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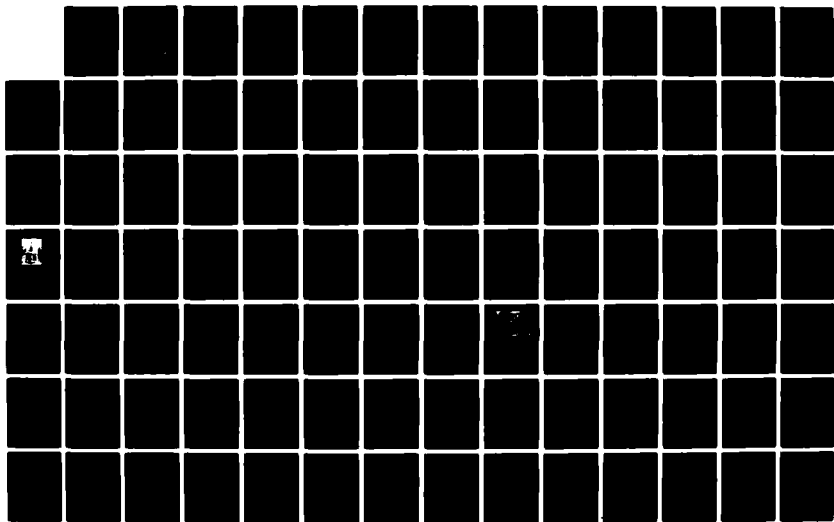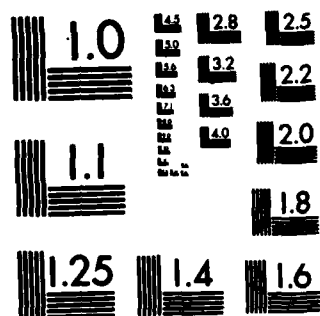   CA MARINE PHYSICAL LAB V P SIMMONS 15 JAN 83
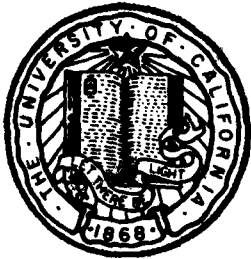UNCLASSIFIED   MPL-U-11/83 N00014-75-C-0749   F/G 20/1   NL

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INVESTIGATIONS OF THE 1 KHZ SOUND ABSORPTION IN SEA WATER

Vernon Pitkin Simmons

SIO REFERENCE 83-1

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INVESTIGATIONS OF THE 1 KHZ SOUND ABSORPTION IN SEA WATER

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER SIO Reference 83-1	2. GOVT ACCESSION NO. AD-A124888	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) INVESTIGATIONS OF THE 1 KHZ SOUND ABSORPTION IN SEA WATER		5. TYPE OF REPORT & PERIOD COVERED Summary
		6. PERFORMING ORG. REPORT NUMBER MPL-U-11/83
7. AUTHOR(s) Vernon Pitkin Simmons		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0749
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of California, San Diego, Marine Physical Laboratory of the Scripps Institution of Oceanography, San Diego, California 92152		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research, Department of the Navy, Code 220, 800 North Quincy Street, Arlington, Virginia 22217		12. REPORT DATE 15 January 1983
		13. NUMBER OF PAGES 145 pages
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Document cleared for public release and sale; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered r Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

sound absorption, seawater, boric acid

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Using a combination of sound absorption data from a large spherical resonator and relaxation frequency data from the temperature jump technique, it has been demonstrated that there is an increased sound absorption in sea water below approximately 1 kHz. The absorption mechanism has been traced to a chemical relaxation of boric acid. Observed and calculated data are in general agreement when a two step, three state boric acid ionization reaction is postulated. The observed sound absorption is attributed to the unimolecular second step of this reaction, with the faster bimolecular first

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step being of low sound absorption magnitude and under diffusion control. The magnitude of the observed sound absorption is approximately nine times greater than the absorption calculated by considering only the contribution from the high frequency magnesium sulfate effect. There is an effect of bicarbonate on the low frequency absorption presumably through the buffering effect on the hydroxyl ion.

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LIST OF SYMBOLS

A	Coefficient matrix defined in equations (1-12) to (1-14).
a_H	Activity of hydrogen ion.
a_{OH}	Activity of hydroxyl ion.
a_{H_2O}	Activity of water.
B	Unit diagonal matrix.
C	Concentration.
c	Phase velocity.
c_p	Specific heat capacity at constant pressure.
d	Thickness of the wall of the spherical resonator.
E_a	Arrhenius energy of activation.
f	Frequency.
f_m	Frequency of a radial mode of oscillation for a resonator.
f_r	Relaxation frequency.
ΔH^o	Standard enthalpy change for a reaction.
i	Square root of -1.
j	Normal reaction mode.
K	Equilibrium constant.
K_p	Equilibrium constant at pressure p.
K_w	Equilibrium constant for water.
K_γ	Activity coefficient equilibrium constant.
K_Σ	Total equilibrium constant.

K'	Apparent equilibrium constant.
K_1'	Wave number.
k_{12}	Rate constant.
M	Molal concentration.
m	Mode number.
n	Number of reaction steps.
P	Pressure
p^K	Negative of the common log of the equilibrium constant.
q	Unit normalization factor.
R	Perfect gas constant.
R_1	Radius of the spherical resonator.
S	Entropy.
s	State number.
T	Absolute temperature.
t	Time.
$\bar{v}$	Complex sound velocity.
V	Volume.
$\bar{V}^o$	Standard partial molal volume.
$\bar{V}^{o\bullet}$	Standard partial molal volume in NaCl solution.
$\Delta\bar{V}^o$	Standard volume change for a reaction.
ΔV_j	Volume change in normal mode j for reaction in new coordinate system.
$\Delta\bar{V}'$	Apparent volume change for a reaction.

α	Amplitude absorption coefficient.
β_o	Compressibility for pure solvent.
β_r	Chemical compressibility.
β_s	Adiabatic compressibility.
Γ	Ionic strength of solvent.
γ_i	Activity coefficient of the ith reactant or the jth product.
θ	Parameter to define extent of reaction.
λ	Wave length.
υ	Stoichiometric coefficient.
$\Delta\xi_s$	Extent of reaction for a particular state s.
ρ	Density.
σ	*Dissociation constant.*
τ	Relaxation time.
τ_I	Relaxation time for the first step of a multistep reaction.
τ_{II}	Relaxation time for the second step of a multistep reaction.
τ_i	Indicator relaxation time.
ω	Angular frequency.
Φ	Transfer function.
ϵ	Error factor in equation (3-3).
$\Delta\bar{\kappa}^0$	Standard partial molal isothermal compressibility.
Π	Transformation matrix defined in equation (I-25).

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ACKNOWLEDGMENTS

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ABSTRACT OF THE DISSERTATION

Investigation of the 1 kHz Sound Absorption in Sea Water

by

Vernon Pitkin Summons

Doctor of Philosophy in Oceanography

University of California, San Diego, 1975

Professor Fred N. Spiess, Co-Chairman

Doctor Frederick H. Fisher, Co-Chairman

Using a combination of sound absorption data from a large spherical
resonator and relaxation frequency data from the temperature jump technique,
it has been demonstrated that there is an increased sound absorption in sea
water below approximately 1 kHz. The absorption mechanism has been
traced to a chemical relaxation of boric acid. Observed and calculated data
are in general agreement when a two step, three state boric acid ionization
reaction is postulated. The observed sound absorption is attributed to the
unimolecular second step of this reaction, with the faster bimolecular first

step being of low sound absorption magnitude and under diffusion control. The

magnitude of the observed sound absorption is approximately nine times

greater than the absorption calculated by considering only the contribution

from the high frequency magnesium sulfate effect. There is an effect of

bicarbonate on the low frequency absorption presumably through the buffering

effect on the hydroxyl ion.

I. HISTORICAL BACKGROUND AND STATEMENT OF THE PROBLEM

Ever since the first scientific measurements of sound absorption in the ocean by Stephenson (1935) indicated that absorption values were markedly larger than fresh water values, there has been great interest in explaining and understanding the anomalies noted. With the advent of World War II, a strong priority was established to explain the increased sound absorption in sea water. Observing that standard shear and volume viscous effects discussed by Herzfeld and Litovitz (1959) were not sufficient explanation and the magnitude of the structural relaxation of water, as proposed by Hall (1948), was too small, Liebermann (1949) proposed a chemical mechanism related to the displacement of ionic equilibria by the pressure front of a sound wave. That same year, Leonard, Combs and Skidmore (1949) published data which confirmed that below approximately 70 kHz in $4^{o}C$ sea water the anomalous increase in sound absorption was due to magnesium sulfate. Subsequent work by Wilson (1951) indicated that the acoustic pressure absorption was caused by a unimolecular $MgSO_4$ reaction. In a later article, Barthel (1952) reviewed Wilson's data and observed that an ionic dissociation of $MgSO_4$ was at least as likely as a unimolecular process. Observing the effect of dielectric constant on $MgSO_4$ sound absorption, Bies (1953) stated that ionic dissociation was probably the most important mechanism. The exact reaction process of the $MgSO_4$ was not adequately resolved until the work of Eigen (1957) indicated a two or three step reaction process coupling both ionic

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dissociation and unimolecular steps could be used to explain a majority of the observed data. A more definitive paper by Eigen and Tamm (1962) on $MgSO_4$ has achieved general acceptance of a three step reaction process; however, only two of the proposed three relaxation times could be located. The work of Atkinson and Petrucci (1966) indicated that a small amplitude intermediate reaction could be observed in the data, thus providing the missing relaxation time and thus confirming the Eigen and Tamm model.

In 1964, Thorp (1965) compiled a series of open ocean sound absorption data at frequencies below the $MgSO_4$ absorption peak. The data represented observations by eight different authors primarily for the Atlantic and Mediterranean area. When absorption versus frequency was plotted, there appeared to be an increase in absorption below 1 kHz which was up to ten times greater than the $MgSO_4$ effect, which is the basis for the Schulkin and Marsh (1962) curve, figure 1. The general shape of the curve is reminiscent of the chemical effects caused by $MgSO_4$ at higher frequencies. Experimental studies in Lake Superior by Browning, Jones, Mellen and Thorp (1968) indicated a similar excess absorption in fresh water. In an attempt to explain both ocean and Lake Superior absorption, Fisher (1970) postulated a multistep bicarbonate absorption. Although additional work did not substantiate the proposed multistep bicarbonate absorption for fresh water, the proposal did lead to temperature jump studies by Yeager, Fisher, Miceli and Bressel (1973) which did confirm a low frequency relaxation in sea water. The original observations in Lake Superior were not confirmed by data from

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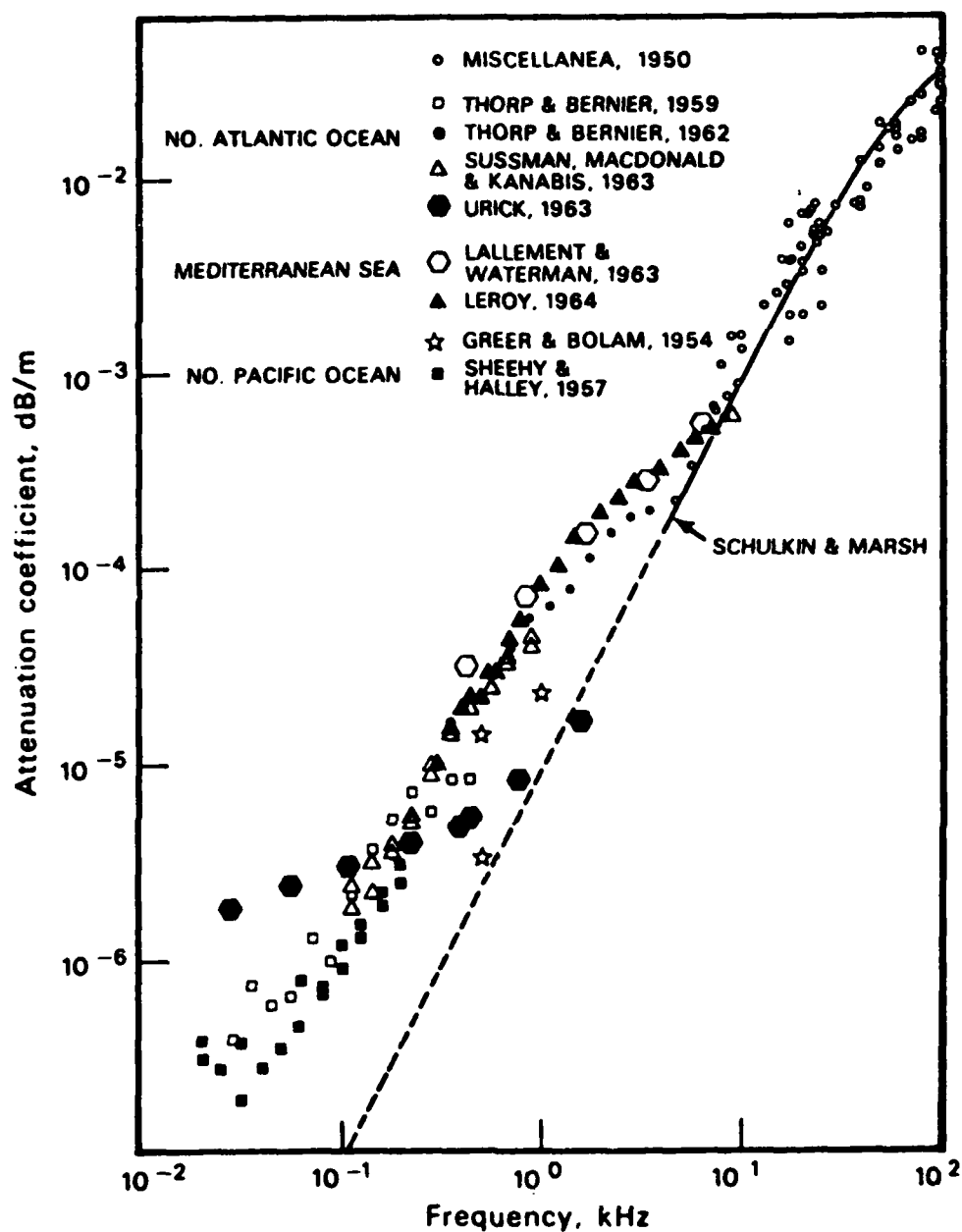
Figure 1

Sound absorption plot developed by Thorp. Absorption coefficient versus frequency plot constructed by Thorp (1965) from data sources listed. The Schulkin and Marsh (1962) calculated curve is based on a depth of 1220 m, temperature of $4^{\circ}C$ and salinity of 35°/oo.

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Lake Tanganyika (Browning, Gorman, Jones, Thorp, Mellen and Weigle, 1972) and a review of the Lake Superior data casts doubt on the validity of these measurements. Thorp's oceanic data have received independent confirmation by Skretting and Leroy (1971) whose work in the Western Mediterranean actually predates Thorp's studies. The original at-sea data of Thorp (1965) were critically reviewed by Goodman and Berman (1971) and they concluded that the increased absorption could be an artifact introduced by the method used to analyze the raw data. Berman and Guthrie (1972) noted the extreme difficulty in measuring sound absorption at 1 kHz where absorption is of the order of 0.06 dB/km and long ranges are required to get significant absorption over spreading losses. They also noted unresolved problems such as boundary scattering, inhomogeneity scattering and sound channel leakage. Urick (1967) observed that the increased absorption could possibly be attributed to shock wave effects inherent in the propagation of explosive pulses used in generating the acoustic energy for most of the data. Beam (1971) reported that absorption measurements using CW sources, which generally eliminate the explosive shock wave problem, in the Atlantic were slightly less than Thorp's data. Recent data from Lovett (1975) using CW sources indicate that absorption in the North Pacific is less than Thorp's but still greater than the $MgSO_4$ effects. The work of Mellen and Browning (1975) indicates that there is a noticeable variability between ocean areas, with data from the Atlantic, Mediterranean and Baffin Bay generally agreeing with Thorp but data from the Gulf of Aden and the North Pacific are respectively 0.6 and 0.41

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times Thorp's values. In summary, the at-sea data generally indicate some increase in absorption over the expected $MgSO_4$ effect at low frequency. Because of the inherent difficulties in data collection and analysis of oceanic data, the magnitude of the absorption is in doubt and the general mechanism is unresolved, although there is a strong case for variability among water masses.

Examining the low frequency absorption problem using laboratory techniques, Yeager, Fisher, Miceli and Bressel (1973) conducted temperature-jump studies on Lyman and Fleming (1940) artificial sea water and Standard Copenhagen Sea Water. Results indicated that artificial and standard sea water had a characteristic relaxation time which corresponded to the 1 kHz absorption frequency observed in the Thorp data. Removing boron, in the form of boric acid, from the artificial sea water eliminated the observed relaxation time and dilution of standard sea water with sodium chloride solution shifted the relaxation time to higher values; however, the original relaxation time could be restored by addition of boron to give the original sea water concentration of 4.2×10^{-4} molal. No reaction mechanism was proposed to account for the observed data but because of the importance of boric acid to the buffering of sea water, it was observed that the equilibrium could be quite complicated and include some carbonate dependence. In a subsequent discussion, Fisher and Levison (1973) proposed a two step reaction for boric acid based on additional temperature jump studies. A theoretical study by Garland, Patel and Atkinson (1973) using a sophisticated computer model

proposed an excess absorption around 8 kHz which was attributed to a magne-
sium bicarbonate hydration reaction. Garland et al (1973) did not consider
the boron effects and their proposed reaction mechanism gave an absorption
value which was smaller than that observed by Thorp. The calculated
relaxation frequency was not compatible with observed data. There was also
a proposal by Knoche (1972) that an aluminum sulfate complex was responsible
for excess sound absorption in the 1 kHz region. Yeager et al (1973) noted
that Knoche's estimate of aluminum concentration in sea water was up to one
thousand times greater than published values and that when the lower concen-
tration was used the calculated excess sound absorption became too small to
explain the observed data. To confirm this calculation, temperature jump
work was conducted on artificial sea water with 0.5 mg/liter of Al, but no
relaxation was noted in the 1 - 10 kHz region.

The majority of data presently available indicates that there is an
increase in open ocean sound absorption below about 1 kHz; however, the
magnitude of the excess absorption is a matter of great conjecture and even
the existence of the increased absorption is not accepted by all acousticians.
The possible importance of boron to sound absorption in sea water has been
shown by Yeager et al (1973) but the exact reaction mechanism and possible
influence on sound absorption remains to be defined. The difficulties of
measuring sound absorption in the presence of scattering, boundary losses,
multipath arrivals, etc., inherent in ocean measurements showed the need
for a laboratory approach under realistic but controlled circumstances where

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required parameters can be varied to define mechanisms. Accordingly, a laboratory study was undertaken to determine the magnitude of the low frequency sound absorption in sea water, define the causes of this absorption and to delineate the reaction process responsible for low frequency sound absorption in the ocean.

The laboratory results confirm the increased sound absorption below 1 kHz previously observed in the ocean and the increase is directly related to the presence of boric acid in sea water. To adequately explain the data, a two step, three state boric acid model is postulated with the increased absorption being related to the unimolecular second step. The presence of bicarbonate in sea water is shown to affect the reaction and thus the sound absorption; however, the mechanism is not clearly understood at this time. The overall results of this work are not only important for the understanding of sound absorption in sea water but also provide a greater understanding and new aspects of boric acid chemistry in dilute aqueous solution.

II. THEORY

The early acoustic research conducted to explain the increased
sound absorption in sea water below 100 kHz was instrumental in the develop-
ment of techniques to study fast reaction kinetics in aqueous solutions and
opened up new aspects of the chemistry of sea water. Subsequent work has
been able to trace this increased sound absorption to the ionization of mag-
nesium sulfate in sea water and another confirmation of multistate ion pairs
in aqueous solution. The understanding of multistate equilibria was not only
important to the understanding of sound propagation but answered many
questions regarding the chemistry of ionic solutions. This study concerns
the lower frequency sound absorption in sea water and the results should
prove as interesting and useful to the study of acoustics, oceanography and
chemistry as the higher frequency relaxation.

Basic kinetic theory is covered in depth by a variety of authors, but
the work of Gardiner (1969), Caldin (1964), Amdur and Hammes (1966),
Stuehr and Yeager (1965) and Eigen and De Maeyer (1963) have been found to
be especially appropriate. The latter reference offers a unified approach
which has been generally followed in this work.

Virtually all kinetic studies deal with a "chemical relaxation" process
whereby a chemical reaction is studied as a function of its response to a small
amplitude perturbation from an initial equilibrium state. Specific tracers are
followed as the system responds to a new equilibrium state or relaxes to the

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initial state after a short duration perturbation. In most cases that can be handled readily, the small amplitude perturbation approximation is invoked and only linear relaxation processes are considered. The process is characterized by a "relaxation time" which is characteristic of the reaction being observed and specific external conditions. For a single step reaction the relaxation times can be related directly to the rate constants of the reaction. For the more complicated multistep reactions, there is a relaxation time for each step but these relaxation times can only be indirectly related to the rate constants of each step.

For a one step reaction such as

$$A + B \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} C \tag{2-1}$$

the rate equation would be represented by

$$\frac{d(C)}{dt} = -\frac{d(A)}{dt} = -\frac{d(B)}{dt} = k_{12}(A)(B) - k_{21}(C) \tag{2-2}$$

where the concentration variables are defined as the equilibrium values (A_e) plus the small perturbation term (ΔA).

$$(A) = (A_e) + (\Delta A)$$

$$(B) = (B_e) + (\Delta B) \tag{2-3}$$

$$(C) = (C_e) + (\Delta C)$$

Substituting equation (2-3) into (2-2) and using the stoichiometric conservation of mass and the time independence of the equilibrium values, one obtains

$$\frac{d\Delta C}{dt} = -\left\{ k_{12}[(A_e) + (B_e)] + k_{21} \right\} \Delta C = -\frac{\Delta C}{\tau} \tag{2-4}$$

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where τ is the characteristic relaxation time. Integration of the first order linear differential equation gives

$$\Delta C = \Delta C_o e^{-t/\tau} \tag{2-5}$$

The relaxation time expression is readily obtained and the individual rate constants may be evaluated. The more complicated multistep process is handled in a similar manner but the solutions become linear matrices which must be solved as an eigenvalue problem.

When considering the perturbation forcing term, it is convenient to express equation (2-4) as

$$\frac{d\Delta C}{dt} + \frac{1}{\tau} \Delta C = \frac{1}{\tau} \overline{\Delta C} \tag{2-6}$$

where $\overline{\Delta C}$ is related to the forcing term, be it a transient or a periodic function. The complete solution of this nonhomogeneous equation would then be the sum of the natural response and forced solution. For a transient forcing term the initial displacement is determined by the forcing term and the response to the system depends on the characteristics of the system. The harmonic forcing term applicable to sound absorption may be represented by

$$\overline{\Delta C} = A_e^{i \omega t} \tag{2-7}$$

and the driven term will assume the same harmonic oscillation but with a different complex amplitude term which includes phase shift information. Inserting the forcing and forced expression into equation (2-6), a complex transfer function Φ relating the two terms can be represented as

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$$\Delta C = \frac{\overline{\Delta C}}{(1 + i\omega\tau)} = \Phi \overline{\Delta C} \qquad (2-8)$$

or

$$\Delta C = \frac{A_e^{i(\omega t - \phi)}}{(1 + \omega^2\tau^2)^{1/2}} \qquad (2-9)$$

where ϕ is the phase angle. From the latter expression it can be seen that the driven term generally lags the driving term and the phase angle increases with increased frequency to a maximum of 90°. $\omega\tau = 1$ when the phase is 45°. The amplitude, operating in the reverse manner, goes to zero as frequency increases, figure 2. This means that at high frequency the driven term remains virtually fixed regardless of the amplitude of the driver.

To directly address the acoustic case, the pressure and density variations of the sound wave will be represented by

$$\exp[i\omega(t - x/\overline{v})] \qquad (2-10)$$

where $\overline{v}$ is the complex velocity which may be represented as

$$1/\overline{v} = 1/c + \alpha/i\omega \qquad (2-11)$$

with c being the phase velocity and α being absorption. The complex sound velocity has been related to the dynamic adiabatic compressibility (β_s) by

$$\overline{v} = (\rho\beta_s)^{-1/2} \qquad (2-12)$$

As shown by Eigen and De Maeyer (1964) and Liebermann (1949), the dynamic adiabatic compressibility is the sum of the static compressibility β_0 and chemical compressibility β_r, which is related to the chemical relaxation. The Φ is the transfer function derived in equation (2-8).

