids is negligible, this in turn is virtually equal to the energy of activation for the process.

A complication arises from the fact that the energies of activation for many processes are dependent on the dielectric constant of the solvent. The dielectric constant itself varies with temperature, so it is not uncommon for workers to keep the dielectric constant fixed by using mixtures of solvents. In systems involving solvent interactions of a specific chemical nature, however, the validity of this procedure is very doubtful.

II. EXPERIMENTAL METHODS FOR THE STUDY OF RELAXATION IN LIQUIDS

A. Ultrasonic Absorption

An examination of the general curve for relaxational absorption per wavelength (Fig. 2) indicates that the two regions of linear dependence are separated in frequency by a factor of approximately 10-fold. Thus, in contrast to optical spectroscopy, ultrasonic absorption measurements must be made over a very wide range of frequencies to characterize fully even a single relaxation process.

Present day techniques are sufficient to permit the investigation of acoustical relaxation in liquids over the frequency range 10 kc to 500 mc. These techniques²³ are listed in Table 2. The accuracies listed in this table become

Table 2: Methods for the measurement of ultrasonic absorption

method	frequency range for aqueous solutions ²⁴ (mc/s)	accuracy over 50% of useable range
A. Progressive wave		
1. pulse two-transducer	10-300	5%
2. pulse-reflector	10-300	5%
3. optical diffraction	5-100	5%
4. radiation pressure	3-60	5%-10%
B. Standing wave		
1. interferometer	10-100	5%-10%
C. Reverberation		
1. resonance	0.01-1	10%
2. statistical	0.1-3	10%
D. Direct		
1. streaming	0.5-5	10%
2. calorimetric		

²³A brief description of these techniques is given in the Appendix.

²⁴Range providing an accuracy of at least $\pm 20\%$.

become considerably poorer as the limits of frequency for the methods are approached. Furthermore, the majority of the methods require considerable technique and are far more time consuming than comparable measurements in optical absorption spectroscopy. This is particularly true of the techniques available for measurements at frequencies less than 5 mc and greater than 60 mc. Until considerable refinements are made in the techniques available for measurements in these regions, physical chemists are not likely to make extensive use of acoustical absorption for the study of the kinetics of fast reactions despite the major importance of the results of such measurements.

In addition to ultrasonic absorption, the velocity also reflects the relaxation processes. The velocity dispersion, however, is usually very small in electrolytic solutions and very difficult to measure. Fox and Marion²⁵ measured the dispersion associated with a MgSO_4 solution by driving a transducer simultaneously at its fundamental and a harmonic and then measuring the shift in phase of the two acoustical signals after the signals had been transmitted through a given distance. Further details will be given later in this report in conjunction with a discussion of experimental studies of polyvalent sulfates.

B. Step Function Techniques for Relaxation Studies in Liquids

The kinetics of fast chemical reactions can also be studied by step function techniques. The equilibrium system

²⁵F. Fox and T. Marion, J. Acoust. Soc. Am. 25, 661 (1953).

is perturbed by a sudden change in temperature, pressure, or electric field, and the readjustment of the system to an equilibrium state followed as a function of time.

Consider an equilibrium of the form, for example,



The equilibrium constant is dependent upon pressure, temperature, and field strength. The application of an instantaneous impulse or "jump" of pressure, temperature, or field strength will cause the degree of dissociation (α) to shift with the time dependence given by the equation

$$\Delta\alpha = (\Delta\alpha)_0 e^{-t/\tau} \quad (118)$$

where $\Delta\alpha$ is the shift in α at time t and $(\Delta\alpha)_0$ is the shift in α predicted on the basis of the dependence of the equilibrium constant on pressure, temperature, and/or electric field strength. This is shown schematically in Figure 6 for the application of a rectangular jump of magnitude I .

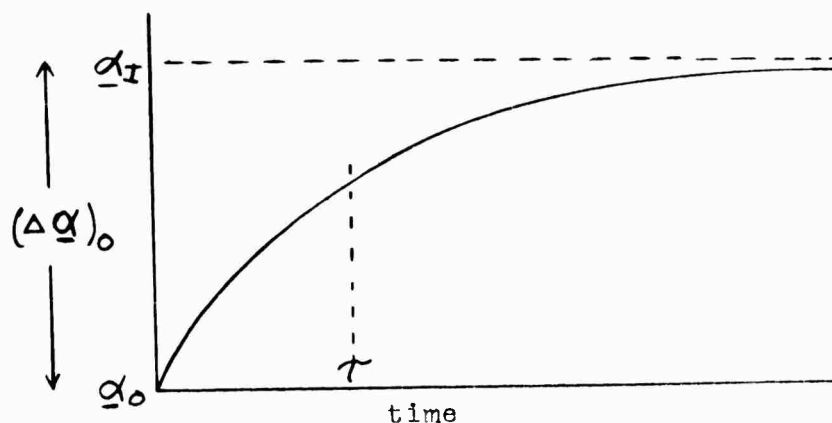


Figure 6: Effect of an abrupt impulse upon the degree of dissociation

1. Pressure Step-Functions

A chemical equilibrium depends upon pressure if the corresponding reaction involves a change in volume ΔV . For example, for the dissociation reaction considered above, the volume change is given by

$$\Delta V = \bar{V}_{A^+} + \bar{V}_{B^-} - \bar{V}_{AB} \quad (119)$$

where \bar{V}_i are the partial molal volumes of the species indicated by the subscripts. From the dependence of the equilibrium constant upon pressure we have the relation

$$\frac{\partial \alpha}{\partial P} = \frac{\alpha(1-\alpha)}{1+(1-\alpha)} \frac{\Delta V^\circ}{RT} \quad (120)$$

where ΔV° is the volume difference of reactants and products.

If the reaction involves the recombination of hydrated ions to a neutral molecule--as is the case for the ionic dissociation reaction--the volume change may be quite significant. For example, for



$\Delta V^\circ = 22 \text{ cm}^3/\text{mole}$.²⁶ Under such circumstances, the change in α is produced primarily by the pressure dependence of the equilibrium and by the temperature change associated with the substantially adiabatic pressure step.

The pressure step-function technique has been applied²⁷⁻²⁹

²⁶M. Eigen, Disc. Faraday Soc. 17, 194 (1954).

²⁷H. Strehlow and M. Becker, Z. Elektrochem. 63, 457 (1959).

²⁸H. Wendt and H. Strehlow, *ibid.*, 64, 131 (1960).

²⁹H. Strehlow and H. Wendt, Trans. Faraday Soc., to be submitted.

to the study of ionic dissociation in, for example, the aqueous FeCl_3 system. Experimentally, the system is under a pressure of about 50 atm, which is suddenly released to 1 atm by means of a bursting diaphragm. The time needed for the pressure step amounts to 50 microsec. After the pressure step, the system approaches the new equilibrium state with a relaxation time τ as described in eq. 118. The rate of approach of the system to its new equilibrium value can be followed by observing the conductivity changes. The relative conductivity change caused by the reaction after a pressure step of 50 atm is of the order of 1%. A pressure step technique has been developed at Western Reserve University for the study of fast electrode processes.³⁰

2. Temperature Step-Function

The temperature dependence of a dissociation equilibrium is described by the well known van't Hoff relation

$$\frac{\partial \alpha}{\partial T} = \frac{\alpha(1-\alpha)}{1+(1-\alpha)} \cdot \frac{\Delta H^\circ}{RT} \quad (121)$$

where ΔH° is the standard enthalpy of reaction.

Since sound waves in aqueous solutions at normal temperatures and sound amplitudes do not give rise to easily measured temperature changes, periodical variations in temperature at high frequencies or impulses of short duration can hardly be realized. On the other hand, it is possible to change the temperature step-wise within a very short time (10^{-7} second). This procedure, which is known as the "temperature jump" approach to relaxational processes, allows a direct oscillo-

³⁰E. Yeager, Transactions of the Symposium on Electrode Processes, John Wiley and Sons, New York, 1961, Chapter 6.

graphic observation of the exponential curve of $\Delta\alpha$ as given in eq. 118. A temperature rise of several degrees centigrade may be brought about by the use of high current impulses, which may be effected within a short time. The duration of the high tension impulse must be short in relation to the time lag of the system under investigation. The rapid temperature rise following the impulse is followed by observing oscillographically the change in imbalance of a conductance bridge. The method is limited to moderately concentrated solutions, since the use of excessively high field strengths is to be avoided. Complete experimental details as well as a fuller theoretical treatment are given in the literature by Czerlinski and Eigen.^{31,32,33}

Gerischer has recently considered the absorption of a high energy microwave pulse in a system as a means of obtaining a temperature step. The absorption of optical energy in the visible or infrared appears attractive as a means of producing a temperature rise. Ultraviolet radiation should be avoided in order to prevent photodecomposition.

3. Wien Effect II

The influence of electrical field density E on the degree of dissociation was first reported by Wien and Schiele.³⁴ It is generally known as the dissociation field effect or the

³¹G. Czerlinski and M. Eigen, Z. Elektrochem. 63, 652 (1959).

³²G. Czerlinski, H. Diebler, and M. Eigen, Z. physik. Chem. (Frankfurt) 19, 246 (1959).

³³L. De Maeyer, Z. Elektrochem. 64, 65 (1960).

³⁴M. Wien and J. Schiele, Physik. Z. 32, 545 (1931).

second Wien effect. According to Onsager,³⁵ the dependence is given to a first approximation by

$$\frac{\partial \alpha}{\partial |E|} = \frac{\alpha(1-\alpha)}{1+(1-\alpha)} \cdot \frac{|z_A|\mu_A + |z_B|\mu_B}{\mu_A + \mu_B} |z_A z_B| \frac{\epsilon^2}{2Dk^2T^2} \quad (122)$$

where z = ionic charge, μ = ionic mobility, ϵ = electrical charge, D = dielectric constant of the solvent, k = Boltzmann constant, and $|E|$ = the absolute value of the field strength.

For uni-univalent electrolytes this reduces to

$$\frac{\partial \alpha}{\partial |E|} = \frac{\alpha(1-\alpha)}{1+(1-\alpha)} \cdot \frac{9.64}{DT^2} \frac{\text{cm}}{\text{volt}} \quad (123)$$

In aqueous solutions this approximation is valid for field strengths up to several hundred kv/cm. For acetic acid with a field strength of 200 kv/cm, the change in the degree of dissociation, as determined from the increase in conductivity at these field strengths, is about 12%.³⁶ With strong fields the use of a periodic variation of the field density is prohibited because of resulting progressive heating. It is necessary to apply very short electrical impulses of variable duration. Upon the application of a sudden electrical field impulse $|E|$, the degree of dissociation α changes from its static value to that determined by eq. 118. Measurement of the change in conductance with time, oscillographically or otherwise, provides a method of determining τ for the dissociation process.

³⁵L. Onsager, J. Chem. Phys. 2, 599 (1933).

³⁶J. Schiele, Physik. Z. 34, 60 (1933).

Details of the experimental apparatus are given in the literature.^{37,38}

As of date, no one appears to have considered the use of a magnetic field for the same purpose; i.e. a magnetic field step function. Such does not appear to be out of the question. The method will probably be more complex than those just described.

III. PRESENT STATE OF RELAXATION PROCESSES IN ELECTROLYTES

A. Measurements

Strong 1-1 valent electrolytes such as KCl, NaCl, KBr, and KI, show no excess absorption over that of distilled water within the accuracy of the measuring apparatus. The accuracy is estimated³⁹ to range from the order of magnitude of water ($\Delta\alpha/r^2 = \pm 25 \times 10^{-17}$) at very low frequencies (10 to 100 kc/s) and $\pm 5\%$ from 5 mc/s to 100 mc/s. In several instances, "negative" absorption at high frequencies has been reported with certainty, e.g. for NaBr and NaI above 50 mc/s³⁹ and for sodium and potassium acetate above 15 mc/s.^{40,41} A 5 M solution of NaBr at 83 mc/s showed a 30% reduction in the absorption coefficient relative to pure water, with the magnitude of the effect

³⁷M. Eigen and J. Schoen, Z. Elektrochem. 59, 483 (1955).

³⁸L. De Maeyer, Z. Elektrochem. 64, 65 (1960).

³⁹G. Kurtze and K. Tamm, Acustica 3, 33 (1953).

⁴⁰R. Barrett and R. Beyer, Phys. Rev. 84, 1060 (1951).

⁴¹R. Barrett, R. Beyer, F. McNamara, J. Acoust. Soc. Am. 26, 966 (1954).

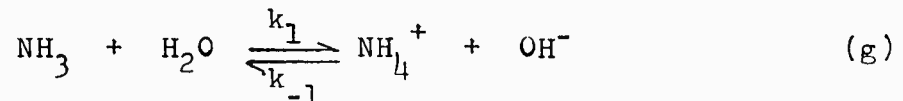
dependent upon the concentration. A possible explanation⁴⁰ based upon the Hall model⁴² for ultrasonic absorption in water is that the ions shift the equilibrium of H_2O molecules between their two postulated configurations. According to the Hall model, the excess absorption of ultrasonic waves in water over that expected on the basis of shear viscosity and thermal conductivity is associated with the perturbing of the equilibrium. The shift produced by the salt favors the more compact structure and is such as to lower the absorption. This would indicate that some error is introduced in treating the absorption coefficient as the sum of that due to solute and that to solvent. The magnitude of this non-additive effect does not appear to be great and is not expected in any case to involve a change approaching the magnitude of the absorption of pure water. Thus, if the total absorption of the solution is high compared to water, the lack of strict additivity can be ignored.

For weak and partially hydrolyzed 1-1 valent electrolytes, in several instances anomalously high absorption and the presence of a relaxation frequency have been reported. This was first observed in salts containing the acetate radical. For example, in sodium and potassium acetates the results of Barrett, Beyer and McNamara⁴¹ by a radiation pressure technique indicated that there was a relaxation frequency at a frequency below the limit of their measuring apparatus (10 mc/s). In both sodium and potassium acetates, the absorption of the

⁴²L. Hall, Phys. Rev. 73, 775 (1948).

solutions above 15 mc/s fell below that of pure water.

Ammonium hydroxide⁴³ was the first 1-1 electrolyte found to have very high excess absorption. Since the dissociation equilibrium constant K_C is of the order 10^{-5} , the degree of dissociation in a 1 M solution is only about 0.3%. The equilibrium in this electrolyte is of the type*



The acoustic perturbation of this equilibrium is assumed to account for the observed relaxation process. From the expression for the relaxation time for a dissociation reaction (eq. 91), it follows that at very low concentrations the relaxation frequency depends only upon k_1 , while at higher concentrations the relaxation frequency is proportional to $\alpha \gamma_{\pm}^2 c k_{-1}$ where γ_{\pm} is the mean activity coefficient. Kurtze and Tamm found that the relaxation frequency increased from 20 mc/s to 60 mc/s in going from a concentration of 0.5 M to 5 M. Increasing concentration also increased the magnitude of the maximum absorption per wavelength, but not in a linear fashion.

Carnevale and Litovitz⁴⁴ made a study of the effect of high pressure on this relaxation and found that with increase in pressure, the magnitude of the absorption decreased while the relaxation frequency increased. These effects may be explained by the pressure dependence of β_r and τ , which in

⁴³K. Tamm, G. Kurtze, and R. Kaiser, *Acustica* 4, 380 (1954).

⁴⁴E. Carnevale and T. Litovitz, *J. Acoust. Soc. Am.* 30, 610 (1958).

* It is generally assumed that $\text{NH}_3 \cdot \text{H}_2\text{O}$ is an intermediate in this reaction, and that the dissociation of the latter is the measured step.

turn depend upon the relative changes with pressure of the ΔV , k_1 , k_{-1} , and/or α terms. Thus

$$\beta_r = \frac{C}{RT} (\Delta V^\circ)^2 \frac{\alpha(1-\alpha)}{2-\alpha} \quad (124)$$

and

$$f_r = \frac{1}{2\pi} [k_1 + 2\alpha \gamma_{\pm}^2 C k_{-1}] = \frac{k_1}{2\pi} [1 + 2\frac{(1-\alpha)}{\alpha}] \quad (125)$$

By way of illustration the authors give the following data for 0.1 M NH_4OH at 45°C.

Table 3: Pressure dependence of the $\text{NH}_3 \cdot \text{H}_2\text{O}$ relaxation⁴⁴

Pressure kg/cm ²	f_r mc	k_1 sec ⁻¹ x 10 ⁻⁵	k_{-1} liter/mol-sec x 10 ⁻¹⁰	K_C mol/liter x 10 ⁵
1	20.6	9.1	4.7	1.9
1117	38.7	28.6	5.5	5.2
2030	52.9	55.5	5.3	10.6

The recombination of the ions NH_4^+ and OH^- is diffusion controlled. The effect of pressure on the diffusion coefficients and thus k_{-1} should be relatively small, and this is indeed true.

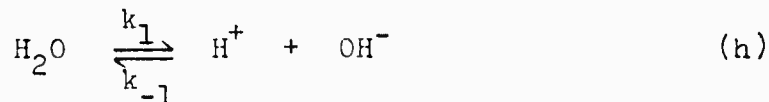
The order of this rate constant is consistent with the frequency of collisions between ions in solution. From calculations⁴⁵ based on formulas given by Debye⁴⁶ these rate

⁴⁵M. Eigen, Disc. Faraday Soc. 17, 194 (1954).

⁴⁶P. Debye, Trans. Electrochem. Soc. 82, 265 (1942).

constants indicate that the ammonium and hydroxyl ions combine spontaneously with ions of opposite charge if the partners approach each other within a distance of 5 Å. This distance is consistent with the normal radii of hydrated ions as indicated by more detailed considerations.⁴⁷

The rate constants for the water dissociation reaction



have been determined by Eigen and his coworkers⁴⁸ by Wien Effect II relaxation studies. This relaxation process is not observed acoustically because of the extremely small degree of dissociation for water. For the neutralization process the rate constant k_{-1} is 1.5×10^{11} liter mole⁻¹ sec⁻¹, whereas for the dissociation $k_1 = 2 \times 10^{-5}$ sec⁻¹. This is to be compared with the dissociation process when H₂O is associated with NH₃, in which case the rate constant for the dissociation of NH₃·H₂O is 4×10^5 sec⁻¹.

2-1, 1-2, 3-1 valent electrolytes, other than acetates and cyanides, show little or no excess absorption at low frequencies.³⁹ Specific examples of salts of these types include Na₂CO₃, K₂SO₄, MgCl₂ and AlCl₃. The absorption of solutions of these salts is so close to that of water that differences are measurable only above 10 mc/s. Solutions of acetates, however, have high absorption and in several cases exhibit relaxation frequencies. The data of Bazulin⁴⁹ indicate a relaxation process in zinc acetate

⁴⁷M. Eigen, Z. physik. Chem. Frankfurt, 1, 176 (1954).

⁴⁸M. Eigen, Z. Elektrochem. 59, 986 (1955).

