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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

KINETIC RELAXATION STUDIES OF

AQUEOUS BORIC ACID SOLUTIONS

AND RELATED SYSTEMS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

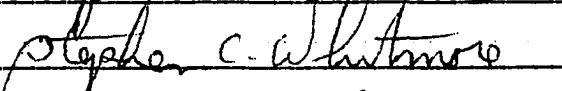
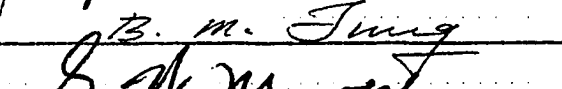
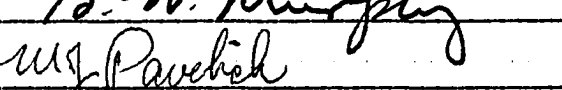
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Norman, Oklahoma

1976

KINETIC RELAXATION STUDIES OF
AQUEOUS BORIC ACID SOLUTIONS
AND RELATED SYSTEMS

APPROVED BY


DISSERTATION COMMITTEE

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DEDICATION

TO MY DEAREST PARENTS

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PART I:
THEORETICAL PREDICTION OF
THE RELAXATION SPECTRA OF
AQUEOUS BORIC ACID AND
RELATED SYSTEMS

I. INTRODUCTION:

A. The Chemistry of Boron and Boric Acid:

The boron atom has the gas-phase electron configuration of $1s^2, 2s^2, 2p^1$. Despite its $2s^2 2p^1$ electronic structure, boron is always trivalent and never monovalent. This is because the total energy released in the formation of three bonds in a BX_3 compound exceeds the energy of formation of one bond in a BX compound by more than enough to provide for promotion of boron to a hybridized valence state of the sp^2 type, and these three sp^2 hybrid orbitals lie in one plane at 120° angles. Therefore, the chief oxidation state of boron is +3 and the element normally combines with oxygen to form three triangular-planar bonds by sp^2 orbital hybridization. The boron-oxygen radius ratio is 0.20^1 and from spatial considerations alone, boron would be expected to occur in three- or fourfold coordination. The transition to tetrahedral sp^3 orbital hybridization is accomplished by the acceptance of an electron-pair from a base into the low-energy fourth orbital of the boron valence shell. The measured B-O bond distances in trigonal borates range from 1.28 to 1.44 Å and the mean is 1.37 Å.²⁻⁵ The average tetrahedral bond length is 1.48 Å while the individual values vary from 1.42 to 1.54 Å.⁶⁻⁸

Boron may be considered a typical metalloid having properties

intermediate between the metals and the electronegative non-metals. The tendency for boron is to form anionic rather than cationic complexes.

Boric acid is formed by hydrolysis of boron halides or boron hydrides. The acid forms white needle-like crystals in which there are $B(OH)_3$ units linked together by hydrogen bonds to form layers of nearly hexagonal symmetry. These layers are $3.18 \text{ \AA}$ apart, which accounts for the pronounced basal cleavage.

Boric acid is moderately soluble in water with a large negative heat of solution so that the solubility increases markedly with temperature. It is a very weak and exclusively monobasic acid which acts not as a proton donor but as a Lewis acid, accepting the OH^- ion. The formation of the hydroxyborate ion, $B(OH)_4^-$, on ionization of boric acid, $B(OH)_3$, is spontaneous.

When both the hydroxyborate ion and its conjugate acid are present in solution, the result is polymerization and the formation of water. However, at boric acid concentrations less than 0.025 M ,⁹⁻¹⁰ essentially only mononuclear species $B(OH)_3$ and $B(OH)_4^-$ are present. But at higher boric acid concentrations the polymeric species such as $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{-2}$, and $B_5O_6(OH)_4^-$ become predominant. It is commonly acknowledged that the equilibria between boric acid, monoborate ions and polyborates in aqueous solution is rapidly reversible.

B. Historical Background:

The importance of boric acid and borax as solid standards for the preparation of buffer solutions has been responsible for numerous determinations of the dissociation constant of boric acid at various

temperatures and pressures. Both the theoretical calculation and a variety of different experimental methods such as conductivity, colorimetry, and electromotive force measurement (with hydrogen electrodes, glass electrodes, silver electrodes, or quinhydrone electrodes) have been used.^{9, 11-31, 33}

In addition to the numerous equilibrium constants measured, the following thermodynamic quantities have also been determined: the Gibb's free energy change, ΔG° , the enthalpy change, ΔH° , the entropy change, ΔS° , the constant pressure heat capacity change, ΔC_p° , and their temperature dependences, associated with the ionization of boric acid at infinite dilution.^{17, 24, 34}

Smisko and Mason have measured the heat of solution, the heat of dilution, and the heat of formation of boric acid at 25°C in aqueous solutions.³² Ward and Millero have studied the apparent molal volume of boric acid and its temperature dependence at infinite dilution.³³ They have also determined the volume change accompanying the dissociation process of boric acid.

From the survey of the literature, it is found that some investigations concerning the equilibria of certain polyborate systems have also been carried out and the corresponding K_{eq} determined.^{19, 28-31} Mesmer, Baes, Jr., and Sweeton have evaluated the ΔH and ΔS values for the association reaction of some polynuclear species.

Although many studies regarding the equilibrium constants and thermodynamic properties have been carried out on both mononuclear and polynuclear boric acid systems, little attention has been paid to the "behavior" of those systems. As far as the kinetic field is concerned, only very limited information is available from the

literature. For the boric acid system, Gilkerson, Anderson, et al.^{35-36, 29} and Kouta have either measured or estimated the rate constants. For polyborate systems, some of the over-all reaction rate constants^{29, 34} have been reported in the literature.

C. Boric Acid and Seawater Sound Absorption:

The oceans cover about 71% of the surface of Earth. But the knowledge concerning this enormous environment of seawater is quite limited. Most studies done in the past have concentrated on the "static" aspects of seawater, such as the physical properties, chemical composition, and thermodynamics of equilibrium states. As far as the study of the "dynamics" of these equilibrium states is concerned, it has been largely ignored. Hence, for a better understanding of seawater, a thorough kinetic study of seawater is necessary.

Sound absorption has long been used as a convenient and powerful technique for the study of fast reactions. Seawater absorbs sound waves strongly over a wide frequency range. The excess sound absorption of seawater at higher frequencies may be explained in terms of a multi-step, ion association reaction involving hydrated magnesium and sulfate ions. However, more recent oceanic measurements have revealed another area of excess absorption in the low frequency region below 10 KHz, which implies the possibility of additional chemical relaxations. The detailed reaction mechanism responsible for this low frequency sound absorption is still unknown and remains to be solved.

The major inorganic components of seawater are Cl^- , Na^+ , SO_4^{2-} , Mg^{+2} , Ca^{+2} , K^+ , HCO_3^- , Br^- , Sr^{+2} , B(OH)_3 , B(OH)_4^- , Si(OH)_4 , and F^- . The concentration of boron in seawater is 4.4×10^{-4} M. Although not in high concentration, the boric acid system is very important. This is because boric acid, together with carbonate and silicate, has a buffering effect in seawater and thus controls the pH. As a consequence, it affects directly many of the other chemical equilibria. Unfortunately, detailed kinetic information concerning boric acid is extremely scarce, and the role boric acid plays in seawater kinetics is not clear. Therefore, it would be of great interest to obtain relaxation data for the boric acid system, in order to determine its importance in sound absorption in the sea.

II. OBJECTIVES:

Since the available information concerning the kinetics of boric acid and its related systems is quite limited, a thorough study of the kinetics of those systems is necessary. The main objectives of this research are as follows:

- A. By taking advantage of the limited data available in the literature plus the reasonable assumed values, predict theoretically the kinetic relaxation spectrum of each system considered.
- B. From the experimental results, check the theoretical relaxation spectra.
- C. By use of the experimental relaxation spectra, determine the reaction mechanism.
- D. Once the reaction mechanism is specified, determine the forward and backward rate constants, and the equilibrium constants as well as the associated energy terms.

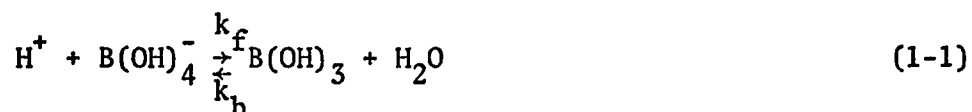
III. THEORY:

A. The Boric Acid System:

1. Chemical Relaxation and the Relaxation Time:

When a chemical reaction which is originally in equilibrium is suddenly perturbed by a change in some external parameter such as temperature, pressure, and electric field, then the reaction system is no longer in its originally equilibrium state. As a consequence, the reaction starts to adjust itself by moving toward a new equilibrium state.

Consider the following reaction:



which, for the purpose of simplicity, we can express in the form of:



Now, suppose that the system is initially at equilibrium, and then the conditions are suddenly disturbed. Let the initial concentrations of A, B, and C be a_0 , b_0 , and c_0 , and let the equilibrium concentrations corresponding to the new conditions be $\bar{a}$, $\bar{b}$, and $\bar{c}$. Let us also suppose that the reaction moves to the right, that is, $a_0 > \bar{a}$, $b_0 > \bar{b}$,

and $\bar{c} > c_0$. Suppose also that the concentrations at any time, t , ($t > 0$) as the system relaxes or shifts to the new equilibrium conditions be a , b , and c . Now, the actual concentrations at any time t will differ from the final equilibrium values by an amount, x , so that:

$$x = a - \bar{a} = b - \bar{b} = \bar{c} - c \quad (1-3)$$

The net forward rate at time t is then given by:

$$(dc/dt) = k_f ab - k_b c \quad (1-4)$$

where k_f is the forward rate constant of the reaction, and k_b is the backward rate constant of the reaction.

Since from equation (1-3), $x = \bar{c} - c$, or:

$$c = \bar{c} - x$$

Substituting this relationship into eqn.(1-4), we get:

$$(d/dt)(\bar{c} - x) = k_f ab - k_b c$$

$$\text{or: } (d\bar{c}/dt) - (dx/dt) = k_f ab - k_b c \quad (1-5)$$

Since $(d\bar{c}/dt) = 0$, eqn.(1-5) becomes:

$$-(dx/dt) = k_f ab - k_b c \quad (1-6)$$

and when the reaction reaches its new equilibrium state, (dx/dt) becomes zero, so that: $0 = k_f \bar{a} \bar{b} - k_b \bar{c}$

$$\text{or: } k_f \bar{a} \bar{b} = k_b \bar{c} \quad (1-7)$$

The forward rate in terms of x may be derived by substituting eqn.(1-3) into eqn.(1-6) and by using the relationship of eqn.(1-7),

$$\begin{aligned} -(dx/dt) &= k_f (\bar{a} + x)(\bar{b} + x) - k_b (\bar{c} - x) \\ &= k_f [\bar{a}\bar{b} + (\bar{a} + \bar{b})x + x^2] - k_b (\bar{c} - x) \end{aligned} \quad (1-8)$$

Since the perturbation is small, the displacement from equilibrium is small, and the x^2 term can be dropped, so that from eqns.(1-8) and (1-7), we get:

$$-(dx/dt) = [k_f (\bar{a} + \bar{b}) + k_b] x \quad (1-9)$$

The quantity in square brackets is a constant for any given condition. So eqn.(1-9) expresses a first-order attainment of equilibrium. For small perturbations, $x \ll c$, the rate at which a chemical system relaxes is proportional to the difference between the actual concentrations (at any time t) and the equilibrium concentrations, that is:

$$-(dx/dt) = kx \quad (1-10)$$

where k is the proportionality constant. (called the over-all first-order constant)

Now, define:

$$\tau \equiv (1/k) \quad (1-11)$$

where τ is the reciprocal of the proportionality constant, has the unit of time, and is called the relaxation time.

Comparing equations (1-9), (1-10), and (1-11), the relaxation time for the reaction (1-2) is then:

$$(1/\tau) = k_f(\bar{a} + \bar{b}) + k_b \quad (1-12)$$

or for our special reaction (1-1), eqn.(1-12) becomes:

$$(1/\tau) = k_f\{[\bar{H}^+] + [\bar{B(OH)}_4^-]\} + k_b \quad (1-13)$$

The relaxation time can then be expressed in terms of a relaxation frequency, f_r , by: ³⁷⁻³⁹

$$\tau = (1/2\pi f_r) \quad (1-14)$$

2. Relation of the Excess Absorption per Wavelength to the Thermodynamic Parameters:

For the single-step chemical reaction, such as:



the equilibrium constant, K_{eq} , can be expressed as:

$$K_{eq} = \frac{[\bar{D}]^{v_D}}{[\bar{A}]^{v_A} [\bar{B}]^{v_B}} \cdot \frac{\gamma_D^{v_D}}{\gamma_A^{v_A} \gamma_B^{v_B}} = \frac{k_f}{k_b} \quad (1-16)$$

where $[\bar{A}]$, $[\bar{B}]$, $[\bar{D}]$ are the equilibrium concentrations of A, B, and D, respectively, and v_A , v_B , v_D are the corresponding stoichiometric coefficients; γ_A , γ_B , and γ_D are the activity coefficients of A, B, and D, respectively.

Let X stand for the advancement of the reaction. Assuming that the reaction moves to the right, we have:

$$\delta X = -(1/v_A) \cdot \delta[\bar{A}] = -(1/v_B) \cdot \delta[\bar{B}] = (1/v_D) \cdot \delta[\bar{D}] \quad (1-17)$$

The adiabatic compressibility of a fluid can be written as:⁴⁰

$$\beta = \beta_{\infty} + \beta_r^* \quad (1-18)$$

where β_{∞} is the instantaneous compressibility (that is, the limiting value of β as $f \rightarrow \infty$); and β_r^* is the frequency dependent relaxational compressibility, which can be further expressed as:

$$\beta_r^* = \beta_r / (1 + j\omega\tau) \quad (1-19)$$

where τ is the relaxation time, and β_r , a real number called the time independent relaxational adiabatic compressibility, is defined as:

$$\beta_r \equiv \beta_{\infty} - \beta_0 \quad (1-20)$$

where β_0 is the static adiabatic compressibility (that is, the limiting value of β as $f \rightarrow 0$).

The time independent part of the relaxational adiabatic compressibility can then be expressed by:⁴⁰

$$\beta_r = -(1/V) [(\partial V/\partial P)_T + (\partial V/\partial T)_P (\partial T/\partial P)_S] \quad (1-21)$$

where $(\partial V/\partial P)_T$ and $(\partial V/\partial T)_P$ are the volume changes associated with the shift of the chemical equilibrium, the volumes of all other components

being constant.

Using the following relationships:

$$(\partial V/\partial P)_T = (\partial V/\partial X)_T (\partial X/\partial P)_T \quad (1-22)$$

$$(\partial T/\partial P)_S = (\partial V/\partial S)_P = (\partial V/\partial T)_P (\partial T/\partial S)_P \quad (1-23)$$

$$(\partial T/\partial S)_P = (\partial T/\partial H)_P (\partial H/\partial S)_P = (1/C_p)(T) = (T/C_p) \quad (1-24)$$

and

$$(1/V)(\partial V/\partial X)_T = \Delta V \approx \Delta V^\circ \quad (1-25)$$

where $\Delta V^\circ = v_D \bar{V}_D^\circ - v_A \bar{V}_A^\circ - v_B \bar{V}_B^\circ$; and $\bar{V}_i^\circ$ is the partial molal volume of species i.

Also:

$$\begin{aligned} (\partial X/\partial P)_T &= (\partial X/\partial K)_T (\partial K/\partial P)_T = (\partial X/\partial K)_T (\partial K/K \cdot \partial P)_T \cdot K \\ &= (\partial X/\partial K)_T (\partial \ln K/\partial P)_T \cdot K \\ &= (\partial X/\partial K)_T (-\Delta V^\circ/RT) \cdot K \end{aligned} \quad (1-26)$$

Then eqn. (1-21) becomes:

$$\beta_T = (\partial X/\partial K)_T \cdot K [(\Delta V^\circ)^2/RT] - (1/V)(\partial V/\partial T)_P (\partial V/\partial T)_P (T/C_p) \quad (1-27)$$

Since

$$\begin{aligned} (\partial V/\partial T)_P &= (\partial V/\partial X)_P (\partial X/\partial T)_P \\ &= (\partial V/\partial X)_P (\partial X/\partial K)_P (\partial K/\partial T)_P \end{aligned} \quad (1-28)$$

and

$$(\partial \ln K/\partial T)_P = (\Delta H^\circ/RT^2)$$

$$\text{or: } (\partial K/\partial T)_P = K \cdot (\Delta H^\circ/RT^2), \quad (1-29)$$

substituting eqns. (1-25), (1-29) into (1-28), one obtains:

$$(\partial V/\partial T)_P = (V \cdot \Delta V^\circ \cdot \Delta H^\circ/RT^2) K (\partial X/\partial K)_P \quad (1-30)$$

From eqns. (1-30) and (1-27), we get:

$$\beta_T = (\partial X/\partial K)_T K [(\Delta V^\circ)^2/RT] - (\partial X/\partial K)_P K (\partial V/\partial T)_P (\Delta H^\circ \cdot \Delta V^\circ/C_p RT) \quad (1-31)$$

From eqn. (1-16), we have:

$$\begin{aligned}
(\partial K/\partial X)_T &= \{ [\bar{A}]^{\nu_A} [\bar{B}]^{\nu_B} \}^{-1} \cdot (\partial/\partial X) \{ [\bar{D}]^{\nu_D} \} \\
&+ \{ [\bar{D}]^{\nu_D} / [\bar{B}]^{\nu_B} \} \cdot (\partial/\partial X) \{ [\bar{A}]^{-\nu_A} \} \\
&+ \{ [\bar{D}]^{\nu_D} / [\bar{A}]^{\nu_A} \} \cdot (\partial/\partial X) \{ [\bar{B}]^{-\nu_B} \}
\end{aligned} \tag{1-32}$$

where the activity coefficient terms such as $(\partial \ln \gamma_i / \partial X)$ have been omitted since the perturbation is small, and the activity coefficients can be considered constant.

Also:

$$(\partial/\partial X) \{ [\bar{D}]^{\nu_D} \} = \nu_D \cdot [\bar{D}]^{\nu_D-1} \cdot \{ d[\bar{D}]/dX \} \tag{1-33}$$

$$(\partial/\partial X) \{ [\bar{A}]^{-\nu_A} \} = \{ -\nu_A / [\bar{A}]^{\nu_A+1} \} \cdot \{ d[\bar{A}]/dX \} \tag{1-34}$$

$$(\partial/\partial X) \{ [\bar{B}]^{-\nu_B} \} = \{ -\nu_B / [\bar{B}]^{\nu_B+1} \} \cdot \{ d[\bar{B}]/dX \} \tag{1-35}$$

Substituting eqns. (1-17), (1-33), (1-34), and (1-35) into eqn. (1-32),

we obtain:

$$\left(\frac{\partial K}{\partial X} \right)_T = K \cdot \left\{ \frac{\nu_D^2}{[\bar{D}]} + \frac{\nu_A^2}{[\bar{A}]} + \frac{\nu_B^2}{[\bar{B}]} \right\}$$

or:

$$K \cdot \left(\frac{\partial X}{\partial K} \right)_T = \left\{ \frac{\nu_D^2}{[\bar{D}]} + \frac{\nu_A^2}{[\bar{A}]} + \frac{\nu_B^2}{[\bar{B}]} \right\}^{-1} \tag{1-36}$$

The excess absorption per wavelength, μ_{chem} , is related to the compressibilities by:⁴¹

$$\mu_{\text{chem}} \equiv \alpha' \lambda = \pi \cdot \frac{\beta_r}{\beta_o} \cdot \frac{\omega \tau}{1 + (\omega \tau)^2} \tag{1-37}$$

where λ is the wavelength, ω is the angular frequency, and α' is the excess sound absorption defined as:⁴²

$$\alpha' \equiv \alpha_{\text{soln}} - \alpha_{\text{solv}} \tag{1-38}$$

where α_{soln} , and α_{solv} are the sound absorptions of solution and of solvent, respectively.

Therefore, from eqns.(1-31), (1-36), and (1-37), one obtains:

$$\mu_{\text{chem}} = \frac{\pi}{\beta_0} \cdot \frac{\Delta V^\circ}{\sum_i \frac{v_i^2}{RT \Sigma [\bar{C}_i]}} \cdot [\Delta V^\circ - (\Delta H^\circ / C_p) (\partial V / \partial T)_p] \cdot \frac{\omega \tau}{1 + (\omega \tau)^2} \quad (1-39)$$

where:

$$\sum_i \{v_i^2 / [\bar{C}_i]\} \equiv \{v_D^2 / [\bar{D}]\} + \{v_A^2 / [\bar{A}]\} + \{v_B^2 / [\bar{B}]\}$$

Since by definition, the thermal expansion coefficient, θ , is given by:

$$\theta \equiv (1/V) (\partial V / \partial T)_p$$

or: $(\partial V / \partial T)_p = \theta V$, (1-40)

substituting eqn.(1-40) into (1-39), we get:

$$\mu_{\text{chem}} = \frac{\pi \Delta V^\circ}{\beta_0 \sum_i \frac{v_i^2}{RT \Sigma [\bar{C}_i]}} \cdot [\Delta V^\circ - \frac{\Delta H^\circ \cdot \theta \cdot \bar{V}}{C_p}] \cdot \frac{\omega \tau}{1 + (\omega \tau)^2} \quad (1-41)$$

Since $\omega = 2\pi f$, equation (1-41) becomes:

$$\mu_{\text{chem}} = \frac{\pi \cdot \Delta V^\circ}{\beta_0 \sum_i \frac{v_i^2}{RT \Sigma [\bar{C}_i]}} \cdot [\Delta V^\circ - \frac{\Delta H^\circ \cdot \theta \cdot \bar{V}}{C_p}] \cdot \frac{2\pi f \tau}{1 + (2\pi f \tau)^2} \quad (1-42)$$

When $f = f_r$, where f_r is the relaxation frequency, then μ_{chem} becomes μ_{max} , this gives us the equation:

$$\mu_{\text{max}} = \frac{\pi \Delta V^\circ [\Delta V^\circ - \frac{\Delta H^\circ \cdot \theta \cdot \bar{V}}{C_p}]}{2 \beta_0 \sum_i \frac{v_i^2}{RT \Sigma [\bar{C}_i]}} \quad (1-43)$$

From eqn.(1-43) and (1-42), we have:

$$\mu_{\text{chem}} = 2\mu_{\text{max}} \cdot \frac{(2\pi f\tau)}{1+(2\pi f\tau)^2} \quad (1-44)$$

In aqueous solutions, the values of enthalpy changes normally encountered are very small, so that:

$$\Delta V^\circ \gg (\Delta H^\circ \cdot \theta \cdot \bar{V}/C_p)$$

or: $\Delta V^\circ - (\Delta H^\circ \cdot \theta \cdot \bar{V}/C_p) \approx \Delta V^\circ \quad (1-45)$

Then eqn(1-43) can be simplified to:

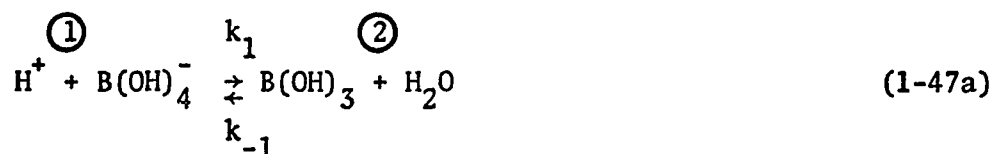
$$\mu_{\text{max}} = \frac{\pi(\Delta V^\circ)^2}{2\beta_o RT \sum_i \frac{v_i^2}{i[\bar{C}_i]}} \quad (1-46)$$

Therefore, by taking advantage of the suitable values of T, P, K_{eq} , k_f , k_b , ΔH° , $C_{\text{B(OH)}_3}$, pH, and ΔV° , etc. using eqns.(1-13), (1-14), (1-43), and (1-44), the values of f_r , μ_{max} , and μ_{chem} can be calculated.

B. The Boric Acid and Sodium Borate System:

1. Determination of the Relaxation Times:

The system studied is:



where k_i and k_{-i} ($i = 1, 2$) are the forward and backward rate constants, respectively, of reaction i ; the symbol $\textcircled{i}$ ($i = 1, 2, 3, 4$) used to indicate

the state number.

The related rate equations of (1-47a,b) can then be written as:

$$(d[H^+]/dt) = k_{-1}[B(OH)_3] - k_1[H^+][B(OH)_4^-] \quad (1-48a)$$

$$(d[B(OH)_3]/dt) = k_1[H^+][B(OH)_4^-] - k_{-1}[B(OH)_3] \quad (1-48b)$$

$$(d[Na^+]/dt) = k_{-2}[NaB(OH)_4] - k_2[Na^+][B(OH)_4^-] \quad (1-48c)$$

$$(d[NaB(OH)_4]/dt) = k_2[Na^+][B(OH)_4^-] - k_{-2}[NaB(OH)_4] \quad (1-48d)$$

An extent of reaction parameter, $\Delta\xi_s$, is now defined for each state S:

$$[A] = [\bar{A}] + \sum_s v^{(s)} \Delta\xi_s \quad (1-49)$$

where: $[A]$ = instantaneous concentration of constituent A

$[\bar{A}]$ = steady state value of constituent A

$\Delta\xi_s$ = movement of A in state S from its steady state value due to perturbation of the reaction system

$v^{(s)}$ = stoichiometric coefficient of A in state S and is zero for any state in which A does not appear

For the reaction system considered, the following relationships can be obtained:

$$[H^+] = [\bar{H}^+] + \Delta\xi_1 \quad (1-50a)$$

$$[B(OH)_3] = [\bar{B(OH)}_3] + \Delta\xi_2 \quad (1-50b)$$

$$[B(OH)_4^-] = [\bar{B(OH)}_4^-] + \Delta\xi_1 + \Delta\xi_3 \quad (1-50c)$$

$$[Na^+] = [\bar{Na}^+] + \Delta\xi_3 \quad (1-50d)$$

$$[NaB(OH)_4] = [\bar{NaB(OH)}_4] + \Delta\xi_4 \quad (1-50e)$$

Substituting eqn. (1-50a-e) into eqn. (1-48a-d), we can obtain:

$$\Delta\dot{\xi}_1 = -k_1\{[\bar{H}^+] + [\bar{B(OH)}_4^-]\Delta\xi_1 + k_{-1}\Delta\xi_2 - k_1[\bar{H}^+]\Delta\xi_3 \quad (1-51a)$$

$$\Delta\dot{\xi}_2 = k_1\{[\bar{H}^+] + [\bar{B(OH)}_4^-]\Delta\xi_1 - k_{-1}\Delta\xi_2 + k_1[\bar{H}^+]\Delta\xi_3 \quad (1-51b)$$

$$\Delta\dot{\xi}_3 = -k_2[\bar{Na}^+]\Delta\xi_1 - k_2\{[\bar{Na}^+] + [\bar{B(OH)}_4^-]\Delta\xi_3 + k_{-2}\Delta\xi_4 \quad (1-51c)$$

$$\Delta\dot{\xi}_4 = k_2[\bar{Na}^+]\Delta\xi_1 + k_2\{[\bar{Na}^+] + [\bar{B(OH)}_4^-]\Delta\xi_3 - k_{-2}\Delta\xi_4 \quad (1-51d)$$

where $\Delta\dot{\xi}_s = (d\Delta\xi_s/dt)$, and in deriving these differential equations,

the following conditions have been used:

- a. Assumed that the perturbations due to the sound wave, $\Delta\xi_s$, are very small, so that higher order terms such as $\Delta\xi_s \cdot \Delta\xi_t$ or $(\Delta\xi_s)^2$ may be ignored.
- b. Used the equilibrium conditions such as:

$$\{d[\overline{B(OH)_3}]/dt\} = k_1 [\overline{H^+}] [\overline{B(OH)_4^-}] - k_{-1} [\overline{B(OH)_3}] \quad (1-52a)$$

and

$$\{d[\overline{NaB(OH)_4}]/dt\} = k_2 [\overline{Na^+}] [\overline{B(OH)_4^-}] - k_{-2} [\overline{NaB(OH)_4}] \quad (1-52b)$$

.
.
.
etc.

Eqns. (1-51a-d) are a set of coupled, first order differential equations whose solution we wish to obtain. This is done by solving the eigenvalue problem for the set.⁴³⁻⁴⁵

Let us now express eqns. (1-51a-d) in matrix notation:

$$\begin{bmatrix} \Delta\dot{\xi}_1 \\ \Delta\dot{\xi}_2 \\ \Delta\dot{\xi}_3 \\ \Delta\dot{\xi}_4 \end{bmatrix} = \begin{bmatrix} -k_1\{[\overline{H^+}] + [\overline{B(OH)_4^-}]\} & k_{-1} & -k_1[\overline{H^+}] & 0 \\ k_1\{[\overline{H^+}] + [\overline{B(OH)_4^-}]\} & -k_{-1} & k_1[\overline{H^+}] & 0 \\ -k_2[\overline{Na^+}] & 0 & -k_2\{[\overline{Na^+}] + [\overline{B(OH)_4^-}]\} & k_{-2} \\ k_2[\overline{Na^+}] & 0 & k_2\{[\overline{Na^+}] + [\overline{B(OH)_4^-}]\} & -k_{-2} \end{bmatrix} \begin{bmatrix} \Delta\xi_1 \\ \Delta\xi_2 \\ \Delta\xi_3 \\ \Delta\xi_4 \end{bmatrix} \quad (1-53)$$

where $[\Delta\dot{\xi}_s]$ and $[\Delta\xi_s]$ are the column vectors.

For the purpose of simplicity, eqn. (1-53) can be expressed in the following form: $[\Delta\dot{\xi}_s] = [A][\Delta\xi_s]$ (1-54)

If the eigenvalues of the coefficient matrix, $[A]$, are λ_j , then: $[A][m_j] = \lambda_j[m_j]$ (1-55)

where $[m_j]$ are the column vectors which are basis vectors of the new

coordinate system.

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Equation (1-55) can be rewritten in the form:

$$\{[A] - \lambda_j [E]\} [m_j] = 0 \quad (1-56)$$

where $[E]$ is the identity matrix. That is, all the cross terms disappear and only the diagonal elements are non-zero and equal unity.

If a solution $[m_j] \neq 0$ exists, then we have:

$$\det.\{[A] - \lambda_j [E]\} = 0 \quad (1-57)$$

By using the relationship of eqn.(1-57), from eqn.(1-53) one obtains:

$$\begin{vmatrix} -k_1\{[\overline{H}^+] + [\overline{B(OH)}_4^-]\} - \lambda & k_{-1} & -k_1[\overline{H}^+] & 0 \\ k_1\{[\overline{H}^+] + [\overline{B(OH)}_4^-]\} & -k_{-1} - \lambda & k_1[\overline{H}^+] & 0 \\ -k_2[\overline{Na}^+] & 0 & -k_2\{[\overline{Na}^+] + [\overline{B(OH)}_4^-]\} - \lambda & k_{-2} \\ k_2[\overline{Na}^+] & 0 & k_2\{[\overline{Na}^+] + [\overline{B(OH)}_4^-]\} & -k_{-2} - \lambda \end{vmatrix} = 0 \quad (1-58)$$

which can be simplified by writing:

$$\begin{vmatrix} -k_1 a - \lambda & k_{-1} & -k_1 c & 0 \\ k_1 a & -k_{-1} - \lambda & k_1 c & 0 \\ -k_2 b & 0 & -k_2 d - \lambda & k_{-2} \\ k_2 b & 0 & k_2 d & -k_{-2} - \lambda \end{vmatrix} = 0 \quad (1-59)$$

$$\text{where: } a = \{[\overline{H}^+] + [\overline{B(OH)}_4^-]\} \quad (1-60a)$$

$$b = [\overline{Na}^+] \quad (1-60b)$$

$$c = [\overline{H}^+] \quad (1-60c)$$

$$d = \{[\overline{Na}^+] + [\overline{B(OH)}_4^-]\} \quad (1-60d)$$

Expanding eqn.(1-59), gives:

$$\lambda^4 + (k_1 a + k_{-2} + k_{-1} + k_2 d) \lambda^3 + (k_1 k_{-2} a + k_1 k_2 a d + k_{-1} k_{-2} + k_{-1} k_2 d - k_1 k_2 b c) \lambda^2 = 0 \quad (1-61a)$$

$$\text{or: } \lambda^2 [\lambda^2 + (k_1 a + k_{-2} + k_{-1} + k_2 d) \lambda + (k_1 k_{-2} a + k_1 k_2 a d + k_{-1} k_{-2} + k_{-1} k_2 d - k_1 k_2 b c)] = 0 \quad (1-61b)$$

Since $\lambda \neq 0$,

$$\lambda^2 + (k_1 a + k_{-2} + k_{-1} + k_2 d) \lambda + (k_1 k_{-2} a + k_1 k_2 a d + k_{-1} k_{-2} + k_{-1} k_2 d - k_1 k_2 b c) = 0 \quad (1-62)$$

$$\text{or: } \lambda^2 + B\lambda + C = 0 \quad (1-63)$$

where:

$$B = k_1 a + k_{-2} + k_{-1} + k_2 d \quad (1-64a)$$

$$C = k_1 k_{-2} a + k_1 k_2 a d + k_{-1} k_{-2} + k_{-1} k_2 d - k_1 k_2 b c \quad (1-64b)$$

The solution of eqn. (1-63) is:

$$\lambda = (1/2) [-B \pm (B^2 - 4C)^{\frac{1}{2}}] \quad (1-65)$$

By using the relationships of eqns. (1-65), (1-64a-b), (1-60a-d), and also the following relations:

$$K_A = k_1 + k_2 \quad (1-66a)$$

$$K_B = k_{-1} + k_{-2} \quad (1-66b)$$

$$K_C = k_1 - k_2 \quad (1-66c)$$

$$K_D = k_{-1} - k_{-2} \quad (1-66d)$$

$$K_E = K_C [\overline{B(OH)_4}] + K_D \quad (1-66e)$$

$$K_F = k_1 [\overline{H^+}] \quad (1-66f)$$

$$K_G = k_2 [\overline{Na^+}] \quad (1-66g)$$

$$K_H = K_A [\overline{B(OH)_4}] \quad (1-66h)$$

We obtain:

$$\lambda_1 = (1/2) [-(K_F + K_H + K_G + K_B) - \sqrt{K_E^2 + (K_F + K_G)^2 + 2(K_F - K_G)K_E}] \quad (1-67a)$$

and

$$\lambda_2 = (1/2) [-(K_F + K_H + K_G + K_B) + \sqrt{K_E^2 + (K_F + K_G)^2 + 2(K_F - K_G)K_E}] \quad (1-67b)$$

The eigenvalue is related to the relaxation time by:

$$\tau_j \equiv (-1/\lambda_j) \quad (1-68)$$

Therefore, from eqn. (1-68), the corresponding relaxation time, τ_j , can be obtained.

An alternative way to solve this eigenvalue problem is to make a coordinate transformation on eqn.(1-54) in such a way that all cross terms disappear, that is, in the transformed coefficient matrix, [B], only the diagonal elements may be non-zero. That is,

$$[B] = [M^{-1}] [A] [M] \quad (1-69)$$

where [M] is the transformation matrix, and $[M^{-1}]$ is the inverse matrix of [M]. The constants λ_j are the diagonal elements of matrix [B] and have units of sec^{-1} ; they are the eigenvalues of the coefficient matrix [A].

2. Evaluation of the Relaxation Spectra:

For a coupled, multi-step reaction, eqn.(1-43) has the general form:

$$\mu_{\max}^j = \frac{\pi \Delta V_j^\circ \left[\Delta V_j^\circ - \frac{\Delta H_j^\circ \cdot \theta \cdot \bar{V}}{C_p} \right]}{2\beta_o RT \Sigma \frac{(v_i^2)_s}{s[\bar{C}_i]_s}} \quad (1-70)$$

and eqn.(1-44) becomes:

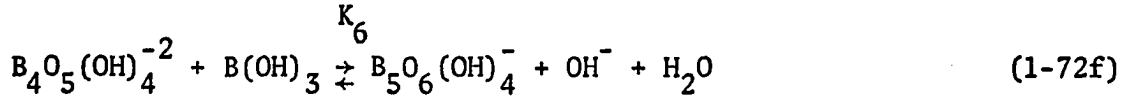
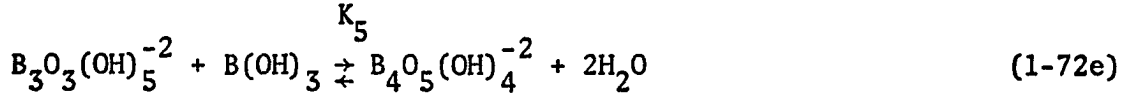
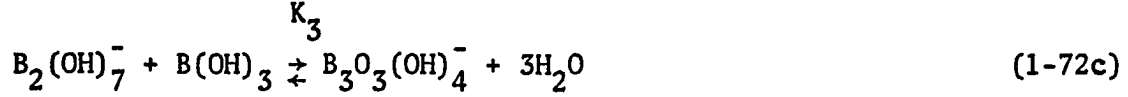
$$\mu_{\text{chem}} = \Sigma_j 2\mu_{\max}^j \left[\frac{2\pi f \tau_j}{1 + (2\pi f \tau_j)^2} \right] \quad (1-71)$$

Therefore, from the suitable thermodynamic parameters, the related relaxation spectra can be evaluated using equations (1-67a-b), (1-68), (1-14), (1-70), and (1-71).

C. The Boric Acid and Polyborate System:

1. Distribution of the Concentrations of Various Species in Equilibrium:

Consider the following polyborate system:



Where K_i ($i=1,2,3,4,5,6$) is the equilibrium constant of reaction i , and can be expressed in the following form:

$$\frac{[\text{H}^+][\text{B(OH)}_4^-]}{[\text{B(OH)}_3]} = K_1 \quad (1-73a)$$

$$\frac{[\text{B}_2(\text{OH})_7^-]}{[\text{B(OH)}_4^-][\text{B(OH)}_3]} = K_2 \quad (1-73b)$$

$$\frac{[\text{B}_3\text{O}_3(\text{OH})_4^-]}{[\text{B}_2(\text{OH})_7^-][\text{B(OH)}_3]} = K_3 \quad (1-73c)$$

$$\frac{[\text{B}_3\text{O}_3(\text{OH})_5^{-2}]}{[\text{B}_3\text{O}_3(\text{OH})_4^-][\text{OH}^-]} = K_4 \quad (1-73d)$$

$$\frac{[\text{B}_4\text{O}_5(\text{OH})_4^{-2}]}{[\text{B}_3\text{O}_3(\text{OH})_5^{-2}][\text{B(OH)}_3]} = K_5 \quad (1-73e)$$

$$\frac{[\text{B}_5\text{O}_6(\text{OH})_4^-][\text{OH}^-]}{[\text{B}_4\text{O}_5(\text{OH})_4^{-2}][\text{B(OH)}_3]} = K_6 \quad (1-73f)$$

The total analytical concentration of boric acid, $C_{B(OH)_3}$, is then given by:

$$\begin{aligned} C_{B(OH)_3} = & [B(OH)_3] + [B(OH)_4^-] + 2[B_2(OH)_7^-] \\ & + 3[B_3O_3(OH)_4^-] + 3[B_3O_3(OH)_5^{-2}] \\ & + 4[B_4O_5(OH)_4^{-2}] + 5[B_5O_6(OH)_4^-] \end{aligned} \quad (1-74)$$

Rewrite eqns.(1-73a-f) in the following form :

$$[B(OH)_4^-] = \frac{K_1 [B(OH)_3]}{[H^+]} \quad (1-75a)$$

$$[B_2(OH)_7^-] = \frac{K_1 K_2 [B(OH)_3]^2}{[H^+]} \quad (1-75b)$$

$$[B_3O_3(OH)_4^-] = \frac{K_1 K_2 K_3 [B(OH)_3]^3}{[H^+]} \quad (1-75c)$$

$$[B_3O_3(OH)_5^{-2}] = \frac{K_1 K_2 K_3 K_4 [OH^-] [B(OH)_3]^3}{[H^+]} \quad (1-75d)$$

$$[B_4O_5(OH)_4^{-2}] = \frac{K_1 K_2 K_3 K_4 K_5 [OH^-] [B(OH)_3]^4}{[H^+]} \quad (1-75e)$$

$$[B_5O_6(OH)_4^-] = \frac{K_1 K_2 K_3 K_4 K_5 K_6 [B(OH)_3]^5}{[H^+]} \quad (1-75f)$$

Substituting eqns.(1-75a-f) into (1-74), we obtain:

$$\begin{aligned} C_{B(OH)_3} = & [B(OH)_3] + \frac{K_1 [B(OH)_3]}{[H^+]} + \frac{2[B(OH)_3]^2 \cdot \frac{2}{1} \Pi K_i}{[H^+]} + \frac{3[B(OH)_3]^3 \cdot \frac{3}{1} \Pi K_i}{[H^+]} \\ & + \frac{3[OH^-] [B(OH)_3]^3 \cdot \frac{4}{1} \Pi K_i}{[H^+]} + \frac{4[OH^-] [B(OH)_3]^4 \cdot \frac{5}{1} \Pi K_i}{[H^+]} + \frac{5[B(OH)_3]^5 \cdot \frac{6}{1} \Pi K_i}{[H^+]} \end{aligned} \quad (1-76)$$

where $\Pi_{1}^n K_i \equiv K_1 \cdot K_2 \cdot K_3 \cdots K_n$

Now, let $x = [B(OH)_3]$, and rearrange eqn. (1-76), to obtain:

$$\begin{aligned} & \frac{5 \cdot \overset{6}{\underset{1}{\Pi K_i}}}{[H^+]} \cdot x^5 + \frac{4 [OH^-] \cdot \overset{5}{\underset{1}{\Pi K_i}}}{[H^+]} \cdot x^4 + \frac{3 \cdot \overset{3}{\underset{1}{\Pi K_i}} + 3 [OH^-] \cdot \overset{4}{\underset{1}{\Pi K_i}}}{[H^+]} \cdot x^3 \\ & + \frac{2 \cdot \overset{2}{\underset{1}{\Pi K_i}}}{[H^+]} \cdot x^2 + \frac{[H^+] + K_1}{[H^+]} \cdot x - C_{B(OH)_3} = 0 \end{aligned} \quad (1-77)$$

Equation (1-77) is in the form of:

$$Ax^5 + Bx^4 + Cx^3 + Dx^2 + Ex + F = 0 \quad (1-78)$$

and can be solved by taking advantage of computer programming techniques.

Once the concentration of $[B(OH)_3]$ has been determined, the concentrations of the polyborate species can then be obtained using eqns. (1-75a-f).

2. The Relaxation Times and the Relaxation Spectra of the Polyborate System:

Consider a reaction mechanism consisting of R elementary chemical reactions which involve N chemical species, then the reactions can be symbolized by:

$$\sum_{i=1}^N v_{i\alpha} B_i = 0, \quad \alpha = 1, 2, 3, \dots, R \quad (1-79)$$

where B_i is the i -th chemical species, and $v_{i\alpha}$ are the stoichiometric coefficients which are taken as negative for reactants and positive for products.

Let ξ_α be the advancement of the α -th reaction. Then for a

single reaction, the number of moles of the i-th species is given by:

$$n_i = n_i^{\circ} + v_i \xi \quad (1-80)$$

where n_i° is the number of moles of species i present when $\xi = 0$.

If the species i is involved in several reactions, then eqn. (1-80) can be written in the general form of:

$$n_i = n_i^{\circ} + \sum_{\alpha=1}^R v_{i\alpha} \xi_{\alpha} \quad (1-81)$$

Setting the equilibrium state as the reference state, we have:

$$n_i = \bar{n}_i + \sum_{\alpha=1}^R v_{i\alpha} \Delta \xi_{\alpha} \quad (1-82)$$

or:

$$C_i = \bar{C}_i + (1/V) \sum_{\alpha=1}^R v_{i\alpha} \Delta \xi_{\alpha} \quad (1-83)$$

where the molar concentration, C_i , is related to the number of moles, n_i , and the volume of the solution, V , by: $C_i = n_i/V$, and $\Delta \xi_{\alpha} = \xi_{\alpha} - \bar{\xi}_{\alpha}$.

For any single α -th reaction, eqn. (1-80) can be expressed by:

$$C_i = C_i^{\circ} + (1/V) v_{i\alpha} \xi_{\alpha} \quad (1-84)$$

or:

$$C_i - C_i^{\circ} = (1/V) v_{i\alpha} \xi_{\alpha} \quad (1-85)$$

Differentiation with respect to time t , gives the rate of the α -th reaction:

$$(\partial/\partial t)_{T,P} (C_i - C_i^{\circ}) = (\partial/\partial t)_{T,P} [(1/V) v_{i\alpha} \xi_{\alpha}]$$

or:

$$(1/v_i) (\partial C_i / \partial t)_{T,P} = (1/V) (\partial \xi_{\alpha} / \partial t)_{T,P}$$

So that the rate can be written as:

$$\text{Rate} = (1/V) (\partial \xi_{\alpha} / \partial t)_{T,P} \quad (1-86)$$

This is the time rate of change of the concentration of any species which appears as a product in the α -th reaction with a stoichiometric coefficient of unity.

Now let k_{α} and $k_{-\alpha}$ stand for the forward and backward rate constants respectively for the α -th reaction, and a_j , $a_{j'}$, the activities of the species of the reactants and the products respectively. Then we can write the rate equation as:

$$\text{Rate} = (1/V)(\partial \xi_{\alpha} / \partial t)_{T,P} = k_{\alpha} \prod_j a_j^{-\nu_{j\alpha}} - k_{-\alpha} \prod_{j'} a_{j'}^{\nu_{j'\alpha}} \quad (1-87)$$

For the validity of eqn.(1-87) it is necessary that the reactions in (1-79) be written as elementary reactions in the kinetic sense, so that the order of the reaction can be inferred from the stoichiometric coefficients.

At equilibrium, the rates of the forward and backward reactions are equal, so that we have:

$$k_{\alpha} \cdot \prod_j \bar{a}_j^{-\nu_{j\alpha}} = k_{-\alpha} \cdot \prod_{j'} \bar{a}_{j'}^{\nu_{j'\alpha}} \equiv r_{\alpha} \quad (1-88)$$

which defines r_{α} , the exchange rate of the reaction.

From eqns.(1-88) and (1-87), we obtain:

$$(1/V)(\partial \xi_{\alpha} / \partial t)_{T,P} = r_{\alpha} \left[\prod_j (a_j / \bar{a}_j)^{-\nu_{j\alpha}} - \prod_{j'} (a_{j'} / \bar{a}_{j'})^{\nu_{j'\alpha}} \right] \quad (1-89)$$

which can be written in the form of :

$$(1/V)(\partial \xi_{\alpha} / \partial t)_{T,P} = r_{\alpha} \cdot \prod_j (a_j / \bar{a}_j)^{-\nu_{j\alpha}} \cdot \left[1 - \prod_{i=1}^N (a_i / \bar{a}_i)^{\nu_{i\alpha}} \right] \quad (1-90)$$

in which the product over i is over both reactants and products of the reaction α .

The quotient of activities for reaction α is defined as:

$$Q_{\alpha} \equiv \prod_i a_i^{\nu_{i\alpha}} \quad (1-91)$$

and the equilibrium constant is:

$$K_{\alpha} \equiv \prod_i \bar{a}_i^{\nu_{i\alpha}} \quad (1-92)$$

Thus, eqn.(1-90) becomes:

$$(1/V)(\partial \xi_{\alpha}/\partial t)_{T,P} = r_{\alpha} \cdot \prod_j (a_j/\bar{a}_j)^{-\nu_{j\alpha}} [1 - (Q_{\alpha}/K_{\alpha})] \quad (1-93)$$

Using G_{α} for the reaction free energy, we have:

$$\begin{aligned} G_{\alpha} &= (\partial G/\partial \xi_{\alpha})_{T,P,\xi_{\beta}} = \sum_{i=1}^N \nu_{i\alpha} \mu_i \\ &= -RT \ln K_{\alpha} + RT \ln Q_{\alpha} = RT \cdot \ln(Q_{\alpha}/K_{\alpha}) \end{aligned} \quad (1-94)$$

$$\text{that is: } Q_{\alpha}/K_{\alpha} = \exp.[G_{\alpha}/RT] \quad (1-95)$$

Near equilibrium, $G_{\alpha}/RT \ll 1$, then eqn.(1-94) becomes:

$$Q_{\alpha}/K_{\alpha} = \exp.[G_{\alpha}/RT] = 1 + [G_{\alpha}/RT] + \dots \approx 1 + [G_{\alpha}/RT] \quad (1-96)$$

Substituting eqn.(1-96) into (1-93), we get:

$$(1/V)(\partial \xi_{\alpha}/\partial t)_{T,P} = -(r_{\alpha} G_{\alpha}/RT) \quad (1-97)$$

where the continued product over j in eqn.(1-93) has been set equal to unity to avoid including higher order terms.

Since the reaction α may be coupled with all the reactions in the mechanism, the rate of the reaction will in general be a function of all of the advancements, ξ_{β} , where $\beta = 1, 2, 3, \dots, R$.

$$G_{\alpha} = \sum_{\beta=1}^R (\partial G_{\alpha}/\partial \xi_{\beta})_{T,P,\xi_{\gamma \neq \beta}} \cdot \Delta \xi_{\beta} \quad (1-98)$$

Define:

$$G_{\alpha\beta} \equiv (\partial G_{\alpha}/\partial \xi_{\beta})_{T,P,\xi_{\gamma \neq \beta}} \quad (1-99)$$

that is:

$$G_{\alpha\beta} = (\partial/\partial \xi_{\beta}) G_{\alpha} = (\partial/\partial \xi_{\beta}) \sum_{i=1}^N \nu_{i\alpha} \mu_i$$

$$= \sum_{i=1}^N v_{i\alpha} (\partial \mu_i / \partial \xi_\beta) = \sum_{i=1}^N \sum_{j=1}^N v_{i\alpha} (\partial \mu_i / \partial C_j) (\partial C_j / \partial \xi_\beta) \quad (1-100)$$

From eqn. (1-84) one obtains:

$$(\partial C_j / \partial \xi_\beta) = (v_{j\beta} / V) \quad (1-101)$$

The chemical potential can be expressed as:

$$\mu_i = \mu_i^\circ + RT \ln C_i + RT \ln \gamma_i \quad (1-102)$$

Differentiating it with respect to C_j , we have:

$$(\partial \mu_i / \partial C_j) = RT(\delta_{ij} / C_j) + RT(\partial \ln \gamma_i / \partial C_j) \quad (1-103)$$

where δ_{ij} is the Kronecker delta.

Substituting eqns. (1-101), (1-103), into (1-100), we obtain:

$$G_{\alpha\beta} = (RT/V) \left[\sum_{i=1}^N (v_{i\alpha} v_{i\beta} / \bar{C}_i) + \sum_{i=1}^N \sum_{j=1}^N v_{i\alpha} v_{j\beta} (\partial \ln \gamma_i / \partial C_j) \right] \quad (1-104)$$

Defining:

$$\sum_{i=1}^N (v_{i\alpha} v_{i\beta} / \bar{C}_i) \equiv g_{\alpha\beta} \quad (1-105)$$

and

$$\sum_{i=1}^N \sum_{j=1}^N v_{i\alpha} v_{j\beta} (\partial \ln \gamma_i / \partial C_j) \equiv g'_{\alpha\beta} \quad (1-106)$$

eqn. (1-104) becomes:

$$G_{\alpha\beta} = (RT/V) (g_{\alpha\beta} + g'_{\alpha\beta}) \quad (1-107)$$

and consequently,

$$G_\alpha = \sum_{\beta=1}^R G_{\alpha\beta} \cdot \Delta \xi_\beta = (RT/V) \sum_{\beta=1}^R (g_{\alpha\beta} + g'_{\alpha\beta}) \cdot \Delta \xi_\beta \quad (1-108)$$

Substituting eqn. (1-108) into (1-97), we have: ^{47, 48}

$$(\partial \xi_\alpha / \partial t)_{T,P} = -r_\alpha \sum_{\beta=1}^R (g_{\alpha\beta} + g'_{\alpha\beta}) \cdot \Delta \xi_\beta \quad (1-109)$$

If matters are arranged so that the γ_i are independent of the concentrations of the reacting species, then $g'_{\alpha\beta} = 0$, and eqn. (1-109) becomes:

$$(\partial \xi_\alpha / \partial t)_{T,P} = -r_\alpha \sum_{\beta=1}^R g_{\alpha\beta} \cdot \Delta \xi_\beta \quad (1-110)$$

It is this form which is very convenient for the computation of the relaxation times.

Assume that the solution to the eqn.(1-110) has the form:

$$\Delta \xi_{\alpha} = \sum_{\epsilon=1}^R m_{\alpha\epsilon} e^{-\lambda_{\epsilon} t} \quad (1-111)$$

Differentiation and insertion of this result into eqn.(1-110), gives:

$$\sum_{\epsilon=1}^R m_{\alpha\epsilon} \lambda_{\epsilon} e^{-\lambda_{\epsilon} t} = r_{\alpha} \sum_{\beta=1}^R \sum_{\epsilon=1}^R g_{\alpha\beta} m_{\beta\epsilon} e^{-\lambda_{\epsilon} t} \quad (1-112)$$

which upon elimination of certain terms on both sides, reduces to:

$$\lambda_{\epsilon} m_{\alpha\epsilon} = r_{\alpha} \sum_{\beta=1}^R g_{\alpha\beta} m_{\beta\epsilon} \quad (1-113)$$

Rearrangement using the Kronecker delta brings this equation to the following form:

$$\sum_{\beta=1}^R (r_{\alpha} g_{\alpha\beta} - \lambda_{\epsilon} \delta_{\alpha\beta}) m_{\beta\epsilon} = 0 \quad (1-114)$$

Non-trivial solutions exist only if the λ_{ϵ} are the roots of the determinantal equation:

$$|r_{\alpha} g_{\alpha\beta} - \lambda \delta_{\alpha\beta}| = 0 \quad (1-115)$$

Now, suppose we have an R-step mechanism in which all the steps are thermodynamically independent, and the relaxation times are well separated. Then: $\tau_1 \ll \tau_2 \ll \tau_3 \dots \dots \dots$ etc.

$$\text{i.e.: } r_1 g_{11} \gg r_2 g_{22} \gg r_3 g_{33} \dots \dots \dots \text{ etc.}$$

For the first approximation, let us set all the $r_{\alpha} = 0$, except r_1 ; this reduces the determinantal eqn.(1-115) to:

$$(r_1 g_{11} - \lambda_1)(-\lambda)^{R-1} = 0 \quad (1-116)$$

which yields the first approximation for the λ_{α} :

$$\text{i.e. } \lambda_1 = r_1 g_{11} ; \lambda_{\alpha} = 0 \ (\alpha \neq 1) \quad (1-117)$$

To obtain λ_2 , divide the first row of the determinant (1-115) by r_1 , and let $r_1 \rightarrow \infty$. All the other r_α are set equal to zero except r_2 . This brings eqn.(1-115) to the form:

$$(-\lambda)^{R-2} \begin{vmatrix} g_{11} & g_{12} \\ r_2 g_{21} & r_2 g_{22} - \lambda_2 \end{vmatrix} = 0 \quad (1-118)$$

which gives:

$$\lambda_2 = (r_2 D_2 / g_{11}) \quad (1-119)$$

where D_2 is the sub-determinant. That is,

$$D_2 \equiv \begin{vmatrix} g_{11} & g_{12} \\ g_{21} & g_{22} \end{vmatrix} \quad (1-120)$$

Repetition of the procedure shows that in general we can write:

$$\lambda_i = (r_i D_i / D_{i-1}) \quad (1-121)$$

where D_i is the i -th principal sub-determinant of the g determinant.

$$D_i = \begin{vmatrix} g_{11} & g_{12} & g_{13} & \cdots & g_{1i} \\ g_{21} & g_{22} & g_{23} & \cdots & g_{2i} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ g_{i1} & g_{i2} & g_{i3} & \cdots & g_{ii} \end{vmatrix} \quad (1-122)$$

For consistency, define:

$$D_0 \equiv 1$$

Then the relaxation time, τ_ϵ , is related to the λ_ϵ by:

$$\tau_\epsilon = (1/\lambda_\epsilon) \quad (1-123)$$

In the case of multi-step reactions with step number exceeding 4 or 5, the calculation of the relaxation times becomes extremely tedious. Therefore, in practice, the actual calculation was completed using computer techniques.

After the τ_j values have been obtained, the relaxation spectra

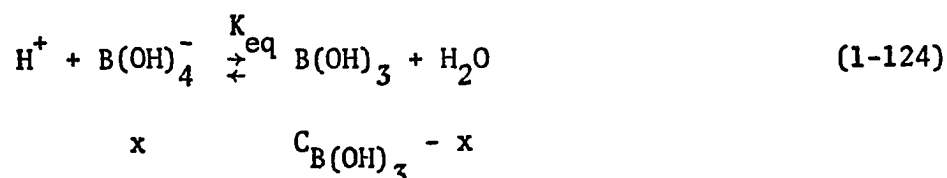
can be calculated using eqns.(1-14), (1-70), and (1-71).

IV. CALCULATIONS:

A. The Boric Acid System:

1. Relation Between the Equilibrium Constant and the Equilibrium Concentrations:

The boric acid system can be written as:



where $C_{\text{B(OH)}_3}$ is the total analytical concentration of boric acid, x is the number of moles of boric acid converted into the hydroxyborate ion, and K_{eq} is the equilibrium constant of the reaction, which can be expressed by:

$$\frac{[\text{B(OH)}_3]}{[\text{H}^+][\text{B(OH)}_4^-]} = K_{\text{eq}} \quad (1-125)$$

or:

$$\frac{C_{\text{B(OH)}_3} - x}{[\text{H}^+] \cdot x} = K_{\text{eq}} \quad (1-126)$$

Rearranging this equation, gives:

$$x = \frac{C_{\text{B(OH)}_3}}{[\text{H}^+]K_{\text{eq}} + 1} \quad (1-127)$$

Since $x = [\text{B(OH)}_4^-]$, eqn. (1-127) becomes:

$$[\text{B(OH)}_4^-] = \frac{C_{\text{B(OH)}_3}}{[\text{H}^+]K_{\text{eq}} + 1} \quad (1-128)$$

Combining equation (1-128) with (1-125), we get:

$$[\text{B(OH)}_3] = \frac{[\text{H}^+] K_{\text{eq}} C_{\text{B(OH)}_3}}{[\text{H}^+] K_{\text{eq}} + 1} \quad (1-129)$$

Therefore, by knowing the values of the total analytical boric acid concentration, pH of the solution, and the equilibrium constant, the related species concentrations of $[\text{B(OH)}_3]$ and $[\text{B(OH)}_4^-]$ can be determined using eqns. (1-128) and (1-129).

2. Constants Used in the Calculation:

The following constants were obtained from the literature:⁴⁹⁻⁵¹
the equilibrium constant, $K_{\text{eq}} = 1.722 \times 10^9 \text{ l} \cdot \text{mole}^{-1}$; the forward rate constant, $k_f = 1.35 \times 10^{10} \text{ M}^{-1} \cdot \text{sec}^{-1}$; the backward rate constant, $k_b = 7.8397 \text{ sec}^{-1}$ (which was calculated using k_f/K_{eq}); and the reaction enthalpy change, $\Delta H^\circ = -3.36 \text{ Kcal/mole}$.

The temperature and the pressure of the system were assumed at $t = 25^\circ\text{C}$ and $p = 1 \text{ atm}$.

3. Variables Used in the Calculation:

The total analytical concentrations of boric acid have been assigned the following values: $C_{\text{B(OH)}_3} = 4.4 \times 10^{-4} \text{ M}$; $4.4 \times 10^{-3} \text{ M}$; 0.01 M ; and 0.025 M .

The acidities of the solution were adjusted at pH = 3.0; 3.5; 4.0; 4.5; 5.0; 5.5; 6.0; 6.5; 7.0; 7.5; 8.0; 8.5; 9.0; 9.5; 10.0; 10.5; 11.0; 11.5; and 12.0.

The volume change of the reaction was found in the literature

to be: $\Delta V^\circ = 35.45$ ml/mole. However, for comparison, the values of $\Delta V^\circ = 20$; 30; and 40 ml/mole were also used.

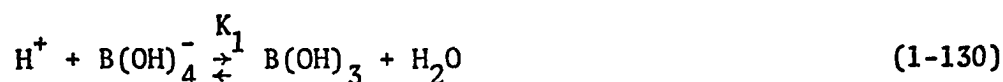
4. Various Terms Calculated:

By use of equations(1-128), (1-129), (1-13), (1-14), (1-43), and (1-44), the following terms have been calculated: the concentrations of the species $[B(OH)_3]$, $[B(OH)_4^-]$, and the corresponding values of percentage of boric acid converted into those species; the relaxation time, τ ; the relaxation frequencies, f_r ; the maximum sound absorption values $\mu_{\max}$ and the corresponding $\log \mu_{\max}$ values; the amplitude of relaxation, $Ampl.$; and the absorption due to chemical relaxation μ_{chem} and the corresponding $\log \mu_{\text{chem}}$ values.

B. The Boric Acid and Sodium Borate System:

1. Relation Between the Equilibrium Constants and the Equilibrium Concentrations:

The system can be represented by:



and the equilibrium constants are:

$$\frac{[B(OH)_3]}{[H^+][B(OH)_4^-]} = K_1 \quad (1-132)$$

$$\frac{[NaB(OH)_4]}{[Na^+][B(OH)_4^-]} = K_2 \quad (1-133)$$

The total analytical concentration of boric acid is the sum of the concentration of each component species, that is,

$$C_{B(OH)_3} = [B(OH)_3] + [B(OH)_4^-] + [NaB(OH)_4] \quad (1-134)$$

and also:

$$C_{Na} = [Na^+] + [NaB(OH)_4] \quad (1-135)$$

where C_{Na} is the total analytical concentration of sodium in solution.

Rearranging eqn. (1-132), we have:

$$[B(OH)_4^-] = \frac{[B(OH)_3]}{K_1 [H^+]} \quad (1-136)$$

From eqns. (1-133), (1-135), and (1-136), one obtains:

$$[NaB(OH)_4] = \frac{K_2 C_{Na} [B(OH)_3]}{K_1 [H^+] + K_2 [B(OH)_3]} \quad (1-137)$$

Substituting eqns. (1-137), and (1-136) into (1-134), and rearranging the order, we get:

$$\{K_1 K_2 [H^+] + K_2\} [B(OH)_3]^2 + \{K_1^2 [H^+]^2 + K_1 [H^+] + K_1 K_2 C_{Na} [H^+] - K_1 K_2 C_{B(OH)_3} [H^+]\} \cdot [B(OH)_3] - C_{B(OH)_3} K_1^2 [H^+]^2 = 0 \quad (1-138)$$

which can be simplified by writing:

$$A[B(OH)_3]^2 + B[B(OH)_3] + C = 0 \quad (1-139)$$

$$\text{with: } A = K_2 \{K_1 [H^+] + 1\}$$

$$B = K_1 [H^+] \{K_1 [H^+] + 1 + K_2 C_{Na} - K_2 C_{B(OH)_3}\}$$

$$C = -K_1^2 [H^+]^2 C_{B(OH)_3}$$

The solution of eqn. (1-139) is:

$$[B(OH)_3] = (1/2A) \left[-B \pm \sqrt{B^2 - 4AC} \right] \quad (1-140)$$

where only the "positive" value can be accepted since the species concentration has no "negative" value. Once the $[B(OH)_3]$ concentration is obtained, the other species concentrations can be evaluated using

eqns. (1-136), (1-137), and (1-135).