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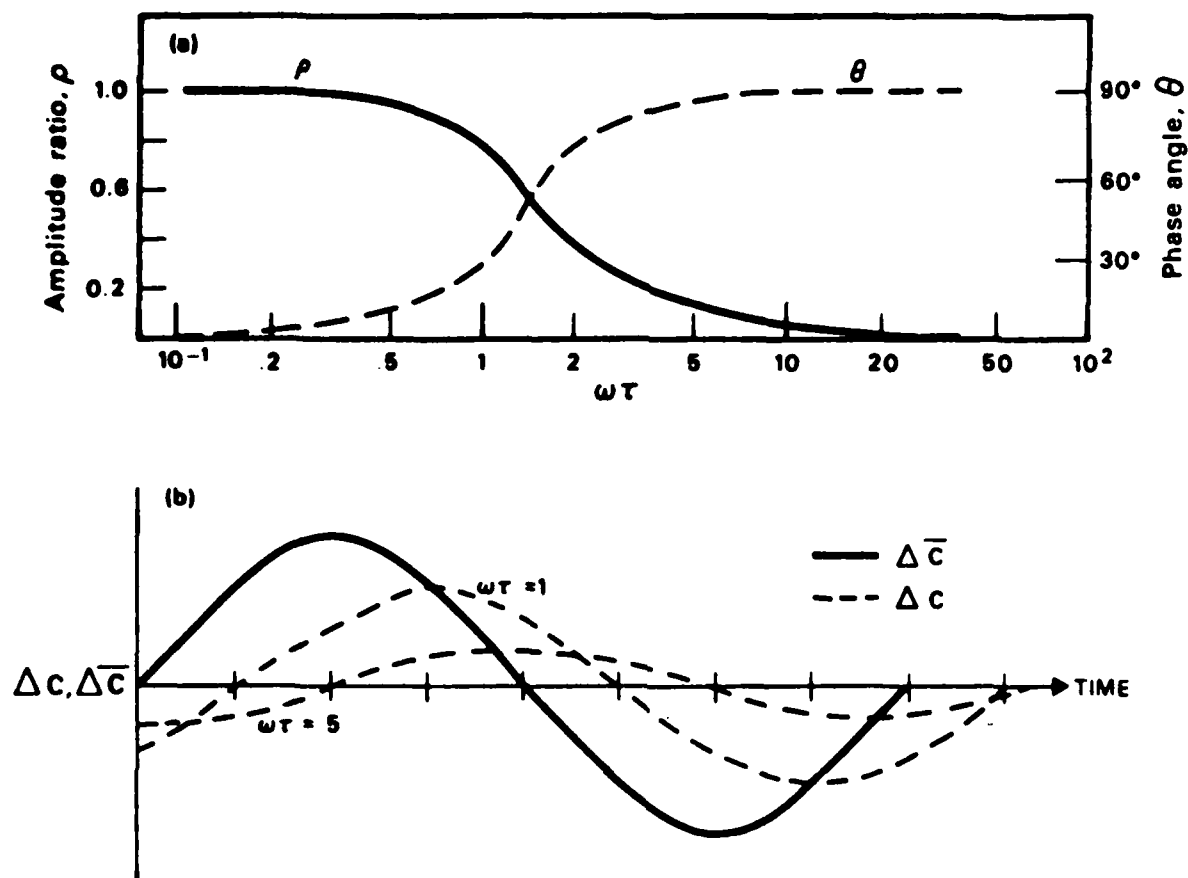
Figure 2

Amplitude and phase response of resonator to harmonic oscillation. Figure 2a
is the amplitude ratio (ρ) and phase angle (θ) response of the solution in a
spherical resonator as plotted against the angular excitation frequency (ω) times
the relaxation time (τ). As the excitation frequency increases the phase angle
goes to a maximum of 90° and the amplitude ratio goes to zero. Figure 2b
shows the response of the system (ΔC) to the driving term ($\Delta \bar{C}$) as $\omega\tau$ is
increased. At low excitation frequency the system follows the driving term
very closely but as excitation frequency is increased the system lags farther
behind the driving term and the amplitude is progressively reduced.

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$$\beta_s = \beta_o + \beta_r \Phi - \beta_r \tag{2-13}$$

Equating equations (2-11) and (2-12), inserting equation (2-13) and separating real and imaginary terms, one obtains

$$C \simeq C_o \left[1 - \frac{1}{2} \frac{\beta_r}{\beta_o} \frac{1}{1 + \omega^2 \tau^2} \right] \tag{2-14}$$

$$\alpha \lambda = \frac{\pi \beta_r}{\beta_o} \frac{\omega \tau}{1 + \omega^2 \tau^2} \tag{2-15}$$

Equation (2-14) is an expression for the velocity dispersion caused by a chemical relaxation and equation (2-15) is the excess sound absorption per wave length for the relaxation. Both expressions can be used to evaluate a chemical relaxation; however, the velocity dispersion in most liquids is extremely small ($< 1\%$) and is difficult to measure when operating at very low frequencies. The excess absorption per wave length has a maximum value when the angular frequency is equal to the relaxation time. It may also be seen that when excess absorption per wave length ($\alpha \lambda$) is plotted against frequency on a log-log plot a characteristic hyperbolic shape will result, as shown in figure 3. It must also be noted that equation (2-15) has been derived for pressure absorption and not for energy absorption. A derivation for energy would place a two in the numerator on the right side of equation (2-15). The differences in the pressure and energy derivation have been confused by several experimenters. A simple rearrangement of equation (2-15) gives

$$\frac{\alpha}{f^2} = \frac{2 \pi^2}{c} \frac{\beta_r}{\beta_o} \frac{\tau}{1 + \omega^2 \tau^2} \tag{2-16}$$

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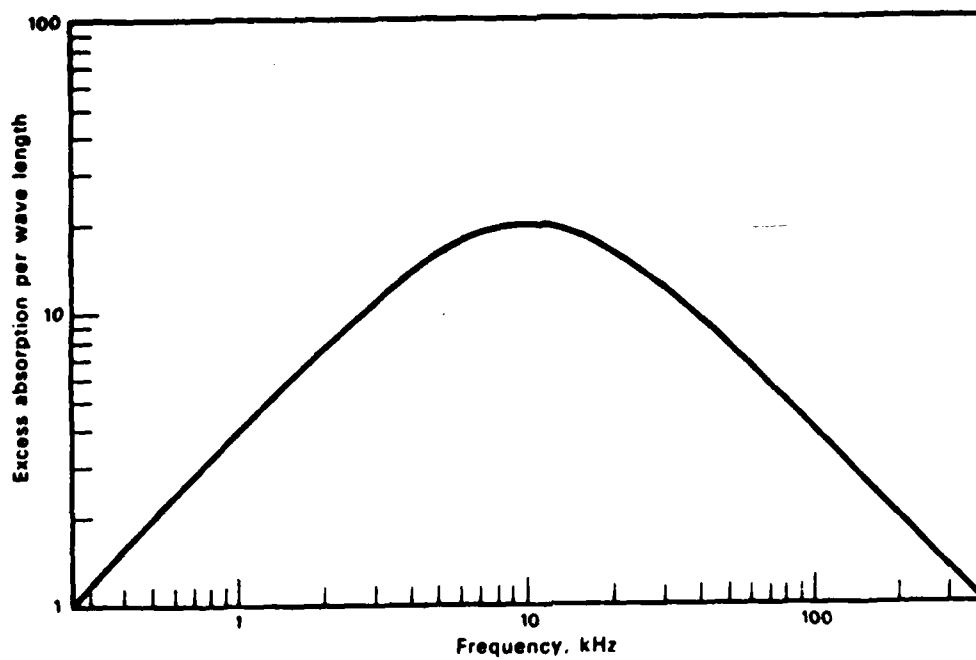
Figure 3

Characteristic plot of excess sound absorption per wave length ($\alpha \lambda$) against

frequency. The curve represents an arbitrary relaxation frequency of 10 kHz

and $\pi \beta_r / \beta_0$ equal to ten.

It is now necessary to evaluate the chemical compressibility in terms of known quantities. Following the derivation by Stuehr and Yeager (1965), the relaxational adiabatic compressibility can be represented as

$$\beta_r = - \frac{1}{V} \left[\left(\frac{\partial V}{\partial P} \right)_T + \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial T}{\partial P} \right)_S \right] \qquad (2-17)$$

The second term on the right is small for most aqueous solutions and is generally dropped; however, the derivation of the second term follows in an analogous manner to that used for the first term. The first term may be expanded around a parameter θ which is a measure of the amount of the system in the various states.

$$- \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = - \frac{1}{V} \left(\frac{\partial V}{\partial \theta} \right)_T \left(\frac{\partial \theta}{\partial K} \right)_T \left(\frac{\partial K}{\partial P} \right)_T \qquad (2-18)$$

For a reaction such as

$$\upsilon_A A + \upsilon_B B + \cdots + \upsilon_i I \rightleftharpoons \upsilon_P P + \upsilon_Q Q + \cdots + \upsilon_j J \qquad (2-19)$$
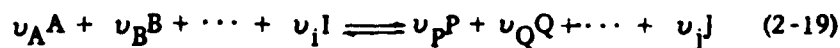
it has been shown by Stuehr and Yeager (1965) that

$$\left(\frac{\partial \theta}{\partial K} \right)_T = \frac{1}{K} \left[\sum_j \frac{\upsilon_j^2}{C_j} + \sum_i \frac{\upsilon_i^2}{C_i} + \sum_j \upsilon_j \left(\frac{\partial \ln \lambda_j}{\partial \theta} \right)_T \right.$$

$$\left. - \sum_i \upsilon_i \left(\frac{\partial \ln \lambda_i}{\partial \theta} \right)_T \right] \qquad (2-20)$$

where C is the concentration of reactant or product as noted and λ is the reactant or product activity coefficient. Using the definition of change in partial molal volume,

$$\Delta V^0 = \sum_j \upsilon_j \bar{V}_j^0 - \sum_i \upsilon_i \bar{V}_i^0 \qquad (2-21)$$

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it may be shown by appropriate differentiation that

$$\frac{1}{V}\left(\frac{\partial V}{\partial \theta}\right)_T \cong \Delta V^o \tag{2-22}$$

The Planck (1887) equation can be used to further simplify equation (2-18)

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V^o}{RT} \tag{2-23}$$

Equation (2-18) may now be represented by

$$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{\Delta V^o}{RT} K\left(\frac{d\theta}{dK}\right) \Delta V^o \tag{2-24}$$

A similar derivation would give

$$-\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_S = -\frac{\Delta V^o}{RT} K\left(\frac{d\theta}{dK}\right) \frac{\Delta H^o}{C_P}\left(\frac{\partial V}{\partial T}\right)_P \tag{2-25}$$

When substitution is made into equation (2-15) the final result would be

$$\alpha \lambda = \frac{\pi \Delta V^o}{\beta_o RT} K\left(\frac{d\theta}{dK}\right)\left[\Delta V^o - \frac{\Delta H^o}{C_P}\left(\frac{\partial V}{\partial T}\right)_P\right] \frac{\omega \tau}{1 + \omega^2 \tau^2} \tag{2-26}$$

In the case of a multistep reaction a linear affine coordinate transformation

must be performed on equation (2-6) to determine the spectrum of relaxation

times. The exact transformation procedure is discussed in depth by Eigen

and Tamm (1962); however, the derivation by Garland, Patel and Atkinson

(1973), using the energy relation, is perhaps the most straightforward and

easiest to understand. Recently, Adams (1974) developed a successive

approximation method to evaluate the multistep reaction process which would

also be applicable to this problem. The absorption per wave length is now a

sum of values represented by

$$\alpha \lambda = \frac{\pi}{\beta_o} \sum_{K=1}^{n} \left(\beta_K \frac{\omega \tau_K}{1 + \omega^2 \tau^2_K} \right) \qquad (2\text{-}27)$$

where n is the number of reaction steps. The chemical compressibility

must now be reevaluated in terms of the transformed coordinate system '

and the relaxation times are also represented in the new coordinate system.

III. EXPERIMENTAL METHODS

I. INTRODUCTION

The experimental apparatus and techniques used in this work were
selected to provide definitive data on the magnitude of low frequency sound
absorption in sea water and to allow formulation of a plausible explanation of
the absorption. Only the resonator technique developed by Leonard (1950)
and Kurtze and Tamm (1953) give acceptable sound absorption data at fre-
quencies below the megahertz range. The tuning fork resonator proposed by
Andreae, Jupp and Vincent (1960) would appear to be optimum for the 1 kHz
region but the accuracy of the method is not presently acceptable and the
concentration of solutions used is higher than that desired in this work. The
largest spherical resonator previously used was a 50 liter glass sphere with
a fundamental radial mode of oscillation of approximately 3 kHz. Early work
by Moen (1951), using spherical glass resonators, indicated that absorption
losses within the sphere tended to increase at low frequency and that the fre-
quency of initial increase was related to sphere diameter. Greenspan (1972)
calculated that this increased absorption was caused by acoustic coupling be-
tween the glass sphere and the liquid, along with tangential wall stresses and
boundary layer effects at and near the fundamental. Losses are considered
to be low enough to be acceptable for modes greater than the third mode.
There is also an observed residual loss at higher frequencies which remains
unexplained but is probably attributable to wall losses not considered to

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date. Despite the stated difficulties, Greenspan observed that the spherical resonator is superior to all other available configurations because of its optimum symmetry and reduced wall losses and tangential effects. In view of the considerations cited, attempting to obtain accurate resonator absorption data down to 1 kHz is presently considered impractical, as a chamber with a volume of approximately one million liters would be required and supporting equipment would be difficult to handle. As a compromise, a 200 liter sphere was obtained with a fundamental mode at 2 kHz, in which acceptable data were obtained down to approximately 6 kHz. This lower frequency limit is considered acceptable because the shape of the chemical absorption curve is known from equation (2-15) and can be used to infer data to lower frequency from high frequency information if the relaxation frequency of the process can be determined by other means. The problem of the unexplained wall losses of the resonator becomes less important when relative measurements are used to determine the absorption in a known chemical system as related to the absorption in a reference solution such as pure water or sodium chloride solution.

The field of chemical kinetics offers a variety of techniques to obtain the relaxation time (hence the relaxation frequency) to support the resonator work. In addition, these techniques provide excellent information about the dynamics of the system being studied. The pressure jump method used by Strehlow and Becker (1959) would be most applicable but was not chosen because of stability problems in the equipment and the design problems inherent

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in the construction of the pressure tube. The upper frequency range of this equipment is just in the 1 kHz area and does not provide sufficient over-lapping coverage with the resonator. The temperature jump equipment used by Yeager et al (1973) provides the desired frequency overlap and meets all other requirements of the study. The simplicity of operations allows collection of a large amount of data over short periods of time and the equip-ment has been proven reliable under heavy use. In that the temperature jump uses Joule heating to perturb a reaction, the implicit assumption is that the pressure effects of the resonator and Joule heating effects of the temperature jump perturb the same reaction. This assumption is considered reasonable in view of data presently available. It must also be pointed out that the temperature jump data depend on a change in solution pH and thus, relaxation frequency results can only be expected for acid or base reactions.

Several other fast reaction techniques were reviewed but not con-sidered applicable at this time. The dielectric relaxation method used by Pottel (1964) for $BeSO_4$ is applicable to a wide frequency range but the boric acid dielectric relaxation results of Gilkerson (1957, 1962) proved to be unreproducible. Bell and Robinson (1962) noted Gilkerson's difficulties and carried out theoretical calculations which indicate that the technique may not be applicable to weak acids. Pressure conductivity work has recently been attempted on boric acid with minimal success. The small dissociation con-stant causes intolerably high cell resistances and in the pH adjusted systems, the solution used to adjust the pH dominated over the boric acid effects. With

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new cell designs, the conductivity work may prove successful at some time in the future. The polarographic technique used by Kuta (1957) may prove useful but results for boric acid reported to date do not agree with other methods as observed by Bell, Edwards and Jones (1967).

2. SPHERICAL RESONATOR

a. <u>Principles of Operation.</u> The spherical resonator technique is one of the stationary methods of studying chemical kinetics by means of sound absorption. Aside from some sophistication in electronic components, the technique has remained virtually unchanged from the system used by Leonard (1950). Understanding of the resonator has been greatly enhanced by the work of Greenspan (1972) and the difficulties of the system recognized. Despite the problems cited in an earlier section, the spherical resonator is presently the only system capable of providing reasonably accurate medium and low frequency sound absorption data for aqueous solutions.

The resonator technique involves exciting a liquid filled container to an equilibrium level by means of a harmonic driving force and then observing the rate of decay of the energy after the excitation source has been secured. The rate of decay is a measure of the sound absorbed by the liquid and a contribution from wall losses. The effect of wall losses and other systematic losses can be minimized by using a reference solution of known absorption characteristics to establish base line decay rates and referencing data from all other solutions to this base line. Acoustic losses outside the resonator

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are minimized by suspending the resonator by fine piano wires to reduce coupling of energy to the support stand and by placing the resonator system in a vacuum chamber to alleviate acoustic coupling to the surrounding environment. The 200 liter resonator, support stand and vacuum chamber are shown in figure 4.

Only the radial modes of oscillation are used to determine decay rates because they should experience minimum wall losses. Circumferential modes and glass modes experience increased absorption because of high shear losses at the liquid-glass interface. An elementary equation for the frequency of the various radial modes (f_m) may be obtained using the wave equation and matching pressure and velocity conditions at the liquid-glass interface. The expression developed by Leonard (1950) is

$$f_m = \frac{k_1'm c_1}{2\pi} \qquad (3-1)$$

where

$$K_1'm = \frac{m\pi}{R_1} + \frac{\epsilon}{R_1} \qquad (3-2)$$

and

$$\tan \epsilon = m\pi \bigg/ \left[1 - \frac{\rho_1}{\rho_2} - \frac{\rho_1}{\rho_2} R_1 \frac{c_1 m\pi}{c_2 R_1} c_0 + \left(\frac{c_1 m\pi d}{c_2 R_1} \right) \right] \qquad (3-3)$$

In these expressions m is the mode number, ρ the density, R_1 the radius of the liquid sphere, d the glass wall thickness and ϵ a correction factor for the liquid-glass interaction. Subscripts (1) refers to conditions in the liquid and (2) to the condition in the glass. As noted by Wilson (1951), the calculated mode spacing and observed mode spacing are in only general

Figure 4

Vacuum chamber, support stand and 200 l resonator used in the sound absorption study. The support stand consists of two scissor jacks used to provide a vertical lift to the inner support ring. The support ring held four piano wires which support the resonator during the data collection run. The vacuum chamber was lowered by means of an overhead hoist. Two guide rails ensure that proper clearance is maintained between the support stand and the vacuum chamber during the lowering process.

agreement. The simplistic model cited above does not consider all modes of oscillation of the sphere and the coupling of these modes at the filling hole. The work of Baker (1961), Prasad (1964) and Kalnins (1964) using thin shell theory as related to spheres is applicable to understanding the resonator, but not even a rudimentary model has been proposed which is applicable to a water filled sphere with a filling hole. The best that can be said is that if the filling hole is a small solid angle of the complete sphere, the effects on the radial modes should be minimized. A full explanation of resonator dynamics must await additional work on thin shell theory.

Location of the radial modes is a difficult task. At low frequency where the decay rate is slower the modes are fairly distinct, a given mode can be found with relatively little difficulty; but at higher frequency, coupling with circumferential modes becomes more noticeable and mode discrimination becomes more difficult. Even at low frequency the radial modes seldom appear as a pure exponential decay. In a majority of cases the slow decay rate will be preceded by a very fast decay followed by an increase in signal level. This "carrot top" pattern has been a strong clue to determine the radial modes. It is postulated that the initial fast decay is related to the radpily decaying glass modes followed by the radial mode.

b. Preparation of Samples and the Resonator. All samples were prepared using analytic reagent grade chemicals and deionized water. Artificial sea water solutions were made using the Lyman and Fleming (1940) formulation. When using the 12 liter sphere, solutions were prepared in the

laboratory and then transferred to the sphere. Because of the increased size and weight of the 50 and 200 liter spheres, chemicals were mixed directly in the spheres. No special effort was undertaken to preclude equilibration of atmospheric carbon dioxide with the solutions.

Prior to filling the spheres, the inside surface of the vessel was cleaned with a potassium chromate, sulfuric acid solution. The sphere was then rinsed several times with pure water and drying of the inside surface observed to detect any film formation on the surface which would indicate the surface was not wetting properly. When satisfied that the surface was clean, the solution was poured directly into the vessel.

Degassing of the solution was performed in the sphere. An expansion chamber was placed above the sphere and a vacuum pulled on the system using the apparatus shown in figure 5. To enhance degassing and to ensure removal of bubbles clinging to the inside surface of the sphere, the filled sphere was sonically degassed using a 39 kHz ceramic crystal. The sphere was placed on the crystal and the crystal driven at resonance by an oscillator through a 200 watt amplifier. Degassing was judged to be completed when no additional bubbles could be seen and when a sharp rap near the neck of the sphere produced only what appeared to be vapor cavitation excitation. The period of degassing varied from 48 to 96 hours depending upon the solution.

During the degassing stage, water vapor is continually being removed from the system and collected in the freeze trap protecting the vacuum pump. No salts are considered lost by this method and any salts lost through splashing
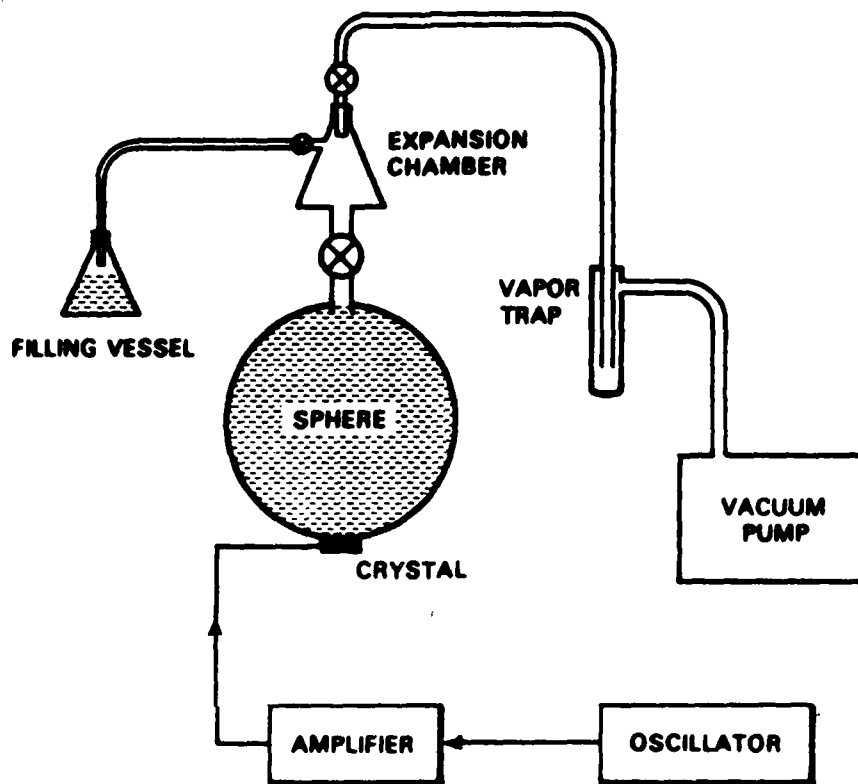
Figure 5

Resonator degassing diagram. Block diagram of equipment used to degas the
spherical resonator.

into the expansion chamber are considered to be minimal. As a result of this water loss, fresh water must be added by means of a supply bottle during the degassing phase. Upon completion of degassing a strong density gradient has been shown to exist near the neck of the sphere. To obtain a homogeneous solution, stirring is conducted under vacuum using a slender rod rotating through a vacuum seal placed on the neck of the sphere. Stirring is conducted until no visible density striation structure is noted. The earlier work of Leonard (1950) and Wilson (1951) was apparently done without benefit of stirring.

Upon completion of stirring the sphere is capped with a plug contain-ing a glass bead thermistor and an overflow piping system. The thermistor was located well up in the neck of the sphere and used in conjunction with a Wheatstone bridge to measure temperature of water in the sphere. This placement of the thermistor also provided a very sensitive means of detecting any vacuum leak in the system during the progress of a data collection run. The small overflow vacuum pipe was connected to a flask to collect water forced out of the sphere by heat expansion as the temperature was changed between runs. A hard vacuum was pulled on the entire overflow system prior to sealing.

After the sphere had been sealed, it was raised off its support struc-ture by piano wires to reduce external loss of sound energy outside the resonator. The 12 liter sphere was supported using a stand similar to that used by Leonard (1950) but the 50 and 200 liter sphere support stand had to be

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significantly strengthened as shown in figure 4. The complete system was then enclosed in a suitable vacuum chamber. To facilitate temperature control, the inside of the vacuum chamber was lined with copper tubing and water from a large temperature controlled bath circulated through the tubing to control and change temperature as desired. The entire vacuum chamber was enclosed in a thermally insulated box which acted as an environmental chamber. The box was equipped with a refrigeration unit to allow low temperature degassing and data collection along with a heater to provide temperature stability. This arrangement also reduced the time required for the resonator to achieve any desired temperature. Upon reaching the desired temperature, the vacuum chamber was pumped down and measurements could then be made.

c. Experimental Procedure. Sound absorption was measured using the apparatus shown in the block diagram in figure 6. A Hewlett Packard frequency synthesizer, model 3320B, provided a frequency modulated signal through a Hewlett Packard counter, model 5212A, to a H. H. Scott decade amplifier. The amplified signal was then passed to a Spencer Kennedy decay rate meter, model 507. The decay rate meter was used only as a gating circuit to open and close the transmit line at equal selected intervals. The meter also provided a trigger signal to the oscilloscope each time the circuit was opened. The gated frequency signal was then passed to the transmit crystal on the spherical resonator.