⁴⁹P. Bazulin and J. Merson, Compt. rend. U.S.S.R. 21, 690 (1939).

solutions of concentrations ranging from 0.05 to 0.15 M with a relaxation frequency in the vicinity of 10 mc/s. The data of Barrett, Beyer and McNamara⁴¹ show for copper acetate a relaxation frequency at about 18 mc/s. This frequency depends on concentration over the experimental range 0.0005 to 0.3 M. The accuracy of the radiation pressure method, however, was not sufficiently great to determine the exact concentration dependence. Leonard and Wilson report⁵⁰ for a 0.02 M solution of magnesium acetate a relaxation frequency in the vicinity of 70 kc/s with an absorption per wavelength of the same order of magnitude as the highly absorbing divalent sulfates.

Excess relaxational absorption in potassium cyanide solutions has been observed in the authors' laboratory and will be the subject of a future technical report.

The only example of a 3-1 valent electrolyte studied that shows a relaxation process is $\text{La}(\text{NO}_3)_3$, which exhibits very high values of excess absorption per wavelength.¹³ Kurtze and Tamm believe that this relaxation is also due to a dissociation process, but in view of the complex nature of an aqueous solution of this substance, no information as yet is available as to the specific step involved. The high absorption is probably related to the large ΔV for this reaction, which is estimated to be $40 \text{ cm}^3/\text{mole}$. With increasing concentration the relaxation frequency increases from 50 mc/s at 0.15 M to 90 mc at 0.3 M.

⁵⁰U. Wilson and R. Leonard, Absorption of Ultrasonic Waves in Solutions of Magnesium Sulfate, Tech. Report No. 4, (Office of Naval Research Contract N6-onr-27507), Dept. of Physics, University of California, Los Angeles, Calif., June, 1951.

Spedding and Atkinson⁵¹ have reported for $\text{Nd}(\text{NO}_3)_3$ an adiabatic compressibility in the 1 mc/s region which shows an amazingly large dependence on frequency. At 1 mc/s, the apparent molal compressibility is 1.30×10^{-2} ($\text{cm}^3 \text{ bar}^{-1} \text{ mole}^{-1}$) and at 2 mc/s is 1.20×10^{-2} units at 25°C. The explanation of these data is not clear, but they may indicate a relaxation process in the vicinity of 10^6 c/s.

Na_3PO_4 is an example of a 1-3 valent electrolyte that has a relaxation process. The relaxation frequency⁴³ is approximately 50 mc/s at 0.01 M and shifts to above 100 mc/s at 0.1 M.

In sharp contrast to the solutions of salts of other valencies, the 2-2 valent electrolytes, and in particular the divalent sulfates, nearly all show anomalously high absorption at some frequencies and many exhibit one or more relaxation processes. The mechanism of the relaxation processes in these solutions was in doubt for many years.

The problem of abnormal sound absorption associated with MgSO_4 was first encountered in absorption measurements in the sea, although early workers did not realize that the minor constituent MgSO_4 in sea water was responsible for this abnormal absorption. The first reported absorption measurements in sea water appear to be those of Stephenson,⁵² who made determinations at 20 and 40 kc/s. Other measurements were made during

⁵¹F. Spedding and G. Atkinson, Chap. 22 in W. Hamer, ed., The Structure of Electrolytic Solutions, John Wiley and Sons, New York, 1959, p. 334.

⁵²E. Stephenson, The Absorption Coefficient of Sound in Sea Water, Report S-1466, NRL, August 12, 1938.

World War II by Everest and O'Neil⁵³ and by Eckart.⁵⁴ In all cases, the absorption in sea water at the lower frequencies was found to be at least an order of magnitude greater than that in fresh water. In 1948, Liebermann⁵⁵ extended the range of the measurements to about 1 mc/s. The method used was to mount large crystals onto the hulls of ships and to make send-receive pulse measurements over several miles path length. These results are shown graphically in Figure 7, in which α has been plotted versus frequency. It is clear from the shape of the curve drawn through the experimental points that there is a relaxational effect with a relaxation frequency of about 120 kc/s.

The relaxation process was at first attributed by Liebermann⁵⁵ to a shift in the pressure-sensitive equilibrium involving the dissociation of Na^+Cl^- ion pairs. He also advanced a theory based upon this assumption which predicted a proportionality of the absorption coefficient α to $(C_p - C_v)$, the specific heat at constant pressure minus that at constant volume. This theory has not been supported by experiment, however, since sodium chloride solutions were found to have little absorption beyond that due to an increase in viscosity.⁵⁶ It was subsequently shown by Leonard and Wilson^{50,56,57} that

⁵³F. Everest and H. O'Neil, Attenuation of Underwater Sound, NDRC, C4-sr30-494 UDCWR, July 6, 1944.

⁵⁴C. Eckart, Attenuation of Sound in the Sea, NDRC Report U-236, Project NS-140 UCDWR, July 6, 1944.

⁵⁵L. Liebermann, J. Acoust. Soc. Am. 20, 868 (1948).

⁵⁶R. Leonard, The Absorption of Sound in Liquids by a Resonator Method, Tech. Report No. 1 (Office of Naval Research Contract N-6-onr-27507) University of California, Los Angeles, Calif., June, 1950.

⁵⁷O. Wilson and R. Leonard, J. Acoust. Soc. Am. 26, 223 (1954).

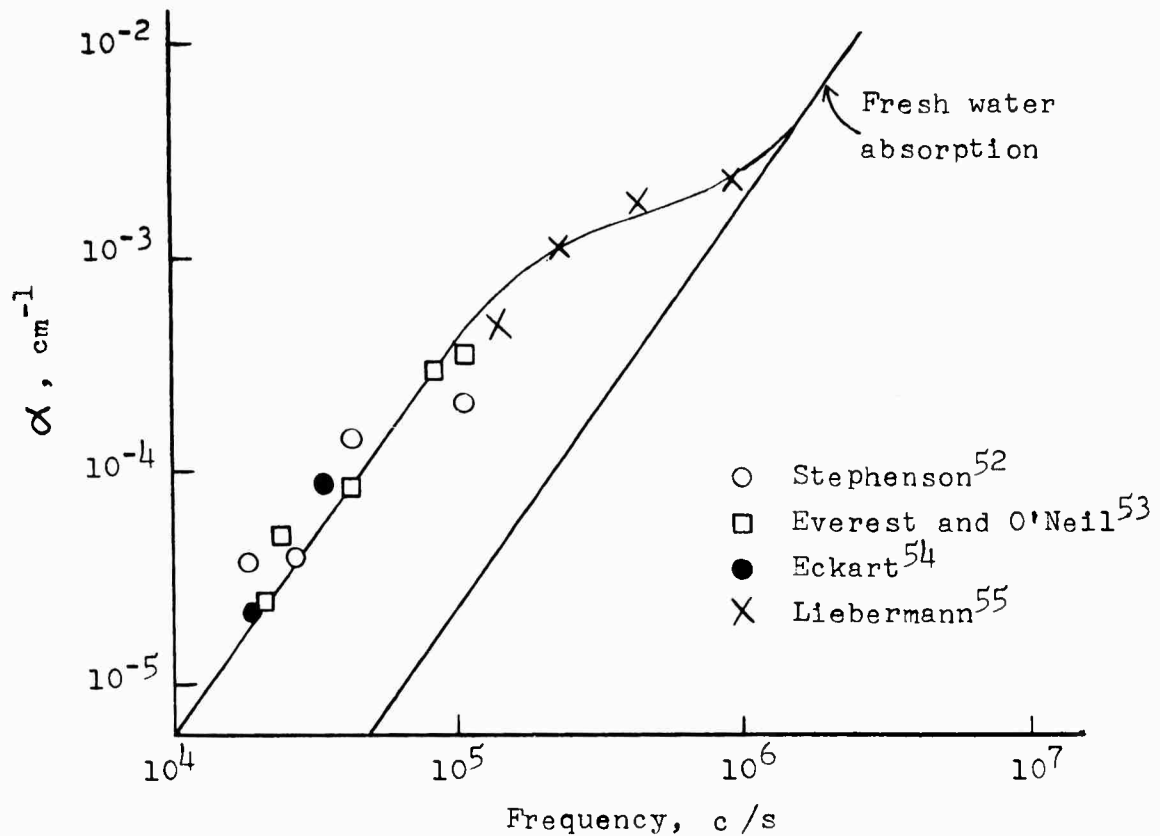


Figure 7: Absorption in sea water (from Markham, Beyer, and Lindsay⁵⁸)

the excess absorption in sea water was due to the presence of a small amount of MgSO_4 (0.02 M). He found that a 0.02 M MgSO_4 solution more than accounts for the excess absorption and that the lower value actually observed in sea water is due to the presence of the larger amounts of NaCl , which has the

⁵⁸J. Markham, R. Beyer, and R. Lindsay, Rev. Modern Phys. 23, 404 (1951).

effect of depressing the magnitude of the absorption due to MgSO_4 .⁵⁶ The data of Leonard and Wilson^{50,57} and Kurtze and Tamm³⁹ further showed that the relaxation frequency of 120 kc/s at 20°C is almost independent of concentration from 0.003 M to 0.1 M, and that the excess absorption is proportional to the concentration over this same range. In this connection Kurtze and Tamm define an absorption cross-section³⁹ $Q = \frac{2\alpha}{NC}$ where C is the concentration of solute in moles cc^{-1} and N is Avogadro's number. The absorption cross-section can be visualized as the molecular cross-sectional area normal to the direction of propagation of a plane wave through which the energy absorbed by a single electrolyte molecule passes. Where the absorption is proportional to concentration, the absorption cross-section Q will be the constant; where the absorption increases less rapidly than the concentration, Q decreases.

In addition, Kurtze and Tamm³⁹ found a less prominent, secondary relaxation peak in MgSO_4 solutions around 200 mc/s at 0.01 to 0.1 M.⁴³ Their data for 0.01 M MgSO_4 are reproduced in Figure 8.

With increasing temperature, the relaxation frequencies are shifted to higher values in accordance with eq. 116. From the temperature dependence of ω_r , Leonard and Wilson⁵⁰ obtained for the apparent heat of activation 7.6 kcal mole⁻¹, and Kurtze and Tamm³⁹ 6.5 kcal mole⁻¹. The magnitude of $(\alpha\lambda)_{\text{max}}$ remained approximately constant over the temperature range.

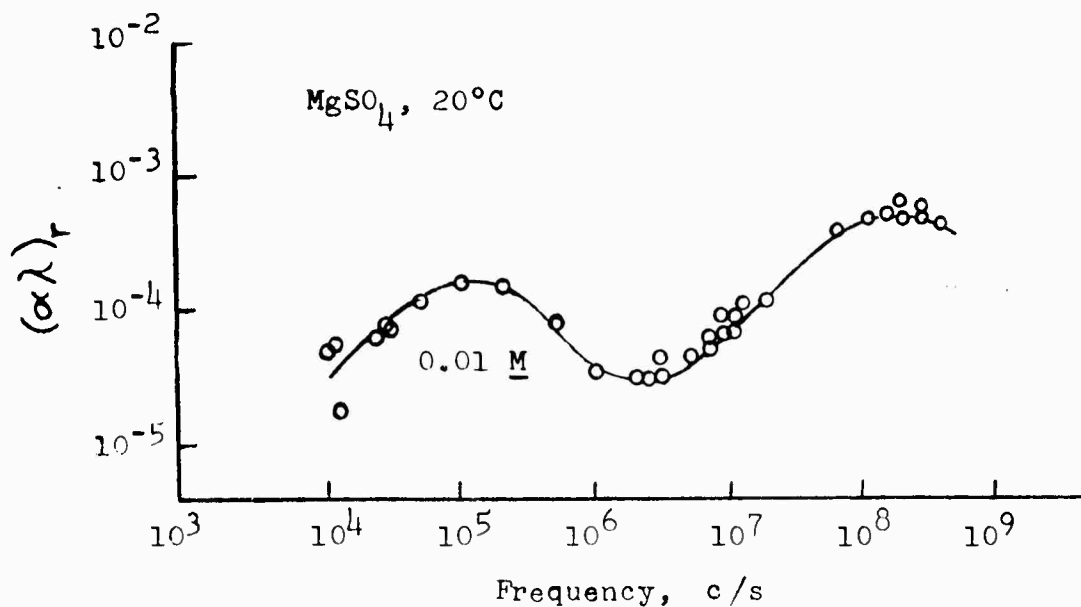


Figure 8: Absorption in MgSO_4 according to Kurtze and Tamm^{39,43,59}

To obtain more information about the nature of the reaction, Kurtze and Tamm³⁹, Bies⁶⁰, Fisher⁶¹, among others made extensive studies of the effects of pH, ionic strength, common ions, dielectric constant, and pressure on the relaxation. With respect to the effect of hydrogen-ion concentration, Kurtze and Tamm found that the magnitude of the absorption decreased as HCl was added, and that the relaxation frequency was shifted upward slightly. For example, the addition of 0.1 M HCl decreased the excess absorption by 10-fold, while the relaxation frequency approached 200 kc/s.

⁵⁹K. Tamm and G. Kurtze, *Nature* 168, 346 (1951).

⁶⁰D. Bies, *J. Chem. Phys.* 23, 428 (1955).

⁶¹F. Fisher, *J. Acoust. Soc. Am.* 30, 442 (1958).

Laidler and Eyring have derived general equations describing the effect of dielectric constant and ionic strength upon the rates of reaction between different species.⁶² The effects of these two parameters upon rate constants are summarized in Table 4.⁶³ This table does not take into account specific interactions of reacting species with solvent molecules.

Table 4: Effect of dielectric constant and ionic strength upon the rate of reaction⁶³

Reaction Type	Increasing Dielectric Constant	Increasing Ionic Strength
dipole - dipole	increase	no effect
ion - ion		
same sign	increase	increase
opposite sign	decrease	increase
ion - molecule	decrease	increase

Kurtze and Tamm found that the addition of NaCl to MgSO₄ solutions decreased the magnitude of the absorption according to the rule

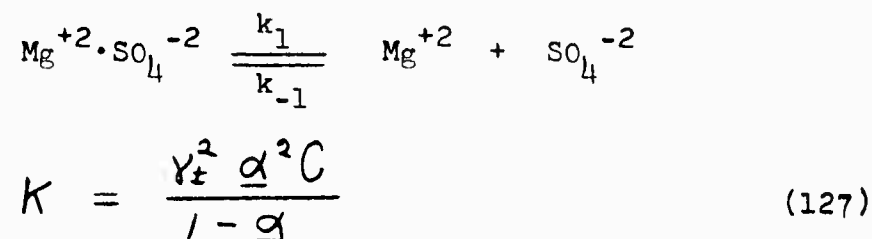
$$\alpha = \frac{\alpha_0 c_{\text{MgSO}_4}}{c_{\text{MgSO}_4} + 0.21 c_{\text{NaCl}}} \quad (126)$$

where α_0 is the absorption in the absence of NaCl.³⁹ No change in the relaxation frequency was observed.

⁶²K. Laidler and H. Eyring, Ann. N. Y. Acad. Sci. 39, 303 (1940).

⁶³K. Laidler, Chemical Kinetics, McGraw Hill Book Co., Inc., New York, 1950, p. 132.

Consider the equilibrium constant for the dissociation of an ion complex, i.e.



The effect of adding to the solution neutral ions, such as those of sodium chloride, will reduce the activity coefficient of the magnesium and sulfate ions, γ_{\pm} . If the overall concentration of the magnesium sulfate and the equilibrium constant remain unchanged, this will result in an increase of the value of α , the degree of dissociation. The effect of this upon the sound absorption due to a reaction involving the associated ions in the magnesium sulfate solution would be not only to decrease the magnitude of $(\alpha\lambda)_{\text{max}}$ in accordance with eq. 87 but also to decrease the relaxation frequency according to eq. 91. This latter prediction is contrary to the observations of Kurtze and Tamm as well as measurements in the authors' laboratory which will be discussed in a future technical report. Thus, a dissociation of ion pairs does not appear likely as the mechanism for the excess absorption.

Kurtze and Tamm also found that the addition of 0.01 M MgCl_2 or Na_2SO_4 nearly doubled the magnitude of the absorption in the vicinity of the relaxation frequency, while the effect of further addition of these salts was additive.³⁹

In liquids with a smaller dielectric constant than water, the energy of dissociation is larger and the relaxation process should be shifted to lower frequencies if a dissociation

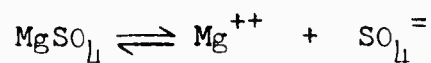
process is rate determining. Tamm, Kurtze and Kaiser⁴³ made measurements in 0.2 M MgSO_4 solutions in which the dielectric constant was varied by the use of water-methanol and water-ethanol mixtures as solvent. The result of these investigations was that the relaxation frequency did shift to lower frequencies as the dielectric constant was lowered. For example, the 0.2 M MgSO_4 in 10% by volume ethyl alcohol solution ($D = 73.5$) had a relaxation frequency of about 60 kc/s, and the magnitude of the maximum absorption per wavelength was about 50% higher than that for pure water as solvent. The effect of methanol-water mixture was similar. These workers suggested that the increase in the magnitude of the maximum absorption was due to an increase in the percent of undissociated molecules. The relaxation frequencies are given for several dielectric constants in Table 5.

Bies⁶⁰ carried out measurements in dilute solutions of magnesium sulfate over the concentration range 0.001 to 0.02 M in solvents of dielectric constant 67.0 and 56.5. The dielectric constant was varied by using dioxane-water mixtures. The relaxation frequencies observed by Leonard and Wilson⁵⁰ in water solutions ($D = 78.5$) were compared with those in the mixed solvent systems. The results of these experiments are shown in Table 5. It is seen that the relaxation frequency first increased, then decreased, with decreasing dielectric constant. No explanation was afforded for this unusual dependence of the relaxation frequency on dielectric constant. In agreement with the data of Leonard and Wilson for water solutions, the relaxation frequency increased with concentration in the mixed solvent systems. Furthermore, it was found that the magnitude

Table 5: Effect of dielectric constant and concentration on the primary relaxation frequency in MgSO_4 at 25°C .

concentration <u>M</u>	relaxation frequency, kc/s				
	$D = 78.5^{50}$	67^{60}	56.5^{60}		
0.001					110
0.0015			175		
0.002	135				130
0.0025			185		
0.003	130				135
0.005			200		155
0.0052	140				
0.008	140		230		
0.01	130		240		
0.014	138				
0.02					
	$D = 78.5$	77.0	76.0	73.5	71.0
0.2 ⁴³	~ 140	80	70	60	~ 50

of the excess absorption increased considerably as the dielectric constant was decreased. For example, at 0.005 M, the magnitude of $(\alpha\lambda)_{\text{max}}$ was 15×10^{-6} , 27×10^{-6} , and 34×10^{-6} at the dielectric constants 78.5, 67.0, and 56.5, respectively. Bies was able to show that such results as the increase in absorption in solutions of lower dielectric constant, dependence of the relaxation frequency on concentration, salt effects³⁹, etc., in dilute MgSO_4 solutions could be explained on the basis of a dissociation reaction of the type



Fisher⁶⁴ measured the absorption in a 0.5 M MgSO₄ solution from 100 to 600 kc/s by a resonator method which allowed the application of high static pressure. He found that the absorption at 20,000 psi was only one-fourth of that at atmospheric pressure. The observed relaxation frequency in this solution was 192 kc/s, and it remained constant with pressure within the accuracy of the experiment, which was estimated to be 10%. More recently⁶⁵, Fisher has reported his findings on the dependence of the relaxation frequency on pressure at various dielectric constants for the solvent. The dielectric constant was varied by using dioxane-water mixtures. His results are shown in Table 6 for 0.5 M MgSO₄ at 25°C. It is seen that in the mixed solvent systems, the relaxation frequency decreases with pressure,

Table 6: Effect of dielectric constant and pressure on the primary relaxation frequency in 0.5 M MgSO₄ at 25°C

solvent	dielectric constant	relaxation frequency, kc/s 1 atm.	relaxation frequency, kc/s 15,000 psi	reference
water	78	192	192	64
13% dioxane	67	160	105	65
25% dioxane	56	200	187	65

the effect being the most pronounced in the solution of dielectric constant 67. Perhaps the most surprising result is that at

⁶⁴F. Fisher, J. Acoust. Soc. Am. 30, 442 (1958).