2. Constants Used in the Calculation:

The following constants were obtained from the literature:⁴⁹⁻⁵²
the equilibrium constant of reaction (1-130), $K_1 = 1.722 \times 10^9 \text{ M}^{-1}$; the equilibrium constant of reaction (1-131), $K_2 = 0.57 \text{ M}^{-1}$; the forward rate constants for both reactions are $k_{f1} = 1.35 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ and $k_{f2} = 1.215 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ (assumed value in case I) or $k_{f2} = 2.7 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ (assumed value in case II); the reaction enthalpy change $\Delta H_1^\circ = -3.36 \text{ Kcal/mole}$ and $\Delta H_2^\circ = -0.09 \text{ Kcal/mole}$; the volume change of reaction (1-130) $\Delta V_1^\circ = 35.45 \text{ ml/mole}$.

In addition to the constants shown above, the temperature and pressure of the system were also specified at $t = 25^\circ\text{C}$ and $p = 1 \text{ atm}$.

3. Variables Used in the Calculation:

The volume change of the association reaction of sodium borate, ΔV_2° , has been set at $\Delta V_2^\circ = 0.04; 1.0; 5.0 \text{ ml/mole}$. The total analytical concentration of boric acid, $C_{\text{B(OH)}_3}$, is set at the following values: $C_{\text{B(OH)}_3} = 4.4 \times 10^{-4} \text{ M}; 4.4 \times 10^{-3} \text{ M}; 0.01 \text{ M};$ and 0.025 M . The total analytical concentration of sodium, C_{Na} , is set at $C_{\text{Na}} = 0.1 \text{ M}; 0.48 \text{ M}; 0.5 \text{ M}; 0.8 \text{ M};$ and 1.0 M . The acidities of the solution are: $\text{pH} = 3.0; 4.0; 5.0; 6.0; 7.0; 8.0; 9.0; 10.0; 11.0;$ and 12.0 .

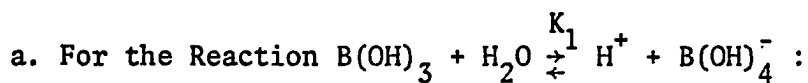
4. Various Terms Calculated:

The values of the equilibrium species concentrations, $[\bar{C}_i]$; the relaxation times, τ_1 , τ_2 ; the relaxation frequencies, $f_r^{(1)}$, $f_r^{(2)}$; the maximum sound absorption, $\mu_{\max}^{(1)}$, $\mu_{\max}^{(2)}$ and their corresponding $\log \mu_{\max}^{(1)}$, $\log \mu_{\max}^{(2)}$ terms; and the amplitude of relaxation, $\text{Ampl.}^{(1)}$, $\text{Ampl.}^{(2)}$ have been determined using the related constants and variables mentioned previously.

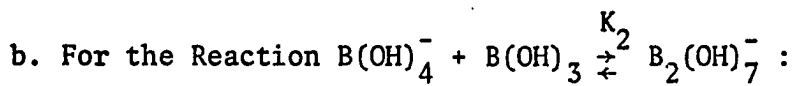
C. The Boric Acid and Polyborate System:

1. Constants Used:

The following constants were used: $t = 25^\circ\text{C}$; $p = 1 \text{ atm}$; $K_{\text{eq}}^{(i)}$; $k_f^{(i)}$; $k_b^{(i)}$; $\Delta V_{(i)}^\circ$; and $\Delta H_{(i)}^\circ$ with $i = 1, 2, 3, 4, 5, 6$.

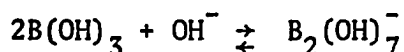


In the related literature, the following values can be found: ⁴⁹⁻⁵¹
 $K_1 = 5.808 \times 10^{-10} \text{ moles/liter}$; $k_{b1} = 1.35 \times 10^{10} \text{ M}^{-1}\text{sec}^{-1}$; $k_{f1} = K_1 \cdot k_{b1}$
 $= 7.841 \text{ sec}^{-1}$; $\Delta H_1^\circ = 3.36 \text{ Kcal/mole}$; $\Delta V_1^\circ = -35.45 \text{ ml/mole}$.



(1) Calculation of K_2 :

For the following reaction: ⁵³



we have:

$$\Delta H^\circ = -9.2 \text{ Kcal/mole}$$

$$\Delta S^\circ = -9.1 \text{ cal/deg.mole}$$

$$\begin{aligned}\text{So: } \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = (-9.2 \times 10^3) - (298.15)(-9.1) \\ &= -6486.835 \text{ cal/mole}\end{aligned}$$

$$\text{and } \ln K = (\Delta G^\circ / -RT) = (-6486.835 / -1.987 \times 298.15) = 10.950$$

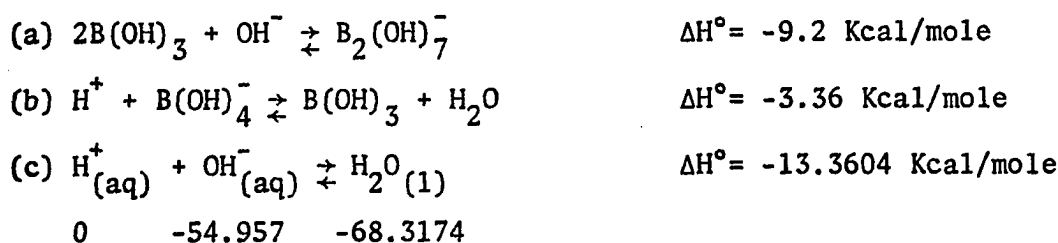
$$\text{or } K = 5.693 \times 10^4 \text{ M}^{-2}$$

Therefore:

$$\begin{aligned}K_2 &= \frac{[B_2(OH)_7^-]}{[B(OH)_3][B(OH)_4^-]} \\ &= \frac{[B_2(OH)_7^-]}{[B(OH)_3]^2 [OH^-]} \cdot \frac{[B(OH)_3]}{[H^+][B(OH)_4^-]} \cdot K_w \\ &= (5.693 \times 10^4)(5.808 \times 10^{-10})^{-1} \cdot 10^{-14} = 0.980 \text{ liter/mole}\end{aligned}$$

(2) Calculation of ΔH_2° :

Consider the following reactions: ^{49, 53, 54}



(a)+(b)-(c) gives:

$$\Delta H_2^\circ = (-9.2) + (-3.36) - (-13.3604) = 0.8004 \text{ Kcal/mole}$$

(3) Calculation of ΔV_2° :

From the literature, we have the following partial molal volumes: ^{51, 55}

$$\bar{V}^\circ_{B(OH)_3} = 39.22 \text{ ml/mole}$$

$$\bar{V}^\circ_{H^+} = -5.4 \text{ ml/mole}$$

$$\text{and since: } \Delta V_1^\circ = [\bar{V}^\circ_{H^+} + \bar{V}^\circ_{B(OH)_4^-}] - [\bar{V}^\circ_{B(OH)_3} + \bar{V}^\circ_{H_2O}]$$

$$-35.45 = [(-5.4) + \bar{V}_{B(OH)_4}^\circ] - [(39.22) + (18.02)]$$

or: $\bar{V}_{B(OH)_4}^\circ = 27.19 \text{ ml/mole}$.

Also from the literature we know that cubic metaboric acid, $B_3O_3(OH)_3$, which contains three purely tetrahedral borate groups, has a M.W. of 131.433 and a density of $\rho = 2.487 \text{ gm/cm}^3$.⁵⁶

So, we can calculate the crystal volume of each tetrahedral group occupied as:

$$\left(\frac{1}{2.487}\right)(131.433)\left(\frac{1}{3}\right) = 17.616 \text{ cm}^3/\text{tetrahedral group} .$$

Since $B_2(OH)_7^-$ contains two tetrahedral groups, its crystal volume

is: $V_{B_2(OH)_7}^{\text{crystal}} = 17.616 \times 2 = 35.232 \text{ cm}^3/\text{mole}$.

In general, $\bar{V}_{\text{ion}}^\circ$ is about 77% larger in water than in the crystal,⁵⁵

that is, $\bar{V}_{\text{ion}}^\circ \approx 1.77 \bar{V}_{\text{crystal}}^\circ$.

Therefore: $\bar{V}_{B_2(OH)_7}^\circ \approx (1.77) \times (35.232) = 62.361 \text{ cm}^3/\text{mole}$,

and $\Delta V_2^\circ = \bar{V}_{B_2(OH)_7}^\circ - \bar{V}_{B(OH)_3}^\circ - \bar{V}_{B(OH)_4}^\circ$
 $= (62.361) - (39.22) - (27.19) = -4.049 \text{ ml/mole}$.

(4) Calculation of k_{f2} and k_{b2} :

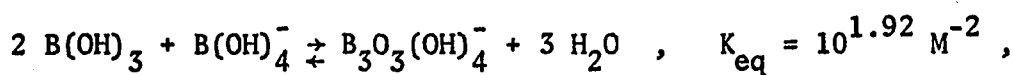
The k_{f2} can be estimated as $6 \times 10^2 \text{ M}^{-1}\text{sec}^{-1}$, so that:

$$k_{b2} = (k_{f2}/K_2) = (6 \times 10^2 / 0.980) = 6.122 \times 10^2 \text{ sec}^{-1} .$$

c. For the Reaction $B_2(OH)_7^- + B(OH)_3 \xrightleftharpoons{K_3} B_3O_3(OH)_4^- + 3 H_2O$:

(1) Calculation of K_3 :

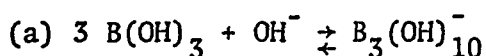
Since for the reaction:⁵⁷



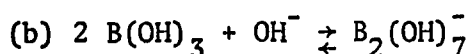
$$\begin{aligned} K_3 &= \frac{[\text{B}_3\text{O}_3(\text{OH})_4^-]}{[\text{B(OH)}_3][\text{B}_2(\text{OH})_7^-]} \\ &= \frac{[\text{B}_3\text{O}_3(\text{OH})_4^-]}{[\text{B(OH)}_3]^2[\text{B(OH)}_4^-]} \times \frac{[\text{B(OH)}_4^-][\text{B(OH)}_3]}{[\text{B}_2(\text{OH})_7^-]} \\ &= (10^{1.92}) \times (1/0.980) = 84.874 \text{ liter/mole} . \end{aligned}$$

(2) Calculation of ΔH_3° :

For the reactions: ⁵³



$$\Delta H^\circ = -14.4 \text{ Kcal/mole}$$



$$\Delta H^\circ = -9.2 \text{ Kcal/mole} .$$

So (a)-(b) gives:

$$\Delta H_3^\circ = (-14.4) - (-9.2) = -5.2 \text{ Kcal/mole} .$$

(3) Calculation of ΔV_3° :

From literature, we also have the following information. ⁵⁶

Monoclinic metaboric acid which contains 1 tetrahedral boron and 2 trigonal borons, has a density of $\rho = 2.044 \text{ gm/cm}^3$.

From which, we have:

$$(1/2.044) \times (131.433) = 64.302 \text{ cm}^3 / 1 \text{ tetrahedral and 2 trigonal groups} .$$

And for orthorhombic metaboric acid (containing tricoordinate boron), with $\rho = 1.784 \text{ gm/cm}^3$ gives:

$$(1/1.784) \times (131.433) \times (1/3) = 24.558 \text{ cm}^3 / \text{triangular group}$$

Since $B_3O_3(OH)_4^-$ contains 1 tetrahedral group and 2 trigonal groups,

$$\bar{V}_{B_3O_3(OH)_4^-}^\circ = 1.77 \times 64.302 = 113.815 \text{ cm}^3/\text{mole}$$

$$\begin{aligned} \text{and } \Delta V_3^\circ &= \bar{V}_{B_3O_3(OH)_4^-}^\circ + 3\bar{V}_{H_2O}^\circ - \bar{V}_{B_2(OH)_7^-}^\circ - \bar{V}_{B(OH)_3}^\circ \\ &= (113.815) + 3(18) - (62.361) - (39.22) = 66.234 \text{ cm}^3/\text{mole} \end{aligned}$$

(4) Calculation of k_{f3} and k_{b3} :

The k_{f3} can be estimated at $3 \times 10^3 \text{ M}^{-1}\text{sec}^{-1}$.

$$\text{Thus: } k_{b3} = (k_{f3}/K_3) = (3 \times 10^3 / 84.874) = 35.347 \text{ sec}^{-1}.$$

d. For the Reaction $B_3O_3(OH)_4^- + OH^- \xrightleftharpoons{K_4} B_3O_3(OH)_5^{-2}$:

(1) Calculation of K_4 :

From the literature, we have:

$$\frac{[B_3O_3(OH)_5^{-2}]}{[B(OH)_3]^3 [OH^-]^2} = 10^{11.7} \text{ M}^{-4}$$

$$\text{and } \frac{[B(OH)_4^-]}{[B(OH)_3] [OH^-]} = 10^{5.18} \text{ M}^{-1}.$$

Therefore:

$$\begin{aligned} K_4 &= \frac{[B_3O_3(OH)_5^{-2}]}{[OH^-] [B_3O_3(OH)_4^-]} \\ &= \frac{[B_3O_3(OH)_5^{-2}]}{[B(OH)_3]^3 [OH^-]^2} \times \frac{[B_2(OH)_7^-] [B(OH)_3]}{[B_3O_3(OH)_4^-]} \\ &\quad \times \frac{[B(OH)_4^-] [B(OH)_3]}{[B_2(OH)_7^-]} \times \frac{[B(OH)_3] [OH^-]}{[B(OH)_4^-]} \end{aligned}$$

$$= (10^{11.7}) \times (1/84.874) \times (1/0.980) \times (1/10^{5.18}) = 3.981 \times 10^4 \text{ liter/mole} .$$

(2) Calculation of ΔV_4° :

$B_3O_3(OH)_5^{-2}$ contains 2 tetrahedral groups and 1 triangular group,⁵⁶ so its crystal volume can be estimated as:

$$V_{B_3O_3(OH)_5^{-2}}^{\text{crystal}} = 2(17.616) + 1(24.558) = 59.79 \text{ cm}^3/\text{mole} ,$$

and the ionic volume in solution is:

$$\bar{V}_{B_3O_3(OH)_5^{-2}}^\circ \approx 1.77 \times 59.79 = 105.828 \text{ cm}^3/\text{mole} .$$

Since⁵⁵ $\bar{V}_{OH^-}^\circ = 1.4 \text{ cm}^3/\text{mole} ,$

$$\begin{aligned} \Delta V_4^\circ &= \bar{V}_{B_3O_3(OH)_5^{-2}}^\circ - \bar{V}_{B_3O_3(OH)_4^-}^\circ - \bar{V}_{OH^-}^\circ \\ &= (105.828) - (113.815) - (1.4) = -9.387 \text{ cm}^3/\text{mole} . \end{aligned}$$

(3) Calculation of ΔH_4° , k_{f4} , and k_{b4} :

ΔH_4° can be assumed to have the value of -10.12 Kcal/mole, and k_{f4} estimated to be $3.5 \times 10^7 \text{ M}^{-1}\text{sec}^{-1}$, so that k_{b4} can be calculated as:

$$k_{b4} = (k_{f4}/K_4) = (3.5 \times 10^7 / 3.981 \times 10^4) = 8.792 \times 10^2 \text{ sec}^{-1} .$$

e. For the Reaction $B_3O_3(OH)_5^{-2} + B(OH)_3 \xrightleftharpoons{K_5} B_4O_5(OH)_4^{-2} + 2 H_2O$:

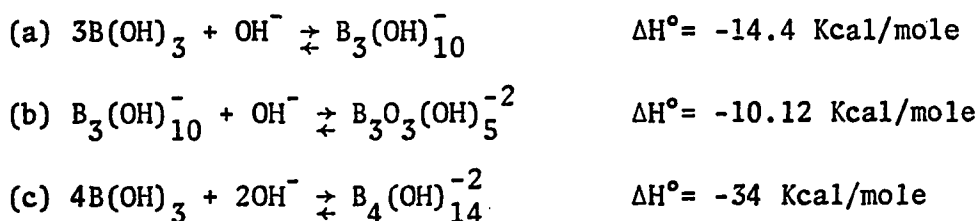
(1) Calculation of K_5 :

$$\text{Since }^{58} \frac{[B_4O_5(OH)_4^{-2}]}{[B(OH)_3]^4 [OH^-]^2} = 10^{13.5} \text{ M}^{-5}$$

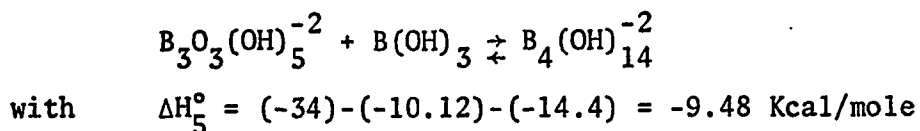
$$\begin{aligned}
K_5 &= \frac{[B_4O_5(OH)_4]^{-2}}{[B(OH)_3][B_3O_3(OH)_5]^{-2}} \\
&= \frac{[B_4O_5(OH)_4]^{-2}}{[B(OH)_3]^4[OH^-]^2} \times \frac{[B(OH)_3]^3[OH^-]^2}{[B_3O_3(OH)_5]^{-2}} \\
&= (10^{13.5}) \times (1/10^{11.7}) = 63.096 \text{ liter/mole}
\end{aligned}$$

(2) Calculation of ΔH_5° :

For the following reactions, we have the ΔH° 's listed: ⁵³



Then (c)-(b)-(a) gives:



(3) Calculation of ΔV_5° :

Since $B_4O_5(OH)_4^{-2}$ contains 2 tetrahedral groups and 2 triangular groups, we have:

$$V_{B_4O_5(OH)_4^{-2}}^{\text{crystal}} = 2(17.616) + 2(24.558) = 84.348 \text{ cm}^3/\text{mole}$$

and $\bar{V}_{B_4O_5(OH)_4^{-2}}^\circ = 1.77 \times 84.348 = 149.296 \text{ cm}^3/\text{mole}$

Consequently: $\Delta V_5^\circ = \bar{V}_{B_4O_5(OH)_4^{-2}}^\circ + 2\bar{V}_{H_2O}^\circ - \bar{V}_{B_3O_3(OH)_5^{-2}}^\circ - \bar{V}_{B(OH)_3}^\circ$

$$= (149.296) + 2(18) - (105.828) - (39.22) = 40.248 \text{ ml/mole}$$

(4) Calculation of k_{f5} and k_{b5} :

Using the estimated value of $k_{f5} = 2 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$, we obtain:

$$k_{b5} = (k_{f5}/K_5) = (2 \times 10^3 / 63.096) = 31.698 \text{ sec}^{-1}$$

f. For the Reaction $\text{B}_4\text{O}_5(\text{OH})_4^{-2} + \text{B}(\text{OH})_3 \xrightleftharpoons{K_6} \text{B}_5\text{O}_6(\text{OH})_4^{-} + \text{OH}^{-} + \text{H}_2\text{O}$:

(1) Calculation of K_6 :

Since ⁵⁸

$$\frac{[\text{B}_5\text{O}_6(\text{OH})_4^{-}]}{[\text{B}(\text{OH})_3]^5 [\text{OH}^{-}]} = 10^{7.39} \text{ M}^{-5},$$

$$\begin{aligned} K_6 &= \frac{[\text{B}_5\text{O}_6(\text{OH})_4^{-}] [\text{OH}^{-}]}{[\text{B}(\text{OH})_3] [\text{B}_4\text{O}_5(\text{OH})_4^{-2}]} \\ &= \frac{[\text{B}_5\text{O}_6(\text{OH})_4^{-}]}{[\text{B}(\text{OH})_3]^5 [\text{OH}^{-}]} \times \frac{[\text{B}(\text{OH})_3]^4 [\text{OH}^{-}]^2}{[\text{B}_4\text{O}_5(\text{OH})_4^{-2}]} \\ &= (10^{7.39}) \times (1/10^{13.5}) = 7.762 \times 10^{-7}. \end{aligned}$$

(2) Calculation of ΔV_6° :

Since $\text{B}_5\text{O}_6(\text{OH})_4^{-}$ contains 1 tetrahedral group and 4 triangular groups, its crystal volume is:

$$V_{\text{B}_5\text{O}_6(\text{OH})_4^{-}}^{\text{crystal}} = 1 \times (17.616) + 4 \times (24.558) = 115.848 \text{ cm}^3/\text{mole}$$

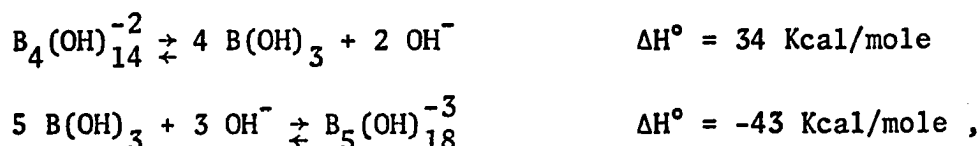
and $\bar{V}_{\text{B}_5\text{O}_6(\text{OH})_4^{-}}^\circ \approx 1.77 \times 115.848 = 205.051 \text{ cm}^3/\text{mole}$

Therefore, we have:

$$\begin{aligned}
\Delta V_6^\circ &= \bar{V}_{B_5O_6(OH)_4}^\circ + \bar{V}_{OH^-}^\circ + \bar{V}_{H_2O}^\circ - \bar{V}_{B_4O_5(OH)_4}^\circ - \bar{V}_{B(OH)_3}^\circ \\
&= (205.051) + (1.4) + (18) - (149.296) - (39.22) \\
&= 35.935 \text{ ml/mole} .
\end{aligned}$$

(3) Estimation of ΔH_6° , k_{f6} , and k_{b6} :

From the following equations and their corresponding ΔH° values: 53



we obtain:

$$\Delta H_6^\circ = (34) + (-43) = -9 \text{ Kcal/mole} .$$

Using the estimated value of $k_{f6} = 1 \times 10^2 \text{ M}^{-1}\text{sec}^{-1}$, the k_{b6} can be calculated as:

$$k_{b6} = (k_{f6}/K_6) = (1 \times 10^2 / 7.762 \times 10^{-7}) = 1.288 \times 10^8 \text{ M}^{-1}\text{sec}^{-1} .$$

2. Variables Used:

The total analytical concentrations of boric acid were set as follows: $C_{B(OH)_3} = 0.025 \text{ M}; 0.05 \text{ M}; 0.1 \text{ M}; 0.112 \text{ M}; 0.2 \text{ M}; 0.3 \text{ M}; 0.4 \text{ M}; 0.5 \text{ M}; 0.6 \text{ M};$ and 1.0 M . The acidities of the solution were $\text{pH} = 3.0; 4.0; 5.0; 6.0; 7.0; 8.0; 9.0; 10.0; 11.0;$ and 12.0 . The frequencies used were $f = 1 \text{ to } 10^{13} \text{ Hz}$.

3. Terms Calculated:

The following terms have been calculated:

τ_i , $f_r^{(i)}$, $\mu_{\max}^{(i)}$, $\log \mu_{\max}^{(i)}$, $\text{Ampl.}^{(i)}$, $\log f$, μ_{chem} , and $\log \mu_{\text{chem}}$.

Where i indicates the reaction number ranging from 1 to 6 .

V. RESULTS AND DISCUSSIONS:

A. The Boric Acid System:

The results have been shown through various tables and diagrams. The percentage distribution of boric acid converted into various component species is found to be dependent on the solution pH values and independent of the total analytical boric acid concentrations. When the solution pH equals 5 or below, there is practically no hydroxyborate species, $[\text{B}(\text{OH})_4^-]$, produced by boric acid; and all boric acid appear in the molecular form of $[\text{B}(\text{OH})_3]$ in solution. When the solution acidity reaches $\text{pH} = 7.0$, the amount of the ionic component species $[\text{B}(\text{OH})_4^-]$ begins to increase and the amount of the molecular species $[\text{B}(\text{OH})_3]$ starts to decrease. At $\text{pH} \approx 9.25$, the concentrations of $[\text{B}(\text{OH})_3]$ and $[\text{B}(\text{OH})_4^-]$ are nearly the same. Above that pH value, the concentration of the species $[\text{B}(\text{OH})_4^-]$ continues to increase and that of the species $[\text{B}(\text{OH})_3]$ continues to decrease, until the former reaches 100% and the latter drops to 0% of the total boric acid concentration. This extreme case occurs at a pH near 12.0.

Increasing the total boric acid concentration will increase the sound absorption peak value. This is especially true in the pH range from 3.0 to 5.0. However, when the pH reaches 6.0 or higher values,

changing the total analytical boric acid concentration does not affect the magnitude of the sound absorption peak but does shift the position of the relaxation frequency slightly. Changing the pH will alter the sound absorption peak magnitude of the reaction system, and will sometimes affect its relaxation frequency value.

An increase in the ΔV° value will increase the sound absorption peak value since the magnitude of the $\mu_{\max}$ value is proportional to the ΔV° values.

It has been found that the relaxation frequencies for the boric acid system range from 2.4 KHz to about 53.6 MHz and that the excess sound absorption values, α' , are from 6.5×10^{-11} dB/cm to 6.5×10^{-6} dB/cm. This indicates that although some of the relaxation frequencies are experimentally available in the laboratory, the α' values are too small to be detected. Thus, it can be expected that for the boric acid system, there will be no measurable excess sound absorption.

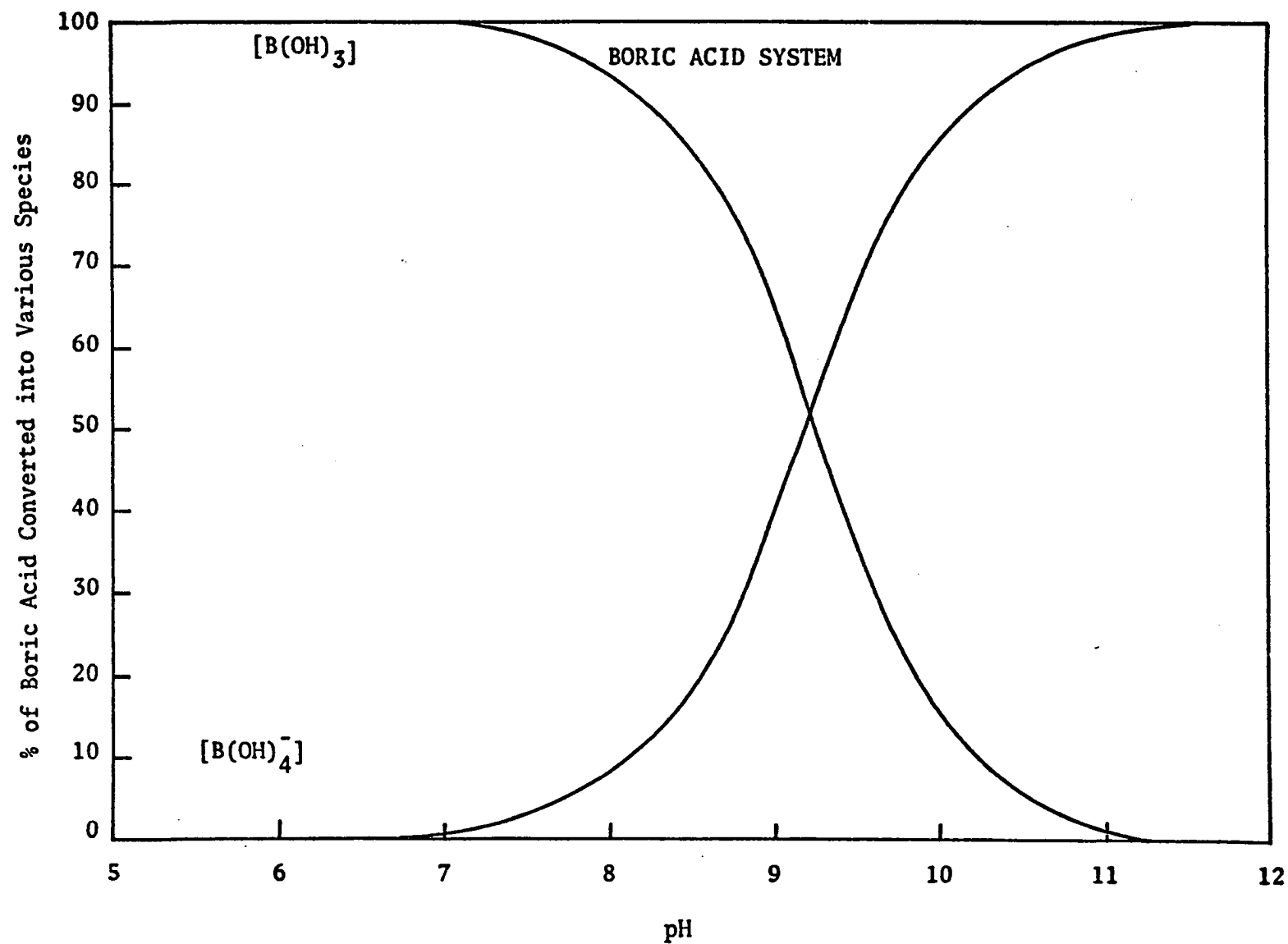


Figure 1-1: The Distribution of Species $[B(OH)_3]$ and $[B(OH)_4^-]$ of Boric Acid System at $C_{B(OH)_3} = 4.4 \times 10^{-4}$ to 0.025 M