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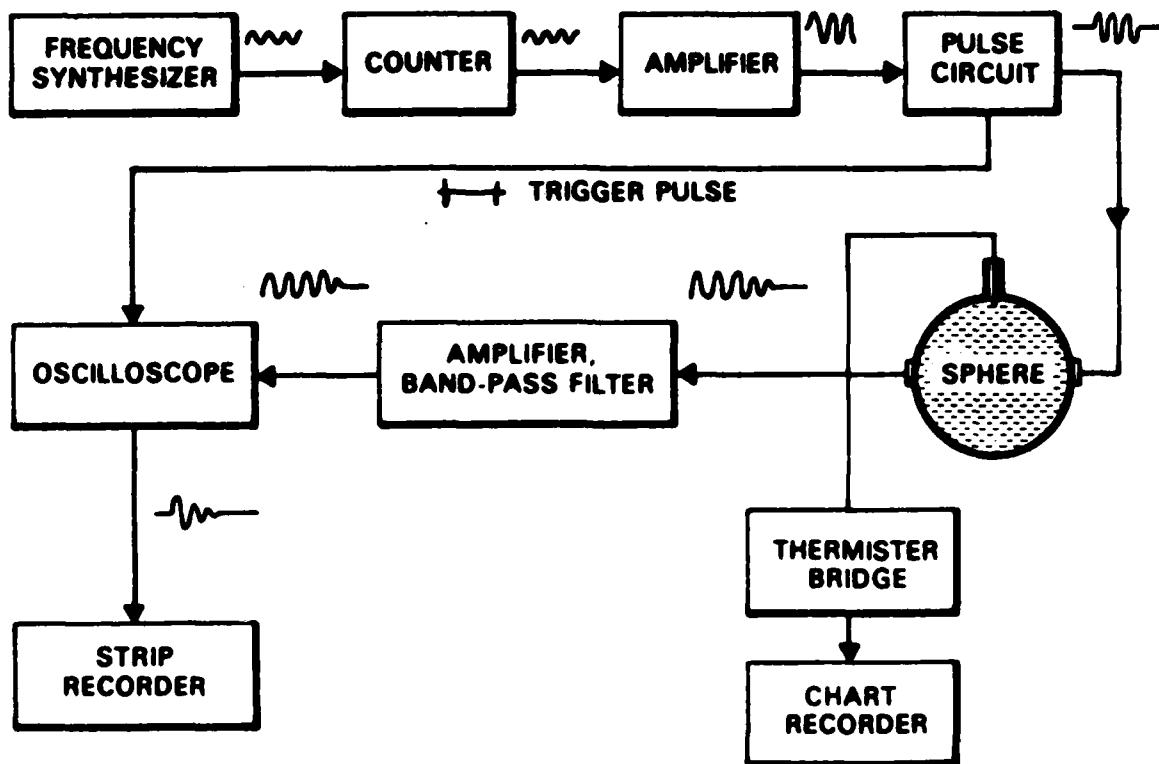
Figure 6

Block diagram of experimental equipment used with the spherical resonator.

Most of the spheres used had three ceramic crystals cemented to the exterior of the sphere using EPON-6 epoxy. The crystals were rods fabricated by Channel Industries, Inc. of 5400 ceramic material. They had resonant frequencies of 100, 200, and 300 kHz respectively. Two crystals were cemented in a vertical orientation on one side of the sphere with the remaining crystal diametrically opposed. The transmitting crystal was selected to be compatible with the excitation frequency and any opposed crystal used as the receiver.

The received signal was transmitted through a bandpass filter and amplifier to a Tektronics Model 535 oscilloscope for viewing. For frequencies above 10 kHz a Wandel u. Goitermann receiver, model AT443, was used with a band pass of 500 Hz below 100 kHz and a 3.5 kHz band pass above 100 kHz. For frequencies below 10 kHz a Brüel and Kjaer Audio Frequency Spectrometer, model 2111, was used with 1/3 octave filters. The filters were tuned to the excitation frequency of the transmit crystal. Selected decay rate signals were recorded on a Brüel and Kjaer model 2305 chart recorder using a 50 dB logarithmic potentiometer. Using selected attenuators, the recording system was initially calibrated to ensure accuracy of the data and the recorder was calibrated several times during the course of the data collection program. Records made on the chart recorder were compared to data taken by photography of the oscilloscope trace. The maximum error detected was on the order of 5% which is considered well within experimental tolerance.

All data were collected by manually sweeping the desired frequency interval at a rate of approximately 0.5 cycles per second and viewing the oscilloscope. When a good mode was detected, the decay rate was recorded on the chart recorder. The initial data run on a new resonator was conducted using a deionized, pure water medium. Modes were observed and decay rates recorded. These data then become the reference to which all further data are compared. Desired chemicals can now be added to the water or the resonator drained and the desired solution added. Disregarding density differences, the radial mode frequency for any mode in a specific resonator is a function primarily of sound velocity in the fluid. By knowing the temperature and salinity of the solution, a sound velocity can be obtained and thence the change in mode frequency from the reference can be approximated. In practice, once an identical mode is located in a new solution, a constant multiplication factor can be applied to locate all other modes. This system works very well in practice and is a great time saver. An attempt was made to use a NaCl solution as a reference and adjust the NaCl concentration to give the same sound velocity as the solution to be examined. Theoretically this would place all the modes at the same frequency for both solutions and allow a mode for mode decay rate matching. In practice the attempt was a failure because the NaCl concentration could not be controlled well enough to exactly duplicate sound velocity and the temperature dependence of sound velocity of the two solutions are divergent.

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A variety of sound velocity equations are available including those developed by Weissler and Del Grosso (1951), Wilson (1960A,B), Del Grosso and Mader (1972) and Millero and Kubinski (1975). A review of previous work by the latter authors indicates the variability between the various formulations is small and the appropriate choice depends on the particular conditions encountered. In virtually every case the data upon which the empirical equations are based were determined by measurements in the mHz region. As pointed out by Horton (1974) and seen in an earlier section of this study, to obtain truly accurate sound velocity at low frequency, the sound dispersion of $MgSO_4$ (approximately 3.5 cm/sec) and any lower frequency relaxation must also be considered. Because the data used in this study do not require extremely accurate sound velocities, the equation developed by Wilson (1960B) was used.

The observed decay rate in dB/sec is converted to a plane wave absorption coefficient (α) expressed (Wilson, 1951) in nepers/meter as follows:

$$\alpha \text{ (nepers/meter)} = \frac{0.1151}{c \text{(meters/second)}} \text{ Decay Rate (dB/second)} \qquad (3-4)$$

For plotting purposes the square law frequency dependence is removed by dividing α by frequency squared (f^2). A combined log-log plot of α/f^2 versus frequency is constructed for the reference solution and for the unknown solution. A sample lot is provided in figure 7. Consistent with the assumption that the radial modes experience the least absorption, a smooth curve is drawn through the lowest data points for each solution. Using the

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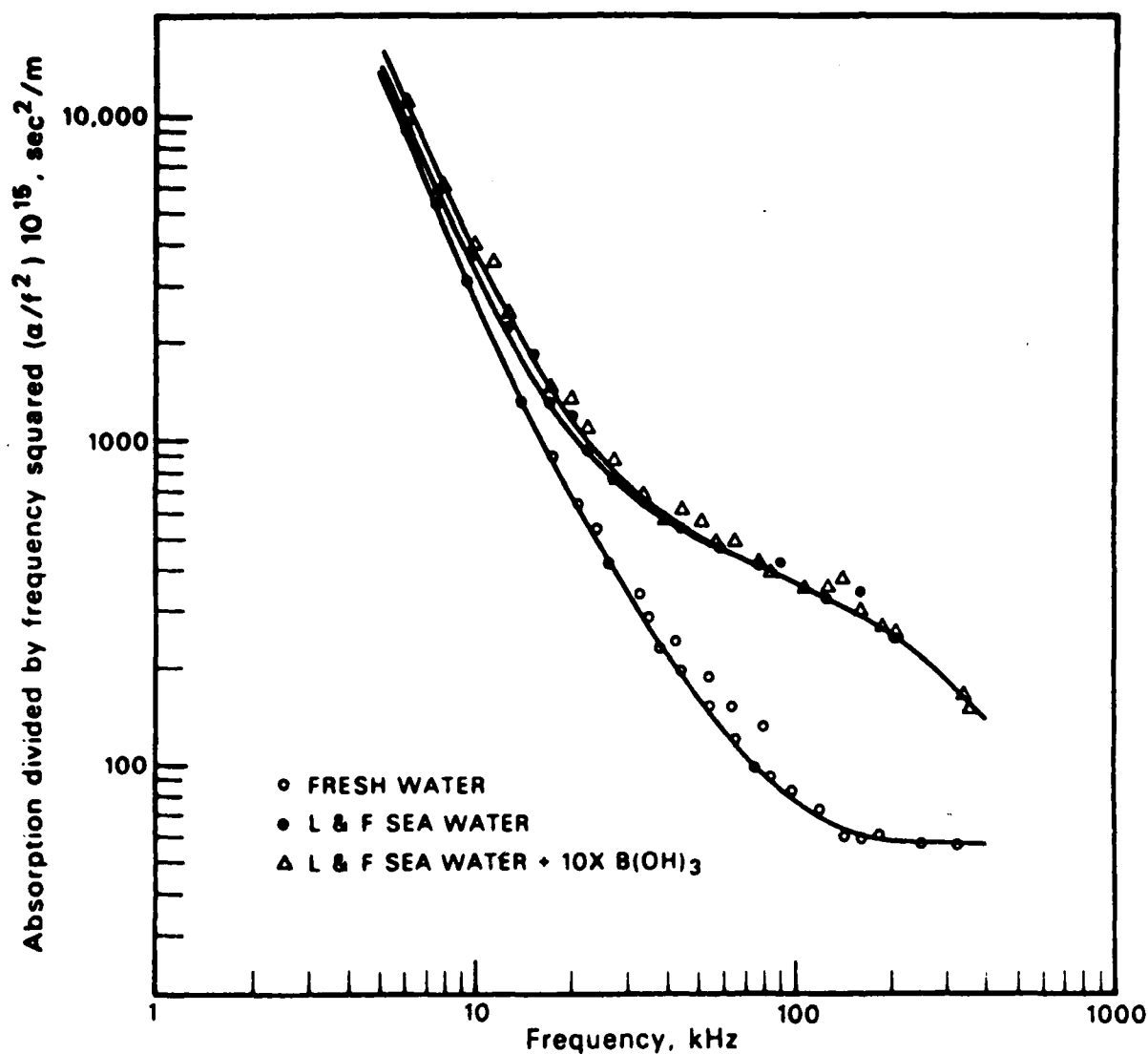
Figure 7

Plot of sound absorption divided by frequency squared. Representative plot

of excess sound absorption divided by frequency squared plotted against fre-

quency. The open circles are values for pure water, which is the reference

solution. The closed circles are for Lyman and Fleming sea water. The

open triangles are for Lyman and Fleming sea water with ten times the sea

water concentration of boric acid. All data were collected at a temperature

of 36°C in the 200 liter resonator.

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following expression, the excess absorption per wave length $(\alpha\lambda)$ can then be calculated.

$$\alpha\lambda = cf\left[\left(\frac{\alpha}{f^2}\right)_{solution} - \left(\frac{\alpha}{f^2}\right)_{reference}\right] \qquad (3\text{-}5)$$

Taking the difference between the α/f^2 curves for the unknown solution and the reference solution at select frequencies, and using equation (3-5), a second log-log plot is now made by plotting $\alpha\lambda$ data against frequency. If a relaxation is present, a hyperbola characteristic of equation (2-15) should be formed. Because the frequency of the lowest usable mode for the 200 liter sphere is on the order of 6 kHz, the data will be obtained only on the high frequency side of the symmetric hyperbola. However, knowing the overall shape of the curve and the relaxation frequency from the temperature jump work, the complete curve can be drawn using sound absorption data only at frequencies above the relaxation frequency. Although the approach is not optimum, it is the only practical approach presently available.

3. TEMPERATURE JUMP

a. Principles of Operation. The temperature jump technique is one of the transient methods of studying chemical kinetics as opposed to the stationary harmonic approach used in the spherical resonator. The technique is particularly well suited to reaction studies because small samples are used, the equipment is reliable, easy to operate and results are obtained quickly. In-depth discussions of the technique are provided by Czerlinski (1966), Eigen and De Maeyer (1963) and Calden (1975).

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A schematic of the temperature jump equipment is shown in figure 8. In operation, a 0.05 microfarad capacitor is charged to high voltage, up to 35 kV, by a power supply. Upon firing a spark gap, the voltage is discharged through a cell containing the ionic solution to be studied and an optically active indicator which is used to follow the reaction by optical means. Specially designed electrodes within the cell provide a uniform electric discharge and uniform Joule heating of the sample contained within a 2.5 cm^3 volume between the electrodes. A monochromatic light source set to a particularly strong absorbance wave length of the indicator is transmitted through the cell and received by a photomultiplier circuit. The voltage output of this circuit is directly proportional to the absorbance of the indicator in the cell. This output is presented on a storage oscilloscope for viewing and data collection. The change in vertical deflection with time is determined from the oscilloscope trace and plotted on semi-log paper for analysis. Using equation (2-5), where ΔC is now the actual vertical deflection in arbitrary units and $\overline{\Delta C}$ is the initial value, the slope of the semi-log plot will be the reciprocal relaxation time. If more than one relaxation time were present, the semi-log plot would be a series of line segments as opposed to a single straight line. A schematic of the perturbation temperature jump and resultant response of the solution is shown in figure 9.

Ideally the temperature rise should be a pure step function, however, in actuality it is a ramp or exponential rise, depending on the
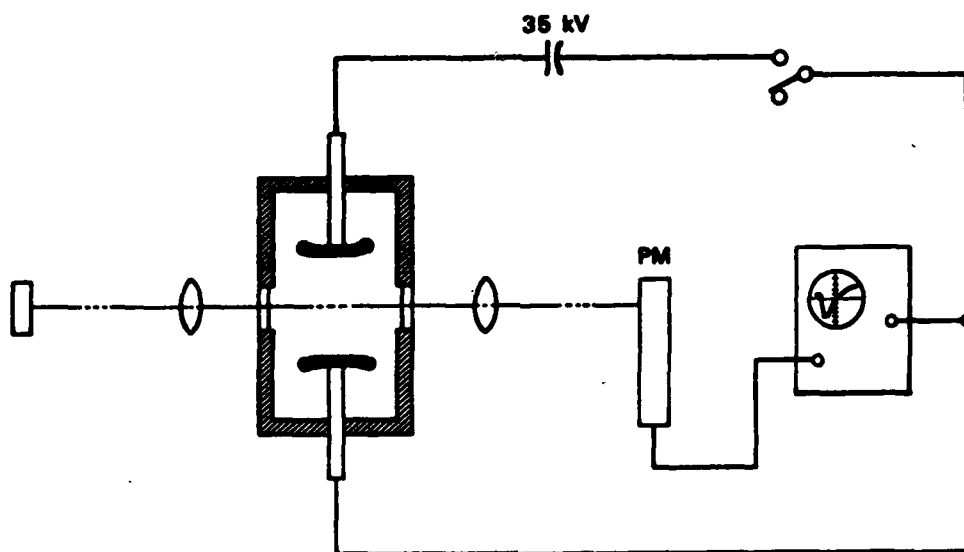
Figure 8

Block diagram of the temperature jump equipment.
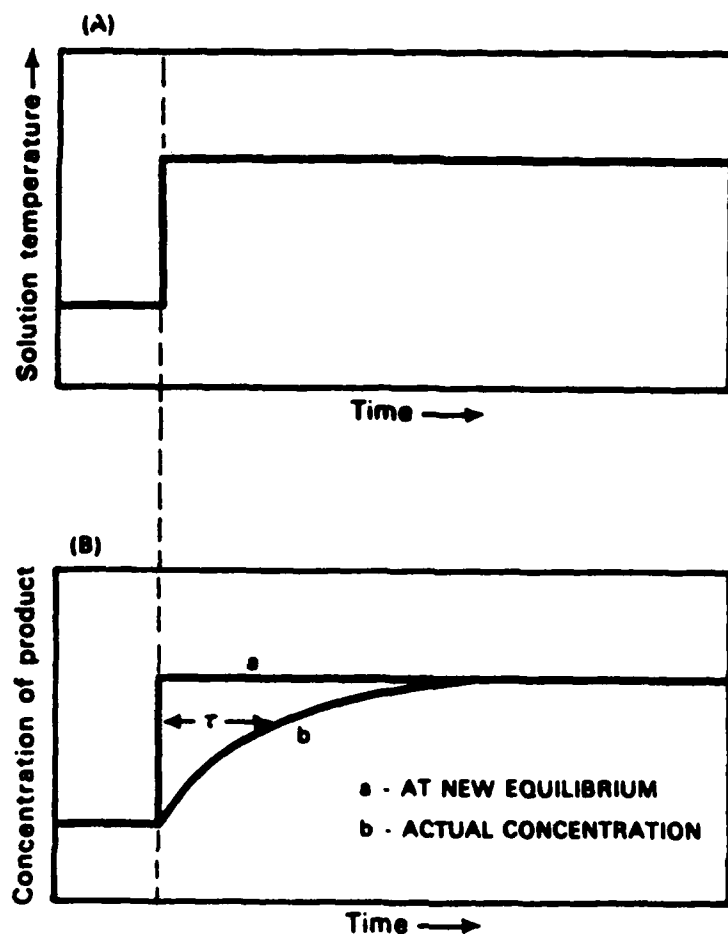
Figure 9

Principle of the temperature jump technique.   Figure 9(A) indicates the ideal

temperature response of the system after the electrical charge is discharged

through the solution.   Figure 9(B) indicates the new equilibrium value in re-

sponse of the system to the new equilibrium value.   The relaxation time (τ) is

the time required for the system to come to $1/e$ of its original equilibrium

value.

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equipment used. As a result, there is a heating time constant which provides a lower limit to the relaxation times which can be observed. For the equipment and solutions used in this study the time constant was on the order of 15 μsec which would convert to a relaxation frequency of approximately 10 kHz. The temperature rise within the solution depends on the specific heat of the solution, the discharge voltage applied to the cell and the resistance of the cell containing the solution. For most solutions examined by this study the temperature rise was 3.5^{o}C. The solution will hold its new equilibrium temperature for approximately one second before conduction of heat within the cell brings the sample back to the base temperature of the water jacket which surrounds the cell. The selection of the proper organic indicator to follow the reaction is critical. The indicator must respond very rapidly to the new equilibrium value, have an absorbance change appropriate to the reaction being followed, the absorbance change should follow the Beer-Lambert law and the indicator must not complex with any of the reactants or products in the solution. The proper indicator may be selected by referring to the books by Bates (1964) and Bishop (1972). The relaxation times of several common indicators have been determined by Massey and Schelly (1974) and Eigen and Hammes (1960). In a majority of cases the indicator relaxation time is on the order of 0.75 μsec which is adequate for the studies conducted. One continuing difficulty of the optical system used is the noise output of the system. Because of the shot noise produced by the background illumination and other related factors, the oscilloscope is really

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measuring a signal to noise level. The system is designed to optimize this level but fluctuations tend to limit the accuracy of the data collected. One other problem that may be noted is the rapid increase in pressure during the temperature step. There is the possibility of shock wave formation within the cell and cavitation effects (bubble formation) can occur. The severity of this problem increases as the base temperature increases and the magnitude of the temperature jump is increased. For the work conducted in support of this study, the minimal temperature rise and moderate base temperatures did not appear to cause cavitation or bubbles.

      b. <u>Preparation of Samples.</u> All temperature jump samples were prepared from the same lot of analytical reagent grade chemicals used in the resonator work. Chemicals were weighed on a Mettler balance and mixed with deionized water having a specific resistance of 15 megohms. After adequate mixing, the pH of the solution was adjusted using NaOH. The pH measurements were made using a Beckman Research pH meter and a Ag/AgCl glass reference electrode. Samples were placed in polyethylene containers and a vacuum pulled on the open containers to remove residual air bubbles and degas the samples. Containers were then closed and transported to the temperature jump equipment.

      Prior to using the sample, a specific amount of pH sensitive indicator was added. The primary indicators were phenol red, cresol red, and phenol-thaline, depending on the pH of the solution. Cresol purple and brilliant yellow were also used to examine indicator effect on the reaction. Indicator

concentrations were generally on the order of 10^{-5} molar. The solution pH was rechecked prior to filling the cell. The temperature jump cell was cleaned with distilled water and rinsed with the solution prior to filling. The cell was then filled slowly and agitated to remove residual bubbles from the wall. The filled cell was then placed in the temperature jump machine and allowed to come to the base temperature prior to commencement of data collection.

    c. <u>Measurements and Analysis</u>. All data were taken using a polaroid camera attached to a Tektronics 564 storage oscilloscope with type 3A3 insert. The oscilloscope was set to sweep upon receipt of the capacitor discharge trigger from the temperature jump equipment. Sweep speed and vertical deflection were adjusted to provide the optimum signal for any section of the trace to be examined. The trace on the scope was recorded on film for analysis. To ensure reproducibility of data, only the data from the first ten jumps were used. Repeated temperature jumps can destroy the solution or the indicator, and thus were avoided.

    Each polaroid picture was examined by establishing a reference line based on the asymptote of the observed signal. A smooth line was drawn through the observed signal trace and deflection from the reference line recorded at intervals along the horizontal time sweep. The deflection values were then plotted against time on semi-log paper and a curve fit to the data. A straight line fit would indicate a single relaxation with the data point scatter being indicative of closeness of fit. Significant breaks in the curve would

indicate two or more closely coupled relaxations. In all data examined a straight line fit was determined to be optimum. The slope of the curve then gives the reciprocal of the relaxation time as stated by equation (2-5).

IV. EXPERIMENTAL RESULTS

1. LOW FREQUENCY SOUND ABSORPTION AND RELAXATION FREQUENCY DATA

a. Background. As previously noted, the general shape of the
Thorp low frequency absorption curve, figure 1, is not unlike the $MgSO_4$
chemical relaxation absorption curve observed at higher frequency. The
possibility of a low frequency relaxation was supported by the temperature
jump data published by Yeager et al (1973), wherein sea water was shown to
have a relaxation frequency near 1 kHz which could be indirectly related to
boric acid concentration. Subsequent work by Fisher and Levison (1973)
tended to confirm the importance of boric acid to the observed relaxation.
The earlier work by Wilson (1951) indicated that synthetic sea water contain-
ing NaCl, $MgCl_2$, $MgSO_4$ and KCl followed the high frequency $MgSO_4$
relaxation very closely, but natural sea water tended to deviate from the
theoretical curve at lower frequency (figure 10). This deviation could
possibly be related to the presence of a lower frequency relaxation absorption
due to another salt in natural sea water, or simply experimental error.

The existence of a relaxation frequency in sea water, observed by
temperature jump methods, that is close to that deduced by Thorp from
acoustic data does not in itself confirm Thorp's data nor define a mechanism.
As shown by equation (2-26), the magnitude of chemical related relaxation
sound absorption depends on the concentration of the chemically active species
and the change in molal volume ($\Delta \overline{V}^o$) in response to a pressure
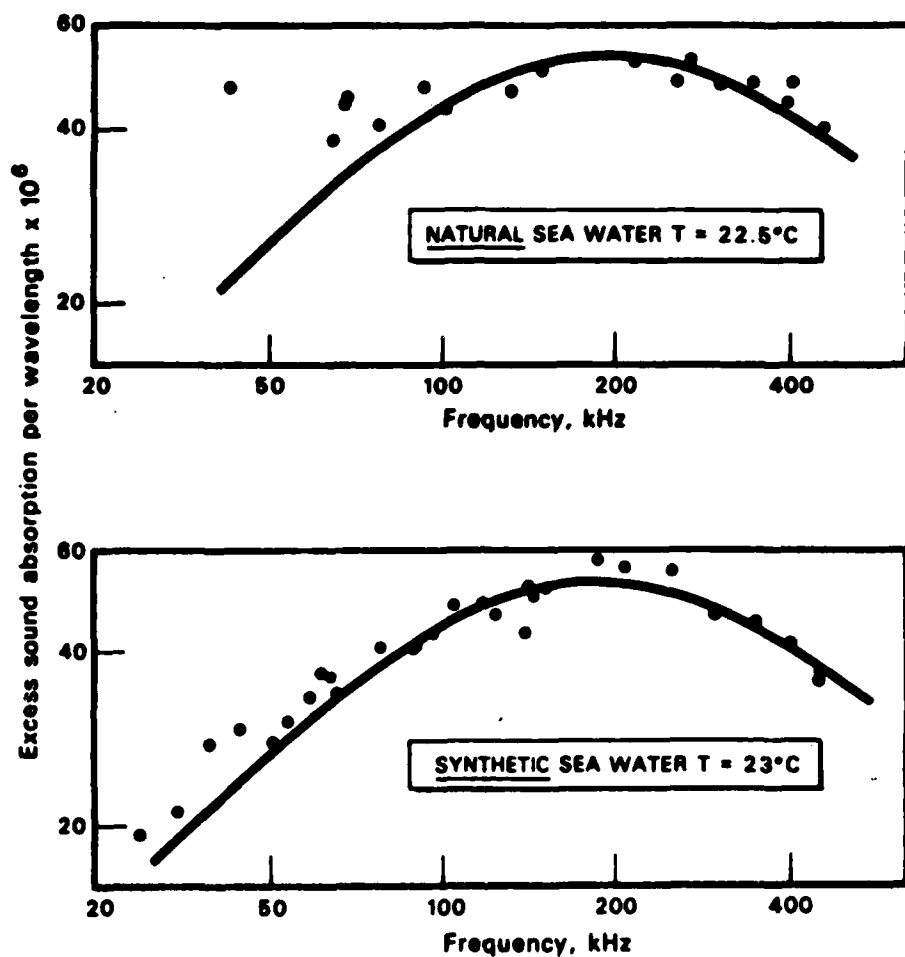
Figure 10

Sound absorption data from Wilson. Excess sound absorption per wave length

($\alpha \lambda$) versus frequency taken from the work of Wilson (1951). The upper

figure is data from natural sea water at a temperature of 22.5°C. The lower

figure is for a synthetic sea water at a temperature of 23°C.

perturbation. The small concentration of boric acid in sea water (4.2×10^{-4} molal) must be balanced by a large change in molal volume before this reaction could be seriously considered. Data by Disteche and Disteche (1967) and Ward and Millero (1974A,B) indicate that the $\Delta \overline{V}^0$ value is approximately 35 cc/mole. Substitution of these values into equation (2-26), assuming the reaction mechanism used by Anderson, Eyring and Whittaker (1964) and dissociation constants for boric acid from Lyman (1957), a value of 5.6×10^{-5} was obtained for $\alpha\lambda$. This value was more than the value of 1.2×10^{-5} derived from the Thorp data. The problem was to confirm the sound absorption data in the laboratory and define the cause.

      b. <u>Resonator Sound Absorption Data.</u> In order to learn the technique and to assure validity of the system, initial data runs were made on a 12 liter spherical resonator originally used by Leonard in 1949. Base line data were established using pure deionized water and then data collected with Lyman and Fleming (1940) (L & F) artificial sea water in the resonator. The resultant $\alpha\lambda$ plot in figure 11 clearly shows the $MgSO_4$ relaxation centered at 215 kHz and a very slight upturn at lower frequency. To examine the importance of boric acid, additional data runs were conducted with boric acid deleted from the artificial sea water. Although not conclusive, because of the low frequency limit of the 12 liter resonator, data in figure 11 would indicate that the low frequency upturn had been eliminated.