⁶⁵F. Fisher, J. Acoust. Soc. Am. 32, 1510 (1960).

atmospheric pressure, the relaxation frequency first decreases, then increases with decreasing dielectric constant. This behavior is as puzzling as, and exactly opposite to, that observed by Bies⁶⁰ for concentration less than 0.02 M where the relaxation frequency was found to first increase, then decrease as the dielectric constant was lowered. No explanation is immediately obvious for either set of data. Some of the difficulty with respect to Fisher's data at atmospheric pressure, at least, could be removed by noting that Fox and Marion⁶⁶ have reported the relaxation frequency in 0.53 M MgSO_4 as 160 kc/s at 25°C. As of 1960, Fisher was engaged in repeating his earlier measurements⁶⁴ in water solutions ($D = 78$) in order to clarify the situation.*

Due to the small velocity dispersion in liquids, the detection of velocity dispersion in the vicinity of a relaxation frequency is not easily measured. The magnitude of the expected difference in velocity at frequencies well below and well above the relaxation frequency is given by

$$\frac{\Delta c}{c} = D = \frac{(\alpha\lambda)_{\max}}{\pi} \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \quad (128)$$

In 1953 Taskoprulu⁶⁷ reported a value of $(0.37 \pm 0.15) \times 10^{-3}$ for $\frac{\Delta c}{c}$ in a 1 M MgSO_4 solution from 5 to 15 mc/s. This value was obtained by averaging the results of several measurements by the optical diffraction method. The reported value is

⁶⁶F. Fox and T. Marion, J. Acoust. Soc. Am. 25, 661 (1953).

⁶⁷N. Taskoprulu, Rev. Fac. Sci. Istanbul, A18, 337 (1953).

* More recent data received too late for inclusion in this report are found in F. Fisher, Techn. Memorandum No. 46 (Office of Naval Research Contract Nonr-1866(24), Harvard University, Cambridge, Mass. (March, 1962)).

open to serious question, because of the unusually large value over a relatively small frequency range well above that where the primary relaxation process is effective. Furthermore, the indicated error is almost 50% of the measurement.

Almost simultaneously, Fox and Marion reported a more reasonable value for the dispersion.⁶⁶ They measured the dispersion directly as the difference in velocity of two harmonically related sound waves which traversed the same acoustic path and were detected at the same point. The acoustic path could be varied from 75 to 165 cm. With dispersion present the phase relations changed by an amount that depended upon the path-length and the dispersive properties of the medium. They measured the dispersion as a function of concentration over the range 0.1 to 0.53 M for the first and third harmonic frequencies of a fundamental frequency of 157 kc/s with an estimated accuracy of 3 parts in 10⁵. The measured dispersion between the fundamental and third harmonic for a 0.53 M solution was $\frac{\Delta c}{c}$

= 2.8×10^{-4} in the vicinity of 25°C. Fox and Marion obtained the total dispersion $(c_{\infty} - c_0)/c_0$ by a graphical method and reported the value 13.6×10^{-4} per mole/liter. This compares favorably with the value for the total dispersion calculated from eq. 128. Fox and Marion used Tamm and Kurtze's value of $(\alpha\lambda)_{\max} = 4.5 \times 10^{-4}$ neper per wavelength for a 0.1 M solution. This leads to a calculated dispersion of 14.3×10^{-4} per mole/liter.

Anomalous absorption has been reported in many other 2-2 valent electrolytes. One of these which has been studied in nearly the same detail as magnesium sulfate is manganous sulfate,

for which Kurtze and Tamm reported a primary relaxation frequency of about 3 mc/s³⁹ and a secondary relaxation frequency of about 300 mc/s⁴³, the same value as for MgSO₄. The presence of the low frequency relaxation process was confirmed by Smithson and Litovitz⁶⁸ who made measurements in solutions of concentrations varying from 0.05 to 0.20 M. In addition, these authors reported a third, less pronounced relaxation process with a relaxation frequency in the vicinity of 30 mc/s. This frequency appeared to be, within the accuracy of the measuring apparatus, independent of concentration. They also determined the activation energy for the primary relaxation, the concentration dependence of the relaxation frequencies and the absorption cross-section Q, and the effects of changing the dielectric constant and using D₂O as a solvent.

Although the specific nature of the process responsible for the relaxation was not then known, the apparent activation energy associated with the primary relaxation process was calculated with the assumption that one of the rate constants was much larger than the other. Under this condition, the change in the rate constant with temperature is reflected in the variation of the relaxation frequency with temperature according to eq. 116 and 117. Smithson and Litovitz⁶⁸ varied the temperature of the solution and observed an apparent activation energy for the process associated with the 3-mc relaxation frequency of 7.8 kcal mole⁻¹. In addition to the isocomposition situation, measurements were also made under isodielectric conditions

⁶⁸J. Smithson and T. Litovitz, J. Acoust. Soc. Am. 28, 462 (1956).

under which the dielectric constant of the solution was kept constant by adding methanol with each temperature change. The activation energy under these conditions was 8.7 kcal/mole, which was somewhat above the values obtained for either pure water or methanol as solvent. No activation energy was found for the 30 mc/s process, which may have been overshadowed by the shift with temperature of the larger maxima on either side.

Verma and Kor^{69,70} on the other hand, measured the variation of the relaxation frequency with temperature in water solutions of 0.1 M MnSO_4 and found that the relaxation frequency changed from 3.0 mc/s at 20°C to 4.0 mc/s at 60°C. This small shift of relaxation frequency corresponds to an experimental activation energy of only 0.82 kcal mole⁻¹. No explanation is given for the large difference with respect to Smithson and Litovitz's results, although it should be pointed out that the latter's measurements were over the temperature range 5 to 50°C. The authors of this report favor the value of Smithson and Litovitz as being more reasonable. Again, it should be pointed out that measurements of activation energy without identification of the specific process responsible for the absorption are complicated by the inability to associate the observed activation energy with a given rate constant.

The low frequency (primary) relaxation process was found by Smithson and Litovitz⁶⁸ to be slightly dependent on the concentration. The relaxation frequency increases from 3.3 mc/s at

⁶⁹G. Verma and S. Kor, Proc. Phys. Soc. (London) 72, 81 (1958).

⁷⁰S. Kor and G. Verma, J. Chem. Phys. 29, 19 (1958).

0.05 M to 3.8 mc/s at 0.2 M. A more complicated dependence of the primary relaxation frequency in MnSO_4 upon concentration has been reported by Verma and Kor⁶⁹. According to the data of these authors, the primary relaxation frequency increases with increasing concentration from 0.0025 to 0.02 M, is independent of concentration from 0.02 to 0.1 M, and again increases with concentrations above 0.1 M. An idea of the magnitude of the concentration dependence of the relaxation frequency in dilute solutions is given by the reported relaxation frequencies of 2.5, 2.7, 2.9 and 3.2 mc/s at the concentrations 0.0025, 0.005, 0.01 and 0.02 M, respectively, at 25°C. Similar behavior is observed by Verma and Kor for solutions of dielectric constants 56.5 and 48 over the same concentration range. No explanation is given for this unusual concentration dependence in water-dioxane solutions.

Smithson and Litovitz found that the magnitude of the excess absorption increased linearly with concentration to about 0.1 M. Above this concentration, the absorption increased less rapidly than the concentration. The use of D_2O as a solvent in place of water caused no change in the relaxation frequency from its value in water solutions at either 25° or 35°C. The measured value of $(\alpha\lambda)_r$ increased by about 40%. Thus, the rupture of hydrogen bonds with solvent molecules does not appear to be the rate step controlling the relaxation frequency.

The effect of dielectric constant on the primary relaxation process has been studied by Smithson and Litovitz⁶⁸ and by Verma and Kor⁶⁹. Smithson and Litovitz found that the primary relaxation frequency decreased as the dielectric constant was decreased. The dielectric constant was varied by using methanol-water

mixtures. At 25°C, for example, the relaxation frequency varied from 3.32 mc/s at $D = 78.5$ to 2.84 mc/s at $D = 64.6$ for a 0.1 M solution. Similar effects were reported at other temperatures from 5° to 45°C. The magnitude of the excess absorption per wavelength increased by 35% with the addition of 15% methanol to the solvent.

The effect of decreasing the dielectric constant was to increase the secondary (31 mc/s) relaxation frequency. For a 0.1 M solution at 25°, this frequency increased from 31.1 mc/s with $D = 78.5$ to 39.4 mc/s with $D = 64.6$. Here, too, the magnitude of the excess absorption increased greatly with decreasing dielectric constant.

Verma and Kor⁶⁹ reported exactly the opposite effect of decreasing dielectric constant on the primary relaxation frequency. According to their data over the frequency range 1-6 mc/s, the relaxation frequency continuously increased from 3.1 mc/s at $D = 78.5$ to 4.0 mc/s at $D = 48$ for a 0.02 M solution at 25°C. Similar results were reported for the effect of dielectric constant on the relaxation frequency of 0.0025, 0.005, and 0.01 M MnSO_4 . The differences in experimental conditions with respect to the work of Smithson and Litovitz were that Verma and Kor's measurements were carried out in more dilute solutions (0.0025 to 0.02 M) and that the latter workers varied the dielectric constant by using water-dioxane mixtures rather than methanol-water. It is difficult to explain the opposite results on the basis of different solvents alone. On the other hand, there is no obvious reason why solutions of concentration 0.02 M and below should be affected by the dielectric constant in a manner

opposite to 0.10 M MnSO_4 . More recently, Kor and Verma⁷¹ have made measurements in 0.5 M MnSO_4 at 25°C in solutions of dielectric constant 78.5, 56.5 and 48.0. The dielectric constant was varied from that of pure water by using 25% and 35% dioxane-water mixtures. In these solutions, the relaxation frequency decreased with decreasing dielectric constant, in agreement with the results of Smithson and Litovitz in 0.1 M MnSO_4 . Table 7 gives the relaxation frequencies for solutions of different concentrations and dielectric constants. The relaxation frequencies given for 0.5 M MnSO_4 have been deduced from the wavelength absorption curves of Kor and Verma.

An examination of the relaxation frequencies in water solutions at different concentrations indicates that the relaxation frequency does indeed appear to increase with concentration to about 0.02 M, is almost independent of concentrations to 0.1 M, and then increases again with increasing concentration. The increase is not great, however, and one wonders how accurately the relaxation frequency can be determined, particularly in the solutions below 0.02 M. The authors of this technical report are of the opinion that the optical method used by Kor and Verma is no more accurate than the pulse-echo technique for measuring absorption. Below 10 mc/s, the measured sound attenuation must be corrected for divergence of the sound beam.* The divergence is more noticeable the lower the frequency or the lower the overall measured absorption. It is possible, therefore, that

⁷¹S. Kor and G. Verma, J. Chem. Phys. 35, 1512 (1961).

*See e.g. J. Pinkerton, Proc. Phys. Soc. B62, 286 (1949).

Table 7: Effect of dielectric constant and concentration on the primary relaxation process in MnSO_4 at 25°C

concentration moles liter ⁻¹	dielectric constant	relaxation frequency, mc/s	$(\alpha\lambda)_{\text{max}}$ $\times 10^4$	reference
0.0025	78.5	2.5*	1	69
	56.5	3.0	-	
	48.0	3.2	-	
0.01	78.5	2.9*	3	69
	56.5	3.2	-	
	48.0	3.7	-	
0.02	8.5	3.2*	6	69
	56.5	3.4	-	
	48.0	4.0	-	
0.05	78.5	3.28	7.2	68
	78.5	3.32	15	
	71.4	3.11	--	
0.10	78.5	3.32	15	68
	71.4	3.11	--	
	64.6	2.84	--	
0.15	78.5	3.50	20	68
	78.5	3.50	20	
	78.5	3.50	20	
0.20	78.	3.83	27	68
	78.	3.83	27	
	78.	3.83	27	
0.50	78.	7	44	71
	56.5	3.1	46	
	48.0	1	75	

*The trends with decreasing dielectric constant are open to question because of difficulties associated with measuring relaxation frequencies in such dilute solutions, particularly below 5 mc.

the measured absorption is somewhat higher than the true value at the very lowest frequencies (< 3 mc/s) employed by Verma and Kor. This effect would be more noticeable in the solutions of lowest overall absorption (highest dielectric constant) and would result in an apparent shift of the maximum in the $(\alpha\lambda)$ curves to a slightly lower frequency. A crucial test of the effect of the dielectric constant on relaxation frequency in dilute solutions of MnSO_4 would be to repeat the measurements at various dielectric constants for solutions below 0.02 M at some higher temperature so that the measured relaxation frequencies were in the range 5-10 mc/s, where the effects of beam divergence should be negligible.

Carstensen⁷² and Schmid and Pessel⁷³ have measured the velocity dispersion in rather concentrated solutions of MnSO_4 by high precision difference techniques^{74,75}. These methods permit the determination of the difference in velocity between distilled water and the salt solution. Although the velocity of sound in distilled water cannot be agreed upon to better than $\pm 0.1\%$, Carstensen estimates that velocity differences can be determined with a precision of 5 parts in 10^5 . For a 0.5 M MnSO_4 solution, Carstensen measured a difference in velocity of 2.5 meters/s over the frequency range 0.3 to 10 mc/s. This corresponds to a velocity dispersion $\frac{\Delta c}{c}$ of 33×10^{-4} per mole/liter. This

⁷²E. Carstensen, J. Acoust. Soc. Am. 26, 862 (1954).

⁷³G. Schmid and H. Pessel, Naturwiss. 44, 257 (1957).

⁷⁴E. Carstensen, J. Acoust. Soc. Am. 26, 858 (1954).

⁷⁵G. Schmid and W. Schmidt, Naturwiss. 42, 123 (1955).

is in excellent agreement with the value 35×10^{-4} anticipated from eq. 128 on the basis of the magnitude of $(\alpha\lambda)_{\max}$. The values of the dispersion reported by Schmid and Pessel are in substantial agreement for 0.5 M MnSO_4 over the frequency range 0.35 to 16 mc/s.

The reported data for velocity dispersion in 2-2 valent electrolytes - with the exception of the questionable value of Taskoprulu⁶⁷ for MgSO_4 - are collected in Table 8. In the fifth column are the experimentally measured values of the velocity dispersion; these are to be compared with the total dispersion D_{∞} calculated from eq. 128 from the known value of $(\alpha\lambda)_{\max}$. In all cases, the measured dispersion is divided by the concentration of the solution to give the dispersion per mole/liter. The values of dispersion for different temperatures are more comparable than would be expected, since the magnitude of the maximum absorption per wavelength and hence the total dispersion does not change appreciably with temperature^{39,50,72}. The final column in Table 8 contains the literature reference for the experimental dispersion.

In addition to these salts which already have been discussed in some detail, several other divalent sulfates have been found to have one or more relaxation processes. A variety of acoustical approaches have been used in their study. Romanenko, for example, used finite amplitude sawtooth waves.⁷⁶ A measurement of the relative amounts of higher harmonics present within the solution then yields information about relaxation processes,

⁷⁶E. Romanenko, Soviet Physics - Acoustics 6, 375 (1961).

Table 8: Velocity dispersion in 2-2 electrolytes

salt	concentration moles/liter	T °C	f_r mc/s	$\frac{\Delta c}{c} \times 10^4$ experimental	per \underline{M} calc. from eq. 128	reference
MgSO ₄	0.53	25	0.160	13.6	14.3 ^a	66
MnSO ₄	0.50	9.5	2.7	33	35 ^b	72
		12	3.1	36	35 ^b	73
		18	4.2	31	35 ^b	72
		25	5.4	34	35 ^b	73
		35	9	--	35 ^b	72
CoSO ₄	0.50	20	0.435	22 ^c	18 ^d	73
		39	1.2	22 ^c	18 ^d	73
		35	1.1	18	18 ^d	72
		35	1.1	13	17 ^e	72
		35	1.1	14	14 ^f	72
MgS ₂ O ₃	0.50	38	1.1 ^c	5.4 ^c	5.7 ^g	73

^a calculated from $(\alpha\lambda)_{\max} = 45 \times 10^{-4}$ per \underline{M} ³⁹

^b " " " = 110×10^{-4} per \underline{M} ⁷²

^c estimated from the dispersion data of Schmid and Pessel⁷³

^d calculated from $(\alpha\lambda)_{\max} = 55 \times 10^{-4}$ per \underline{M} ⁷²

^e " " " = 54×10^{-4} per \underline{M} ⁷²

^f " " " = 42×10^{-4} per \underline{M} ⁷²

^g " " " = 18×10^{-4} per \underline{M} ³⁹

if present but abnormal absorption associated with finite amplitude waves must be considered. This technique has been successfully applied to the study of e.g. MnSO_4 solutions.⁷⁷ Romanenko reported a relaxation frequency of 3.3 mc/s for 0.5 M MnSO_4 at 21°C.

In addition to the relaxation processes occurring in the divalent sulfates, $\text{Al}_2(\text{SO}_4)_3$ has been examined and found to exhibit very high excess absorption per wavelength with a relaxation frequency which is concentration dependent.⁴³ At a concentration of 0.01 M, the relaxation frequency is in the vicinity of 30 mc/s, while at 0.5 M, the relaxation frequency has shifted to above 200 mc/s.

A summary of the known acoustic relaxation data is included in Table 9 for all types of electrolytes. The second column contains the primary and secondary relaxation frequencies, if two are found. The fourth column gives the mechanism which is thought to account for the relaxation process.

Several general comments may be made about the relaxation phenomena in 2-2 electrolytes. They are all characterized by an almost linear dependence of $(\alpha\lambda)$ upon concentration up to about 0.1 M. The relaxation frequencies themselves cover a wide range, but for a given cation the primary relaxation frequency is relatively independent of the nature of the anion. Thus, magnesium sulfate, thiosulfate, and chromate have relaxation frequencies in the vicinity of 1.5×10^5 c/s. Furthermore, the relaxation frequencies are almost independent of concentration.

⁷⁷E. Romanenko, Soviet Physics - Acoustics 6, 508 (1961).