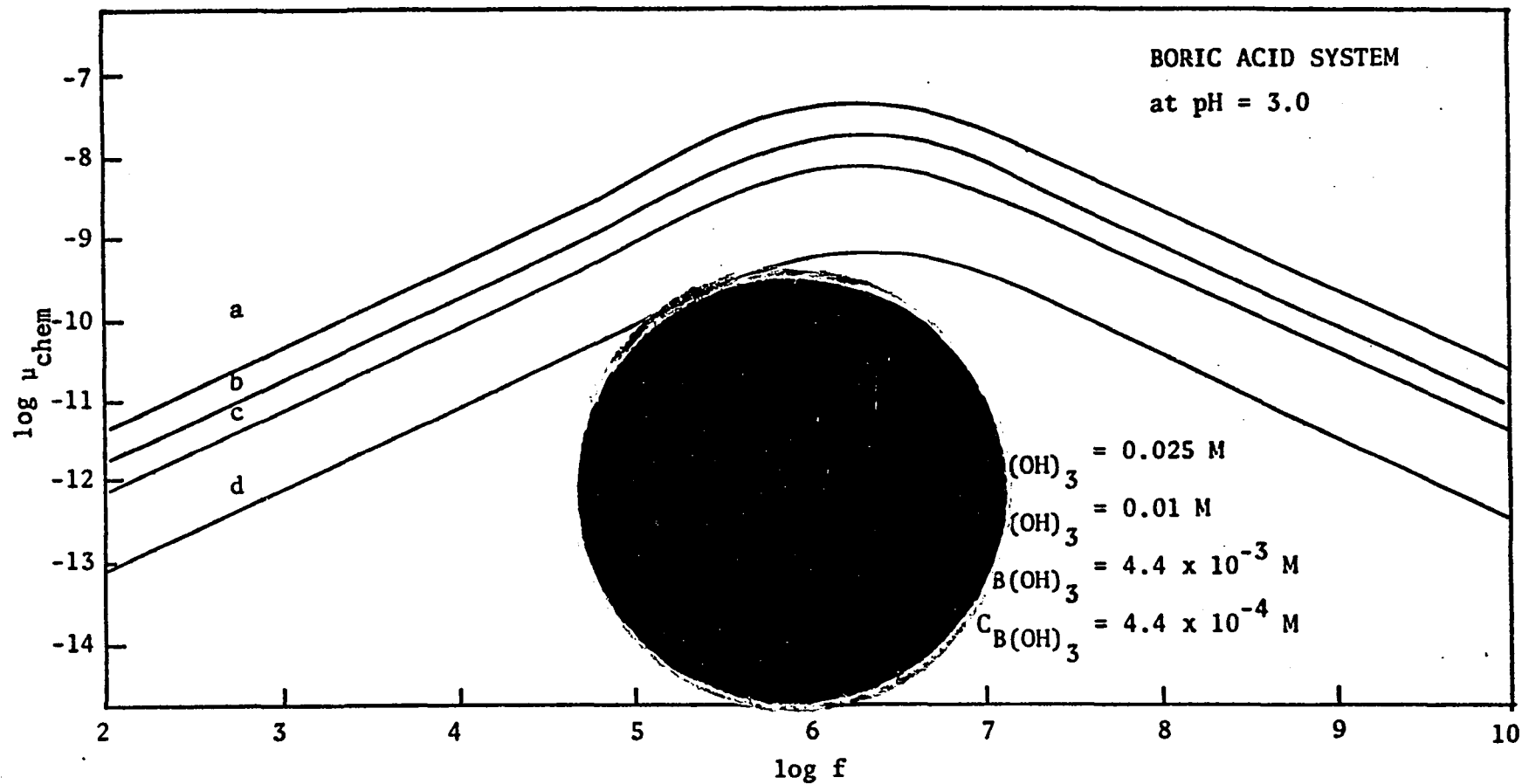


Figure 1-2: The Relaxation Spectra of Boric Acid System at Solution pH=3.0

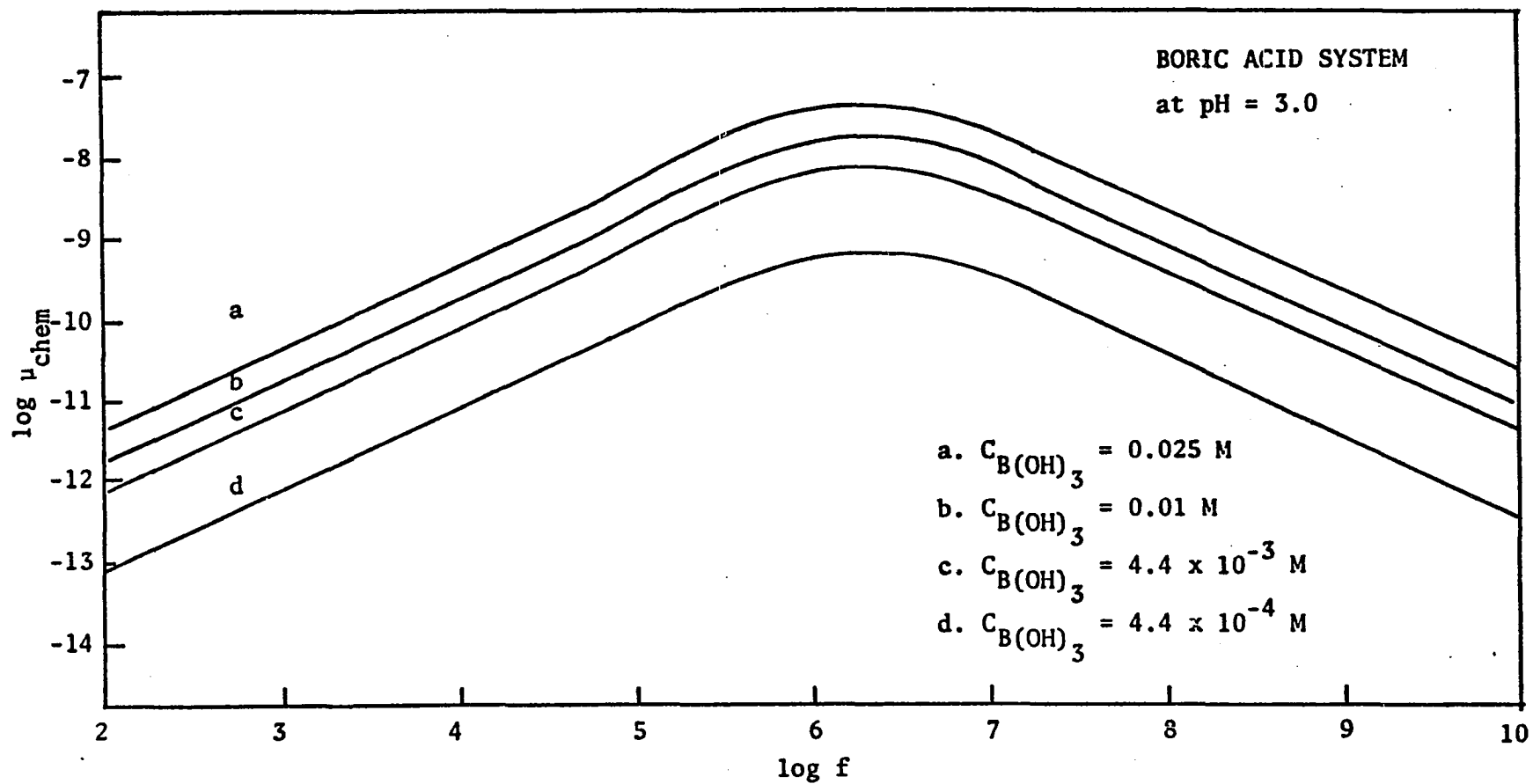


Figure 1-2: The Relaxation Spectra of Boric Acid System at Solution pH=3.0

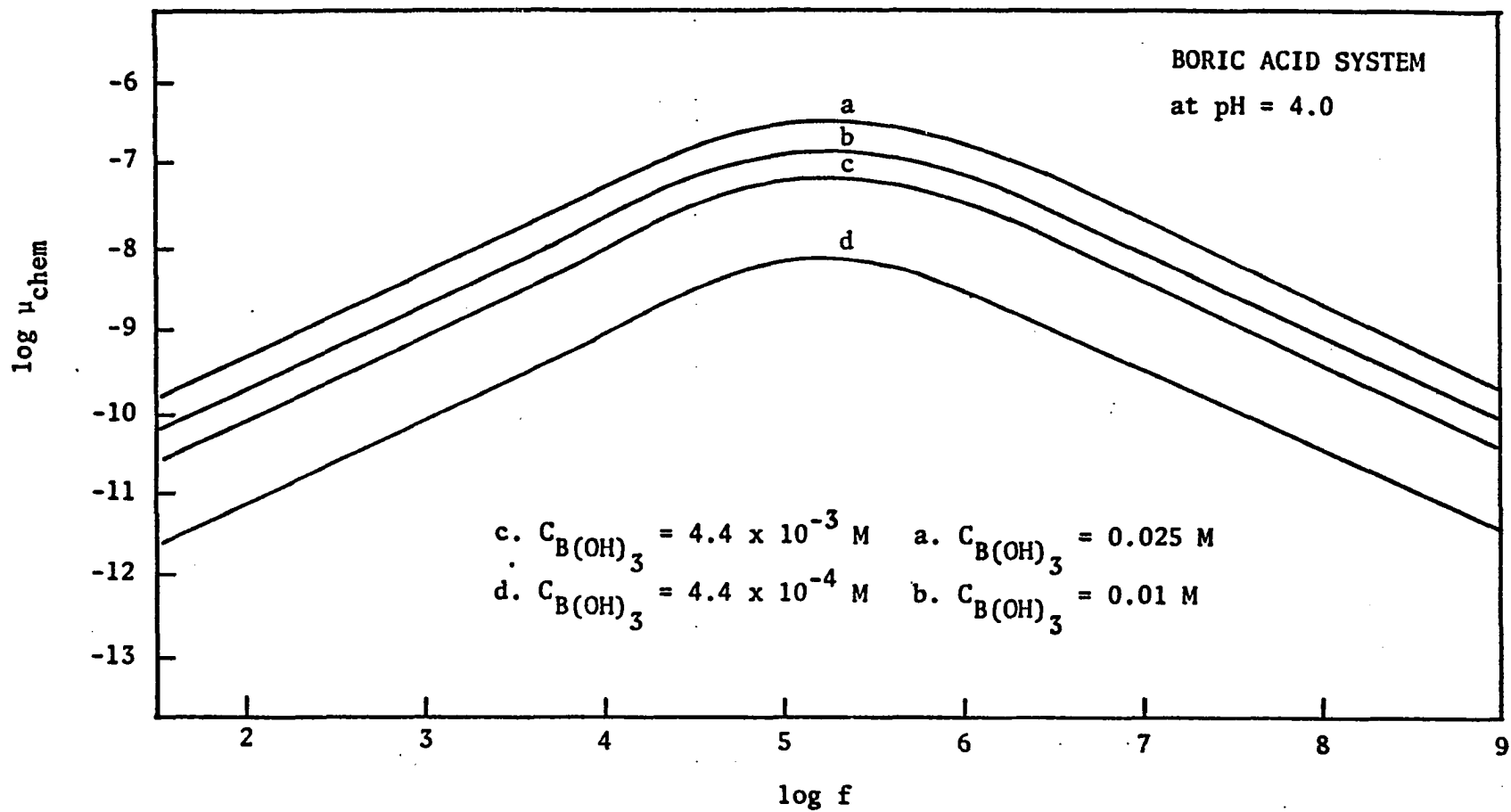


Figure 1-3: The Relaxation Spectra of Boric Acid System at Solution pH=4.0

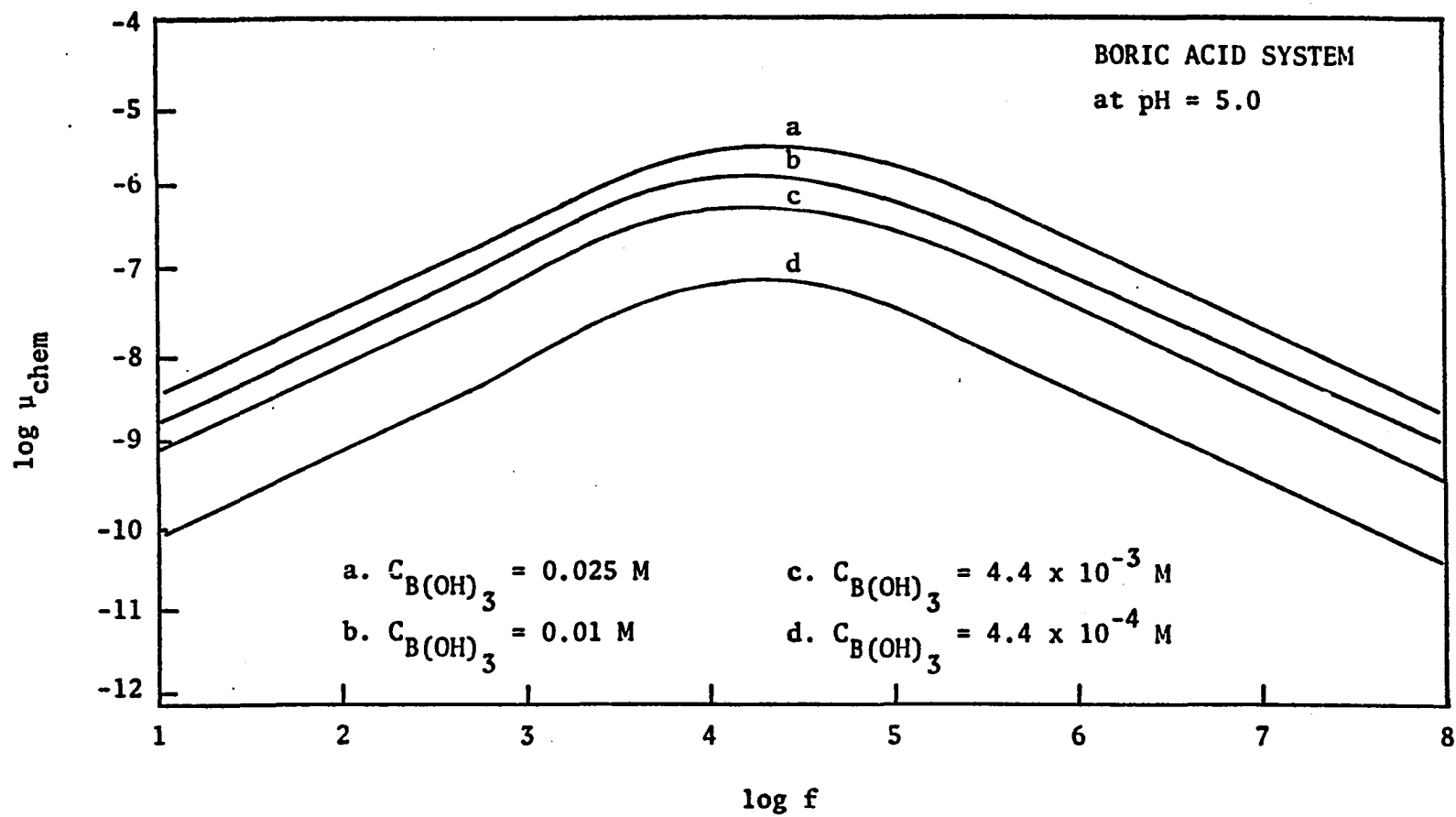


Figure 1-4: The Relaxation Spectra of Boric Acid System at Solution pH=5.0

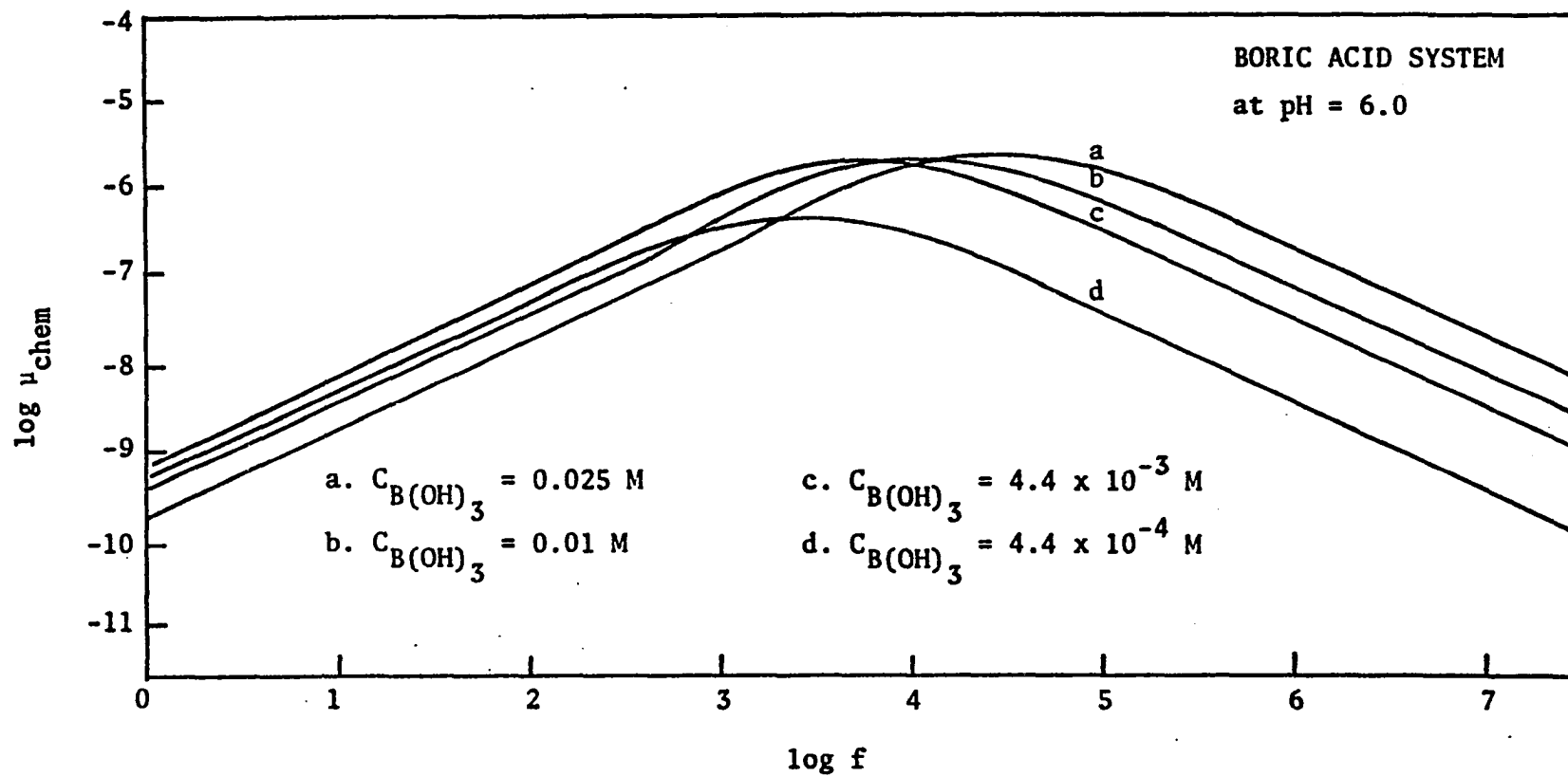


Figure 1-5: The Relaxation Spectra of Boric Acid System at Solution pH=6.0

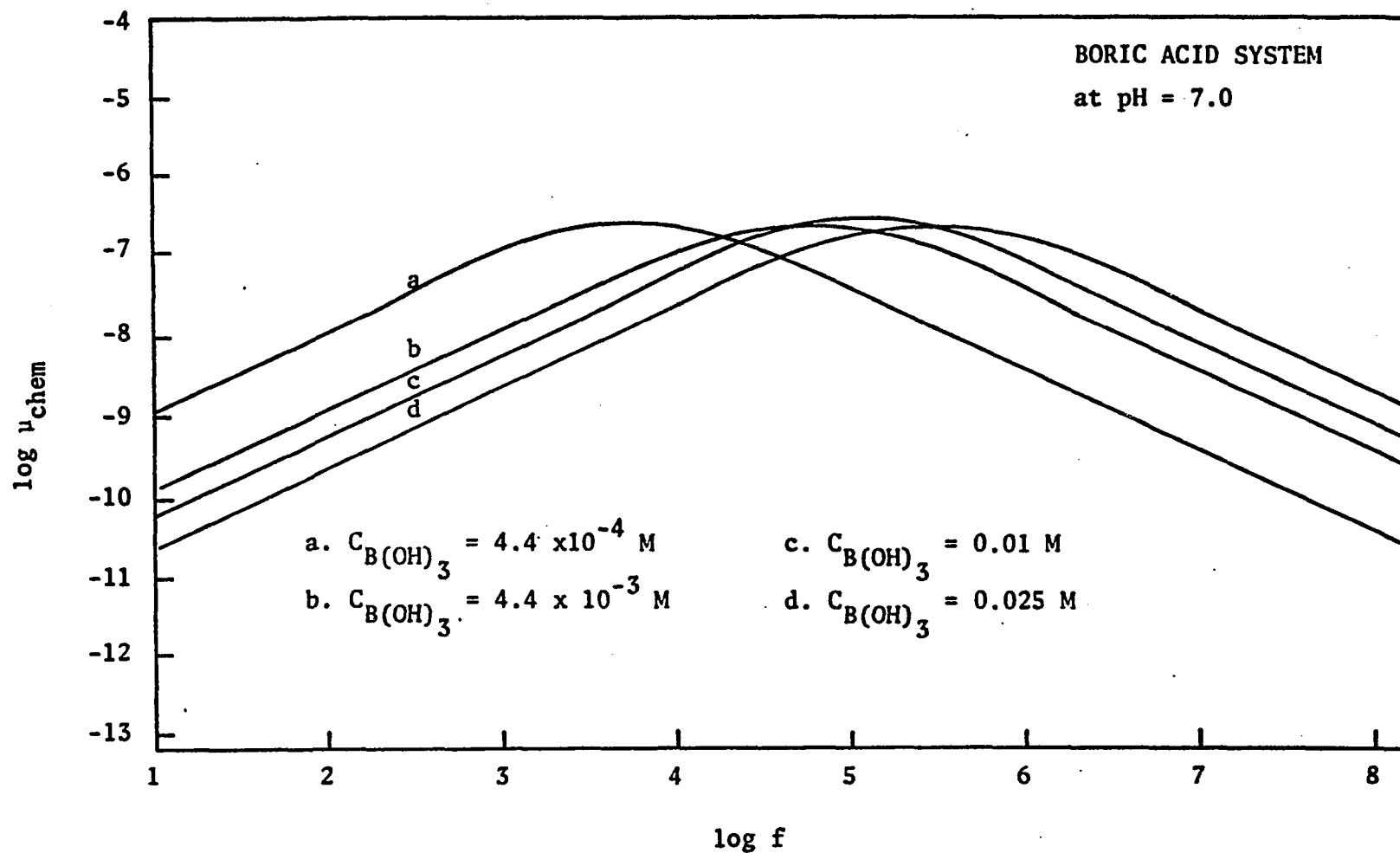


Figure 1-6: The Relaxation Spectra of Boric Acid System at Solution pH=7.0

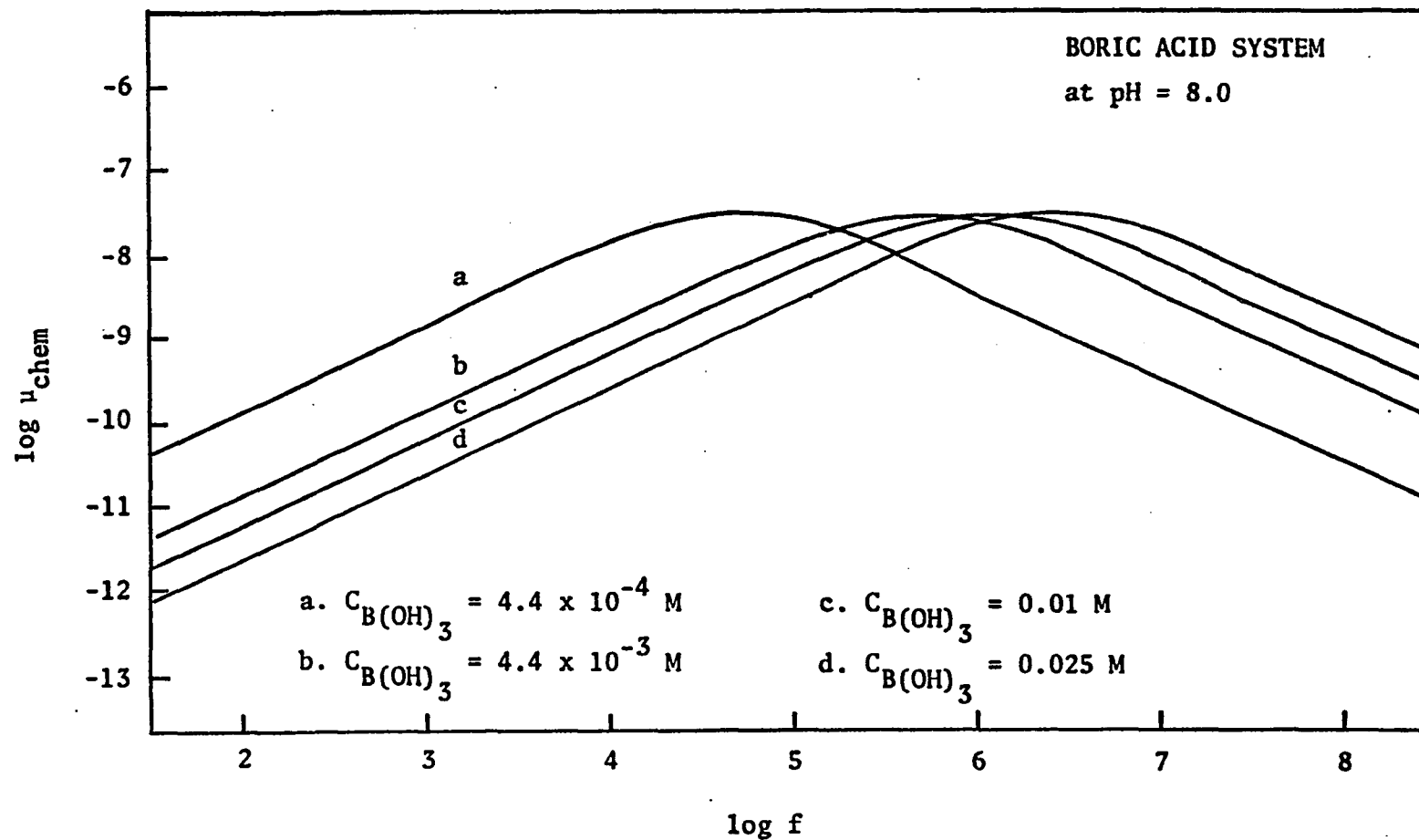


Figure 1-7: The Relaxation Spectra of Boric Acid System at Solution pH=8.0

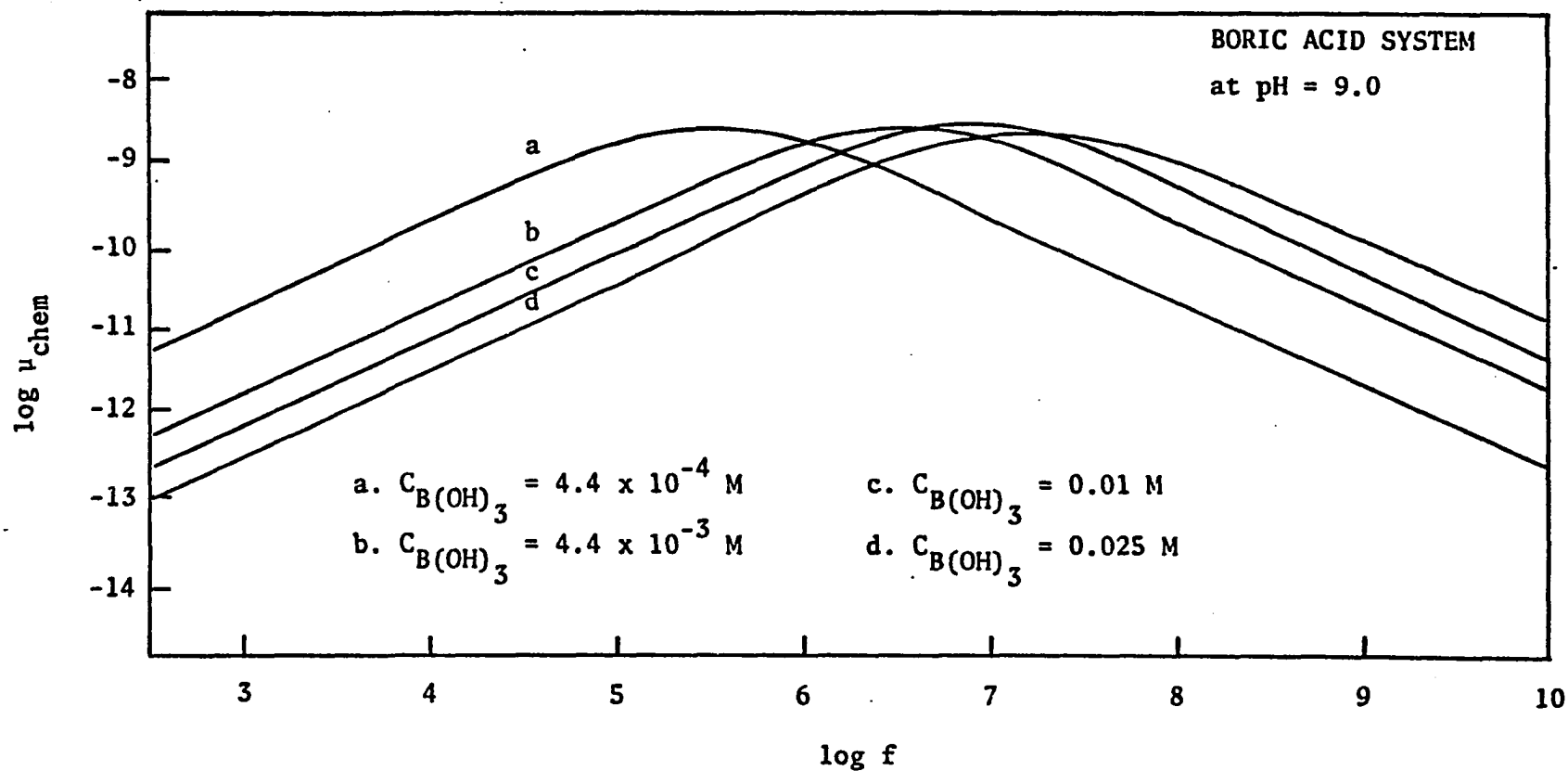


Figure 1-8: The Relaxation Spectra of Boric Acid System at Solution pH=9.0

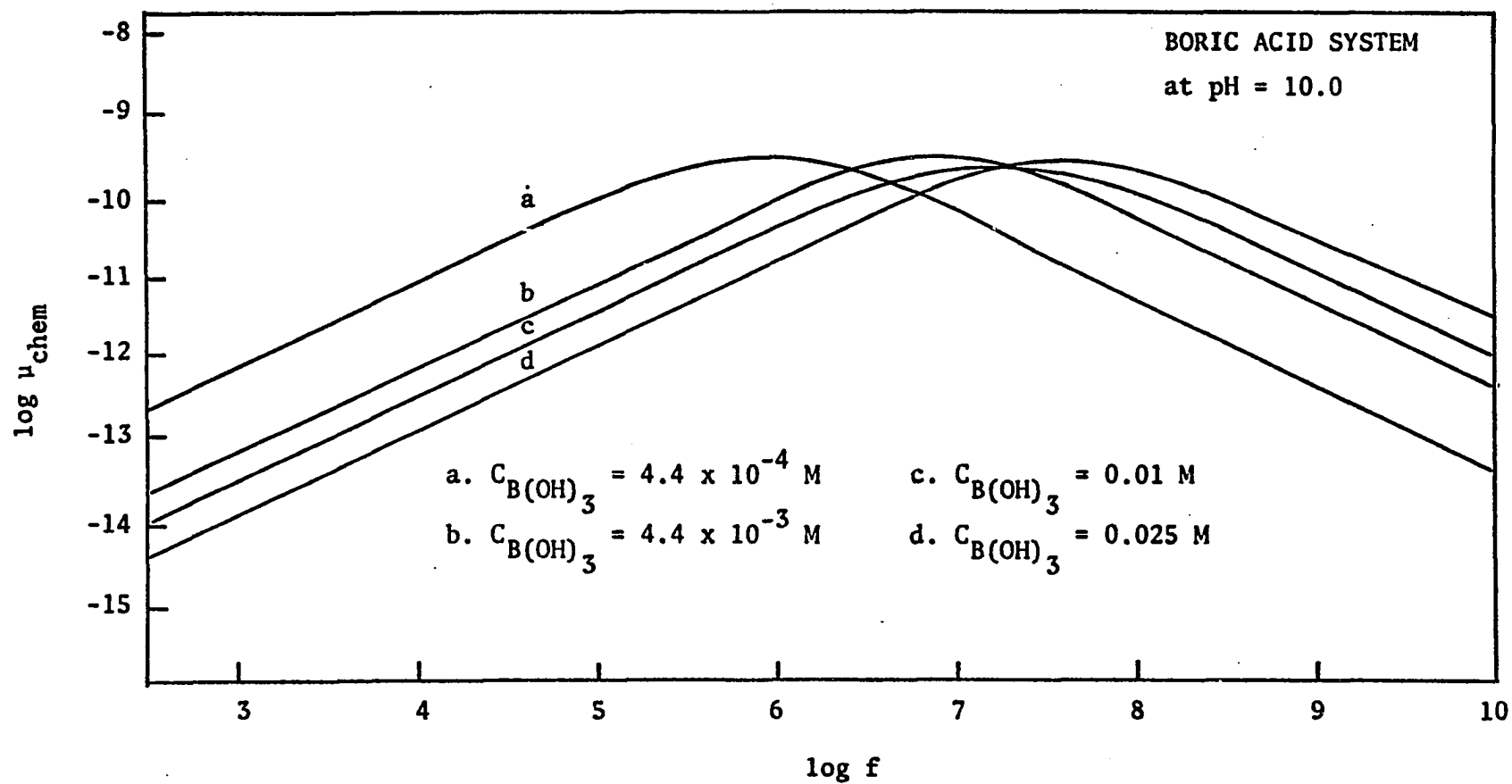


Figure 1-9: The Relaxation Spectra of Boric Acid System at Solution pH=10.0

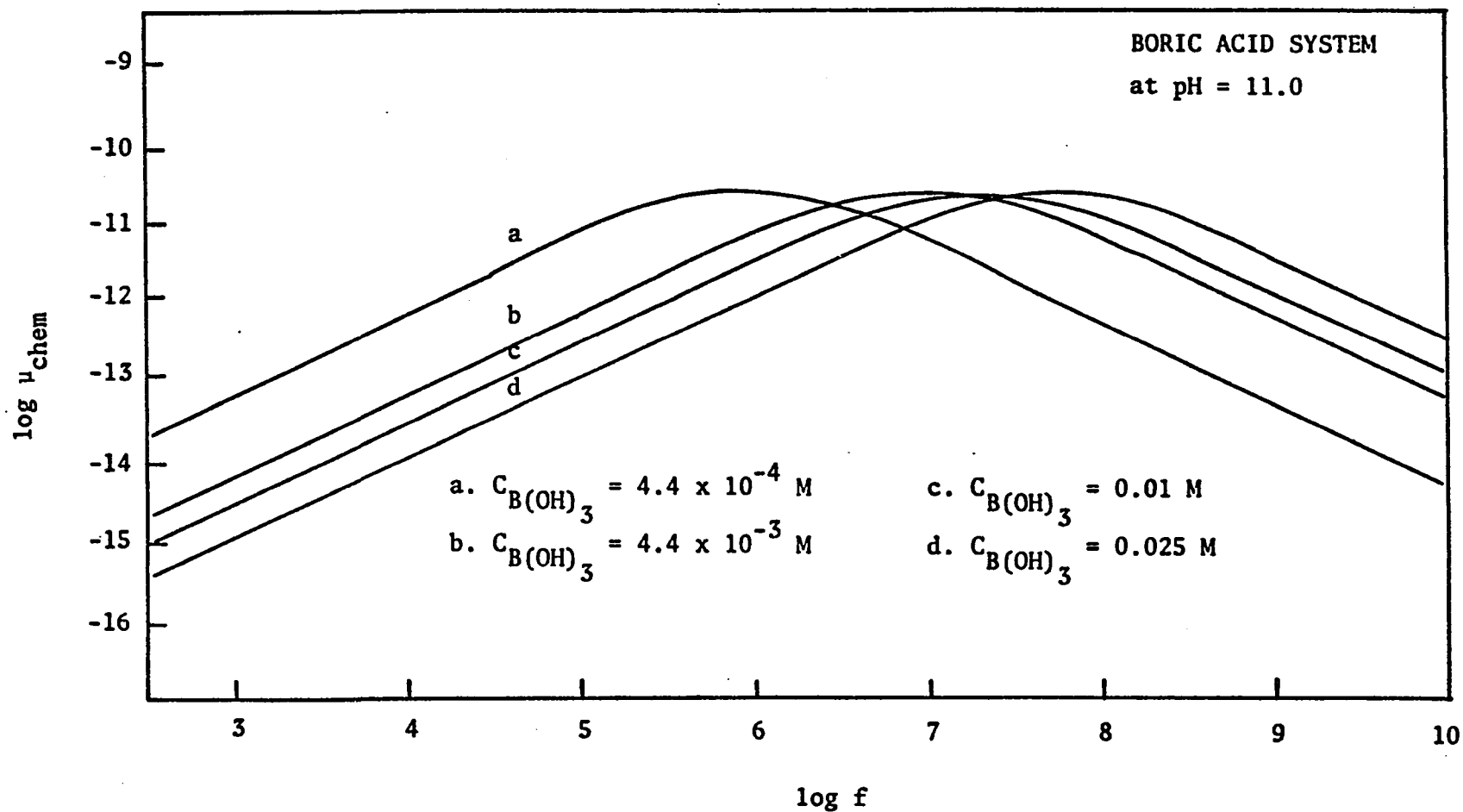


Figure 1-10: The Relaxation Spectra of Boric Acid System at Solution pH=11.0

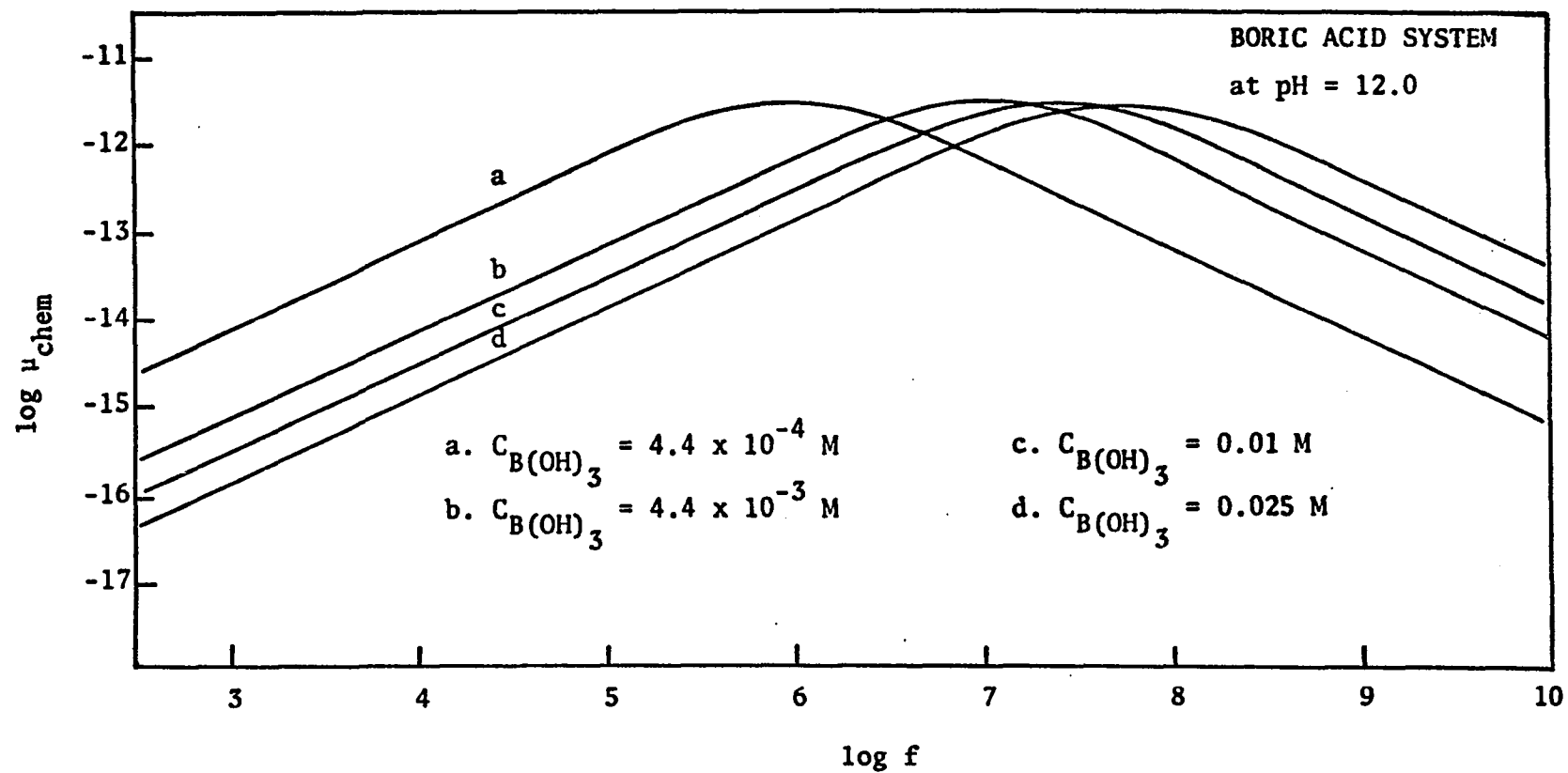


Figure 1-11: The Relaxation Spectra of Boric Acid System at Solution pH=12.0

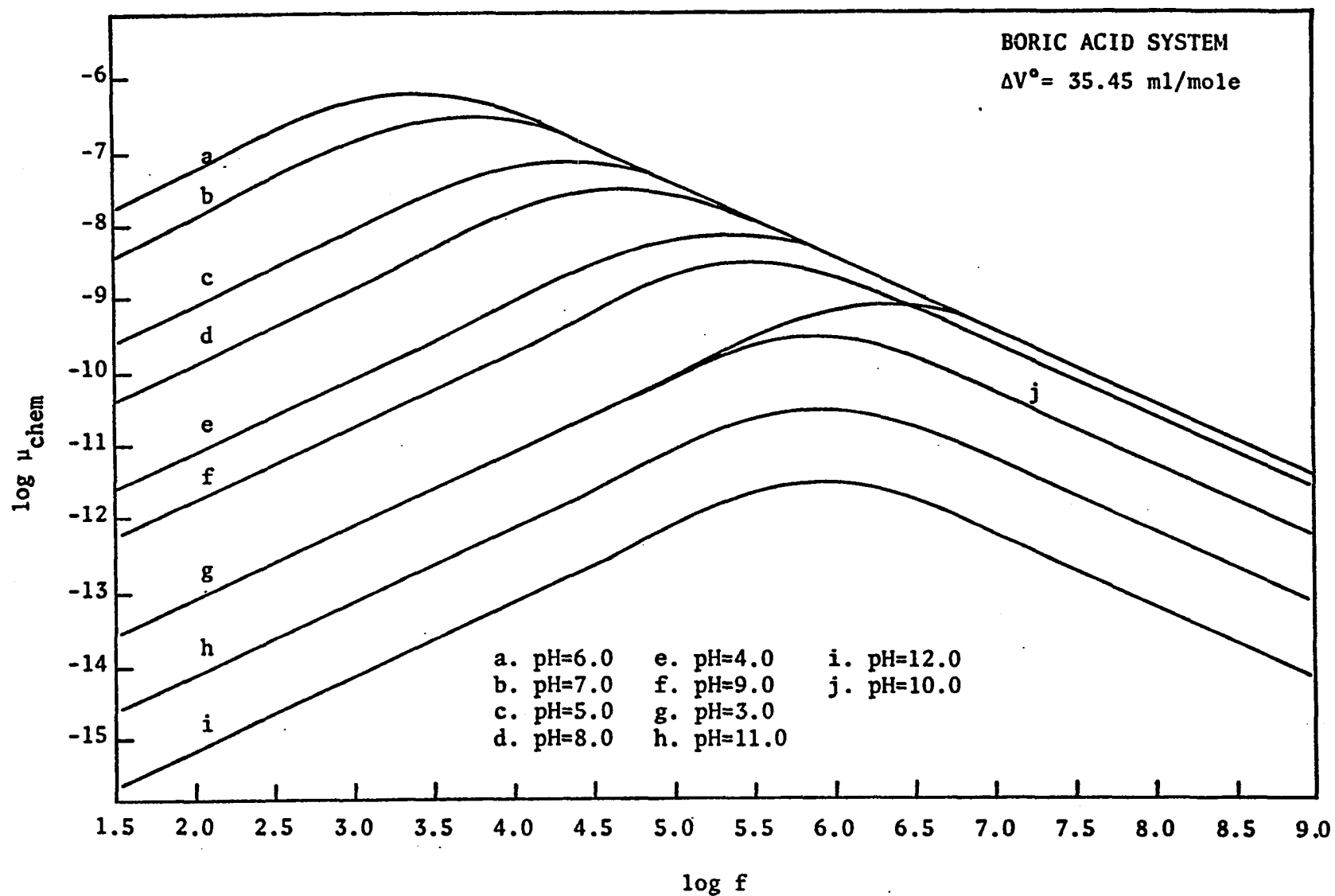


Figure 1-12: The Relaxation Spectra of Boric Acid System at
Total Boric Acid Concentration of $4.4 \times 10^{-4} \text{ M}$

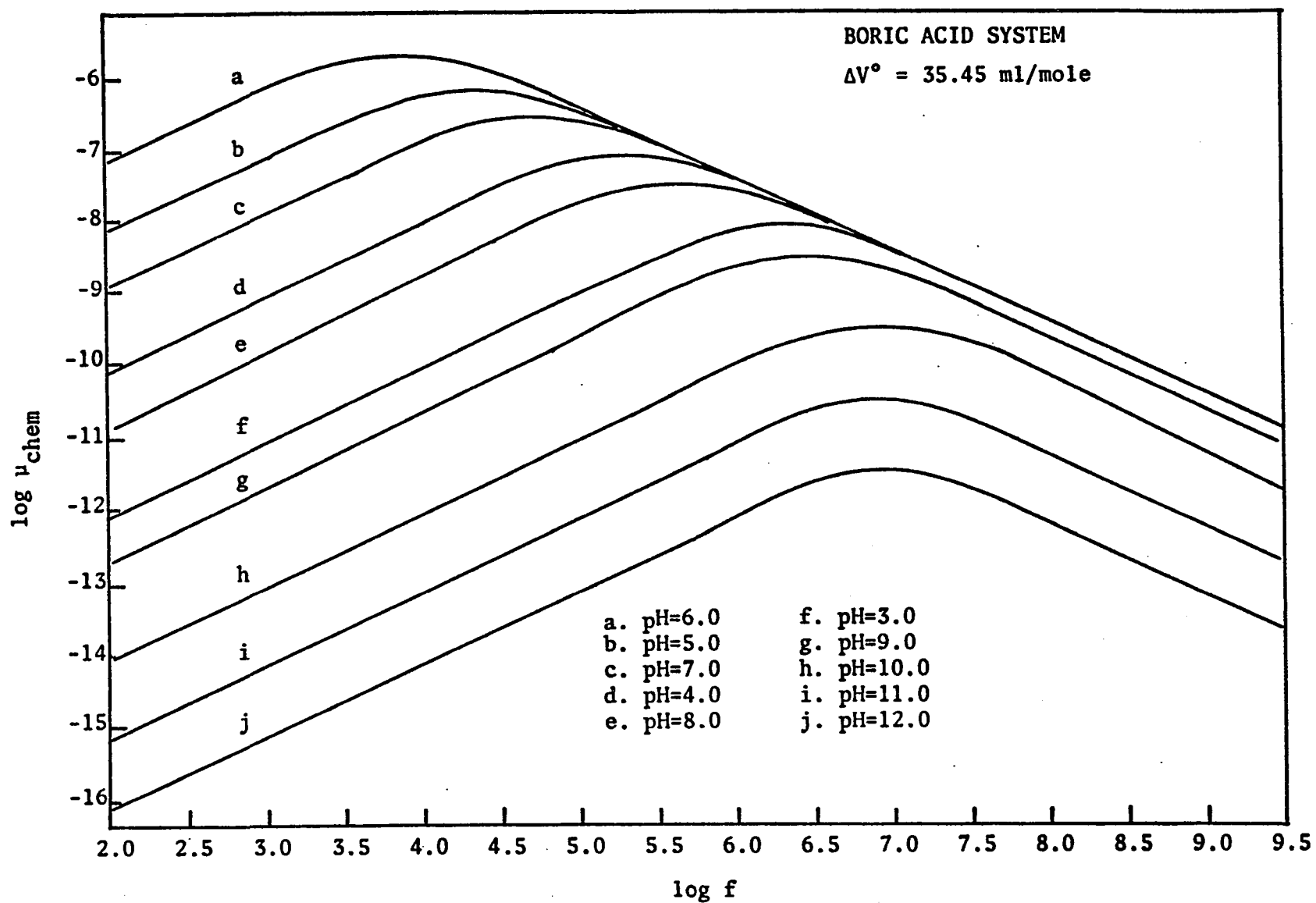


Figure 1-13: The Relaxation Spectra of Boric Acid System
at Total Boric Acid Concentration of $4.4 \times 10^{-3} \text{ M}$

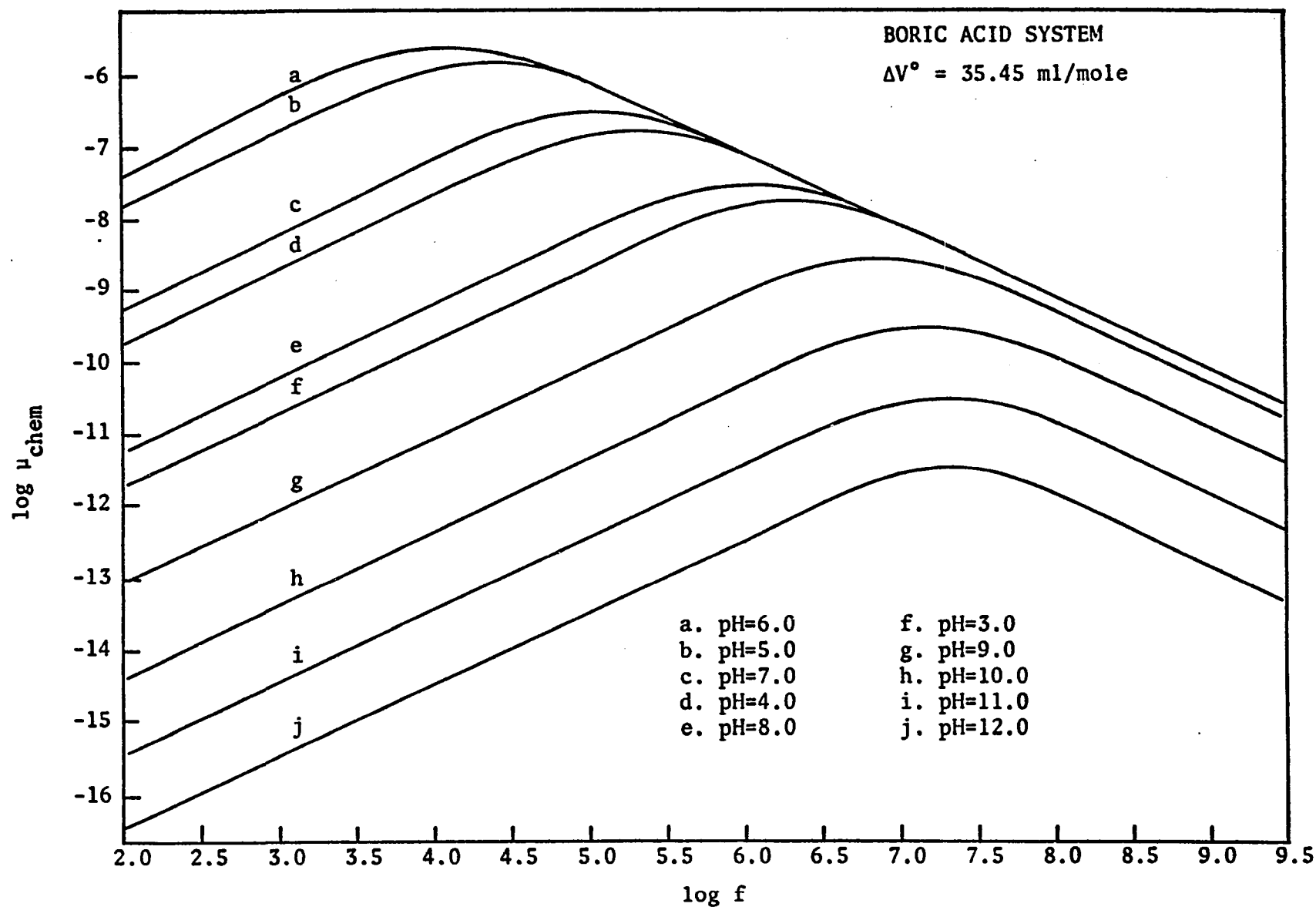


Figure 1-14: The Relaxation Spectra of Boric Acid System
at Total Boric Acid Concentration of 0.01 M

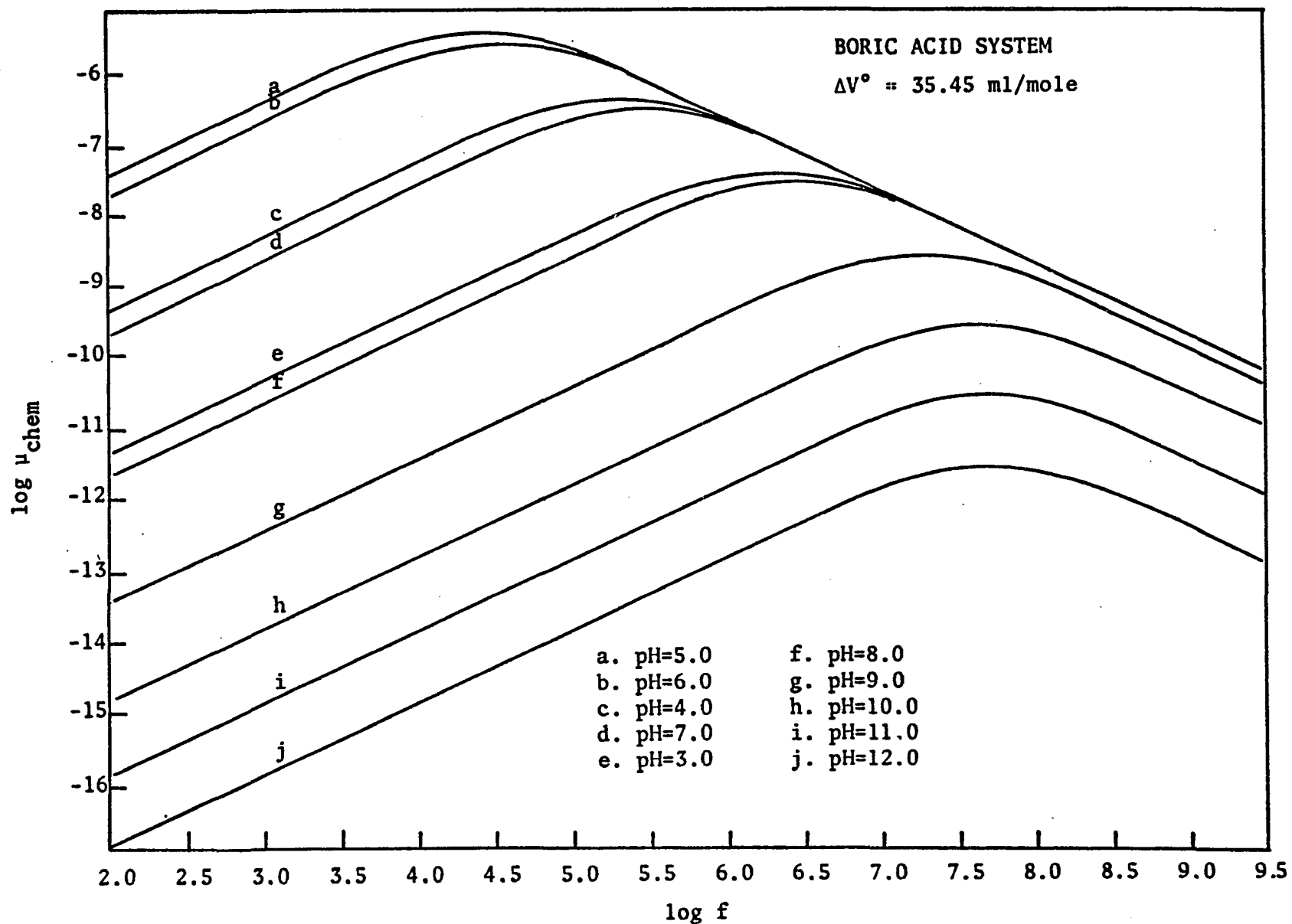


Figure 1-15: The Relaxation Spectra of Boric Acid System
at Total Boric Acid Concentration of 0.025 M

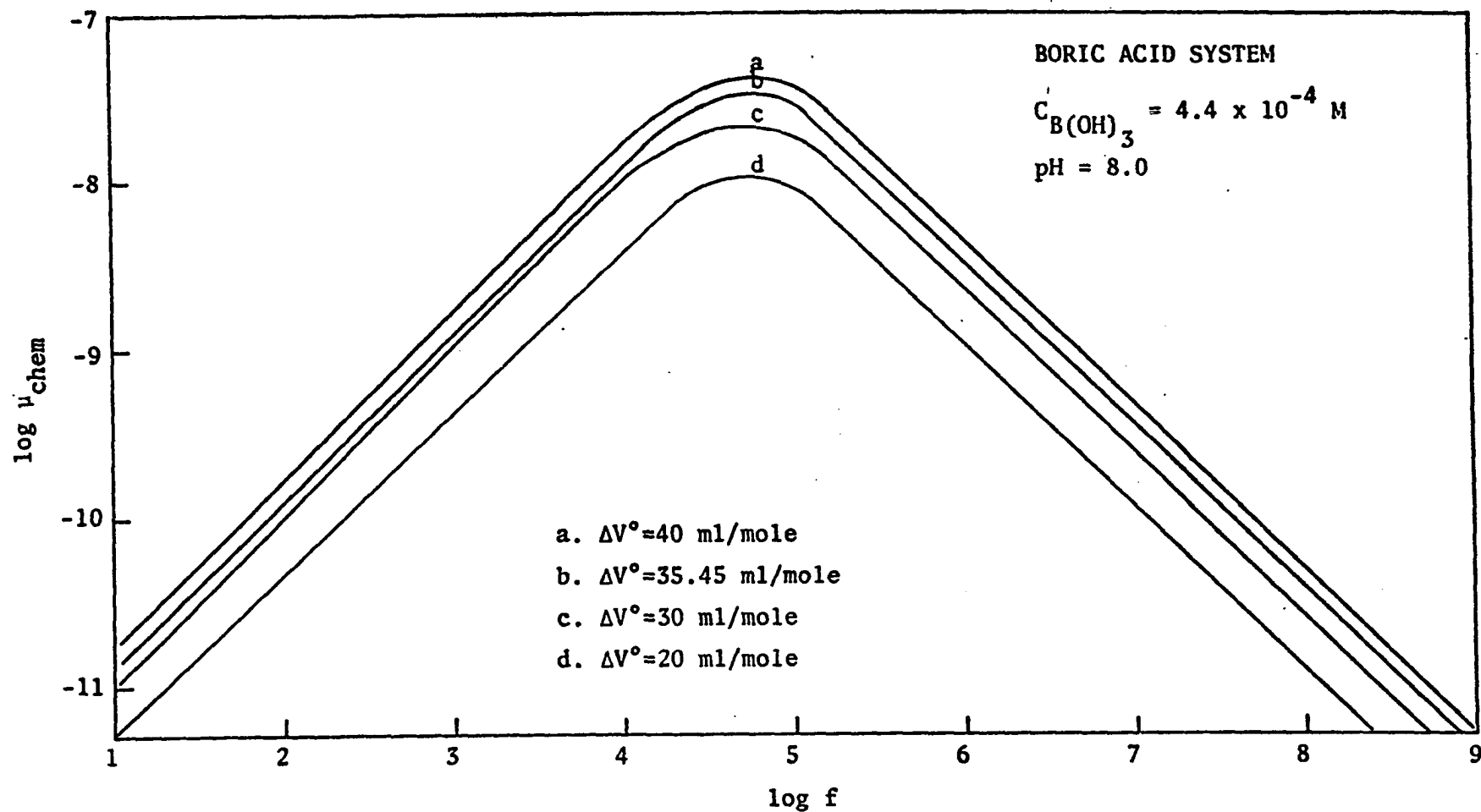


Figure 1-16: The Effect of the Reaction Volume Change on the Relaxation Spectra of Boric Acid System

B. The Boric Acid-Sodium Borate System:

Two different rate constant values have been assigned to the association reaction between sodium ion and hydroxyborate ion. They were $k_{f2} = 1.215 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ for the system I, and $k_{f2} = 2.7 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ for the system II. However, the difference between these rate constants will not change the distribution pattern of the various species of the system, but will only affect the relaxation spectra of the system.

The percentage distribution pattern of the various species will be affected by the solution pH values and the total sodium concentrations, C_{Na} values. The total boric acid concentration, $C_{\text{B(OH)}_3}$, has no effect on the distribution pattern as far as the pH and C_{Na} values remain constant. The effect of C_{Na} values on the % distribution is small when compared with that of the pH effect. At the pH value below 8.5, changing in C_{Na} value will change the % distribution of $[\text{B(OH)}_3]$ and $[\text{NaB(OH)}_4]$ slightly, but the distribution of $[\text{B(OH)}_4^-]$ species will remain the same. The $[\text{B(OH)}_3]$ concentration will decrease and that of $[\text{NaB(OH)}_4]$ will increase upon increasing the C_{Na} concentration. However, in the range of pH = 9.0 to 12.0, the concentrations of all three component species will be influenced by the C_{Na} values. Below pH = 6.0, practically, all the dissolved boric acid appear in the molecular form of $[\text{B(OH)}_3]$, and no $[\text{B(OH)}_4^-]$ and $[\text{NaB(OH)}_4]$ species exist regardless of the total boric acid concentration and the total sodium concentration in solution. At solution pH above 6.0, the $[\text{B(OH)}_4^-]$ concentration and the $[\text{NaB(OH)}_4]$ concentration start to increase until they reach their certain maximum values. Meantime, the $[\text{B(OH)}_3]$ concentration will decrease since certain amount of the

$[B(OH)_3]$ species now appear in the form of $[B(OH)_4^-]$ and $[NaB(OH)_4]$. In the same pH range, increasing the C_{Na} value will increase the $[NaB(OH)_4]$ concentration and decrease the $[B(OH)_4^-]$ concentration, considerably. But only slight change has been observed for the distribution of $[B(OH)_3]$ species. This happens between pH = 9.0 and 12.0 .

The effect of pH values on the relaxation spectra are shown in figure(1-19) and figure(1-24). It has been found that at different pH values, the relaxation peaks have their different magnitudes. However, at the frequency around $f = 10^8$ Hz, no matter what the pH value the system has, they all give the same excess sound absorption value of $\mu_{chem} \approx 10^{-10.5}$ nepers.

As shown in figure(1-21), the increase in the total boric acid concentration has no effect on the first peak value of the relaxation spectra except shifts the corresponding relaxation frequency values slightly. However, the second peak value is increased upon increasing the $C_{B(OH)_3}$ concentrations.

At constant $C_{B(OH)_3}$ and pH values, increasing the total sodium concentration will increase the second relaxation peak. This can be seen in figure(1-20). The ΔV_2^0 value also has the same effect on the second relaxation peak magnitude as C_{Na} does.

For the comparison purpose, the relaxation spectra of the boric acid-sodium borate system(I) and/or system(II) have been drawn together with that of the boric acid system on the same diagram. It has been found that for the first case (that is, system I), the number of the relaxation peak has increased by one, but in the second case (that is, system II), the relaxation spectra for the boric acid system

and that for the boric acid-sodium borate system are the same. This can be realized since at the second case, the k_{f2} has the value of $2.7 \times 10^3 \text{ M}^{-1}\text{sec}^{-1}$ which is very small compared with that of the $k_{f1} = 1.35 \times 10^{10} \text{ M}^{-1}\text{sec}^{-1}$. As a consequence, the association reaction between the Na^+ ion and the B(OH)_4^- ion can be ignored.

It is found that the relaxation frequencies for this system range from 2.7 KHz to 5.3×10^3 MHz, which are partly experimentally available in the laboratory. However, the maximum α' value for the system is about 1.7×10^{-2} dB/cm, which is still too small to be detected accurately. Therefore, it can be expected that for the boric acid-sodium borate system, no excess sound absorption can be obtained through ultrasonic relaxation method.

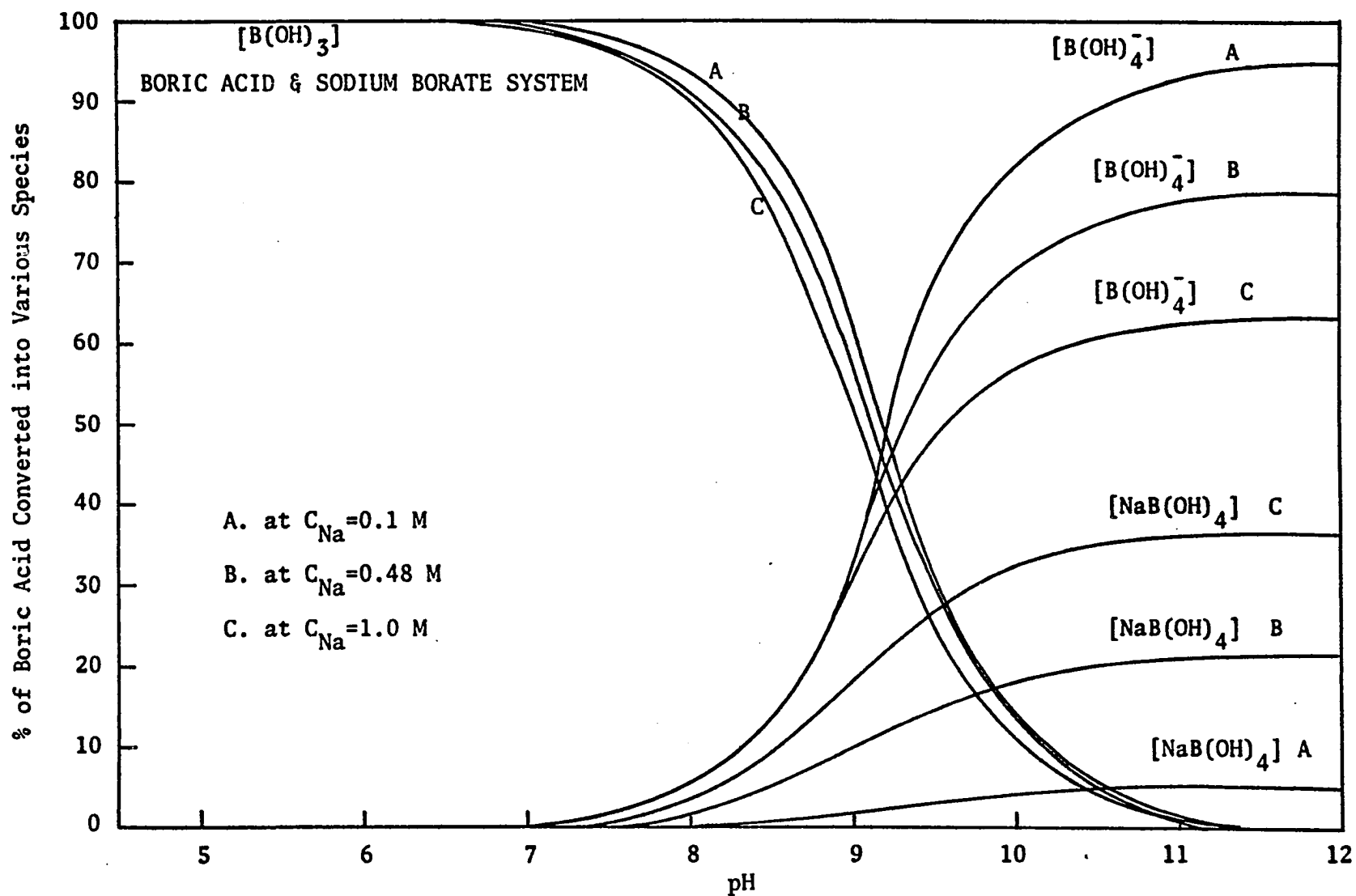


Figure 1-17: The Distribution of the Various Species of Boric Acid & Sodium Borate System at $C_{B(OH)_3} = 4.4 \times 10^{-4}$ to 0.025 M.

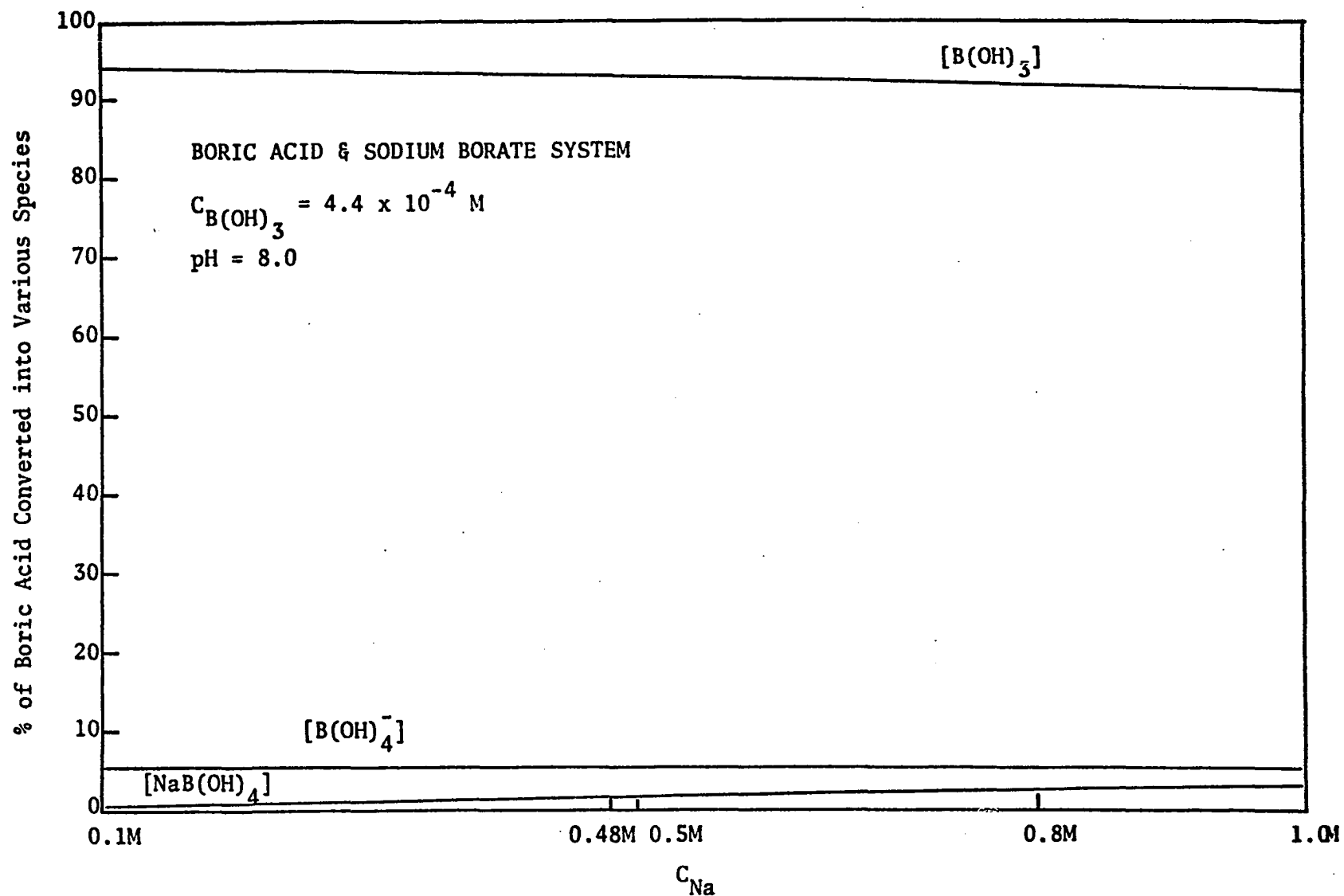


Figure 1-18: The Effect of the Total Sodium Concentration on the Distribution of the Various Species of Boric Acid & Sodium Borate System.

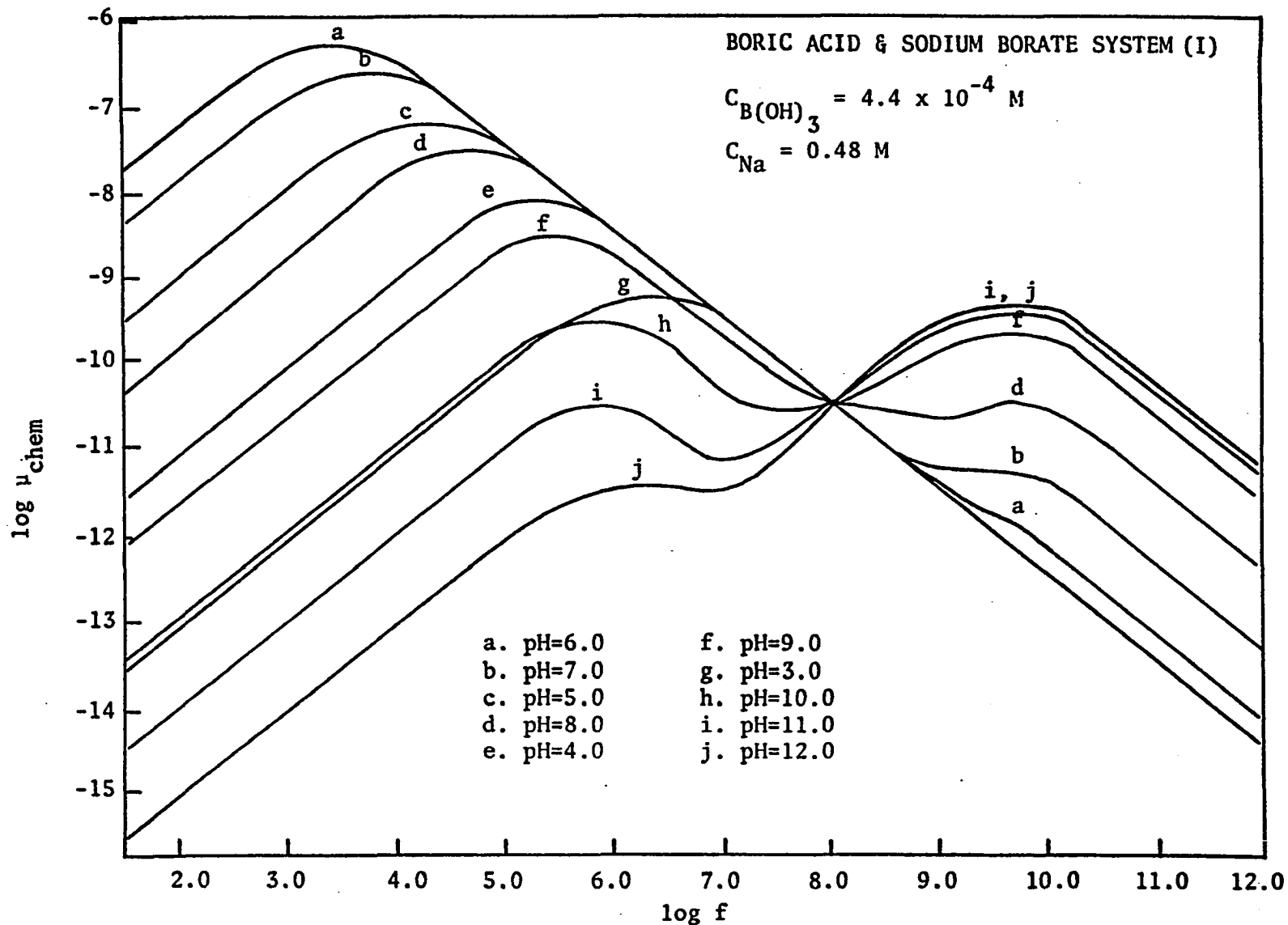


Figure 1-19: The Effect of Solution pH on the Relaxation Spectra of Boric Acid & Sodium Borate System.

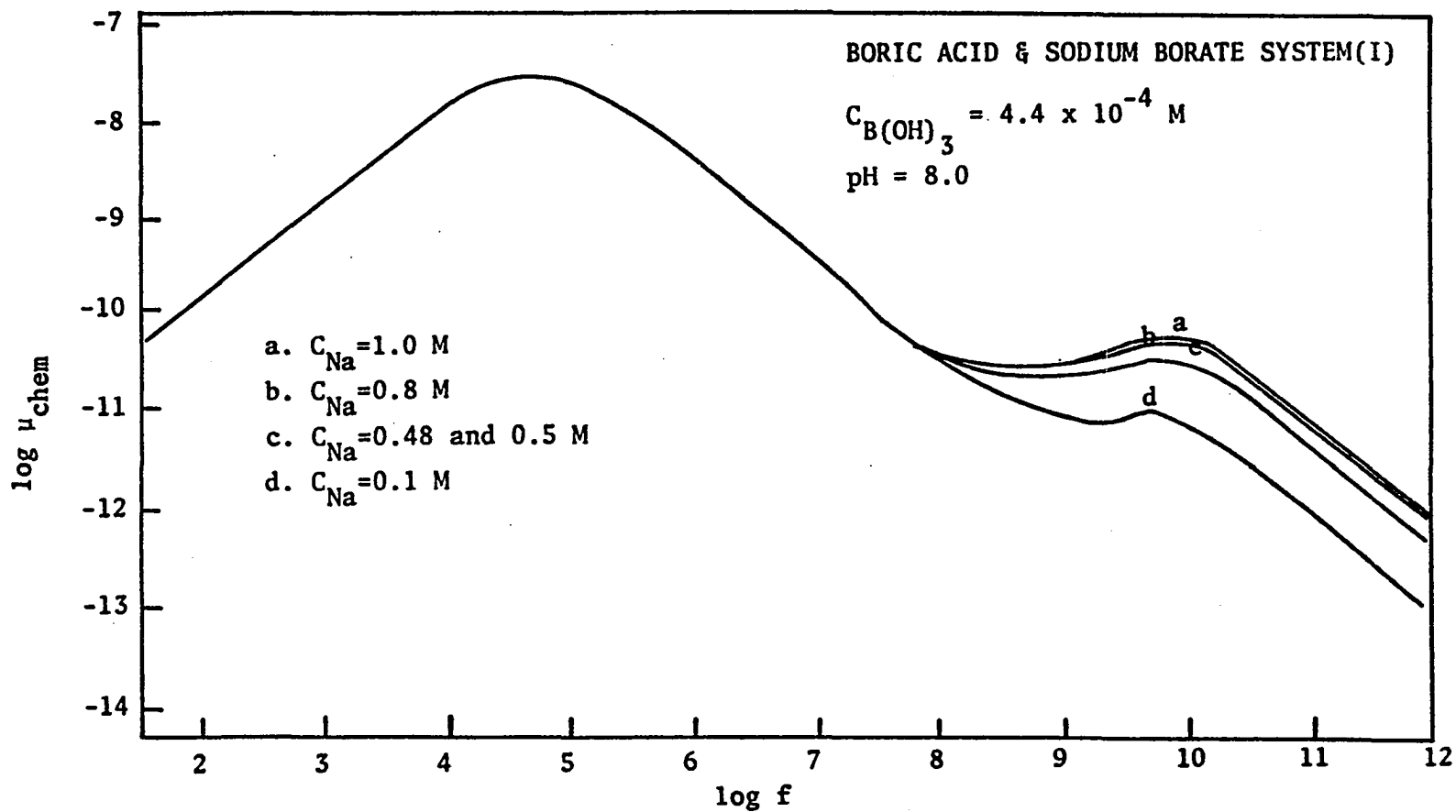


Figure 1-20: The Effect of the Total Sodium Concentration on the Relaxation Spectra of Boric Acid & Sodium Borate System(I).

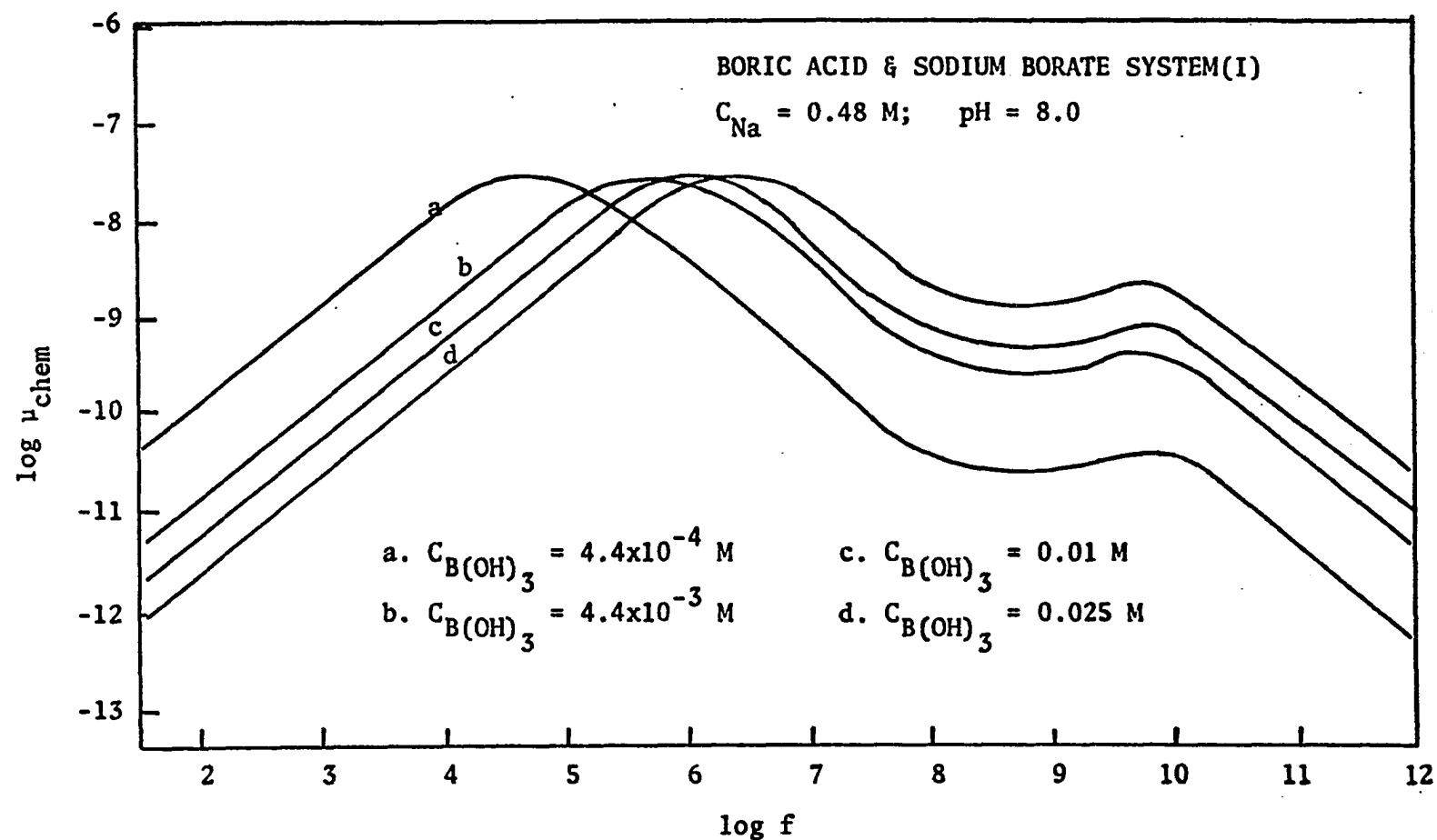


Figure 1-21: The Effect of the Total Boric Acid Concentration on the Relaxation Spectra of Boric Acid & Sodium Borate System.

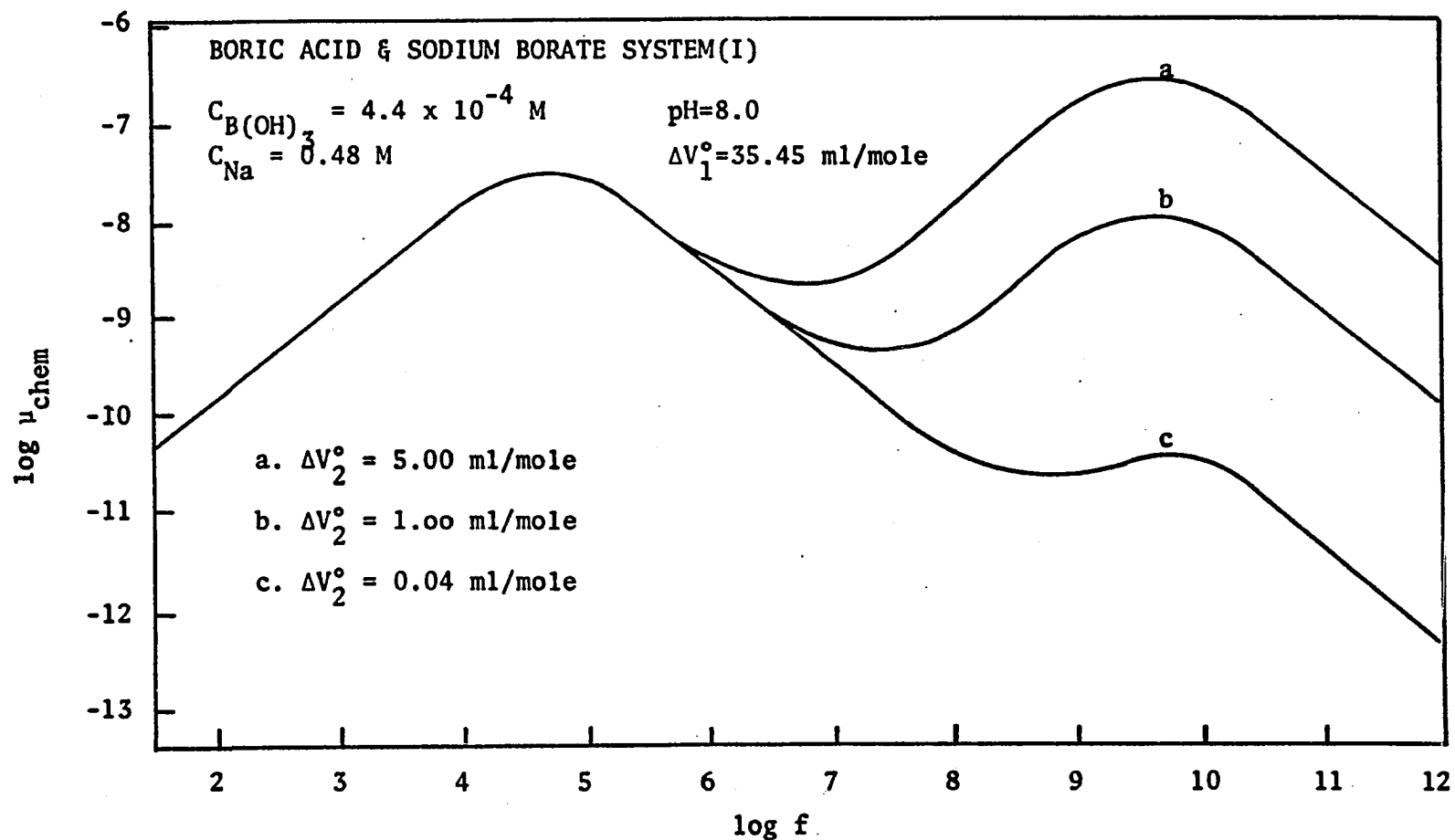


Figure 1-22: The Effect of the ΔV_2° Values on the Relaxation Spectra of Boric Acid & Sodium Borate System.

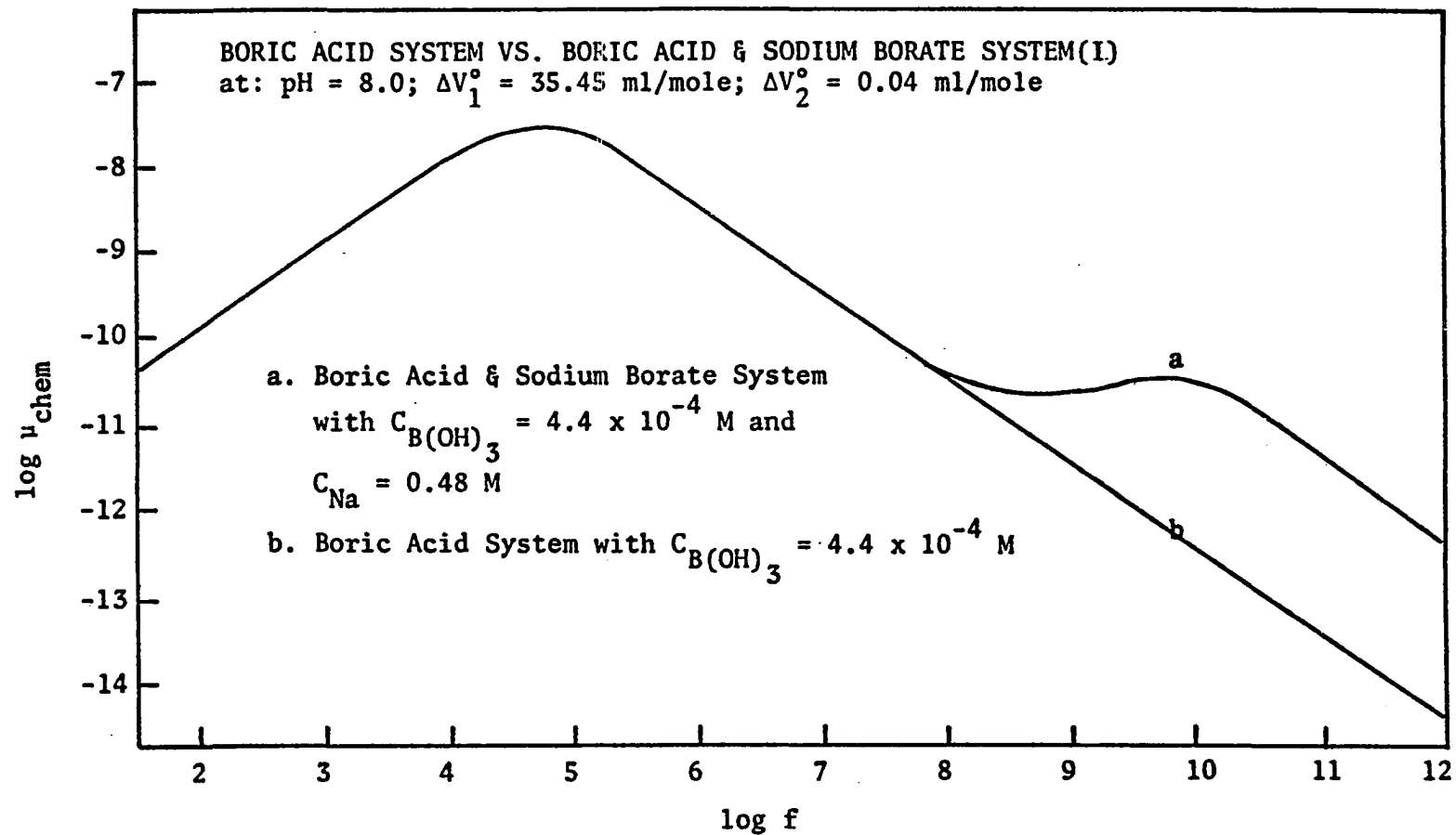


Figure 1-23: The Comparison of the Relaxation Spectra of Boric Acid System with That of the Boric Acid & Sodium Borate System(I).

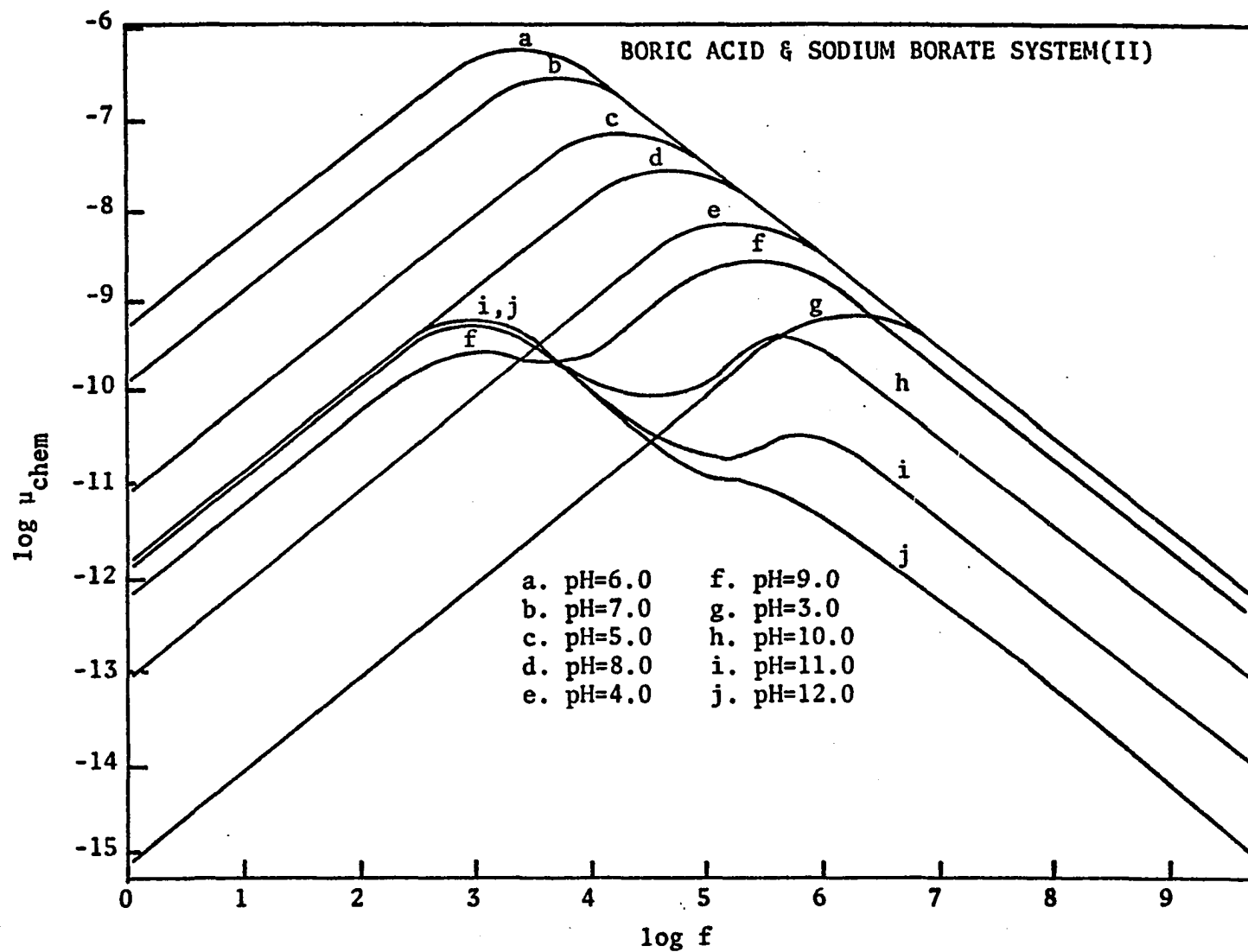


Figure 1-24: The Relaxation Spectra of Boric Acid & Sodium Borate System(II) with $C_{B(OH)_3} = 4.4 \times 10^{-4}$ M and $C_{Na} = 0.48$ M.