      In order to confirm the 12 liter resonator data and to obtain additional data at low frequency, a 50 liter resonator (originally from Leonard's

Figure 11

Sound absorption in the 12 l resonator with Lyman and Fleming sea water at 31°C. Excess sound absorption per wave length ($\alpha\lambda$) based on data collected at 31°C in the 12 liter spherical resonator. The closed circles are for the Lyman and Fleming artificial sea water with boric acid. The dashed line is the $\alpha\lambda$ curve for the higher frequency relaxation.

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laboratory) was employed and similar data runs conducted. As shown in figure 12, the low frequency deviation of L & F artificial sea water from sea water without boric acid has become quite noticeable. Because the low frequency data limit of this resonator is approximately 9 kHz, sufficient data cannot be obtained to estimate the magnitude of the absorption in the artificial sea water, nor can the boric acid absorption mechanism be adequately studied. The results of the 12 and 50 liter resonators have demonstrated the existence of the low frequency sound absorption in sea water and give positive confirmation to the importance of boric acid to this absorption. These data provided justification for going to a 200 liter resonator with a low frequency data cutoff of approximately 6 kHz and point up the need for additional temperature jump data to support the resonator work.

The 200 liter resonator data for Lyman and Fleming artificial sea water with and without boric acid are presented in figures 13 to 17 for select temperatures. Plots were constructed by making a template of the theoretical $\alpha\lambda$ curve for a single frequency relaxation using equation (2-15) as shown in figure 3. The template was fitted to the data from the solution without boric acid and the heavy dashed curve drawn. A solid line is now drawn through the data points for the complete artificial sea water down to a frequency of 6 kHz. The difference between these two lines is now obtained and plotted. The apex of the theoretical $\alpha\lambda$ curve template is now placed at the appropriate relaxation frequency obtained from supporting temperature jump studies and the template moved along the line of the ordinate until a match is

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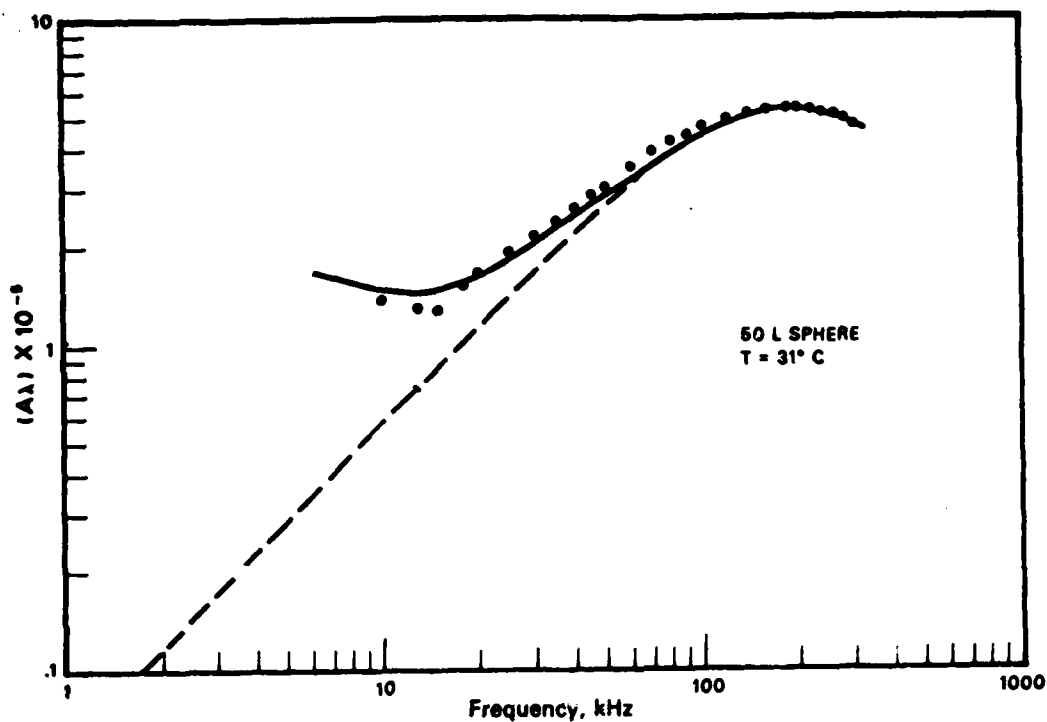
Figure 12

Sound absorption in the 50 l resonator with Lyman and Fleming sea water at 34°C. Excess sound absorption per wave length ($\alpha\lambda$) based on data collected at 34°C in the 50 liter spherical resonator. The closed circles are for Lyman and Fleming artificial sea water with boric acid. The dashed line is the curve for the higher frequency relaxation.
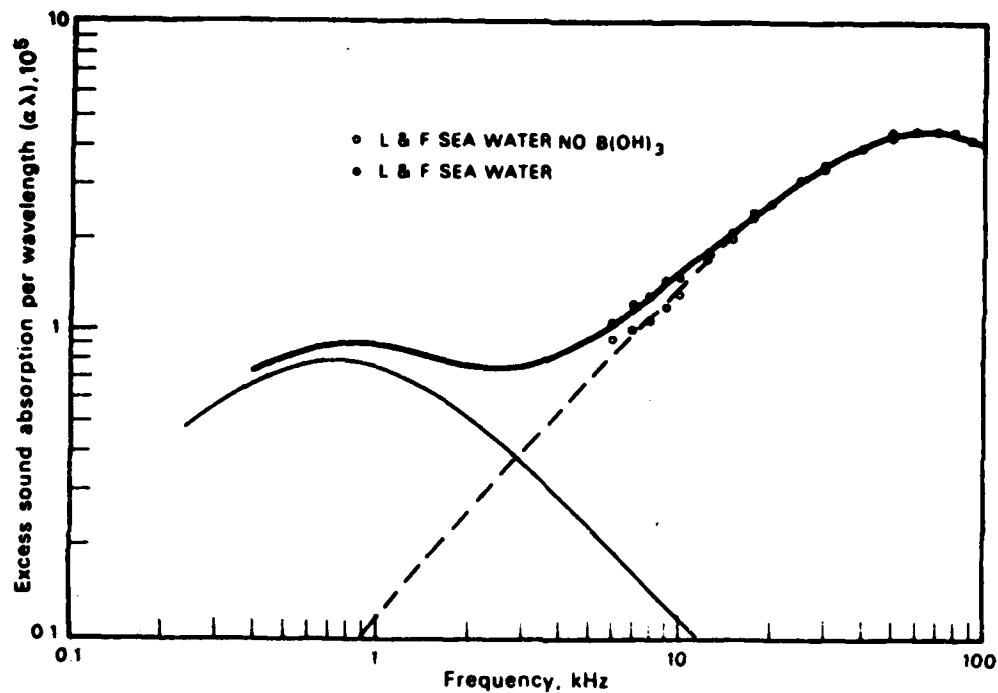
Figure 13

Sound absorption in the 200 l resonator with Lyman and Fleming sea water at 4°C. Excess sound absorption per wave length ($\alpha\lambda$) based on data collected at 4°C in the 200 liter spherical resonator. Open circles are for Lyman and Fleming artificial sea water without boric acid. The closed circles are for the same sea water with boric acid. The light dashed line is the high frequency relaxation curve, with the light solid line being the relaxation curve attributed to boric acid. The heavy solid line is the composite curve for the two relaxations.
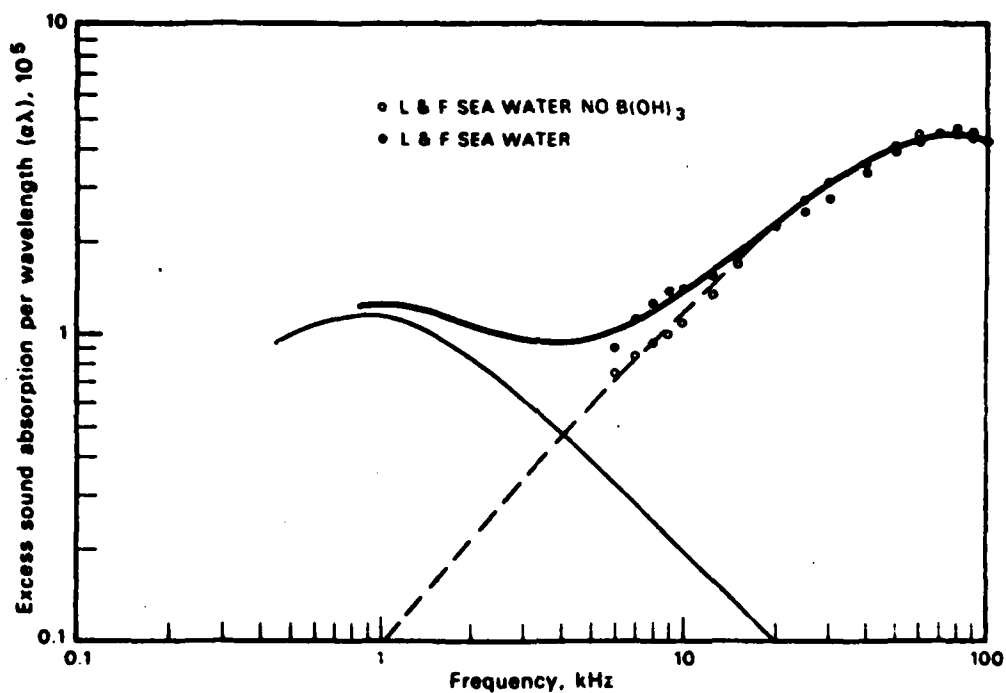
Figure 14

Sound absorption in the 200 l resonator with Lyman and Fleming sea water at
9°C. Excess sound absorption per wave length ($\alpha\lambda$) based on data collected
at 9°C in the 200 liter spherical resonator. Open circles are for Lyman and
Fleming artificial sea water without boric acid. The closed circles are for the
same sea water with boric acid. The light dashed line is the high frequency
relaxation curve, with the light solid line being the relaxation curve attributed
to boric acid. The heavy solid line is the composite curve for the two relaxa-
tions.
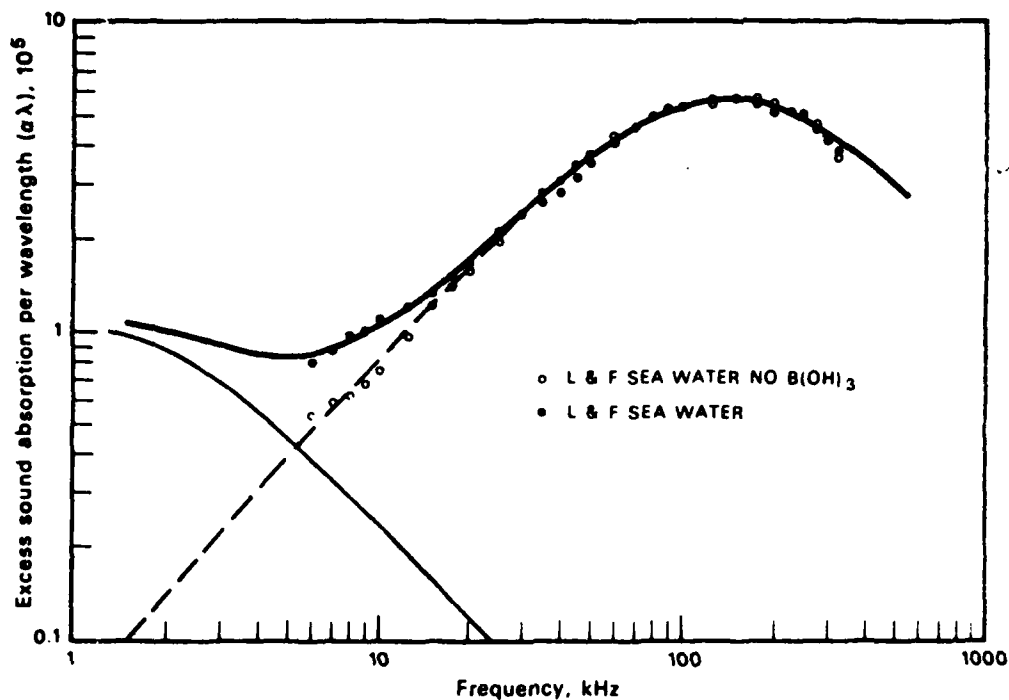
Figure 15

Sound absorption in the 200 l resonator with Lyman and Fleming sea water at 20°C. Excess sound absorption per wave length ($\alpha\lambda$) based on data collected at 20°C in the 200 liter spherical resonator. Open circles are for Lyman and Fleming artificial sea water without boric acid. The closed circles are for the same sea water with boric acid. The light dashed line is the high frequency relaxation curve, with the light solid line being the relaxation curve attributed to boric acid. The heavy solid line is the composite curve for the two relaxations.
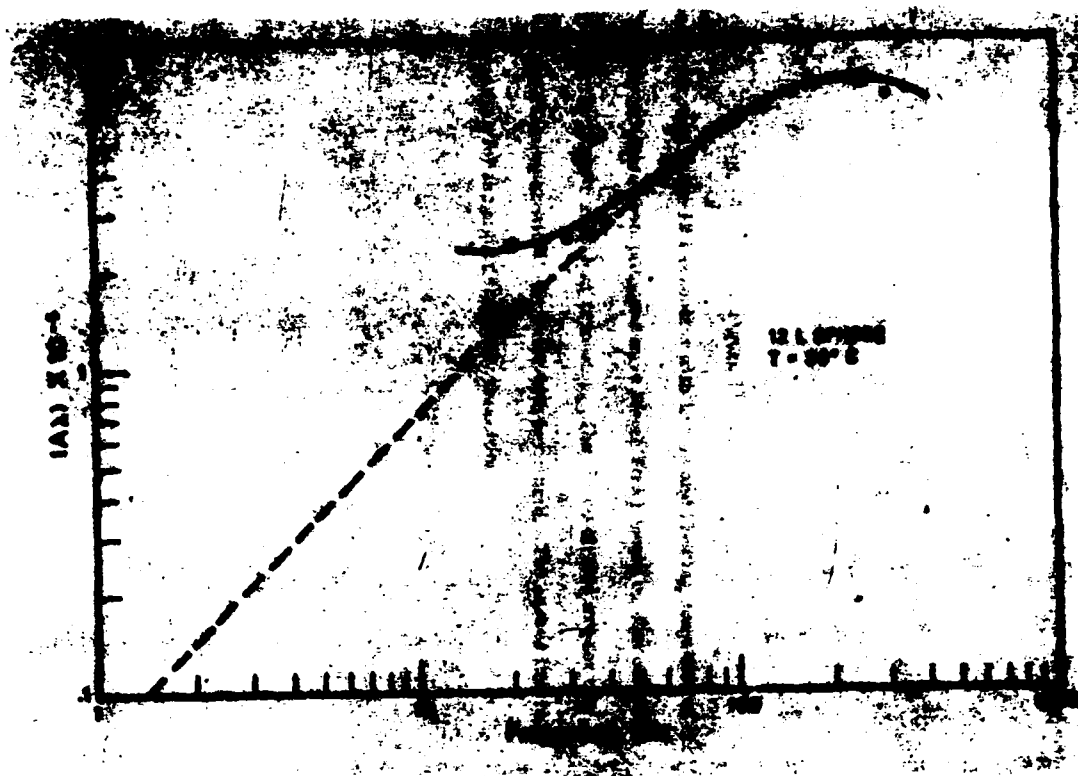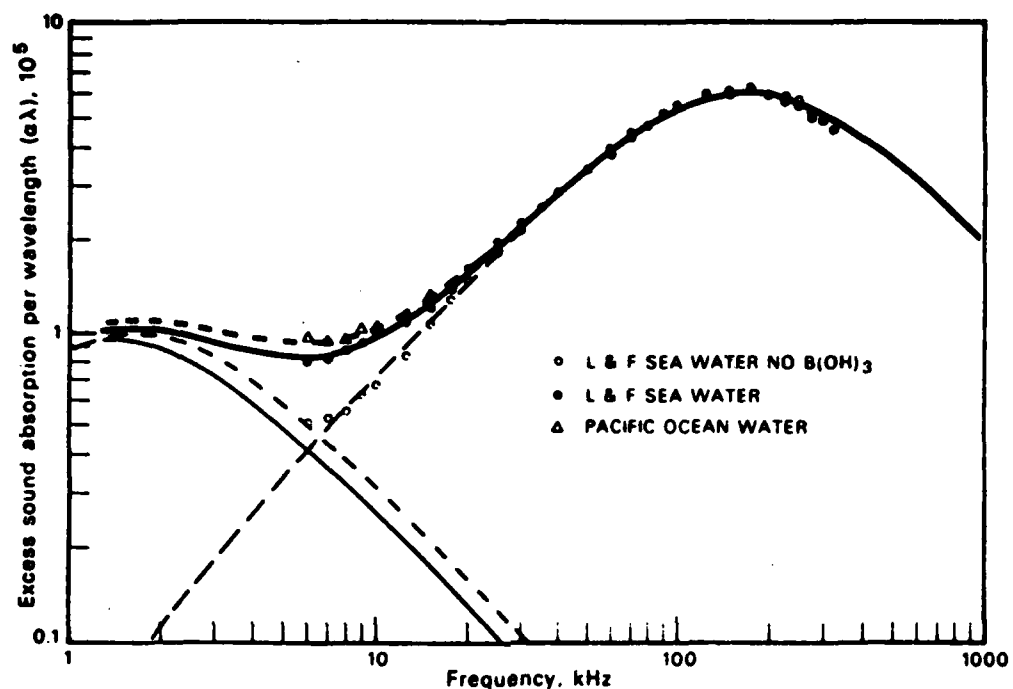
Figure 16

Sound absorption in the 200 l resonator with Lyman and Fleming sea water at 28.5°C. Excess sound absorption per wave length ($\alpha\lambda$) based on data collected in the 200 liter spherical resonator. The closed and open circles represent data for Lyman and Fleming artificial sea water with and without boric acid respectively taken at 28.5°C. The triangles represent data for near shore Pacific Ocean water taken at 25°C.

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Figure 17

Sound absorption in the 200 l resonator with Lyman and Fleming sea water at 36°C. Excess sound absorption per wave length ($\alpha \lambda$) based on data collected at 36°C in the 200 liter spherical resonator. The closed circles represent data for Lyman and Fleming sea water. The open circles are for the same solution without boric acid. The triangles are for the solution with five times the sea water concentration of boric acid and the closed squares are for the same solution with ten times the sea water concentration of boric acid.

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obtained with $\alpha\lambda$ values previously plotted. The light line is then drawn. The heavy solid line, which represented the composite effect, is now completed below 6 kHz by adding the values of the dashed and light lines and is considered to represent what the full absorption data would look like if lower frequency absorption data were available. Although the plot represents a composite of temperature jump data and sound absorption data, the approach is considered appropriate and represents the only means of approaching the problem with existing laboratory equipment.

In figure 16, data from actual sea water are compared with the Lyman and Fleming formulation. The agreement between the two solutions is very strong at the high frequency relaxation but some deviation is noted at low frequency with $\alpha\lambda$ values being larger for the actual sea water. The low frequency variation is not explained; however, the actual sea water used was obtained at Scripps Pier in relatively shallow water and is probably not representative of the general Pacific Ocean water. Although there is no reason to expect any significant variation in boric acid concentration, the Scripps Pier water did have a salinity of 33.6°/oo which is not representative of Pacific Ocean near surface water where the salinity is 35°/oo. The actual sea water data were collected at 25°C while the artificial sea water data were obtained at 28.5°C. This small temperature difference is insufficient cause to explain the observed difference. It should be noted that consideration of the estimated 10% error in measurement of the decay rate data could explain only part of the difference. In summary, although some low frequency variability is noted

the data presented indicate that the artificial sea water is sufficiently close to natural sea water to satisfy the purposes of this work.

Figure 17 presents data on the effect of boric acid concentration to the observed $\alpha\lambda$ values. Selecting the higher temperature to gather this data allowed a better look at the resultant curves and increased accuracy. The important thing to note is that $(\alpha\lambda)_{max}$ does not increase in direct relation to the concentration of boric acid. A ten-fold increase in boric acid concentration produced only a two-fold increase in $(\alpha\lambda)_{max}$. The importance of this observation will be addressed more completely when the reaction mechanism is discussed.

A review of the data presented in figures 11 to 17 would provide the following points: (1) The increase in sound absorption at low frequency is directly related to the presence of boric acid. (2) The Lyman and Fleming artificial sea water is sufficiently close to natural sea water to justify use of the former in these studies. (3) The absorption increase with increased boric acid concentration is not a linear relationship.

The next set of absorption data was collected using a 0.725 M NaCl solution with boric acid. The objective was to examine the influence of boric acid in a medium that was of the same ionic strength of sea water. NaCl was selected because it is a major constituent of sea water and it does not exhibit any sound absorption (Kurtze and Tamm, 1953). The base line absorption data were collected using NaCl dissolved in pure deionized water. Boric acid was then added to the system and the resultant $\alpha\lambda$ data are presented in

figure 18. Frequencies up to 350 kHz were examined but no increase in absorption was noted and the data were not plotted. The low frequency absorption was very evident. It will be noted that an increase in boric acid concentration caused an increase in relaxation frequency, based on temperature jump data, but there was no increase in the maximum $\alpha\lambda$ values. In fact, a small decrease was noted. This is in contrast to artificial sea water where increased boric acid concentration tended to increase $\alpha\lambda$.

A third series of data was collected on boric acid in pure deionized water. These data show that boric acid exhibits the low frequency absorption by itself and indicate the importance of pH to the absorption effect. As in the case of NaCl solution, only the low frequency data are shown in figure 19, as nothing was noted at higher frequency. When boric acid was added to pure water the resultant pH was approximately 6.1 and no excess absorption could be noted. As pH was increased by the addition of NaOH, the excess absorption tended to increase. The data are not considered to be of high accuracy because the relaxation frequency could not be obtained from the temperature jump technique for such a low ionic strength medium. The assumption has been made that the relaxation frequency in NaCl solution is similar to that in fresh water, and the former values were used. The assumption would be correct if the boric acid reaction did not react with the NaCl and if no effect could be attributed to the increased ionic strength. Neither case is completely satisfied. Byrne and Kester (1974) noted that up to 3% of total boron in sea water could be complexed to form sodium borate. Although there is some
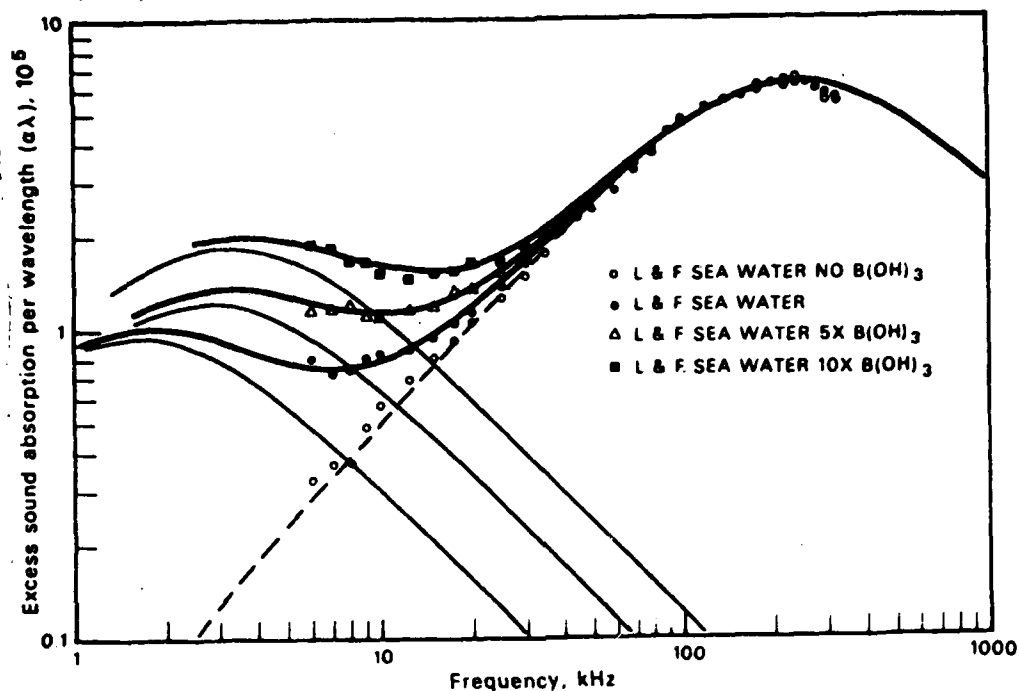
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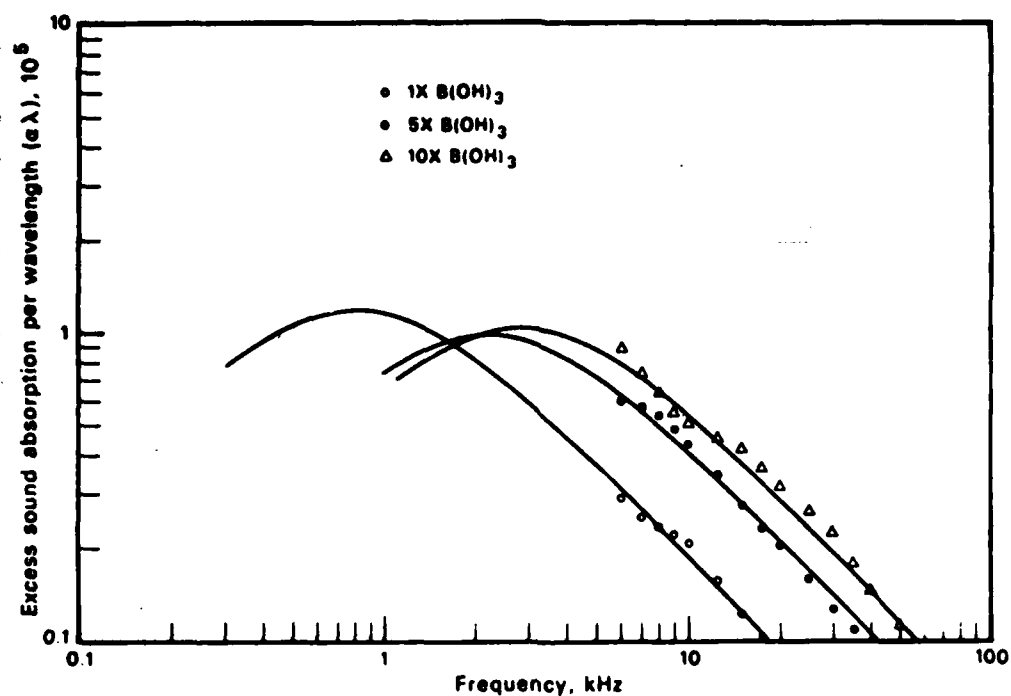
Figure 18

Sound absorption in the 200 l resonator with boric acid in NaCl solution at 25°C. Excess sound absorption per wave length ($\alpha\lambda$) based on data collected at 25°C in the 200 liter spherical resonator. The solution was 0.725 M sodium chloride with boric acid at one, five and ten times sea water concentration as noted in the figure. The pH was adjusted to 8.0 by addition of NaOH.