Table 9: Relaxation frequencies in aqueous solutions at 20°C.

electrolyte	relaxation frequencies	concentration* moles/liter	probable mechanism	references
NH ₃ ·H ₂ O	3 x 10 ⁷	1.0	hydrolysis	43
Na acetate	1 x 10 ⁷	0.1	"	41,#
K acetate	1 x 10 ⁷	0.1	"	41,#
Cu acetate	2 x 10 ⁷	0.3	"	41
Zn acetate	2 x 10 ⁷	0.15	"	49,56
La(NO ₃) ₃	5 x 10 ⁷	0.15	"	43
Na ₃ PO ₄	5 x 10 ⁶	0.01	"	39
BeSO ₄	10 ⁴ 3 x 10 ⁸		{ ** a,b plus hydrolysis	39,87 43
NiSO ₄	10 ⁴		** b	39
MgSO ₄	1.3 x 10 ⁵ 2 x 10 ⁸		** b ** a	39,50 43
MgS ₂ O ₃	2 x 10 ⁵		** b	39
MgCrO ₄	2 x 10 ⁵ 2 x 10 ⁸		** b ** a	39 43
CuSO ₄	1.5 x 10 ⁵	>0.05	** b	39
CaCrO ₄	2 x 10 ⁵		** b	39
CoSO ₄	4 x 10 ⁵ 2 x 10 ⁸		** b ** a	39 43
MnSO ₄	3 x 10 ⁶ 3 x 10 ⁷ 2 x 10 ⁸		** b - ** a	39,68 68 43
KCN	4.5 x 10 ⁵ 9.5 x 10 ⁵	0.01 0.05	hydrolysis	##

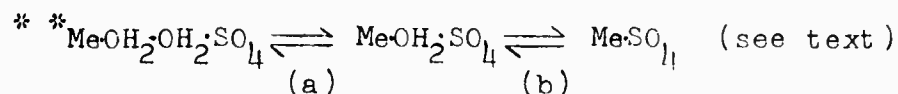
See also M. Krishnamurthi and M. Suryanayama, J. Phys. Soc. (Japan) 15, 345 (1960).

Frequencies are for 25°C. These values will be discussed in a future technical report by the present authors.

Table 9: continued

electrolyte	relaxation frequencies	concentration* moles/liter	probable mechanism	reference
ZnSO ₄	1 x 10 ⁸		* *a,b	43
Al ₂ (SO ₄) ₃	~10 ⁸		hydrolysis	43

* No strong concentration dependence unless concentration specified.



Where energies of activation have been determined for the primary process, they all (with the exception of the value obtained by Verma⁶⁹⁻⁷⁰ for MnSO₄) fall in the range 6 to 9 kcal/mole. In addition, a secondary relaxation process has been observed in many cases. The secondary relaxation frequency seems to be independent of the nature of the cation, and is in the vicinity of 2 or 3 x 10⁸ c/s.

B. Mechanisms

2-2 electrolytes.

Any postulated mechanism for the relaxation in 2-2 electrolytes such as MgSO₄ must explain the following facts concerning the primary relaxation process.

1. The primary relaxation frequency is strongly dependent on the nature of the cation and appears to be relatively independent of the anion.

2. The primary relaxation frequency is almost independent of concentration of electrolyte.

3. Neither $MgCl_2$ nor K_2SO_4 themselves show large excess absorption, but a mixture of the two is strongly absorbing.

4. In all cases, the anion associated with the relaxational cationic system contains oxygen.

5. The magnitude of the excess absorption decreases with increasing ionic strength while the relaxation frequency remains constant.

6. The effect of the addition of salts containing an ion common to the relaxing species is to increase the magnitude of the absorption.

7. Increasing the pH causes a decrease in the magnitude of the absorption while increasing slightly the relaxation frequency.

8. The use of D_2O as solvent increases the absorption, the relaxation frequency remaining constant.

9. With decreasing dielectric constant the relaxation frequency decreases somewhat, while the magnitude of the absorption greatly increases.

10. With increasing pressure, the relaxation frequency in water solutions remains constant while the absorption decreases.

The treatments of excess sound absorption associated with a dissociation process⁷⁸ and a relaxing ionic atmosphere⁷⁹ have already been discussed in relation to excess sound absorption in magnesium sulfate solutions. In an attempt to distinguish between the unimolecular and dissociation reactions, Wilson and Leonard⁸⁰ plotted $(\alpha\lambda)_{\max}$ against $C_0(1-\alpha)$, which is the concentration dependence expected for a unimolecular reaction involving ion-pairs, and against $\frac{\alpha(1-\alpha)\lambda \pm C}{2 - (2-\lambda)\alpha}$ for the dissociation

⁷⁸L. Liebermann, Phys. Rev. 76, 1520 (1949).

⁷⁹L. Hall, J. Acoust. Soc. Am. 24, 704 (1952); M. Eigen, Disc. Faraday Soc. 24, 25 (1957).

⁸⁰O. Wilson and R. Leonard, Absorption of Ultrasonic Waves in Solutions of Magnesium Sulfate, Tech. Report No. 4, (Office of Naval Research Contract N6-onr-27507), Dept. of Physics, University of California, Los Angeles, Calif., June, 1951.

reaction. The conclusion reached by these authors was that the experimental data fitted the concentration dependence for the unimolecular reaction, but gave poor agreement with that for the dissociation reaction. Furthermore, the fact that the relaxation frequency was found to be almost concentration independent was further evidence for a unimolecular type reaction. It should, however, again be pointed out that Wilson and Leonard obtained the concentration dependence for the dissociation reaction by introducing the activity coefficients into the equilibrium constant for the dissociation process, whereas they should have been used in the rate expressions as well (cf. eq. 90). When this is done, the concentration dependence is given by $\frac{\alpha C(1-\alpha)}{2-\alpha}$. The predicted variation of $(\alpha\lambda)_{\max}$ fits this concentration dependence equally as well as that for the unimolecular reaction. Therefore, it is not possible on the basis of the concentration dependence of $(\alpha\lambda)_{\max}$ alone to determine the nature of the mechanism responsible for the anomalous sound absorption in magnesium sulfate solutions.

A theoretical treatment of the first absorption maximum (120 kc/s) in terms of a one-step dissociation equilibrium has been given by Bies.⁸¹ The theoretical treatment given earlier in this report for a dissociation reaction (eq. 91), however, indicates that the relaxation frequency should increase with the product $\frac{\alpha^2}{1-\alpha} C_0$ in the range where $\frac{\alpha^2}{1-\alpha} C_0 k_{-1} > k_1$.

⁸¹D. Bies, J. Chem. Phys. 23, 428 (1955).

Barthel⁸² and Kurtze and Tamm⁸³ have pointed out that the activity coefficient γ_{\pm} is known to decrease with increasing concentration in 2-2 valent salts and this may compensate for the concentration term, yielding an almost concentration-independent relaxation time. On the other hand, it may be considered highly fortuitous that the effects of decreasing activity coefficients almost exactly balance the concentration term for nearly all the divalent sulfates. In any event, the dissociation theory of Bies cannot explain the behavior of these solutions for concentrations above 0.01 M.

A series of papers by Eigen on the subject of the mechanism for the anomalous absorption⁸⁴⁻⁸⁶ finally culminated in the description of a mechanism which, more than any other, explains the observed behavior of the relaxation processes in 2-2 valent electrolytes.⁸⁷⁻⁸⁸ This mechanism explains the relaxation phenomena as being due to the step-wise loss of water from the hydration layers separating cation from anion in hydrated ion-pairs. The mechanism is shown schematically as

⁸²R. Barthel, J. Acoust. Soc. Am. 24, 313 (1952).

⁸³G. Kurtze and K. Tamm, Acustica 3, 33 (1953).

⁸⁴M. Eigen, G. Kurtze, and K. Tamm, Z. Elektrochem. 57, 103 (1953).

⁸⁵M. Eigen, Disc. Faraday Soc. 24, 25 (1957).

⁸⁶C. Czerlinski, H. Diebler, and M. Eigen, Z. physik. Chem. Frankfurt 19, 246 (1959).

⁸⁷H. Diebler and M. Eigen, ibid. 20, 299 (1959).

⁸⁸M. Eigen, Z. Elektrochem. 64, 115 (1960).

takes place quickly ($\tau_2 \cong 10^{-9}$ sec.) and is approximately the same for all 2-2 valent oxygen-containing electrolytes. Eigen associates this step with the high frequency (~ 200 mc/s) maximum in the absorption curves of many of these electrolytes. The third step, the replacement by the anion of the second water molecule in the inner coordination sphere of the cation, proceeds more slowly with a velocity which is specific for a given cation. This is considered to be the process which causes the low-frequency absorption maximum in the divalent sulfates (e.g. in the case of MgSO_4 , $\tau_1 \cong 10^{-6}$ sec.).

This last mechanism has been used in the discussion of the relaxation spectrum of BeSO_4 .⁸⁷ A quantitative interpretation is rendered difficult by the fact that the reaction is complicated by hydrolysis. Nevertheless, a qualitative discussion can be made on the basis of the known relaxation times. For a 0.2 M solution a value of $\tau_2 = 2 \times 10^{-9}$ sec is indicated by sound absorption measurements.⁹¹ The low frequency rise in absorption⁸³ indicates a relaxation frequency of 10^3 c/s; this relaxation was found by the temperature step-function technique⁸⁷ to have a relaxation time $\tau_1 = 8 \times 10^{-4}$ sec. No experimental data exist for τ_3 ; Diebler and Eigen⁸⁷ estimate from theoretical considerations that $\tau_3 = 7 \times 10^{-10}$ sec.

It may be worthwhile to make some general comments about mechanism (j). According to Eigen⁸⁸, the rate constants k_2 and k_{-2} are, for a given valence type, not dependent on the

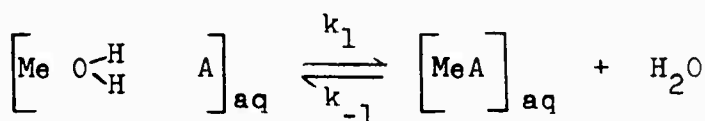
⁹¹K. Tamm, G. Kurtze, and R. Kaiser, *Acustica* 4, 380 (1954).

individual electrolyte. This is also true of the rate constants for the diffusion-controlled process $I \rightleftharpoons II$. The conversion $II \rightleftharpoons III$ occurs very rapidly, and for all the 2-2 electrolytes studied in detail to date, the rate constants k_2 and k_{-2} are of the order 10^9 sec^{-1} . At least for the divalent oxygen-containing anions under consideration, individual differences are not expected for metal ions of the same valence type, since the metal and anion are still separated by two water layers.

On the other hand, specific influences (such as the radius of the cation, degree of covalent character of the bond, or crystal field stabilization) are expected to be reflected in the rate constants k_1 and k_{-1} . That this is actually the case is shown in Table 10, in which are tabulated the forward and reverse rate constants for the loss of hydration water from between 2-2 valent ion-pairs. The rate constants differ for the various cations by several orders of magnitude. The directly measured rate constants are those designated by k_{-1} , i.e. the rate constant for the insertion of a water molecule between the magnesium and sulfate in the MgSO_4 ion pair. According to Table 10, they are very strongly dependent on the nature of the metal ion, and virtually independent of the nature of ligand ($\text{SO}_4^{=}$, $\text{S}_2\text{O}_3^{=}$, $\text{CrO}_4^{=}$). The rather close correlation between rate constant and ionic radius is particularly noteworthy; in general, the rate constants increase with increasing ionic radius.

The reverse rate constants k_1 can be evaluated from the equilibrium constant for this step. According to Eigen⁸⁸, the equilibrium constant is obtained from the absolute magnitude

Table 10: Rate constants for 2-2 electrolytes⁸⁸



Me	A	k_{1-1} sec ⁻¹	k_{-1-1} sec ⁻¹	$r_o +$ A	ΔE_a^* kcal mole ⁻¹
Be ⁺⁺	SO ₄ ⁼	1 x 10 ²	1.3 x 10 ³	0.35	
Cu ⁺⁺	SO ₄ ⁼	~ 10 ⁴	1 x 10 ⁶	0.72	
Ni ⁺⁺	SO ₄ ⁼	1 x 10 ⁴	1 x 10 ⁵	0.78	8 ⁸³
Mg ⁺⁺	SO ₄ ⁼	1 x 10 ⁵	8 x 10 ⁵	0.78	6.5, ⁸³ 7.6 ⁸⁰
Mg ⁺⁺	S ₂ O ₃ ⁼	1 x 10 ⁵	1.5 x 10 ⁶	0.78	
Mg ⁺⁺	CrO ₄ ⁼	1 x 10 ⁵	1.5 x 10 ⁶	0.78	
Co ⁺⁺	SO ₄ ⁼	2 x 10 ⁵	2.5 x 10 ⁶	0.82	6 ⁸³
Mn ⁺⁺	SO ₄ ⁼	4 x 10 ⁶	2 x 10 ⁷	0.91	7.8 ⁶⁸ , 0.8 ⁶⁹
Ca ⁺⁺	SO ₄ ⁼	~ 10 ⁷	~ 10 ⁸	0.99	

*Apparent activation energy deduced from the variation of the relaxation time with temperature.

of the relaxational absorption. The details of the calculation of the equilibrium constant from the magnitude of the absorption are by no means clear. In any case, an independent estimate of the volume change ΔV appears to be necessary. It will be shown in a mathematical analysis of mechanism (j) that the volume change is essentially the same as that for the ions combining to yield ion pairs.

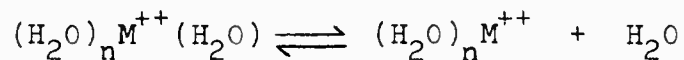
It may be of interest to speculate on why only the divalent sulfates, thiosulfates, and chromates have exhibited relaxation

processes which are characterized by mechanism (j). Certainly the high charge-density of these salts is important in order to form reasonably stable hydrated ion-pairs in sufficient amounts to be detected acoustically. Salts such as sodium sulfate or magnesium chloride would be expected to have higher degrees of dissociation and decreased stability of water-bridged ion pairs of the type shown in reaction j. Both of these effects would tend to reduce the measured absorption, since the magnitude of the relaxational absorption is proportional to both τ and to $(1 - \alpha)C$. (See eq. 25). An decrease in τ by one or two orders of magnitude or slight increases in the degree of dissociation, particularly where the degree of dissociation approaches unity, would decrease the magnitude of the relaxational absorption so that it would not normally be detected, even if the process were characterized by a relatively large ΔV° .

The role of oxygen in these ion pairs may be to stabilize the formation of the bridged ion pairs through hydrogen bonding, but it does not necessarily follow that the anion must contain oxygen. Aqueous solutions involving the very electronegative fluoride ion, for example, may form ion pairs in sufficient quantities to be observed acoustically.

It is interesting to speculate on possible mechanisms for the loss of the last water from between the M^{++} and A^-

ions on the basis of the S_N1 and S_N2 mechanisms.⁹² If one considers first a S_N1 (i.e. dissociation) process, a situation may be imagined wherein the water molecules within the primary hydration layer of structure III of reaction j are in constant rotation about the M^{++} ion. Periodically during this rotation, one of the primary water molecules dissociates from the aggregate:

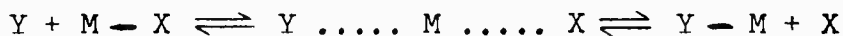


This may be assumed to occur slowly and be rate determining. At some time in the rotation of the "hole" left by the lost water, the A^- anion takes its place in the coordination sphere of the metal. By this means the coordination number of the cation is restored to its initial value. This step would be expected to occur rapidly.

If the process occurs by a S_N2 (displacement) mechanism, one can imagine a situation such as the following. The water molecules in the primary hydration sphere of the M^{++} ion again are assumed to be in rotation. At some instant, the anion

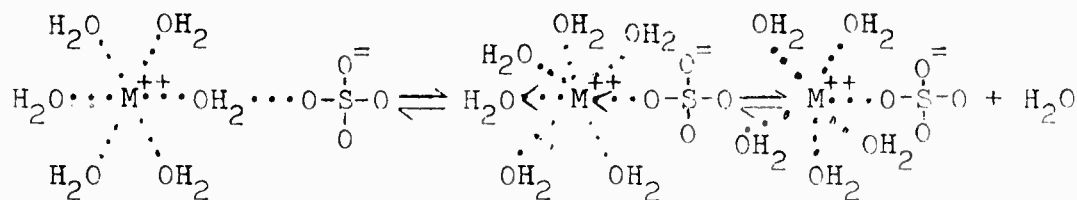
92 The notation S_N1 and S_N2 is commonly used as shorthand for nucleophilic substitution by dissociation and displacement mechanisms, respectively. A S_N1 mechanism is one in which the first step is a slow unimolecular dissociation $M-X \rightleftharpoons M + X$ followed by a rapid coordination of M with a second reagent $M + Y \rightarrow M - Y$. As an intermediate there exists the metal ion of a coordination number reduced by one.

The S_N2 (displacement) mechanism involves a bimolecular rate determining step in which one nucleophilic reagent displaces another.



The coordination number of the metal ion increases by one in the transition state.

penetrates to within the inner coordination sphere of the metal ion and weakens the metal attraction to the water molecules. One of these is then displaced in order to restore the initial coordination number of the metal:



A quantitative interpretation of the effects of dielectric constant, common ion, pH, pressure, etc. upon mechanism (j) is complicated by the fact that eq. 58 and 68 describing the relaxational absorption and relaxation time for a simple unimolecular process are no longer applicable to this system of coupled consecutive reactions. It was previously shown in the discussion of more complex reactions by matrix analysis that, for even the relatively simple system

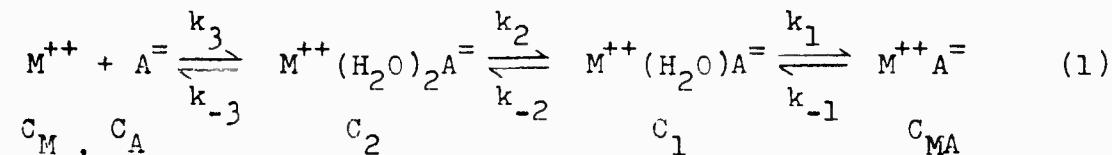


the relaxation time associated with the conversion $\text{A}_1 \rightleftharpoons \text{A}_2$ is not independent of the kinetic parameters associated with the conversion $\text{A} \rightleftharpoons \text{A}_1$. The expression $\tau^{-1} = k_1 + k_{-1}$ for the second process is valid only under the special assumption $k_2 \gg k_{-2}$ (eq. 105), i.e. A is of negligible concentration. In general it is recognized⁹³ that $\tau_1^{-1} = k_f + k_r$ is justified only

⁹³See, for example, M. Eigen, *Disc. Faraday Soc.* 24, 25 (1957) and R. Davies and J. Lamb, *Proc. Phys. Soc.* 69B, 293 (1956).

in a very few special cases, and that ordinarily one must take into account the previous steps in deriving specific equations for the relaxation time and excess absorption associated with a particular step.

A simplified mechanism for the processes of interest in solutions of the divalent sulfates may be represented as



in which M^{++} and A^{-} represent the metal cation and anion; $M^{++}(H_2O)_2A^{-}$, $M^{++}(H_2O)A^{-}$, and $M^{++}A^{-}$ are the hydrated ion pairs, the cation and anion of which are separated by two, one and no water molecules, respectively.