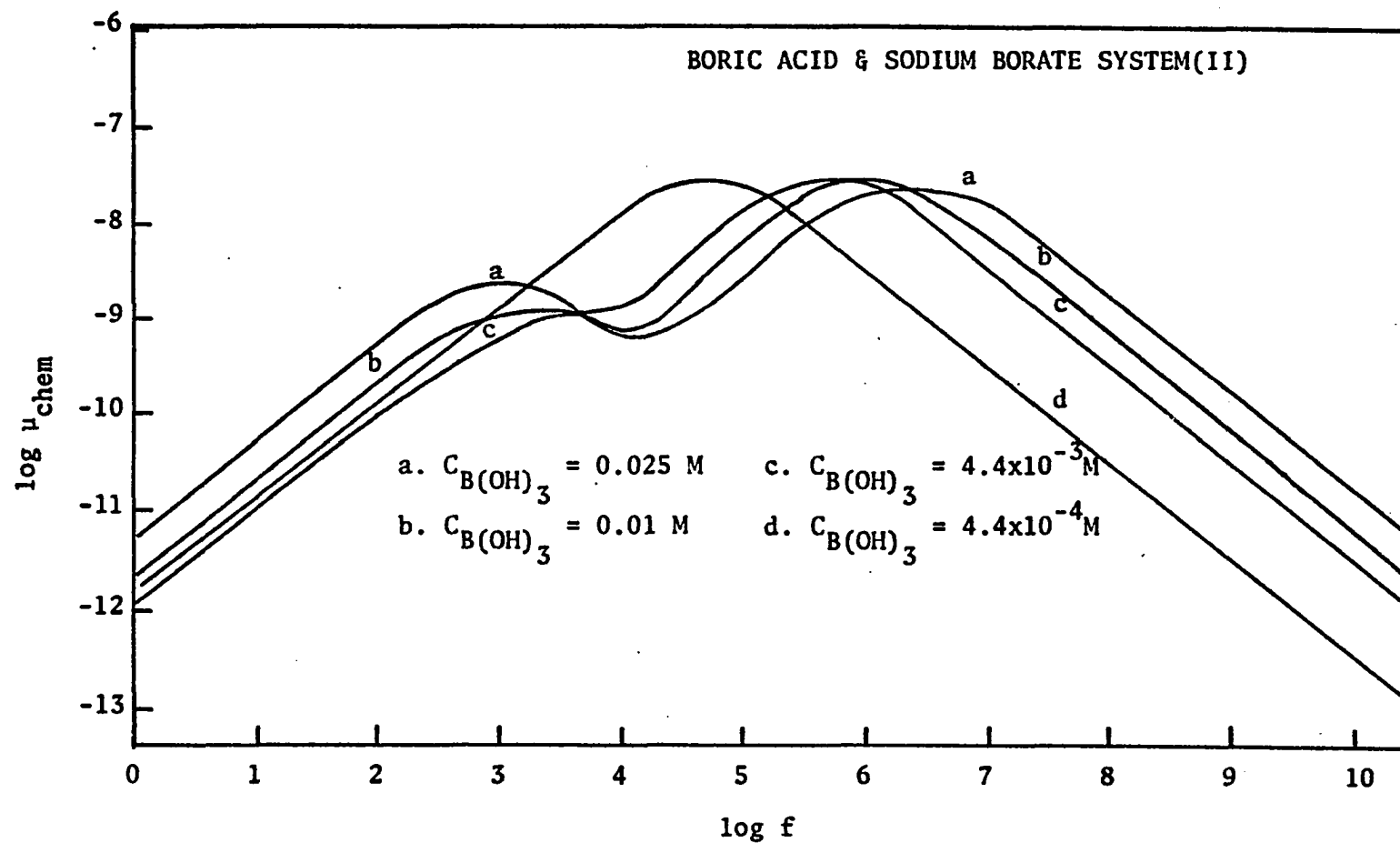


Figure 1-25: The Relaxation Spectra of Boric Acid & Sodium Borate System(II) with $C_{Na} = 0.48 \text{ M}$ and at Solution pH = 8.0.

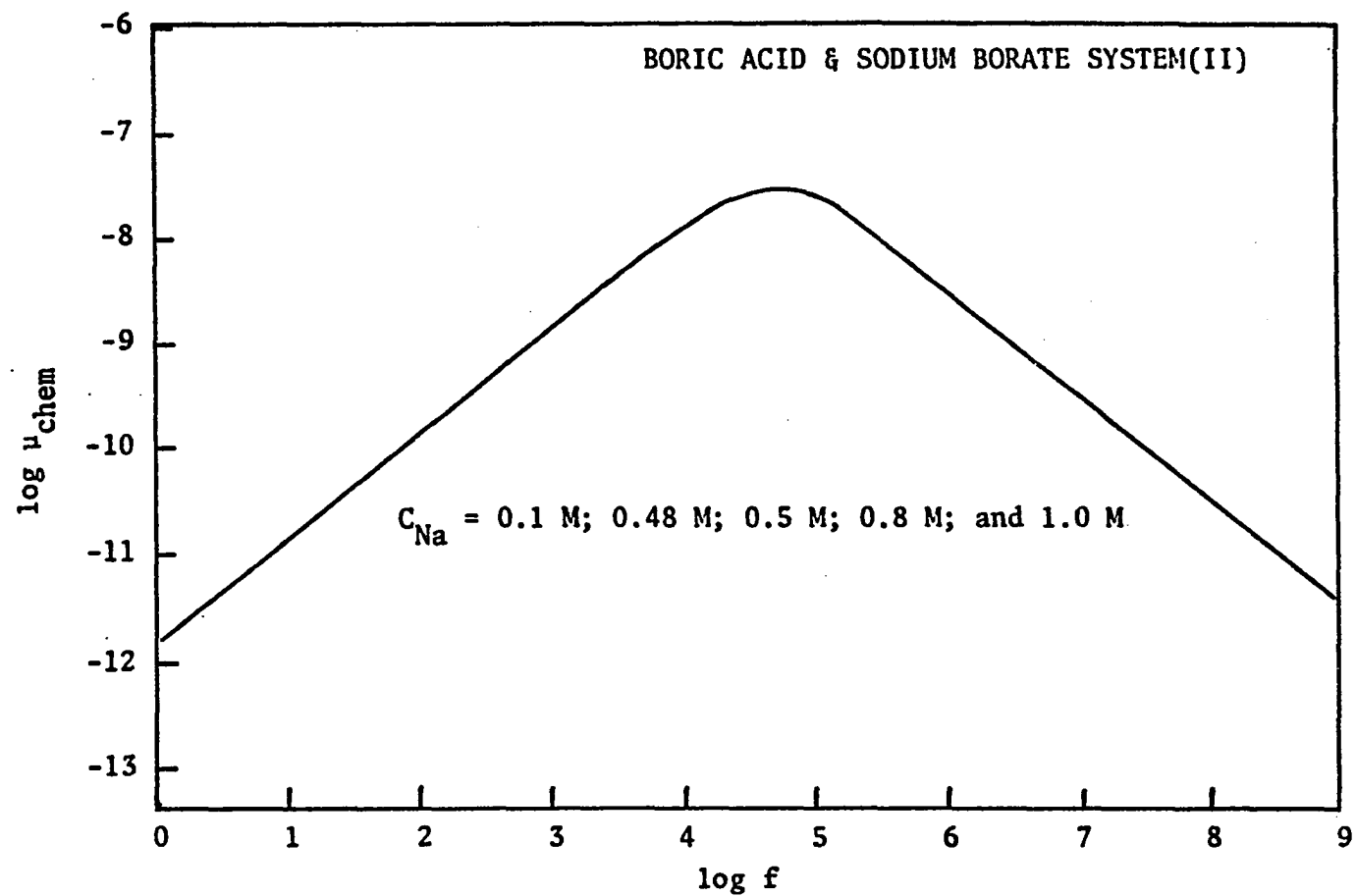


Figure 1-26: The Relaxation Spectra of Boric Acid & Sodium Borate System(II) with $C_{B(OH)_3} = 4.4 \times 10^{-4} \text{ M}$ and at Solution pH=8.0

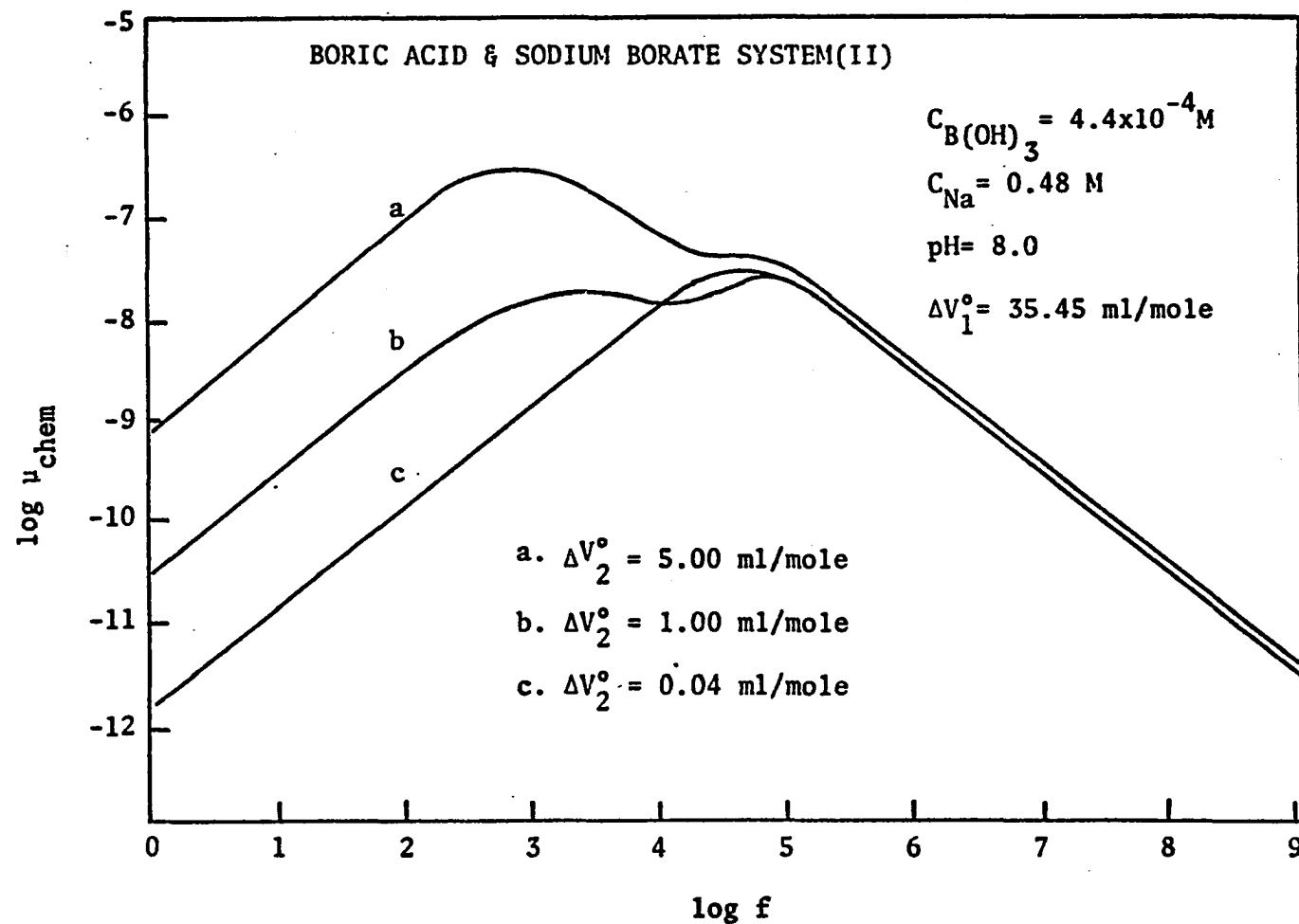


Figure 1-27: The Effect of ΔV_2° on the Relaxation Spectra of Boric²Acid & Sodium Borate System(II)

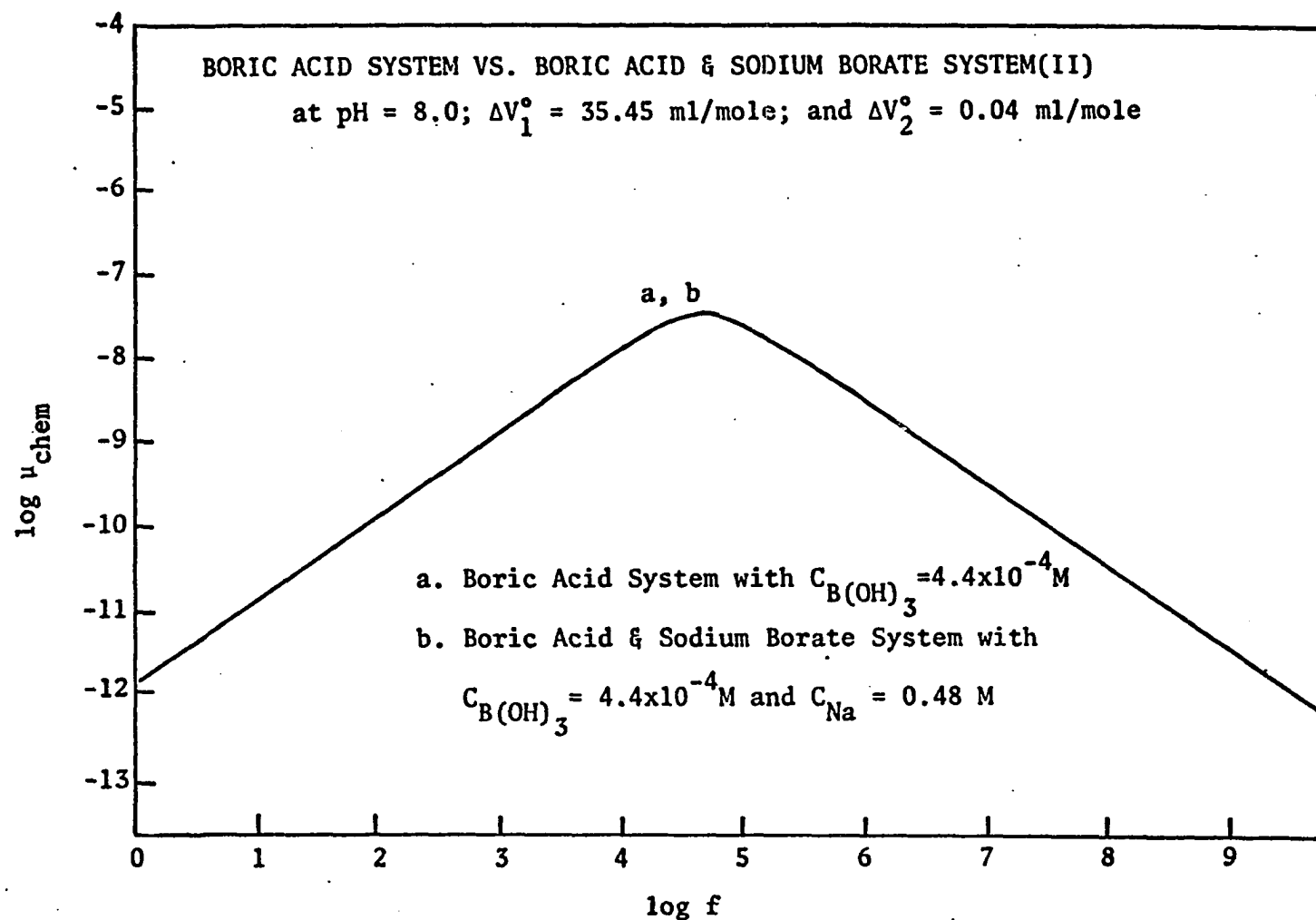


Figure 1-28: The Comparison of the Relaxation Spectra of Boric Acid System Vs. Boric Acid & Sodium Borate System(II)

C. The Boric Acid and Polyborate System:

The distribution of various polyborate species is influenced by two main factors. The first factor is the total analytical concentration of boric acid present in the solution, and the second factor is the solution pH value. At solution pH values around 3.0 or 4.0, the only important species in solution is $[B(OH)_3]$ regardless of the total boric acid concentration. When the pH value is equal to or above 5.0, polynuclear species such as $[B_3O_3(OH)_4^-]$ and $[B_5O_6(OH)_4^-]$ start to appear in amounts depending on the total boric acid concentration in solution. At a solution pH of 8.0, nearly all of the polynuclear species are present in some amount. But after that pH value, the variety of polyborates starts to decrease. At the extreme case of pH=12.0, only two polyborate species, $[B_3O_3(OH)_5^{2-}]$ and $[B_4O_5(OH)_4^{2-}]$, exist in solution.

As far as the effect of total boric acid concentration on the distribution pattern of polynuclear species is concerned, it can be seen from figures (1-38) to (1-48) that when the total boric acid concentration is below 0.025 M, all the polynuclear species such as $[B_2(OH)_7^-]$, $[B_3O_3(OH)_4^-]$, $[B_3O_3(OH)_5^{2-}]$, and $[B_4O_5(OH)_4^{2-}]$ appear in a negligible amount and can be ignored. In other words, polyborates become important only when the total boric acid concentration exceeds 0.025 M. This result is consistent with that indicated in the literature.⁹⁻¹⁰ In a given pH range, the concentrations of various polyborate species will increase upon increasing the total boric acid concentration. Among all the polynuclear species,

only the following polyborates appear in appreciable amounts: $[B_4O_5(OH)_4]^{-2}$, $[B_3O_3(OH)_4]^{-}$, and $[B_3O_3(OH)_5]^{-2}$. $[B_2(OH)_7]^{-}$ always appears in small quantity regardless of the total boric acid concentration since this species is quite unstable compared with that of the trimer or tetramer. The $[B_5O_6(OH)_4]^{-}$ species becomes important only when the total boric acid concentration reaches 0.4 M or more. The concentration of $[B_3O_3(OH)_5]^{-2}$ becomes considerable only at higher pH values.

Generally speaking, increasing the total boric acid concentration will increase the amplitude of the relaxation spectra. This can be seen from figures (1-49) to (1-52). The solution pH value also has a strong influence on the relaxation spectra pattern. At pH 9.0 or 10.0, the excess sound absorption has its highest value; and around pH=5.0 or less, its lowest. Most of the relaxation spectra have two peaks. However, in some of them the second peak is vague, and the system can be treated as one peak.

For the polyborate system, the maximum excess sound absorption has the value of $\mu_{\max} = 10^{-0.95}$ nepers (or $\alpha' = 1.3 \times 10^{-4}$ dB/cm) which is too small to be measured experimentally. The corresponding frequency is at $f = 10^{1.3}$ Hz (or 20 Hz) which is also extremely low and is experimentally unavailable. In the frequency range from 500 KHz to 100 MHz or above, which is experimentally feasible in our laboratory, the corresponding maximum excess sound absorption value of the polyborate system is about $\mu_{\max} = 10^{-4.5}$ nepers (or $\alpha' = 9.2 \times 10^{-4}$ dB/cm) which is still too small to be measured experimentally. Consequently, it can be predicted that for the polyborate system

there should be no excess sound absorption which can be detected using available ultrasonic relaxation techniques.

The detailed results will be shown through the tables and figures on the following pages.

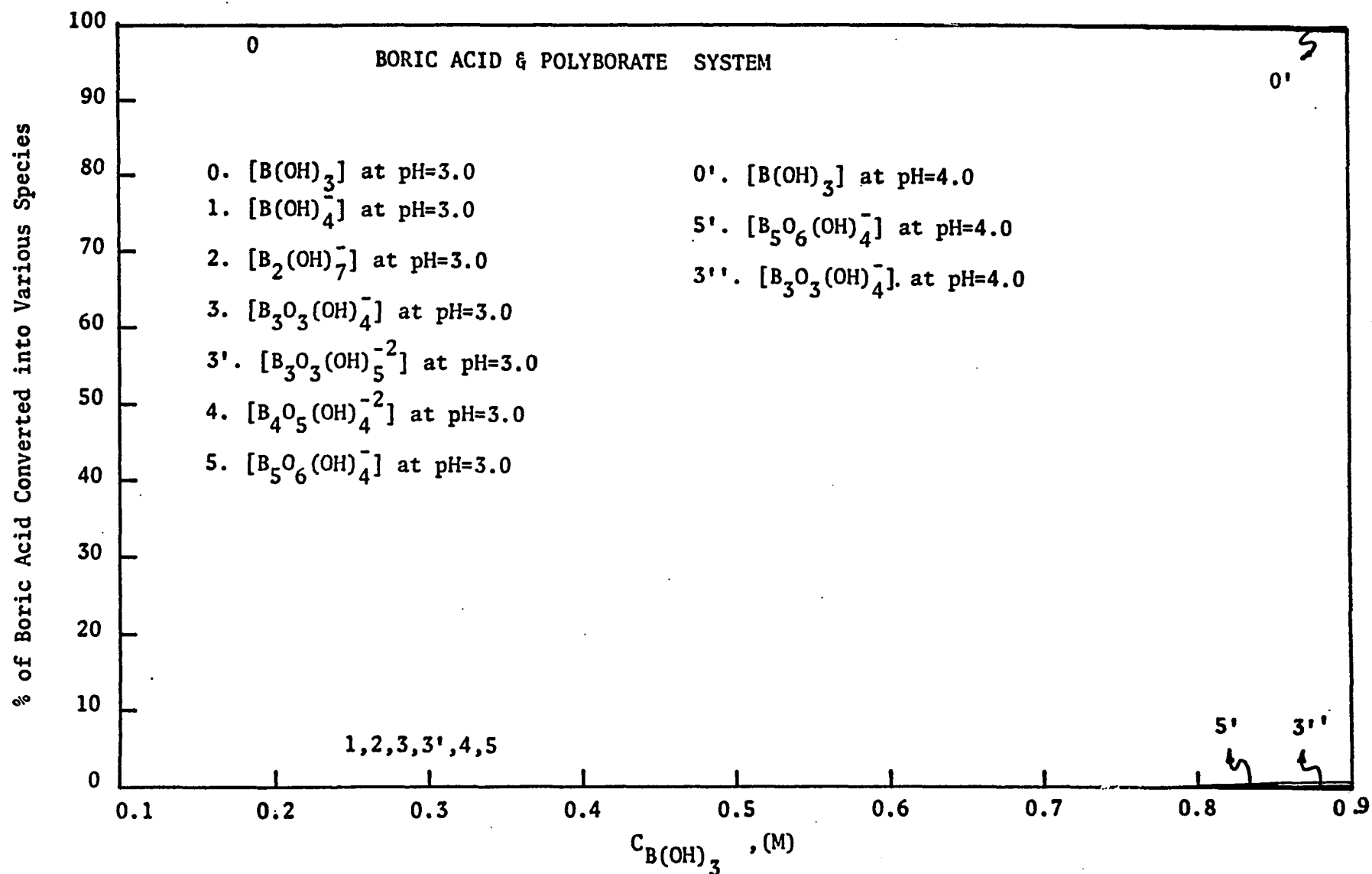


Figure 1-29: The Distribution of Various Species of Boric Acid & Polyborate System at Solution pH=3.0 and pH=4.0

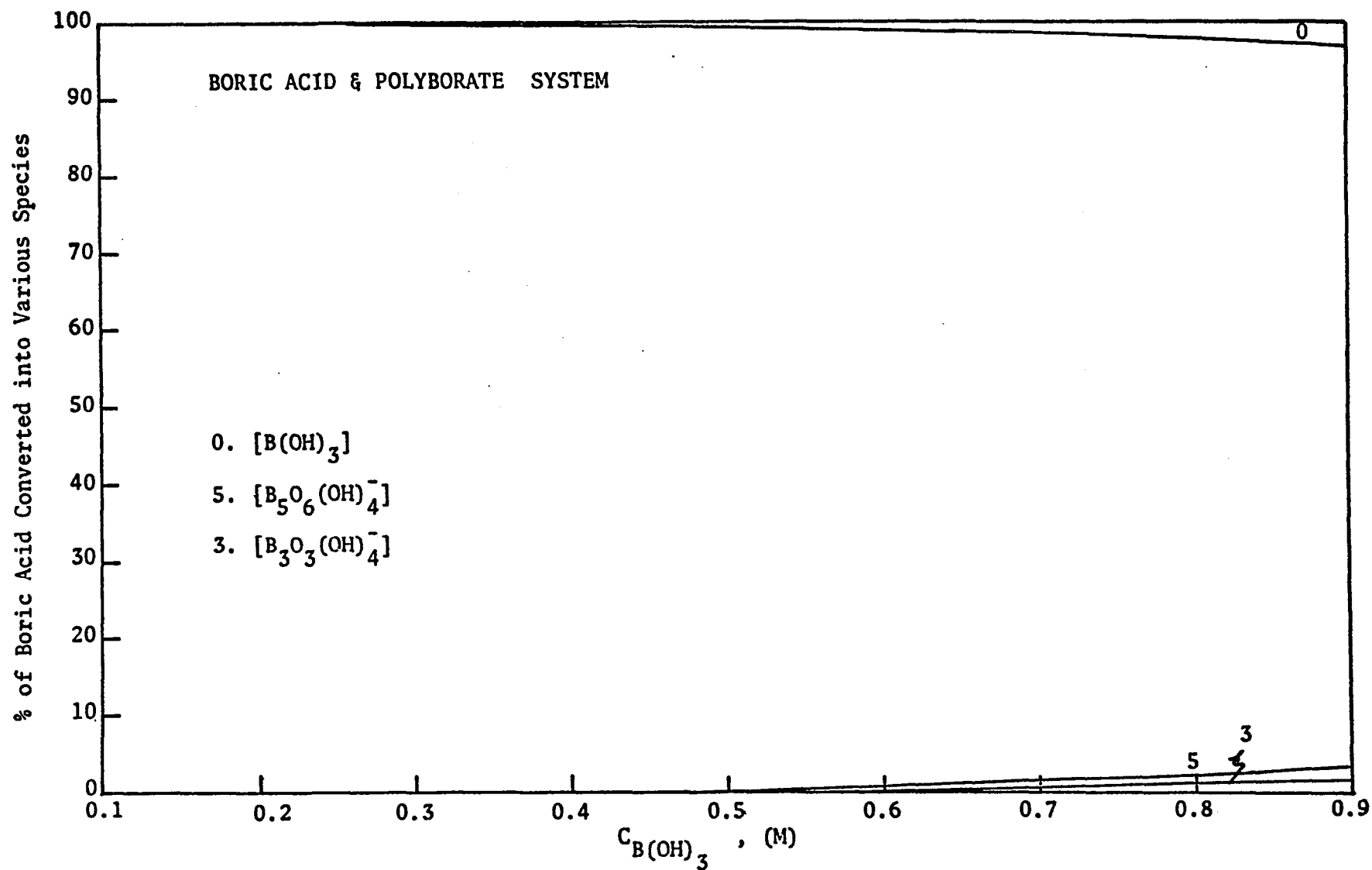


Figure 1-30: The Distribution of Various Species of Boric Acid & Polyborate System at Solution pH=5.0

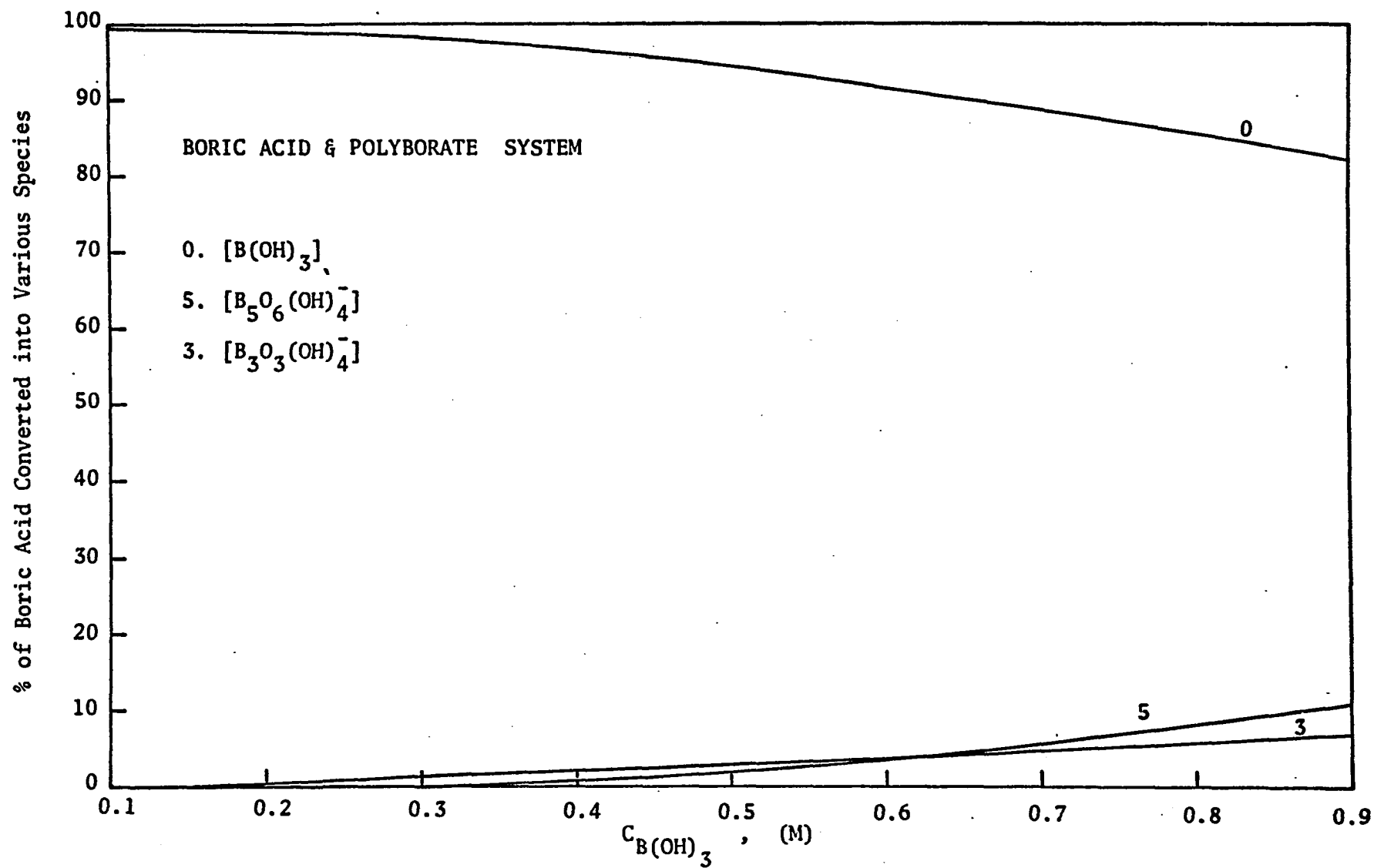


Figure 1-31: The Distribution of Various Species of Boric Acid & Polyborate System at pH=6.0

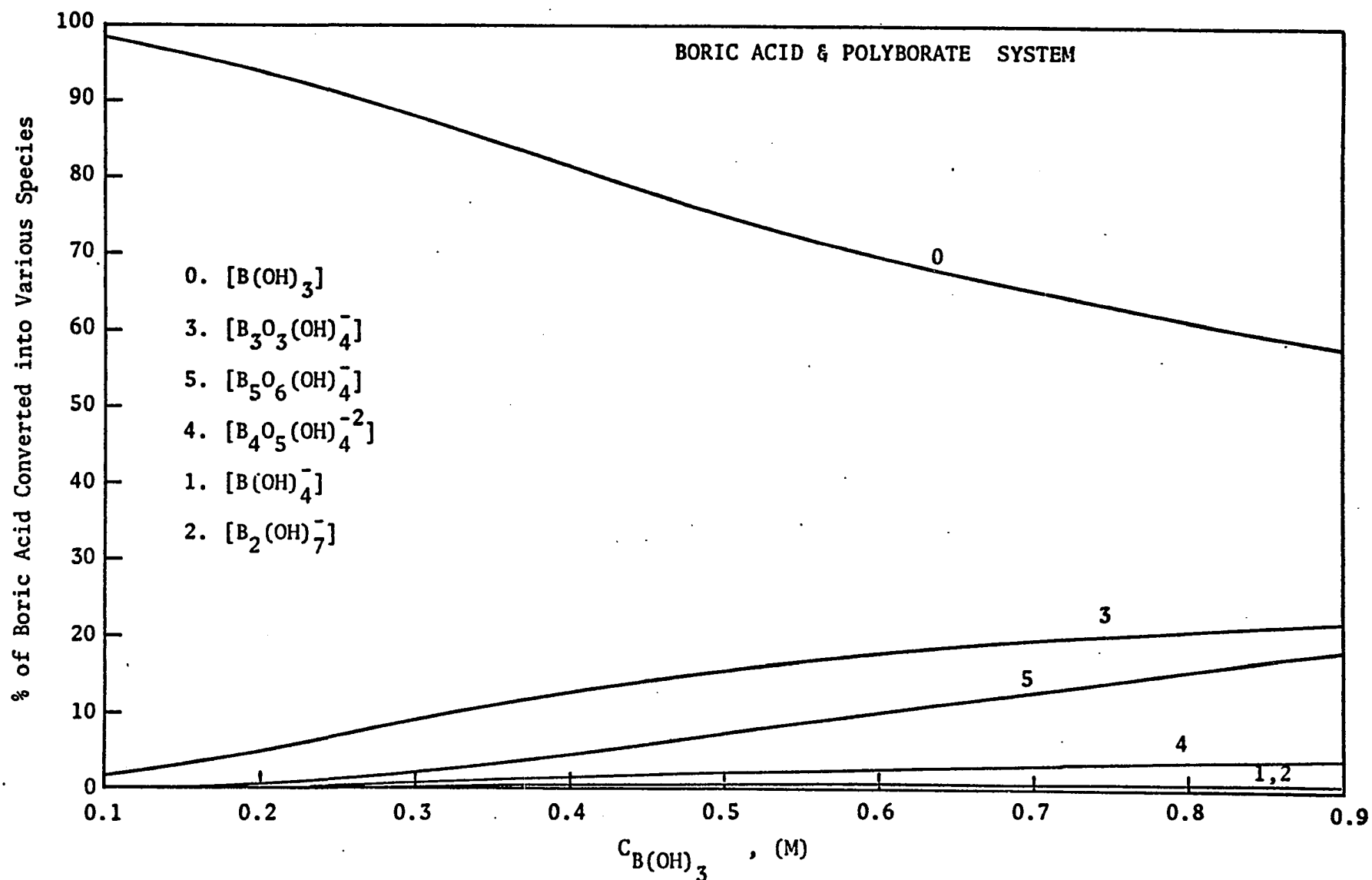


Figure 1-32: The Distribution of Various Species of Boric Acid & Polyborate System at Solution pH=7.0

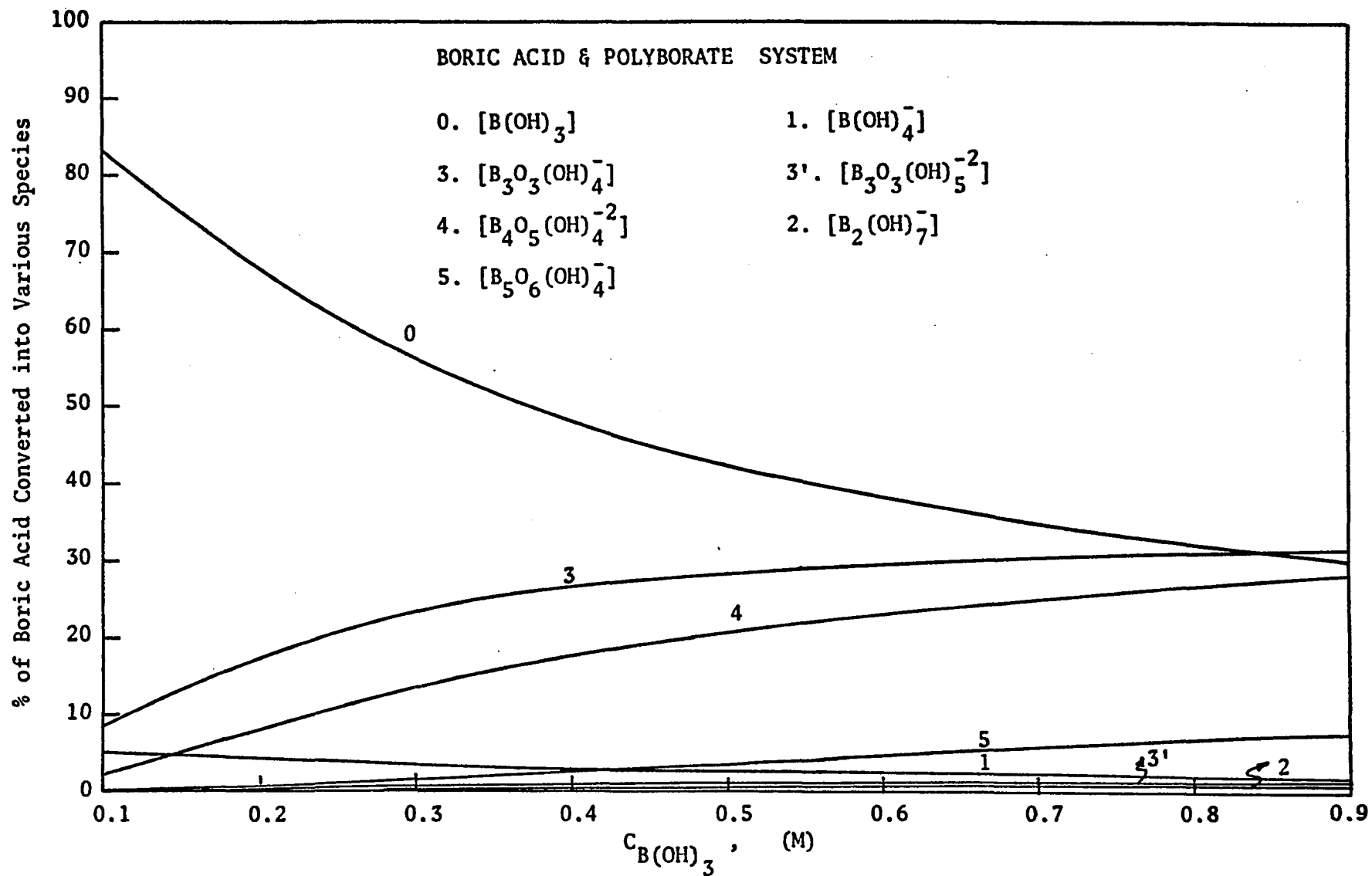


Figure 1-33: The Distribution of Various Species of Boric Acid & Polyborate System at Solution pH=8.0

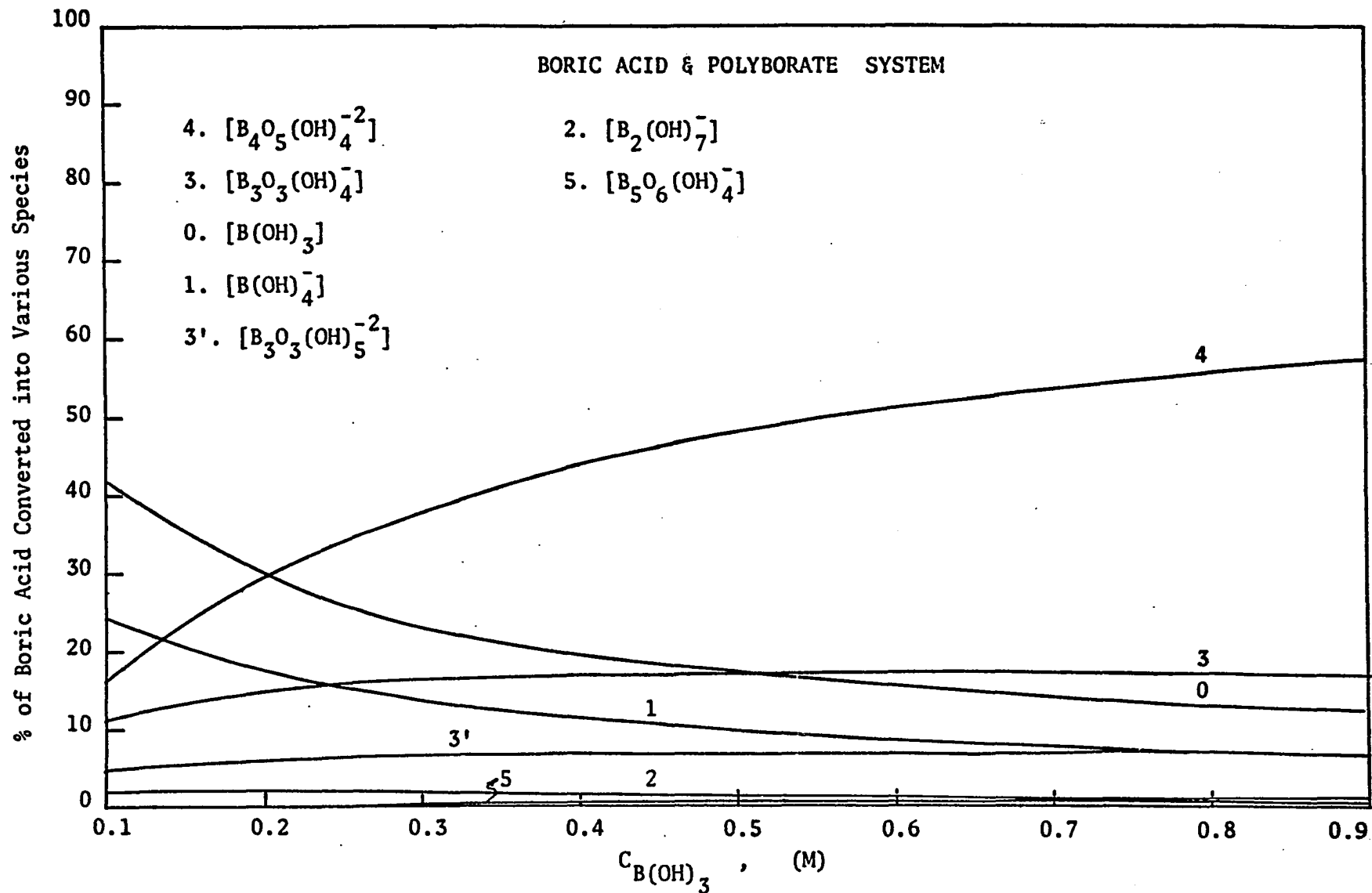


Figure 1-34: The Distribution of Various Species of Boric Acid & Polyborate System at Solution pH=9.0

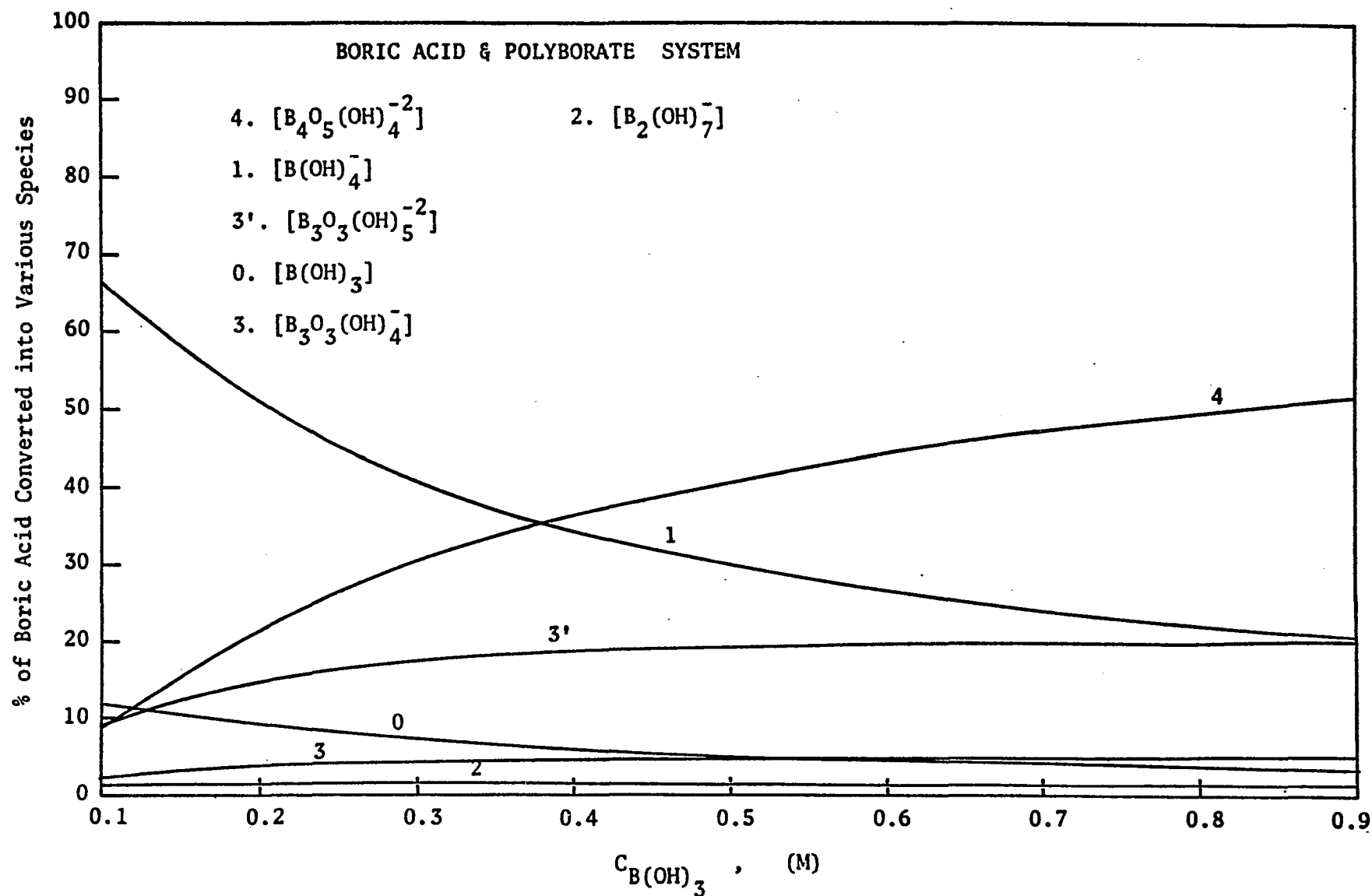


Figure 1-35: The Distribution of Various Species of Boric Acid & Polyborate System at Solution pH=10.0

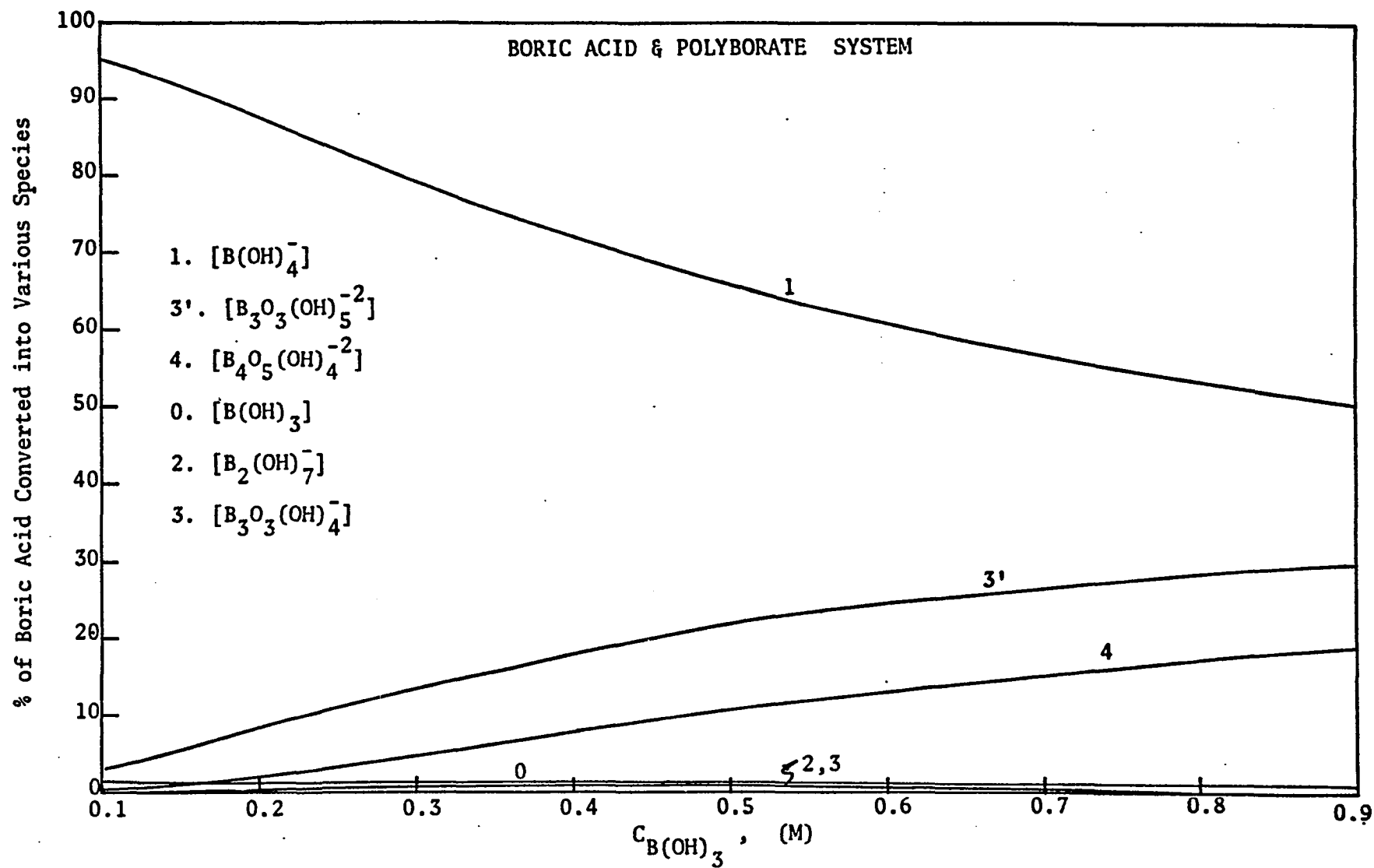


Figure 1-36: The Distribution of Various Species of Boric Acid & Polyborate System at Solution pH=11.0

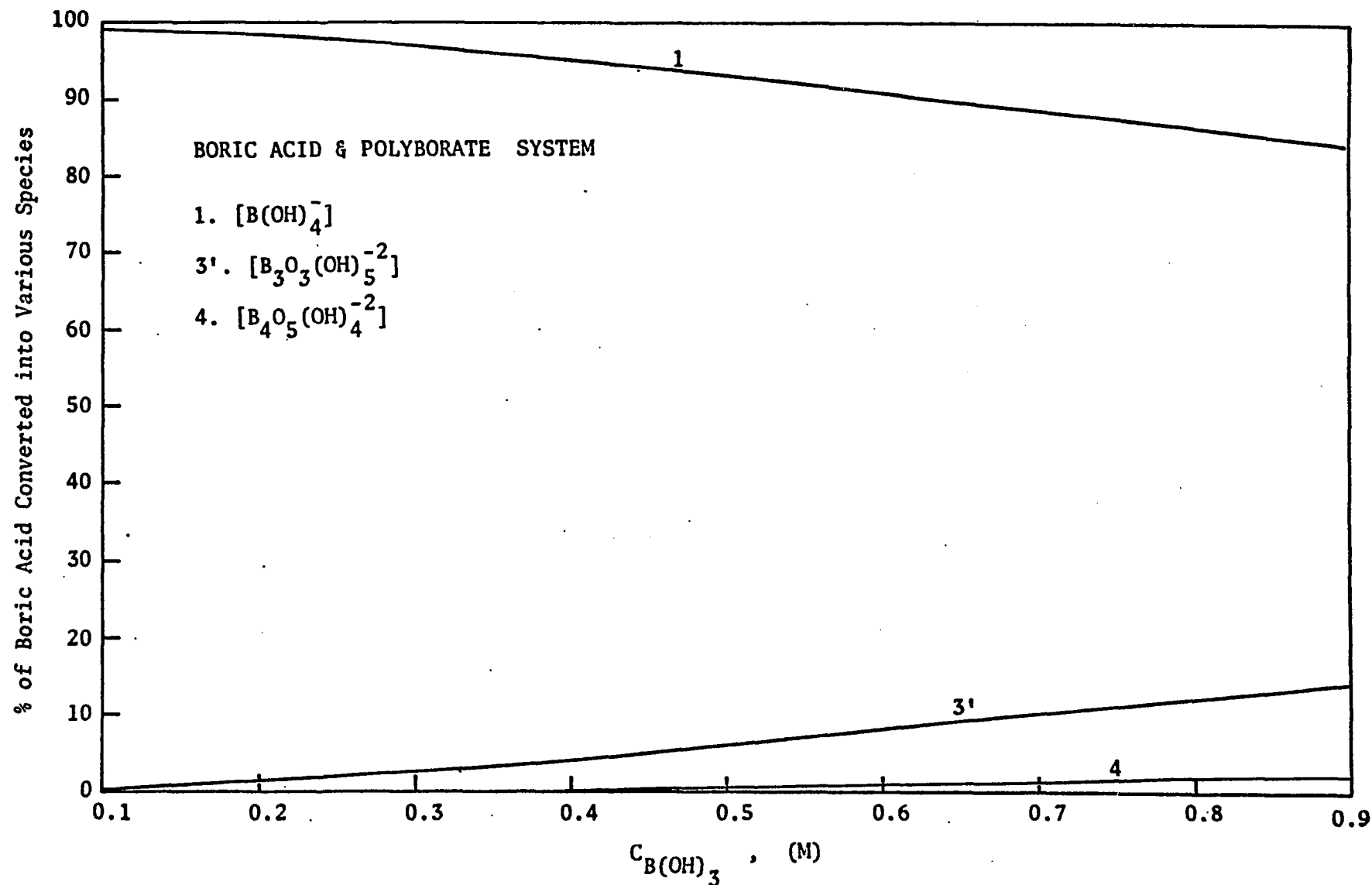


Figure 1-37: The Distribution of Various Species of Boric Acid & Polyborate System at Solution pH=12.0

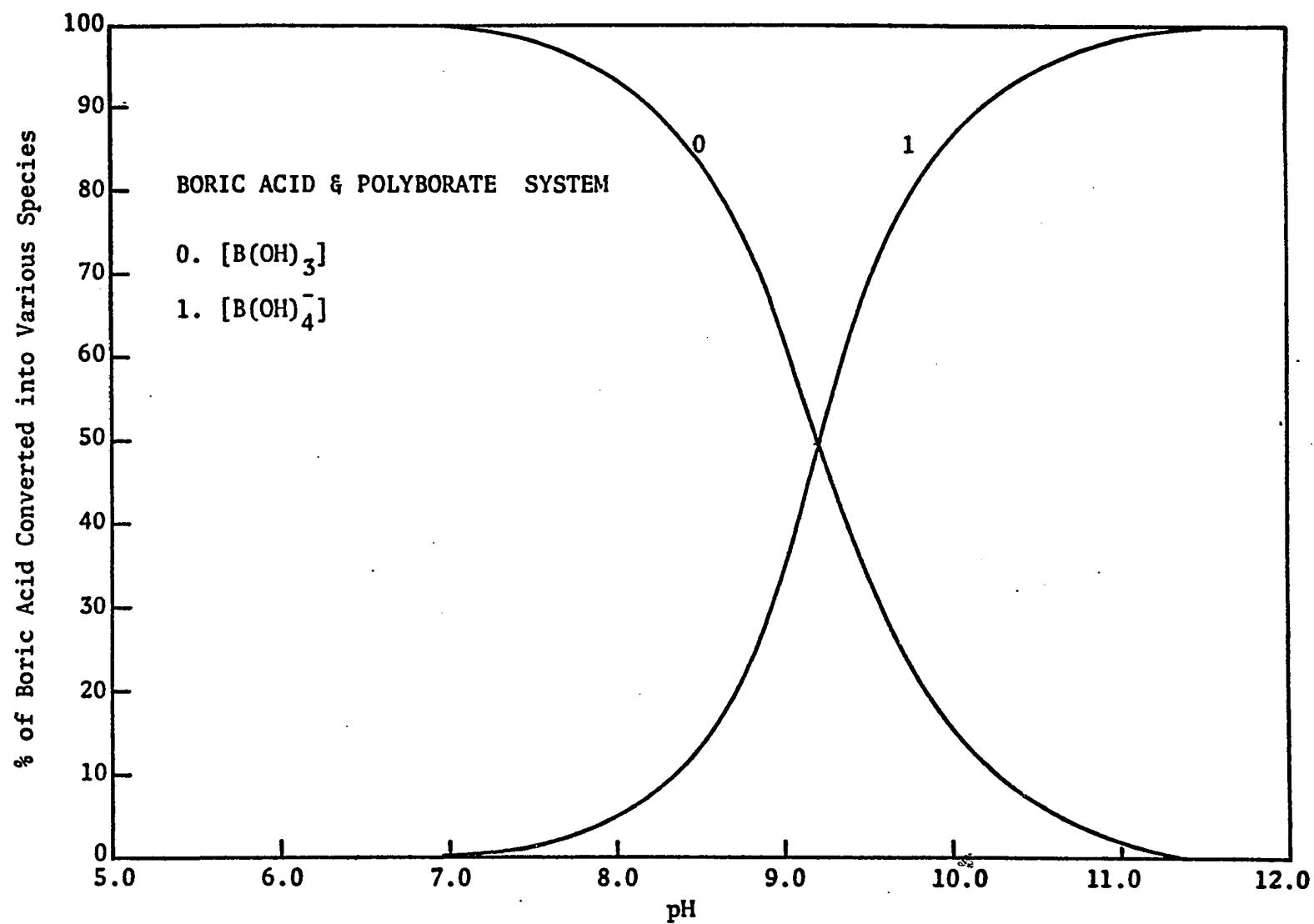


Figure 1-38: The Distribution of Various Species of Boric Acid & Polyborate System at Total Boric Acid Concentration of 4.4×10^{-4} M

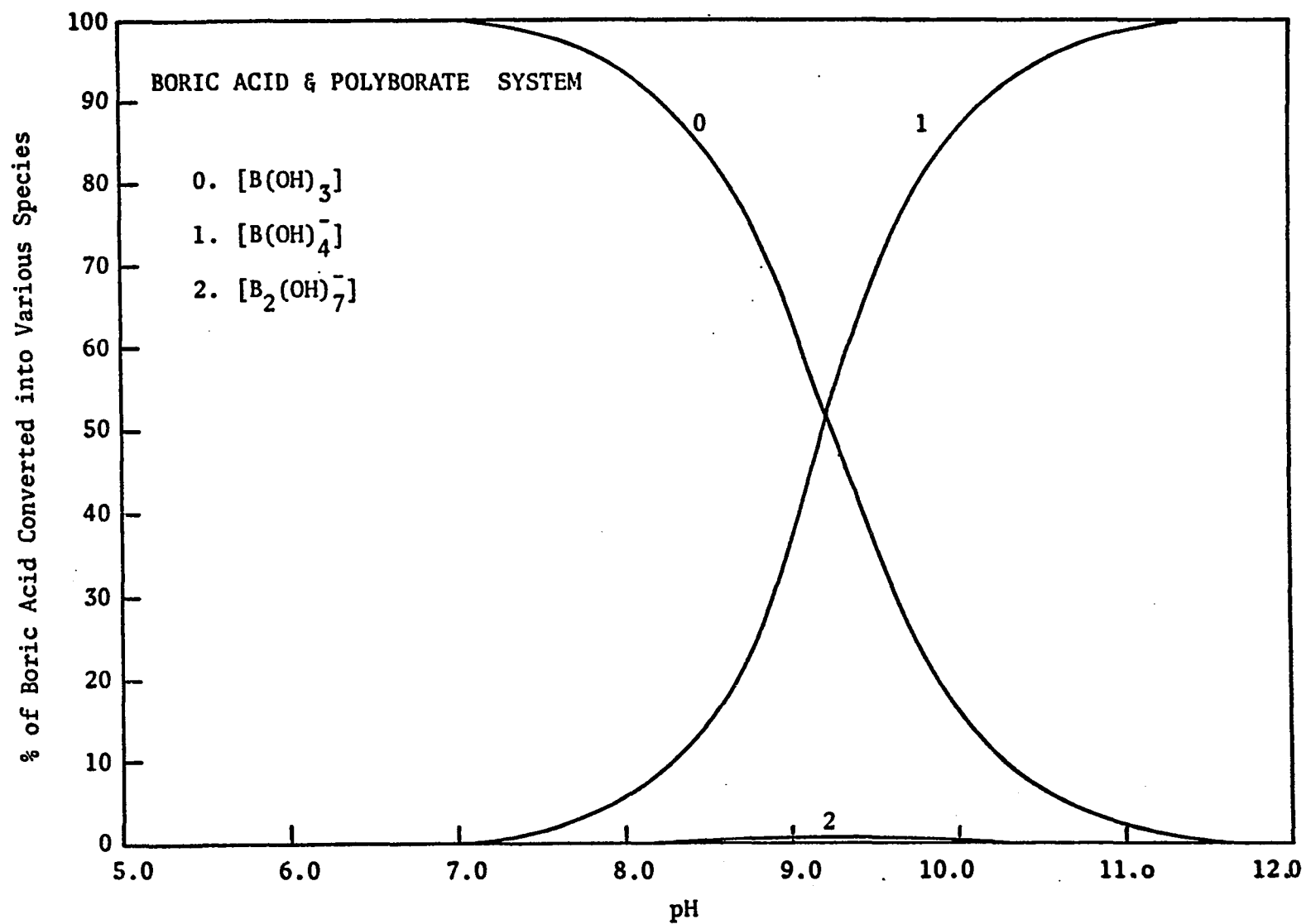


Figure 1-39: The Distribution of Various Species of Boric Acid & Polyborate System at Total Boric Acid Concentration of 4.4×10^{-3} M

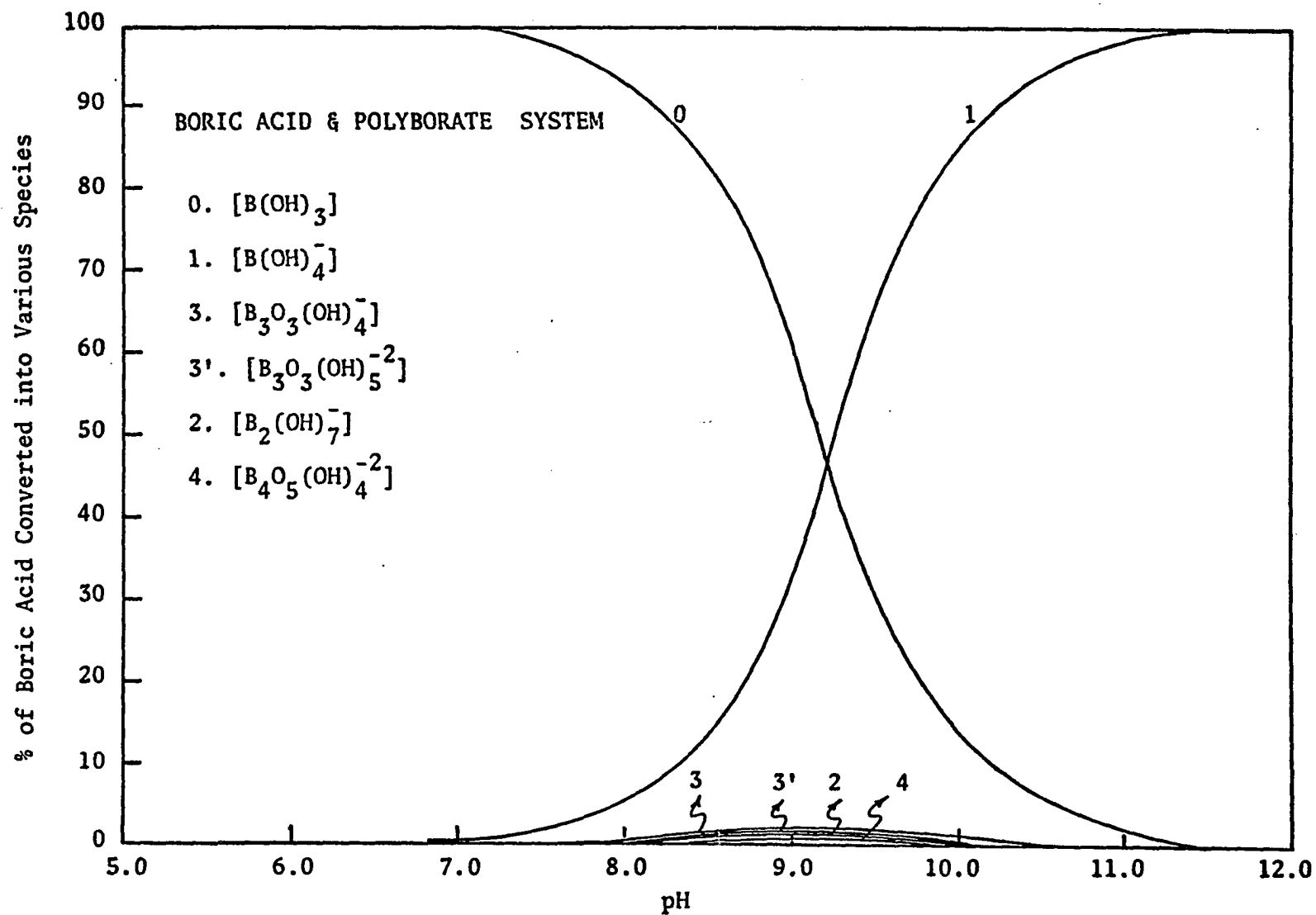


Figure 1-40: The Distribution of Various Species of Boric Acid & Polyborate System at Total Boric Acid Concentration of 0.025 M