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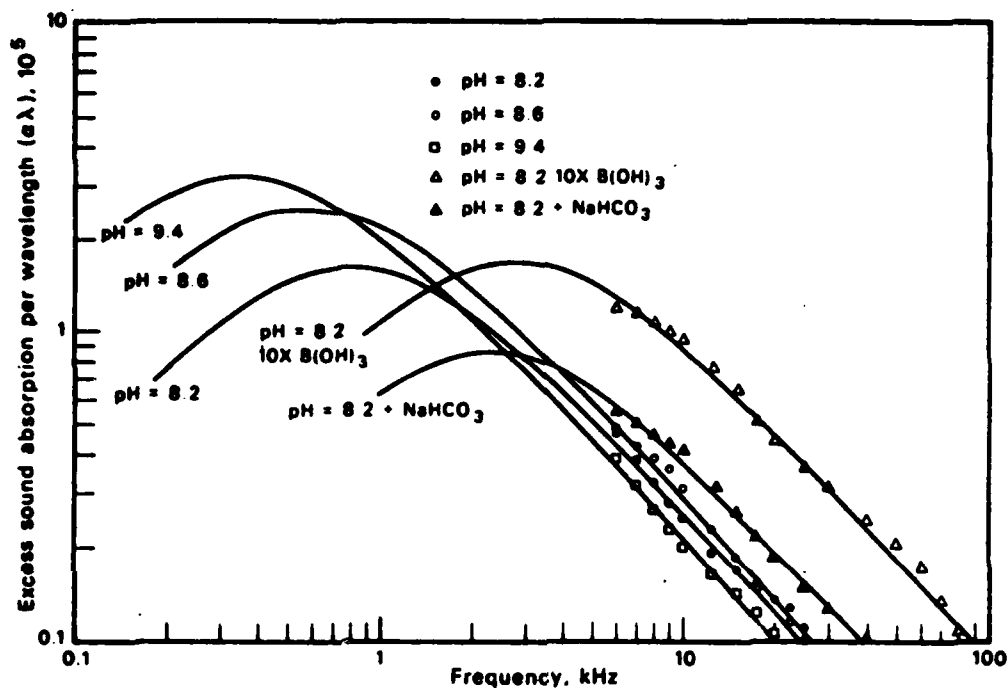
Figure 19

Sound absorption in the 200 l resonator with boric acid in pure water at 25°C.

Excess sound absorption per wave length ($\alpha\lambda$) based on data collected at

25°C in the 200 liter spherical resonator. The closed circles, open circles

and open squares are data points collected in a solution of boric acid at sea

water concentration in deionized water. The solution pH, adjusted with NaOH,

was as noted. The open triangles are data for deionized water solution with

ten times the sea water concentration of boric acid. The closed triangles are

data from a deionized water solution with boric acid and sodium bicarbonate

at sea water concentration.

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controversy about their results, up to 10% of the borate ion '. NaCl solution could be so tied up. As a result, the exact relaxation frequency is in doubt. The data presented does indicate several interesting facts. In the first case, an increase in pH does tend to increase the maximum value of $\alpha\lambda$, but because of the decrease in relaxation frequency, the excess absorption at frequencies greater than 2 kHz is not appreciably affected. Second, increasing the boric acid concentration by a factor of ten did not appreciably increase the maximum value of $\alpha\lambda$, although a shift in relaxation frequency was noted. Thirdly, the addition of $NaHCO_3$ to obtain sea water concentration tended to reduce the maximum $\alpha\lambda$ value and the relaxation frequency was increased. These data would indicate the importance of carbonate to the low frequency sound absorption. The lack of any excess absorption at pH 6.1 is attributed to the very small ionization of boric acid in this pH range.

Garland, Patel and Atkinson (1973) have proposed a relaxation mechanism of magnesium, carbonate and sulfate to explain any low frequency excess absorption in the region of 8 kHz. Data from the 200 liter resonator do not support any excess absorption in this region. Separate runs in the 12 and 50 liter spheres on a solution of $MgCl_2$, $NaHCO_3$, Na_2SO_4 and NaCl indicated no excess absorption at low frequency. Temperature jump data on an identical solution also failed to indicate a relaxation frequency in the expected region. It must be noted that a 8 kHz relaxation frequency is very near the resolution limit of the temperature jump apparatus used and the temperature jump results are not confirming in themselves. However, neither the resonator nor

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temperature jump data will support the theoretical low frequency relaxation proposed by Garland et al (1973).

c. <u>Accuracy of Resonator Data.</u> The overall accuracy of resonator data cannot be readily ascertained. Wilson (1951) observed that decay rates could be measured with an accuracy of 5%. This estimate is for the decay rate once the mode is located and does not consider the error in locating the identical mode in various solutions. For any given run only the lowest decay rates are used and no average of observed data would be meaningful. An attempt to produce replicate runs of sufficient number to be statistically significant would be extremely time consuming. The following observations are considered germane to this problem: (1) On any individual temperature run, individual modes could be readily relocated and decay rates varied by an average of 3%. (2) For runs in different solutions, the identical mode shape could generally be located based on the change in sound velocity. (3) As shown in Table 1, the observed $MgSO_4$ relaxation frequency and $\alpha\lambda$ values for the 200 liter sphere are very close to the interpolated values obtained from Wilson. These three subjective observations indicate that the resonator data are probably accurate to plus or minus 15 - 20% as a conservative esti-mate.

d. <u>Temperature Jump Results.</u> The temperature jump apparatus provides a direct measure of reaction relaxation time (τ) which is related to relaxation frequency (f_r) by $f_r = 1/2\pi\tau$. Because the temperature jump effect depends on Joule heating, solutions must have a reasonably high ionic

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Table 1

Comparison of $MgSO_4$ Relaxation Frequencies and Maximum

$\alpha\lambda$ Values for Natural Sea Water from Wilson (1951) and for

Lyman and Fleming Artificial Sea Water from this Work

Temperature °C	Natural Sea Water		Lyman and Fleming Sea Water	
	Relaxation Frequency kHz	$(\alpha\lambda)_{max}$ x 10^5	Relaxation Frequency kHz	$(\alpha\lambda)_{max}$ x 10^5
4	70	4.2	69	4.5
9	86	4.3	86	4.3
20	141	5.1	145	5.7
28.5	197	5.8	185	6.1
36	235	6.6	240	6.3

strength. The low ionic strength of boric acid in pure water precludes direct observation in this medium.

To follow the reaction, organic pH indicator solutions were used as follows:

Phenol Red   pH $\leq$ 7.5

Cresol Red   7.5 < pH < 8.5

Phenolphthalein   pH $\geq$ 8.5

All indicator concentrations were less than 2×10^{-5} molar. The importance of indicator type and concentration is addressed in a later section. The base temperature for the majority of data was $18.5^{\circ}C$ with a final temperature of $22^{\circ}C$.

The data presented in figure 20 are for boric acid in 0.725 M NaCl solution. The concentrations are 1, 2, and 10 times the sea water values for solution pH values from 7.0 to 9.0 at 0.5 pH intervals. The pH was adjusted by addition of NaOH to the solution. For any desired pH there is a strong dependency of relaxation frequency on boric acid concentration. This dependency would tend to rule out the possibility of a one step unimolecular reaction, as will be discussed later. There is also an apparent dependency of relaxation frequency on pH for any given concentration. The curves are not linear, with a greater decrease in relaxation frequency at higher pH values. Data of Yeager et al (1973) for standard sea water indicate no change in relaxation frequency with pH up to 8.54, then a fairly sharp decrease. These results are not inconsistent with the data shown. The decrease in relaxation
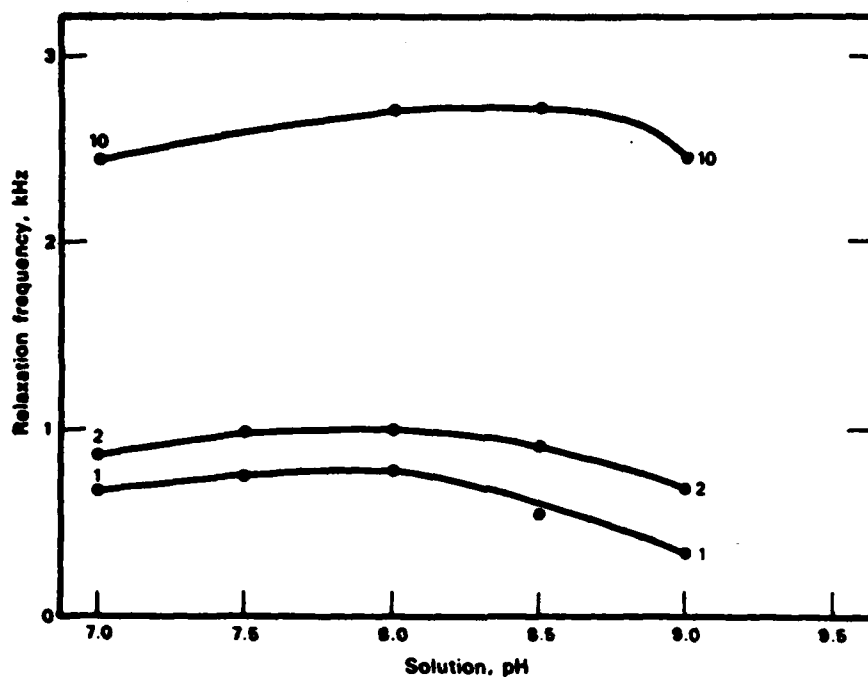
Figure 20

Relaxation frequency pH dependence. Effect of boric acid concentration and solution pH on the observed temperature jump relaxation frequency in a 0. 725 M NaCl solution at a base temperature of 18. 5°C. The numbers on the curves indicate boric acid concentration based on sea water concentration being unity.

frequency at high pH values is probably related to the increased contribution of the hydroxyl ion to the boric acid concentration dependence as pH increases.

Table 2 provides temperature jump data used to support the resonator work. All data are for a solution adjusted to a pH of 8.0. Comparison of the NaCl solution data to the artificial sea water data indicates an increased relaxation frequency for the sea water samples. The standard sea water demonstrates a relaxation frequency that is slightly higher than the artificial sea water. Although not shown in the table, no relaxation was noted in Lyman and Fleming artificial sea water without boric acid. Nor was any relaxation noted in a solution of $MgCl_2$, $NaHCO_3$, Na_2SO_4 and NaCl or a solution of $MgCl_2$, $NaHCO_3$ and NaCl. Garland et al (1973) had proposed a relaxation frequency of 8 kHz for these solutions. Additional temperature jump data will be discussed in following sections.

e. Accuracy of Temperature Jump Data. The relaxation frequencies obtained from temperature jump are normally considered to be plus or minus 20% (Eigen and De Maeyer, 1963). In the case of data presented herein, each data point represents the average of a minimum of four jumps. The variability for a series of measurements was generally less than 10%. Solutions of sea water concentration boric acid in NaCl solution have been measured three times in different solutions over a period of three months. The observed relaxation frequencies were 0.773 kHz, 0.770 kHz and 0.762 kHz respectively. As the buffering capacity of the solution increases, by adding $NaHCO_3$, the temperature jump trace becomes more erratic and more difficult to

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Table 2

Temperature Jump Relaxation Frequencies for

Various Solutions at a Temperature of $22^{\circ}C$

Solution	Boric Acid Concentration (times sea water value)	pH	Relaxation Frequency kHz
NaCl	1	8.0	0.77
NaCl	5	8.0	2.07
NaCl	10	8.0	1.71
L&F Sea Water	1	8.0	1.17
L&F Sea Water	5	8.0	2.61
L&F Sea Water	10	8.0	3.02
Standard Sea Water	1	7.6	1.35
Standard Sea Water	2	7.6	1.89
Standard Sea Water	5	7.6	2.76

evaluate. In the sea water case, the full plus or minus 20% error is considered appropriate but for boric acid NaCl solutions the error is more on the order of 10%.

2. CHEMISTRY OF BORIC ACID

Boron is an element of significant academic interest and of commercial importance for select industrial application. The full chemistry of boron is a subject unto itself, as addressed in the book by Muetterties (1967). In this study, only aqueous solutions of boric acid will be treated.

Boric acid enters sea water primarily by the weathering of igneous rock. Once in the ocean, boric acid is generally a conservative quantity. The boron/chlorinity ratio of approximately 0.232 B $(mgkg^{-1})/Cl(^o/oo)$ is virtually constant in both horizontal and vertical extent (Uppstrom, 1974), with some minor variation noted in the region of the oxygen minimum. It is noted, however, that methods to analyze boron in sea water are considered to be of questionable accuracy. Considering that boric acid is a major factor in establishing the buffering capacity of sea water, the study of this compound has received nowhere near the attention of the carbonate system and is often overlooked in studies of sea water buffering.

Surprisingly little is known about the structure of boric acid in aqueous solution. Edwards, Morrison, Ross and Schultz (1955) have shown that boric acid should be properly considered a Lewis acid (electron pair acceptor). They also note that by comparison with x-ray data on the minerals teepleite and brandylite, by Raman spectrum and nuclear magnetic resonance,

the borate ion should be written as $B(OH)_4^-$ and it has a tetrahedral symmetry. The basic $B(OH)_3$ molecule has been shown by Raman spectrum to be trigonal planar. It is generally agreed that these two species are the primary forms of boron in sea water. Extensive work by Edwards (1953) and Ingri (1962, 1963A) have shown that as concentration of boric acid increases there is a strong tendency to form polyborates. The critical threshold of concentration is vaguely defined to be 0.025 M by Ingri, Lagerstrom, Frydman and Sillen (1957) and 0.01 M by Mesmer, Baes and Sweeton (1972). In any case this is not a serious consideration in sea water as Hansson (1973A) has estimated less than 0.001% of boron is in the polyborate form. The formation of poly- borates does limit some experimental work as to what concentrations can be examined. Although there is no evidence for complexing of $B(OH)_3$ in sea water, it has been postulated that the borate ion complexes with magnesium and calcium (Dyrssen and Hansson, 1973) and sodium (Byrne and Kester, 1974). There is no indication for complexing of boric acid with silicate (Seward, 1974) or for the formation of floride compounds such as BF_4^- (Moriguchi and Hosokawa, 1971). Aqueous boric acid does complex with certain organic polyhydroxyl compounds to form a strong acid (Gast and Thompson, 1958). This organic complexing is the basis for the quantitative analysis of boron in sea water.

The ionization mechanism of boric acid has not been adequately de- fined nor have the rate constants been fully evaluated. Using the acid-base equilibrium scheme developed by Eigen (1964), Yeager (1975) proposed the

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general diagram shown in figure 21. Selection of the proper leg of this re-action to fit experimental conditions is fairly subjective. Observing that the pH of sea water is around 8.0, where the hydroxyl ions are in excess over the hydrogen ions, and by estimation of the diffusion controlled rate constants, it is postulated that step 2 to 3 is probably the more important and appropriate in sea water. Personal communication from Yeager confirms this estimate. Bell, Edwards and Jones (1967) noted that the obvious change in coordination number of boron from three to four could substantiate a three state, two step ionization process. Although several mechanisms were proposed, there wasn't sufficient experimental evidence to either confirm the two step process or define the intermediate reactants and products.

To complete the discussion of the ionization of boric acid, it is noted that several experimenters have proposed a second and possibly third dis-sociation based on potentiometric titration. Lyman (1957) interpreted features in his sea water results as being caused by a second dissociation and calcu-lated pK'_{2B} values which ranged from 9.11 to 11.17, depending on solution temperature and salinity. In reviewing this data, Edmond and Gieskes (1970) questioned the validity of the results and attributed the data to the alkaline error of the glass electrode used by Lyman or possibly to the formation of poly-anions. As a result, there is no firm evidence for high order dissoci-ation of boric acid in sea water; however, the possibility cannot be completely ruled out.
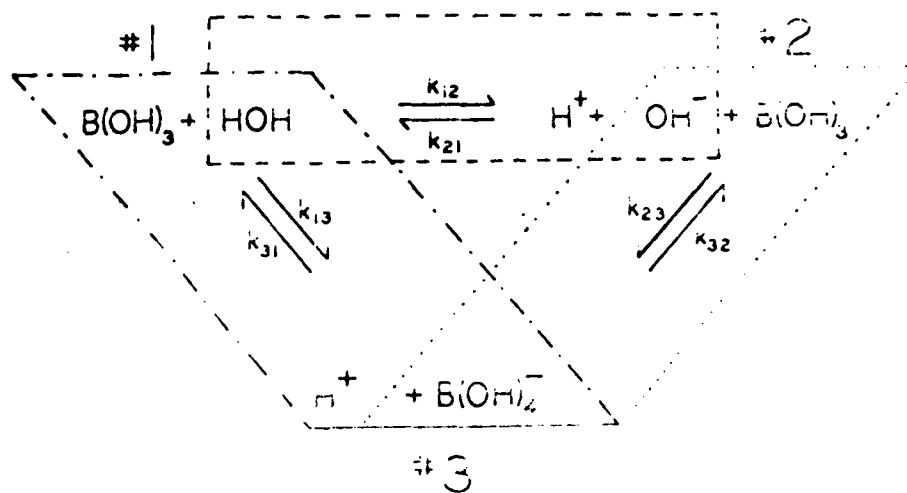
Figure 21

Boric acid ionization triangle. Boric acid reaction triangle indicating the

possible ionization paths for a one step reaction.

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3. BORIC ACID REACTION PATH AND KINETICS

As previously discussed and in agreement with the work of Anderson, Eyring and Whittaker (1964), the basic boric acid reaction in sea water will be represented by

$$B(OH)_3 + OH^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} B(OH)_4^- \qquad (4-1)$$
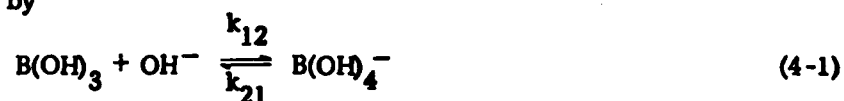
The equilibrium constants for this reaction are from the potentiometric derived equilibrium values obtained by Owen (1934) for pure water solutions, Owen and King (1943) for NaCl solutions and from Lyman (1957) for sea water, by using the equilibrium constant for pure water from Harned and Owen (1958) as done by Anderson et al (1964). The experimental data of Hansson (1973A,B) can also be used; however, the revised pH scale developed and used by Hansson (1973C) is not directly related to the NBS scale used in this work and the HSO_4^- error has not been considered in Hansson's pH values as pointed out by Bates (1975). With the reactant and product concentration values available, equation (2-4) can be used to determine the relaxation time for the one step boric acid reaction.

$$1/\tau = k_{12} \left\{ \left[B(OH)_3 \right] + \left[OH^- \right] \right\} + k_{21} \qquad (4-2)$$

If this reaction were to hold, plotting the reciprocal relaxation time data against the concentration of reactants should give a straight line. The slope of the line would be the forward rate constant (k_{12}) and the intercept on the $1/\tau$ axis as the reactant concentration goes to zero would be the back rate constant (k_{21}). Figure 22 represents such a plot and it is evident that the curve is not straight for either the NaCl solution or for sea water values. The
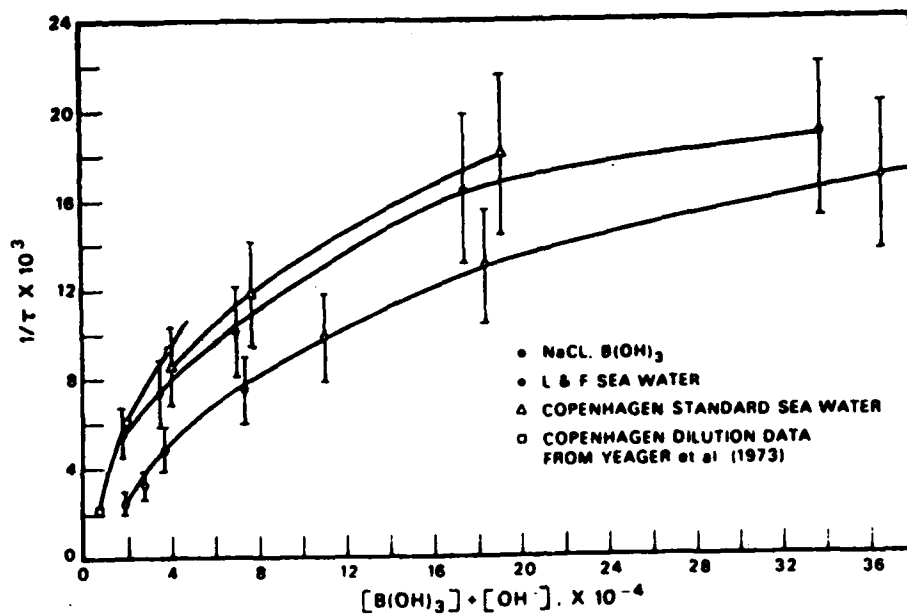
Figure 22

Concentration versus frequency for a one step reaction. A plot of concentration of boric acid plus hydroxyl ion concentration against reciprocal relaxation time for various solutions as noted. Error bars indicate a ±20% variability in relaxation time.

failure of the observed data to produce a straight line is the initial indication that the one step reaction may not hold for the boric acid reaction in NaCl solution or sea water.

The sound absorption data can also be examined to see if the one step reaction is applicable. Using equation (2-26) it can be seen that as the concentration of reactants increase, in particular the concentration of $B(OH)_3$, the observed $\alpha\lambda$ values should increase as a direct relation. Thus a ten times increase in $B(OH)_3$ should produce very nearly a ten times increase in

. As noted in figure 18 for the NaCl solution, $\alpha\lambda$ does not increase with $B(OH)_3$ concentration. For artificial sea water presented in figure 15, there is an increase in $\alpha\lambda$ by a factor of approximately two but this is far below the factor of ten expected. Despite the difficulties in obtaining the $\alpha\lambda$ data and the number of potential errors, there is little doubt but what a ten-fold increase in $\alpha\lambda$ would be detected if present.

In summary, neither the temperature jump relaxation times nor the resonator sound absorption data will support a one step ionization process for boric acid. In fact, the data is suggestive of a two step process as originally proposed by Bell et al (1967).

As noted in section IV, 2., the best that can be said about boric acid is that $B(OH)_3$ and $B(OH)_4^-$ are the primary constituents in aqueous solution at sea water concentration. The presence of a polyborate intermediate step is very unlikely due to the low concentration of boric acid in sea water. Any intermediate step between $B(OH)_3$ and $B(OH)_4^-$ must be of extremely low

concentration or it would have been detected by the techniques used by

Edwards (1953) and others. Noting that the ionization of boric acid requires a

transformation from a trigonal planar $B(OH)_3$ molecule to a tetrahedral $B(OH)_4^-$

ion, it is attractive to consider the intermediate state as an encounter complex.

The postulate is that the planar $B(OH)_3$ molecule encounters a hydroxyl ion in a

diffusion controlled process forming a loosely bonded complex. The trans-

formation to the tetrahedral $B(OH)_4^-$ ion, with resultant change in coordination

number, would then be the second step of the reactant. The first step under

diffusion control would be very rapid and not represent a large change in molal

volume. The second step would be much slower and give the major contribution

to the change in molal volume by the formation of the larger tetrahedral ion.

The reaction could then be written as

$$B(OH)_3 + OH^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} B(OH)_3\,OH^- \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} B(OH)_4^- \qquad (4\text{-}3)$$
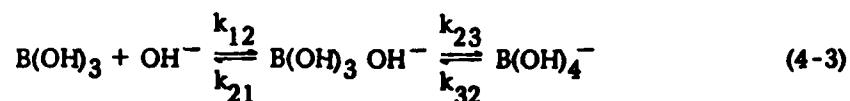
The exact structure of the intermediate step is open to interpretation and up

to this point its existence is based on circumstantial evidence. It was

especially encouraging, that Yeager (1975) independently arrived at the same

conclusion without full availability of the data presented above.

4. COMPARISON OF OBSERVED DATA TO THE PROPOSED REACTION
   MECHANISM

As discussed in section II, to resolve a two step reaction, a co-

ordinate transformation must be made and an eigenvalue problem solved.