Eigen⁸⁵ has theoretically treated this system in terms of normal reaction coordinates⁹⁴ as outlined earlier (pp. 26-30). An alternate approach is used here, which is an extension of the

method used in connection with the discussion of the unimolecular and dissociation mechanisms (pp. 15-25). For convenience, let the concentrations of the various species in reaction (1) be represented by the symbols C_M , C_A , C_2 , C_1 , and C_{MA} respectively.

Equilibrium constants can be defined for each of the steps in the reaction:

$$K_1 = \frac{C_{MA}}{C_1} = \frac{k_1}{k_{-1}} \quad (129)$$

⁹⁴S. Benson, The Foundation of Chemical Kinetics, McGraw-Hill Book Co., Inc., New York, 1960, pp. 39-42.

$$K_2 = \frac{C_1}{C_2} = \frac{k_2}{k_{-2}} \quad (130)$$

$$K_3 = \frac{C_2}{C_M C_A \gamma_{\pm}^2} = \frac{k_3}{k_{-3}} \quad (131)$$

where all activity coefficients have been assumed to be unity except that for the separate ions.⁹⁵ One can write the usual kinetic expression for the final step

$$\frac{dC_{MA}}{dt} = \dot{C}_{MA} = k_1 C_1 - k_{-1} C_{MA} \quad (132)$$

The other reactions will be assumed to be fast relative to the last step. As in the treatment for the simple unimolecular and dissociation reactions discussed in an earlier section of this report, the rate constants and concentrations are assumed to undergo periodic variations from their equilibrium values

$$k_j = k_j^0 + (\delta k_j) e^{i\omega t} \quad (133)$$

$$C_j = C_j^0 + (\delta C_j) e^{i\omega t} \quad (134)$$

If one substitutes these into eq. 132, expands, and neglects second order perturbation terms, there results

⁹⁵It cannot be emphasized too strongly that the activity coefficient γ_{\pm} used in this report is the "true" activity coefficient, which takes into account incomplete dissociation of the electrolyte. In practical work, the activity coefficient most frequently encountered is the stoichiometric mean molal activity coefficient γ_{\pm} , which does not take into account the degree of dissociation of the electrolyte. The equilibrium constant for a dissociation reaction is then

$$K = \frac{\gamma_{\pm}^2 C_0}{1 - \alpha} = \frac{\gamma_{\pm}^2 \alpha^2 C_0}{1 - \alpha}$$

The degree of dissociation α can be calculated from this equation, and then the true activity coefficient by

$$\gamma_{\pm} = \frac{\gamma_{\pm}}{\alpha}$$

$$i\omega\delta C_{MA} = k_1\delta C_1 + C_1\delta k_1 - k_{-1}\delta C_{MA} - C_{MA}\delta k_{-1} \quad (135)$$

The magnitudes of the various concentration perturbations are related through the material balance equation

$$-\delta C_{MA} = \delta C_M + \delta C_2 + \delta C_1 \quad (136)$$

The quantities δC_2 and δC_M may be expressed in terms of δC_1 by differentiating the equilibrium constants; one then obtains

$$\delta C_2 = \frac{\delta C_1}{K_2} - \frac{C_2}{K_2} \delta K_2 \quad (137)$$

and

$$\delta C_M = \frac{1}{2} \left[\frac{\delta C_1}{C_M K_{23} \gamma_{\pm}^2} - \frac{C_M}{K_{23}} \delta K_{23} \right] \quad (138)$$

where K_{23} is used to represent the product $K_2 K_3$. Substitution of these into eq. 136 yields

$$\delta C_1 = \frac{-\delta C_{MA} + A_2 \delta K_2 + A_3 \delta K_{23}}{A_1} \quad (139)$$

where

$$A_1 = 1 + \frac{1}{K_2} + \frac{1}{2K_{23} \gamma_{\pm}^2 C_M} \quad (140)$$

$$A_2 = \frac{C_2}{K_2} \quad \text{and} \quad A_3 = \frac{C_M}{2K_{23}} \quad (141)$$

Eq. 139 may now be substituted into eq. 135:

$$\delta C_{MA} = \frac{k_{-1} C_1 \delta K_1 + \frac{k_1}{A_1} (A_2 \delta K_2 + A_3 \delta K_{23})}{\left(i\omega + \frac{k_1}{A_1} + k_{-1} \right)} \quad (142)$$

which has been simplified by

$$k_{-1} \delta K_1 = \frac{k_{-1} \delta k_1 + k_1 \delta k_{-1}}{k_{-1}} \quad (143)$$

The relaxation time may be evaluated in the usual manner from the equation

$$\delta \dot{c}_{MA} = k_1 \delta c_1 - k_{-1} \delta c_{MA} \quad (144)$$

$$\text{where } \delta c_1 = - \frac{\delta c_{MA}}{A_1}$$

so that

$$\delta \dot{c}_{MA} = - \left(\frac{k_1}{A_1} + k_{-1} \right) \delta c_{MA} \quad (145)$$

Comparison with eq. 42 shows that

$$\tau^{-1} = \frac{k_1}{A_1} + k_{-1} \quad (146)$$

If this and the relation

$$\frac{dK_1}{dP} \cong \frac{\delta K_1}{\delta P} = - \left(\frac{\Delta V_1^\circ}{RT} \right) K_1 \quad (147)$$

for the differential equilibrium constants are substituted into eq. 142, the result is

$$\frac{\delta c_{MA}}{\delta P} = - \frac{k_{-1} K_1}{RT} \left(\Delta V_1^\circ c_1 + \frac{C_2}{A_1} \Delta V_2^\circ + \frac{C_M}{2A_1} \Delta V_{23}^\circ \right) \tau \cdot \left(\frac{1}{1 + i\omega\tau} \right) \quad (148)$$

$$\text{where } \Delta V_{23}^\circ = \Delta V_2^\circ + \Delta V_3^\circ$$

This can now be related to the relaxational compressibility through eq. 11, 23, and 64, so that

$$(\alpha\lambda)_r = \frac{\pi \beta_r}{\gamma \beta_o} \cdot \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (149)$$

$$= \frac{\pi k_{-1}K_1}{\beta_o RT} \left[c_1 \Delta V_1^o + \frac{c_2}{A_1} \Delta V_2^o + \frac{c_M}{2A_1} \Delta V_{23}^o \right] \tau \cdot$$

$$\cdot \frac{\partial v}{\partial n_{MA}} \cdot \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (150)$$

where the ratio of specific heats γ has been assumed to be unity. This may be simplified through some assumptions concerning the relative sizes of the terms. One may make

assumptions concerning the relative values of the equilibrium constants K_1 and K_2 . The fact that the relaxation time (eq. 146) is found experimentally to vary with concentration is an indication that the $1/K_2$ term in A_1 (eq. 140) is negligible, i.e. $K_2 > 1$. A decision as to the magnitude of K_1 is contingent upon deciding whether most of the ion pairs are in the form $M(H_2O)A$ or MA . This depends on the relative magnitudes of the ion-ion and ion-solvent interactions. Unfortunately, this decision is not easily made on a theoretical basis alone. In the remainder of this derivation, it will be assumed first that $K_1 > 1$, and then the resultant expression for the relaxational absorption per wavelength will be rederived with $K_1 < 1$. From the values of k_1 and k_{-1} in Table 10, it is evident that Eigen⁸⁸ has assumed the latter case.

For the present, it is assumed that

$$K_{12} > K_1 > 1 \quad \text{and} \quad \Delta V_1^{\circ} > \frac{1}{K_1 K_2} \Delta V_2^{\circ} \quad (151)$$

If one considers dilute solutions, the approximation may be made that

$$A_1 = \frac{1}{2\underline{\alpha} c_0 \gamma_{\pm}^2 K_{23}} \quad (152)$$

where $\underline{\alpha}$ is the time-average degree of dissociation defined by

$$\underline{\alpha} = \frac{c_M}{c_0} \quad (153)$$

Under these conditions, eq. 150 becomes

$$(\alpha\lambda)_r = \frac{\pi^{k-1} K_1 C_1 \Delta V_{123}^{\circ}}{\beta_0 RT} \cdot \tau \cdot \frac{\partial V}{\partial n_{MA}} \cdot \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (154)$$

where

$$\Delta V_{123}^{\circ} = \Delta V_1^{\circ} + \Delta V_2^{\circ} + \Delta V_3^{\circ} \quad (155)$$

The concentration C_1 may now be related to the total salt concentration C_0 as follows:

$$C_0 = C_M + C_2 + C_1 + C_{MA} \quad (156)$$

or

$$C_0 = \alpha C_0 + \frac{C_1}{K_2} + C_1 + K_1 C_1 \quad (157)$$

which rearranges to

$$C_1 \cong \frac{1}{K_1} (1 - \alpha) C_0 \quad (158)$$

The substitution of this into eq. 154 yields

$$(\alpha\lambda)_r = \frac{\pi (1 - \alpha) C_0}{\beta_0 RT} \Delta V_{123}^{\circ} \tau^{k-1} \frac{\partial V}{\partial n_{MA}} \cdot \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (159)$$

Consider now the product τ^{k-1} . Combination of eq. 146 and 152 yields

$$\tau^{k-1} = \frac{1}{1 + 2\alpha C_0 \gamma_{\pm}^2 K_{123}} \quad (160)$$

where

$$K_{123} = K_1 K_2 K_3 \quad (161)$$

and

$$\alpha C_0 \gamma_{\pm}^2 K_{123} = \frac{C_{MA}}{\alpha C_0} = \frac{1 - \alpha}{\alpha} \quad (162)$$

Therefore, eq. 160 becomes

$$\tau_{k-1} = \frac{\alpha}{2 - \alpha} \quad (163)$$

and eq. 159

$$\left(\alpha\lambda\right)_r = \frac{\pi}{\beta_0 RT} \cdot \frac{\alpha C_0 (1 - \alpha)}{2 - \alpha} \Delta V_{123}^{\circ} \frac{\partial V}{\partial n_{MA}} \cdot \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (164)$$

where

$$\Delta V_{123}^{\circ} = \Delta V_1^{\circ} + \Delta V_2^{\circ} + \Delta V_3^{\circ} = \bar{V}_{MA} - (\bar{V}_M + \bar{V}_A) \quad (165)$$

The quantity $\frac{\partial V}{\partial n_{MA}}$ remains to be evaluated.

One can write for the volume of the reacting species

$$V = \bar{V}_{MA} n_{MA} + \bar{V}_M n_M + \bar{V}_A n_A + \bar{V}_1 n_1 + \bar{V}_2 n_2 \quad (166)$$

Differentiation with respect to n_{AB} yields

$$\frac{\partial V}{\partial n_{MA}} = \bar{V}_{MA} + \bar{V}_M \frac{\partial n_M}{\partial n_{MA}} + \bar{V}_A \frac{\partial n_A}{\partial n_{MA}} + \bar{V}_1 \frac{\partial n_1}{\partial n_{MA}} + \bar{V}_2 \frac{\partial n_2}{\partial n_{MA}} \quad (167)$$

The material balance for the change in number of moles of reactants and products is

$$\frac{\partial n_M}{\partial n_{MA}} + \frac{\partial n_1}{\partial n_{MA}} + \frac{\partial n_2}{\partial n_{MA}} = -1 \quad (168)$$

or

$$\frac{\partial n_M}{\partial n_{MA}} \left(1 + \frac{\partial n_1}{\partial n_M} + \frac{\partial n_2}{\partial n_M} \right) = -1 \quad (169)$$

The changes in number of moles are governed by the following restrictions

$$\frac{n_2}{n_M} = \text{constant} = K_3 C_M \gamma_{\pm}^2 \quad (170)$$

and

$$\frac{n_1}{n_M} = \text{constant} = K_{23} C_M \gamma_{\pm}^2 \quad (171)$$

From these, it follows that

$$\frac{\partial n_1}{\partial n_M} = K_{23} C_M \gamma_{\pm}^2 \quad (172)$$

and

$$\frac{\partial n_2}{\partial n_M} = K_3 C_M \gamma_{\pm}^2 \quad (173)$$

Substitution of eq. 172 and 173 into 169 yields

$$\frac{\partial n_M}{\partial n_{MA}} = - \frac{1}{1 + K_3 C_M \gamma_{\pm}^2 (K_2 + 1)} \quad (174)$$

If eq. 167 is written in the form

$$\frac{\partial v}{\partial n_{MA}} = \bar{v}_{MA} + \frac{\partial n_M}{\partial n_{MA}} \left(\bar{v}_M + \bar{v}_A + \bar{v}_1 \frac{\partial n_1}{\partial n_M} + \bar{v}_2 \frac{\partial n_2}{\partial n_M} \right) \quad (175)$$

and the appropriate differentials substituted from eq. 172, 173, and 174, there results

$$\frac{\partial v}{\partial n_{MA}} = \bar{v}_{MA} - \frac{1}{1 + K_3 C_M \gamma_{\pm}^2 (K_2 + 1)} \left[\bar{v}_M + \bar{v}_A + \bar{v}_1 K_{23} C_M \gamma_{\pm}^2 + \bar{v}_2 K_3 C_M \gamma_{\pm}^2 \right] \quad (176)$$

If one neglects the terms involving $C_M \gamma_{\pm}^2$, this becomes

$$\frac{\partial v}{\partial n_{MA}} \cong \bar{v}_{MA} - (\bar{v}_M + \bar{v}_A) = \Delta v_{123} \quad (177)$$

Substitution of eq. 177 into eq. 164 then results in

$$(\alpha\lambda)_r = \frac{\pi}{\beta_0 RT} \frac{\alpha C_0 (1 - \alpha)}{2 - \alpha} \cdot (\Delta V_{123}^\circ)^2 \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (178)$$

This equation is identical to eq. 87 derived for the relaxational absorption for a simple dissociation reaction. That is, when the rate-determining step (unimolecular) is coupled to a series of faster prior steps, the theoretical treatment approximates to a situation in which the intermediate steps can be neglected. The relaxation time, however, is not independent of the equilibrium parameters of the intermediate steps.

The relaxation time may be approximated as

$$\tau^{-1} = k_{-1} + 2\alpha C_0 \gamma_{\pm}^2 K_{23} k_1 \quad (179)$$

As the concentration of electrolyte approaches zero, the relaxation time is given by

$$\tau^{-1} = k_{-1} \quad (180)$$

As the concentration is increased, the relaxation time decreases according to

$$\tau^{-1} = k_{-1} + 2\alpha C_0 \gamma_{\pm}^2 K_{23} k_1 = \frac{k_{-1} (2 - \alpha)}{\alpha} \quad (181)$$

A limiting value for the relaxation time is reached at concentrations above which the degree of dissociation α is approximately constant.

The expression for the relaxational absorption per wavelength will now be rederived with the assumption

$$K_2 \gg 1 \gg K_1 \quad (182)$$

The concentration C_1 (eq. 158) then becomes

$$c_1 \cong (1 - \alpha) c_0 \quad (183)$$

i.e. most of the ion-pairs are in the form $M(H_2O)A$. Substitution of eq. 183 into eq. 154 yields

$$(\alpha \lambda)_r = \frac{\pi k_{-1} K_1 (1 - \alpha) c_0}{\beta_0 RT} \cdot \Delta V_{123}^\circ \cdot \frac{\partial V}{\partial \eta_{MA}} \cdot \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (184)$$

the remainder of the derivation (eqs. 160-177) remains unchanged, so that

$$(\alpha \lambda)_r = \frac{\pi K_1}{\beta_0 RT} \frac{\alpha c_0 (1 - \alpha)}{2 - \alpha} (\Delta V_{123}^\circ)^2 \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (185)$$

This expression is the same as eq. 178 with the exception of the presence of K_1 in the numerator. Thus, if 182 correctly represents the relative magnitudes of the equilibrium constants, a knowledge of the volume change ΔV_{123} associated with the dissociation process allows K_1 to be calculated from the magnitude of the relaxation absorption. The relaxation time (eqs. 179-181) remains unchanged.

On the basis of these equations describing the excess absorption and relaxation time associated with the removal of the last water of hydration from between the cation and anion in the hydrated ion pairs, it is now possible to discuss the effect of concentration, ionic strength, etc. on mechanism (j). Eq. 144 for the relaxation time for the last step in this mechanism indicates that the relaxation frequency should increase slightly with increasing concentration of active electrolyte. The effect is not expected to be great because $k_{-1} \gg 2\alpha c_0 \gamma_{\pm}^2 K_{23} k_1$, and for very dilute solutions, the relaxation frequency should be practically independent of concentration.

This is in accordance with the experimental results of Leonard and Wilson^{57,80} and Kurtze and Tamm⁸³ for the independence of the relaxation frequency upon concentration in dilute solutions, and is further supported by the findings of Fisher⁶¹ for MgSO_4 and of Smithson and Litovitz⁶⁸ for MnSO_4 that the relaxation frequency increases only slightly with concentration.

The effect of increasing the ionic strength by adding a salt such as sodium or potassium chloride is to decrease significantly the mean activity coefficient γ_{\pm} . This in turn causes an increase in the degree of dissociation α , so that $C_0(1 - \alpha)$ and hence $(\alpha\lambda)_r$ decrease. The results of experiments by the present authors on the effect of a large excess of potassium chloride on the relaxation process in magnesium sulfate will be discussed in a future technical report.

This mechanism will also explain the effect of adding salts with ions common to the relaxing species, for example, the addition of MgCl_2 or K_2SO_4 to MgSO_4 solutions. Eqs. 178 and 185 are based on the assumption that $C_M = C_A$. A careful examination of the derivation of this equation indicates that anything which increases the ion-pair concentration will also increase the excess absorption. Chemically, the equilibrium is shifted in the direction of forming more ion-pairs. As a result, the quantity $(1 - \alpha)$ and hence the relaxational absorption increase. The effect of common ions upon the relaxation frequency is expected to be very slight, since $2\alpha C_0 \gamma_{\pm}^2 k_{23} k_1 < k_{-1}$. A slight decrease is anticipated, since both α and γ_{\pm} decrease.

The experiments of Smithson and Litovitz⁶⁸ with respect to the substitution of D_2O for water as solvent are quite informative.

The fact that the 3 mc/s relaxation frequency in MnSO_4 does not change under this condition is evidence that the rupture of a hydrogen bond is not the step associated with k_{-1} . This is consistent with mechanism j. The fact that the excess absorption is about 30% greater in D_2O solutions than in water solutions cannot be explained on the basis of the difference in dielectric constants, since these differ by less than 1%. Smithson and Litovitz are of the opinion⁶⁸ that, since many salts are slightly less soluble in D_2O than in water,⁹⁶ the degree of dissociation might be less. An increase in the ion pair concentration brought about by a small decrease in the degree of dissociation could account for the increased absorption. The 30 mc/s relaxation process, which is not observed when D_2O is the solvent, possibly does involve the breaking of an O-H bond.