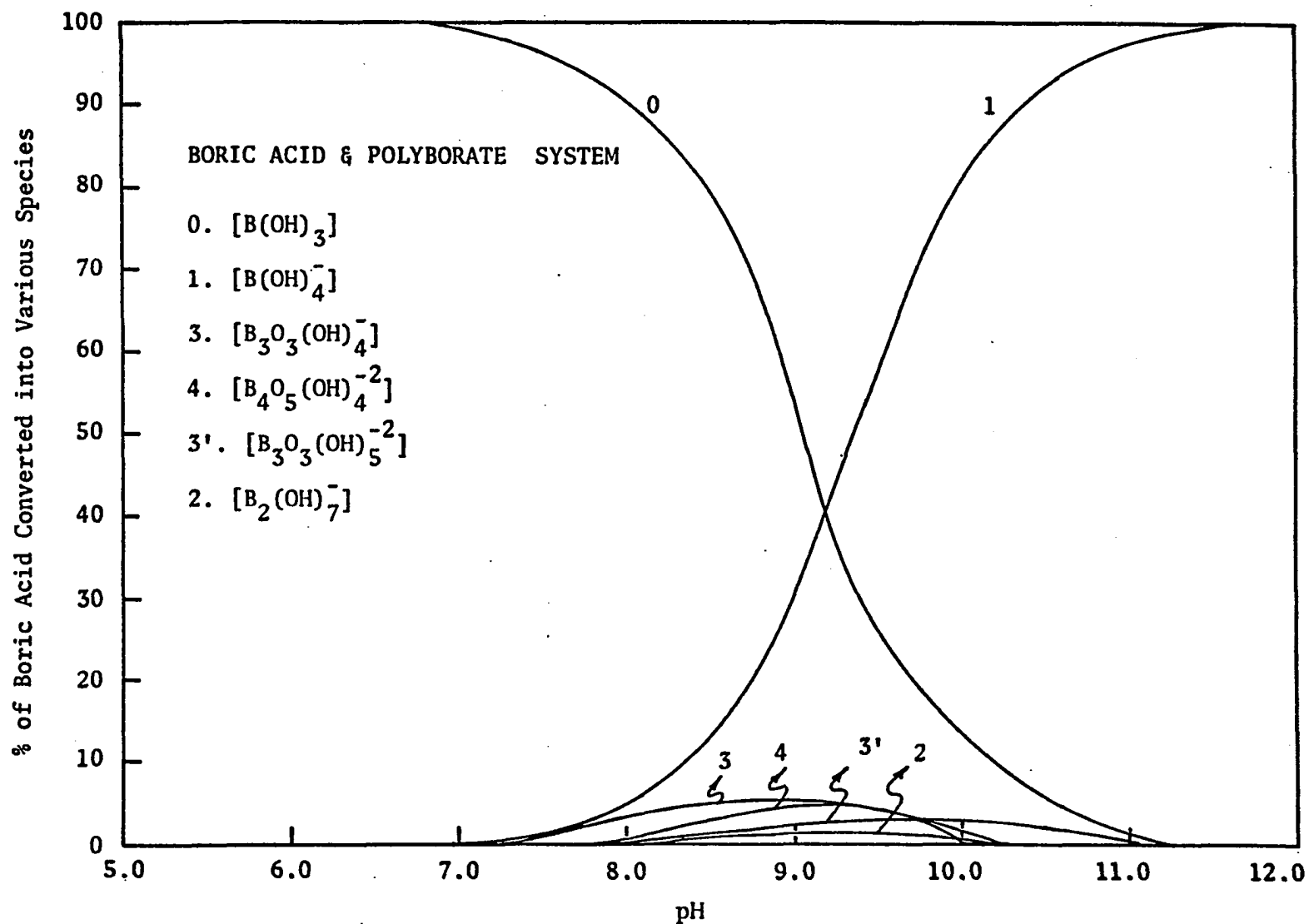


Figure 1-41: The Distribution of Various Species of Boric Acid & Polyborate System at Total Boric Acid Concentration of 0.05 M

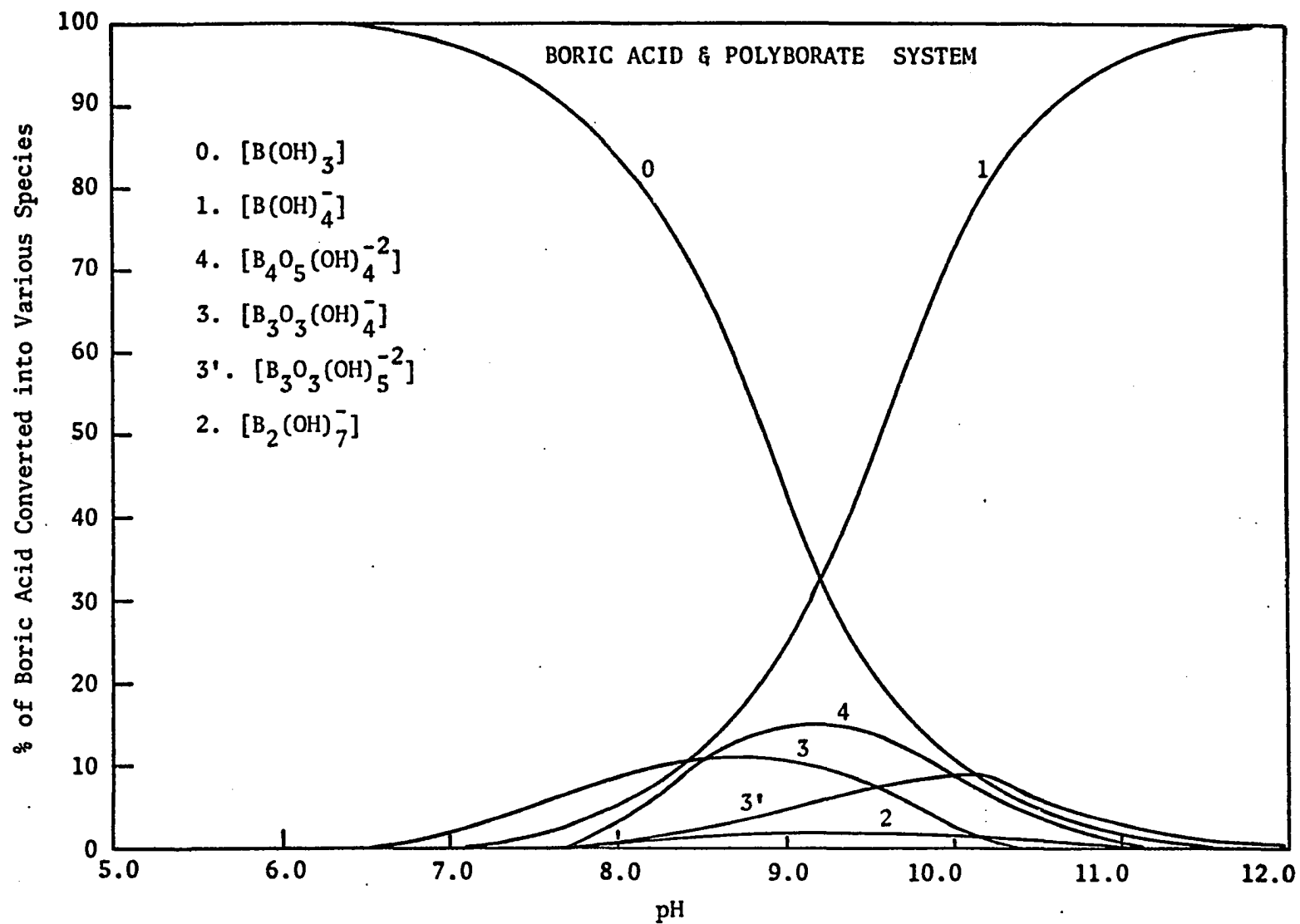


Figure 1-42: The Distribution of Various Species of Boric Acid & Polyborate System at Total Boric Acid Concentration of 0.1 M

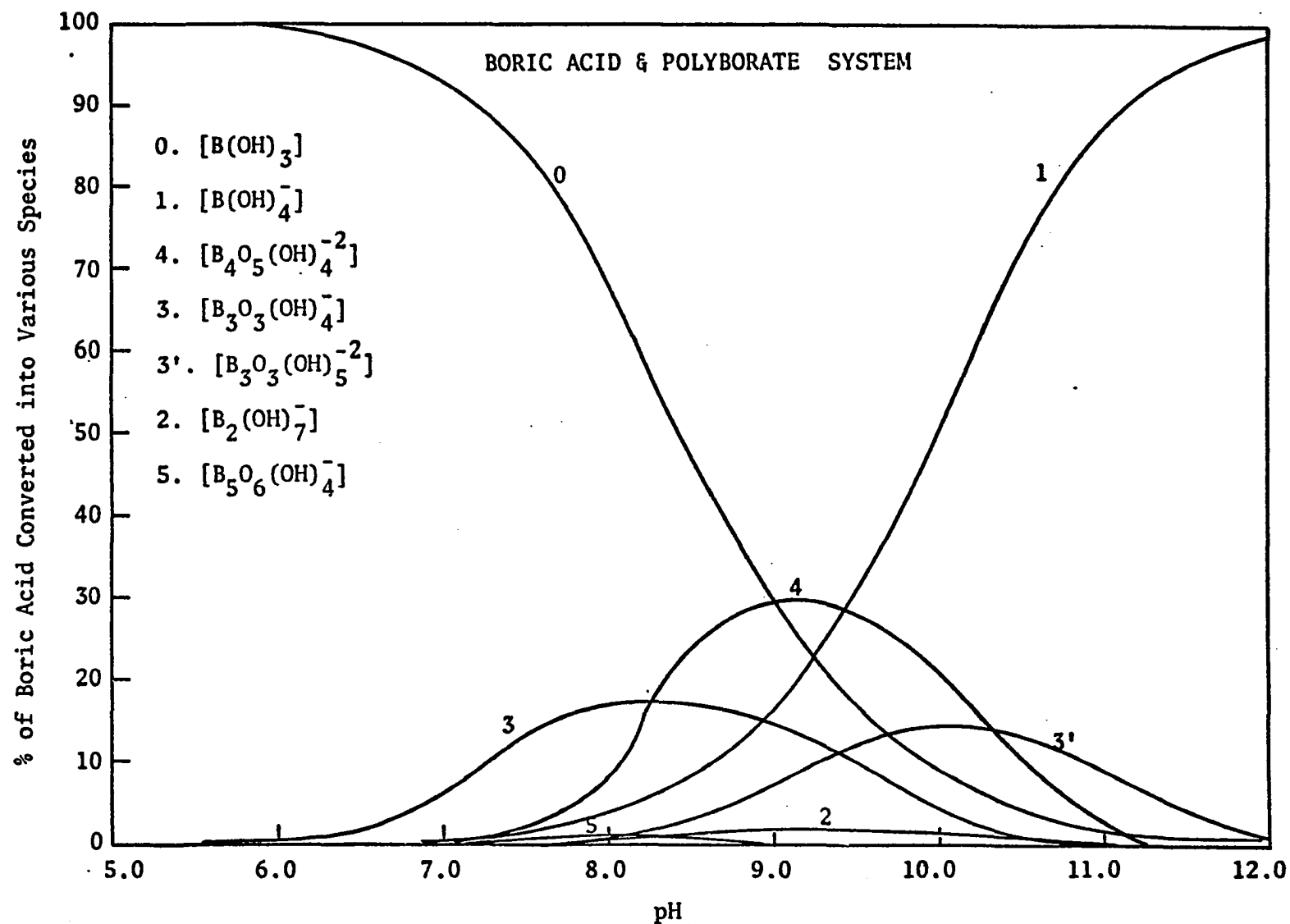


Figure 1-43: The Distribution of Various Species of Boric Acid & Polyborate System at Total Boric Acid Concentration of 0.2 M

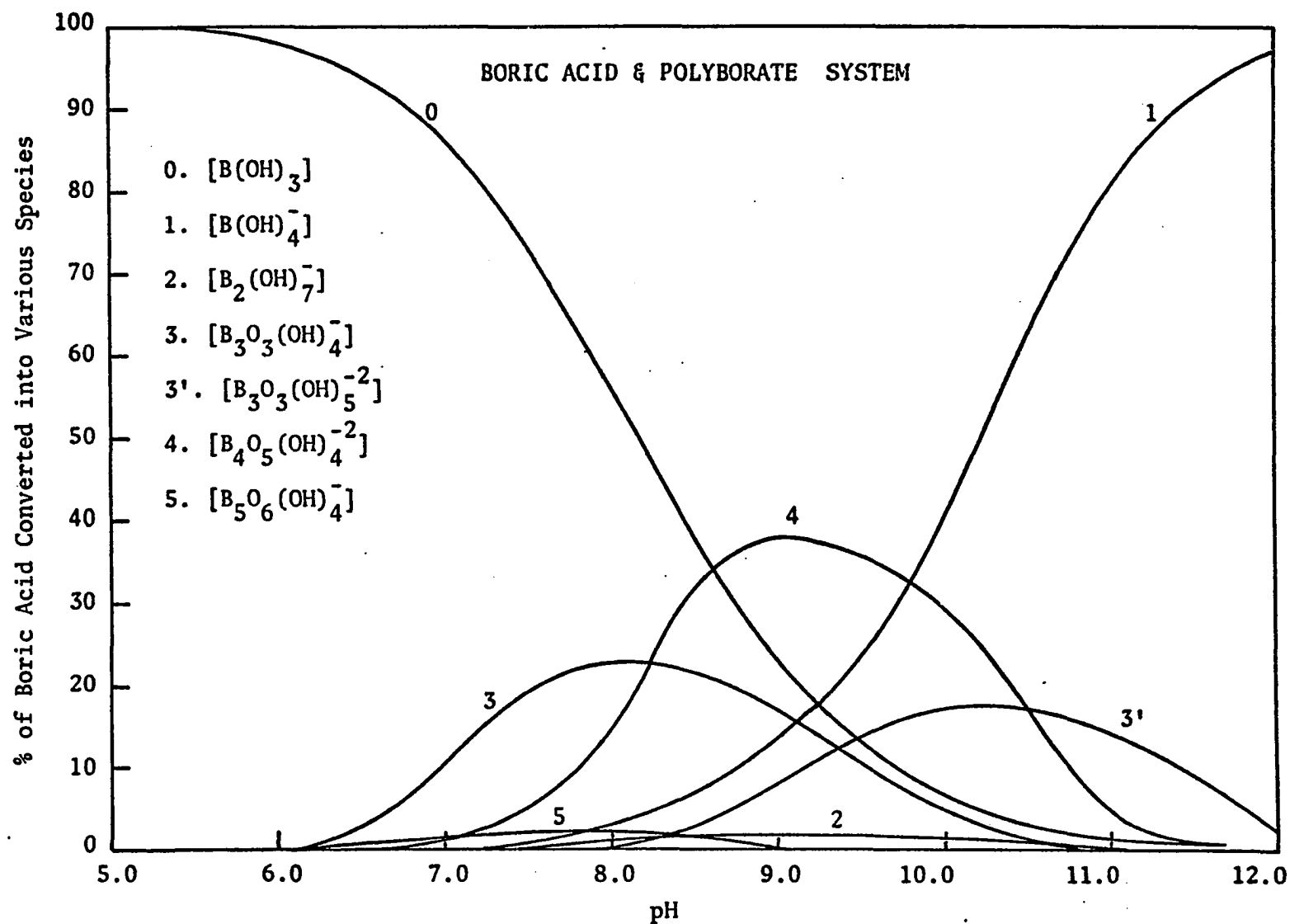


Figure 1-44: The Distribution of Various Species of Boric Acid & Polyborate System at Total Boric Acid Concentration of 0.3 M

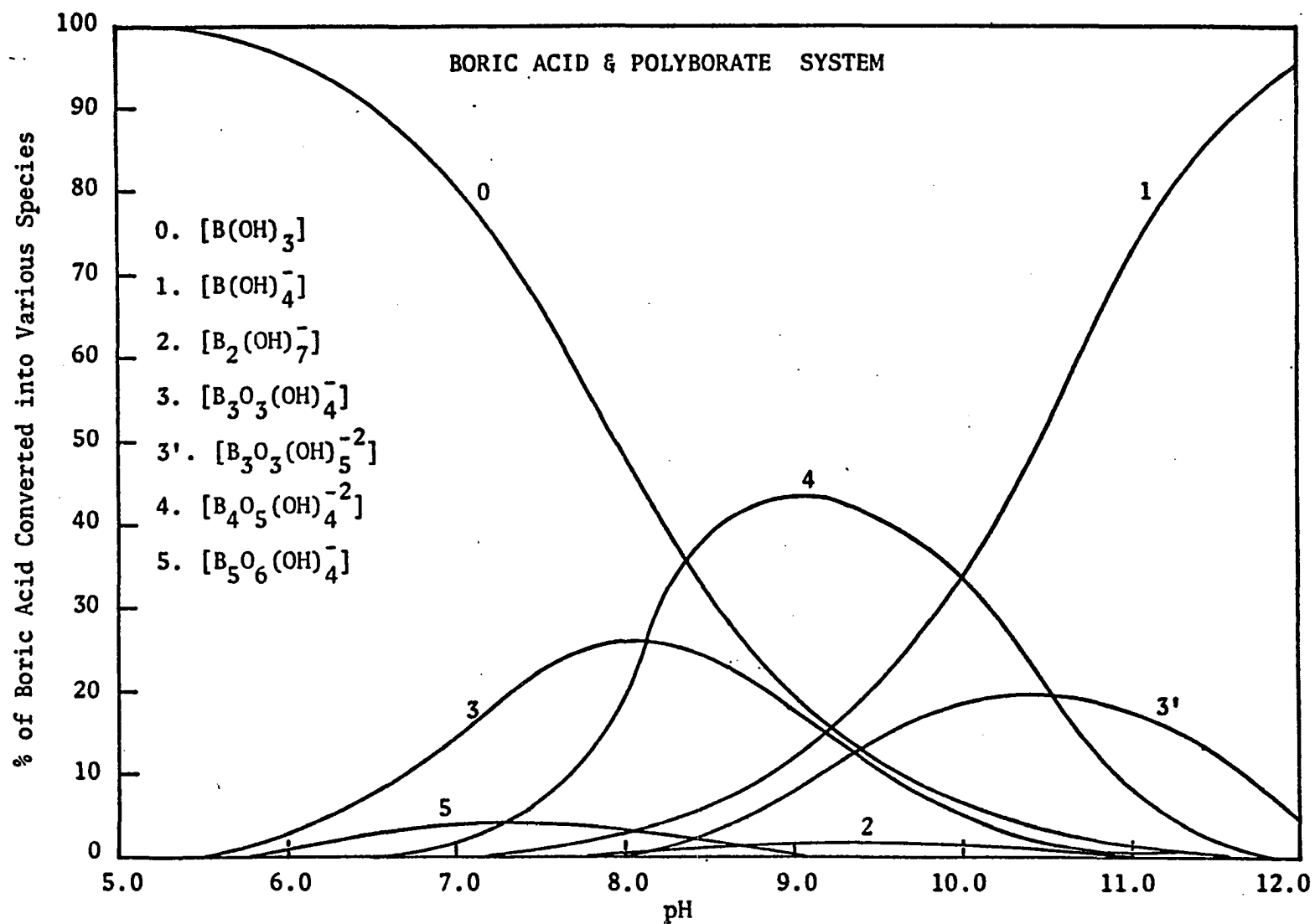


Figure 1-45: The Distribution of Various Species of Boric Acid & Polyborate System at Total Boric Acid Concentration of 0.4 M

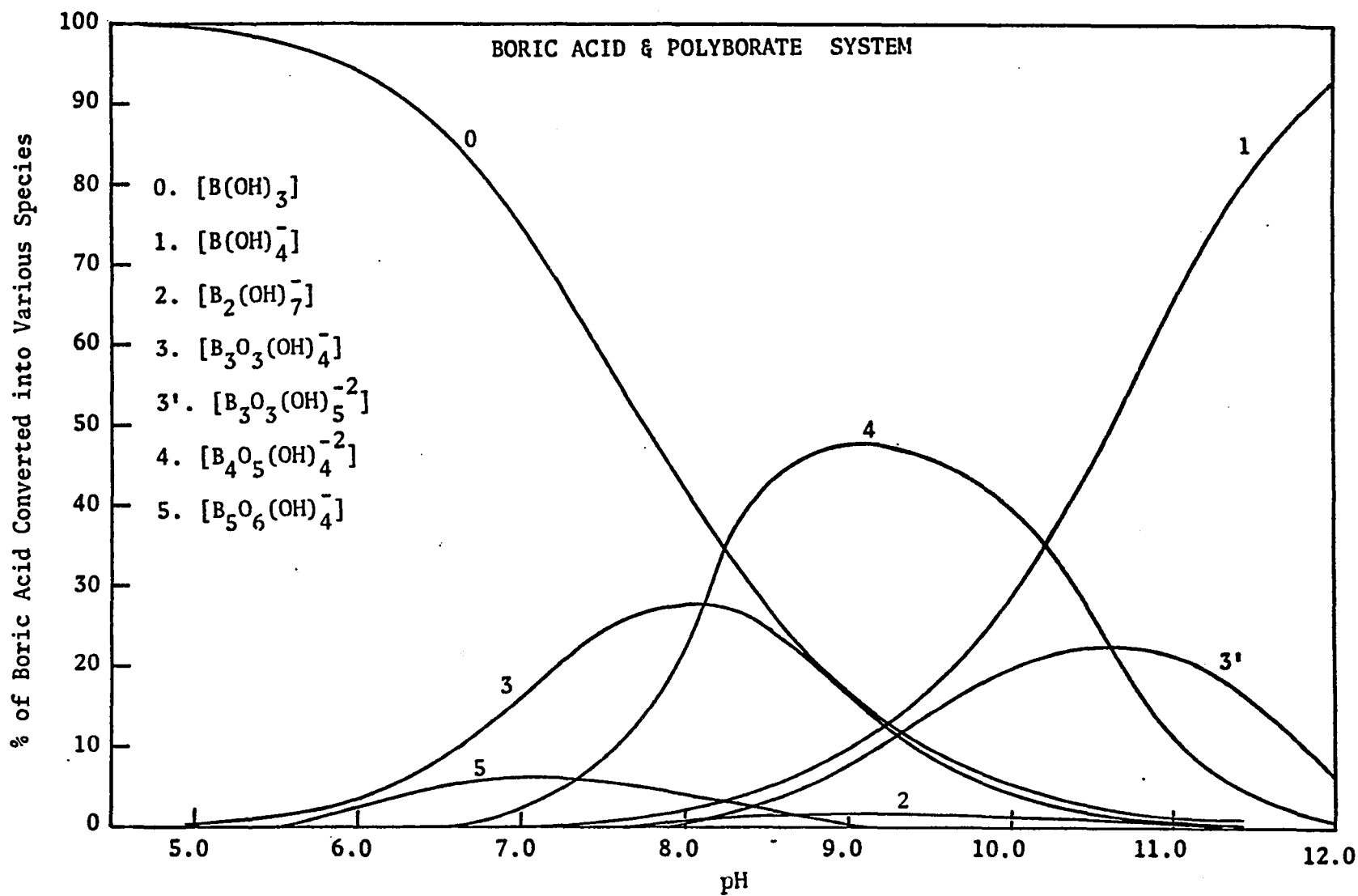


Figure 1-46: The Distribution of Various Species of Boric Acid & Polyborate System at Total Boric Acid Concentration of 0.5 M

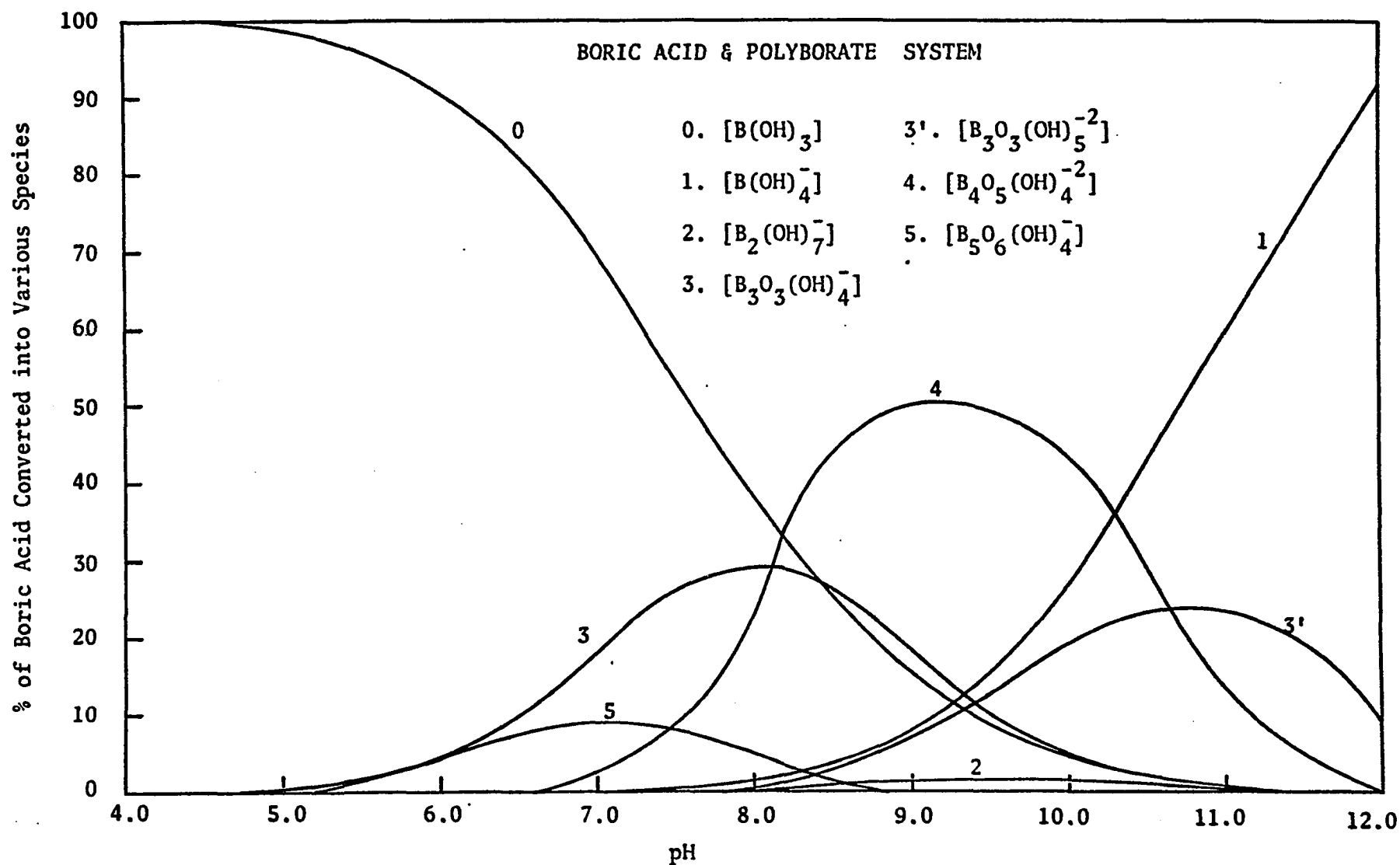


Figure 1-47: The Distribution of Various Species of Boric Acid & Polyborate System at Total Boric Acid Concentration of 0.6 M

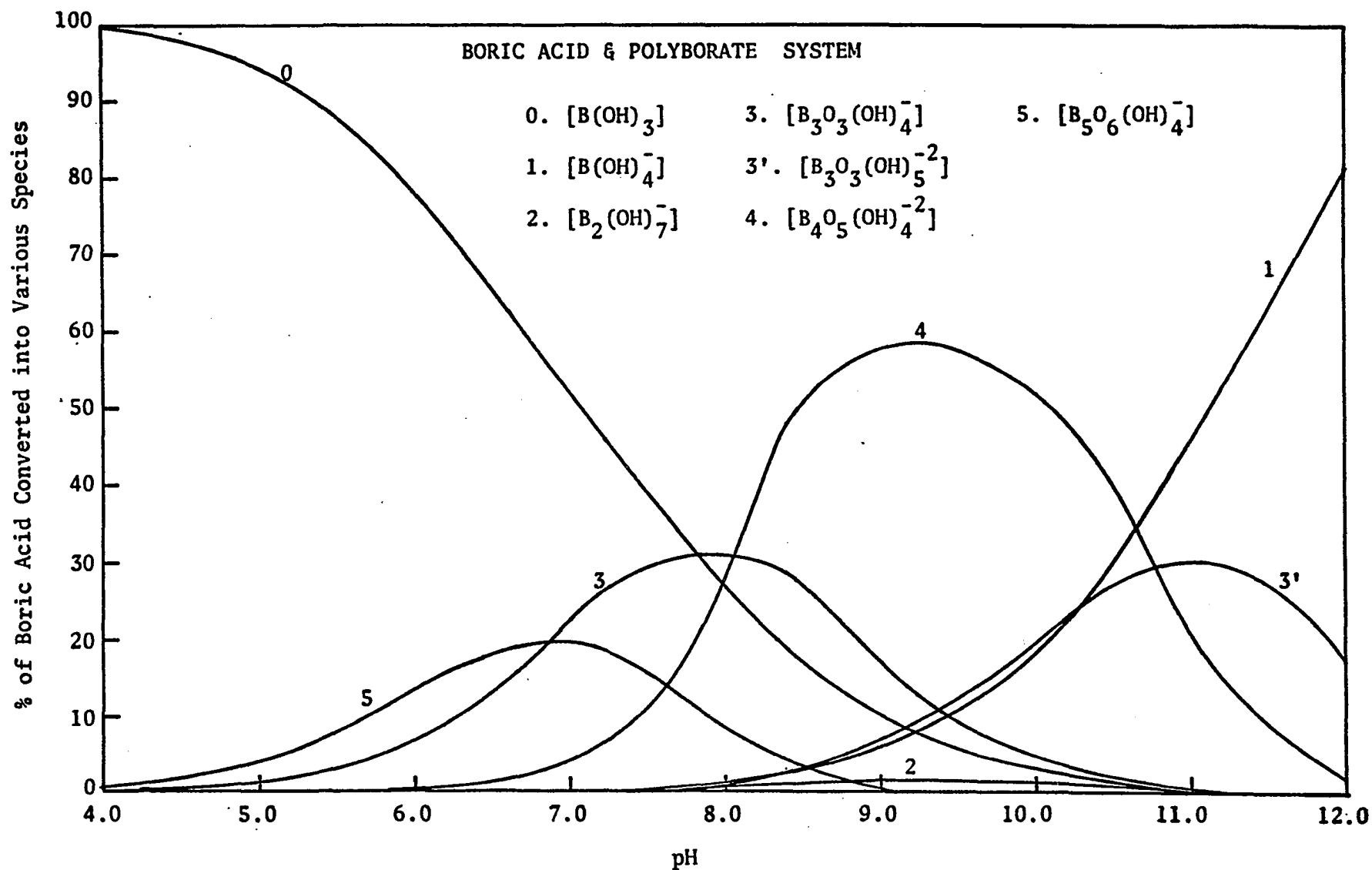


Figure 1-48: The Distribution of Various Species of Boric Acid & Polyborate System at Total Boric Acid Concentration of 1.0 M

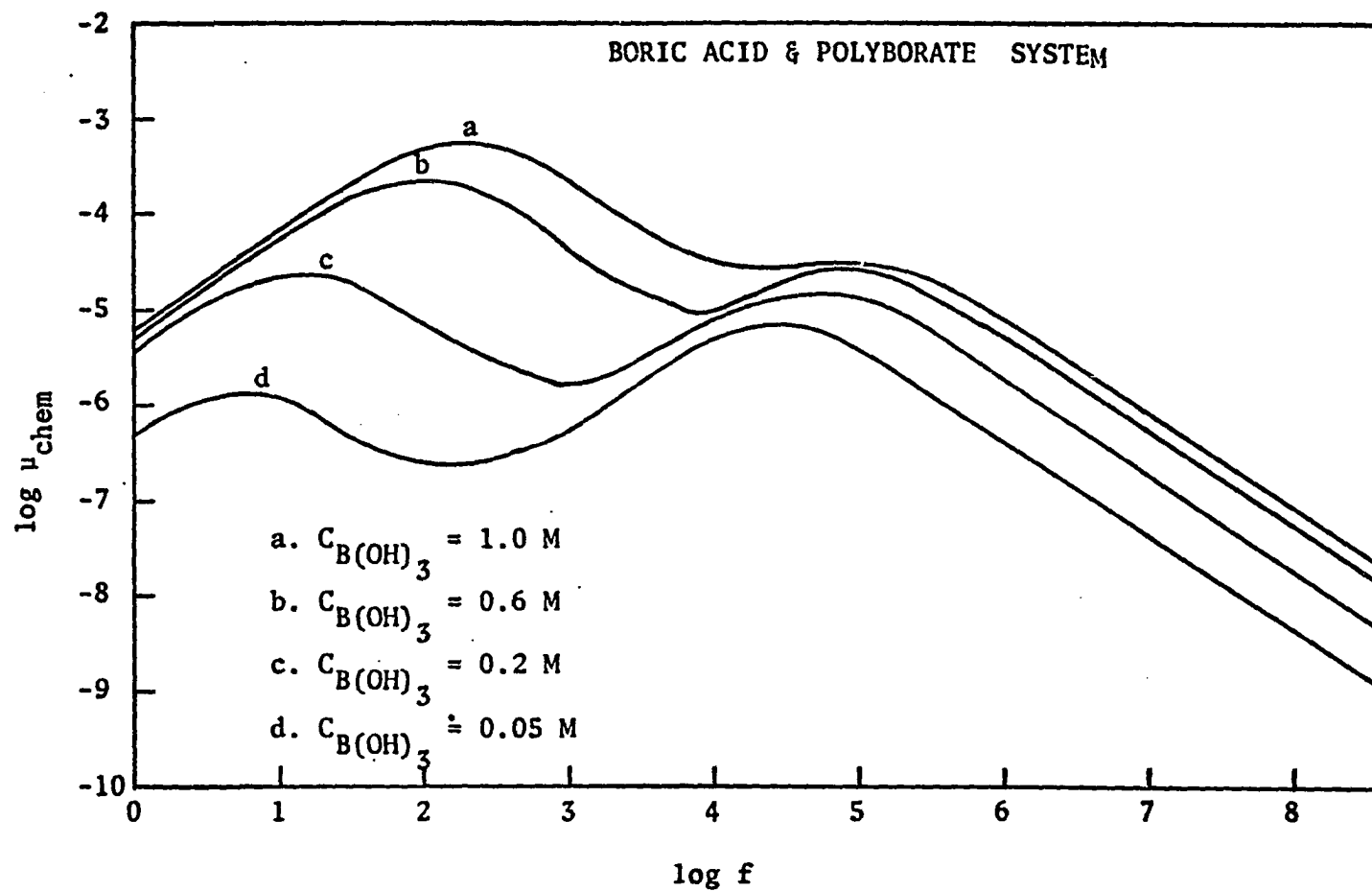


Figure 1-49: The Relaxation Spectra of Boric Acid & Polyborate System at Solution pH=5.0

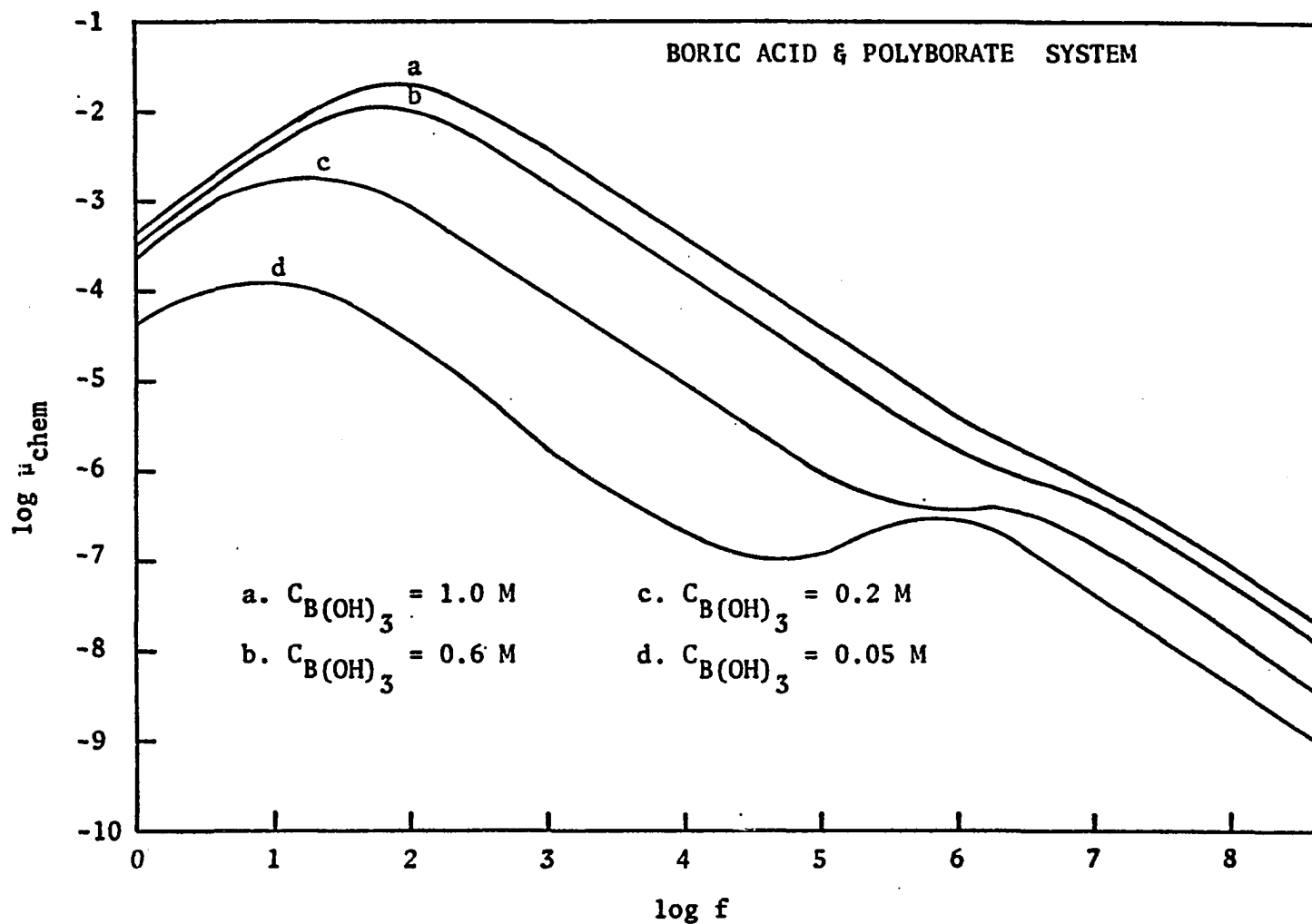


Figure 1-50: The Relaxation Spectra of Boric Acid & Polyborate System at Solution pH=7.0

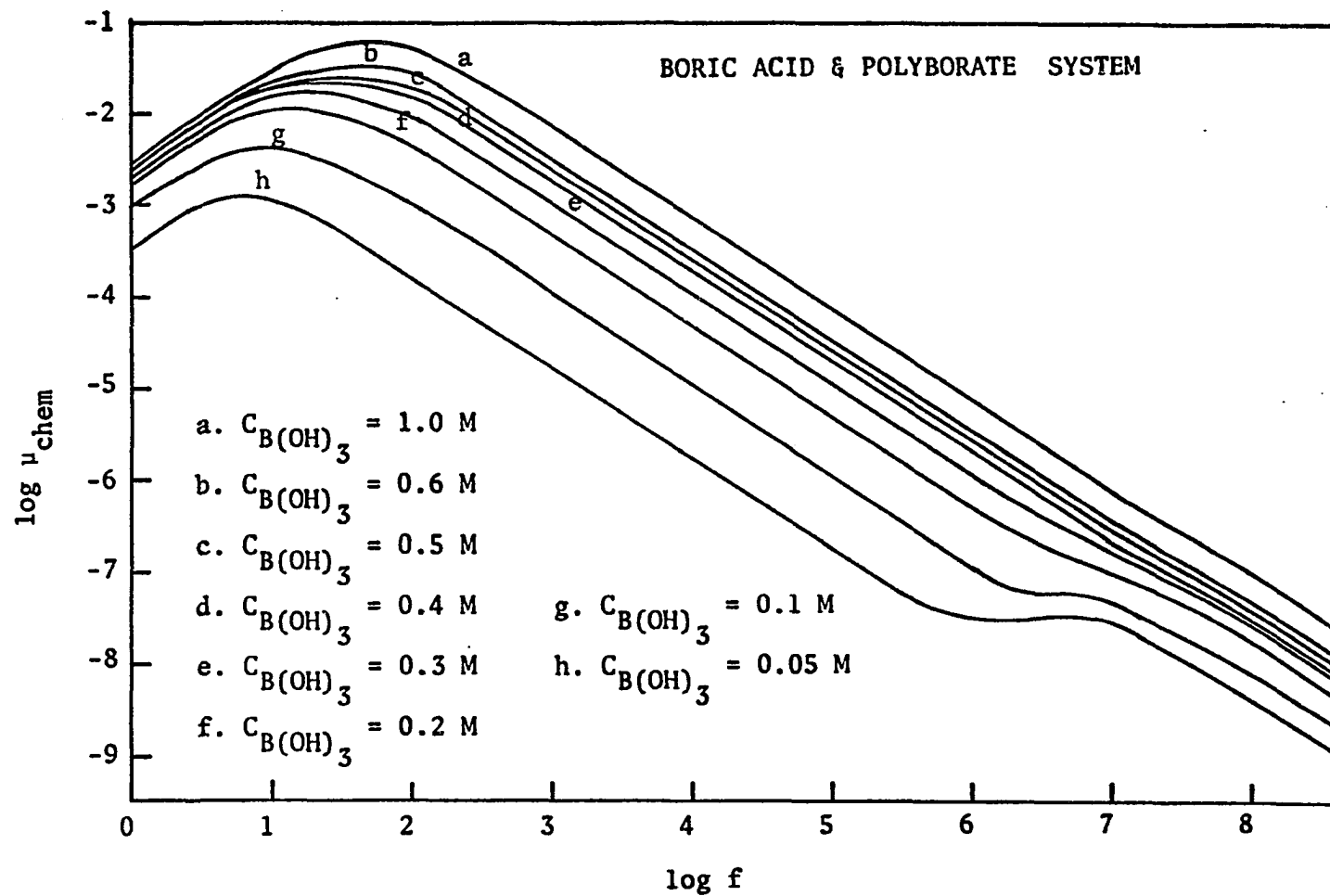


Figure 1-51: The Relaxation Spectra of Boric Acid & Polyborate System at Solution pH=8.0

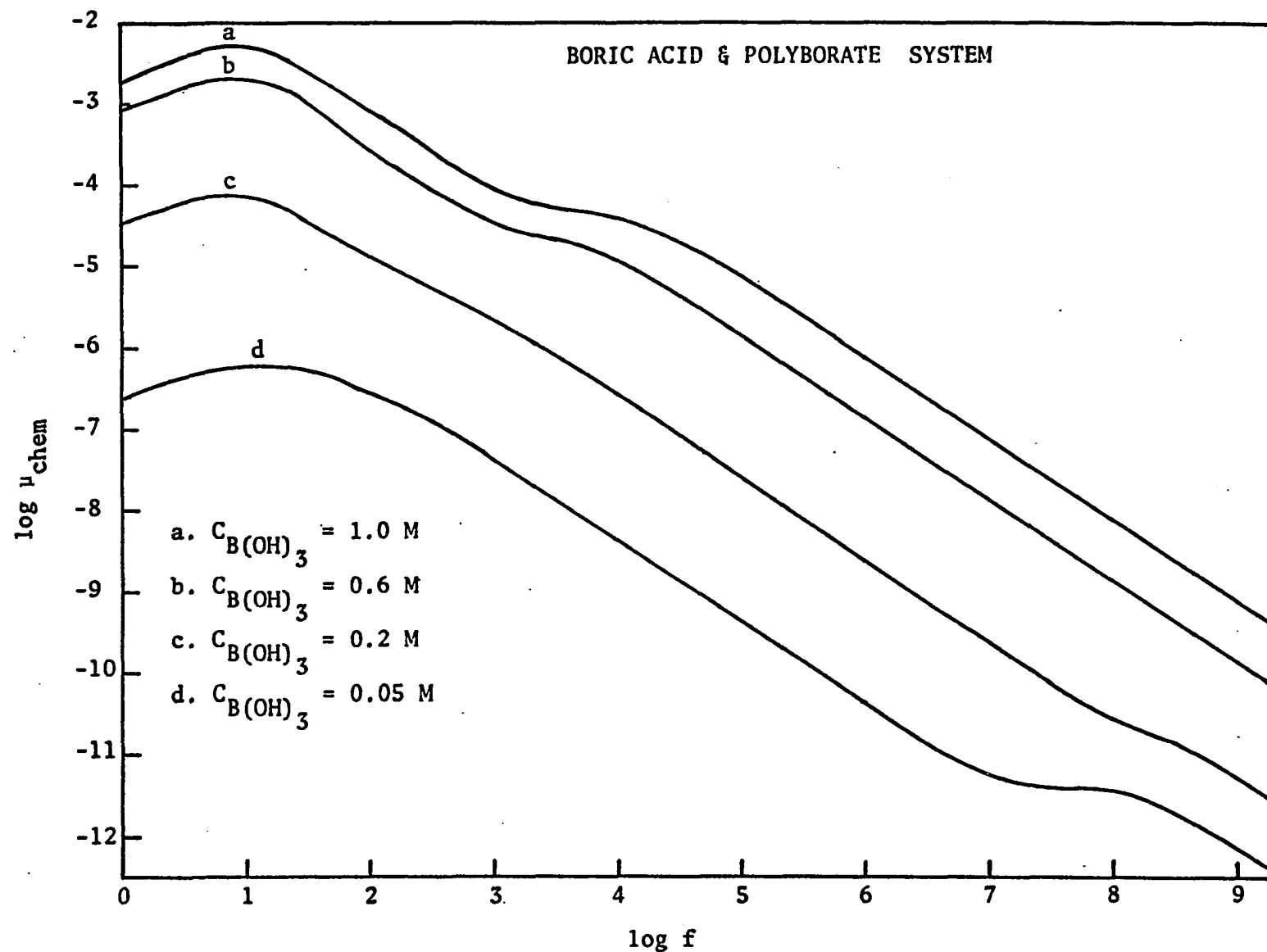


Figure 1-52: The Relaxation Spectra of Boric Acid & Polyborate System at Solution pH= 12.0

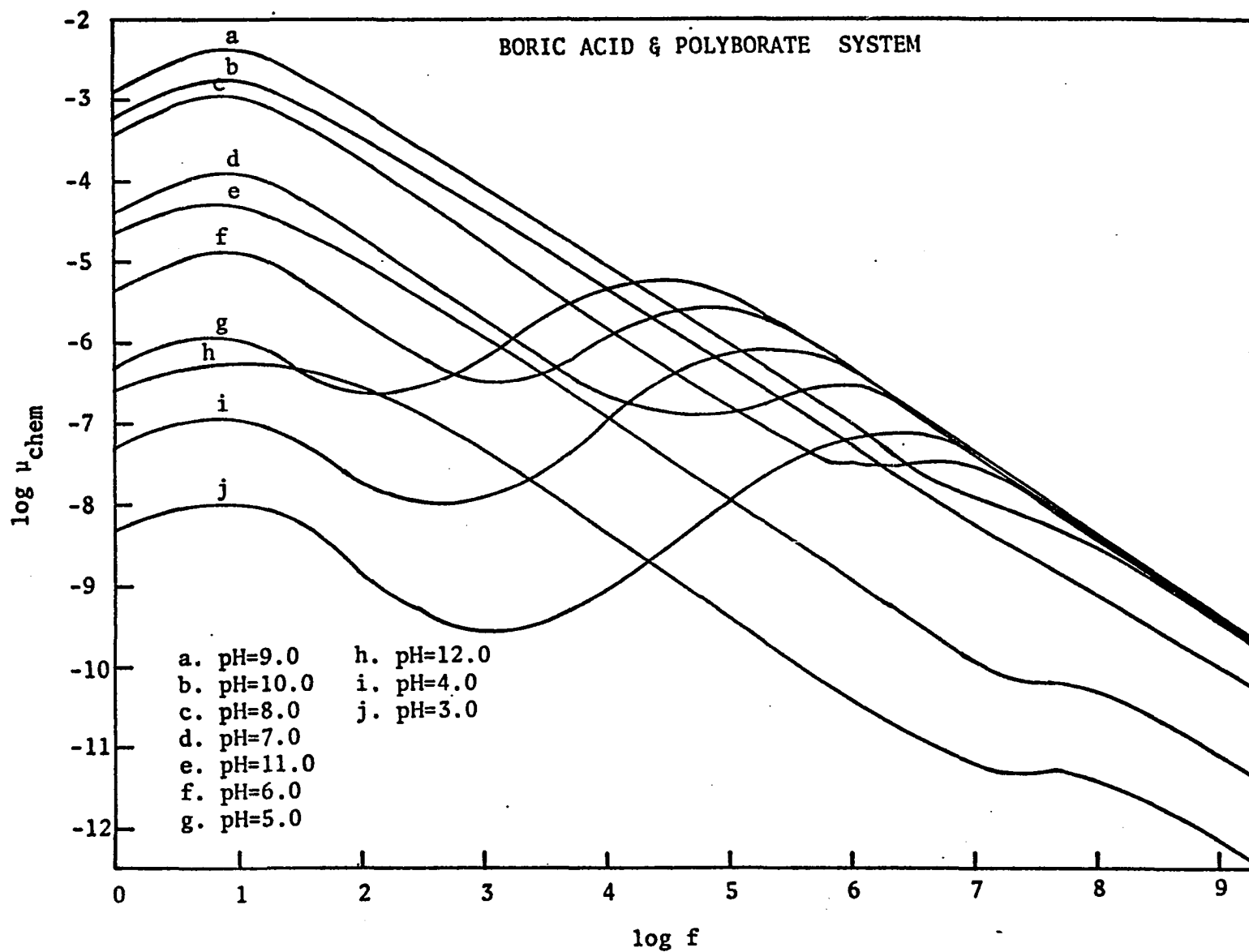


Figure 1-53: The Relaxation Spectra of Boric Acid & Polyborate System at Total Boric Acid Concentration of 0.05 M

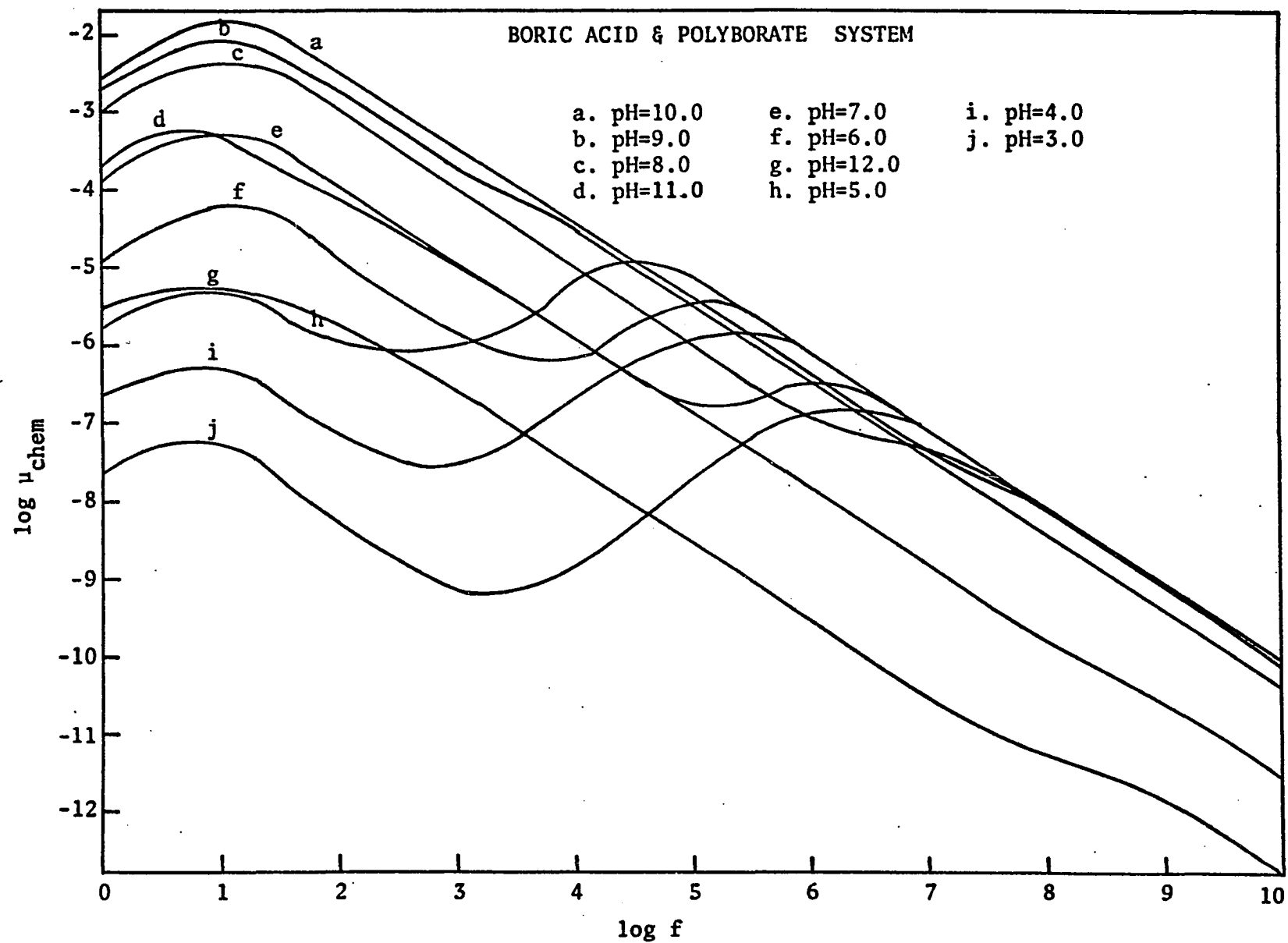


Figure 1-54: The Relaxation Spectra of Boric Acid & Polyborate System at Total Boric Acid Concentration of 0.1 M

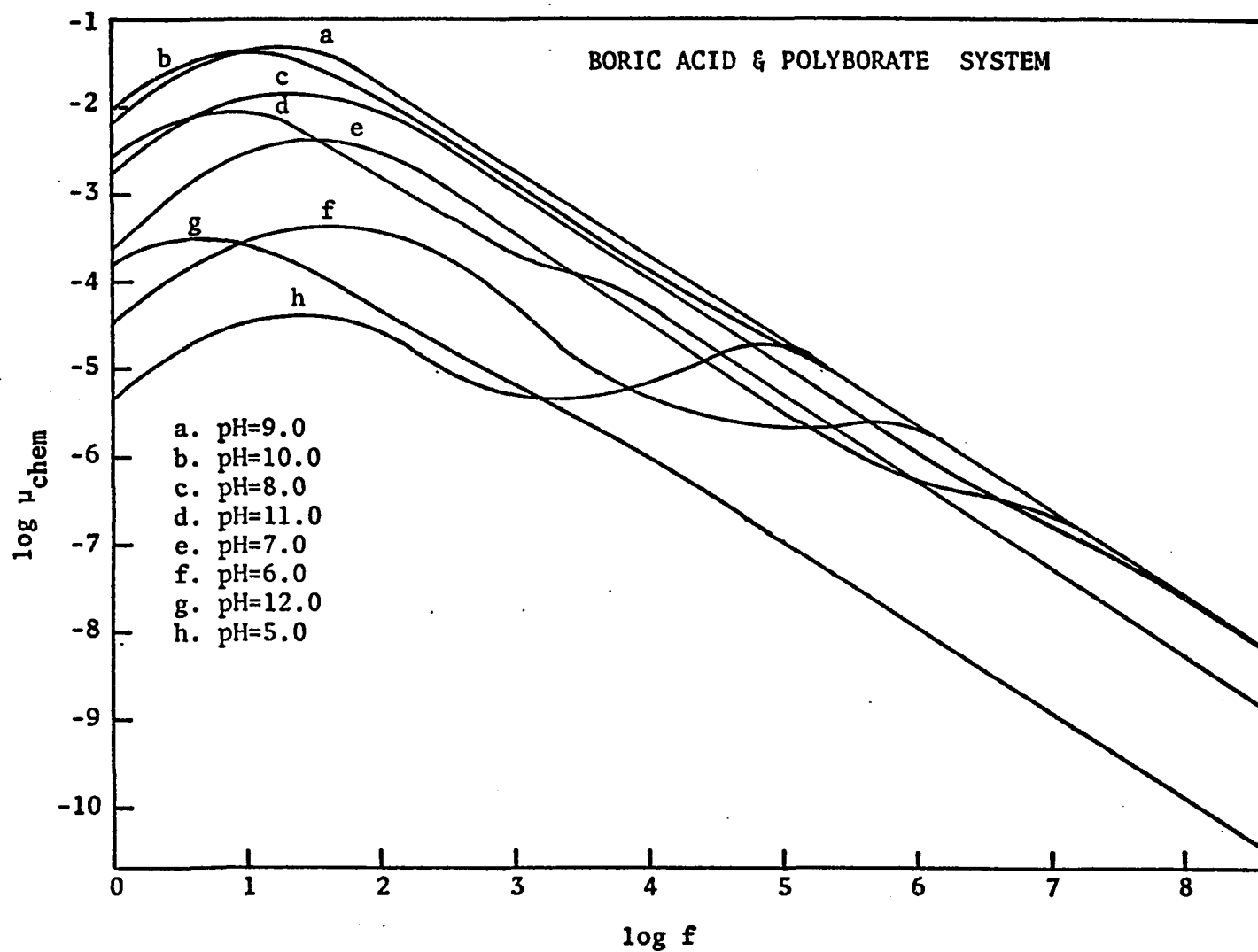


Figure 1-55: The Relaxation Spectra of Boric Acid & Polyborate System at Total Boric Acid Concentration of 0.3 M

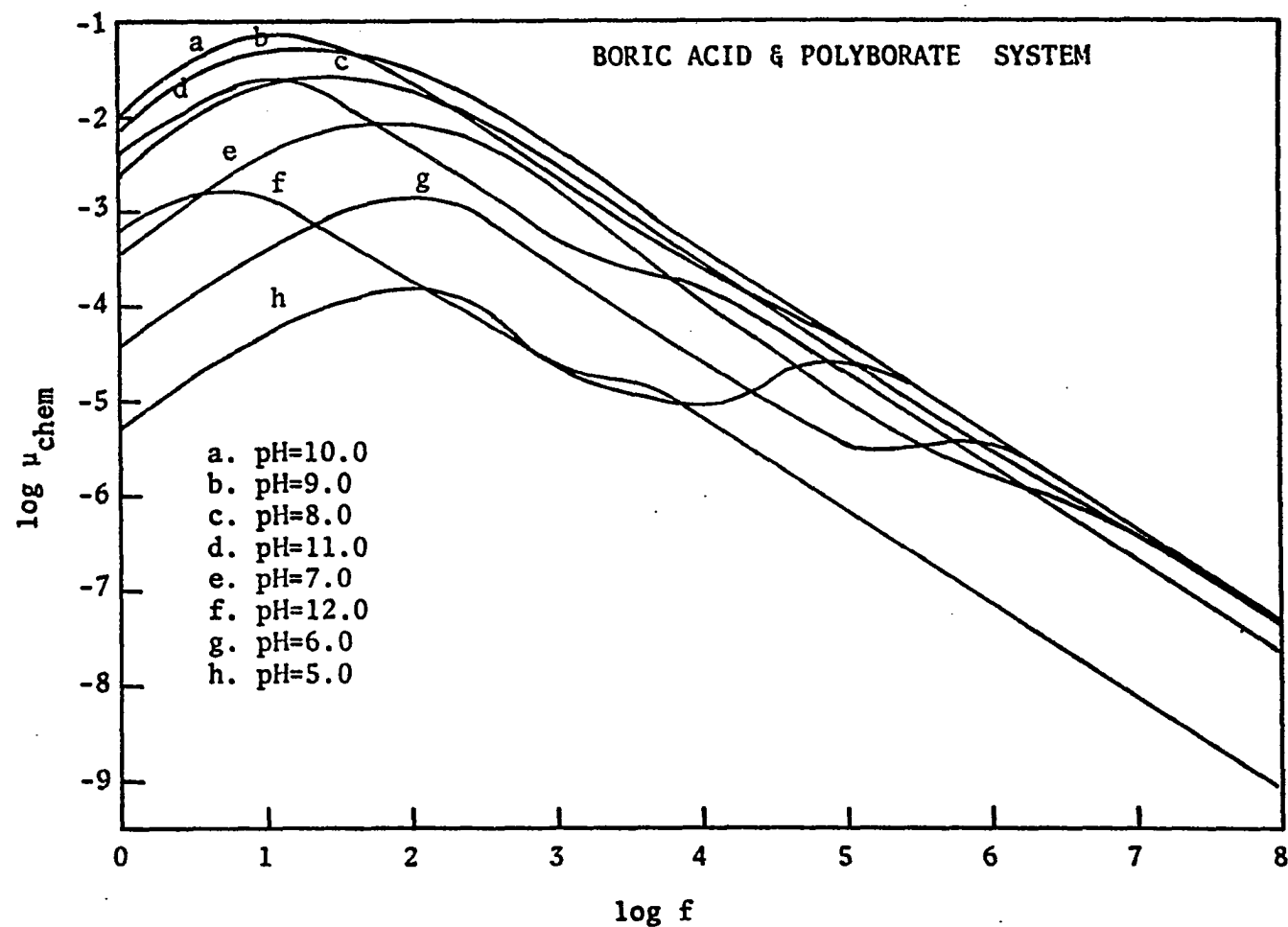


Figure 1-56: The Relaxation Spectra of Boric Acid & Polyborate System at Total Boric Acid Concentration of 0.5 M

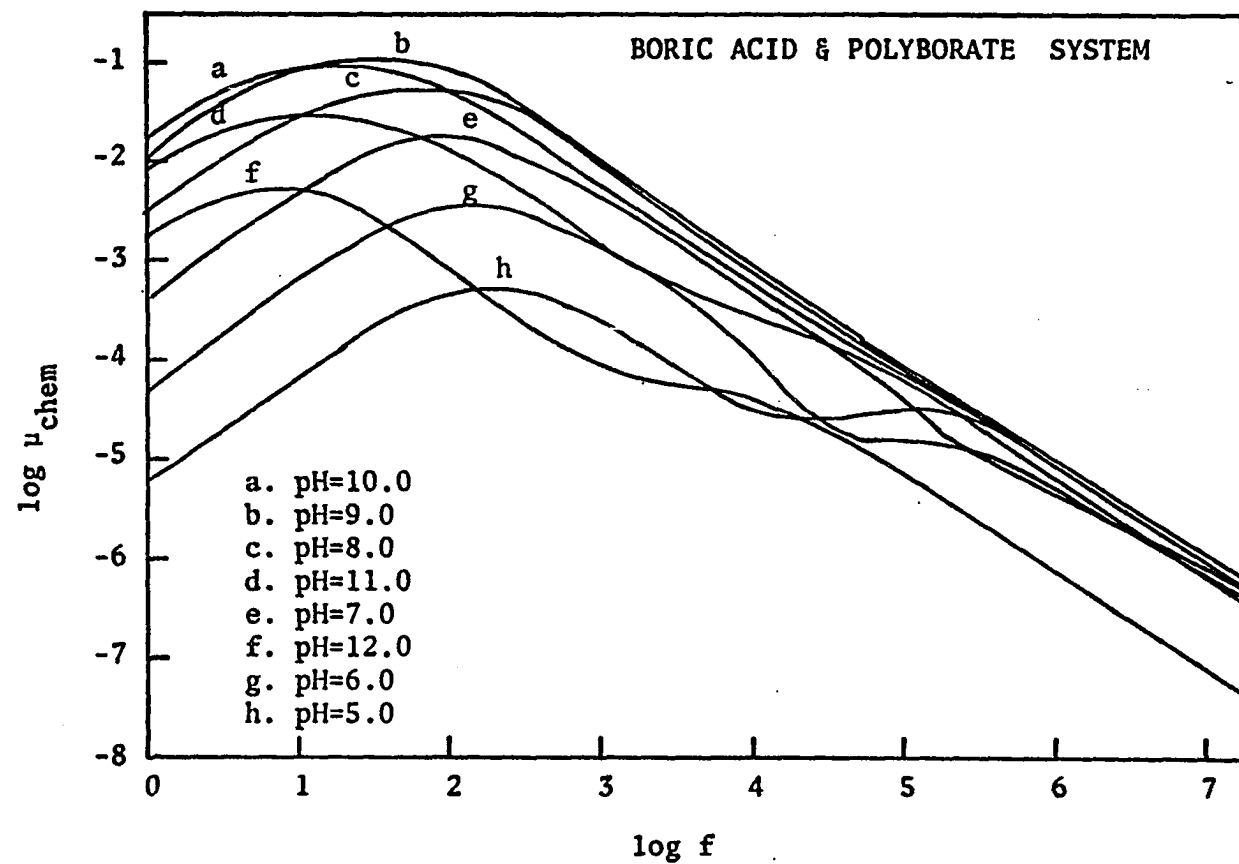


Figure 1-57: The Relaxation Spectra of Boric Acid & Polyborate System at Total Boric Acid Concentration of 1.0 M

D. Concluding Remarks:

For accurate ultrasonic measurements of a chemically reacting system in our laboratory, the relaxation frequency of the system should be higher than 500 KHz, and the excess sound absorption, α' , should be greater than 0.5 dB/cm. For the boric acid system, the boric acid-sodium borate system, and the boric acid-polyborate system, although theoretical studies can be accomplished, the experimental measurements using ultrasonic relaxation technique are not practical due to either too low a relaxation frequency value or too small an excess sound absorption value, or both. However, some other techniques such as the temperature-jump method can be used to measure the relaxation frequencies. The calculations show that the relaxation frequencies of these systems fall in the low frequency region.