Techniques to perform this operation have been well established by Eigen (1957)

and Eigen and Tamm (1962). The later approach by Garland, Patel and Atkinson (1973) is considered to be the more general and is used in this discussion. The complete derivation of the relaxation spectrum for equation (4-3) is contained in Appendix I. Only pertinent comments and equations will be presented herewith.

In order to resolve the relaxation time spectrum of a multistep process, the individual relaxation times must be separated by at least two orders of magnitude. In equation (4-3) it has been assumed that the first reaction is diffusion controlled and thus, much faster than the second step. Accordingly, the first step is almost completed before the second step gets completely underway. As shown in Appendix I, the fast first step may be represented by

$$1/\tau_I = k_{12} \left\{ [B(OH)] + [OH^-] \right\} + k_{21} \qquad (4-4)$$

with the slow second step represented by

$$1/\tau_{II} = k_{23} \left\{ \frac{[B(OH)_3] + [OH^-]}{(1/K_1) + [B(OH)_3] + [OH^-]} \right\} + k_{32} \qquad (4-5)$$

Assuming that the observed relaxation time is τ_{II}, then by knowing the term in brackets on the right and plotting this term against $1/\tau_{II}$ it would be possible to evaluate the rate constants. The first step equilibrium constant (K_1) is not known. The total equilibrium constant (K_Σ) has been determined and for a two step process it can be represented as a product of the constants for the individual steps by

$$K_\Sigma = K_1 K_2 \qquad (4-6)$$

or by

$$K_\Sigma = K_1 + K_1 K_2 \qquad\qquad (4\text{-}7)$$

as used by Hemmes (1972) for formulation of inner, outer sphere complexes.
It will subsequently be shown that, for the reaction in question, the two repre-
sentations give virtually the same representation as K_1 is much smaller than
$K_1 K_2$. The concentration of $B(OH)_3$ and OH^- can be determined from the K_Σ
value and pH measurements of the solution. The applicable concentration data
along with the corresponding temperature jump relaxation times are fed into a
computer and by iteration on the value of K_1, a first order least square fit is
performed on the parameters in equation (4-5). After each iteration, the
slope (equated to k_{23}) and the intercept (equated to k_{32}) values are examined
and the second step equilibrium constant is formed as $K_2 = k_{23}/k_{32}$. By use
of equation (4-6), the calculated K_2 value along with the iteration K_1 value are
used to calculate a proposed K_Σ. The proposed K_Σ is compared with the
measured K_Σ and an error parameter defined which becomes the basis for
the next iteration of K_1. The process is continued until the proposed and
actual K_Σ values agree to within an error of say 0.1%. The data presented
in figure 22 can now be plotted in such a manner that a straight line is ob-
tained, figure 23. The presence of a straight line on this plot does not directly
confirm a two step process, but does indicate that the data can be explained by
a two step process.

The iteration process provides an evaluation of the rate constants
k_{23} and k_{32} and the equilibrium constants K_1 and K_2. The rate constants for
the first step can be inferred by knowledge of the diffusion controlled rate

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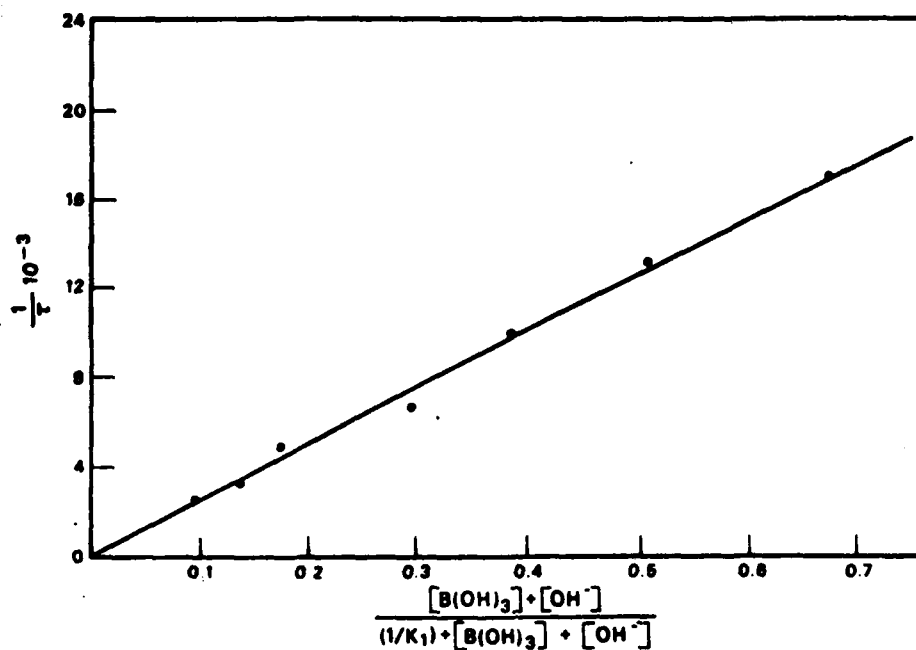
Figure 23

Concentration versus frequency for a two step reaction. A plot of the concentration term for the slow second step of a two step reaction against the reciprocal relaxation time. Data points have been calculated for a 0.725 M NaCl, boric acid solution at $22^{\circ}C$ with pH adjusted to 8.0 by the addition of NaOH. Although unclear in the figure, the curve does not pass through zero but has a slightly positive intercept on the ordinate.

constant of the first step. Using the von Smoluchowsky question applicable to equation (4-3), Anderson et al (1964) predicted that k_{12} should be on the order of $10^{-10} M^{-1} sec^{-1}$. Yeager (1975) has proposed a value for k_{12} of $3 \times 10^{-10} M^{-1} sec^{-1}$. This later quantity can be used with the calculated value to K_1 to evaluate k_{21}. The concentration of the second and third states in equation (4-3) may also be calculated from the rate and equilibrium constants obtained.

Before addressing the calculated rate constants, etc., it is appropriate to review the means by which the relevant concentration values were obtained. Most total equilibrium constants (K_Σ) for boric acid are written as $K_\Sigma^* = [H^+] [B(OH)_4^-] / [B(OH)_3]$. The K_Σ value for equation (4-3) is obtained by taking $10^{pK_w - pK_\Sigma^*}$ to give $K_\Sigma = [B(OH)_4^-] / [B(OH)_3] [OH^-]$. The equilibrium constant for water (pK_w) was taken from Harned and Owen (1958) and the value for NaCl solution was also used for sea water. The above procedure should be applicable for both thermodynamic and apparent equilibrium constants. The calculated value of hydroxyl ion concentration was derived from the pH measurements. Assuming that pH is a measure of hydrogen ion activity (Bates, 1964), then hydroxyl ion activity (a_{OH}) can be obtained by knowledge of K_w and the activity of water (a_{H_2O}). This latter term is available from Lyman (1957) for sea water and has been applied without correction to NaCl solution. Using the activity coefficient for hydrogen (γ_H) in sea water as obtained by Culberson, Pytkowicz and Hawley (1970) or Lyman (1957) and the activity coefficient equilibrium constant $(K\gamma)$ defines as

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$K_\gamma = \gamma_H \gamma_{OH} / a_{H_2O}$ by Harned and Owen (1958); the activity coefficient of hydroxyl ion (γ_{OH}) is obtained. This latter value together with a_{OH} gives the concentration of hydroxyl ion in solution. Because of the lack of adequate data, sea water and NaCl solutions have been treated as being identical for this calculation. As pointed out by Kester and Pytkowicz (1967) and Pytkowicz, Kester and Burgener (1966), pH measurements in sea water do not yield a true thermodynamic hydrogen ion activity due to liquid junction and asymmetry potentials. Thus, the approach taken is not completely satisfactory and some small error can be expected. It is also noted that only apparent equilibrium constants (K_Σ') are available for boric acid in sea water. This means that the concentration of $B(OH)_4^-$ represents all the complexed borate ion as well as the free ion (Gieskes and Edmond, 1972). In passing, it is noted that Platford (1969) has shown that the activity coefficient of $B(OH)_3$ in dilute solutions is nearly one. The activity coefficient of $B(OH)_4^-$ is generally in doubt, but Millero (1974) quotes a measured value of 0.35. Using the more general Garrels and Thompson (1962) approach, the singly charged borate ion would be expected to have an activity coefficient of 0.68. The activity coefficients should not play a major role in the calculations because there is no net charge change between reactants and products.

With due consideration for the assumptions previously noted, Table 3 provides calculated rate and equilibrium constants for equation (4-3). The best data are for the Lyman and Fleming artificial sea water at a pH of 8.0 and for the boric acid, NaCl solution at a pH of 8.0. Because of the limited

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Table 3

Calculated Rate Constants and Equilibrium Constants for the

Two Step Boric Acid Reaction for a Temperature of $25^{\circ}C$

Solution	pH	k_{23} $\sec^{-1}$	k_{32} $\sec^{-1}$	K_1	K_2	K_Σ
NaCl, B(OH)$_3$	8.0	2.5×10^5	9.6×10^1	5.6×10^2	2.6×10^2	1.5×10^5
Standard Sea Water	7.6	2.5×10^4	1.6×10^2	1.3×10^3	1.5×10^2	1.9×10^5
L&F Sea Water	8.0	2.2×10^4	1.7×10^2	1.6×10^3	1.2×10^2	1.9×10^5
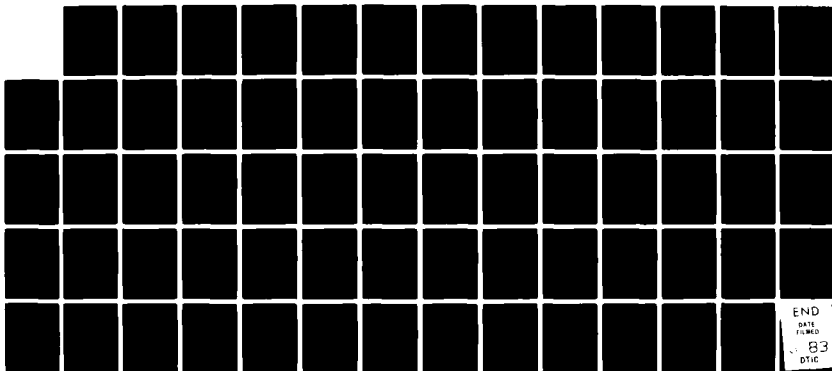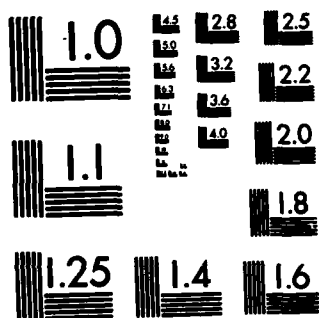
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number of data points for the Copenhagen Standard Sea Water, the values presented are of lesser accuracy. The results are quite consistent with expectations. A change in pH does affect the rates but not significantly. The errors in the calculated equilibrium constants are probably on the order of plus or minus 20%.

Given the rate and equilibrium constants, it is now possible to calculate sound absorption in the form of $\alpha\lambda$ to compare with the observed resonator data. To make these calculations, the change in molal volume ($\Delta\overline{V}^o$) must be known. Following the work of Ward and Millero (1974A), the $\Delta\overline{V}^o$ for the complete reaction in equation (4-3) can be represented by

$$\Delta\overline{V}^o = \overline{V}^o\,[B(OH)_4^-] - \overline{V}^o\,[OH^-] - \overline{V}^o\,[B(OH)_3] \qquad (4\text{-}8)$$

$$\Delta\overline{V}^o = \overline{V}^o\,[NaB(OH)_4^-] - \overline{V}^o\,[H_2O] + \overline{V}^o\,[NaCl]$$
$$- \overline{V}^o\,[B(OH)_3] \qquad (4\text{-}9)$$

Using values from Ward and Millero (1974A) and Harned and Owen (1958), a value of -35.45 ml/mol is obtained for the pure water case. Values for NaCl solution and sea water are not as readily obtained. Because of the presence of the electrolyte in NaCl and sea water solutions the molal volumes of the molecules are modified by electrostriction, etc. There is also the effect of ion-pairing and other complex formations that will affect the molal volumes. Fortunately there are some direct measurements of the molal volumes in 0.725 M NaCl solutions. Values for the terms in equation (4-9) have been taken from the following sources: $\overline{V}^o\,[B(OH)_3]$, Ward and Millero (1974B); $\overline{V}^o\,[HCl]$ and $\overline{V}^o\,[NaCl]$, Millero (1971); and $\overline{V}^o\,[H_2O]$, Owen and Brinkley

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(1941). There is no published value for $\overline{V}^O[NaB(OH)_4]$ in NaCl solution.

Millero (1969) proposed a formula to calculate the change in molal volume when a transfer is made from pure to sea water. The formulation appears to be most appropriate to single element ions, with multielement ions showing a marked deviation which is attributed to ion-pairing. Because of this uncertainty, his formulation was not used but rather the following expression from Owen and Brinkley (1941) employed.

$$\overline{V}^{O*} = \overline{V}^O + A_V \sqrt{\Gamma} \qquad (4\text{-}10)$$

A_V is a constant for the molecule considered and Γ is the ionic strength of the solvent. The resultant value for $\overline{V}^O[NaB(OH)_4]$ was 22.99 ml/mol. Substituting the prescribed values into equation (4-9), the $\Delta\overline{V}^{O*}$ in NaCl solutions are evaluated as -35.78 ml/mol. Following the recommendation of Owen and Brinkley (1941), this same value is applied to sea water. As pointed out by Millero (1971), this assumption is not entirely justified because of ion interaction in sea water; however, the current lack of conclusive data on boric acid and borate ions in sea water precludes any other approach.

With this choice for the overall change in molal volume, the next problem is to estimate the volume changes for each step of equation (4-3). If the first step is viewed as an ion association, then the derivation of Hemmes (1972), based on the Bjerrum (1926) and Fuoss (1958) relations, could be considered. However, the lack of a charge change in equation (4-3) greatly reduces the applicability of these expressions and the only term that would have to be considered is the density factor when changing from molal to molar

units. If this is the case, then the $\Delta \overline{V}^o$ for the first step would be approximately -2 ml/mol. Even if step 1 to 2 in figure 21 is assumed, the $\Delta \overline{V}^o$ would be less than -4 ml/mol. As cited previously, the assumption is that the large change in molal volume is attributed to the second step and the assumption of minor contribution from the first step would appear to be justified.

Using the rate constants from Table 3, determining reactant concentrations by the method described and initially assuming that all of the $\Delta \overline{V}^o$ is attributed to the second step of equation (4-3), it is possible to calculate $(\alpha \lambda)_{max}$ using the following expression developed in Appendix I.

$$\alpha \lambda_{max} = \frac{\pi (\Delta \overline{V}_j)^2}{2 \beta RT \sum_s \left\{ (m_j^{(s)})^2 / [C_s] \right\}} \tag{4-11}$$

where j is the mode number (equals 2 for the slow relaxation) and s is the state number as described in Appendix I. Calculated $\alpha \lambda_{max}$ values are compared with those observed from the resonator work in Table 4. The agreement is very good with the calculated values being slightly less than the observed but within the estimated experimental error. This agreement is a confirmation of the two step reaction process.

The calculated low frequency maximum $\alpha \lambda$ values tabulated in Table 4 show several points of interest. For the Lyman and Fleming sea water there is an increase of $\alpha \lambda$ with temperature up to 28.5^oC, but a lower value is calculated for 36^oC. This break is related in part to the temperature dependence of the total equilibrium constant and the assumption that the

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Table 4

Calculated Maximum $\alpha\lambda$ Values for the Boric Acid

Relaxation as Compared to Maximum $\alpha\lambda$ Values

Observed in the 200 1 Resonator for Various Solutions

Solution	pH	Temperature ^{o}C	Concentrated $B(OH)_3$ (times sea water value)	Calculated $(\alpha\lambda)_{max}$ x 10^5	Observed $(\alpha\lambda)_{max}$ x 10^5
L&F Sea Water	8.0	4°	1	0.63	0.81
" " "	8.0	9°	1	0.85	0.91
" " "	8.0	20°	1	1.03	1.00
" " "	8.0	28.5^o	1	1.42	0.96
" " "	8.0	36°	1	1.13	0.95
" " "	8.0	36°	5	1.11	1.23
" " "	8.0	36°	10	1.53	1.86
NaCl + $B(OH)_3$	8.0	25°	1	1.12	1.17
" "	8.0	25°	5	0.75	1.00
" "	8.0	25°	10	0.83	1.05
Pure Water + $B(OH)_3$	8.2	25°	1	1.71	1.63
"	8.2	25°	10	1.67	1.68
"	8.6	25°	1	3.24	2.55
"	9.4	25°	1	2.04	3.20
Pure Water + $NaHCO_3$, $B(OH)_3$	8.2	25°	1	--	0.86

diffusion controlled rate constant (k_{12}) is independent of temperature. It is also noted that with increased $B(OH)_3$ concentration the maximum $\alpha\lambda$ values either increase or decrease depending on the solution. This fact is related to the change in total equilibrium constants between the various solutions. The slight dip at the five times concentration is not yet understood. The observed results do not confirm this behavior.

In order to estimate what the effect of a small $\Delta\overline{V}^o$ for the first step would have on the calculated $\alpha\lambda$ values for the second step, $\Delta\overline{V}^o$ values of 2, 4, and 6 ml/mol were inserted for the first step and the $\alpha\lambda$ values recalculated. The results are shown in Table 5 for representative runs. In general, the changes are very small and the observed $\alpha\lambda$ values give no indication as to the value of $\Delta\overline{V}^o$ for the first step. Table 5 also lists the calculated relaxation frequency and $\alpha\lambda_{max}$ values for the first reaction as a function of the assumed $\Delta\overline{V}^o$ for the first step. The predicted relaxation frequency is on the order of 10 MHz and $\alpha\lambda$ is generally less than 1×10^{-6}. Both of these parameters are outside the range of the spherical resonator or the temperature jump equipment. To measure these high relaxation frequencies an ultrasonic device such as used by Carstensen (1954) or a pulsed device such as that used by Boumgartner and Hess (1974) could be employed. Atkinson (1975) advised that no relaxation was noted in the region from 1 to 50 mHz for boric acid in a NaCl solution. The technique used was pulsed sound absorption. The lack of a detectable relaxation frequency in this region is attributed to the low $\alpha\lambda$ values at the calculated frequency which were

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Table 5

Calculated Changes in Relaxation Frequency and $(\alpha\lambda)_{max}$

Values Caused by Attributing Various $\Delta\overline{V}^o$ Values to the

First Step of the Two Step Boric Acid Reaction

Total $\Delta\overline{V}^o = -35.78/mol/mol$

Solution	Temperature ^{o}C	$\Delta\overline{V}_1^o$ ml/mol	Relaxation Frequency MHz	$(\alpha\lambda)_{1\,max}$ x 10^5	$(\alpha\lambda)_{2\,max}$ x 10^5
L&F Artificial Sea Water	20°	0	4.75	7.48×10^{-7}	1.09
		2	4.75	4.4×10^{-4}	1.05
		4	4.75	1.79×10^{-3}	1.01
$B(OH)_3$ NaCl	25°	0	8.64	9.2×10^{-9}	0.98
		2	8.64	1.43×10^{-5}	0.96
		4	8.64	5.78×10^{-4}	0.94

below the detection threshold of the pulse instrument. This information would confirm that a very small $\Delta \overline{V}^{O}$ must be attributed to the first step of the reaction; however, no value can be readily estimated.

In summary, it has been shown that the one step dissociation process for boric acid does not fit either the temperature jump or the sound absorption data. A two step, three state model will fit the data within experimental error. The calculated sound absorption is in good agreement with observed data, even though several strenuous assumptions have been made in obtaining the calculated values.

5. EFFECTS OF OTHER SALTS IN SEA WATER

The resonator sound absorption data coupled with temperature jump information have clearly shown the importance of boric acid to the low frequency relaxation in sea water. It must be noted, however, that there is a striking difference in relaxation frequency for the standard and artificial sea water as compared to boric acid in NaCl solution as shown in figure 22. This difference is well outside experimental error. In an attempt to resolve this discrepancy, Lyman and Fleming artificial sea water was synthesized in steps and temperature jump data were taken after each constituent was added. The NaCl concentration was continually adjusted to maintain sea water ionic strength and pH was adjusted to 8.0 by addition of NaOH. The results are shown in Table 6. It must be remembered that artificial sea water without boric acid demonstrated no low frequency relaxation frequency. As indicated in Table 6, the relaxation frequencies indicate no major variation until $NaHCO_3$

Table 6

Relaxation Times and Frequencies for

Lyman and Fleming Sea Water Constituents

pH = 8.0

Constituent Added	Relaxation Time 10^{-6} sec	Relaxation Frequency kHz
$B(OH)_3$, NaCl	206	0.77
+ $SrCl_2$, NaF	237	0.67
+ KB_r	233	0.68
+ KCl	239	0.67
+ $CaCl_2$	238	0.67
+ Na_2SO_4	201	0.79
+ $MgCl_2$	232	0.69
+ $NaHCO_3$	120	1.32

was added to the system. Clearly the bicarbonate is involved in the boric acid

relaxation reaction. As stated in an earlier section, the vertical deflection of

the output from the temperature jump sensors is seriously reduced for a

strongly buffered system such as boric acid and bicarbonate, and as a result

errors in data reduction are increased. However, the observed relaxation

frequency change upon addition of the bicarbonate is beyond any effects due to

experimental error. As shown in Table 7, the relaxation frequency for a

solution of $NaHCO_3$ and $B(OH)_3$ at sea water concentrations in NaCl solution is

approximately three times greater than the same solution without $NaHCO_3$.

Addition of $MgCl_2$ and $CaCl_2$ to the solution tended to decrease the relaxation

frequency as noted. This change is probably caused by the reduction in free

HCO_3^- by ion-pair formation with both Mg^{++} and Ca^{++}, as suggested by

Garrels and Thompson (1962) and reviewed by Pytkowicz and Hawley (1974) and

Whitfield (1974). To a lesser extent, there is some complexing of these

elements with the borate ion. This point will be discussed later. Exactly how

the bicarbonate affects the boric acid is unknown. There is no evidence for

complex formation of bicarbonate with either $B(OH)_3$ or the $B(OH)_4^-$ ion. Hence

the effect must be through the buffering capacity of bicarbonate on the hydroxyl

ion of equation (4-3). Figure 24 represents an attempt by Yeager to consider

all the possible interactions of carbonate to the simple boric acid reaction.

The complications are quite overwhelming and not likely to be resolved in the

near future. The only hope may be a sort of decoupled evaluation of the two

separate reactions such as done for the magnesium, sulfate, carbonate system

Table 7

Relaxation Times and Frequencies for Various Solutions

pH = 8.0

Solution Composition	Relaxation Time 10^{-6} sec	Relaxation Frequency kHz
$B(OH)_3$, $NaHCO_3$, $NaCl$	70	2.26
$B(OH)_3$, $NaCl$	206	0.77
$B(OH)_3$, KCl	206	0.77
$B(OH)_3$, $CaCl_2$, $NaCl$	238	0.67
$B(OH)_3$, $MgCl_2$, $NaCl$	243	0.65
$B(OH)_3$, $MgCl_2$, $CaCl_2$, $NaCl$	245	0.65
$B(OH)_3$, $MgCl_2$, $NaHCO_3$, $NaCl$	133	1.20
$B(OH)_3$, $CaCl_2$, $NaHCO_3$, $NaCl$	159	0.99
$B(OH)_3$, $CaCl_2$, $MgCl_2$, $NaHCO_3$, $NaCl$	124	1.27
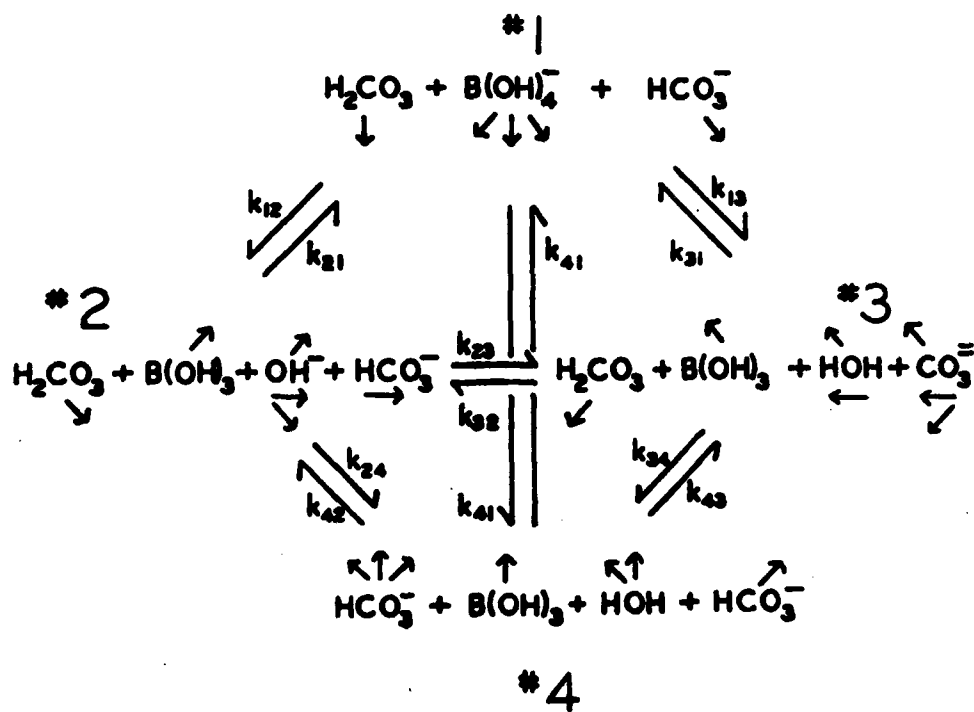
Figure 24

Boric acid and carbonate reaction schematic. A diagram of possible reaction paths for the coupling of carbonate to boric acid in sea water as proposed by Yeager.

by Garland et al (1973).