The effects of high static pressure⁶⁴ on this mechanism can be explained on the basis of the change in the pressure-sensitive variables: γ_{\pm} , the mean ionic activity coefficient; α , the degree of dissociation; and ΔV , the volume change for the reaction. It should be pointed out that the quantity $(\Delta V^\circ)^2$ in eqs. 178 and 185 actually consists of the product of the volume change ΔV° obtained from the variation of the equilibrium constant with pressure (eq. 147) times a volume change ΔV which is deduced from the variation of the volume with the number of moles of ion pairs n_{MA} (eq. 167). The first of these is referred to a standard state of one atmosphere and

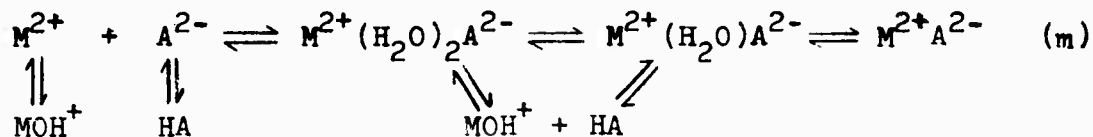
⁹⁶R. Eddy and A. Menzies, J. Phys. Chem. 44, 207 (1940).

is pressure independent. The second ΔV is both concentration and pressure dependent (cf. eq. 176). Eq. 178 shows that a decrease with pressure of ΔV and/or an increase of α will reduce the magnitude of the absorption. Negligible effect is expected upon the relaxation frequency, since the pressure dependence of the rate constants k_1 and k_{-1} is small. Furthermore, the term in the relaxation frequency containing the degree of dissociation and the activity coefficient is much smaller than the directly measured k_{-1} .

Experiments which involve varying the solvent and hence the dielectric constant are open to some criticism since the proposed mechanism involves the solvent itself in the rate-determining step. It may be, for example, that the cation preferentially coordinates with the water, and that the reaction mechanism is relatively insensitive to the bulk solvent as long as some water is present. The results of such experiments may then lead to ambiguous interpretation if one attempts a correlation such as that afforded by Table 4 for reactions in solution. As Smithson and Litovitz point out⁶⁸, the theoretically deduced dependence of a rate of reaction between two dipoles upon the dielectric constant does not necessarily apply to a reaction involving ion pairs. It is probable, however, that the increased absorption often observed in solutions of lower dielectric constant is associated with a higher degree of ion association, i.e. an increase in the number of ion pairs.

The influence of pH on these relaxation processes is not so simply explained. In the derivation of eqs. 178 and 185, no competing reactions were considered. It is entirely possible,

however, that various side reactions may influence the relaxation process; for example:



pH sensitive

independent of pH

It may be argued that increasing hydrogen ion concentration converts most $SO_4^{=}$ in magnesium sulfate solutions to the form HSO_4^- . This would result in a decrease in the absorption due to the smaller number of ion pairs and a slight decrease in the relaxation frequency. These are the effects experimentally observed. Evidence for the existence of competing equilibria such as those indicated by reaction m is afforded by the observed hydrolysis of many of these systems. Hydrolysis would be expected in some cases to give rise to further relaxation processes coupled to the general relaxation scheme. This, in fact, appears to be the true situation. It has already been pointed out, for example, that the relaxation mechanism in solutions of $BeSO_4$ ⁸⁷ is complicated by observed relaxation effects due to hydrolysis processes.

In view of the marked success of mechanism j in explaining the observed relaxation effects in 2-2 valent electrolytes, it is somewhat surprising that several workers appear not to have accepted this mechanism or even to have commented directly on it in their recent publications. For example, Kor and Verma⁹⁷ continue to speculate on the nature of the reaction in poly-

⁹⁷S. Kor and G. Verma, J. Chem. Phys. 35, 1512 (1961).

valent sulfate solutions but give no consideration to mechanism j proposed by Eigen. Furthermore, they consider only simple electrostatic interactions. Even more recently, Suryanarayana⁹⁸ has tabulated the apparent variation with concentration of the forward and reverse rate constants in solutions of magnesium and manganese sulfate on the assumption that a simple dissociation mechanism were responsible for the relaxation process. This paper gives no indication of familiarity with mechanisms proposed by Eigen.

Eigen⁸⁸ and Pearson⁹⁹ have emphasized the fact that crystal field theory should afford some correlations of the rate of removal of the last water in mechanism j with the electronic structure of the cation. Certain predictions concerning the rate of the conversion III \rightleftharpoons IV in mechanism j can be made on the basis of an electrostatic model. These predictions are shown in Table 11 and refer to the relative tendencies toward S_N1 and S_N2 mechanisms⁹⁹ as the sizes and charges of the various species are changed.

By either mechanism one would expect a decrease in the rate of reaction as the charge of the leaving group increases or the size decreases. This is in rather good agreement with what is

⁹⁸M. Suryanarayana, J. Phys. Chem. 66, 360 (1962).

⁹⁹R. Pearson, J. Phys. Chem. 63, 321 (1959).

Table 11: Effect of charges and sizes on rates of reaction⁹⁹

Condition	Effect on Rate Constant	
	S _N 1	S _N 2
increased positive charge of central atom	decrease	opposing effects
increased size of central atom	increase	increase
increased size of entering group	no effect	decrease
increased negative charge of entering group	no effect	decrease
increased negative charge of leaving group	decrease	decrease
increased size of leaving group	increase	opposing effects

found experimentally. Furthermore, as the size of the central ion diminishes and its charge increases, it may be expected that the rate of reaction by either mechanism would decrease. This is indeed found to be the case in general with respect to inorganic substitution reactions in general.¹⁰⁰

An electrostatic theory using point charges, or uniformly charged spheres, however, cannot be taken as a complete explanation for the behavior of complex ions.⁹⁹ The well known reactivity of, for example, iron (III) complexes compared to

¹⁰⁰F. Basolo and R. Pearson, Mechanisms of Inorganic Reactions, John Wiley and Sons., Inc., New York, 1958, Chapter 3.

the inertness of those of cobalt (III) are more easily explained on the basis of crystal field theory. This theory is also applicable in explaining the differences not only between the various transition metal ions, but also between the transition and non-transition ions in general.

Furthermore, the mechanism for the relaxation process in 2-2 valent sulfates, i.e. the step-wise removal of water molecules from between the cation and anion in ion pairs, has received support from considerations^{88,98} based on crystal field theory. The essence of this theory is that the five d orbitals, which are equal in energy in the gaseous metal ion, acquire quite different energies in the presence of the electrostatic field due to ligands (the crystal field). The electrons of a central atom with an incomplete electronic shell are not spherically distributed about the central atom. Instead the electrons will preferentially occupy the orbitals which lie furthest away from the ligands. This will lead to an increased stabilization of the complex ion beyond that which a simple model based on spherical charge distribution would predict. In other words, by preferentially filling the low-energy d orbitals, the d electrons can stabilize the system compared to random filling of the d orbitals as required by the simple electrostatic theory. The gain in bonding energy achieved in this way is the crystal field stabilization energy (CFSE). Complexes in which more of the electrons are in the lower energy d orbitals are more stable than complexes in which all of the d orbitals are equally filled.

One of the advantages of the crystal field theory is that many properties can be correlated and in some cases quantitative

predictions made. The CFSE can be calculated by using wave functions and perturbation theory; this is absolute but complicated. Energy differences between orbitals, however, can be calculated from measurements of the energy splitting obtained in the visible absorption spectra of complexes.

The quantity $10 Dq$ is defined as the energy separation between the lower and upper levels. Since from symmetry considerations, the d_{xy} , d_{xz} , and d_{yz} are equal in energy, as are the $d_{x^2-y^2}$ and d_{z^2} levels, an assignment can be made of $-4 Dq$ for the energy of the former and $+6 Dq$ for the latter for octahedral complexes. These numbers follow because of the rule that the CFSE must be zero if all levels are equally occupied.⁹⁹

An approximate value for $10 Dq$ is given by

$$10 Dq = \frac{5eqa^4}{3r^5} \quad \text{or} \quad 10 Dq = \frac{5e\mu a^4}{r^6}$$

where e is the charge on the electron, q or μ is the charge or dipole moment of one ligand, r is the distance from the center of the ion to the center of the ligand, and a^4 is the average value of the fourth power of the radius of the d electrons.

Basolo and Pearson¹⁰⁰ have pointed out that it should be possible to estimate the contribution to the total activation energy due to crystal field stabilization. To do this, one must evaluate the total electrostatic energy of the transition state in which an extra ligand has been added in the case of a displacement (S_N2) mechanism, or one ligand is partly removed in the case of a dissociation (S_N1) mechanism. Exact calculation becomes very difficult because of the irregular geometry of the

complexes in question. Moreover, calculation of the crystal field activation energy is dependent on the mechanism and therefore on the nature of the transition state. Different values will be obtained for calculations based on a strong crystal field as compared to a weak field. (For a discussion of this problem, see Chapter 3 in Basolo and Pearson.)

For the present purpose, values of the crystal field stabilization energy calculated for a ligand in the presence of a weak field are shown¹⁰⁰ in Table 12. The rate constants for mechanism j are shown for comparison. There appears to be some correlation between the rate constants and the CFSE. The cations characterized by slower rate constants are those expected to be the most stable according to crystal field theory. The position of Cu^{++} in this table is the most obvious anomaly. It is probable that crystal field stabilization is only a partial explanation of the observed order of rate constants.

An interesting correlation exists between the rate constants for mechanism j and calculated heats of solvation of individual ions. Enthalpies of solution may be calculated from the Born-Haber cycle:

$$\Delta H_s = -U + \Delta H_+ + \Delta H_- \quad (186)$$

where ΔH_s is the heat of solvation of a salt, U is the lattice energy of the solid crystal, and ΔH_+ and ΔH_- are the individual heats of solvation for cations and anions. The lattice energy is given by

$$U = U_0 + \int_0^T (C_p \text{ salt}) dT - \sum_{\text{ions}} \int_0^T (C_p \text{ gas ions}) dT \quad (187)$$

Table 12: Relation of the rate constants to the crystal field stabilization energy and enthalpy of hydration of cations.

MeA	k_1 sec ⁻¹	k_{-1} sec ⁻¹	CFSE ¹⁰⁰ kcal (g ion) ⁻¹	$-\Delta H_1$ kcal (g ion) ⁻¹ for cation
BeSO ₄	1 x 10 ²	1.3 x 10 ³		-
CuSO ₄	10 ⁴	1 x 10 ⁶	34	536
ZnSO ₄	-	-		528
NiSO ₄	3 x 10 ⁴	1 x 10 ⁵	67	516
MgSO ₄	1 x 10 ⁵	8 x 10 ⁵		490
MgS ₂ O ₃	1 x 10 ⁵	1.5 x 10 ⁶		490
MgCrO ₄	1 x 10 ⁵	1.5 x 10 ⁶		490
CoSO ₄	2 x 10 ⁵	2.5 x 10 ⁶	45	504
FeSO ₄	-	≥ 4 x 10 ⁶ *	22	500
MnSO ₄	4 x 10 ⁶	2 x 10 ⁷	0	479
CdSO ₄	-	2 x 10 ⁸ *	0	462
CaSO ₄	~10 ⁷	~10 ⁸		410

*These values will be discussed in a future technical report by the present authors.

Bernal and Fowler¹⁰¹ estimated the individual cationic enthalpies of solvation by the following procedure. In small ions, the energy of hydration may be assumed to be essentially coulombic and thus inversely proportional to the ionic radius.

¹⁰¹Bernal and Fowler, J. Chem. Phys. 1, 515 (1933).

If the ionic radius of the cation is about the same as that for the anion (as in KF), the individual heats of hydration can be obtained by dividing the measured heat of hydration of the salt by two. The value thus obtained ($-95.5 \text{ kcal g-ion}^{-1}$ for K^+ and F^-) must be corrected for the different spatial arrangement of water around cations and anions. This arises from the non-central location of the dipole in a water molecule. The result is $-97 \text{ kcal g-ion}^{-1}$ for the enthalpy of solvation of F^- . On this basis, heats of hydration of cations other than potassium may be obtained from experimental heats of hydration of salts containing the fluoride ion. Although the exact procedure used by Bernal and Fowler is open to some criticism,¹⁰² the values thus obtained should at least show significant relative differences for different cations.

Conway and Bockris¹⁰³ tabulate the results of various methods of calculating individual heats of solvation. Some of Bernal and Fowler's results are reproduced in Table 12. Comparison with the rate constants for mechanism j shows that there is a very strong correlation of the individual ionic heats of solvation with the rate constants k_1 and k_{-1} . The latter increase with more positive enthalpies of solvation.

Protolytic reactions

The relaxation processes in electrolytes of types other than 2-2 valent, particularly 1-1 electrolytes, have already

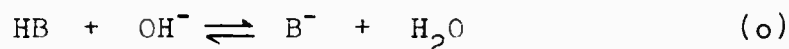
¹⁰²J. O'M. Bockris (Ed.), Modern Aspects of Electrochemistry, Vol. I, Butterworths Scientific Publications, London, 1954, p. 74.

¹⁰³Bockris, op. cit., p. 52.

been mentioned as being primarily associated with protolytic reactions. We are here concerned with, for example, the dissociation equilibrium of a weak acid (HB) in water solution



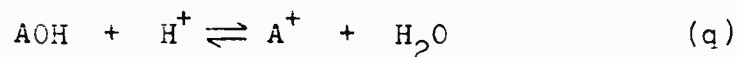
where B^- is a base in the usual sense, e.g. an acid anion or a basic anhydride such as NH_3 . Weak acids can also be involved in reaction with hydroxyl ions according to the scheme



Analogous considerations also exist for weak bases of the type AOH:



and



Rate constants for many of the reactions corresponding to eqs. n to q can be determined by the various relaxation methods. These include the Wien Effect II (field dissociation effect), temperature jump, pressure jump, as well as acoustic absorption.¹⁰⁴ Several rate constants as determined by these techniques are collected in Table 13. The first column contains the reaction under consideration; the second, the specific rate constants for the indicated ion recombination; the third, the specific rate constant for dissociation; the fourth, the method of study; and finally, the pertinent literature references. The relaxation time for these reactions is given by

¹⁰⁴For a brief discussion of these methods, see pp. 33-40.

Table 13: Rate constants for protolytic reactions

Reaction	k_R $M^{-1} \text{sec}^{-1}$	k_D sec^{-1}	Method of study	Reference
$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$	1×10^{11}	$\sim 10^9$	sound absorption	105
$H^+ + HCOO^- \rightleftharpoons HCOOH$	5×10^{10}	$\sim 10^7$	-	106 [†]
$H^+ + CH_3COO^- \rightleftharpoons CH_3COOH$	4.5×10^{10}	8×10^5	Wien Effect II	107
$H^+ + HSO_3^- \rightleftharpoons SO_2 \cdot H_2O$	2×10^8 *	3.4×10^6 *	sound absorption	108
$H^+ + HCO_3^- \rightleftharpoons CO_2 \cdot H_2O$	5.6×10^4 *	4.3×10^{-2} *	-	109 [†]
$H^+ + HS^- \rightleftharpoons H_2S$	7.5×10^{10}	4.3×10^3	Wien Effect II	110
$H^+ + F^- \rightleftharpoons HF$	1×10^{11} *	6.7×10^7 *	"	110
reaction v, meta	4.2×10^{10}	1.9×10^2	"	110
reaction v, para	3.6×10^{10}	2.6×10^3	"	110
$H^+ + OH^- \rightleftharpoons H_2O$	1.4×10^{11}	2.5×10^{-5}	"	111, 112, 113
$(CH_3)_3NH^+ + OH^- \rightleftharpoons (CH_3)_3N \cdot H_2O$	1×10^{10}	6×10^5	-	106 [†]
$NH_4^+ + OH^- \rightleftharpoons NH_3 \cdot H_2O$	3×10^{10}	5×10^5	sound absorption	105, 107
$HCN + OH^- \rightleftharpoons CN^- + H_2O$	3.6×10^9	5.0×10^4	"	**

*See text for a discussion of these values.

[†]The authors fail to indicate what method was used to determine these rate constants, and defer description of the experimental work to a later paper apparently not yet published (106, 109).

**These rate constants will be discussed in a future technical report by the present authors.

$$\tau^{-1} = k_D + (C_+ + C_-)k_R = k_D + 2\alpha Ck_R \quad (188)$$

(cf. eq. 87). In most cases, k_D is sufficiently smaller than $2\alpha Ck_R$, so that the measured relaxation time gives k_R directly. The constant k_D is then calculated from the known value of the dissociation equilibrium constant.

A particularly important subject is the determination of the specific rate constants for neutralization reactions:



In order to eliminate any effects of the anion and cation associated with the acid and base, respectively, the rate constants for this reaction have been determined from the dissociation of very pure water. The self-dissociation of water is not detected acoustically via eq. (87) and (89) because of the extremely small degree of dissociation α . This reaction has been studied by the dissociation field effect by Eigen and De Maeyer.¹¹¹

¹⁰⁵M. Eigen, Z. physik. Chem. (Frankfurt) 1, 176 (1954).

¹⁰⁶M. Eigen, J. Johnson, and A. Wittig, quoted in M. Eigen, Z. Elektrochem. 64, 115 (1960).

¹⁰⁷M. Eigen and J. Schoen, Z. Elektrochem. 59, 483 (1955).

¹⁰⁸M. Eigen, K. Kustin, and G. Maas, Z. physik. Chem. (Frankfurt) 30, 130 (1961).

¹⁰⁹M. Eigen, K. Kustin, and R. Munson, Z. physik. Chem. (Frankfurt), (at press, 1962).

¹¹⁰M. Eigen and K. Kustin, J. Am. Chem. Soc. 82, 5952 (1960).

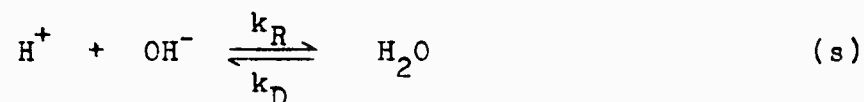
¹¹¹M. Eigen and L. De Maeyer, Z. Elektrochem. 59, 986 (1955).

¹¹²M. Eigen and L. De Maeyer, Proc. Faraday Soc. A247, 505 (1958).

¹¹³M. Eigen and L. De Maeyer in W. Hamer (ed.) The Structure of Electrolytic Solutions, John Wiley and Sons, Inc., N. Y., 1959, Ch. 5.

According to accepted theory, charge transfer associated with hydrogen ions in hydrogen-bonded media occurs through two mechanisms: (1) ordinary ion migration and (2) charge transfer through a chain transfer mechanism. For water, the latter is the predominant mechanism. In aqueous solutions, the charge chain transfer process involves the following: (1) the formation or rearrangement of a hydrogen-bonded structure of orientation favorable for a proton transfer; and (2) the charge transfer within the hydrogen bond. Many workers consider the first step to be rate-determining in water.