PART II:

ULTRASONIC RELAXATION STUDIES OF
AQUEOUS BORIC ACID, AND
BORIC ACID-POLYBORATE SYSTEM BY THE
REGULAR ULTRASONIC PULSE ABSORPTION METHOD

I. INTRODUCTION:

For a few decades, ultrasound has been used as a measurement tool in fast reaction kinetics. The frequency range reached by ultrasonic measurements ranges from about 10 KHz to more than 2 GHz. To measure over such a wide frequency range, various experimental techniques have been developed and used, such as: resonance (0.1-50 KHz); interferometry or reverberation (50 KHz-2 MHz); optical method (Debye-Sears)(1-100 MHz); pulse method (5-500 MHz, can be extended with a special technique to 2 GHz); and Brillouin scattering technique (10-100 GHz).⁶⁰⁻⁶⁷ The corresponding relaxation times span the range from approximately 10^{-5} to below 10^{-11} sec. Thus ultrasonic relaxation spectroscopy represents an important technique for covering a kinetic time spectrum that is not readily accessible by other means.

The passage of a sound wave through a medium provides a means of perturbing a dynamic equilibrium system by the pressure and temperature variations that accompany the wave. The two parameters that determine ultrasonic wave propagation in liquids are the sound velocity c , and the sound absorption α . Both values are frequency dependent. Thus, it is necessary to measure both quantities over a wide frequency range. However, it is very hard to cover such a wide frequency range in a single experimental technique. Therefore, in most cases it is necessary

to use several different types of apparatus.

Ultrasonic absorption measurements involve the following considerations: generation of ultrasonic vibrations, propagation through a fluid, and detection as a function of distance traveled. At low frequencies (<50 KHz), no observable absorption takes place from a plane wave that travels a distance of several meters, whereas, at high frequencies (>100 MHz), practically all the energy is absorbed after a few mm of propagation. Thus, the volume of liquid required is quite small for the high frequency pulse technique, but for most of the lower frequency techniques it is considerable.

In this part of research, the regular ultrasonic pulse absorption technique has been used, which covers a frequency range from 15 MHz to 95 MHz. The reactions studied include the boric acid system and the boric acid-polyborate system.

II. THEORY:

A. Wave Equation:

A sound wave can be treated as a series of compressions and rarefactions travelling along a tube such that molecular planes are displaced from their mean positions. The displacement, ξ , occurs parallel to the direction of the travelling wave and is dependent on position x and time t . That is, $\xi = f(x,t)$

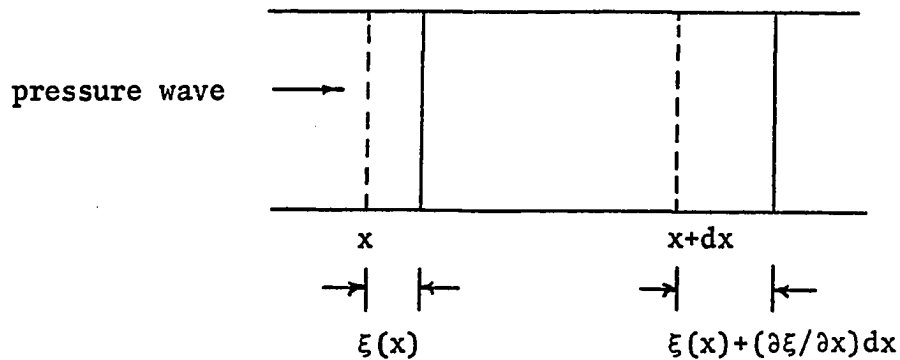


Figure 2-1: Molecular planes displaced by sound wave from equilibrium positions at x and $x+dx$.

Displacement of the fluid contained between the two planes results from a pressure $p+p(x)$ acting in the direction of the wave's progress on the left-hand plane and a pressure $p+p(x)+(\partial p/\partial x)dx$ in the same direction on the right-hand plane. These different pressures on cross-sectional area, s , produce a force which accelerates the mass of fluid.

$$\text{Force} = [p+p(x)]s - [p+p(x)+(\partial p/\partial x)dx]s = -s(\partial p/\partial x)dx \quad (2-1)$$

Also:

$$\begin{aligned} \text{Force} &= (\text{mass}) \times (\text{acceleration}) \\ &= (\rho s dx) (\partial^2 \xi / \partial t^2) \end{aligned} \quad (2-2)$$

$$\text{So:} \quad -s(\partial p/\partial x)dx = (\rho s dx) (\partial^2 \xi / \partial t^2)$$

$$\text{or:} \quad -(\partial p/\partial x) = \rho (\partial^2 \xi / \partial t^2)$$

$$\begin{aligned} \text{Thus:} \quad (\partial^2 \xi / \partial t^2) &= -(1/\rho) (\partial p/\partial x) \\ &= -(1/\rho) (\partial p/\partial v) (\partial v/\partial x) \\ &= -(1/\rho) (v/v) (\partial p/\partial v) (\partial v/\partial x) \end{aligned} \quad (2-3)$$

$$\text{Define:} \quad \beta \equiv -(1/v) (\partial v/\partial p) ,$$

then eqn. (2-3) becomes:

$$(\partial^2 \xi / \partial t^2) = (1/\rho) (1/\beta) (1/v) (\partial v/\partial x) \quad (2-4)$$

$$\begin{aligned} \text{Since:} \quad dv &= s[\xi(x) + (\partial \xi / \partial x)dx + dx - \xi(x)] - sdx \\ &= s(\partial \xi / \partial x)dx \end{aligned}$$

$$\text{and} \quad v = sdx ,$$

$$(dv/v) = [s(\partial \xi / \partial x)dx/sdx] = (\partial \xi / \partial x) \quad (2-5)$$

Substituting eqn. (2-5) into eqn. (2-4), gives:

$$\begin{aligned} (\partial^2 \xi / \partial t^2) &= (1/\beta \rho) (\partial \xi / \partial x) (1/\partial x) \\ &= (1/\beta \rho) (\partial^2 \xi / \partial x^2) \end{aligned}$$

Therefore, for the one-dimensional case of a plane sound wave propagating in the x-direction, the wave equation can be written as:

$$(\partial^2 \xi / \partial t^2) - (1/\beta \rho) (\partial^2 \xi / \partial x^2) = 0 \quad (2-6)$$

where ρ is the fluid density, and β is the adiabatic compressibility.

Since the sound velocity, c , can be expressed by:

$$c = (1/\rho \beta)^{0.5} ,$$

eqn. (2-6) becomes:

$$(\partial^2 \xi / \partial t^2) - c^2 (\partial^2 \xi / \partial x^2) = 0 \quad (2-7)$$

If the source of the sound wave is driven such that it executes periodic displacement, then the solution of eqn.(2-7) gives:

$$\xi = \xi_0 \sin[\omega t - (\omega x/c)] = \xi_0 \exp j[\omega t - (\omega x/c)] \quad (2-8)$$

where:

ω = angular frequency of the wave

$$j = (-1)^{0.5}$$

ξ_0 = displacement amplitude (i.e. maximum displacement)

And:

$$\omega = 2\pi f = 2\pi(c/\lambda) , \quad (2-9)$$

where f is the frequency, and λ is the wavelength.

Substituting eqn.(2-9) into eqn.(2-8), one obtains:

$$\xi = \xi_0 \sin[\omega t - (2\pi x/\lambda)] = \xi_0 \exp j[\omega t - (2\pi x/\lambda)] \quad (2-10)$$

and

$$\dot{\xi} \equiv (\partial \xi / \partial t) = \xi_0 \omega \exp j[\omega t - (2\pi x/\lambda) + (\pi/2)] \quad (2-11)$$

Let:

$$\xi_0 \omega \equiv \dot{\xi}_0 = \text{velocity amplitude}$$

then eqn.(2-11) becomes:

$$\dot{\xi} = \dot{\xi}_0 \exp j[\omega t - (2\pi x/\lambda) + (\pi/2)] \quad (2-12)$$

And: $P = (1/c\beta) \dot{\xi} ,$

where P is the acoustic pressure, that is, the difference between the instantaneous pressure and the equilibrium pressure.

Thus eqn.(2-12) can also be written in the form of:

$$P = P_0 \exp j[\omega t - (2\pi x/\lambda) + (\pi/2)] \quad (2-13)$$

where P_0 is the amplitude of the acoustic pressure.

B. Sound Absorption:

In real systems, the maximum displacement ξ_0 decreases with distance travelled by the wave, and the amplitude of a plane sound

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wave propagating in the x-direction can then be expressed in the form:

$$A(x) = A_0 e^{-\alpha x} \quad (2-14)$$

where: A = amplitude

α = amplitude absorption coefficient, usually expressed in
(nepers/cm)

The average energy density $\bar{E}$ is proportional to the square of amplitude, so eqn.(2-14) can be written in the form:

$$\bar{E} = \bar{E}_0 e^{-2\alpha x} \quad (2-15)$$

Since: $I = c\bar{E}$,

where I is the intensity of a sound beam, equation (2-15) can also be expressed as:

$$I = I_0 e^{-2\alpha x} \quad (2-16)$$

Since both energy and intensity are proportional to ξ_0^2 , the equations for ξ and P are rewritten as follows:

$$\xi = \xi_0 \exp j[\omega t - (2\pi x/\lambda) + (\pi/2)] \exp(-\alpha x) \quad (2-17)$$

$$\text{and } P = P_0 \exp j[\omega t - (2\pi x/\lambda) + (\pi/2)] \exp(-\alpha x) \quad (2-18)$$

C. Forcing Function:

The ultrasonic relaxation technique is a kind of stationary method, in which a constantly oscillating function is applied across the solution. Because of chemical relaxation the system does not follow directly the disturbing function but lags some way behind it. If the frequency of the forcing function (that is, the oscillating disturbance) is sufficiently low, the system can readjust itself rapidly and the concentration changes can effectively keep up with their equilibrium values. In such a case, the concentrations and the forcing function have the same

magnitude and can be represented by curve 1 in figure 2-2. If the frequency of the forcing function is much too high for the system to readjust itself, there will be no observed concentration changes, as indicated by curve 2. If the applied frequency is of the same order of magnitude as the rate at which the changing chemical equilibrium can be set up in the system, there will be an interaction between the system and the forcing function in which energy is absorbed by the system. This case is represented by curve 1 and curve 3 in figure 2-2.

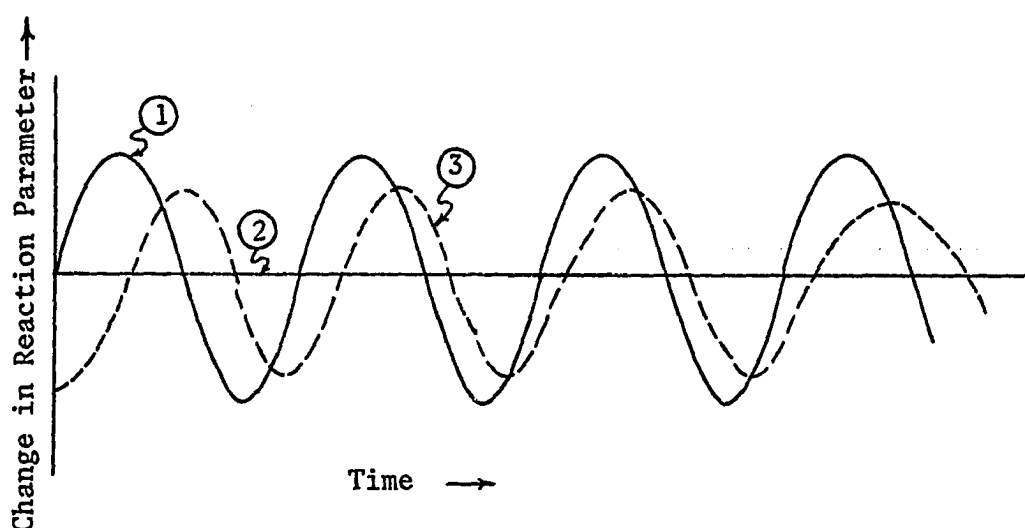


Figure 2-2: Chemical relaxation with a periodic forcing function

D. Excess Absorption and Determination of Ultrasonic Relaxation Spectrum:

The difference in sound attenuation is directly proportional to distance between two measurement points, that is,

$$\Delta(\text{dB}) = \alpha \cdot \Delta x \quad (2-19)$$

where $\Delta(\text{dB})$ is the change in attenuation, Δx is the change in distance, and α is the absorption coefficient of the fluid. Thus a plot of (dB) vs. (x) should be a straight line with slope equal to α .

By use of the pure solvent and the related solution as the fluids under investigation, the corresponding α_{solvent} and α_{solution} can be evaluated.

However, in practice, we are only interested in the excess absorption, α_{chem} , which is defined by:

$$\alpha_{\text{chem}} \equiv \alpha_{\text{solution}} - \alpha_{\text{solvent}} \quad (2-20)$$

or expressed in "absorption per wavelength", μ_{chem} , which is defined as:

$$\mu_{\text{chem}} \equiv \alpha_{\text{chem}} \lambda = \alpha_{\text{chem}} \cdot (c/f) \quad (2-21)$$

where λ is the wavelength, c is the velocity, and f is the frequency.

$$\text{Since: } \tau = (1/2\pi f_r), \quad (2-22)$$

eqn.(1-44) can be rewritten in the form:

$$\mu_{\text{chem}} = 2\mu_{\text{max}} \cdot \frac{(f/f_r)}{1+(f/f_r)^2} \quad (2-23)$$

which gives $\mu_{\text{chem}} \rightarrow \mu_{\text{max}}$, as $f \rightarrow f_r$. Therefore, a plot of μ_{chem} versus f (or μ_{chem} versus $\log f$; or $\log \mu_{\text{chem}}$ versus $\log f$) at μ_{max} gives the corresponding relaxation frequency f_r as indicated in figure 2-3.

An alternative representation of a chemical relaxation is:

$$\frac{\alpha_t}{f^2} = \frac{A}{1+(\frac{f}{f_r})^2} + B \quad (2-24)$$

where: $A = 2\mu_{\text{max}}/cf_r$; B = the constant background absorption due to the solvent; and α_t = total absorption coefficient. Thus by plotting $(\alpha_{\text{chem}}/f^2)$ versus $\log f$, the f_r value can be obtained at the point which corresponds to the frequency of inflection as shown in figure 2-4.

Once f_r has been determined, the relaxation time, τ , can be calculated from eqn. (2-22).

Then from eqn. (1-13), the related rate constants k_f and k_b can be determined.

In the case of multiple-step chemical relaxations, eqns. (2-23) and (2-24) have the general form of:

$$\mu_{\text{chem}} = \sum_i \frac{2\mu_{\text{max}}^i (f/f_{r,i})}{1 + (f/f_{r,i})^2} \quad (2-25)$$

and

$$(\alpha_t/f^2) = \sum_i \left[\frac{A_i}{1 + (f/f_{r,i})^2} \right] + B \quad (2-26)$$

respectively.

Naturally, the analysis of the relaxation spectrum for such case is much more difficult than for the single-step reactions.

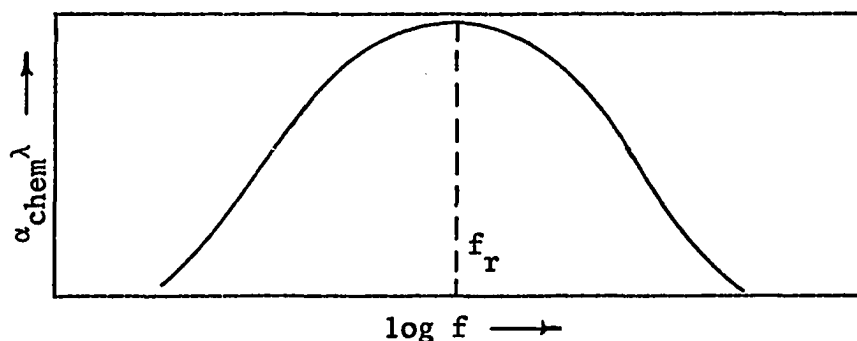


Figure 2-3: Graphical representation of experimental single relaxation curve described by eqn. (2-23).

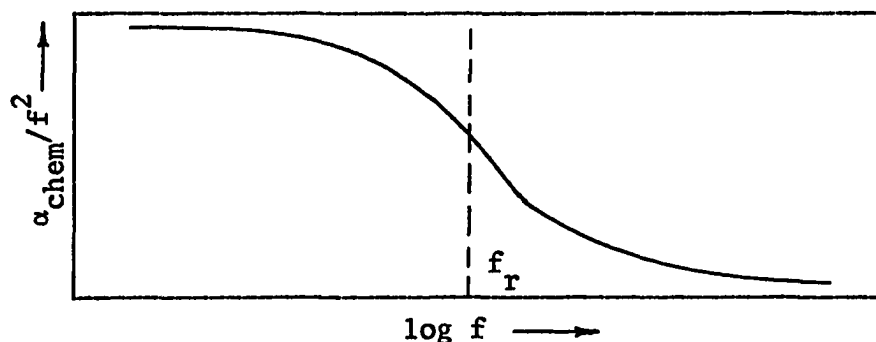


Figure 2-4: Graphical representation of experimental single relaxation curve described by eqn. (2-24).

III. INSTRUMENTATION AND EXPERIMENTATION:

A. Instruments Used:

1. The Cell:

Generally speaking, the cell contains three main parts. They are: micrometer and sending transducer with quartz delay rod; stainless steel cell container with volume around 100 ml; and the receiving transducer. A diagram of the cell and its components are shown in figure(2-5) and figure(2-6).

The piezoelectric transducers used for the generation and detection of the ultrasonic vibrations were X-cut quartz crystals.⁶⁸ The sending and receiving crystals are matched to vibrate at the same fundamental frequency. The fundamental frequency is inversely proportional to the thickness of the transducers. The crystals have been cut, ground, and optically polished so that higher harmonics of the fundamental are also available. The crystals are gold plated to give a better electrical contact. The diameters of the sending and receiving crystals are 1/2 and 1 inch, respectively.

The transmitting crystal is mounted in a crystal holder followed by a 1 inch long quartz rod which serves as an acoustic delay line. The end of the quartz rod is exposed to the solution under investigation.

A very thin coating of "Nonaq" (Fisher, Cat. No. 14-633) is applied to the sending transducer-delay rod interface for good acoustical contact. A sound wave of frequency f ($f=nf_0$, where f_0 is the fundamental frequency of the transducers, n is the n th harmonic and has odd values) is produced by exciting the transmitting crystal with an R.F. pulse of the same frequency. The pulse of the sound wave travels through the quartz delay rod into the solution and is picked up by the receiving crystal mounted at the bottom of the cell chamber, which converts the sound waves back into an R.F. signal. A large part of the signal is reflected back through the delay line so that multiple reflections of the signal occur. The net result, as viewed on an oscilloscope, is a number of equally spaced peaks of decreasing heights, which correspond to the passage of the ultrasonic wave through the solution once, three times, five times, and so on. The peak height decreases exponentially with distance travelled in the same way as the acoustic amplitude does.

The two principal mechanical functions of the cell are to vary the path length precisely between the two crystal transducers and to adjust for non-parallelism of the crystal transducers. The first function can be accomplished by a micrometer driven piston arrangement. The crystal holder is screwed onto the piston and the micrometer head is mounted vertically with respect to the cell container and is anchored by three insert screws. The piston itself is prevented from rotating about its axis by a key and channel arrangement, so that rotating the micrometer screw moves the piston up or down only. The change in path length is measured by a precision micrometer to ± 0.002 mm. The micrometer has a total path length of 50 mm.⁶⁹

Short path lengths are required at high frequency since the absorption is proportional to the frequency squared and becomes quite large at higher frequencies.

The second mechanical function of the cell is to correct for non-parallelism of the crystal transducers. This can be corrected for by the three leveling screws which adjust the position of the sending transducer with respect to the receiving transducer. The adjustment for parallelism is determined by the received pulse amplitude and shape.

The cell container itself has double walls through which water is circulated from a thermostated tank. The temperature of the tank was kept at $25 \pm 0.01^{\circ}\text{C}$.

2. The Pulse Generator and Receiver:

The MATEC Model 6000 R.F. Pulse Generator and Receiver has been used in the research. This provides, in conjunction with appropriate R.F. plug-ins, essential transducer driving waveforms and receiving amplification required when making pulsed ultrasonic attenuation measurements. The instrument features continuously variable pulse width and amplitude controls, broad frequency coverage, and a wide bandwidth, wide dynamic linearity range receiver.

An internal repetition rate generator provides a free running sync source variable from 5 to 500 pulses per second. A 60 MHz high gain I.F. amplifier provides a highly linear means of amplification common to all plug-ins operating above 10 MHz. Besides the high degree of linearity, the I.F. amplifier can

also provide both a very stable center frequency and a constant bandwidth over the full range of receiver gain control. Good linearity, stable center frequency, and constant bandwidth are all prerequisite for successful attenuation measurements with either the exponential comparator technique or the automatic attenuation recorder. The front end or tuner for the receiver is included in the plug-in and has a frequency range matching that of the pulsed oscillator in the same plug-in unit. The frequency range is determined by the R.F. plug-in used. Pulse width is continuously variable from 0.5 to 5 microsecond. The pulse amplitude is also adjustable from zero to maximum. Maximum R.F. amplitude is a function of frequency and plug-in used.

The MATEC Model 960 R.F. Plug-in unit was used together with the main frame to provide R.F. pulse drive and receiver tuning capabilities over the frequency range from 10 to 310 MHz.

3. The Pulse Amplitude Monitor:

The MATEC Model 1235B Ultrasonic Amplitude Indicator has been used as a part of a complete system to measure and record changes in amplitude of pulsed ultrasonic energy in various materials. When used with a suitable R.F. pulse generator and receiver, this instrument will continuously measure and indicate on a linear decibel scale the difference in amplitude between an echo and an internal reference voltage.

The Model 1235B has a maximum full scale sensitivity of 1 dB and an accuracy of ± 0.2 dB over a span of 20 dB.

4. The Attenuator:⁷⁰

The purpose of using this instrument is to control the output peak height of the ultrasonic amplitude so that all the output peaks can be seen on the CRT screen.

5. The Oscilloscope:

Either the Tektronix Type 502 Dual-Beam Oscilloscope or the Type 545A Cathode-Ray Oscilloscope can be used. Both of them are wide-range general purpose laboratory instruments.

6. The Signal Generator:

A Hewlett-Packard Model 608D VHF Signal Generator has been used, which furnishes R.F. signals from 0.1 microvolt to 0.5 volt over the frequency range from 10 to 420 MHz.

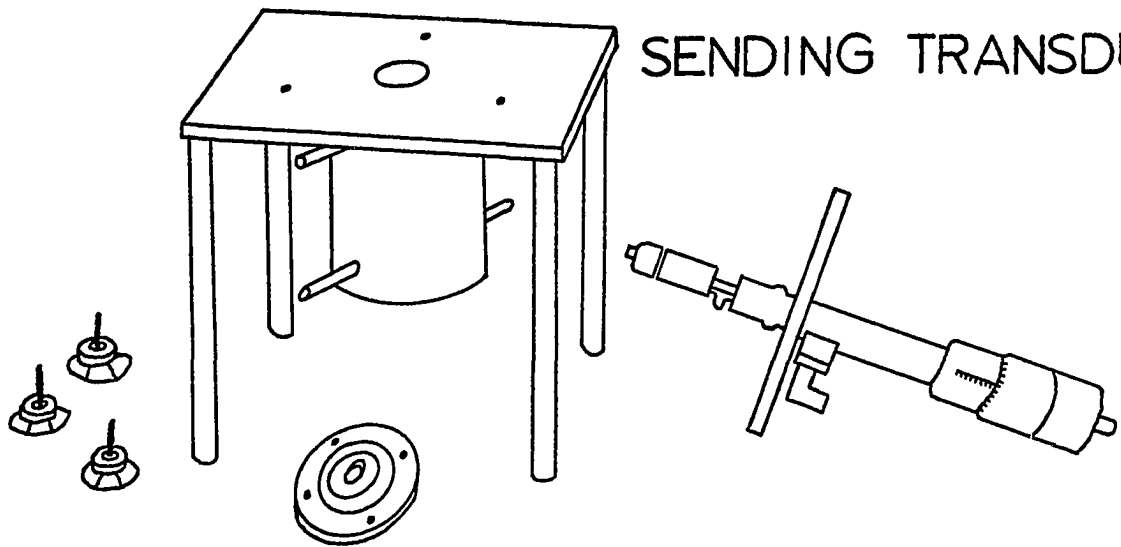
7. The Frequency Counter:

A Hewlett-Packard Model 5327C Frequency Counter is used to measure the frequency.

8. The Thermostated Water Bath:

CELL CONTAINER

MICROMETER &
SENDING TRANSDUCER



RECEIVING TRANSDUCER

Figure 2-5: The main parts of the ultrasonic cell.

ASSEMBLY OF
ULTRASONIC CELL

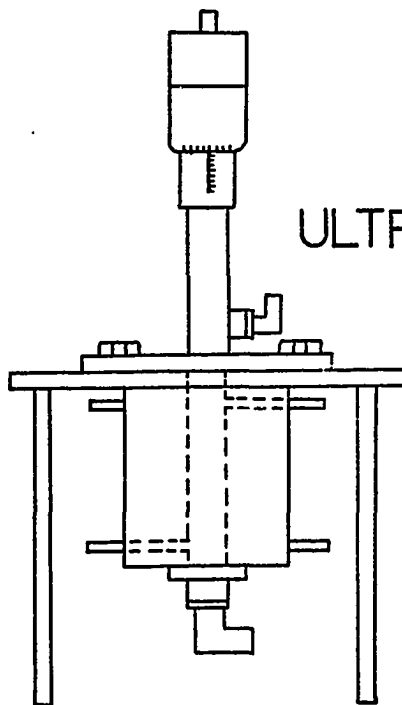


Figure 2-6: The assembly of the ultrasonic cell.

The Model K-4R Lauda/Brinkmann Circulator has been used to circulate the constant-temperature water through the ultrasonic double-wall absorption cell. The temperature of the water bath can be controlled to $\pm 0.01^{\circ}\text{C}$.

B. Chemicals Used:

1. Boric Acid: Baker & Adamson certified, A.C.S. reagent grade of crystal boric acid has been used without further purification.
2. Water: Distilled, deionized, and CO_2 -free water has been used as the solvent.
3. Nitrogen Gas: Pure, saturated nitrogen gas was used to expel all the CO_2 which might exist in the cell and in the solution under investigation.
4. Hydrochloric Acid: Fisher Scientific Company Certified concentrated HCl solution was used to adjust the solution pH.
5. Sodium Hydroxide: Fisher Scientific Company Certified laboratory grade NaOH pellets were used to prepare the concentrated NaOH solution needed for adjusting solution pH.

C. Experimental Procedure:

A block diagram of the ultrasonic absorption apparatus is shown in figure 2-7; and that of the ultrasonic frequency measurement is shown in figure 2-8.

All electronic equipments were warmed up for at least two hours before taking any measurement. The pure, dry nitrogen gas

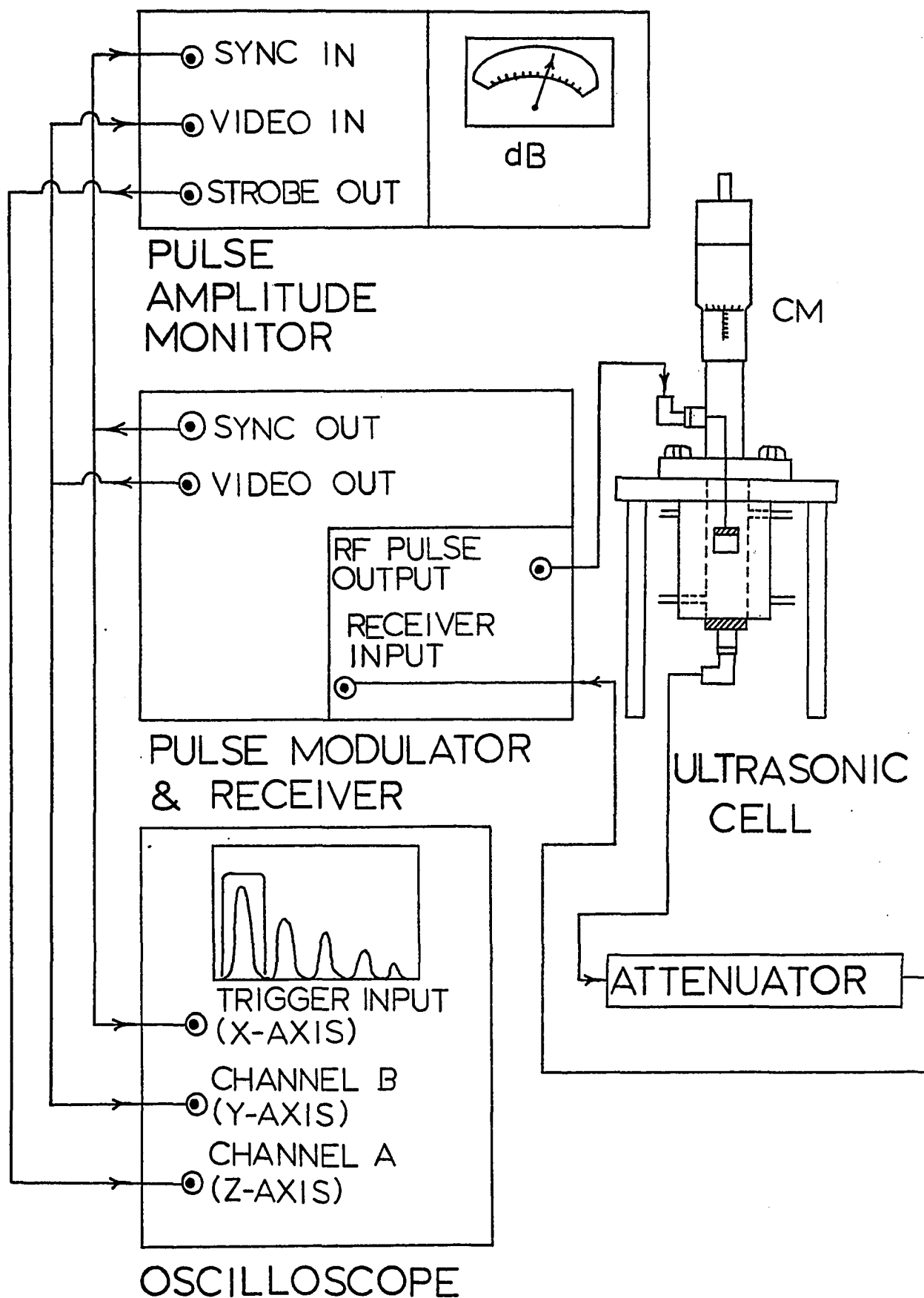


Figure 2-7: Block diagram of the ultrasonic absorption apparatus.

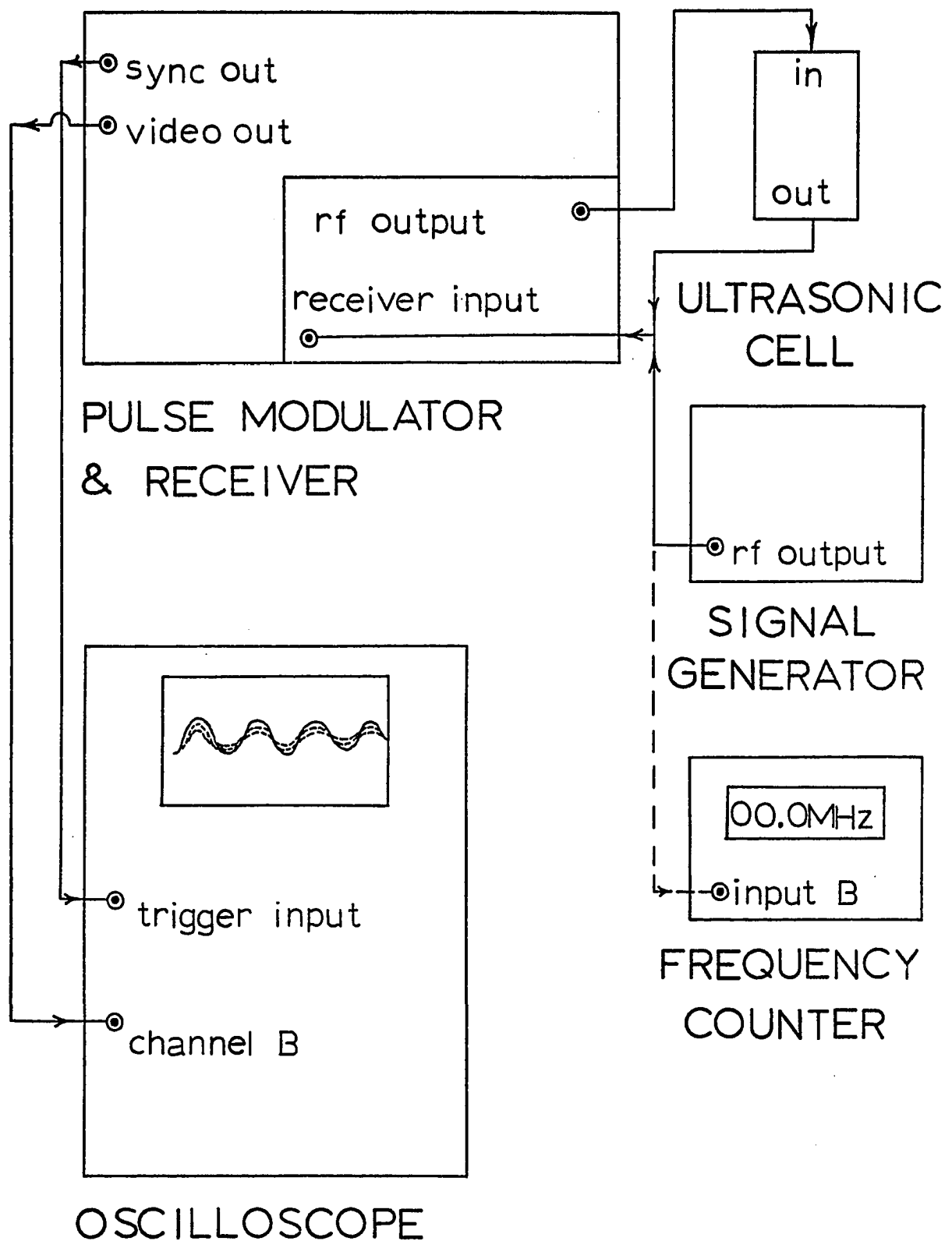


Figure 2-8: Block diagram of the ultrasonic frequency measurement.

has been passed through a bottle of distilled, deionized, CO₂-free water to achieve saturation. The saturated nitrogen gas is then introduced into the solution in the cell and the sample solution is bubbled for at least 20 minutes to expel all the CO₂ which might exist in the solution under investigation. The cell is then sealed with the cover head which contains a micrometer, a sending transducer, and a quartz delay rod. The transmitting crystal, which has a fundamental frequency of 5 MHz, is excited at one of its resonant frequencies by means of the R.F. oscillator. The output of the oscillator is controlled by the pulse generator. In this way intermittent trains of ultrasonic waves are propagated through the sample solution. These waves are then picked up by a receiving crystal which converts these sound waves back into R.F. signals. The output R.F. signals are then fed into the receiver and amplified. The result is displayed both on a pulse amplitude monitor and an oscilloscope CRT screen.

There is a delay generator located in the pulse amplitude monitor to provide a time delay arrangement. The delay is used to determine the time of "gate" opening for echo selection. The selector then linearly passes just one echo. The strobe circuit of the pulse amplitude monitor will then accept the delay output pulse and feeds it as a brightening pulse to the Z-axis of the CRT to identify the echo being selected. Usually the first output peak has always been selected and measured since it has the highest amplitude value. The height of the output cell signal is changed by increasing or decreasing the distance between transducers.

The distance travelled by the sound wave can be found from the micrometer readings; and the sound absorption value dB can be

read out directly from the pulse amplitude monitor. The absorption coefficient α (in dB/cm) is then obtained from the slope of a plot of attenuation dB versus the corresponding distance cm.

A frequency counter is used to measure the frequency of the R.F. signal produced by the receiving transducer. This is done by beating the continuous wave output of the signal generator to resonance against the cell signal using the oscilloscope for detection. The frequency of the signal generator is then measured with the frequency counter.

IV. RESULTS AND DISCUSSIONS:

The results are given in tables(2-1) to (2-5) and in figures (2-9) to (2-10).

For checking the measurement validity, water has been used as the solvent, and its sound attenuation versus distance measured and compared with that in the literature. Since α is an intensive property of the solution, no absolute measurements are required. Relative measurements are sufficient. In order to reduce overall error, at least four repetitions of the measurements are usually made, with alternate directions of motion for the moving transducer.

Instead of plotting attenuation (dB) versus distance (cm), the initial data were used to calculate the absorption coefficient α by a linear least squares computer program. Once the α values have been obtained, the corresponding (α/f^2) values and their average values $(\alpha/f^2)_{\text{avg.}}$ can then be determined. The value of the solvent absorption at each frequency is then calculated from the equation:

$$\alpha_{\text{solvent}} = (\alpha/f^2)_{\text{avg.}} \cdot (f^2) \quad \text{in (neper/cm)} \quad (2-27)$$

where:

$$1 \text{ neper} = 8.686 \text{ dB}$$

The quantity, (α/f^2) , for water and many other pure liquids is found to be independent of frequency over a large frequency range. The value of (α/f^2) taken for water from the experimental result in this laboratory is 20.978×10^{-17} nepers $\cdot$ sec² $\cdot$ cm⁻¹,
71-73
which is quite consistent with that in the literature.

For the boric acid system, the boric acid concentration of 0.025 M has been used since this is the maximum concentration allowable for the polynuclear species to be ignored. The pH of the solution has been adjusted from pH = 3.615 to pH = 12.02; and the ultrasonic frequencies used are from 15 MHz to 95 MHz. For the boric acid and polyborate system, the boric acid concentration has been set at 1.0 M. This concentration is about the highest concentration possible at 25°C due to the limited solubility of boric acid in water. The pH of the polyborate systems studied range from 3.59 to 12.06; and the frequency from 15 MHz to 95 MHz.

From the (α/f^2) values, it is found that for both the boric acid system and the polyborate system, there is no excess sound absorption in the frequency range from 15 MHz to 95 MHz regardless of the solution pH values. This result is in accordance with what was predicted by the theoretical calculations in Part I.

Table 2-1: Attenuation versus distance for water at various frequencies.

25°C; 1 atm

Frequency (MHz):	Distance (cm):	Attenuation (dB):
15	4.0	18
	3.5	17.86
	3.0	17.54
	2.5	17.4
	2.0	17.28
	1.5	16.9
45	4.0	8.3
	3.5	7.1
	3.0	4.95
	2.5	2.85
	2.0	1.1
55	4.0	16.6
	3.5	14.24
	3.0	11.23
	2.5	8.13
	2.0	4.84
	1.5	3.5
65	4.0	17.48
	3.5	14.53
	3.0	11.33
	2.5	6.16
	2.0	1.9
85	3.0	19.05
	2.7	17.09
	2.5	14.88
	2.2	10.88
	2.0	8.18
	1.7	3.67
	1.5	0.85

Table 2-1 (continued):

Frequency (MHz):	Distance (cm):	Attenuation (dB):
95	2.4	15.8
	2.2	13.51
	2.0	10.08
	1.8	6.63
	1.6	3.13
	1.5	1.88

Table 2-2: The values of α and α/f^2 for water at various frequencies.

25°C; 1 atm

Frequency (MHz):	α (dB/cm):	$(\alpha/f^2) \times 10^{17}$ (nepers·sec ² ·cm ⁻¹):
15	0.4217	21.58
45	3.730	21.21
55	5.531	21.05
65	7.906	21.54
85	12.57	20.03
95	16.04	20.46

Table 2-3: The average values of α for water at various frequencies.

at $(\alpha/f^2)_{\text{avg.}} = 20.98 \times 10^{-17}$ nepers·sec²·cm⁻¹

Frequency (MHz):	$\alpha_{\text{avg.}}$ (dB/cm):
15	0.4100
35	2.232
55	5.512
75	10.25
95	16.44

Table 2-4: The values of α and α/f^2 for the boric acid system at various pH values and frequencies.

[Boric Acid] = 0.025 M

pH:	f (MHz):	α (dB/cm):	$(\alpha/f^2) \times 10^{17}$ (nepers $\cdot$ sec 2 $\cdot$ cm $^{-1}$):
3.615	15	0.4267	21.83
	35	2.179	20.48
	55	6.316	24.04
	75	10.66	21.82
	95	15.72	20.05
5.41	15	0.4000	20.47
	35	2.256	21.21
	55	5.894	22.43
	75	10.11	20.69
	95	16.91	21.57
7.04	15	0.4040	20.67
	35	2.150	20.21
	55	5.901	22.46
	75	10.90	22.31
	95	16.29	20.78
8.63	15	0.4594	23.51
	35	2.224	20.90
	55	5.373	20.45
	75	10.11	20.69
	95	16.22	20.69
10.47	15	0.4001	20.47
	35	2.196	20.64
	55	5.845	22.25
	75	10.36	21.20
	95	16.09	20.53
12.02	15	0.4440	22.72
	35	2.350	22.09
	55	6.029	22.94
	75	11.27	23.06
	95	15.82	20.18

Table 2-5: The values of α and α/f^2 for the boric acid-polyborate system at various pH values and frequencies.

[Boric Acid]=1.0 M

pH:	f (MHz):	α (dB/cm):	$(\alpha/f^2) \times 10^{17}$ (nepers $\cdot$ sec 2 $\cdot$ cm $^{-1}$):
3.59	15	0.3900	19.96
	35	2.040	19.17
	55	5.328	20.28
	75	11.14	22.80
	95	16.72	21.32
5.06	15	0.4134	21.15
	35	2.193	20.61
	55	5.772	21.97
	75	11.26	23.05
	95	16.32	20.82
7.01	15	0.4032	20.63
	35	2.363	22.21
	55	5.725	21.79
	75	10.47	21.43
	95	15.83	20.19
8.03	15	0.4210	21.54
	35	2.350	22.09
	55	6.000	22.84
	75	10.38	21.24
	95	16.06	20.48
10.02	15	0.4218	21.58
	35	2.434	22.87
	55	5.852	22.27
	75	10.50	21.49
	95	16.70	21.30
12.06	15	0.4330	22.16
	35	2.260	21.24
	55	5.374	20.45
	75	11.15	22.82
	95	17.52	22.35

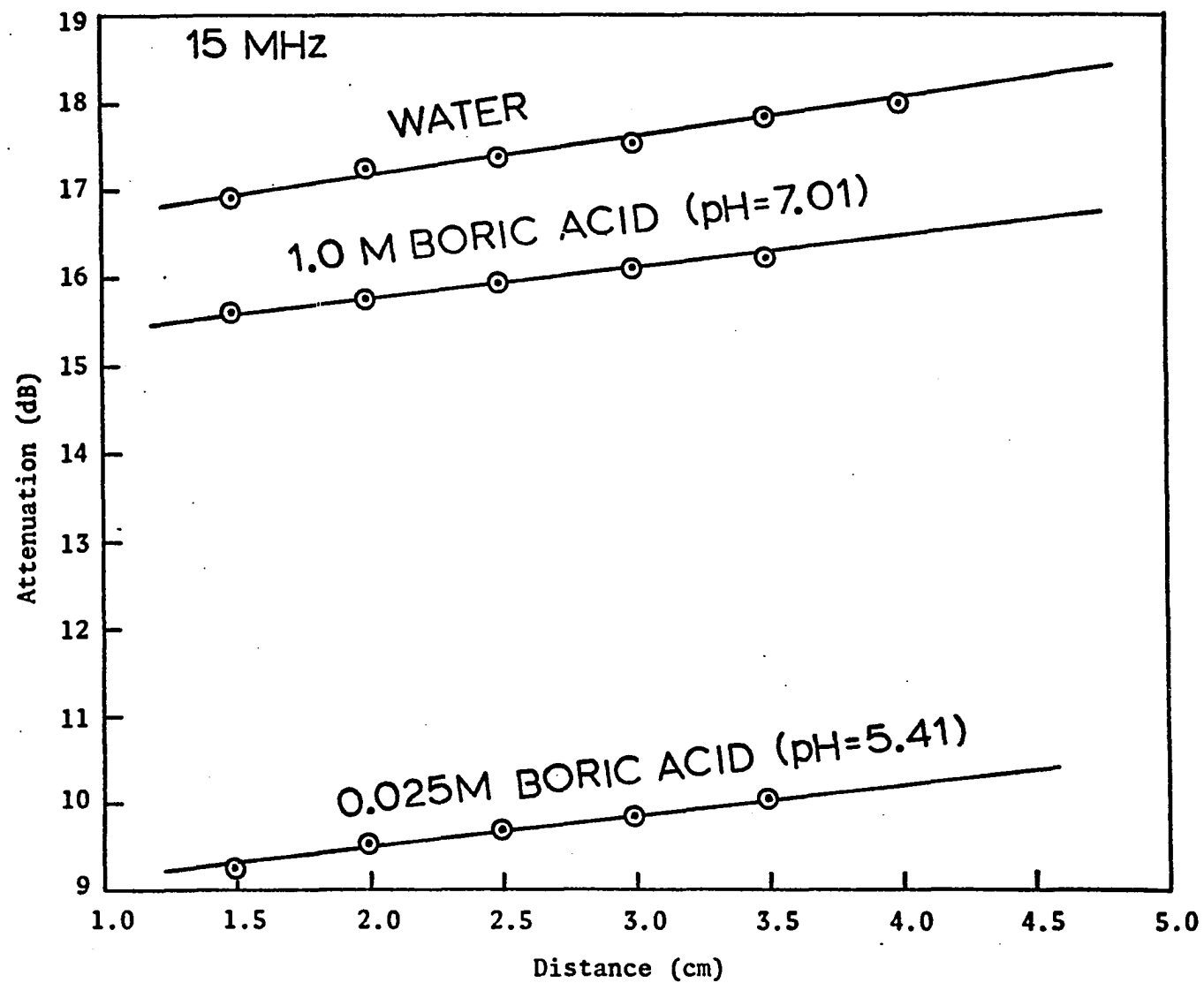


Figure 2-9: The attenuation versus distance for water; 0.025 M boric acid; and 1.0 M boric acid at frequency of 15 MHz.

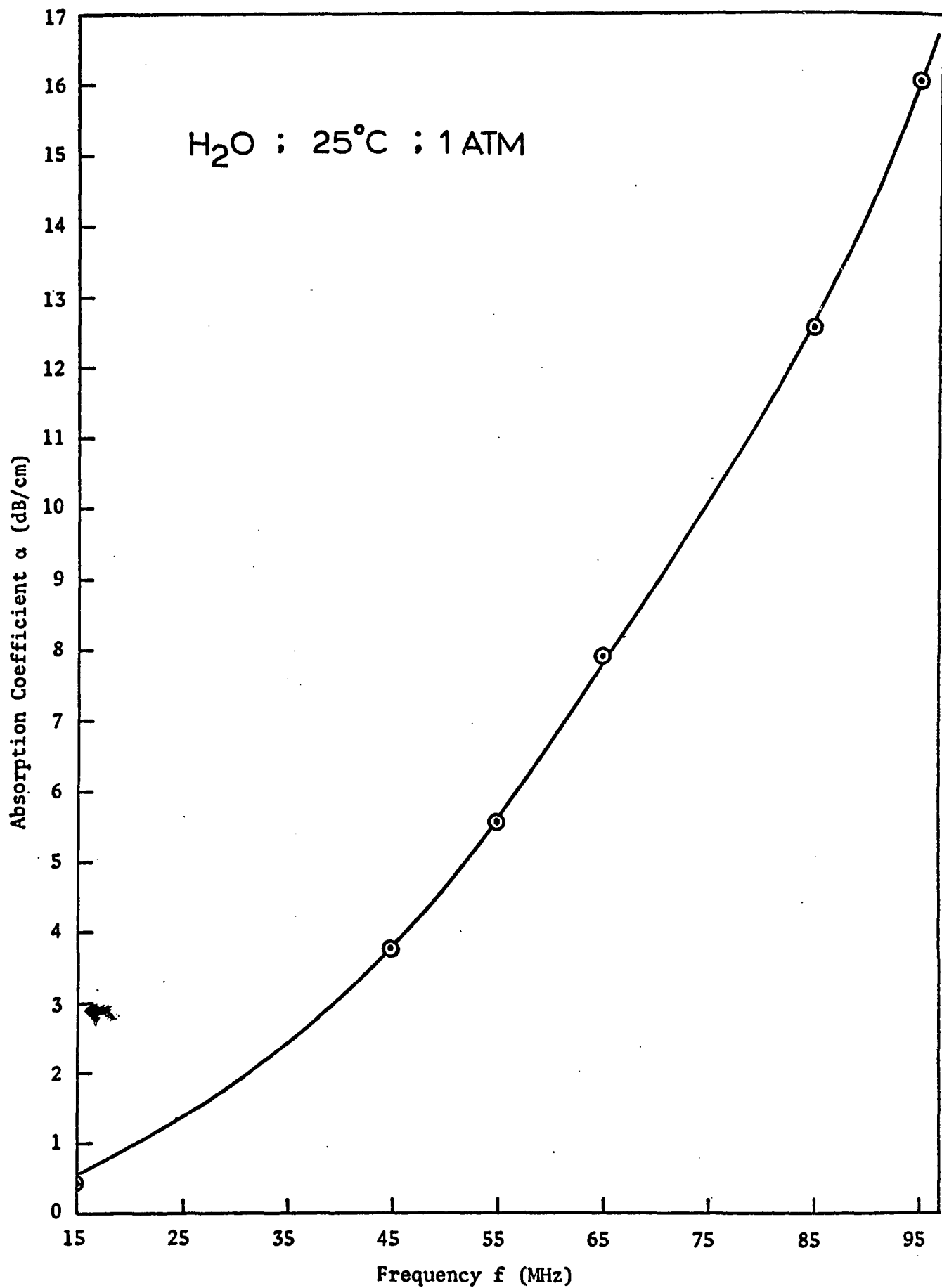


Figure 2-10a: The absorption coefficient versus frequency for water at 25°C and 1 atm.

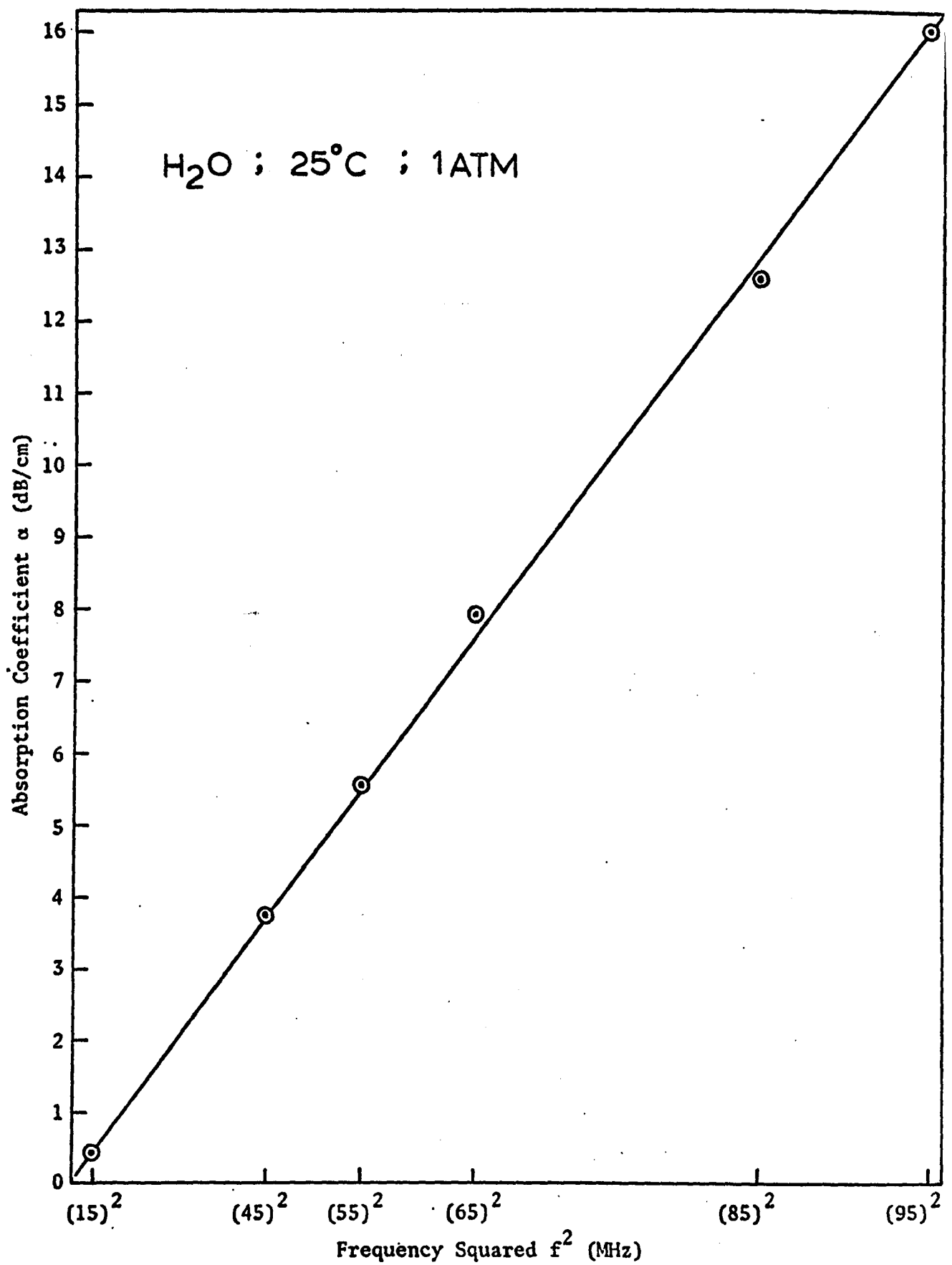


Figure 2-10b: The absorption coefficient versus frequency squared for water at 25°C and 1 atm.

PART III:
ULTRASONIC RELAXATION STUDIES OF
AQUEOUS BORIC ACID, AND
BORIC ACID-POLYBORATE SYSTEM
USING THE ULTRASONIC RESONATOR TECHNIQUE

I. INTRODUCTION:

In this part of the research an ultrasonic resonator technique, which covers the frequency range from 0.5 MHz to 13 MHz with a liquid sample volume of approximately 30 ml, has been employed to measure the ultrasonic excess absorption of the sample solution.

Distilled, deionized and boiled water was used as a reference liquid. Aqueous boric acid solutions of concentration 0.025 M and pH at 5.52; 7.50; and 9.58 were used as the sample solutions for the boric acid system. Aqueous boric acid solutions of concentration 0.6 M and pH at 4.45; 7.41; and 9.40 were used as the sample solutions for the boric acid and polyborate system. The magnitude of half-power bandwidth (HPB or 3-dB bandwidth), Δf , and the corresponding resonance frequency value, f_n , for both the reference liquid and sample solutions have been carefully measured, and their Δf values are then compared to see if there is any excess sound absorption exist for a system.

II. THEORY:

The ultrasonic resonator technique employs a standing sound wave in a cylindrical cavity in the resonator cell.⁷⁴⁻⁷⁹

The resonator cell consists of a liquid sample between two X-cut quartz plates used as transducers. A tunable sine wave oscillator drives the input quartz transducer and produces a standing-wave sound field in the liquid sample at certain characteristic frequencies called resonance frequencies. At these resonance frequencies the output quartz transducer delivers pronounced voltage peaks, as shown in Figure 3-1, which after amplification by a tunable receiver can be measured on a meter and displayed on an oscilloscope screen.

Under the assumption of one-dimensional wave propagation in the liquid sample and ideal reflection at the transducers, the output voltage near a resonance frequency, f_n , can be described by:⁸⁰⁻⁸³

$$V_n^{\text{output}} = V_n^{\text{max}} \left[1 + \frac{\sin^2(\pi f/f_L)}{\sinh^2(\alpha x)} \right]^{-1/2} \quad (3-1)$$

Where:

V_n^{max} = maximum output voltage at the particular peak, and

is proportional to the driving voltage

αx = ultrasonic absorption per pathlength x

f_L = fundamental frequency of the liquid column

And

$$f_L = V_L / 2x \quad (3-2)$$

where V_L is the sound velocity in liquid sample solution.

For small attenuation values ($\alpha x \ll 1$) eqn.(3-1) can be linearized near a peak frequency and sine and hyperbolic sine are approximated by the arguments. This results in the relation between half-power bandwidth, Δf , of a particular peak and the frequency f_n of that peak:

$$(\alpha \lambda / \pi) = (\Delta f / f_n) = (1/Q) \quad (3-3)$$

This equation yields the quality factor, Q , of an "ideal" resonator cell with energy losses due to liquid attenuation only.

In the "real" system, however, the overall quality factor, Q_{real} , should be expressed by:

$$(1/Q_{\text{real}}) = (1/Q_{\text{liquid}}) + (1/Q_{\text{extra}}) \quad (3-4)$$

where Q_{liquid} is the quality factor due to sound absorption in the liquid sample and Q_{extra} summarizes all the additional energy losses in the resonator cell due to beam divergence, scattering, friction effects, imperfect reflection at the quartz surface, transducer mounting, and coupling losses.

The excess sound absorption caused by the relaxation of a chemical reaction is obtained by means of a reference measurement in the same resonator cell at the same resonance frequencies with a suitable reference liquid. This reference liquid should have equal or very similar sound velocity to insure an identical sound field pattern in the resonator cell for

both measurements. The excess absorption per wavelength, $(\alpha\lambda)_{\text{excess}}$, in the liquid is obtained from:

$$(\alpha\lambda)_{\text{excess}} = \pi \cdot \frac{\Delta f_s - \Delta f_r}{f_n} \quad (3-5)$$

where Δf_s and Δf_r are the corresponding HPB values of the n -th resonance peak in the sample solution and reference liquid, respectively. Equation (3-5) holds only if subsequent resonance peaks are well separated, i.e. $\Delta f \ll f_{n+1} - f_n$, where f_n and f_{n+1} are subsequent peak frequencies.

The fundamental frequency, f_L , of the liquid column can be determined with rough approximation by:

$$f_L \approx f_{n+1} - f_n \quad (3-6)$$

The sound velocity in the liquid sample, V_L , can be obtained from f_L and the distance between two quartz transducers, x , which must be determined from a calibration measurement with a liquid of known sound velocity, such as water.