In view of the effect of the sea water concentration of bicarbonate on the boric acid relaxation frequency, the question was asked as to what the effect of atmospheric carbon dioxide (CO_2) equilibration with the boric acid samples would have on the data. Accordingly, a series of boric acid, NaCl solutions were prepared using CO_2 free water and reagents under a nitrogen atmosphere. Samples were transported to the temperature jump equipment in closed containers under a positive nitrogen pressure. Solution was forced into the temperature jump cell by nitrogen pressure and the cell quickly closed and inserted in the equipment. The comparative results shown in Table 8 indicate very little difference in relaxation frequency for CO_2 free samples as compared to the samples where no effort was made to exclude CO_2.

As previously noted, Dyrssen and Hansson (1973) and Byrne and Kester (1974) have reported that the borate ion tends to complex with Mg^{++}, Ca^{++} and Na^+. The results in Table 6 do not indicate any significant shift in relaxation frequency with the addition of the two former elements. To examine the results more closely, various solutions of Mg^{++} and Ca^{++} at sea water concentration were examined by temperature jump and the results presented in Table 7. There is a slight decrease in relaxation frequency as these ions are added, which is to be expected if complexes are formed, but the changes are not significant. When bicarbonate is added to the system, the relaxation frequency tends to increase instead of decrease. This opposite behavior is attributed to the ion-pairing of the carbonate with the ions in question which is

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Table 8

Comparison of Relaxation Frequencies for

$B(OH)_3$, NaCl Solutions with and without CO_2 Equilibration

Solution pH ≈ 8.0

$B(OH)_3$ Concentration (times sea water value)	Relaxation Frequency with CO_2 Equilibration kHz	Relaxation Frequency without CO_2 Equilibration kHz
1	0.77	0.83
2	1.18	1.13
5	2.09	1.89
10	2.74	2.95

apparently straonger than the borate effect. Although the temperature jump
data would support some ion-pairing with the borate ion, the extent of the pair-
ing cannot be estimated from the temperature jump results. In the article by
Byrne and Kester (1974) it was concluded that borate ion did not complex with
the potassium ion. As shown in Table 7, exchanging potassium for sodium did
not change the relaxation frequency. Although the temperature jump data is not
completely definitive on this point, it would appear to indicate that the
potassium and sodium act identically and if there is complexing with one there
must be nearly the same situation with the other.

In summary, although boric acid is the primary cause of the low fre-
quency relaxation in sea water, the carbonate system is a major influence in
determining the relaxation frequency. The interaction of the carbonate with
the boric acid is extremely complex and cannot be adequately treated at this
time. The complexing of the borate ion with Mg^{++}, Ca^{++} and Na^+ is inferred
but the evidence is not definitive. There is also an indication that the borate
ion complexes with K^+.

6. TEMPERATURE DEPENDENCE OF THE REACTION PROCESS

The temperature dependence of the observed relaxation frequency in
the boric acid, NaCl solution has been examined by use of the temperature
jump equipment. The dependence of relaxation frequency on temperature in
the Lyman and Fleming artificial sea water is inferred from this data. The
relaxation frequency data for base temperature of 8, 18.5, and $32^{o}C$ are
presented in Table 9. Using these data, the rate constants and equilibrium

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Table 9

Relaxation Frequency as a Function of Base Temperature

for a Solution of $B(OH)_3$ in 0.725 M NaCl

$B(OH)_3$ Concentration (times sea water value)	$8^\circ C$ Relaxation Frequency kHz	$18.5^\circ C$ Relaxation Frequency kHz	$32^\circ C$ Relaxation Frequency kHz
0.5	0.34	0.39	0.47
1	0.49	0.77	0.75
3	0.96	1.56	1.67
10	2.56	2.70	2.76

constants for the second step of equation (4-3) were calculated using procedures previously described. The results are shown in Table 10.

Although important in the evaluation of the resonator sound absorption data, the temperature dependence of the rate constants can be used to determine the Arrhenius energy of activation (E_a) by use of

$$\frac{d\ln K}{dT} = \frac{E_a}{RT^2} \qquad (4-12)$$

By appropriate rearrangement, equation (4-12) can be represented as

$$\frac{d\ln K}{d(1/T)} = -\frac{E_a}{R} \qquad (4-13)$$

As discussed by Caldin (1964), a plot of log k against 1/T will usually result in a linear curve, the slope of which is directly related to the energy of activation. Plotting data from Table 10 the energy of activation for the back reaction (reaction rate k_{32}) was determined to be 13 ± 2 Kcal/mol. The forward reaction (reaction rate k_{23}) had a zero or slightly positive slope. There is no adequate explanation for this behavior, other than to note that the errors in the temperature jump data are sufficient to mask a very small energy of activation. Thus, there is probably very little energy which can be attributed to the forward step. Values of E_a for the first step in equation (4-3) cannot be readily calculated because of the uncertainty of the diffusion controlled rate constant and the inability to observe this step with the experimental equipment available.

There is no singular interpretation of the energy of activation results; however, for the reaction at hand it is reasonable to say that it is

Table 10

Rate and Equilibrium Constants for a Solution of $B(OH)_3$ in

0.725 M NaCl as a Function of Temperature at pH = 8.0

Temperature $^{\circ}C$	k_{23} m^{-1}	k_{32} m^{-1}	K_1	K_2
8	3.0×10^4	2.8×10^1	3.4×10^2	1.1×10^3
18.5	2.4×10^4	1.2×10^1	6.9×10^2	2.1×10^2
32	2.4×10^4	1.9×10^2	6.7×10^2	1.2×10^2

related to the height of a potential energy barrier. The low energy for the forward step would indicate that the reaction proceeds almost spontaneously to the borate ion, with this being the preferred state. The high back reaction energy implies that there is little tendency for the reaction to return to the intermediate step once the borate ion is formed. These results are considered to be consistent with earlier speculation regarding the two step, three state reaction.

7. IMPORTANCE OF INDICATOR TYPE AND CONCENTRATION OF TEMPERATURE JUMP DATA

The raw data from the temperature jump equipment is actually the change in optical absorbance of a solution containing a color sensitive pH indicator in response to a rapid change in equilibrium conditions. In this case, an increase in temperature changes the equilibrium state of the reaction. The implicit assumption is that the change in absorbance of the indicator is directly coupled to the reaction being observed and the indicator does not contribute to the reaction itself. If the indicator reaction is represented by

$$HIn + OH^- \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} In^- + H_2O \tag{4-14}$$
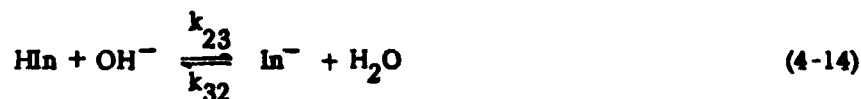
and a single step primary reaction such as

$$B(OH)_3 + OH^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} B(OH)_4^- \tag{4-15}$$
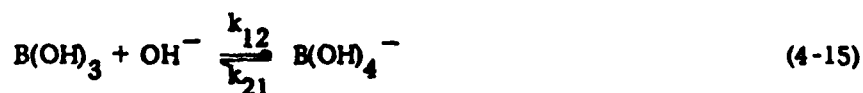
is assumed, a relaxation can be calculated for the coupled equations by using the conservation equations for boron, indicator and charge represented as

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follows

$$\Delta[B(OH)_3] + \Delta[B(OH)_4^-] = 0 \qquad (4-16)$$

$$\Delta[HIn] + \Delta[In^-] = 0 \qquad (4-17)$$

$$\Delta[OH^-] + \Delta[B(OH)_4^-] + \Delta[In^-] = 0 \qquad (4-18)$$

Following the procedure outlined in section II and using the conservation

equations as required to obtain a common variable, the following expression

is obtained for the overall relaxation time.

$$1/\tau = k_{12} \left\{ [B(OH)_3] + [OH^-] \right.$$
$$\left. + \frac{[B(OH)_3] K_2 [HIn]}{\left(\frac{1}{\tau_2 k_{32}} - 1 - K_2[OH^-] - K_2[HIn] \right)} \right\} + k_{21} \qquad (4-19)$$

By comparison with equation (2-4), the third term in the brackets is seen to be

the contribution of the indicator to the overall reaction. The subscripts two

in equation (4-19) refer to indicator values. The quantities required to evalu-

ate this term are not generally known, but a strong inference can be made

from data in the literature. Because cresol red (Cresolsulphonephthalein) was

generally used for the pH 8.0 data runs, the third term in the brackets will be

evaluated for this indicator. Bishop (1972) provides pK_i values for cresol red

at low ionic strength which cannot be applied directly to the 0.725 M NaCl

case. Accordingly, spectrophotometric data were collected on cresol red in

the actual solutions used to gather temperature jump data. An isosbestic plot

was constructed and pK_i of cresol red determined to be 7.82 ± 0.15. The

equilibrium concentration can now be evaluated given the pH of the solution.

The relaxation time (τ_2) for the indicator reaction has not been reported in the

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literature; however, Massey and Schelly (1974) have reported a value of approximately 0.75 μsec for phenolphthalein by use of field effect and temperature jump. Lacking a better number, this value may be assumed for cresol red. The rate constant k_{23} is also not known for cresol red, but Eigen, Hammes and Kustin (1960) have measured a value of approximately $2 \times 10^3 \, sec^{-1}$ for a chlor phenol red indicator. Applying this value to cresol red we now have or have assumed enough to evaluate the indicator term. The result is a value of approximately 1×10^{-6} which is normally two orders of magnitude less than the $B(OH)_3$ concentration. Even considering all of the assumptions employed, it appears safe to say that the indicator contribution would be less than 1%. This conclusion is similar to that reached by Anderson, Eyring and Whittaker (1964) for their work in boric acid at higher concentration. To confirm the calculation, and to determine what differences could be expected for the two step model, the indicator concentration in a solution of boric acid was varied by a factor of ten. The results in Table 11 indicate minimal influence of the indicator, as all values are well within experimental error. An indicator concentration of approximately 2.1×10^{-5} M was used for most actual experimental data.

Although there are no published data to indicate that pH sensitive indicators should react with the various salts in sea water, an attempt was made to use several indicators in identical solutions. Unfortunately the number of common indicators that respond in a given pH range are limited as shown by Bates (1964). The results of the trials made are presented in Table 12. The

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Table 11

Change of Relaxation Time and Frequency with

Indicator Concentration in a Solution of

$B(OH)_3$, $NaCl_2$ at pH = 8.0

Cresol Red Indicator Concentration 10^{-5} molar	Relaxation Time 10^{-6} sec	Relaxation Frequency kHz
0.35	207	0.77
1.05	211	0.75
2.10	211	0.75
4.20	217	0.73

Table 12

Change of Relaxation Frequency with Indicator Type

Indicator	Solution	Solution pH	Relaxation Frequency kHz
Cresol Red	Lyman & Fleming Sea Water	7.6	1.07
Phenol Red	" "	7.6	1.15
Cresol Red	Standard Sea Water	7.6	1.09
Phenol Red	" "	7.6	1.12
Cresol Red	$B(OH)_3$, NaCl	8.5	0.78
Phenolphthalein	" "	8.5	0.82

data indicate no major effect of the type of indicator used, as the variability is within experimental error.

In summary, there is no evidence that the indicator type nor its concentration had any significant effect upon the temperature jump results.

V. DISCUSSION

1. PRESSURE DEPENDENCE OF THE REACTION PROCESS

, A change in pressure has the effect of adjusting the equilibrium constant (K) and there is a change in the volume as measured by the partial molal volumes. These effects are related by the Planck (1887) relation

$$\left(\frac{\partial \ln K}{\partial P}\right) = -\frac{\Delta \overline{V}^0}{RT} \tag{5-1}$$

Secondary effects related to the study at hand would be an adjustment of the pH and a change in sound absorption. It can also be noted that by Le Chatelier's principle, an increase in pressure should tend to force a reaction toward smaller volume which would normally be the ionized form.

Because of the early paucity of data for equilibrium constants, etc., as a function of pressure, Owen and Brinkley (1941) developed expressions based on equation (5-1) that could be used to determine pressure values from atmospheric measurements. Their approach has been recently updated by Lown, Thirsk and Wynne-Jones (1968) based on the observation that the change in partial molal isothermal compressibility ($\Delta \overline{\kappa}^0$) defined by

$$-\Delta \overline{\kappa}^0 = \left(\frac{\partial \Delta \overline{V}^0}{\partial P}\right)_T \tag{5-2}$$

is nearly independent of pressure up to pressures greater than 2000 bars. Equation (5-1) can then be written as

$$-RT\left(\frac{\partial \ln K}{\partial P}\right)_T = \Delta \overline{V}^0 = \Delta \overline{V}_1^0 - \Delta \overline{\kappa}^0 (P-1) \tag{5-3}$$

where the subscript 1 refers to atmospheric conditions and P is the pressure

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in bars. This relation can now be used to determine $\Delta\overline{V}^O$ from atmospheric measurements. Integration of equation (5-3) gives

$$RT\ln\left(\frac{K_p}{K_1}\right) = -\Delta\overline{V}^O(P-1) + \frac{1}{2}\Delta\overline{\kappa}^O(P-1)^2 \qquad (5-4)$$

which allows calculation of the equilibrium constant at pressure (K_p) from atmospheric pressure values. Strictly speaking these relations can only be applied to solutions where water is the solvent.

The study of pressure effect in NaCl solutions and sea water is of extreme importance to oceanography. Disteche and Disteche (1967) used potentiometric measurements to evaluate the pressure effects on equilibrium constants in sea water down to 1000 bars pressure. By using similar techniques Culberson, Kester and Pytkowicz (1967) and Culberson and Pytkowicz (1968) have measured the carbonate and boric acid K values for various sea water samples. The objective of much of this work was to determine the change of pH with pressure and to examine saturation of sea water with respect to various minerals. Thus, the change in the total K for boric acid has been examined in sea water but the pressure dependence of the equilibrium constant for the second step of equation (4-3) is generally unknown. An attempt is made to estimate the pressure effect on this equilibrium; however, the large number of assumptions employed can only lead to very rough approximations.

For the case of boric acid in fresh water, the Lown et al (1968) relations can be applied directly. Using a $\Delta\overline{\kappa}^O$ value of -7.14×10^{-3}

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ml/mol-bar and a $\Delta \overline{V}^o$ value of approximately -38.0 ml/mol at 10^oC (Ward and Millero, 1974A) in equation (5-3), the $\Delta \overline{V}^o$ at 500 atmospheres would be -34.3 ml/mol and at 1000 atmospheres would be 30.122 ml/mol. Based on a total K for boric acid of 1.428×10^5, the pressure values would be 3.109×10^5 and 6.269×10^5 respectively. Assuming that the $\Delta \overline{\kappa}^o$ value would also apply to the second step of equation (4-3), and using a calculated K_2 of 8.94×10^1, the pressure values would be 1.95×10^2 and 3.92×10^2 respectively. The assumption has been made that all of the $\Delta \overline{V}^o$ is attributed to the second step.

The values for a 0.725 M NaCl solution cannot be estimated with great accuracy. The method of Owen and Brinkley (1941) could be used if the partial molal compressibility of $NaB(OH)_4$ were known. Values of $\Delta \overline{\kappa}^o$ are also not available and the fresh water value must be used. The temperature dependence of $\Delta \overline{V}^o$ in the NaCl solution is also not directly available, but the results of Ward and Millero (1974B) would indicate much less change in this solution than observed in fresh water. Thus a value of -35.78 ml/mol will be used for $\Delta \overline{V}^o$ at 10^oC. Employing equation (5-3) the $\Delta \overline{V}^o$ would be 32.08 ml/mol and 27.90 ml/mol for pressures of 500 and 1000 atmospheres respectively. The total K values would be 7.59×10^5 and 14.59×10^5 for the two respective pressures based on an atmospheric K of 3.65×10^5. For a calculated K_2 of 2.09×10^2, the pressure value would be 4.34×10^2 and 8.34×10^2 respectively. The reality of these values is somewhat questionable in view of the assumptions made.

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Attempting to extend the preceding arguments to sea water conditions would probably be unjustified as the Lown relations could not be expected to hold and there is an added complication of pH adjustment caused by the carbonate system. The change in $\Delta \bar{\kappa}^o$ with pressure in sea water can be roughly examined by using the K_B' values for 11.6^oC from Culberson and Pytkowicz (1968) in equation (5-4) along with the $\Delta \bar{V}^o$ value of -35.78 ml/mol for sea water. The resultant $\Delta \bar{\kappa}^o$ values for 500 and 1000 atmospheres are 3.37×10^{-2} and 1.83×10^{-2} ml/mol-bar respectively. It is apparent that the value is not a constant as a function of depth for sea water. Using the same K_B' values in equation (5-1) give values for $\Delta \bar{V}^o$ of -27.22 and 26.47 ml/mol for 500 and 1000 atmospheres respectively. The preceding results imply that there is no adequate way to estimate the change in K for the second step of equation (4-3) as a function of pressure and no direct measurements are available.

The lack of pressure dependent data on the two step boric acid relation in either NaCl solution or in sea water generally precludes any reliable estimate of the pressure effects on the sound absorption data caused by a shift in K_2 and a change in $\Delta \bar{V}^o$. Additional pressure work is called for to remove this ambiguity.

2. COMPARISON OF LABORATORY RESULTS TO FIELD DATA

Prior to making a comparison between observed in situ data and the laboratory results, it is appropriate to review how the open ocean data were collected and analyzed. To achieve the long range sound propagation paths

required to allow measurement of sound absorption values on the order of

0.06 dB/km, experiments were conducted near the deep sound channel axis.

The deep sound channel is a region of sound velocity minimum so that acoustic

energy introduced into the region is focused along the axis much like a lens

focuses light. Although there is leakage out of the sound channel, depending

upon the location of the sound source, most of the energy will be trapped and

projected. Because refraction is used to trap the energy, there is little loss

due to boundary effects as long as the bottom depth exceeds the critical depth.

Although the axis is not completely stationary, it is generally to be found at

depths from 1000 to 1200 meters in the open ocean. In shallow regions or

regions of high ambient temperature or salinity, such as the Mediterranean

or Red Sea, there may be no well defined sound channel; however, the local

conditions may allow long range propagation by other paths. In the early work,

the sound energy was generated by explosive sources detonated by a hydro-

static trigger. The receiver consisted of a series of hydrophones located at

select depths. Although explosive sources are still used, the trend is now to

CW sources which offer greater control of frequency and timing, but at a

higher cost. The received data, recorded at a hydrophone output, are filtered

and smoothed for presentation. After spreading loss of energy is compensated

for, the received energy level is compared to the level of the sound source and

together with range information, absorption is calculated along the path. As

pointed out by Berman and Guthrie (1972), many complications and approxi-

mations are used to obtain the absorption information and some are of

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questionable validity. However, these doubts are generally overcome by the reproducibility of the data as collected by several experimenters over different seasons in different years. The primary points to consider when comparing open ocean data to laboratory data are the following: (1) The data are collected at depth where pressure, pH, temperature, etc. are not the same as near surface values. (2) The acoustic energy traverses regions of changing pressure, pH and temperature but a majority of the travel time is spent at depths greater than the sound channel axis. (3) There is great variability between various ocean areas and the parameters that affect acoustic propagation. (4) The variability of the environment along the acoustic path and the lack of complete understanding of dependent parameters tend to increase experimental error.

A more general problem is the paucity of good data published in the open literature. Aside from the papers by Thorp (1965), Skretting and Leroy (1971), Lovett (1975), Mellen, Browning, Ross and Merklinger (1975) and presentations by Mellen and Browning (1975), most of the data are retained for proprietary use. As a result only select comparisons can be performed with the laboratory data now available.

The composite data presented by Thorp (1965) indicate a relaxation frequency of approximately 1 kHz. Fitting a curve to the data, Thorp (1967) obtained the expression

$$\alpha \frac{dB}{kyd} = \frac{0.1f^2}{1 + f^2} + \frac{40f^2}{4100 + f^2} \tag{5-5}$$

where f is the frequency in kHz. Assuming that the temperature of the deep

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sound channel axis in the Atlantic is $4^{\circ}C$, the calculated absorption would be 0.066 dB/km and $\alpha\lambda$ would be 1.1×10^{-5}. From figure 11, it is seen that the observed $(\alpha\lambda)_{max}$ for Lyman and Fleming sea water was 9.1×10^{-6}. The agreement between these values is perhaps surprising considering the poor definition of the laboratory curves at this low temperature. An accurate comparison would require a pressure correction of the laboratory data to about 140 atmospheres. Regrettably there are no reliable pressure dependent data and this correction cannot be reliably performed.

Skretting and Leroy (1971) obtained absorption data along the deep refracted path in the near isothermal deep water of the Mediterranean. Based on a least square fit to their data, the following equation was developed

$$\alpha \frac{dB}{km} = 0.006f^2 + \frac{0.155(1.7)f^2}{(1.7)^2 + f^2} \tag{5-6}$$

where f is frequency in kHz. From the data plot, the relaxation frequency was estimated to be 1.7 kHz. Using this frequency in equation (5-6), the absorption would be 0.097 dB/km and for a mean water temperature of $13^{\circ}C$, the $(\alpha\lambda)_{max}$ value would be 1.31×10^{-5}. Interpolating between the laboratory data at $9^{\circ}C$ and $20^{\circ}C$, the observed relaxation frequency was 1.1 kHz and the $(\alpha\lambda)_{max}$ value was 1.1×10^{-5}. Although the agreement is very encouraging, the caveat regarding the lack of knowledge of pressure dependency must be restated. For most of the Mediterranean data the mean pressure would probably be on the order of 75 - 100 atmospheres.

Mellen and Browning (1975) provided preliminary data from work in

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the Red Sea, Gulf of Aden and Pacific and Mellen et al (1975) provided final

data for Baffin Bay. Relaxation frequency data were only provided for the

Red Sea; however, temperatures and empirical formulas to calculate attenu-

ation below 10 kHz were provided for each of these bodies. Using this data

along with estimated relaxation frequencies from this work and from Yeager

et al (1973), absorption and $(\alpha\lambda)_{max}$ values were calculated as provided in

Table 13. Despite the variability of in situ values, there is a general agree-

ment with the observed laboratory values; however, the pressure effect must

still be considered as unknown. As a second check, Mellen and Browning

(1975) plotted relaxation frequency versus temperature for the Atlantic,

Red Sea and Mediterranean as shown in figure 25. Adding the data from

Yeager et al (1973) for standard sea water and data from this work for Lyman

and Fleming sea water, the overall agreement is very reassuring. The large

departure of Mediterranean data is unexplained other than to speculate that

the relaxation frequency is too high.

The marked disagreement between the Atlantic and Pacific data is

puzzling. In the sound absorption plot developed by Thorp (1965) (figure 1),

the Greer and Bolan results for the North Pacific indicate less absorption

than comparable results for the North Atlantic and Mediterranean areas.

The Sheehy and Halley results in the North Atlantic are slightly below the

composite plot and as replotted by Mellen and Browning (1975), the Sheehy

and Halley results would support the lower sound absorption in the Pacific.

There is also a lesser disagreement between the Gulf of Aden and the

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Table 13

Comparison of $(\alpha\lambda)_{max}$ Values Observed in Select Open Ocean

Areas as Compared to Laboratory Measurements

at Comparable Temperatures

Ocean Area	Temperature ^oC	Relaxation Frequency kHz	Open Ocean $(\alpha\lambda)_{max}$ x 10^5	Laboratory $(\alpha\lambda)_{max}$ x 10^5
Atlantic	4°	1	1.11	0.91
Mediterranean	13°	1.7	1.31	1.1
Red Sea	22°	1.5	1.47	1.21
Gulf of Aden	15°	1.2	0.82	0.96
Pacific	4°	1	0.47	0.91
Baffin Bay	4°	1	1.1	0.92

Figure 25

Temperature dependence of the relaxation frequency. Points for listed ocean

areas were taken from Mellen and Browning (1975). The triangles are data

from Yeager et al (1973) for standard sea water. The squares are data from

this work representing Lyman and Fleming artificial sea water.

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Mediterranean. The former disparity is of greater importance because of the supposed similarity between the two water masses in regard to large scale features, both in constituents and acoustic paths used to obtain the data. Although the pressure effect on the boric acid reaction has not been resolved, the similarity of deep sound channel axis between the two oceans should preclude this effect as a cause of the variability. It would be attractive to speculate that there was a variance in boric acid concentration between the two oceans; however, this is unlikely for the following reasons: (1) To account for the difference in $\alpha\lambda$ values it is estimated that the boric acid concentration in the Pacific would have to be between one third and one half of that observed in the Atlantic. Results published in Riley and Skirrow (1965) and by Uppstrom (1974) do not support this variability and analysis techniques, although difficult, have an error that is far less than what would have to be postulated to account for this difference. (2) If there were a boric acid concentration difference between the two oceans then there should be a lowering of the relaxation frequency by up to 20%. Once again, although experimental errors are generally large, it is unlikely that a 20% change in relaxation frequency would go unnoticed. As a secondary proposal, it might be stated that there is more complexing of the borate ion in the Pacific than the Atlantic. Although possible, this case is also unlikely as the chemical composition relative to the ions that would form complexes show little variability between the two oceans. As noted by Gast and Thompson (1958), certain organic polyhydroxyl compounds do complex with boric acid

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in sea water, coverting the boric acid to a strong acid. This complexing was the method used to analyze for boric acid until Uppstrom (1968) devised a method using a curcumim complex. Lyman (1957) also noted that organic material in a boric acid solution tended to shift the equilibrium constant slightly but the subject was not pursued at any length. The amount of organic complexing of boric acid in sea water does not seem to be well known nor extensively studied. In one series of temperature jump studies, a tris organic buffer at 0.01 M with NaCl and boric acid was examined. The original intent was to look at boric acid under a highly buffered condition. The results were surprising. At sea water concentration of boric acid, no relaxation frequency could be located. At two times this concentration, the observed relaxation frequency was at 1.2 Hz with nothing in the kHz region. At ten times boric acid concentration, one relaxation frequency was noted at 5.8 Hz and another at 2.1 kHz. With no tris in the solution the relaxation frequency at a pH of 7.5 was 1.75 kHz. The results are unexplained other than to say that boric acid must be complexing with the tris amine buffer. How this relates to the situation in sea water, where organic concentrations are much less, is unknown but warrants further investigation. The last possibility to explain the variability of absorption between the Atlantic and Pacific is the carbonate mechanism. As previously cited, carbonate definitely affects the relaxation frequency and to a lesser extent the absorption. The exact mechanism is unknown and the magnitude of this effect must await further work. The preliminary data indicate that the carbonate effects could not be solely responsible

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for the observed changes in absorption between the two oceans. Although several postulates have been examined, no one single cause appears sufficient to explain the variability between absorption measurements in the Atlantic and Pacific oceans. In fact, this review has revealed more questions than answers.