The relaxation time associated with the reaction



is given by

$$\tau = \frac{1}{k_D + k_R(C_{\text{H}^+} + C_{\text{OH}^-})} \quad (189)$$

where k_D and k_R are the specific rate constants for the self-dissociation of water and the recombination of ions, respectively. In this case,

$$(C_{\text{H}^+} + C_{\text{OH}^-})k_R \gg k_D$$

so that the measured relaxation time (35×10^{-6} sec at 25°C) gives k_R directly. The constant k_D is then calculated from the value of the equilibrium constant

$$K_{\text{H}_2\text{O}} = \frac{C_{\text{H}^+} C_{\text{OH}^-}}{C_{\text{H}_2\text{O}}} = 1.821 \times 10^{-16} \text{ mole liter}^{-1}$$

The value $1.4 \times 10^{11} \text{ M}^{-1} \text{ sec}^{-1}$ is obtained for the rate constant k_R . The dissociation is characterized by a much smaller constant: $k_D = 2.5 \times 10^{-5} \text{ sec}^{-1}$. Nevertheless, if one considers a situation in which no H^+ or OH^- ions are initially present in the 55 moles

liter⁻¹ present in pure water, the equilibrium concentrations of 10⁻⁷ moles liter⁻¹ H⁺ and OH⁻ are attained in less than 10⁻⁴ sec. The apparent activation energies, calculated from the Arrhenius temperature dependence of the rate constant, are 2 to 3 kcal mole⁻¹ for the recombination and about 16 kcal mole⁻¹ for the dissociation process. Further interpretation of these data is given in the literature.¹¹¹⁻¹¹³

The transfer of a proton from a water molecule to a base B⁻ generally occurs much more rapidly than the transfer of a proton from a water molecule to an adjacent one as is involved in the self-dissociation of H₂O. For example, the rate constant k_D for the dissociation of NH₃·H₂O is 5 x 10⁵ sec⁻¹, i.e. a factor of 10¹⁰ more rapid than that for the dissociation of pure water. This factor is probably associated with the presence of the easily accessible unshared electron-pair on NH₃, the difference in size between NH₃ and H₂O, and the difference in electro-negativity of oxygen and nitrogen.

It is interesting to note that the rate constants for the recombination of oppositely-charged ions are in the order of magnitude 10¹⁰-10¹¹ liter mole⁻¹ sec⁻¹. Eigen has emphasized⁸⁸ that these rate constants approach the maximum values for diffusion-controlled reactions. From equations derived by Debye¹¹⁴ for the rates of ionic processes, Eigen^{88,112,113} gives the expression

$$k_R = \frac{4\pi N Z a (D_+ + D_-)}{\exp(Z) - 1} \quad (190)$$

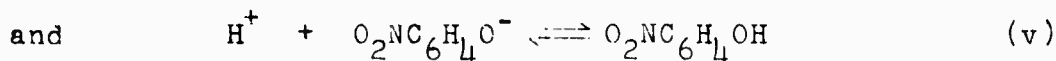
for a diffusion-controlled ionic recombination reaction where

$$Z = \frac{z_+ z_- e^2}{\epsilon a k T} \quad (191)$$

¹¹⁴P. Debye, Trans. Electrochem. Soc. 82, 265 (1942).

N is Avogadro's number, D_+ and D_- are the diffusion coefficients of the cation and anion, respectively, e is the electronic charge, ϵ the dielectric constant, and a is the effective distance to which a cation and an anion must mutually approach for combination to occur. In dilute solutions, the validity of eq. 190 is limited only by the fact that the dielectric constant depends on the effective reaction distance a , and that steric factors may restrict the total number of possible approaches for successful encounters. A comparison of the observed rate constant for the recombination of H^+ and OH^- with that given by eq. 190 shows that a reaction occurs spontaneously whenever the ions approach to within about 7.5 \AA of each other. This distance corresponds to 2 or 3 hydrogen bonds, and is sufficiently large to permit the use of the macroscopic dielectric constant. Individual differences in the specific rates of other diffusion-controlled reactions can probably be explained by the difference in valence types, in the diffusion coefficients of the partners, and, in certain cases, by steric factors.

In a study of steric effects on the rate of ionic recombination, Eigen and Kustin¹¹⁰ carried out measurements in solutions of HF, H_2S , and nitrophenol. The relaxation times were measured by means of the dissociation field effect (Wien Effect II), and correspond to the reactions



The relaxation time corresponding to these reactions is

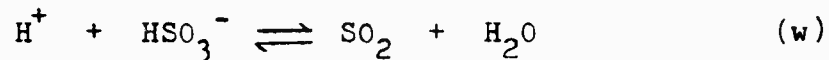
$$\tau^{-1} = k_D + (C_+ + C_-)k_R \quad (192)$$

where C_+ and C_- are the equilibrium concentrations of the cation and anion, respectively. No relaxation time was observed for the HF system; therefore, only a lower limit for the rate constant k_R could be estimated corresponding to the time-constant of the measuring apparatus. This lower limit is $k_R = 1.0 \times 10^{11} \text{ M}^{-1} \text{ sec}^{-1}$. This, however, is also close to the maximum value expected for a diffusion controlled reaction involving the recombination of univalent ions, calculated from eq. 190 with $a = 7.5 \text{ \AA}$. Therefore, $k_R = 1 \times 10^{11} \text{ M}^{-1} \text{ sec}^{-1}$ may be a reasonable value for the recombination of H^+ and F^- ions. The reverse rate constant $k_D = 6.7 \times 10^7$ is then calculated from the known value of the equilibrium constant for reaction t.

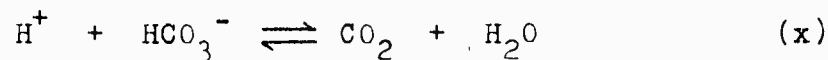
The interpretation of the steric factors associated with the recombination of the H^+ and HS^- ions (reaction u) was made in the following manner. If one assumes an effective reaction distance of 7.5 \AA and approximately the same diffusion coefficients as for H^+ and F^- , one would again expect $k_R = 1 \times 10^{11}$. However, Eigen and Kustin argue that the ion HS^- should be sterically hindered to an extent sufficient to reduce the effective collisions by about 25%. Therefore, a steric factor of about 0.75 is expected, yielding the rate constant $k_R \cong 7.5 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$. That this is in exact agreement with the experimental value is perhaps fortuitous, but it is significant that one can make quite reasonable estimates of the rate constants for diffusion-controlled ionic reactions.

The ionization of solutions of water-soluble gases constitutes an interesting type of protolytic reaction. Two such systems — water solutions of SO_2 and CO_2 — have been studied by

various relaxation techniques. The overall reactions may be represented by



and



for solutions of sulfur dioxide¹⁰⁸ and carbon dioxide,¹⁰⁹ respectively. The relaxation time corresponding to reactions w and x is

$$\tau^{-1} = k_D + (C_{\text{H}^+} + C_{\text{A}^-})k_R \quad (193)$$

Ultrasonic absorption measurements¹⁰⁸ were carried out in acidified solutions of SO_2 by the optical method.¹¹⁵ For a solution of 0.1 M total ionic strength, a single relaxation frequency of approximately 4 mc/s was observed at 20°C. From eq. 193, this yields the rate constants $k_R = 2 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ and $k_D = 3.4 \times 10^6 \text{ sec}^{-1}$. The magnitude of the absorption cross-section¹¹⁶ at this ionic strength was $(Q \lambda)_{\text{max}} = 180 \times 10^{-24} \text{ cm}^3$. Knowledge of this quantity then allows (eq. 87) the calculation of the volume change for the reaction, $\Delta V^\circ = 18 \text{ cm}^3 \text{ mole}^{-1}$, where

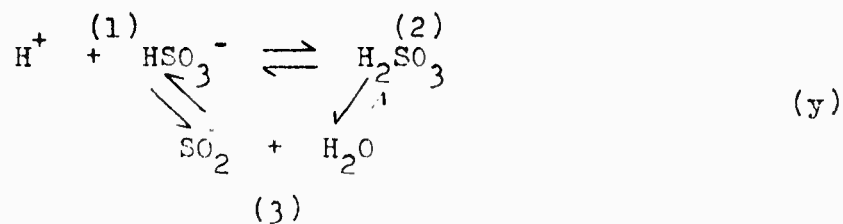
$$\Delta V^\circ = \bar{V}_{\text{SO}_2} + \bar{V}_{\text{H}_2\text{O}} - \bar{V}_{\text{HSO}_3^-} - \bar{V}_{\text{H}^+}$$

A more detailed analysis, however, shows that mechanisms w and x are in fact oversimplifications of a more probable series of

¹¹⁵See the appendix for a brief discussion of the various methods for measuring ultrasonic absorption.

¹¹⁶See p. 49 for the definition of the absorption cross-section.

equilibria and that the rate constants k_D and k_R thus obtained are the "overall" or "effective" rate constants. If one considers mathematically the mechanism



and the analogous reaction for CO_2 , one obtains the relaxation times

$$\tau_1^{-1} = k_{12}(C_{\text{H}^+} + C_{\text{HSO}_3^-}) + k_{21} \quad (194)$$

$$\tau_2^{-1} = \frac{k_{13}K_{12} + k_{23}}{1 + K_{12}(C_{\text{H}^+} + C_{\text{HSO}_3^-})} + k_{31} + k_{32} \quad (195)$$

where the subscripts refer to the rate constants and equilibrium constants for the indicated steps in reaction y. The effective constants k_D and k_R are related to the constants for the individual steps by

$$k_R = k_{13} + \frac{k_{23}}{K_{12}} \quad (196)$$

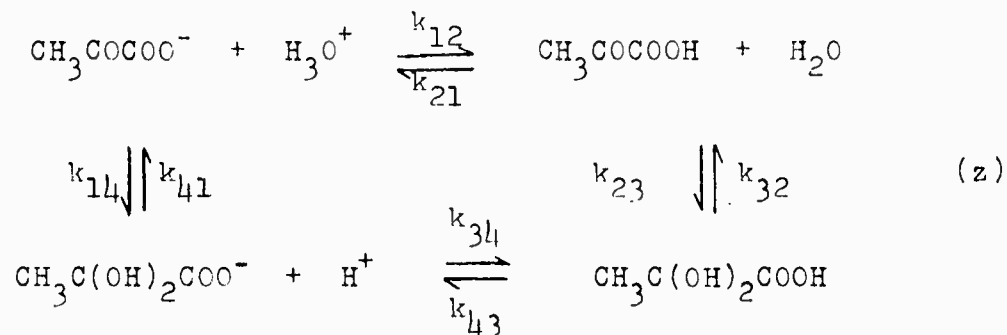
and

$$k_D = k_{31} + k_{32} \quad (197)$$

That is, a simple interpretation of the equilibria y is formal in nature and does not necessarily correspond to the true situation.

A further discussion of the mechanism and rate constants is given in the original paper.¹⁰⁸ Similar arguments with respect to the mechanism and rate constants given in Table 13 apply to reaction x as well.

Eigen and his coworkers have found that α -ketoacids undergo more complicated dissociation processes than do simple acids and bases such as those given in Table 13. On the basis of the relaxational data, the following mechanism is proposed¹¹⁷ for the dissociation of α -ketopropionic acid:



From polarographic measurements,¹¹⁸ the value of k_{12} has been obtained as $1.3 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ for a 0.55 M solution. The other rate constants were obtained from the relaxation times determined by both the pressure jump and temperature jump methods in the vicinity of 25°C . An exact analysis is complicated by the fact that the measured relaxation time involves many of the rate constants and concentrations associated with mechanism z. From measurements involving the temperature-jump method, the relaxation time was found to be 1 sec at $\text{pH} = 3.0$. This corresponds to $k_{32} = 0.5 \text{ sec}^{-1}$. Further details in the interpretation of mechanism z as well as other constants are to be found in the paper.¹¹⁷

¹¹⁷M. Eigen, K. Kustin, and H. Strehlow, Z. physik. Chem. (Frankfurt) 31, 140 (1962).

¹¹⁸M. Becker and H. Strehlow, Z. Elektrochem. 64, 813 (1960).

Thus, the measurement of relaxation times provides a means for determining the kinetic parameters of chemical processes which occur too rapidly to be studied by more conventional techniques. Relaxation times less than 10^{-6} sec are perhaps best measured by ultrasonic absorption methods; times greater than 10^{-6} may be more conveniently studied by the step-function techniques.

Future technical reports from the Ultrasonics Research Laboratories of Western Reserve University will be concerned with the experimental study of specific systems of electrolytic solutions.

APPENDIX

EXPERIMENTAL METHODS FOR THE MEASUREMENT OF ULTRASONIC ABSORPTION IN LIQUIDS

The shape of the relaxational absorption per wavelength curve (Figure 2) is of interest in indicating the frequency range over which absorption due to relaxational processes manifests itself. The two regions of linear variation of $\alpha\lambda$ with frequency are separated in frequency by a factor of approximately 10. While it is possible to study a relaxation process over a 10-fold frequency range by one experimental method, in general the location of the relaxation frequency is not known beforehand. Therefore, as wide a working range as possible is desirable. Present techniques permit the investigation of acoustic relaxation processes over the approximate frequency range 10 kc/s to perhaps 500 mc/s in liquids. In the discussion which follows, an attempt has been made only to indicate the nature of the individual experimental methods. For further details of instrumentation and experimental procedures, the reader is referred to the pertinent literature.

In general, the various methods of measuring absorption and velocity may be divided into techniques using progressive wave, standing wave, and reverberation methods. The first two methods depend on the measurement of the decrease in voltage, amplitude, or energy of the sound wave as a function of distance according to the equation.

$$I = I_0 e^{-2\alpha x} \quad (A - 1)$$

A. Progressive Wave Methods

1. Pulse Methods

In the pulse-echo method of measuring the absorption and velocity of ultrasound, a transducer is excited by short bursts of sonic energy at regular intervals. A reflector some distance away returns the pulses to the transducer. The distance between transducer and reflector is varied by moving one or the other parallel to their common axis by means of a micrometer screw. The echoes from the reflector are detected by the transducer, amplified, and displayed on a cathode ray tube provided with a time base triggered by the original pulse. Velocity and absorption are then deduced from the changes in position and amplitude of the echo as the distance between transducer and reflector is changed. A simplified block diagram of the apparatus is shown in Figure A-1.

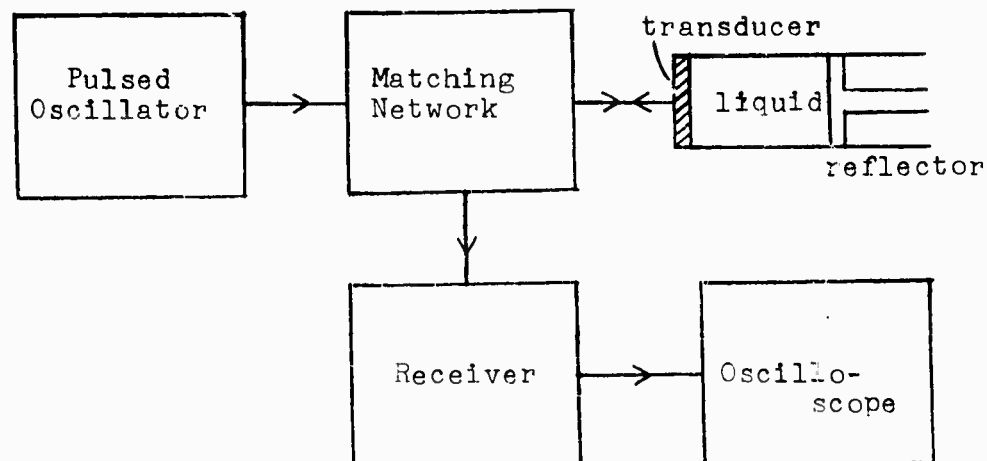


Figure A-1: Pulse-echo apparatus

This method was developed independently by Pellam and Galt¹ and Pinkerton.² Details for the construction and operation of pulse equipment are given by Andreae *et al.*³ for measurements in liquids over a range of frequencies of 1 to 200 mc/s. They estimate the error in an absorption measurement as 3% from 15 to 70 mc/s and somewhat higher outside these limits. This method has also been used successfully by, among others, Teeter,⁴ Litovitz,⁵ and Smithson and Litovitz.⁶

In the two-crystal variation of this technique, the reflecting surface is replaced by a receiver crystal. The essential features of the apparatus remain as in the pulse-echo. Among those who have used the two-crystal technique are Tamm,

¹J. Pellam and J. Galt, *J. Chem. Phys.* 14, 608 (1946).

²J. Pinkerton, *Proc. Phys. Soc. London* B62, 286 (1949).

³J. Andreae, R. Bass, E. Heasell, and J. Lamb, *Acustica* 8, 131 (1958).

⁴C. Teeter, *J. Acoust. Soc. Am.* 18, 488 (1946).

⁵T. Litovitz, *J. Acoust. Soc. Am.* 23, 75 (1951).

⁶J. Smithson and T. Litovitz, *J. Acoust. Soc. Am.* 28, 462 (1956).

Kurtze, and Kaiser;⁷ Andraee, Heasell, and Lamb⁸; and Krebs and Lamb⁹. A hydrophone can be substituted for the receiving crystal.^{10,11}

2. Radiation Pressure

The radiation pressure method depends upon the fact that when sound waves are wholly or partly absorbed or reflected by a plate they exert a pressure on it. If waves of mean energy density E are normally incident on a plate which reflects a proportion a and absorbs a proportion b of the energy, the pressure on the plate is equal to the difference between the energy densities on the two sides, $(2a + b)E$.¹² The maximum value of this quantity is $2E$, and it occurs when a is unity and b vanishes, i.e. when the plate is a perfect reflector. The radiation pressure is proportional to the mean energy density in the beam

$$P_r = kE = k \frac{I}{c} \quad (A - 2)$$

where P_r is the radiation pressure, I is the sound intensity, c the velocity, and k is a proportionality constant. The equipment is shown schematically in Figure A - 2.

To measure absorption^{by} this method,¹³⁻¹⁵ ultrasonic radiation from a quartz crystal is sent vertically upward in a

⁷K. Tamm, G. Kurtze, and R. Kaiser, *Acustica* 4, 380 (1954).

⁸J. Andraee, E. Heasell, and J. Lamb, *Proc. Phys. Soc. (London)* B69, 625 (1956).

⁹K. Krebs and J. Lamb, *Proc. Roy. Soc. (London)* A244, 558 (1958).

¹⁰L. Labaw and A. Williams, *J. Acoust. Soc. Am.* 19, 30 (1947).

¹¹M. Smith, R. Barrett, and R. Beyer, *J. Acoust. Soc. Am.* 23, 71 (1951).

¹²P. Vigoureux, *Ultrasonics*, John Wiley and Sons, Inc., 1951, p. 73.

¹³F. Fox and G. Rock, *J. Acoust. Soc. Am.* 12, 505 (1941).

¹⁴F. Fox and G. Rock, *Phys. Rev.* 70, 68 (1946).

¹⁵E. Hsu, *J. Acoust. Soc. Am.* 17, 127 (1945).