At higher frequencies Δf is predominantly determined by the liquid absorption, and its theoretical value can be expressed by:

$$\Delta f_{\text{theo.}} = (\alpha V_L / \pi) \quad (3-7)$$

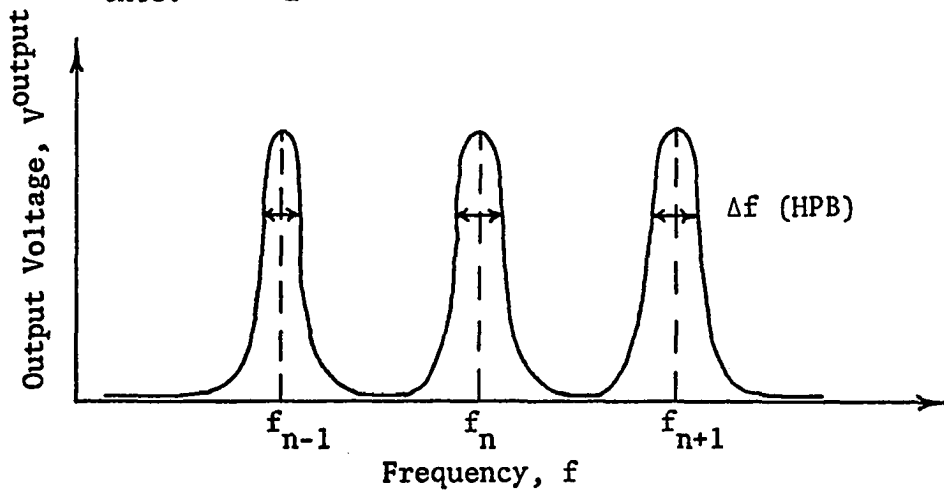


Figure 3-1: Output voltage from the resonator cell.

III. INSTRUMENTATION AND EXPERIMENTATION:

A. Instruments Used:

1. Hewlett-Packard Model 3330 B Automatic Synthesizer:

This instrument provides accurate and stable frequencies from 0.1 Hz to 13,000,999.9 Hz with a resolution of 0.1 Hz.

2. Hewlett-Packard Model 461 A Wideband Amplifier:

It can amplify sinusoidal signal input in the 1 KHz to 150 MHz range.

3. Telonic XD-8A R.F. Detector:

It can detect the R.F. signal with frequency in the range of 0.5 MHz to 300 MHz.

4. Hewlett-Packard Model 5489A Low-Pass Filter:

This is a two-channel active low-pass filter with frequency cut-offs selectable from 1 Hz to 30 KHz.

5. Hewlett-Packard Model 3480B Digital Voltmeter:

The basic measurement capability of this instrument is from ± 0.001 Volt to ± 14.999 Volt.

6. Hewlett-Packard Model 5327C Frequency Counter:

This instrument measures frequency from 0 to 550 MHz.

7. Resonator Cell:

Figure 3-2 shows the detailed structure of the resonator cell.

The cell consists of two nearly equal halves, each of which

contains a 2.0 inch diameter, 0.04 inch thick quartz plate used as the transmitting or receiving transducer with a fundamental frequency of 2.5 MHz. Since the sensitivity of the interferometric principle is based on the multiple reflections of sound waves at the transducers, the mounting of both quartz transducers is quite important, and they must be flat and parallel to optical grade. The two transducers are mounted with teflon gaskets and an o-ring which makes a liquid-tight seal against the edge of each transducer. The R.F. signal input is applied to the sending quartz crystal via a spring contact soldered to an R.F. connector which is mounted on the back-plate of the cell. The side of the quartz plate which is in contact with the sample solution is grounded to the cell by means of "bridges" painted on the teflon gaskets with conductive paint. The crystal-gasket assembly is then held into place by a metal ring which is screwed onto the cell body. Each cell-half is jacketed for water circulation and constant temperature control. The two cell halves are then held together by three screws and, at the same time, are separated by a large o-ring. This large o-ring along with that of the two crystal o-rings mentioned previously seals the sample solution against any leakage. Also, the combination of large o-ring and three screws permits convenient leveling of the two quartz transducers. One of the cell halves has two filling holes with one on the top and the other at the bottom of the cell. The bottom hole is tapped so that chem-inert fittings may be used to fill the cell with a syringe. About

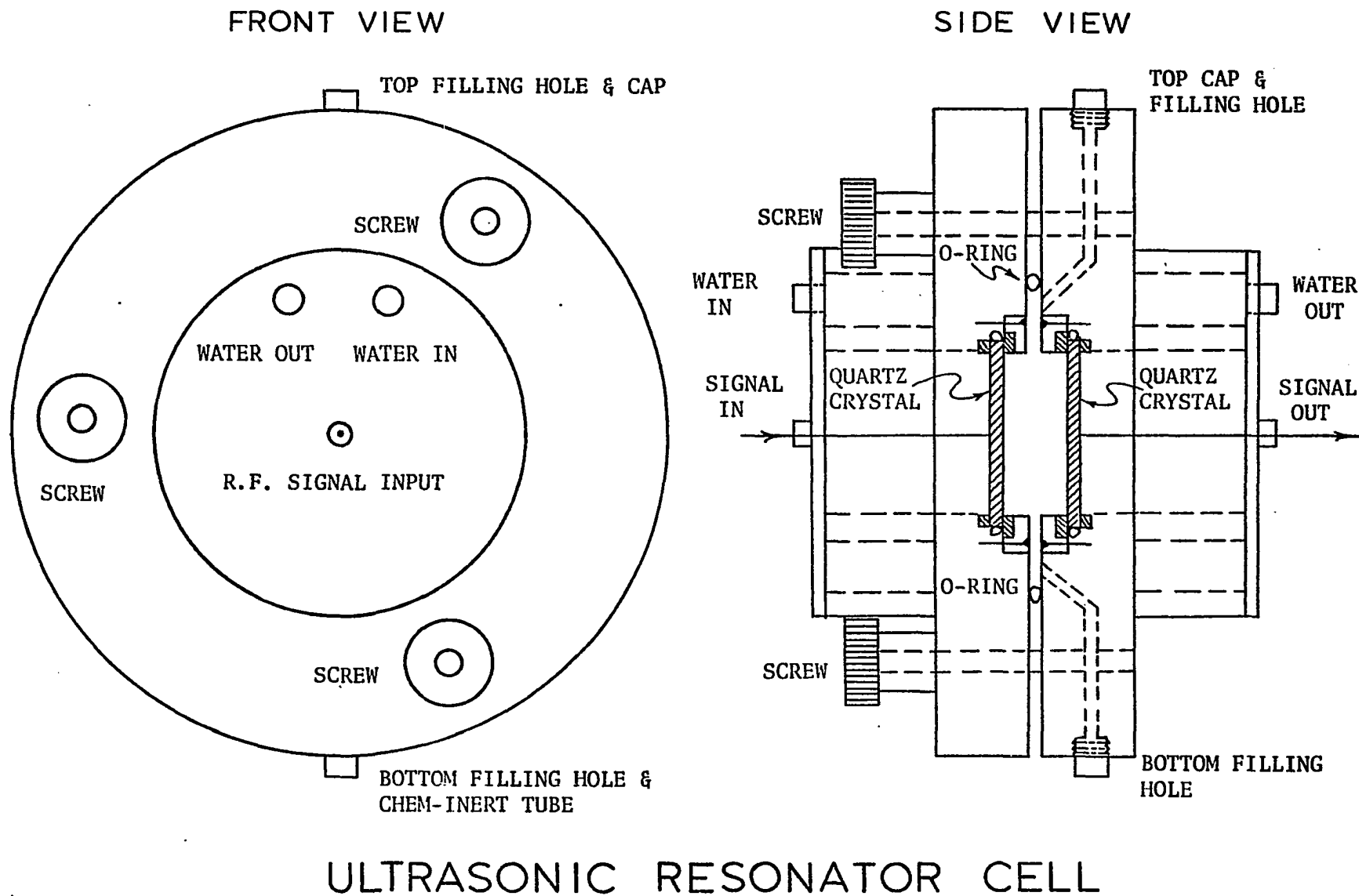


Figure 3-2

30 ml of liquid is needed to fill the cell cavity.

B. Chemical Used and Reaction Systems Studied:

Baker & Adamson A.C.S. Certified Reagent Grade boric acid was used. For the boric acid system, the boric acid concentration has been kept at 0.025 M with the pH adjusted to 5.52; 7.50; and 9.58. For the boric acid and polyborate system, the boric acid concentration is 0.6 M with the pH at the values: 4.45; 7.41; and 9.40. Distilled, deionized, and boiled water has been used as the reference liquid and the solvent for sample solutions.

C. Experimentation:

The detailed block diagram of the apparatus used in the resonance measurement is shown in Figure 3-3. A Hewlett-Packard Model 3330B Automatic Synthesizer is used to produce the accurate and stable R.F. signal which drives the transmitting quartz crystal and generates a standing sound wave in the resonant cavity which holds the sample solution. The frequency of this R.F. signal can be double checked by H.P. 5327C Frequency Counter. The output of the receiving transducer of the resonator cell is amplified by H.P. 461A Wideband Amplifier and detected by the Telonic XD-8A R.F. Detector. The detector puts out a positive D.C. voltage proportional to the magnitude of the input R.F. signal. The output of the detector is then double passed through an H.P. 5489A Low-Pass

Filter, the bandwidth of which is set at 1 Hz. The output from the low-pass filter is then measured on a H.P. 3480B Digital Voltmeter.

The measurement of the excess sound absorption of the liquid sample solution can be accomplished as follows: The frequency of the cell input signal has been carefully adjusted to one of the resonance frequencies of the resonator cell, f_n ; these resonance frequencies can be detected by the sharp maximum in the output of the receiving crystal as can be observed on the digital voltmeter. After the resonance frequency has been obtained, both the maximum output voltage magnitude and the corresponding resonance frequency value have been recorded. The signal frequency is then changed until the output voltage is $\sqrt{0.5}$ times the resonant peak value. Two frequencies can be obtained which correspond to the HPB value, one is higher than the resonance frequency f_n and the other is lower than f_n . The difference between these two frequencies is the Δf value corresponding to the HPB output. The Δf value was measured for both the reference liquid and the sample solution at the same resonance frequency, and the excess sound absorption of the sample solution can then be calculated using equation (3-5).

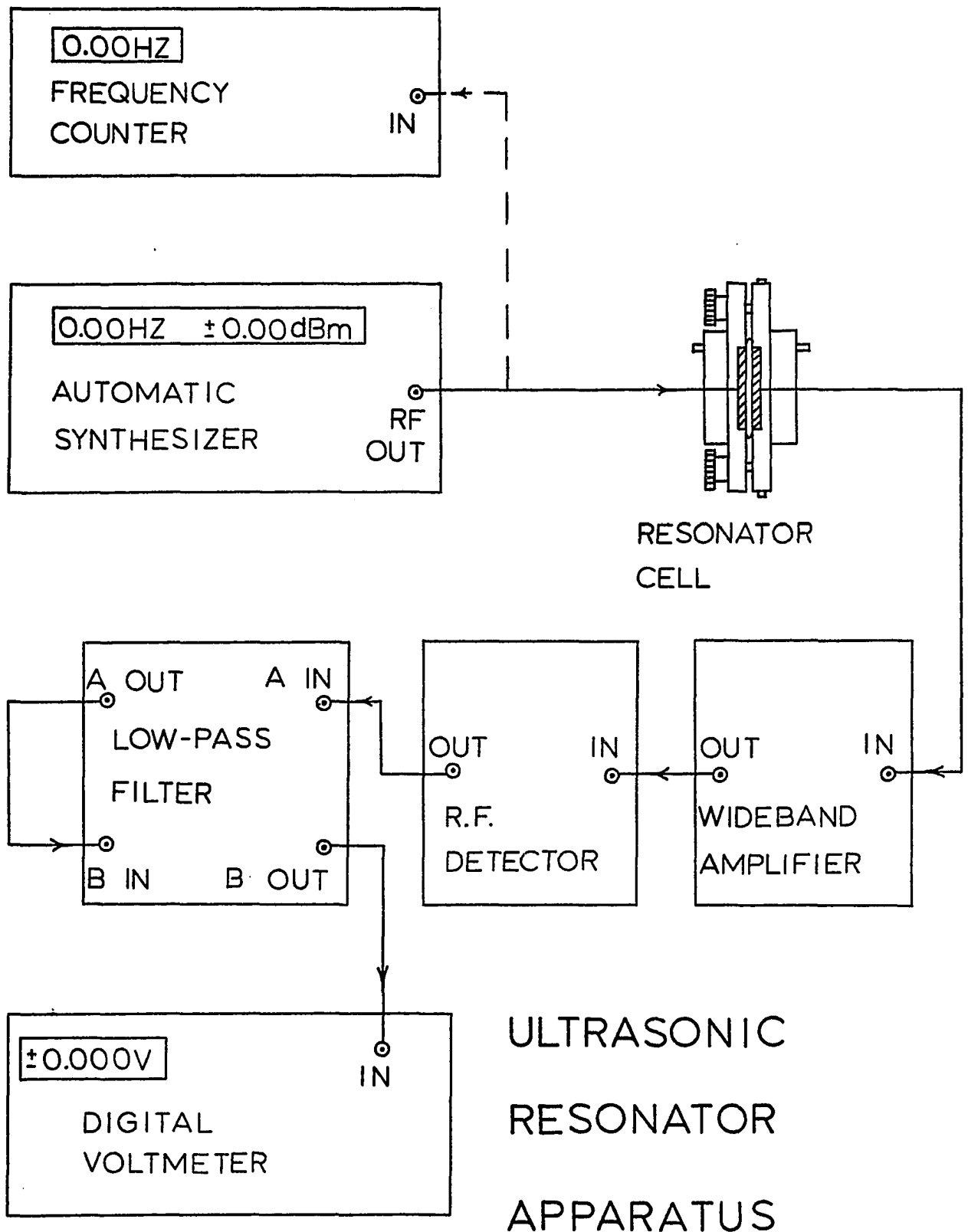


Figure 3-3

IV. RESULTS AND DISCUSSIONS:

The half-power bandwidth value Δf versus the corresponding resonance frequency f_n of water, used as the reference liquid, has been plotted and shown in Figure 3-4. It can be seen from the graph that below a frequency of 1.75 MHz, deviation from the straight line relationship occurs (the lower the frequency, the greater the deviation) and the accuracy of the experimental results starts to decrease. This is because at lower frequencies, the sound absorption is no longer predominantly determined by water (or any reference liquid) only. The effect of resonator cell construction on the sound energy losses becomes greater at such low frequencies, and the cell itself plays a very important role in the process of sound attenuation.

For the aqueous boric acid system, data points of 0.025 M boric acid solution with pH adjusted at 5.52; 7.50; and 9.58 have been plotted and displayed in Figure 3-5 to Figure 3-7. Those data points are then compared with that of the water reference liquid line which has also been shown in the same diagram. Similarly, for aqueous boric acid & polyborate system, data points of 0.6 M boric acid aqueous solution at various pH values have also been plotted and compared with the water reference line shown on

the same diagram, as shown in Figure (3-8) through Figure (3-10). For both systems, it is obvious that no excess sound absorption has been found in the frequency range from 0.5 MHz to 13 MHz. This shows that the experimental result obtained is quite consistent with what has been predicted previously in Part I.

Table 3-1: Resonance frequencies and their corresponding HPB values of water at 25°C.

Resonance Frequency, f_n (KHz):	HPB Δf (KHz):
12624.147	2.180
9077.610	1.460
7687.530	1.370
6284.720	1.020
3405.240	0.400
1913.582	0.300
1135.927	0.204
962.080	0.152
702.960	0.200
530.268	0.260

Table 3-2: Resonance frequencies and their corresponding HPB values of 0.025M boric acid with pH adjusted at 5.52.

Resonance Frequency, f_n (KHz):	HPB Δf (KHz):
12625.492	1.910
9064.580	1.380
3402.868	0.440
1912.404	0.260
1134.049	0.174
961.656	0.149
702.073	0.202
529.777	0.216

Table 3-3: Resonance frequencies and their corresponding HPB values of 0.025 M boric acid with pH adjusted at 7.50.

Resonance Frequency, f_n (KHz):	HPB Δf (KHz):
12622.897	2.320
9063.660	1.570
7697.770	1.300
3401.414	0.499
1911.507	0.244
1135.362	0.310
961.109	0.140
702.979	0.266
529.433	0.200

Table 3-4: Resonance frequencies and their corresponding HPB values of 0.025 M boric acid with pH adjusted at 9.58.

Resonance Frequency, f_n (KHz):	HPB Δf (KHz):
12628.212	2.420
6367.246	0.960
3404.475	0.390
1913.417	0.209
1135.365	0.174
962.092	0.152
702.346	0.168
529.973	0.220

Table 3-5: Resonance frequencies and their corresponding HPB values
of 0.6 M boric acid with pH adjusted at 4.45.

Resonance Frequency, f_n (KHz):	HPB Δf (KHz):
12627.031	2.180
8765.109	1.284
7698.200	1.160
6310.245	1.030
3405.355	0.270
1914.561	0.296
1136.730	0.168
963.688	0.152
704.539	0.166
532.570	0.204

Table 3-6: Resonance frequencies and their corresponding HPB values
of 0.6 M boric acid with pH adjusted at 7.41.

Resonance Frequency, f_n (KHz):	HPB Δf (KHz):
12628.507	2.340
9049.910	1.340
7683.400	0.880
6294.810	0.780
3414.670	0.314
1919.798	0.372
1139.978	0.202
966.496	0.156
706.685	0.195
534.192	0.262

Table 3-7: Resonance frequencies and their corresponding HPB
values of 0.6 M boric acid with pH adjusted at 9.40.

Resonance Frequency, f_n (KHz):	HPB Δf (KHz):
12609.092	1.980
7700.580	1.354
6295.740	1.214
3445.242	0.454
1938.996	0.260
1150.035	0.212
974.987	0.160
712.873	0.212
538.834	0.246

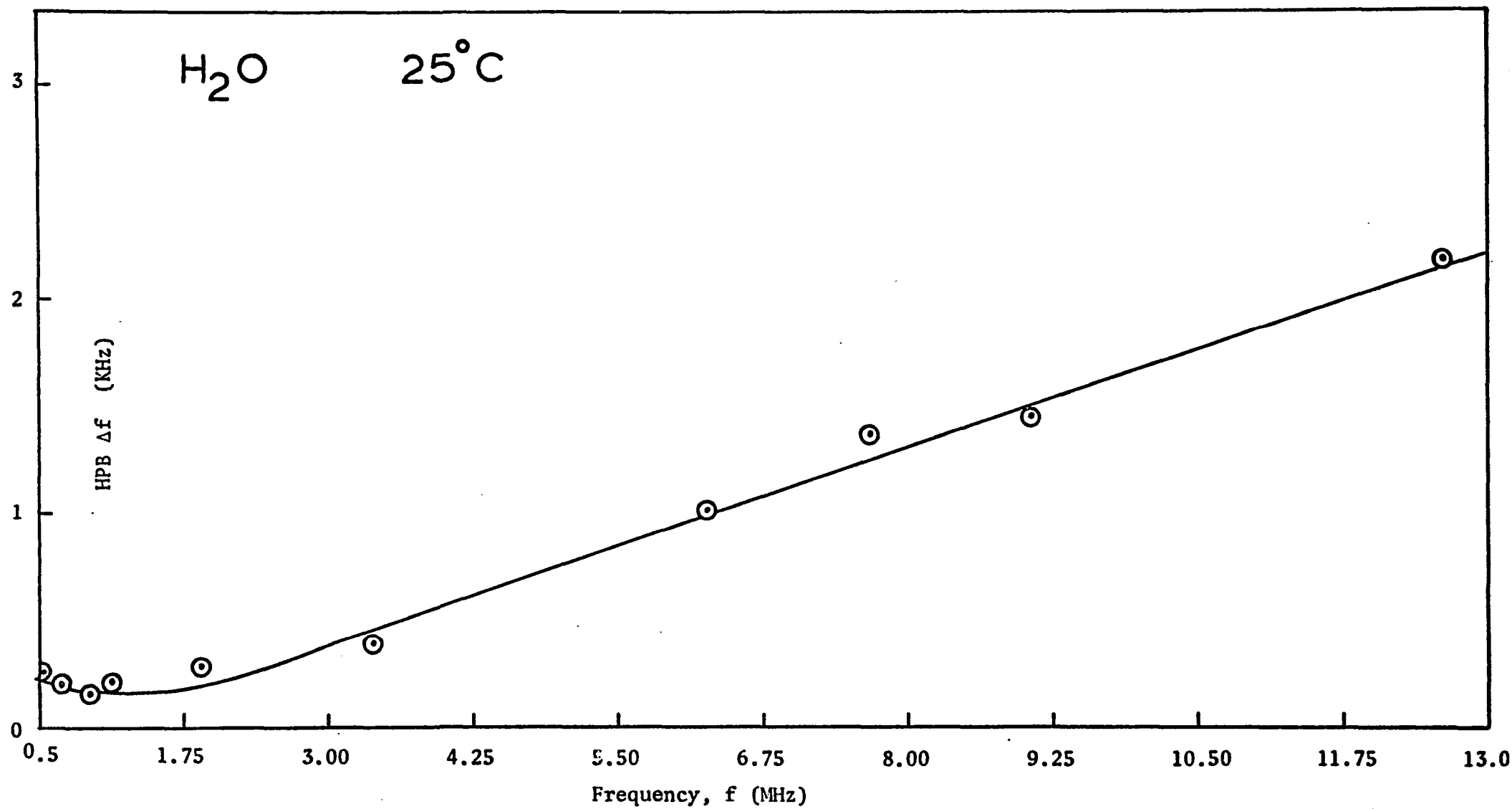


Figure 3-4

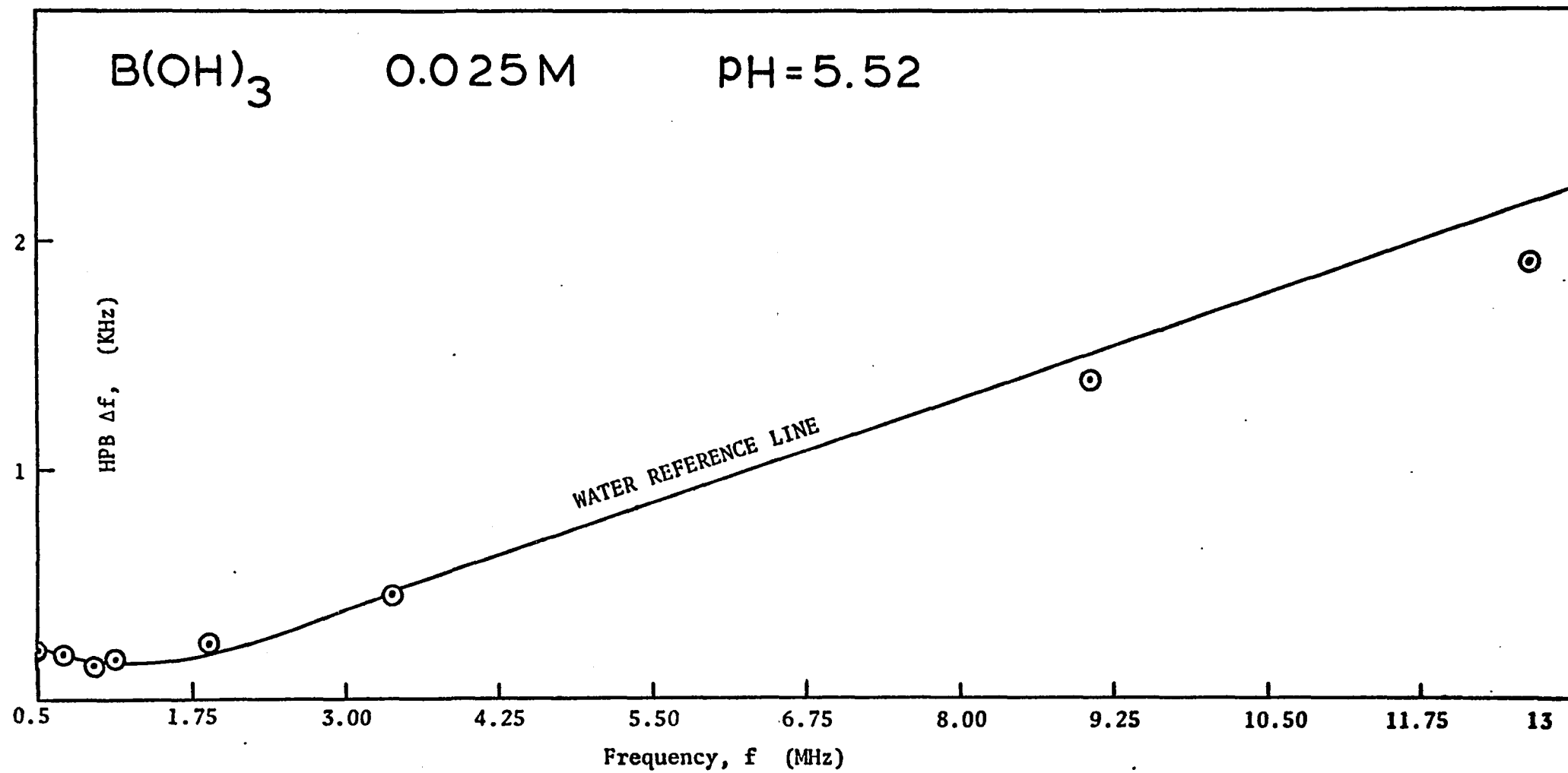


Figure 3-5

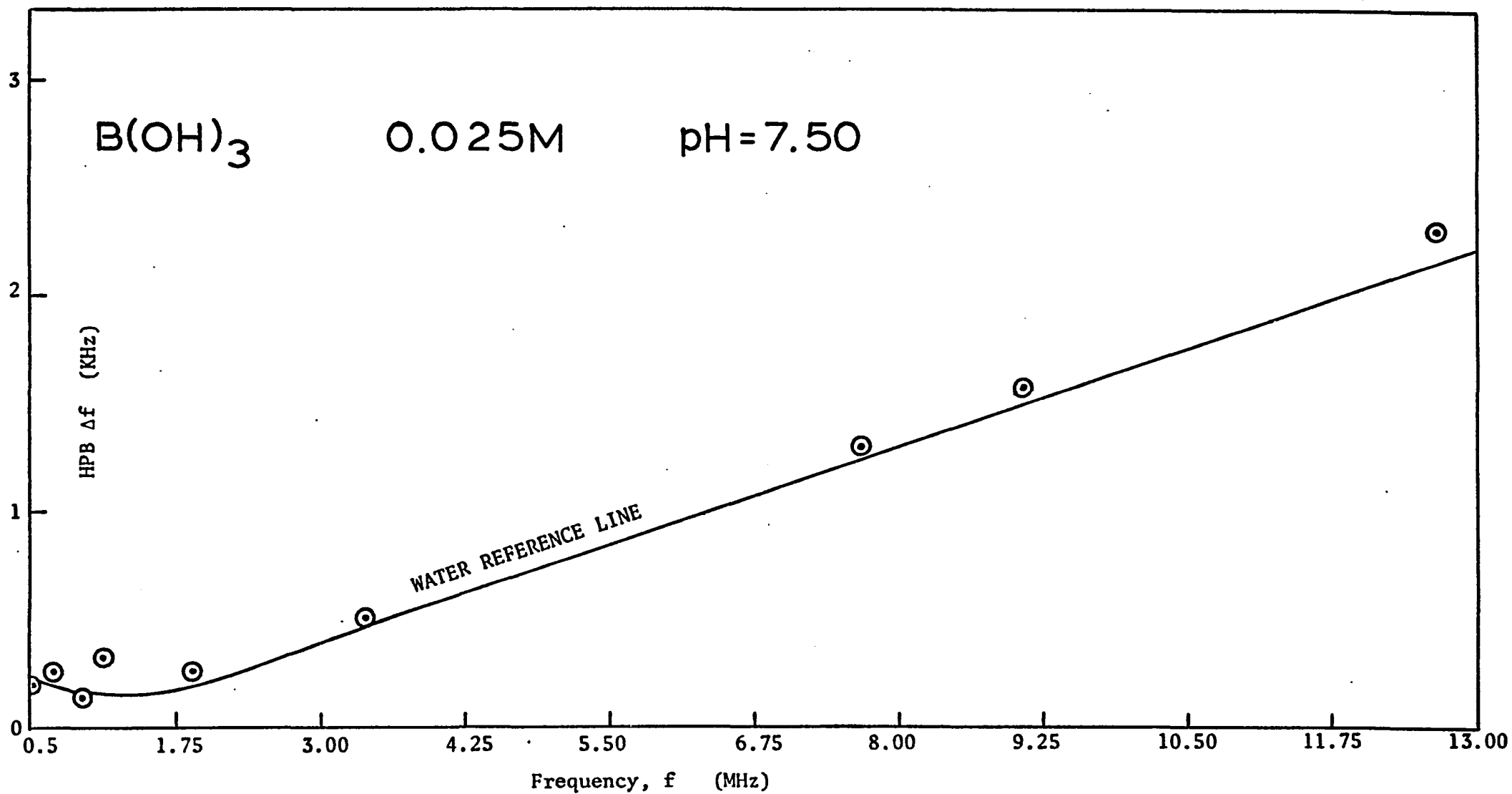
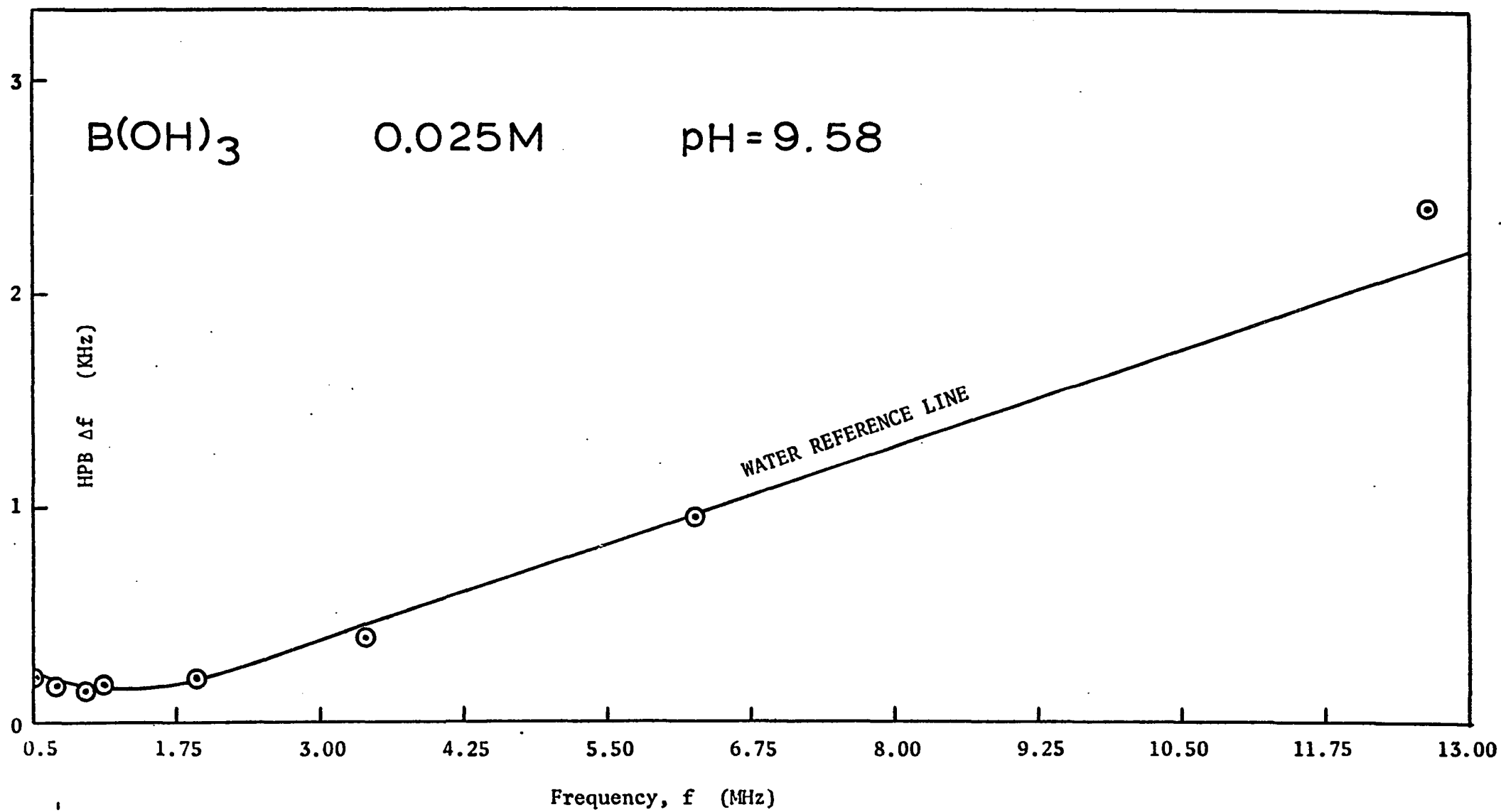


Figure 3-6



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Figure 3-7

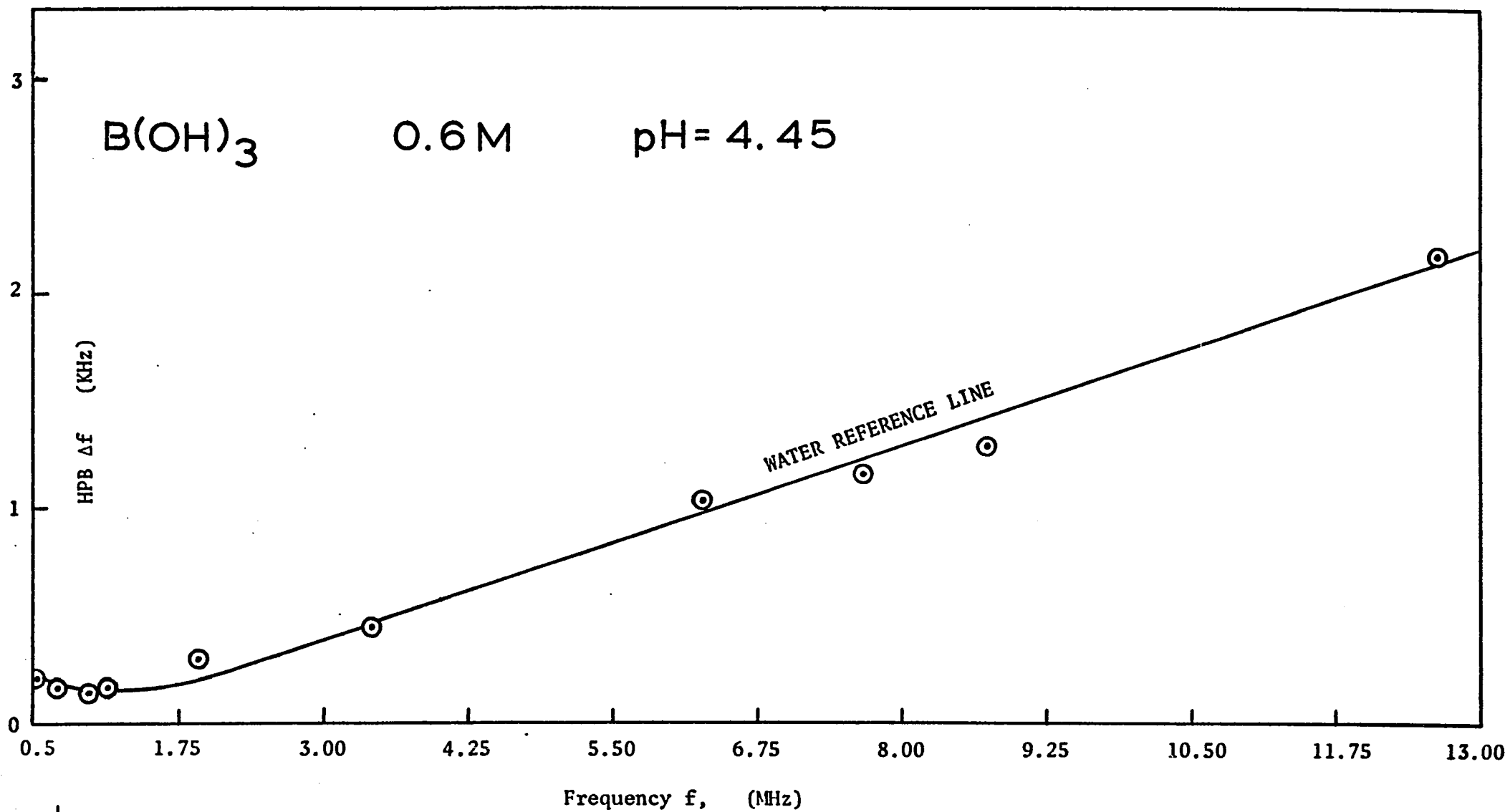


Figure 3-8

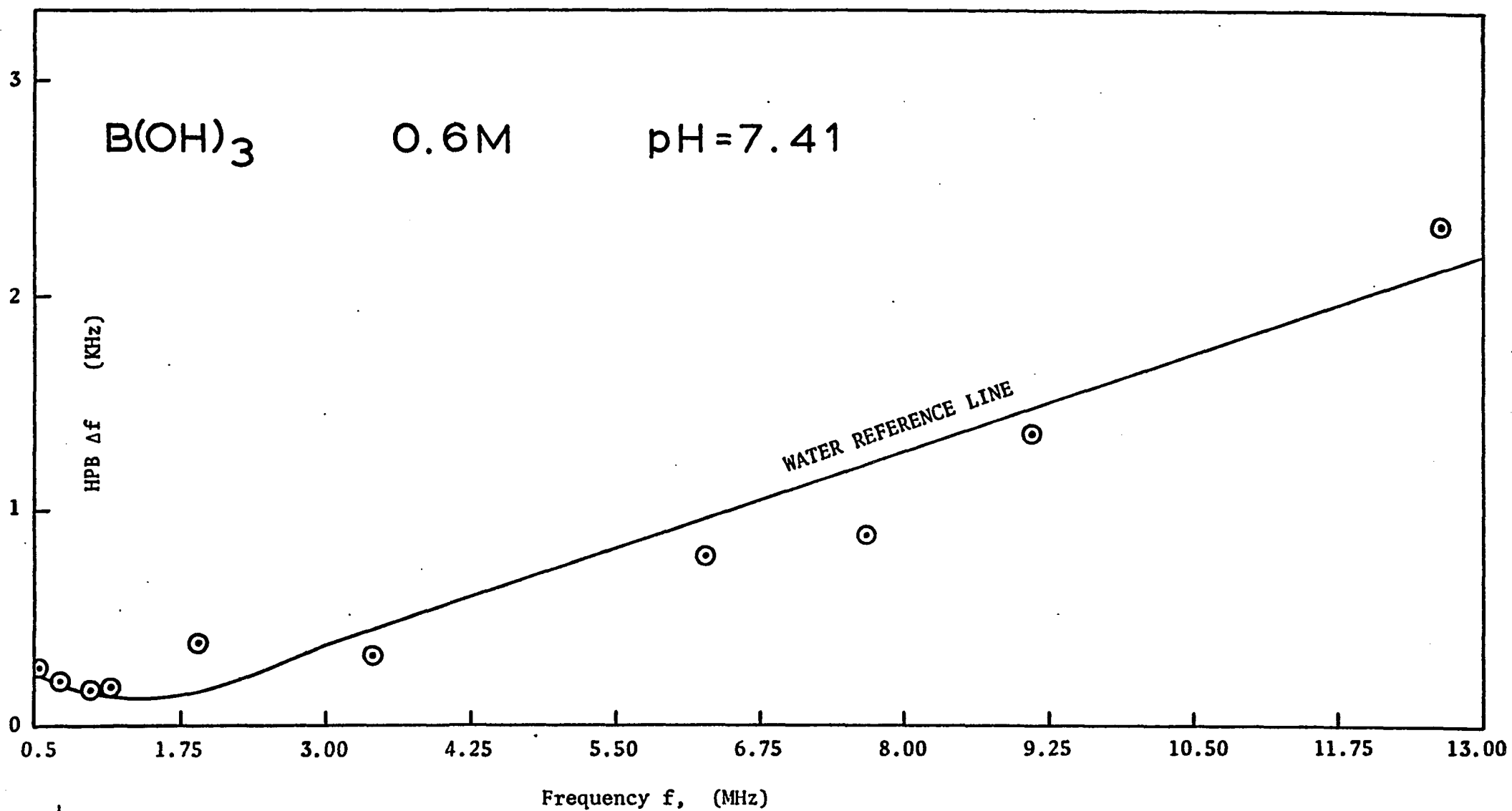


Figure 3-9

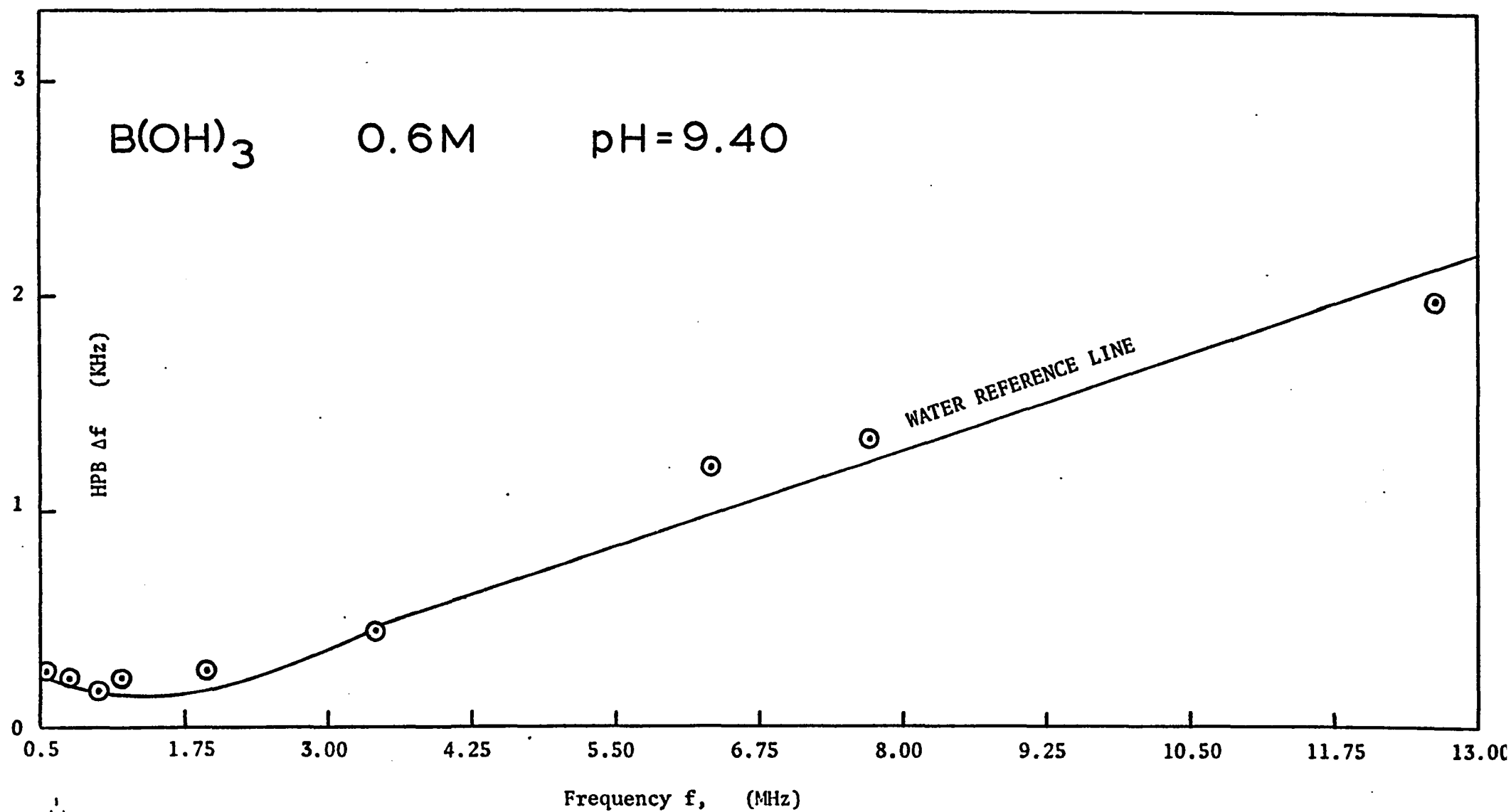


Figure 3-10

PART IV:
TEMPERATURE-JUMP RELAXATION STUDIES OF
AQUEOUS BORIC ACID SOLUTIONS
AND RELATED SYSTEMS

I. INTRODUCTION:

The temperature-jump method is known as a "step relaxation method" depending on a rapid perturbation followed by a shift of the composition of the solution towards the new position of equilibrium. Suppose that a certain fast reaction whose reaction rate we wish to measure comes to an equilibrium, which can be disturbed by a change of some external parameter such as temperature, pressure, or electric field. If such a change of condition is made suddenly, then there will be a time-lag while the system approaches the new position of equilibrium. This time-lag is expressed as a "relaxation time" and is related to the forward and backward rate constants of the reaction.

The fundamental principle of the temperature-jump method is to alter suddenly the temperature of a reaction system originally in chemical equilibrium, and then use some fast-recording detector to follow the course of the resulting change towards the new equilibrium state. From the reaction-time curve, the relaxation time and the rate constants can be evaluated.^{60, 84-86}

Generally, for reactions with half-lives between 10^{-2} and 10^{-6} sec, the temperature-jump method is probably the most versatile, accurate and widely-applicable. The types of reaction that have been investigated include proton transfer, hydrogen-bond formation, ligand

substitution, electron transfer, and reactions of biological interest
such as those of enzymes and polynucleotides. ⁸⁷⁻¹⁰²

In this part of the research, aqueous solutions of boric acid with boric acid concentrations less than 0.025 M, boric acid-NaCl solutions, boric acid-MgCl₂ solutions, boric acid-CaCl₂ solutions, boric acid-NaHCO₃ solutions, and the boric acid-seawater systems have been studied.

II. THEORY:

A. General Statements:

Suppose a solution containing substances coupled by chemical equilibria originally at thermal equilibrium, is suddenly perturbed by a rapid increase in temperature. The concentrations of the chemical species will then shift to new equilibrium values at the higher temperature. The magnitude of the concentration changes is governed by the laws of thermodynamics. For each equilibrium, we have:

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H^\circ}{RT^2} \quad (4-1)$$

where K is the equilibrium constant of the chemical reaction at constant pressure; ΔH° is the standard enthalpy change of the reaction; R is the gas constant and T is the absolute temperature. From the above equation, it is obvious that this method is valid only for reactions in which concentrations of species participating in the equilibrium (and hence the equilibrium constant) are temperature dependent, that is, $\Delta H^\circ \neq 0$, and in which the rate of concentration change is slower than the time required to heat the solution to the new temperature. Obviously, in the case of a sequence of coupled reactions, the system will be perturbed by a temperature-jump if any of the reactions

is characterized by a non-zero enthalpy change. In the case of equilibria which are insensitive to temperature, a perturbation of the system can also be accomplished by coupling the reactions of interest to a temperature dependent reaction. The most common example of this is a "pH jump" which can be achieved by use of a buffer with temperature dependent ionization constants. With this technique pH dependent reactions can be readily perturbed. Other concentration jump methods can also be devised if needed, but in general, equilibrium constants are sufficiently dependent on temperature that this is unnecessary.

The rates of change of the concentrations to their new equilibrium values are characterized by linear first order differential equations, which have solutions in the form of linear combinations of exponentials. Each exponential term is associated with a relaxation time, τ , which may be thought of as a reciprocal first-order rate constant. Thus a complex reaction mechanism is associated with a spectrum of relaxation times. In general, the relaxation times will have a unique dependence on the equilibrium concentrations and the determination of the relaxation times at various concentrations permits postulation of a reaction mechanism. The present time resolution of temperature-jump equipment is about 1 μ sec, but in principle, the method can be extended to even shorter times.

So far, only the perturbation of a system at equilibrium has been considered. In principle relaxation methods can be applied to any system where an overall net change in concentrations does not occur. Therefore, systems in a steady state can also be perturbed,

and the relaxation spectrum can then be determined if the steady state persists for a sufficiently long time. By using a combined stopped flow-temperature jump apparatus, perturbation of steady states with half times as short as milliseconds can be accomplished. Thus the temperature-jump method can be applied to both reversible and essentially irreversible reactions.

B. Temperature Pulse By Joule Heating:

The temperature pulse is obtained by discharge of a high voltage capacitor through the solution in a suitable cell. The temperature pulse is applied to an aqueous solution of low resistance and as a result the solution temperature is raised rapidly by several degrees.

Now, let the current delivered during the discharge of the capacitor have the form:

$$i = \left(\frac{V_0}{R}\right)e^{-t/RC} \quad (4-2)$$

This equation is valid when $RC/2 \gg 2L/R$, which is usually the case.

V_0 is the initial value of the voltage across the capacitor; R is the resistance of the solution between the electrodes; C is the discharge capacitance in farads; and L is the inductance.

If all other impedance losses in the circuit are small compared to that occurring in the solution, the temperature rise rate is:

$$\frac{dT}{dt} = \frac{i^2 R}{4.18 C_p \rho V} \quad (4-3)$$

where C_p and ρ are the specific heat capacity and the density of the

solution, respectively; and V is the volume of the solution that is heated between the electrodes.

Substitution of eqn.(4-2) into (4-3) and integration from $t=0$ to $t=t$ (with constant C_p , ρ , V, and R), yields the relationship:

$$\begin{aligned}\delta T(t) &= \frac{CV_o^2}{8.36C_p\rho V} [1 - e^{-2t/RC}] \\ &= \delta T_\infty [1 - e^{-2t/RC}]\end{aligned}\tag{4-4}$$

where:

$$\delta T_\infty = \frac{CV_o^2}{8.36C_p\rho V}$$

Thus the heating of the solution proceeds exponentially with a characteristic time constant $RC/2$. Typical values of the time constant, $RC/2$, and the total temperature rise, δT_∞ , are 1-10 μsec and 7-8°C, respectively.

C. Detection Of Concentration Changes:

Concentration changes may be detected by several optical methods such as absorption spectrophotometry, fluorimetry, polarimetry, or light-scattering. However, electrical properties, such as conductivity, also might be used, but in order to achieve sufficient sensitivity no inert electrolytes can be present. This is a prohibitive restriction if the temperature perturbation is done with Joule heating.

The total concentration change, δC_t , of a single component of a one step reaction when the temperature jump, δT , is small is:

$$\delta C_t = \delta T \cdot \frac{\partial \ln C_i}{\partial \ln K} \cdot \frac{\Delta H^\circ}{RT^2} \quad (4-5)$$

where the activity coefficients have been neglected, since under the customary conditions for performing kinetic experiments, the activity coefficients are not altered appreciably by the perturbation.

For a single relaxation process:

$$\delta C_i = \delta C_t (1 - e^{-t/\tau}) \quad (4-6)$$

while for multiple relaxation processes, we have:

$$\delta C_i = \sum_j A_j e^{-t/\tau_j} \quad (4-7)$$

where the A_j 's are constants which can be evaluated for a given mechanism. Therefore any optical property which is a linear function of the concentration (for small concentration changes) can be used for the measurement of relaxation times.

For absorption spectrophotometry the equation relating concentration and light intensity, I , transmitted through the solution is:

$$I = I_0 e^{-\epsilon_i C_i \ell} \quad (4-8)$$

where ϵ_i is the molar extinction coefficient of the i -th species, ℓ is the path length of the observation cell in cm, C_i is the concentration in moles/liter, and I_0 is the light intensity before passage through the cell. For small concentration changes,

$$(\delta I/I_0) = -\epsilon_i \ell \delta C_i \quad (4-9)$$

so that the change in light intensity is directly proportional to the concentration change.

D. Analysis Of Data:

If a reaction mechanism is sufficiently simple or the relaxation times are sufficiently separated on the time axis, then by selection of an appropriate time base, a single discrete relaxation time can be observed.

For a single relaxation time and small perturbations, $x \ll c$, the rate at which a chemical system relaxes is proportional to the difference between the actual (at any time t) and equilibrium concentrations (at T_f), that is,

$$-(dx/dt) = (1/\tau)x \quad (4-10)$$

where $x \equiv c - \bar{c}$

From Beer's Law:

$$A = \epsilon \ell c \quad (4-11)$$

where A is the optical absorbance; ϵ is the molar extinction coefficient; ℓ is the path length; and c is the concentration.

Equation (4-11) can be rewritten as:

$$A = \epsilon [x + \bar{c}] \ell$$

$$\text{or: } dA = \epsilon \ell dx$$

$$\text{or: } x = (1/\epsilon \ell) \cdot \Delta A \quad (4-12)$$

Substituting eqn. (4-12) into (4-10), gives:

$$-(d\Delta A/dt) = (1/\tau) \cdot \Delta A \quad (4-13)$$

Integrating eqn. (4-13), one obtains: ¹⁰³⁻¹⁰⁵

$$\Delta A = \Delta A_0 e^{-t/\tau} \quad (4-14)$$

$$\text{or: } \log \Delta A = (-1/2.303\tau)t + \text{constant} \quad (4-15)$$

Since the signal appeared on the oscillograph is proportional to

the absorbance of the solution, that is,

$$\Delta S \propto \Delta A$$

equation (4-14) can be expressed in the form:

$$\Delta S = \Delta S_0 e^{-t/\tau} \quad (4-16)$$

where ΔS is the difference between the signal at $t=t$ and $t=\infty$, and ΔS_0 is the difference between the signal at $t=0$ and $t=\infty$. Therefore a plot of $\log \Delta S$ vs. t should be a straight line with a slope of $-1/2.303\tau$.

In the case of multiple relaxation times, eqn.(4-16) can be written as:

$$\Delta S = \sum_{i=1}^n \Delta S_{0,i} e^{-t/\tau_i} \quad (4-17)$$

A plot of $\log \Delta S$ vs. t will be curved if $i > 1$. However, at sufficiently long times all of the terms of the series except that characterized by the longest relaxation time, the n -th, will go to zero. Therefore, a straight line can be drawn through the curve at long times ($t \rightarrow \infty$) and the relaxation time and $\Delta S_{0,n}$ can be determined. This term can now be subtracted from the series (that is, the straight line subtracted from the curve) and the resultant series (or curve) becomes:

$$\Delta S = \sum_{i=1}^{n-1} \Delta S_{0,i} e^{-t/\tau_i} \quad (4-18)$$

Repetition of this procedure will yield the n relaxation times. In practice, if the relaxation times do not differ by at least a factor of five, resolution of the relaxation spectrum is not possible.

III. INSTRUMENTATION AND EXPERIMENTATION:

A. Instruments Used:

1. Kepeco Model JQE 55-20(M) Power Supply: Used to control the voltage and current of the lamp.
2. Sorensen 230-6P-R&D High Voltage D.C. Power Supply: Used to supply 10 kV high voltage to the capacitor.
3. Electronics Console: Which houses the voltage follower, differential amplifier, inverter, gain amplifier, and spark gap triggering circuit.
4. Lamp and the Bausch & Lomb cat. no. 33-86-79 High-Intensity Monochromator: Supply the high intensity light of certain wavelength.
5. Photomultiplier Tube and Its Housing Chamber.¹⁰⁶
6. Capacitor: Which has the capacity of 0.04 mfd.
7. Tektronix Type 564 Storage Oscilloscope.
8. Fluke Model 412B High Voltage D.C. Power Supply: Supplies the high voltage needed for the photomultiplier tube.
9. T-Jump Cell: The most critical part of the temperature jump apparatus from the aspect of design is the cell which contains the reaction mixture under investigation. The cell is made of Plexiglas (polymethyl methacrylate) and requires about 2 ml of solution. Installed in the middle of the cell are two conical quartz lenses which focus the beam of light and thus considerably

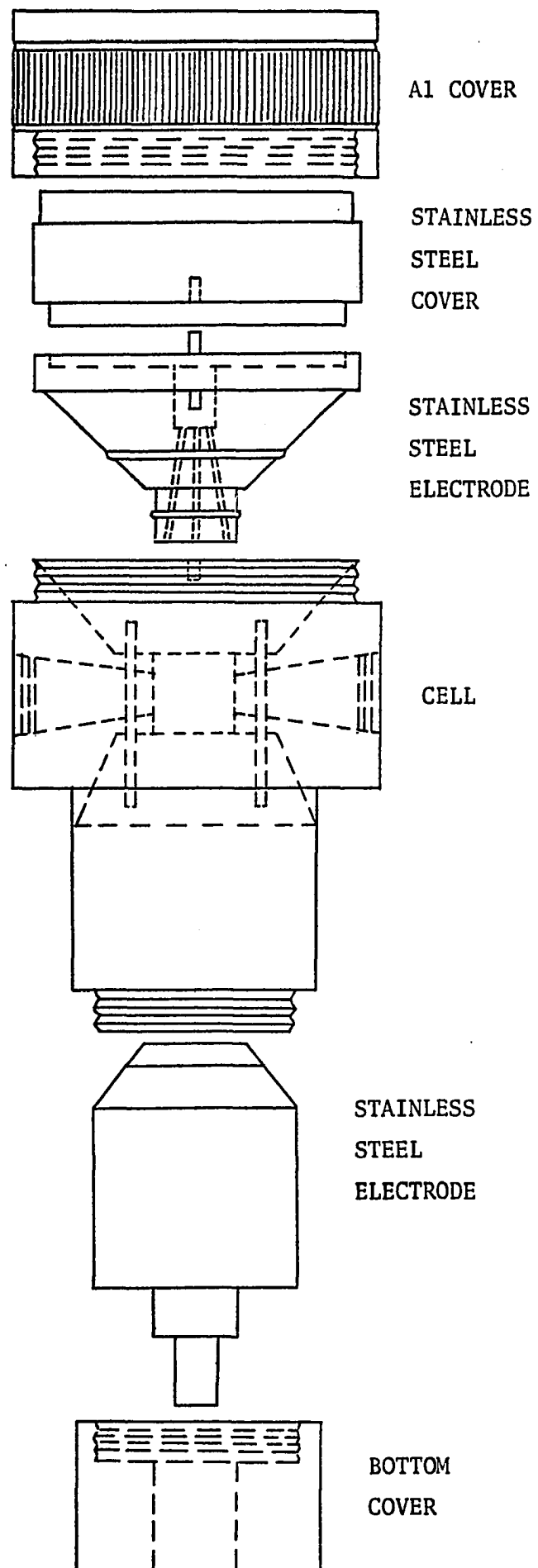
enhance the signal to noise ratio. The observation windows are perpendicular to the path of the discharge. The length of the light path between quartz windows is 7 mm. The faces of the electrodes are 10 mm apart, and the volume of the solution that is heated by the electrical discharge is about 0.14 ml. After the cell has been filled, the top, which consists of the stainless steel electrode and the aluminum cover, is screwed on, and any air bubbles that have been trapped in the lower chamber or beneath the ground electrode are removed. The entire assembly may then be placed in a cylindrical Plexiglas support which is mounted in the light path. Finally, a brass cover which has been connected to the ground is screwed on the top of the entire cell. This brass cover is also in thermal contact with the solution by way of the ground electrode of the cell so that the temperature of the sample solution can return to its initial value within a few minutes after the pulse. A detailed diagram of the cell and its components is shown in Figure 4-1.

B. Chemicals Used:

1. Baker & Adamson A.C.S. Reagent Grade Boric Acid (crystal).
2. G.F. Smith Chemical Co. Reagent Grade Anhydrous Sodium Perchlorate.
3. Indicators: Include Thymol Blue(thymolsulfonephthalein), Phenol Red (phenolsulfonephthalein), Cresol Red (o-cresolsulfonephthalein), and Phenolphthalein (2,2-bis-p-hydroxyphenyl phthalide).
4. Fisher Scientific Co., A.C.S. Certified Sodium Chloride (crystal).
5. Fisher Scientific Co., A.C.S. Certified Calcium Chloride (granular).

T-JUMP CELL AND ITS COMPONENTS

Figure 4-1



6. Mallinckrodt, Analytical Reagent Grade Magnesium Chloride (crystal).
7. Merck & Co., Inc., A.C.S. Reagent Grade Sodium Bicarbonate (powder).
8. Standard Sea-Water P₅₉ with Chlorinity at 19,377 0/00.¹⁰⁷

C. Experimental Procedure:

The complete set-up of the temperature-jump apparatus has been shown in Figure 4-2. All the instruments are warmed up for at least two hours before starting the experiment. The solution has been carefully prepared from distilled, deionized, and boiled water. Some trial runs on the solution have been made by using either Zeiss spectrophotometer or Cary Model 118C spectrophotometer to determine the optimum conditions of wavelength, absorbance and pH. The prepared solution is then transferred to the temperature-jump cell. During this transferring process, care should be taken that no air bubbles are present in the cell. Otherwise electrical breakdown will occur in the cell.

The lamp current and voltage have been set at 8-10 amperes and approximately 20 volts, respectively. However, to accomplish this current value, a corresponding change in the voltage setting may be necessary. The voltage on the Model 412B High Voltage D.C. Power Supply has been set between 250-350 volts. The entrance and exit slits of the Bausch and Lomb Monochromator are initially set at zero, and gradually opened until a signal of 4-6 volts is obtained at the photomultiplier tube output. It is important to adjust these three units so that the maximum amount of light goes through the cell

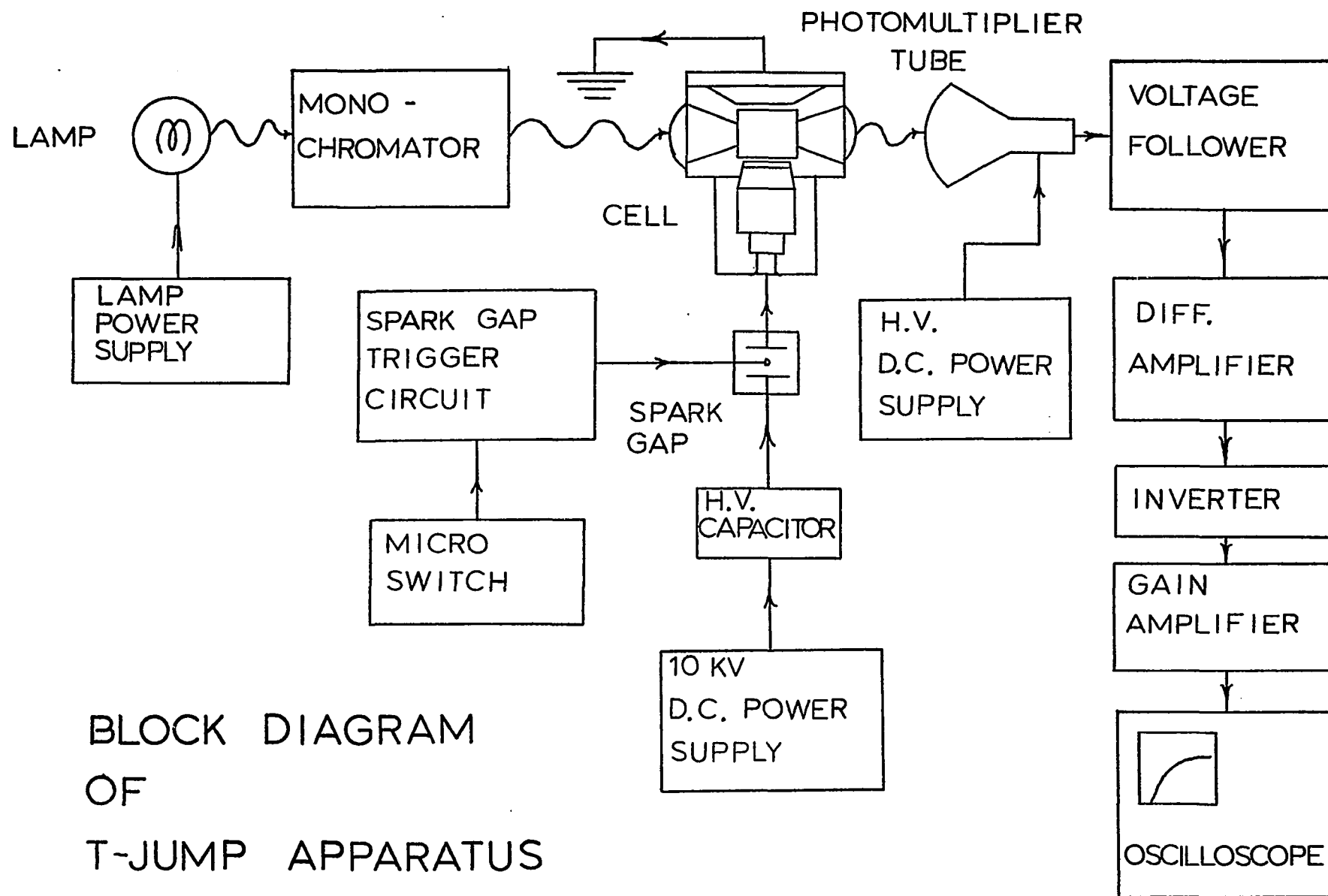


Figure 4-2

under any given set of experimental conditions. For instance, for a sample solution with a relatively narrow absorption band, and a relatively high absorbance, it may be necessary to operate at a small slit width, a high lamp intensity, and a higher voltage at the photomultiplier tube. However, if operating conditions become such that the photocurrent becomes relatively high (because of the high light intensity and the high voltage at the photomultiplier tube), then it may be necessary to check the linearity of the phototube response. This can be done by measuring the P.M.T. voltage with water and two sample solutions of known absorbances in the cell under a given set of conditions.