In reviewing the preceding discussion, Professor Gieskes pointed out the fact that the in situ pH versus depth profile in the Atlantic is different from that observed in the Pacific in the region of the deep sound channel. As shown by Gieskes, Meincke and Wench (1970), the Atlantic demonstrates a gradual decrease in pH with depth to a pH minimum of 8.0 at about 2500 m. In the North Pacific, Park (1966) observed a very rapid decrease in pH with depth to a pH minimum of 7.6 at about 300 m and a gradual pH increase as depth continues to increase. At a depth of approximately 3500 m the pH values for the two oceans approach a common value of approximately 7.9. Although the difference in pH is relatively small, the difference has a large effect on the CO_3^{--} concentration and if the CO_3^{--} were the primary interaction product of the carbonate system with the boric acid, as shown by the results in Table 7, there could be an influence on the sound absorption. To examine this proposal, temperature jump runs were conducted on a solution of $B(OH)_3$, $NaHCO_3$ at sea water concentration and NaCl to give the ionic strength of sea water. Data were collected at pH values of 7.3, 7.6, 7.8, 8.0 and 8.3, with the pH adjusted by the addition of NaOH or NCl as required. Although there is some data scatter in this buffered solution, the results indicate no

significant change in relaxation frequency with pH. These results would indicate that the CO_3^{--} concentration had minimal effect on the observed relaxation frequency and is not the cause of the relaxation frequency shift noted in Table 7 for the case where $NaHCO_3$ was added to the boric acid solution.

Lacking laboratory data on the effect of pressure on sound absorption, some inferences can be drawn from the open ocean results. If the boric acid relaxation responds like the higher frequency $MgSO_4$ relaxation, a decrease in sound absorption would be expected with increased pressure. Examining the results in Table 13, for the Atlantic Ocean data, collected at a mean depth of approximately 1000 meters, the absorption is slightly larger than laboratory measurements. This would indicate that pressure actually increased absorption which is contrary to expectation. Comparing the Atlantic results to the Baffin Bay figures, where the data collection depth was 100 meters, indicates virtually no effect of pressure on the observed open ocean sound absorption. The Pacific Ocean data, on the other hand, indicate a decrease in sound absorption by approximately 50% as compared to the laboratory results. Such a decrease could be expected; however, there is no good way to assess what the change should be. The Mediterranean, Red Sea and Gulf of Aden results represent data collected at shallower depth where the pressure effects are less, but the higher ambient temperatures cause complications in making comparisons to the Atlantic or Pacific results. In general, the Mediterranean and Red Sea absorption results are higher than comparable laboratory

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measurements, which would indicate little pressure dependence. The Gulf of

Aden results are 10% lower than comparable laboratory measurements which

would indicate a small pressure effect for depths of 500 meters. Although

inconclusive because of the scatter of the open ocean data, there is a pre-

liminary indication that the pressure effect on the boric acid sound absorption

is relatively small; however, laboratory work is required to confirm this

speculation.

In summary, despite the paucity of published ocean data, the labora-

tory work is in substantial agreement with the available data on relaxation

frequency and absorption per wave length. The variability between similar

oceans is a question that demands additional work as it appears there is

nothing in this study that can be used to explain it directly. Regardless, there

appears to be little doubt but what boric acid is the primary contribution to the

approximate 1 kHz sound absorption noted in sea water.

3. EMPIRICAL SOUND ABSORPTION EQUATION

One important practical application of this work is to provide data

upon which forecasts of low frequency sound absorption in sea water can be

based. Using a theoretical expression derived by Liebermann (1948), Schulkin

and Marsh (1962) developed an empirical sound absorption expression based

on open ocean and laboratory studies of absorption coupled with the pressure

sound absorption results in $MgSO_4$ as done by Fisher (1958) to give

$$\alpha = \frac{SAf_t f^2}{f_t^2 + f^2} + \frac{Bf^2}{f_t} (1 - 6.54 \times 10^{-4} \, P) \, \text{nepers/meter} \quad (5\text{-}7)$$

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In this expression A and B may be represented by constants, S is the salinity in parts per thousand (^{o}/oo) f is frequency in kHz, P is pressure in atmospheres, and f_t is the temperature dependent $MgSO_4$ relaxation frequency in kHz represented by $f_t = 21.9 \times 10^{[6 - 1520/(t + 273)]}$ where t is in ^{o}C. The equation is considered valid down to 2 kHz and represented the higher frequency $MgSO_4$ relaxation plus viscous effects.

Thorp (1967) developed an expression for the 1 kHz absorption but did not consider temperature dependence or attempt to tie his expression to the higher frequency absorption. Hall (1968) derived a more complete equation but the lack of data for the temperature dependence of the low frequency absorption precluded including this term. Baker (1975) provided yet another expression but temperature dependence was still lacking. Using the results of this work, a more complete expression can be proposed with certain caveats regarding lack of data on pressure dependence and the variability of sound absorption in the various oceans as previously noted.

To derive a sound absorption equation, equation (2-15) can be modified to give

$$\alpha\lambda = \frac{\pi\beta_r}{\beta_o} \frac{f_r f}{f_r^2 + f^2} \tag{5-8}$$

or

$$\alpha = \frac{\pi\beta_r}{c\beta_o} \frac{f_r f^2}{f_r^2 + f^2} \tag{5-9}$$

Using equation (5-8), it is noted that when the actual frequency (f) is equal to the relaxation frequency (f_r) the maximum $\alpha\lambda$ is represented by

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$$(\alpha\lambda)_{max} = \frac{\pi\beta_r}{2\beta_0} \qquad (5\text{-}10)$$

Based on the laboratory results in Table 13, $(\alpha\lambda)_{max}$ is generally 1×10^{-5} which by use of equation (5-10) would give $\pi\beta_r/\beta_0 = 2 \times 10^{-5}$. The temperature dependence of the relaxation frequency can be derived from an empirical fit of an equation to the straight line in figure 25. The empirical equation is $f_r = 0.9\,(1.5^{t/18})$, where t is temperature in $^{\circ}$C. The sound velocity (c) in equation (5-9) is a function of temperature and salinity; how-ever, using the equation developed by Wilson (1960A) for a salinity of $35^{\circ}/oo$ and temperature of 10°C the sound velocity would be approximately 1490 m/sec. Substituting these values into equation (5-9) the results would be

$$\alpha = 1.342 \times 10^{-8}\ \frac{f^2 f_r}{f_r^2 + f^2} \qquad (5\text{-}11)$$

Using the fact that individual discrete relaxations have an additive effect on the sound absorption, the low frequency sound absorption in equation (5-11) can be added to the higher frequency Schulkin and Marsh (1962) relation to give

$$\alpha = 1.342 \times 10^{-8}\ \frac{f^2 f_r}{f_r^2 + f^2}$$
$$+ \left(\frac{SAf_t f^2}{f_t^2 + f^2} + \frac{Bf^2}{f_t}\right)(1 - 6.54 \times 10^{-4}\,P)\ \text{nepers/meter} \qquad (5\text{-}12)$$

The absorption can be converted to dB/kyd by multiplying equation (5-12) by 7.94×10^3.

When using the sound absorption equation presented in equation (5-12)

the following points must be kept in mind: (1) The pressure dependence of the contribution from the $MgSO_4$ relaxation is based on results from work conducted in concentrated $MgSO_4$ solutions and not sea water. The results of Bezdek (1973) cast doubt on this pressure dependence as it relates to sea water. (2) The low frequency contribution is based on laboratory measurements which generally agree with the open ocean observations in the Atlantic, Mediterranean and Baffin Bay but apparently do not agree with the Pacific results. (3) No pressure effects have been allowed for in the low frequency contribution. As discussed previously, the effect of this omission is unknown and awaits additional data. (4) A representative sound velocity has been used to define the constant for the low frequency contribution. A more precise absorption could be obtained by using the observed sound velocity to recalculate the constant.

In summary, the empirical sound absorption expression presented is probably sufficient for most operation applications and its accuracy is consistent with our current knowledge of processes involved. As our understanding of the pressure effects improves and the variability in absorption between the Atlantic and Facific is resolved, the constants in this expression must be updated.

Although not directly related to the sound absorption equation, it has been noted that not only does a chemical relaxation in sea water affect sound absorption but there is an associated velocity dispersion. As pointed out by Horton (1974), the higher frequency $MgSO_4$ relaxation causes a velocity

dispersion of some 3.5 cm/sec and by a similar calculation it can be shown that the boric acid reaction should cause a dispersion of approximately 1.5 cm/sec. Although small in absolute magnitude, these dispersion values are within experimental error claimed by Del Grosso and Mader (1972) for their empirical sound velocity equation and thus should be considered for low frequency use.

4. UNRESOLVED PROBLEMS AND RECOMMENDED ADDITIONAL WORK

In many research problems, the resolution of one question brings to light more questions that must be resolved before our knowledge on the subject is complete. The following is a partial list of remaining work that needs to be conducted.

The foremost need is to define the effects of pressure on the two step, three state boric acid reaction. In particular, the second step, which has been related to the observed sound absorption, must be understood in full detail. Until this question has been resolved, correlation of at-sea data with laboratory work can only be done with restrictive caveats. Obtaining the required data is complicated by the large size of pressure vessel required to do resonator work; however, there is presently little alternative to the resonator approach. It is noted in passing that even the pressure effects of the higher frequency $MgSO_4$ relaxation remains in doubt based on the at-sea work of Bezdek (1973), where observed absorption at depth was 27% less than the calculated values based on laboratory pressure work. Thus, both the

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$MgSO_4$ and $B(OH)_3$ chemical relaxation mechanisms in the ocean require additional pressure work.

The combined temperature jump-resonator approach to measuring sound absorption in sea water is a good approximation but fully tractable data can only be obtained by direct measurement of sound absorption to below 1 kHz. Although the resonator technique can be applied to this low frequency region, the size and weight of the container becomes very large. As discussed with Dr. Fisher, if this path is pursued, then a storage tank from a liquid natural gas ship would probably be the best approach. The container is spherical, of sufficient size and has a good vacuum chamber built around the vessel. The major problem would be modifying the suspension system of the vessel to take the added weight of water. From an engineering standpoint, the easier thing to do would be to refine the tuning fork system used by Andreae, Jupp and Vincent (1960) so that good data can be obtained at low solution concentration.

The temperature jump work should be conducted under pressure to define the effects of pressure on the rate and equilibrium constants of the reaction. Pressure techniques have been discussed by Czerlinski (1966) and a limited number of such systems are available. This approach would complement the pressure work on the change in molal volume and allow much better understanding of the problem.

The carbonate interaction with the boric acid reaction needs much additional study. Probable reaction paths need to be determined and the

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exact effect of the carbonate on the relaxation frequency and sound absorption needs to be defined. This study will not only assist the work at hand, but allow a better understanding of the buffering capacity of sea water. The optimum approach is not known, but additional temperature jump work and pressure temperature jump work would probably be helpful. This would be particularly true if temperature jump work could be conducted down to the nanosecond region, which is within present engineering capabilities.

A kinetic study of the boric acid system in pure water should be undertaken to refine kinetics in a system free of borate complexes. The only system that appears applicable would be the laser temperature jump technique discussed by Caldin (1975). The use of a laser to raise the temperature negates the requirement for a solution of moderately high ionic strength as used with the electric discharge system and would allow studies in pure water. Present laser equipment is of limited power and will not provide as large a temperature rise as desired for this work.

Temperature jump studies or organic complexing with boric acid should be continued to examine the effects on the reaction and as a possible explanation of the variability of acoustic absorption in the Atlantic and Pacific oceans. A complete set of experiments varying the concentration of organic material would define threshold values and allow estimates of the relaxation frequency given a known organic concentration. An effort should be made to duplicate the major organic substances in sea water.

There is also a variety of improvements that should be made to the spherical resonator set-up used in the present study. (1) The frequency excitation source could be a white noise, variable frequency band width oscillator. The composite return sign could then be viewed to determine the slowest decay rate. The band width could then be progressively reduced until the slow decay rate was defined to any desired degree of accuracy. This would insure selection of the slowest decay rate and reduce data collection time. (2) A heater could be used inside the vacuum jar to assist heating of the resonator between temperature runs. This would allow a more rapid change in temperature and the present water heat exchanger could be used to hold the desired temperature during the run. (3) Digital recording and processing of the decay rate data would assist rapid analysis and improve accuracy. It would also provide a real time determination of decay rate and facilitate comparisons of data.

Although slightly beyond the control of the present study, additional at-sea data should be analyzed to provide a better data base for future laboratory work. Not only should existing data be made available, but in future studies field work should include collection and analysis of water samples along the acoustic path. Variability along the path could be defined and become the basis for additional laboratory work.

VI. SUMMARY

The objective of this study was to examine the 1 kHz, low frequency anomalous increase of sound absorption in sea water observed during several open ocean acoustic studies. Supporting objectives were to determine the magnitude of the absorption under laboratory conditions and to define the process responsible for the increased sound absorption. To achieve these objectives, a combination of the spherical resonator and temperature jump technique was employed.

The results clearly demonstrate that there is an increase in sound absorption below approximately 1 kHz in real sea water and in artificial sea water. The increased absorption is directly related to the presence of boric acid in the solution. The observed data will not fit a one step boric acid ionization process but can be explained if a two step ionization process is postulated. Although the intermediate product has not been isolated, pre- sumably because of its small concentration, it is estimated to be an encounter complex formed by the addition of a hydroxyl ion to the boric acid. Based on the observed fact that the ionization of boric acid causes a shift from the trigonal planar $B(OH)_3$ molecule to the tetrahedral $B(OH)_4^-$ ion, it is postu- lated that the first step of the reaction is diffusion controlled and represents little change in molal volume. The second step, thusly, represents the large change in configuration and the major change in molal volume. Accordingly, this second step is related to the observed sound absorption in sea water. The small change in molal volume of the first step would preclude

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detection by standard acoustic absorption technique. Although there is little doubt as to the importance of boric acid to the absorption, it is apparent that the presence of bicarbonate in solution adjusts both the magnitude of the absorption and the relaxation frequency. As of this time, no mechanism can be proposed to explain the bicarbonate effect other than to say that it must be related to the buffering effect on the hydroxyl ion. This work did note what could be considered complexing of the borate ion with magnesium and calcium, but the results cannot give any estimate of the magnitude. The proposed complex with sodium has not been positively confirmed; however, it was noted that sodium and potassium tended to have the same effect on the results.

Open ocean absorption data, collected at depth near the sound channel axis, are in general agreement with the laboratory data and calculated absorption values using the two step boric acid ionization process. Although direct comparisons have been hampered by a lack of data on the effect of pressure on the second step of the reaction, the data agreement is normally better than 20%. The relaxation frequency as a function of temperature is also in very good agreement between the in situ and laboratory work. The observed differences between the absorption in the Atlantic and Pacific are unexplained; however, there are several mechanisms, probably operating in consort, which could explain some of this difference once additional data become available.

The basic objectives of this study have been met. The complete resolution of this problem must await additional research to define the

pressure effects, change in molal volume, determination of good fresh water

values, etc.   These supporting data can be expected to be slow in coming as

the state of laboratory technology has not progressed to the point where

equipment can be readily designed within laboratory constraints.

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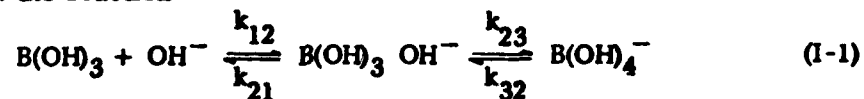Yeager, E. (1975) Personal communications.

APPENDIX I

DERIVATION OF THE TWO STEP BORIC ACID REACTION EQUATIONS

As stated in chapter IV, section 3, the derivation for the two step, three state reaction will follow the development by Garland, Patel and Atkinson (1973).

For the reaction

$$B(OH)_3 + OH^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} B(OH)_3 \ OH^- \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} B(OH)_4^- \qquad (I\text{-}1)$$

the rate equations are represented by

$$\frac{d[B(OH)_3]}{dt} = -k_{12}[B(OH)_3][OH^-] + k_{21}[B(OH)_3 \ OH^-] \qquad (I\text{-}2)$$

$$\frac{d[B(OH)_3 \ OH^-]}{dt} = k_{12}[B(OH)_3][OH^-]$$
$$- (k_{21} + k_{23})[B(OH)_3 \ OH^-] + k_{32}[B(OH)_4^-] \qquad (I\text{-}3)$$

$$\frac{d[B(OH)_4^-]}{dt} = k_{23}[B(OH)_3 \ OH^-] - k_{32}[B(OH)_4^-] \qquad (I\text{-}4)$$

The instantaneous concentration $[A_i]$ is represented by the sum of the steady-state value $[<A_i>]$ and the extent of reaction $\Delta \xi_s$ times the stoichiometric coefficient (v^s). The sum is over the states (s) which contain the reactant.

$$[A_i] = [<A_i>] + \sum_s v^{(s)} \Delta \xi_s \qquad (I\text{-}5)$$

Substituting (I-5) into (I-2) thru (I-4), note that the equilibrium values are time independent,

$$\frac{d[<A_i>]}{dt} = 0 \qquad (I\text{-}7)$$

allowing only first order perturbations

$$(\Delta \xi_s)^2 = 0 \tag{I-8}$$

and noting that equilibrium values can be represented by

$$k_{12}[<B(OH)_3>][<OH^->] = k_{21}[<B(OH)_3 \quad OH^->] \tag{I-9}$$

$$(k_{12} + K_{23})[<B(OH)_3 \quad OH^->] = k_{12}[<B(OH)_3>][<OH^->]$$

$$+ K_{32}[<B(OH)_4^->] \tag{I-10}$$

$$k_{23}[<B(OH)_3 \quad OH^->] = k_{32}[<B(OH)_4^->] \tag{I-11}$$

the resultant expressions are

$$\frac{d\Delta \xi_1}{dt} = -k_{12}\Big([<B(OH)_3>] + [<OH^->]\Big)\Delta\xi_1 + k_{21}\,\Delta\xi_2 \tag{I-12}$$

$$\frac{d\Delta \xi_2}{dt} = k_{12}\Big([<B(OH)_3>] + [<OH^->]\Big)\Delta\xi_1$$

$$- (k_{21} + k_{23})\,\Delta\xi_2 + k_{32}\,\Delta\xi_3 \tag{I-13}$$

$$\frac{d\Delta \xi_3}{dt} = k_{23}\,\Delta\xi_2 - k_{32}\,\Delta\xi_3 \tag{I-14}$$

Equations (I-12) thru (I-14) are coupled, first-order differential equation

which may be solved as an eigenvalue problem by forming the matrix $\mathscr{C}$ with

coefficients from equations (I-12) thru (I-14)

$$\frac{d\overrightarrow{\Delta\xi}}{dt} = \mathscr{C}\overrightarrow{\Delta\xi} \tag{I-15}$$

with $d\overrightarrow{\Delta\xi}/dt$ and $\overrightarrow{\Delta\xi}$ being column vectors. Performing the coordinate

transformation and substituting

$$A = [<B(OH)_3>] + [<OH^->] \tag{I-16}$$

the following determinant must be solved

$$
\begin{bmatrix}
- k_{12}A + 1/\tau & k_{21} & 0 \\
k_{12}A & -(k_{21} + k_{23}) + 1/\tau & k_{32} \\
0 & k_{23} & -k_{32} + 1/\tau
\end{bmatrix} \tag{I-17}
$$

where $1/\tau$ represented the eigenvalues of $\mathcal{E}$ and are the relaxation times. The solution of the matrix is

$$
(1/\tau)^3 + (-k_{23} - k_{32} - k_{12}A - k_{21}) (1/\tau)^2
$$
$$
+ (k_{21}k_{32} + k_{23}k_{12}A + k_{12}k_{32}A) (1/\tau) = 0 \tag{I-18}
$$

One of the roots of this expression is obviously zero and the remaining roots must be evaluated by the quadratic equation. The expression can be simplified by using the approximation

$$
(1 \pm a)^n \cong 1 \pm na \tag{I-19}
$$

which is justified if

$$
\frac{4 (k_{21}k_{32} + k_{23}k_{12}A + k_{12}k_{32}A)}{(k_{23} + k_{32} + k_{21} + k_{12}A)^2} < 1 \tag{I-20}
$$

This is a reasonable approximation for most relaxation processes where the two relaxation times are separated by at least two orders of magnitude. If it is assumed that the first reaction in equation (I-1) is faster than the second reaction, it may be noted that

$$
k_{12}, \; k_{21} \gg k_{23}, \; k_{32} \tag{I-21}
$$

The resultant relaxation times can be represented by

$$
1/\tau_I = k_{21} + k_{12} \left([<B(OH)_3>] + [<OH^->] \right) \tag{I-22}
$$

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$$1/\tau_{II} = k_{32} + k_{23} \left\{ \frac{[<B(OH)_3>] + [<OH^->]}{(1/K_1) + [<B(OH)_3>] + [<OH^->]} \right\} \qquad (I-23)$$

where τ_I corresponds to the faster first step and τ_{II} represents the slower second step. The equilibrium constant K_1 is the value for the first step, represented by

$$K_1 = k_{12}/k_{21} \qquad (I-24)$$

Amdur and Hammes (1966) and Czerlinski (1966) obtained identical results using a slightly modified approach.

To evaluate the eigenvalue problem, the following matrix relation must be solved

$$B = \Pi^{-1} \mathcal{E} \Pi \qquad (I-25)$$

where B is a diagonal matrix, Π is the transformation matrix, and   is the matrix of coefficients from equation (I-12) thru (I-14). The column vectors m_i of the transformation matrix represent the basic vectors for the transformed coordinate system. By rearrangement of equation (I-25) equation

$$\mathcal{E} \overrightarrow{m_j} = -\frac{1}{\tau_j} \overrightarrow{m_j} \qquad (I-26)$$

may be obtained. The individual elements $(m_j^{(s)})$ of the vector $\overrightarrow{m_j}$ represent the contribution of each of the reaction states (s) to the normal reaction mode 1. Solving equation (I-25), the following values of $\overrightarrow{m_j}$ are obtained

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$$\vec{m_j} = \begin{vmatrix} m_j^{(1)} \\ m_j^{(2)} \\ m_j^{(3)} \end{vmatrix} = \begin{vmatrix} q \\ \dfrac{(k_{12}A - 1/\tau_j)\,q}{k_{21}} \\ \dfrac{k_{23}(k_{12}A - 1/\tau_j)\,q}{k_{21}(k_{32} - 1/\tau_j)} \end{vmatrix} \qquad (I\text{-}27)$$

where q is a unit normalization factor. Using equation (2-26) with

$$\frac{d\theta}{dK} = \frac{1}{K \sum\limits_i \left[v_i^2 / [<A_i>] \right]} \qquad (I\text{-}28)$$

which is applicable when activity coefficients are not a major factor, and

looking at the maximum $\alpha\lambda$ values which occur when the observed frequency

equals the relation frequency, one obtains

$$(\alpha\lambda)_{max} = \frac{\pi \left[\Delta V^o - \dfrac{\Delta H^o}{C_p} \left(\dfrac{\theta V}{\theta T} \right)_p \right] \Delta V^o}{2\beta_o RT \sum\limits_i (v_i^2 / [<A_i>])} \qquad (I\text{-}29)$$

Disregarding the enthalpy change because of its small value in comparison

to the change in molal volume and converting to the new coordinate system,

equation (I-29) would become

$$(\alpha\lambda)_{max} = \frac{\pi (\Delta V_j)^2}{2\beta_o RT \sum\limits_s \left\{ (m_j^{(s)})^2 / [<C_s>] \right\}} \qquad (I\text{-}30)$$

where $[<C_s>]$ is the concentration of reactant for the appropriate state.

Representing the $\Delta V_j^{\,o}$ value as

$$\Delta V_1 = \sum_s m_1^{(s)} V_s \qquad (I\text{-}31)$$

for reaction (I-1) the ΔV_j would be

$$\Delta V_j = (m_j^{(2)} + m_j^{(3)}) \; \Delta V_{12} + m_j^{(3)} \; \Delta V_{23} \qquad (I\text{-}32)$$

The individual $\alpha \lambda$ values can now be calculated using the available information.

It will be noted that activity coefficients have not been directly treated by this derivation. As pointed out by Stuehr and Yeager (1965), terms such as $(\partial \ln \gamma_{\pm}^2 / \partial \ln \sigma)_T$, where σ is the dissociation constant, are generally negligible if work is conducted in a solution where much of the ionic strength is attributed to ions which do not react. This is normally the case for equation (I-1). If activity coefficients must be considered, they would be incorporated in the rate constants and the derivation would proceed as noted. Using the activity coefficients from Whitfield (1974) for $B(OH)_3$ and OH^- as 0.65, in equation (I-1) the overall effect of the activity coefficients would cancel.

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July 1982