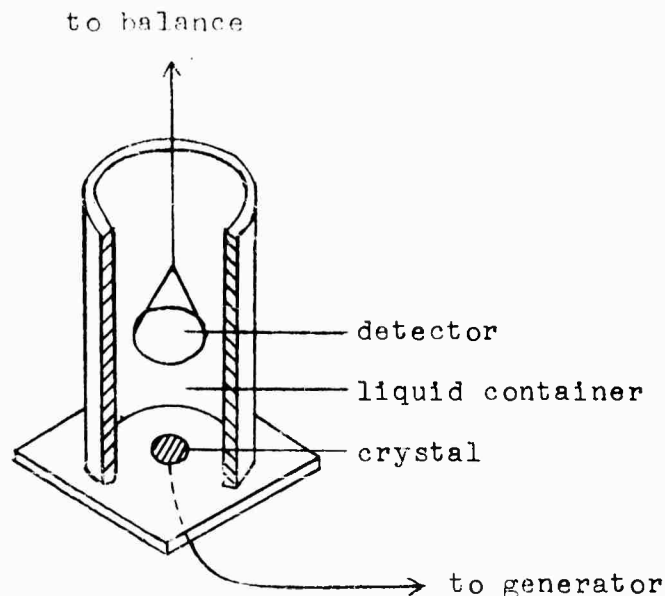


Figure A-2: Diagram of apparatus for absorption measurement by radiation pressure

container filled with the liquid under investigation. A flat metal plate (the detector) is suspended in the beam from one end of a sensitive balance. The difference between the apparent weight of the detector in the presence and absence of the sound beam is proportional to the sound intensity. By changing the separation of the source and detector, a quantity similarly proportional to the intensity at the new position can be measured.

As described, the method must be carefully examined for several sources of error: the effects of the surface tension of the measured liquid on the supporting wire of the detector, the effect of which is to cause a "sticking" of the detector near the position of balance; reflections from the walls of the container or from the face of the detector which may lead to standing waves; and hydrodynamic flow set up by the passage of the sound beam, causing an extra force which is recorded by the detector. With special care, however, these effects may be reduced or eliminated.^{16,17}

¹⁶R. Beyer and M. Smith, J. Acoust. Soc. Am. 18, 424 (1946).

¹⁷M. Smith and R. Beyer, ibid. 20, 608 (1948).

In a later development of this method, Barrett, Beyer, and McNamara¹⁸ eliminated some of these effects by modulating the ultrasonic signal with an audio frequency. The detector plate was then replaced with a condenser microphone and the output of the low frequency voltage measured. The method as described has been operated over the frequency range 9-27 mc/s with an accuracy which is said to be comparable to that of the pulse-echo technique.

3. Optical Method

The optical method depends on the fact, shown independently by Lucas and Biquard¹⁹ and Debye and Sears,²⁰ that parallel light incident on a beam of ultrasonic waves in a liquid or a solid is diffracted by the waves in much the same way as by a ruled grating. The deflection θ of the n^{th} order spectrum is given in terms of the wave-lengths Λ and λ of light and sound by

$$\sin \theta = n \frac{\Lambda}{\lambda} \quad (\text{A} - 3)$$

This effect can be used to determine both velocity and absorption. For velocity measurement, a photograph of the diffraction pattern is taken at a distance d from the sound beam which is sufficiently large for the distance i between consecutive fringes to be measured with accuracy. Replacing $\sin \theta$ of eq. A - 3 by i/d for sufficiently small values of θ gives

$$c = \frac{\Lambda fd}{i} \quad (\text{A} - 4)$$

For the measurement of ultrasonic absorption use is made of the fact that as the light is diffracted, the intensity of the central fringe is a measure of the acoustical intensity. Thus, by measuring light intensity as a function of distance, the absorption coefficient of the sound may be determined. This technique has been used successfully by many workers among

¹⁸R. Barrett, R. Beyer, and F. McNamara, J. Acoust. Soc. Am. 26, 966 (1954).

¹⁹R. Lucas and P. Biquard, J. phys. radium 3, 461 (1932).

²⁰P. Debye and F. Sears, Proc. Natl. Acad. Sci. U.S. 18, 409 (1932).

whom are Biquard,²¹ Willis,²² Sette,²³ and Kurtze and Tamm.²⁴ The latter made measurements over the frequency range 3-100 mc/s, and estimated the accuracy at about $\pm 5\%$.

B. Standing Wave Methods

In the interferometer method, the basic design of which was developed by Pierce²⁵ for measurement of velocity, a flat plate is used as a transducer. A plane reflector is set accurately parallel to the transducer and at a distance which can be varied. As the piston or reflector is moved, standing waves will result within the fluid. The formation of the standing wave field can be recognized through changes in the electrical impedance of the transducer.

The interferometer also has been used to measure absorption. The variation in the current reading in the output amplifier stage of the r.f. generator is proportional to the excess pressure in the sound beam at the face of the crystal. If the reflector is moved through a distance x , the path length is increased by $2x$, and hence the pressure of the returning wave will be decreased by the factor $e^{-2\alpha x}$. This method is useful for liquids in which the absorption coefficient is greater than 0.1 cm^{-1} .

C. Reverberation Methods

At very low frequencies, the progressive and standing wave techniques just described become difficult to use since long path lengths, large volumes of liquid, and large transducers are required. For low-absorbing liquids below 1 mc/s, moreover, decreases in sound amplitude due to divergence of the beam may equal or exceed that due to absorption. The lower limit is thus set by the absorption of the liquid as well as by the physical dimensions of the absorption-measuring device. For example, α/f^2 for water at 25°C is $25 \times 10^{-17} \text{ sec}^2\text{cm}^{-1}$. The path length required at 100 kc/s for the reduction by just 10% of the amplitude of a plane wave is about 1000 meters. Such distances are possible in the laboratory only with a multi-reflection

²¹P. Biquard, Sur l'absorption des ondes ultrasonores par les liquides, Masson, Paris, 1935.

²²F. Willis, J. Acoust. Soc. Am. 19, 242 (1947).

²³D. Sette, J. Chem. Phys. 18, 1592 (1950).

²⁴G. Kurtze and K. Tamm, Acustica 3, 33 (1953).

²⁵G. Pierce, Proc. Amer. Acad. Arts Sci. 60, 271 (1925).

technique, and in fact one must turn to the open seas and lakes if measurements are to be made²⁶ with simple send-receive techniques.

Reverberation measurements within a liquid-filled vessel provide an opportunity to utilize the multiple reflection technique. The absorption coefficient can be calculated from the rate of decay of sound intensity within the vessel. If all losses occur within the bulk of the liquid, the intensity I is dependent in time according to the equation

$$I = I_0 e^{-2\alpha ct} \quad (A-5)$$

where c is the propagation velocity and I_0 is the intensity at zero time. This equation may be rewritten as

$$\alpha = - \frac{(.115}{c} \frac{db}{t}) \quad (A-6)$$

where db is the change in 10 log I which occurs in time t . Thus the measurement of the ringing time t over a fixed decibel range may be directly converted to α .

1. Resonance method (spherical resonator)

A resonator filled with the liquid to be investigated is excited as nearly as possible at a radial normal mode of oscillation. Such a mode is characterized by a minimum of boundary losses. After stopping the excitation the decay constant for the system is measured. In general, the wall (boundary) losses are dependent upon the liquid in the vessel, but to a good approximation a correction for the wall losses can be made by subtracting the decay constant of the same normal mode of oscillation measured when the resonator is filled with a standard liquid of known absorption and nearly the same acoustic impedance. This is particularly ^{true} when the calibrating liquid is water and the measured solutions are dilute salt solutions. In Fig. A-3 is shown a typical arrangement for the spherical resonator method. This method is the result of work by Leonard and

²⁶L. Liebermann, J. Acoust. Soc. Am. 20, 868 (1948).

Wilson²⁷⁻³⁰, Kurtze and Tamm³¹, and Moen³². Leonard and his group used a 12-liter spherical resonator in early work and later a 50-liter resonator over the frequency range 40 kc/s to 400 kc/s, while Kurtze and Tamm worked with a 24-liter resonator from about 10 kc/s to 50 kc/s.

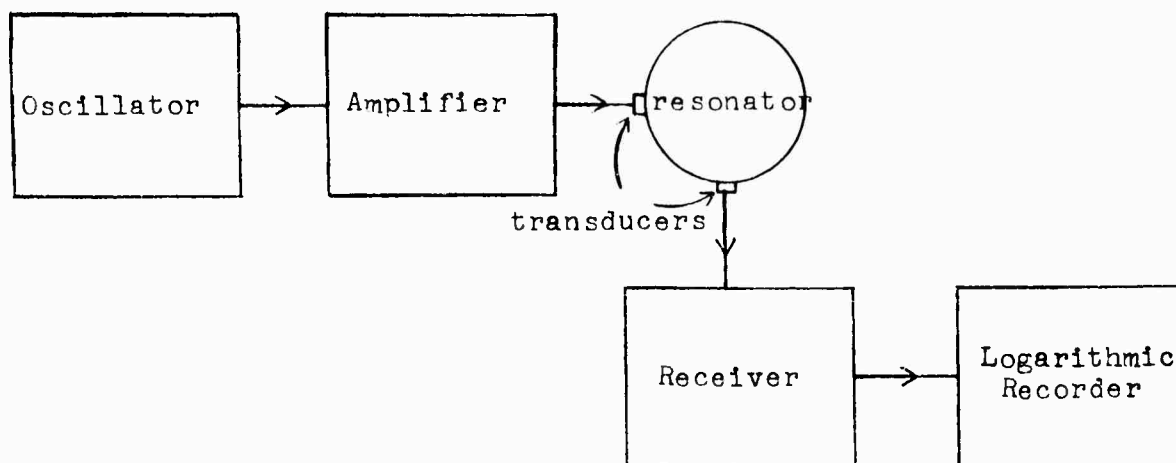


Figure A-3: Spherical resonator apparatus

The work of Karpovich³³ is particularly significant in that he showed that the boundary losses are very much dependent upon the liquid in the resonator. He used a series of calibration

²⁷R. Leonard, J. Acoust. Soc. Am. 18, 252 (1946).

²⁸Ibid. 20, 224 (1948).

²⁹R. Leonard, Absorption in Liquids by a Resonator Method, Tech. Report No. 1 (Office of Naval Research Contract N-6-onr-27507), University of California, Los Angeles, California, June, 1950.

³⁰O. Wilson and R. Leonard, Absorption of Ultrasonic Waves in Aqueous Solutions of Magnesium Sulfate, Tech. Report No. 4 (Office of Naval Research Contract N-6-onr-27507), University of California, Los Angeles, California, June, 1951

³¹G. Kurtze and K. Tamm, Acustica 3, 33 (1953).

³²C. Moen, J. Acoust. Soc. Am. 23, 62 (1951).

³³J. Karpovich, J. Acoust. Soc. Am. 26, 819 (1954).

liquids of widely different absorption coefficients in order to determine wall losses. The accuracy of the method is not great, and depends upon the number of measurements taken as well as the magnitude of the absorption relative to the boundary losses. Karpovich estimates that the accuracy of a smooth curve drawn through the lowest points to be 5-10%.

The limitations of the method are as follows. At very low frequencies absorption coefficients are so small that any error in calculating the wall losses is significant. At high frequencies, the various radial and non-radial modes lie very close together; hence it is difficult to recognize radial modes. Furthermore, the adjustment of the signal generator to a radial mode, because of its sharpness, is difficult. If non-radial modes are excited, wall losses are much greater.

2. Statistical reverberation

This method is similar to the resonance method in that ringing times of a system are measured, but instead of attempting to excite single modes of normal oscillation, a diffuse sound field containing many modes statistically distributed about a selected center frequency is employed. An approximately exponential decay results which is the mean decay of all the excited modes. Since the location of normal modes is not involved, the method may be used at frequencies higher than those normally employed with the single mode method. Mulders³⁴ used aluminum cylinders from 500 to 1500 kc/s, and Kurtze and Tamm³¹ carried out their measurements in aluminum tanks of 100 liter capacity over the frequency range 50-1000 kc/s. The precision of the measurements is comparable to that of the resonance method; the accuracy is contingent on the availability of suitable liquids of known absorption for determining wall losses.

D. Direct Methods

1. Acoustic streaming

Another method for measuring the absorption coefficient of liquids is provided by the rate of acoustic streaming which results when a plane progressive wave is propagated through an attenuating medium. According to Poiseuille, the flow velocity v_0 of a liquid along the axis of a tube of radius r and length d is given by

$$v_0 = \frac{\Delta P r^2}{4 \eta d} \quad (A-7)$$

³⁴C. Mulders, Appl. Sci. Research B1, 149 (1949); B1, 311 (1950).

where ΔP is the difference in pressure between the ends of the tube and η is the coefficient of shear viscosity of the fluid.

This method was first used by Piercy and Lamb³⁵ near 1 mc/s to measure absorption in liquids. Their experimental arrangement is shown in Figure A-4 and involves the use of a beam of progressive waves in a main tube and a small side tube

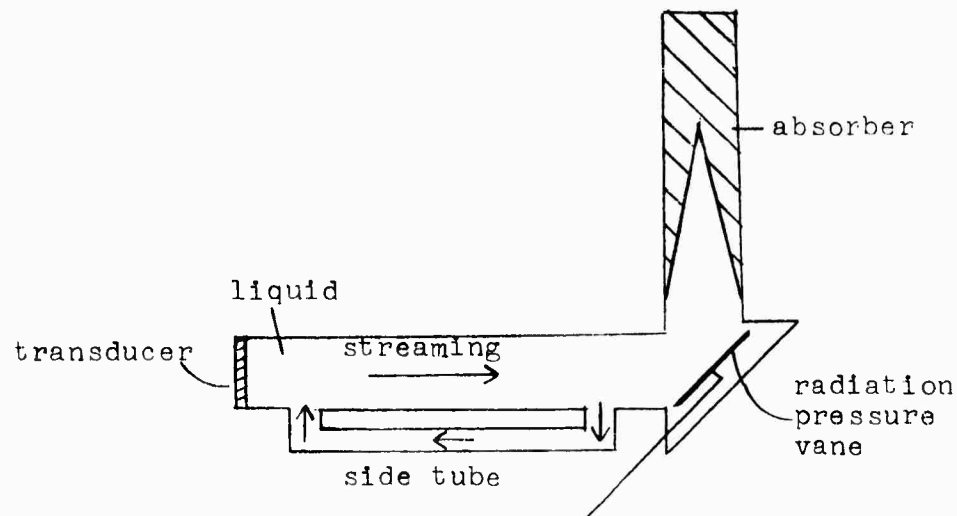


Figure A-4: Apparatus for measurement of ultrasonic absorption from acoustic streaming.

which provides a return path for the streaming. The streaming velocity in the side tube is

$$v_0 = \frac{E_0 r^2 (1 - e^{-2\alpha d})}{4\eta d} \quad (\text{A-8})$$

where E_0 is the acoustic energy density at the end of the side tube nearest the transducer. The pressure difference ΔP arises from the change in radiation pressure due to attenuation of the sound wave over a pathlength d in the tube. The velocity v_0 was obtained by following the motion of small aluminum particles in the side tube by means of a microscope. The energy density E_0 is determined by the radiation pressure vane. At 1 mc/s Piercy and Lamb obtained results good to within about 10%

³⁵J. Piercy and J. Lamb, Proc. Roy. Soc. (London) A226, 53 (1954).

for several liquids. In a later development,³⁶ Hall and Lamb extended the frequency range of this method down to 100 kc/s with an accuracy estimated at $\pm 11\%$ at 130 kc/s in a highly absorbing liquid such as carbon disulfide.

2. Thermal and calorimetric methods

These methods arise from the fact that sound energy absorbed in a medium is converted to thermal energy. This principle has been applied to the measurement of the absorption coefficient in liquids by measuring the temperature rise associated with the sound absorption. It has been shown³⁷ that the initial rate of temperature rise in an absorbing medium is given by

$$\left(\frac{dT}{dt}\right)_0 = \frac{\alpha I}{\rho C_s} \quad (\text{A-9})$$

where I is the acoustic intensity, ρ the density, C_s the heat capacity, and α the absorption coefficient of the medium. Thus, a measurement of the initial temperature rise in the liquid and knowledge of the quantities ρ and C_s , allows the calculation of either the absorption coefficient if the absolute sound intensity is known, or of the intensity if the propagation is carried out in a medium of known absorption. This method has been applied³⁸ essentially as described to the measurement of the absorption coefficient in castor oil in the vicinity of 1 mc/s. Rectangular pulses of sound energy of one second duration were propagated through castor oil. The resulting temperature rise was detected by means of a copper-constantan thermocouple. In practice, corrections must be applied for heat conduction in the thermocouple wires and for boundary losses.

Apparatus is presently under construction in the Ultrasonics Research Laboratories of Western Reserve University for the measurement of ultrasonic absorption by thermal techniques below 1 mc/s. In pure organic liquids such as castor oil, direct measurement of the temperature rise by means of sensitive thermistor probes appears feasible. In the case of solutions of electrolytes, it may be more convenient to measure the change in electrical conductivity associated with the temperature rise.

Parthasarathy and Mathur's^{39,40} variation of the thermal method for measuring ultrasonic absorption has resulted in an

³⁶D. Hall and J. Lamb, Proc. Phys. Soc. B73, 354 (1959).

³⁷W. Fry and R. Fry, J. Acoust. Soc. Am. 26, 294 (1954).

³⁸W. Fry and R. Fry, J. Acoust. Soc. Am. 26, 311 (1954).

³⁹S. Parthasarathy and S. Mathur, Nature 178, 378 (1956).

⁴⁰S. Parthasarathy and S. Mathur, Ann. Phys. 19, 242 (1956).

essentially calorimetric technique. A strong beam of ultrasonic waves is produced in a liquid in a tank which is surrounded by a constant temperature bath. A brass cell with two thin mica windows to permit the passage of sound is filled with the same liquid and placed in the tank. Under ultrasonic radiation, the liquid heats and eventually reaches a constant temperature when the ultrasonic heating is balanced by conduction losses. The temperature difference between the liquid in the cell and that in the tank is then measured with a sensitive thermocouple. The steady-state temperature difference is related to the acoustic intensity and absorption coefficient by

$$I_0(1 - e^{-2\alpha d}) = JH = k\Delta T = K\Theta_1 \quad (\text{A-10})$$

where I_0 is the sound intensity at the first mica window in the cell, d is the length of the cell, H is the heat difference between the tank and cell, J is Joule's mechanical equivalent of heat, Θ_1 is a galvanometer deflection corresponding to the temperature difference ΔT , and k and K are constants.

The method may be used as described if one knows the sound intensity I_0 , or the measurement may be repeated with the cell positioned at some distance x from the first position within the tank. Then

$$I_0(1 - e^{-2\alpha d}) e^{-2\alpha x} = K\Theta_2 \quad (\text{A-11})$$

In this case, neither the proportionality constant nor the absolute sound intensity is needed, since

$$\alpha = \frac{\ln \frac{\Theta_1}{\Theta_2}}{2x} \quad (\text{A-12})$$

Necessary precautions include the proper alignment of the cell so that the movement is along the axis of the sound beam, and the elimination of reflections from the remote end of the tank. Measurements reported by this method in various organic liquids at 5 mc/s are in good agreement with those by other methods.

Further details concerning many of these methods are to be found in the literature.⁴¹

⁴¹See, for example, Z. Elektrochem. 64, 65 (1960) and 64, 73 (1960).

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