The high voltage at the capacitor has been set at 10 kV. The capacitor is installed in the Plexiglas housing unit which also contains the spark gap. The temperature-jump is initiated through the discharge of this capacitor. The discharge can be carried out by triggering the spark gap using a microswitch together with a spark gap triggering circuit. After the 10 kV capacitor has been discharged, a current flows through the solution in the T-Jump cell, and a sudden temperature rise of several degrees occurs. As a consequence, the reaction system under investigation starts to relax and gives a relaxation signal. The relaxation signal then passes through the photomultiplier tube, voltage follower, differential amplifier, inverter, gain amplifier, and finally feeds into the oscilloscope. The oscilloscope can be triggered either by an external triggering system or an internal triggering system. The signal is displayed on the oscilloscope screen and

is recorded on Polaroid Type 47 film.¹⁰⁸ The trace recorded on
the film can then be analyzed and its relaxation time determined.

IV. RESULTS AND DISCUSSION :

A. Boric Acid System:

1. Reaction Mechanisms Assumed:

a. One-Step Reaction Process:

In basic aqueous solution the dissociation of boric acid can be expressed in the following form:



where ① and ② stand for the number of the state.

The rate equation is:

$$\frac{d[\text{B(OH)}_4^-]}{dt} = k_f [\text{B(OH)}_3] [\text{OH}^-] - k_b [\text{B(OH)}_4^-] \quad (4-20)$$

When the system reaches its equilibrium state, we have:

$$\frac{d[\text{B(OH)}_4^-]}{dt} = 0 \quad (4-21)$$

or:

$$k_f [\text{B(OH)}_3] [\text{OH}^-] = k_b [\text{B(OH)}_4^-] \quad (4-22)$$

where k_f and k_b are the forward and backward rate constants, respectively. $[\text{B(OH)}_3]$, $[\text{OH}^-]$, and $[\text{B(OH)}_4^-]$ are the equilibrium concentrations of various species involved.

Now define:

$$[C] = [\bar{C}] + \sum_s v^{(s)} \Delta \xi_s \quad (4-23)$$

where $[C]$ is the instantaneous concentration of substance C; $[\bar{C}]$ is the equilibrium concentration of substance C; $\Delta \xi_s$ is the extent of reaction parameter of state S; and $v^{(s)}$ is the stoichiometric coefficient of substance C in state S.

Using the relationship of eqn.(4-23), for the reaction system(4-19) considered, we can write directly the equations:

$$[B(OH)_3] = [\bar{B(OH)}_3] + \Delta \xi_1 \quad (4-24)$$

$$[OH^-] = [\bar{OH}^-] + \Delta \xi_1 \quad (4-25)$$

$$[B(OH)_4^-] = [\bar{B(OH)}_4^-] + \Delta \xi_2 \quad (4-26)$$

Substituting eqns.(4-24), (4-25), and (4-26) back into eqn.(4-20), and using the relationships of eqn.(4-21) and (4-22), we obtain:

$$\frac{d\Delta \xi_2}{dt} = k_f \{ [\bar{OH}^-] + [\bar{B(OH)}_3] \} \Delta \xi_1 - k_b \Delta \xi_2 + k_f \Delta \xi_1^2 \quad (4-27)$$

Since the perturbation is small, the $\Delta \xi_1^2$ or $\Delta \xi_1^3$ terms can be neglected. Eqn.(4-27) now has the form:

$$\Delta \dot{\xi}_2 = k_f \{ [\bar{OH}^-] + [\bar{B(OH)}_3] \} \Delta \xi_1 - k_b \Delta \xi_2 \quad (4-28)$$

where:

$$\Delta \dot{\xi}_2 \equiv \frac{d\Delta \xi_2}{dt}$$

Since:

$$\Delta \dot{\xi}_1 = -\Delta \dot{\xi}_2$$

we can write:

$$\Delta \dot{\xi}_1 = -k_f \{ [\bar{OH}^-] + [\bar{B(OH)}_3] \} \Delta \xi_1 + k_b \Delta \xi_2 \quad (4-29)$$

Now express eqns.(4-29) and (4-28) in the matrix notation:

$$\begin{bmatrix} \Delta \xi_1 \\ \Delta \xi_2 \end{bmatrix} = \begin{bmatrix} -k_f \{ [\overline{B(OH)_3}] + [\overline{OH^-}] \} & k_b \\ k_f \{ [\overline{B(OH)_3}] + [\overline{OH^-}] \} & -k_b \end{bmatrix} \begin{bmatrix} \Delta \xi_1 \\ \Delta \xi_2 \end{bmatrix} \quad (4-30)$$

This gives:

$$\begin{vmatrix} -k_f \{ [\overline{B(OH)_3}] + [\overline{OH^-}] \} - \lambda & k_b \\ k_f \{ [\overline{B(OH)_3}] + [\overline{OH^-}] \} & -k_b - \lambda \end{vmatrix} = 0 \quad (4-31)$$

where λ is the eigenvalue of the matrix.

Expanding eqn. (4-31), gives:

$$k_b \lambda + k_f \lambda [\overline{OH^-}] + k_f \lambda [\overline{B(OH)_3}] + \lambda^2 = 0 \quad (4-32)$$

Since $\lambda \neq 0$,

$$k_b + k_f \{ [\overline{B(OH)_3}] + [\overline{OH^-}] \} + \lambda = 0 \quad (4-33)$$

or:

$$\lambda = -k_b - k_f \{ [\overline{OH^-}] + [\overline{B(OH)_3}] \} \quad (4-34)$$

Using the relationship:

$$(1/\tau) \equiv -\lambda \quad (4-35)$$

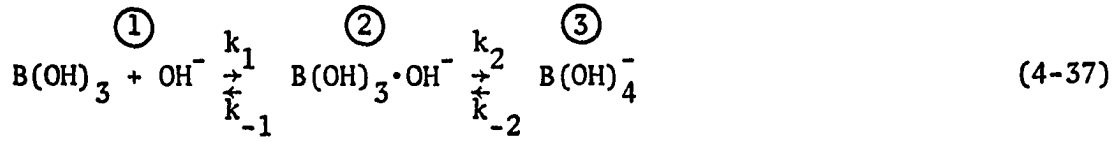
where τ is the relaxation time. Equation (4-34) then becomes:

$$(1/\tau) = k_f \{ [\overline{B(OH)_3}] + [\overline{OH^-}] \} + k_b \quad (4-36)$$

This is the equation which expresses the relation between the relaxation time and the equilibrium concentrations of various species involved in the boric acid one-step reaction process.

b. Two-Step Reaction Process:

The reaction mechanism for a two-step process can be expressed as:



Which has the rate equations:

$$\frac{d[\text{B(OH)}_3]}{dt} = -k_1 [\text{B(OH)}_3] [\text{OH}^-] + k_{-1} [\text{B(OH)}_3 \cdot \text{OH}^-] \quad (4-38)$$

$$\frac{d[\text{B(OH)}_3 \cdot \text{OH}^-]}{dt} = k_1 [\text{B(OH)}_3] [\text{OH}^-] - (k_{-1} + k_2) [\text{B(OH)}_3 \cdot \text{OH}^-] + k_{-2} [\text{B(OH)}_4^-] \quad (4-39)$$

$$\frac{d[\text{B(OH)}_4^-]}{dt} = k_2 [\text{B(OH)}_3 \cdot \text{OH}^-] - k_{-2} [\text{B(OH)}_4^-] \quad (4-40)$$

Since:

$$[\text{B(OH)}_3] = [\overline{\text{B(OH)}}_3] + \Delta\xi_1 \quad (4-41)$$

$$[\text{OH}^-] = [\overline{\text{OH}}^-] + \Delta\xi_1 \quad (4-42)$$

$$[\text{B(OH)}_3 \cdot \text{OH}^-] = [\overline{\text{B(OH)}}_3 \cdot \text{OH}^-] + \Delta\xi_2 \quad (4-43)$$

$$[\text{B(OH)}_4^-] = [\overline{\text{B(OH)}}_4^-] + \Delta\xi_3 \quad (4-44)$$

eqns. (4-38), (4-39), and (4-40) have the following forms:

$$\Delta\dot{\xi}_1 = -k_1 \{ [\overline{\text{B(OH)}}_3] + [\overline{\text{OH}}^-] \} \cdot \Delta\xi_1 + k_{-1} \cdot \Delta\xi_2 \quad (4-45)$$

$$\Delta\dot{\xi}_2 = k_1 \{ [\overline{\text{B(OH)}}_3] + [\overline{\text{OH}}^-] \} \cdot \Delta\xi_1 - (k_{-1} + k_2) \cdot \Delta\xi_2 + k_{-2} \cdot \Delta\xi_3 \quad (4-46)$$

$$\Delta\dot{\xi}_3 = k_2 \cdot \Delta\xi_2 - k_{-2} \cdot \Delta\xi_3 \quad (4-47)$$

In deriving the above equations, the following relationships have also been used:

$$\frac{d[\overline{\text{B(OH)}}_3]}{dt} = \frac{d[\overline{\text{B(OH)}}_3 \cdot \text{OH}^-]}{dt} = \frac{d[\overline{\text{B(OH)}}_4^-]}{dt} = 0 \quad (4-48)$$

(equilibrium concentrations are independent of time)

$$k_1 [\overline{\text{B(OH)}}_3] [\overline{\text{OH}}^-] = k_{-1} [\overline{\text{B(OH)}}_3 \cdot \text{OH}^-] \quad (4-49)$$

$$(k_{-1} + k_2) [\overline{\text{B(OH)}}_3 \cdot \text{OH}^-] = k_1 [\overline{\text{B(OH)}}_3] [\overline{\text{OH}}^-] + k_{-2} [\overline{\text{B(OH)}}_4^-] \quad (4-50)$$

$$k_2 [\overline{\text{B(OH)}}_3 \cdot \text{OH}^-] = k_{-2} [\overline{\text{B(OH)}}_4^-] \quad (4-51)$$

(at equilibrium, the forward reaction rate is equal to the backward reaction rate)

$$\Delta \xi_1^2 = \Delta \xi_2^2 = \Delta \xi_3^2 = 0 \quad (4-52)$$

(because of the small perturbation, higher order terms can be omitted)

Putting eqns. (4-45), (4-46), and (4-47) in matrix notation, we have:

$$\begin{bmatrix} \Delta \dot{\xi}_1 \\ \Delta \dot{\xi}_2 \\ \Delta \dot{\xi}_3 \end{bmatrix} = \begin{bmatrix} -k_1 \{ [\overline{B(OH)}_3] + [\overline{OH}^-] \} & k_{-1} & 0 \\ k_1 \{ [\overline{B(OH)}_3] + [\overline{OH}^-] \} & -(k_{-1} + k_2) & k_{-2} \\ 0 & k_2 & -k_{-2} \end{bmatrix} \begin{bmatrix} \Delta \xi_1 \\ \Delta \xi_2 \\ \Delta \xi_3 \end{bmatrix} \quad (4-53)$$

This gives the determinant:

$$\begin{vmatrix} -k_1 A - \lambda & k_{-1} & 0 \\ k_1 A & -(k_{-1} + k_2) - \lambda & k_{-2} \\ 0 & k_2 & -k_{-2} - \lambda \end{vmatrix} = 0 \quad (4-54a)$$

where:

$$A = [\overline{B(OH)}_3] + [\overline{OH}^-] \quad (4-54b)$$

and λ = eigen value of the matrix

Expanding eqn. (4-54a), gives:

$$[-k_1 A - \lambda] [-(k_{-1} + k_2) - \lambda] [-k_{-2} - \lambda] - [k_{-1}] [k_1 A] [-k_{-2} - \lambda] - [-k_1 A - \lambda] [k_2] [k_{-2}] = 0 \quad (4-55)$$

or:

$$\lambda^3 + (k_{-1} + k_{-2} + k_2 + k_1 A) \lambda^2 + (k_{-1} k_{-2} + k_1 k_{-2} A + k_1 k_2 A) \lambda = 0 \quad (4-56)$$

Since $\lambda \neq 0$,

$$\lambda^2 + (k_{-1} + k_{-2} + k_2 + k_1 A) \lambda + (k_{-1} k_{-2} + k_1 k_{-2} A + k_1 k_2 A) = 0 \quad (4-57)$$

Let:

$$B = k_{-1} + k_{-2} + k_2 + k_1 A$$

$$C = k_{-1} k_{-2} + k_1 k_{-2} A + k_1 k_2 A$$

$$\begin{aligned}\text{Then: } \lambda &= (1/2) [-B \pm \sqrt{B^2 - 4C}] \\ &= (B/2) \{-1 \pm [1 - (4C/B^2)]^{0.5}\}\end{aligned}\quad (4-58)$$

Now, using the relationship:

$$(1-x)^n = 1 - nx + \frac{n(n-1)x^2}{2!} - \frac{n(n-1)(n-2)x^3}{3!} + \dots$$

or:

$$\left(1 - \frac{4C}{B^2}\right)^{0.5} = 1 - \left(\frac{1}{2}\right)\left(\frac{4C}{B^2}\right) + \frac{\left(\frac{1}{2}\right)\left(-\frac{1}{2}\right)}{2!}\left(\frac{4C}{B^2}\right)^2 - \frac{\left(\frac{1}{2}\right)\left(-\frac{1}{2}\right)\left(-\frac{3}{2}\right)}{3!}\left(\frac{4C}{B^2}\right)^3 + \dots \quad (4-59)$$

Since $(4C/B^2)$ is a small number, the approximation of eqn. (4-59) which gives

$$\begin{aligned}[1 - (4C/B^2)]^{0.5} &= \\ &= \end{aligned}\quad (4-60)$$

Substituting eqn. (4-60) into eqn. (4-58) obtains:

$$\lambda = (B/2) \{-1 \pm [1 - (2C/B^2)]\} \quad (4-61)$$

For the "plus" sign:

$$\begin{aligned}\lambda_2 &= (B/2) \{-1 + [1 - (2C/B^2)]\} = (B/2) [-(2C/B^2)] = -C/B \\ &= -\frac{k_{-1}k_{-2} + k_1k_{-2}A + k_1k_2A}{k_{-1} + k_{-2} + k_2 + k_1A}\end{aligned}\quad (4-62)$$

Assume that $k_1, k_{-1} \gg k_2, k_{-2}$; then eqn. (4-62) reduces to the form:

$$\begin{aligned}-\lambda_2 &= \frac{k_{-1}k_{-2} + k_1k_{-2}A + k_1k_2A}{k_{-1} + k_1A} = \frac{k_{-2}(k_{-1} + k_1A)}{k_{-1} + k_1A} + \frac{k_1k_2A}{k_{-1} + k_1A} \\ &= k_{-2} + \frac{k_1k_2A}{k_{-1} + k_1A} = k_{-2} + \frac{k_2}{\frac{k_{-1}}{k_1A} + 1} \\ &= k_{-2} + k_2 \cdot \frac{1}{\left(\frac{k_{-1}A + k_{-1}}{k_1A}\right)} = k_{-2} + k_2 \cdot \frac{k_1A}{k_1A + k_{-1}}\end{aligned}$$

$$\begin{aligned}
\text{Then: } \lambda &= (1/2) [-B \pm \sqrt{B^2 - 4C}] \\
&= (B/2) \{-1 \pm [1 - (4C/B^2)]^{0.5}\}
\end{aligned} \tag{4-58}$$

Now, using the relationship:

$$(1-x)^n = 1 - nx + \frac{n(n-1)x^2}{2!} - \frac{n(n-1)(n-2)x^3}{3!} + \dots$$

or:

$$\left(1 - \frac{4C}{B^2}\right)^{0.5} = 1 - \left(\frac{1}{2}\right) \left(\frac{4C}{B^2}\right) + \frac{\left(\frac{1}{2}\right) \left(-\frac{1}{2}\right) \left(\frac{4C}{B^2}\right)^2}{2!} - \frac{\left(\frac{1}{2}\right) \left(-\frac{1}{2}\right) \left(-\frac{3}{2}\right) \left(\frac{4C}{B^2}\right)^3}{3!} + \dots \tag{4-59}$$

Since $(4C/B^2)$ is a small quantity, we can use the approximation of eqn. (4-59) which gives:

$$\begin{aligned}
[1 - (4C/B^2)]^{0.5} &\approx 1 - (1/2)(4C/B^2) \\
&= 1 - (2C/B^2)
\end{aligned} \tag{4-60}$$

Substituting eqn. (4-60) back into (4-58), one obtains:

$$\lambda = (B/2) \{-1 \pm [1 - (2C/B^2)]\} \tag{4-61}$$

For the "plus" sign:

$$\begin{aligned}
\lambda_2 &= (B/2) \{-1 + [1 - (2C/B^2)]\} = (B/2) [-(2C/B^2)] = -C/B \\
&= - \frac{k_{-1}k_{-2} + k_1k_{-2}A + k_1k_2A}{k_{-1} + k_{-2} + k_2 + k_1A}
\end{aligned} \tag{4-62}$$

Assume that $k_1, k_{-1} \gg k_2, k_{-2}$; then eqn. (4-62) reduces to the form:

$$\begin{aligned}
-\lambda_2 &= \frac{k_{-1}k_{-2} + k_1k_{-2}A + k_1k_2A}{k_{-1} + k_1A} = \frac{k_{-2}(k_{-1} + k_1A)}{k_{-1} + k_1A} + \frac{k_1k_2A}{k_{-1} + k_1A} \\
&= k_{-2} + \frac{k_1k_2A}{k_{-1} + k_1A} = k_{-2} + \frac{k_2}{\frac{k_{-1}}{k_1A} + 1} \\
&= k_{-2} + k_2 \cdot \frac{1}{\left(\frac{k_{-1}A + k_{-1}}{k_1A}\right)} = k_{-2} + k_2 \cdot \frac{k_1A}{k_1A + k_{-1}}
\end{aligned}$$

$$= k_{-2} + k_2 \cdot \frac{A}{A + \frac{k_{-1}}{k_1}} \quad (4-63)$$

Since $k_{-1}/k_1 = K_{21}$, where K_{21} is the equilibrium constant between state 2 and state 1; and also from eqn.(4-54b), eqn. (4-63) becomes:

$$-\lambda_2 = k_{-2} + k_2 \frac{[\overline{B(OH)_3}] + [\overline{OH^-}]}{[\overline{B(OH)_3}] + [\overline{OH^-}] + K_{21}} \quad (4-64)$$

or:

$$\frac{1}{\tau_2} = k_{-2} + k_2 \left\{ \frac{[\overline{B(OH)_3}] + [\overline{OH^-}]}{[\overline{B(OH)_3}] + [\overline{OH^-}] + K_{21}} \right\} \quad (4-65)$$

For the "minus" sign, eqn.(4-61) gives:

$$\begin{aligned} \lambda_1 &= (B/2) \{-1 - [1 - (2C/B^2)]\} = (B/2) [-2 + (2C/B^2)] \\ &= B[-1 + (C/B^2)] = -B + (C/B) \\ &= -(k_{-1} + k_{-2} + k_2 + k_1 A) + \frac{k_{-1}k_{-2} + k_1k_{-2}A + k_1k_2A}{k_{-1} + k_{-2} + k_2 + k_1A} \end{aligned} \quad (4-66)$$

Since $k_1, k_{-1} \gg k_2, k_{-2}$, eqn.(4-66) can be simplified to:

$$\begin{aligned} \lambda_1 &= -(k_{-1} + k_1 A) + \frac{k_{-1}k_{-2} + k_1k_{-2}A + k_1k_2A}{k_{-1} + k_1A} \\ &= -(k_{-1} + k_1 A) + \frac{k_{-2}(k_{-1} + k_1 A)}{k_{-1} + k_1 A} + \frac{k_1k_2A}{k_{-1} + k_1A} \\ &= -k_{-1} - k_1 A + k_{-2} + \frac{k_1k_2A}{k_{-1} + k_1A} \end{aligned} \quad (4-67)$$

Using the assumption $k_1, k_{-1} \gg k_2, k_{-2}$ again, eqn.(4-67) reduces further to:

$$\lambda_1 = -k_{-1} - k_1 A$$

or:

$$-\lambda_1 = k_{-1} + k_1 A \quad (4-68)$$

Thus:

$$\frac{1}{\tau_1} = k_{-1} + k_1 A$$

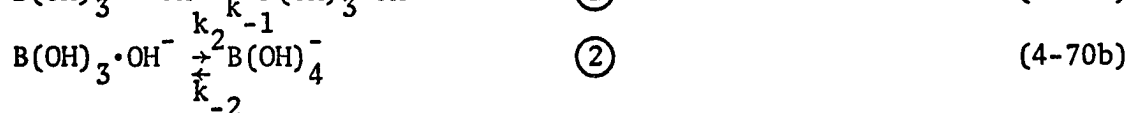
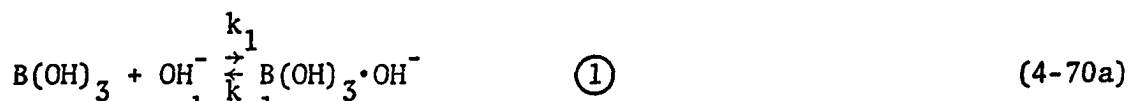
or:

$$\frac{1}{\tau_1} = k_{-1} + k_1 \{ [\overline{B(OH)_3}] + [\overline{OH^-}] \} \quad (4-69)$$

Eqns.(4-65) and (4-69) are equations which express the relations between the relaxation times and the equilibrium concentrations of the various species involved in the boric acid two-step reaction process.

In deriving eqns.(4-65) and (4-69), an alternative method can also be used, which is as follows:

The reactions can be written as:



from which, we can write:

$$g_{11} = \frac{1}{[\overline{B(OH)_3}]} + \frac{1}{[\overline{OH^-}]} + \frac{1}{[\overline{B(OH)_3 \cdot OH^-}]} \quad (4-71)$$

$$g_{12} = \frac{(+1)(-1)}{[\overline{B(OH)_3 \cdot OH^-}]} = \frac{-1}{[\overline{B(OH)_3 \cdot OH^-}]} \quad (4-72)$$

$$g_{22} = \frac{1}{[\overline{B(OH)_3 \cdot OH^-}]} + \frac{1}{[\overline{B(OH)_4^-}]} \quad (4-73)$$

Since:

$$D_0 = 1$$

$$D_1 = g_{11}$$

$$r_1 = k_1 [\overline{B(OH)_3}] [\overline{OH^-}] = k_{-1} [\overline{B(OH)_3 \cdot OH^-}]$$

and

$$\lambda_1 = r_1 D_1 / D_0 = r_1 D_1 ,$$

$$\begin{aligned} \lambda_1 &= k_1 [\overline{B(OH)_3}] [\overline{OH^-}] \cdot \left\{ \frac{1}{[\overline{B(OH)_3}]} + \frac{1}{[\overline{OH^-}]} + \frac{1}{[\overline{B(OH)_3 \cdot OH^-}]} \right\} \\ &= k_1 [\overline{OH^-}] + k_1 [\overline{B(OH)_3}] + k_{-1} \end{aligned} \quad (4-74)$$

Since $\tau = 1/\lambda$, equation (4-74) becomes:

$$(1/\tau_1) = k_{-1} + k_1 \{ [\overline{B(OH)_3}] + [\overline{OH^-}] \} \quad (4-75)$$

which is the same as eqn. (4-69).

Since:

$$r_2 = k_2 [\overline{B(OH)_3 \cdot OH^-}] = k_{-2} [\overline{B(OH)_4^-}] \quad (4-76)$$

$$D_2 = \begin{vmatrix} g_{11} & g_{12} \\ g_{21} & g_{22} \end{vmatrix} = g_{11}g_{22} - g_{12}g_{21} \quad (4-77)$$

$$\lambda_2 = \frac{r_2 D_2}{D_{2-1}} = \frac{r_2 D_2}{D_1} \quad (4-78)$$

and

$$\begin{aligned} \frac{D_2}{D_1} &= \frac{g_{11}g_{22} - g_{12}g_{21}}{g_{11}} = g_{22} - \frac{g_{12}^2}{g_{11}} \\ &= \left\{ \frac{1}{[\overline{B(OH)_3 \cdot OH^-}]} + \frac{1}{[\overline{B(OH)_4^-}]} \right\} - \left\{ \frac{\frac{1}{[\overline{B(OH)_3 \cdot OH^-}]^2}}{\frac{1}{[\overline{B(OH)_3}] + \frac{1}{[\overline{OH^-}] + \frac{1}{[\overline{B(OH)_3 \cdot OH^-}]}}}} \right\} \end{aligned} \quad (4-79)$$

substituting eqn. (4-76), (4-79) into (4-78), gives:

$$\lambda_2 = k_2 + k_{-2} - \left\{ \frac{\frac{k_2}{[\overline{B(OH)_3 \cdot OH^-}]}}{\frac{1}{[\overline{B(OH)_3}] + \frac{1}{[\overline{OH^-}] + \frac{1}{[\overline{B(OH)_3 \cdot OH^-}]}}} \right\}$$

or:

$$\frac{1}{\tau_2} = \lambda_2 = k_{-2} + k_2 \left\{ 1 - \frac{\frac{1}{[\overline{B(OH)_3 \cdot OH^-}]}}{\frac{1}{[\overline{B(OH)_3}] + \frac{1}{[\overline{OH^-}] + \frac{1}{[\overline{B(OH)_3 \cdot OH^-}]}}} \right\}$$

$$\begin{aligned}
&= k_{-2} + k_2 \left\{ \frac{\frac{1}{[\overline{\text{B}(\text{OH})}_3]} + \frac{1}{[\overline{\text{OH}}^-]}}{\frac{1}{[\overline{\text{B}(\text{OH})}_3]} + \frac{1}{[\overline{\text{OH}}^-]} + \frac{1}{[\overline{\text{B}(\text{OH})}_3 \cdot \overline{\text{OH}}^-]}} \right\} \\
&= k_{-2} + k_2 \left\{ \frac{\frac{[\overline{\text{OH}}^-] + [\overline{\text{B}(\text{OH})}_3]}{[\overline{\text{B}(\text{OH})}_3] [\overline{\text{OH}}^-]}}{\frac{[\overline{\text{OH}}^-] + [\overline{\text{B}(\text{OH})}_3]}{[\overline{\text{B}(\text{OH})}_3] [\overline{\text{OH}}^-]} + \frac{1}{[\overline{\text{B}(\text{OH})}_3 \cdot \overline{\text{OH}}^-]}} \right\} \quad (4-80)
\end{aligned}$$

And:

$$K_{21} = \frac{[\overline{\text{B}(\text{OH})}_3] [\overline{\text{OH}}^-]}{[\overline{\text{B}(\text{OH})}_3 \cdot \overline{\text{OH}}^-]}$$

or:

$$\frac{1}{[\overline{\text{B}(\text{OH})}_3 \cdot \overline{\text{OH}}^-]} = \frac{K_{21}}{[\overline{\text{B}(\text{OH})}_3] [\overline{\text{OH}}^-]} \quad (4-81)$$

Therefore, from eqns. (4-80) and (4-81), we obtain:

$$\begin{aligned}
\frac{1}{\tau_2} &= k_{-2} + k_2 \left\{ \frac{\frac{[\overline{\text{OH}}^-] + [\overline{\text{B}(\text{OH})}_3]}{[\overline{\text{B}(\text{OH})}_3] [\overline{\text{OH}}^-]}}{\frac{[\overline{\text{OH}}^-] + [\overline{\text{B}(\text{OH})}_3]}{[\overline{\text{B}(\text{OH})}_3] [\overline{\text{OH}}^-]} + \frac{K_{21}}{[\overline{\text{B}(\text{OH})}_3] [\overline{\text{OH}}^-]}} \right\}
\end{aligned}$$

or:

$$\frac{1}{\tau_2} = k_{-2} + k_2 \left\{ \frac{[\overline{\text{OH}}^-] + [\overline{\text{B}(\text{OH})}_3]}{K_{21} + [\overline{\text{OH}}^-] + [\overline{\text{B}(\text{OH})}_3]} \right\} \quad (4-82)$$

which is the same as equation (4-65).

2. Data Analysis:

Photographs of the oscilloscope trace have been taken for detailed processing of the data. Every temperature-jump trace recorded on film has been carefully analyzed. The logarithm of the signal amplitude, that is, the logarithm of the transmission, ΔS (in mm) and its corresponding time t (in μsec or msec) have been calculated. A plot of $\log \Delta S$ versus t for each trace was made (as shown in Figure 4-3), and its slope has been carefully evaluated using a computer linear least squares fit method. The relaxation time, τ , is then calculated from $\tau = -1/2.303 \times \text{slope}$.

At least six to eight measurements have been made on each sample solution. The relaxation times so obtained are then averaged, and the averaged τ values for the various sample solutions are shown in Table 4-1 through Table 4-4. The τ values obtained are now used to analyze the reaction mechanism of the system. For the one-step process assumed, a plot of $(1/\tau)$ versus $\{[\overline{\text{B}(\text{OH})}_3] + [\overline{\text{OH}}^-]\}$ for each kind of indicator used at various boric acid concentrations has been made, and is shown in Figure 4-4 through Figure 4-7. For the two-step mechanism assumed, $(1/\tau)$ was plotted against $\{[\overline{\text{OH}}^-] + [\overline{\text{B}(\text{OH})}_3]\} / \{K_{21} + [\overline{\text{OH}}^-] + [\overline{\text{B}(\text{OH})}_3]\}$ as shown in Figure 4-8 to Figure 4-11.

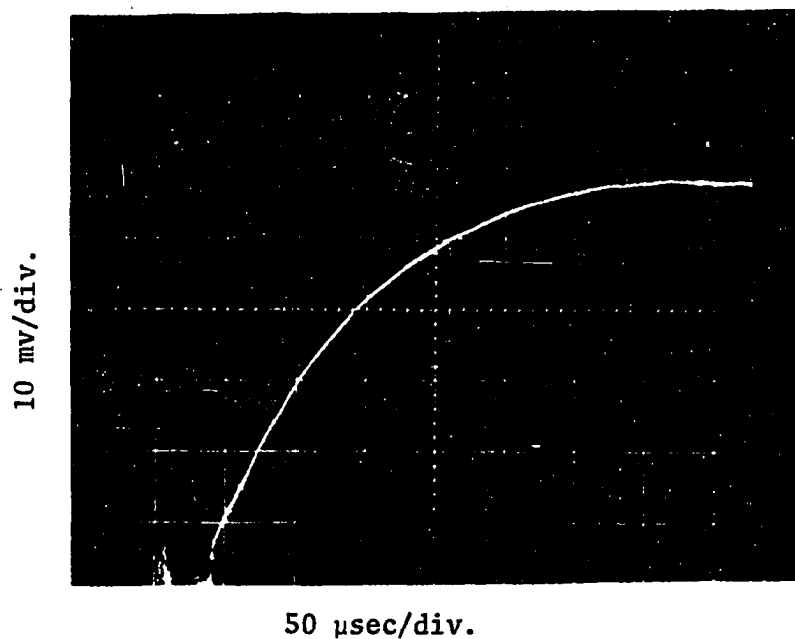
In both cases, the actual calculations of the slope values were carried out by a computer linear least squares technique.

The following constants have been used in the calculations:

for one-step reaction: $K_{\text{eq}} = 5.8072 \times 10^4 \text{ M}^{-1}$ (calc'd)

for two-step reaction: $K_{\text{overall}} = 5.8072 \times 10^4 \text{ M}^{-1}$ (calc'd)

However, since neither the K_{12} value nor the K_{23} value is known,



$C_{B(OH)_3} = 2.2 \times 10^{-3} \text{ M}$; Thymol Blue = $2 \times 10^{-5} \text{ M}$; pH = 8.50
 $NaClO_4 = 0.15 \text{ M}$; $\lambda_{\text{max}} = 596 \text{ nm}$

$\Delta S \text{ (mm)}:$	$\log \Delta S:$	$t \text{ (}\mu\text{sec)}:$
39.5	1.596	11.11
36.5	1.562	20.00
34.5	1.537	23.33
30.5	1.484	37.22
26.5	1.423	49.44
21.5	1.332	68.88
18.5	1.267	83.33
15.5	1.190	100.0
12.5	1.096	117.2
9.5	0.9777	143.8
7.5	0.8751	161.6
4.5	0.6532	200.0
2.5	0.3979	228.3
1.5	0.1761	250.0

Slope = -0.5578×10^{-2} ; $\tau = 77.83 \text{ } \mu\text{sec}$

Figure 4-3a: T-Jump trace of aqueous boric acid system with boric acid conc. at $2.2 \times 10^{-3} \text{ M}$.

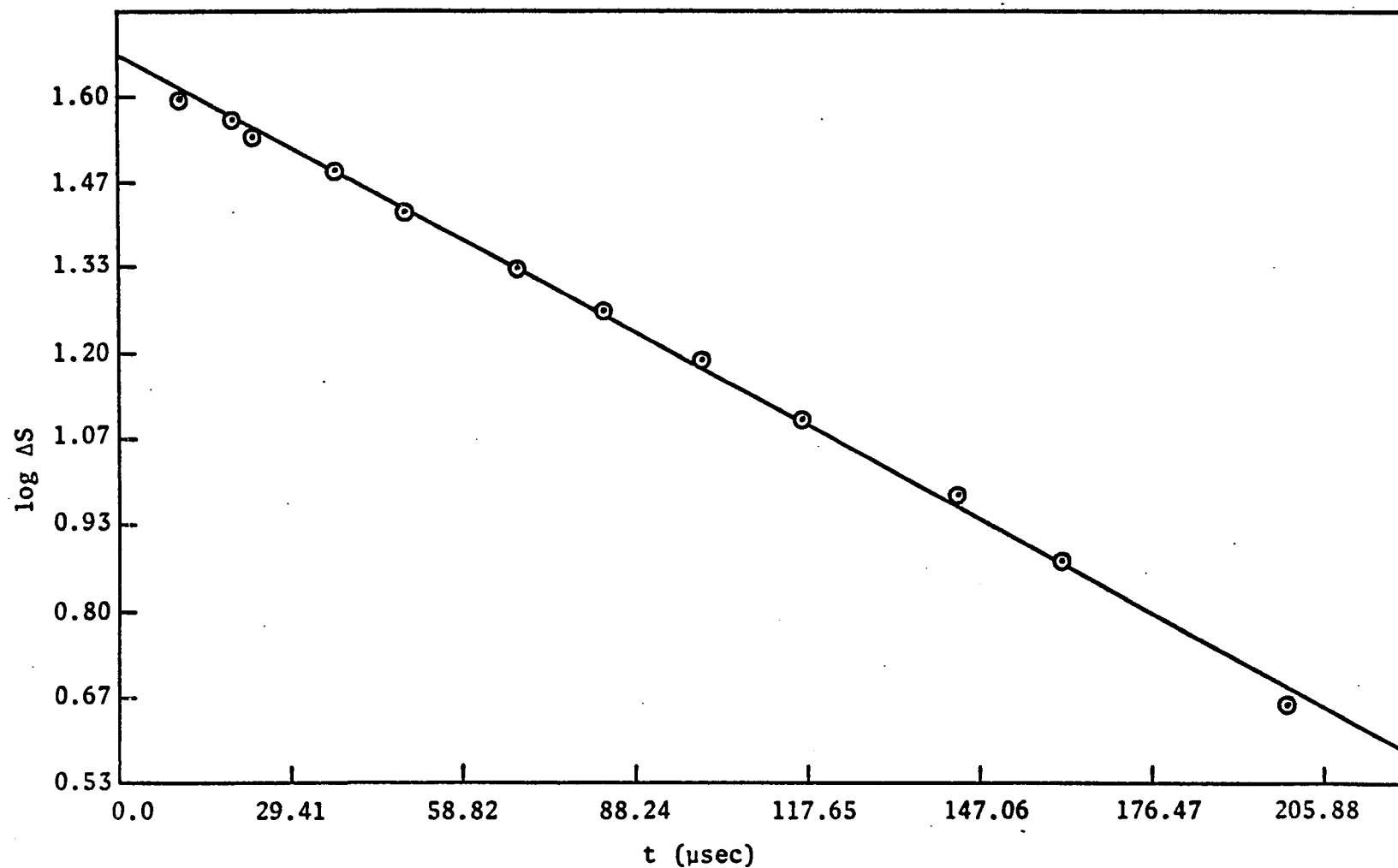


Figure 4-3b: log ΔS vs. t of T-Jump trace of aqueous boric acid system
with boric acid conc. at 2.2×10^{-3} M.

Table 4-1: The relaxation times and their corresponding relaxation frequencies of aqueous boric acid system with Thymol Blue as the indicator.

Indicator: [Thymol Blue] = 2×10^{-5} M

Inert Electrolyte: [NaClO₄] = 0.15 M

$\lambda_{\max}$ = 596 nm

$C_{B(OH)_3}$ (M):	pH:	τ (μ sec):	f_r (KHz):
8.8×10^{-4} (2x)	8.57	125.2 ± 1.4	1.271
1.1×10^{-3} (2.5x)	8.55	113.7 ± 3.6	1.400
1.32×10^{-3} (3x)	8.63	98.65 ± 0.74	1.613
1.32×10^{-3} (3x)	8.56	100.5 ± 0.19	1.584
1.54×10^{-3} (3.5x)	8.60	92.05 ± 0.99	1.729
1.76×10^{-3} (4x)	8.51	84.78 ± 0.58	1.877
1.76×10^{-3} (4x)	8.53	83.82 ± 0.43	1.899
1.76×10^{-3} (4x)	8.56	83.32 ± 0.14	1.910
1.98×10^{-3} (4.5x)	8.55	80.60 ± 0.41	1.975
1.98×10^{-3} (4.5x)	8.53	81.39 ± 0.18	1.956
2.2×10^{-3} (5x)	8.51	76.43 ± 0.58	2.082
2.2×10^{-3} (5x)	8.53	75.92 ± 1.7	2.097
2.2×10^{-3} (5x)	8.50	78.20 ± 0.36	2.035
2.64×10^{-3} (6x)	8.50	70.39 ± 0.55	2.261
2.64×10^{-3} (6x)	8.51	69.19 ± 1.1	2.300
3.52×10^{-3} (8x)	8.52	62.25 ± 0.83	2.557
3.52×10^{-3} (8x)	8.51	63.37 ± 0.59	2.512
4.4×10^{-3} (10x)	8.50	58.56 ± 0.46	2.718
6.16×10^{-3} (14x)	8.50	52.53 ± 0.64	3.030
8.8×10^{-3} (20x)	8.50	49.14 ± 0.49	3.239

Note: 4.4×10^{-4} M = (1x)

Table 4-2: The relaxation times and their corresponding relaxation frequencies of aqueous boric acid system with Phenol Red as the indicator.

Indicator: [Phenol Red] = 2×10^{-5} M

Inert Electrolyte: $[\text{NaClO}_4] = 0.15$ M

$\lambda_{\text{max}} = 558$ nm

$C_{\text{B(OH)}_3}$ (M):	pH:	τ (μsec):	f_r (KHz):
3.74×10^{-4}	(0.85x) 7.56	211.8 ± 9.5	0.7514
6.6×10^{-4}	(1.5x) 7.55	142.3 ± 6.6	1.118
"	" 7.54	144.6 ± 3.4	1.101
8.8×10^{-4}	(2x) 7.54	120.2 ± 6.9	1.325
1.1×10^{-3}	(2.5x) 7.53	102.6 ± 1.6	1.552
1.32×10^{-3}	(3x) 7.52	92.24 ± 0.56	1.725
1.54×10^{-3}	(3.5x) 7.52	84.38 ± 0.65	1.886
"	" 7.51	84.52 ± 0.89	1.883
1.98×10^{-3}	(4.5x) 7.50	75.55 ± 1.1	2.107
"	" 7.49	75.02 ± 0.37	2.122
2.42×10^{-3}	(5.5x) 7.51	68.24 ± 0.71	2.332
"	" 7.52	66.80 ± 0.05	2.383
3.08×10^{-3}	(7x) 7.52	61.91 ± 1.4	2.571
4.4×10^{-3}	(10x) 7.49	55.66 ± 0.98	2.860
7.92×10^{-3}	(18x) 7.51	48.06 ± 0.27	3.312
0.022	(50x) 7.50	41.84 ± 1.3	3.804
"	" 7.49	42.50 ± 0.93	3.745

Note: 4.4×10^{-4} M = (1x)

Table 4-3: The relaxation times and their corresponding relaxation frequencies of aqueous boric acid system with Cresol Red as the indicator.

Indicator: [Cresol Red] = 2×10^{-5} M

Inert Electrolyte: [NaClO₄] = 0.15 M

λ_{max} = 572 nm

$C_{\text{B(OH)}_3}$ (M):	pH:	τ (μsec):	f_r (KHz):
8.8×10^{-4} (2x)	8.08	116.4 ± 8.1	1.368
1.1×10^{-3} (2.5x)	8.06	103.1 ± 1.9	1.544
" "	8.03	109.0 ± 1.8	1.460
1.32×10^{-3} (3x)	8.02	95.00 ± 0.49	1.675
1.54×10^{-3} (3.5x)	8.02	86.24 ± 1.0	1.846
" "	8.01	87.82 ± 0.53	1.812
1.98×10^{-3} (4.5x)	7.99	75.53 ± 0.50	2.107
" "	8.00	76.99 ± 1.2	2.067
2.42×10^{-3} (5.5x)	8.00	69.68 ± 0.63	2.284
2.64×10^{-3} (6x)	7.92	66.82 ± 0.71	2.382
" "	7.98	65.66 ± 0.79	2.424
3.52×10^{-3} (8x)	8.07	60.83 ± 0.61	2.616
5.28×10^{-3} (12x)	8.02	54.33 ± 0.84	2.929
0.022 (50x)	8.00	43.43 ± 0.77	3.665

Note: 4.4×10^{-4} M = (1x)

Table 4-4: The relaxation times and their corresponding relaxation frequencies of aqueous boric acid system with Phenolphthalein as the indicator.

Indicator: [Phenolphthalein] = 2×10^{-5} M

Inert Electrolyte: $[\text{NaClO}_4] = 0.15$ M

$\lambda_{\text{max}} = 553$ nm

$C_{\text{B(OH)}_3}$ (M):	pH:	τ (μsec):	f_r (KHz):
1.54×10^{-3} (3.5x)	9.10	107.0 ± 0.69	1.487
1.76×10^{-3} (4x)	9.03	96.59 ± 0.80	1.648
2.2×10^{-3} (5x)	9.01	87.95 ± 0.43	1.810
2.42×10^{-3} (5.5x)	9.02	82.35 ± 0.30	1.933
" "	9.01	84.65 ± 0.16	1.880
" "	9.00	83.15 ± 1.5	1.914
2.64×10^{-3} (6x)	8.99	80.82 ± 0.33	1.969
" "	9.00	78.19 ± 1.0	2.036
3.08×10^{-3} (7x)	9.01	73.55 ± 0.26	2.164
" "	9.00	72.70 ± 0.10	2.189
3.52×10^{-3} (8x)	9.00	70.39 ± 1.3	2.261
" "	8.99	71.26 ± 0.02	2.233
3.96×10^{-3} (9x)	9.00	66.80 ± 1.0	2.383
5.28×10^{-3} (12x)	9.00	60.87 ± 0.51	2.615
" "	9.02	58.74 ± 0.84	2.709
0.022 (50x)	9.00	42.65 ± 1.9	3.731

Note: 4.4×10^{-4} M = (1x)

Table 4-5: $(1/\tau)$ vs. $\{[B(OH)_3] + [OH^-]\}$ of one-step process of aqueous boric acid system with Thymol Blue as the indicator.

At: $K_{eq} = 5.8072 \times 10^4 \text{ M}^{-1}$

Note: $4.4 \times 10^{-4} \text{ M} = (1x)$

$C_{B(OH)_3}$:	pH:	$(1/\tau) \times 10^{-3} \text{ (sec}^{-1}\text{)}$:	$\{[B(OH)_3] + [OH^-]\} \times 10^4 \text{ (M)}$:
(2x)	8.57	7.987	7.275
(2.5x)	8.55	8.799	9.156
(3x)	8.63	10.14	10.62
"	8.56	9.952	10.94
(3.5x)	8.60	10.86	12.55
(4x)	8.51	11.80	14.85
"	8.53	11.93	14.74
"	8.56	12.00	14.57
(4.5x)	8.55	12.41	16.45
"	8.53	12.29	16.58
(5x)	8.51	13.08	18.55
"	8.53	13.17	18.42
"	8.50	12.79	18.62
(6x)	8.50	14.21	22.34
"	8.51	14.45	22.26
(8x)	8.52	16.06	29.56
"	8.51	15.78	29.66
(10x)	8.50	17.08	37.21
(14x)	8.50	19.04	52.07
(20x)	8.50	20.35	74.38

Plot $(1/\tau)$ vs. $\{[B(OH)_3] + [OH^-]\}$

Slope (k_f) = $(1.57 \pm 0.15) \times 10^6 \text{ sec}^{-1} \text{ M}^{-1}$

Intercept (k_b) = $(9.00 \pm 0.49) \times 10^3 \text{ sec}^{-1}$

$K_{eq} = 1.74 \times 10^2 \text{ M}^{-1}$

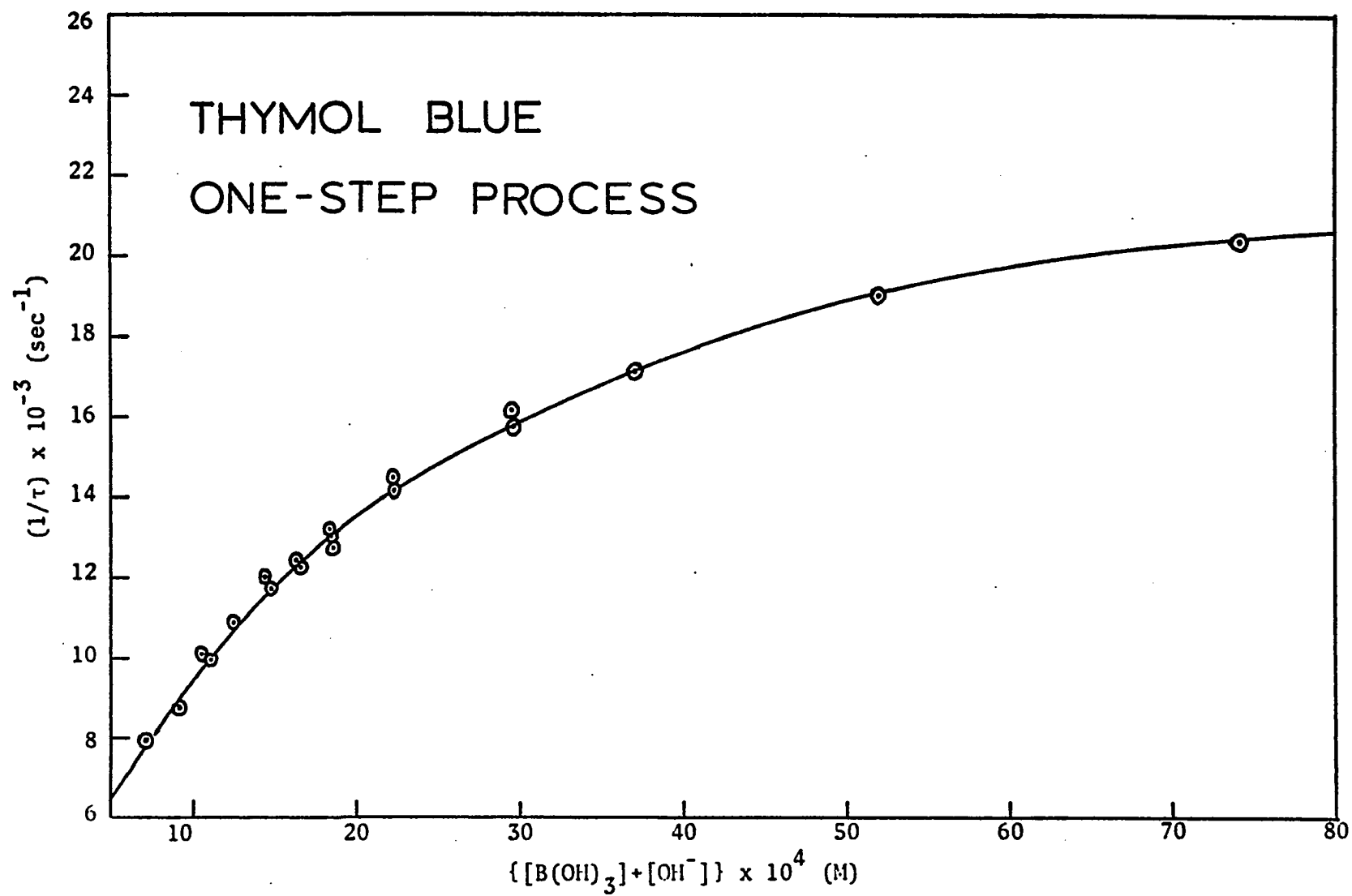


Figure 4-4

Table 4-6: $(1/\tau)$ vs. $\{[B(OH)_3] + [OH^-]\}$ of one-step process of aqueous boric acid system with Phenol Red as the indicator.

At: $K_{eq} = 5.8072 \times 10^4 \text{ M}^{-1}$

Note: $4.4 \times 10^{-4} \text{ M} = (1x)$

$C_{B(OH)_3}$:	pH:	$(1/\tau) \times 10^{-3} \text{ (sec}^{-1}\text{)}:$	$\{[B(OH)_3] + [OH^-]\} \times 10^4 \text{ (M)}:$
(0.85x)	7.56	4.721	3.666
(1.5x)	7.55	7.025	6.470
"	7.54	6.918	6.473
(2x)	7.54	8.322	8.630
(2.5x)	7.53	9.748	10.79
(3x)	7.52	10.84	12.95
(3.5x)	7.52	11.85	15.11
"	7.51	11.83	15.12
(4.5x)	7.50	13.24	19.45
"	7.49	13.33	19.45
(5.5x)	7.51	14.65	23.76
"	7.52	14.97	23.75
(7x)	7.52	16.15	30.22
(10x)	7.49	17.97	43.23
(18x)	7.51	20.81	77.74
(50x)	7.50	23.90	216.0
"	7.49	23.53	216.1

Plot $(1/\tau)$ vs. $\{[B(OH)_3] + [OH^-]\}$

Slope (k_f) = $(6.83 \pm 1.2) \times 10^5 \text{ sec}^{-1} \text{ M}^{-1}$

Intercept (k_b) = $(1.05 \pm 0.10) \times 10^4 \text{ sec}^{-1}$

$K_{eq} = 6.54 \times 10 \text{ M}^{-1}$

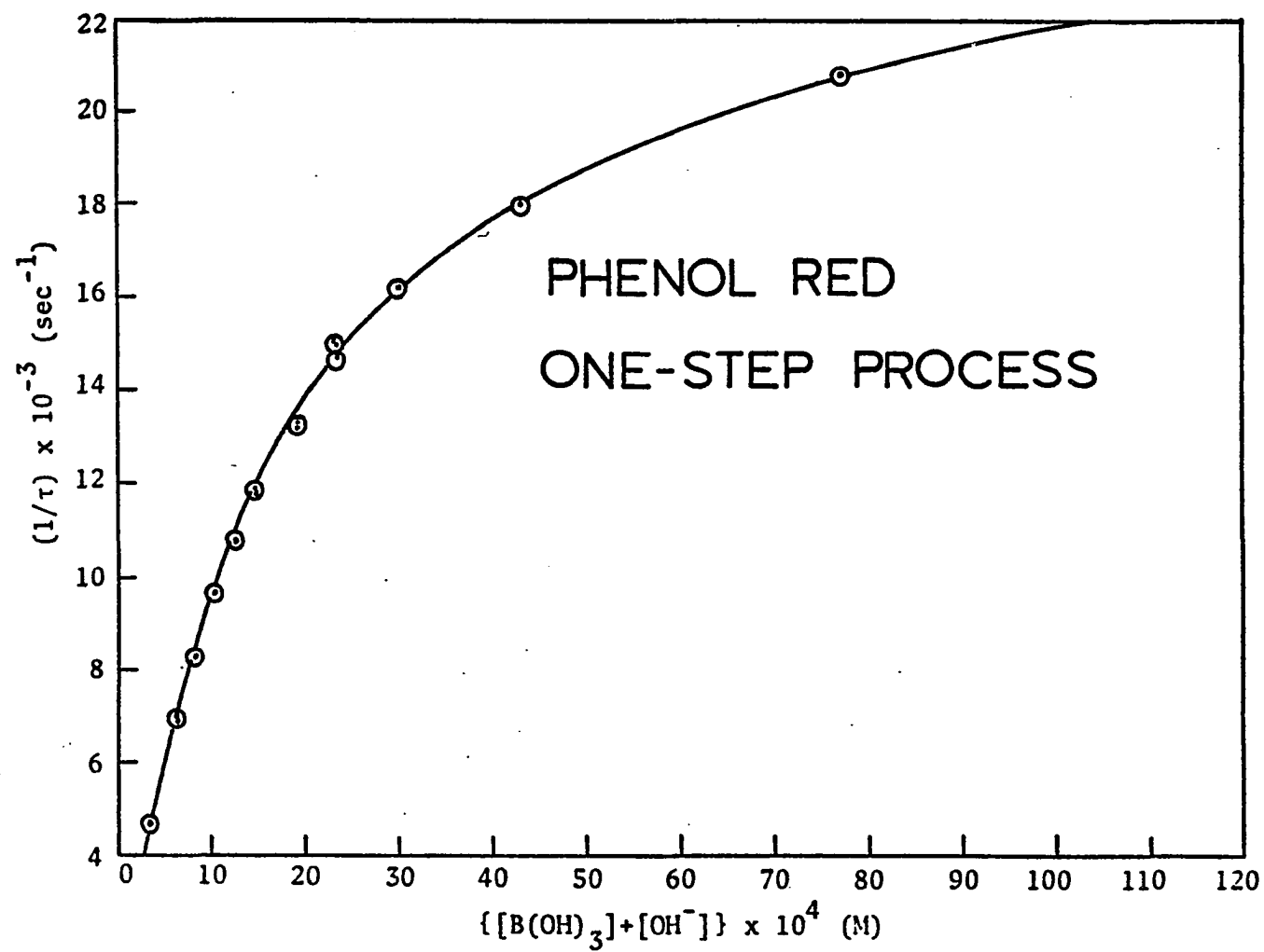


Figure 4-5

Table 4-7: $(1/\tau)$ vs. $\{[B(OH)_3] + [OH^-]\}$ of one-step process of aqueous boric acid system with Cresol Red as the indicator.

At: $K_{eq} = 5.8072 \times 10^4 \text{ M}^{-1}$

Note: $4.4 \times 10^{-4} \text{ M} = (1x)$

$C_{B(OH)_3}$:	pH:	$(1/\tau) \times 10^{-3} \text{ (sec}^{-1}\text{)}:$	$\{[B(OH)_3] + [OH^-]\} \times 10^4 \text{ (M)}:$
(2x)	8.08	8.593	8.238
(2.5x)	8.06	9.700	10.32
"	8.03	9.173	10.37
(3x)	8.02	10.53	12.45
(3.5x)	8.02	11.60	14.53
"	8.01	11.39	14.55
(4.5x)	7.99	13.24	18.75
"	8.00	12.99	18.72
(5.5x)	8.00	14.35	22.88
(6x)	7.92	14.97	25.19
"	7.98	15.23	25.02
(8x)	8.07	16.44	32.96
(12x)	8.02	18.40	49.78
(50x)	8.00	23.03	207.9

Plot $(1/\tau)$ vs. $\{[B(OH)_3] + [OH^-]\}$

Slope (k_f) = $(5.98 \pm 1.2) \times 10^5 \text{ sec}^{-1} \text{ M}^{-1}$

Intercept (k_b) = $(1.14 \pm 0.08) \times 10^4 \text{ sec}^{-1}$

$K_{eq} = 5.24 \times 10 \text{ M}^{-1}$

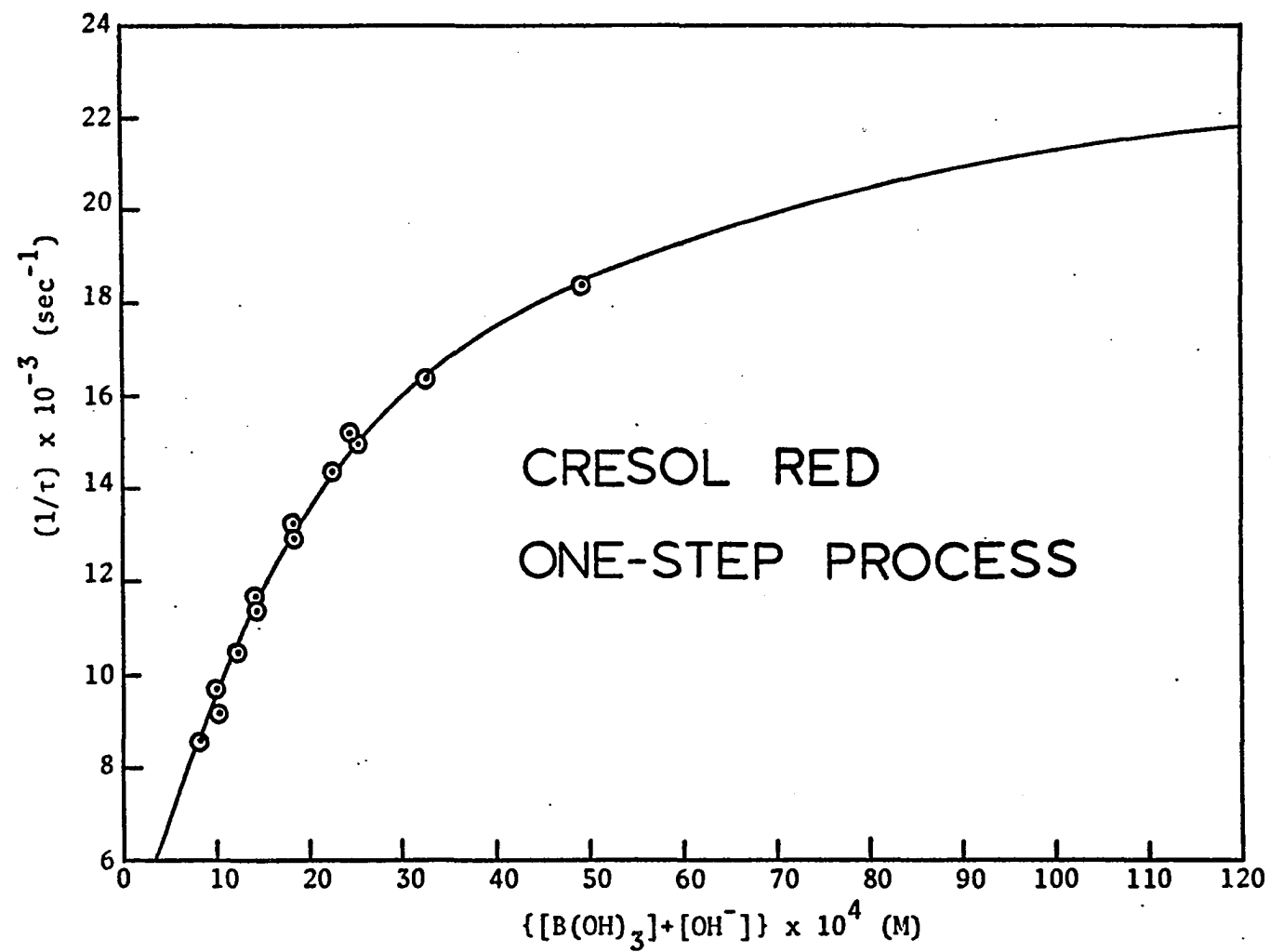


Figure 4-6

Table 4-8: $(1/\tau)$ vs. $\{[B(OH)_3] + [OH^-]\}$ of one-step process of aqueous boric acid system with Phenolphthalein as the indicator.

At: $K_{eq} = 5.8072 \times 10^4 \text{ M}^{-1}$

Note: $4.4 \times 10^{-4} \text{ M} = (1x)$

$C_{B(OH)_3}$:	pH:	$(1/\tau) \times 10^{-3} \text{ (sec}^{-1}\text{)}$:	$\{[B(OH)_3] + [OH^-]\} \times 10^4 \text{ (M)}$:
(3.5x)	9.10	9.343	9.022
(4x)	9.03	10.35	10.96
(5x)	9.01	11.37	13.90
(5.5x)	9.02	12.14	15.15
"	9.01	11.81	15.28
"	9.00	12.03	15.41
(6x)	8.99	12.37	16.94
"	9.00	12.79	16.80
(7x)	9.01	13.60	19.42
"	9.00	13.75	19.58
(8x)	9.00	14.21	22.37
"	8.99	14.03	22.55
(9x)	9.00	14.97	25.15
(12x)	9.00	16.43	33.50
"	9.02	17.02	32.94
(50x)	9.00	23.45	139.3

Plot $(1/\tau)$ vs. $\{[B(OH)_3] + [OH^-]\}$

Slope (k_f) = $(6.08 \pm 0.81) \times 10^5 \text{ sec}^{-1} \text{ M}^{-1}$

Intercept (k_b) = $(1.12 \pm 0.05) \times 10^4 \text{ sec}^{-1}$

$K_{eq} = 5.43 \times 10 \text{ M}^{-1}$

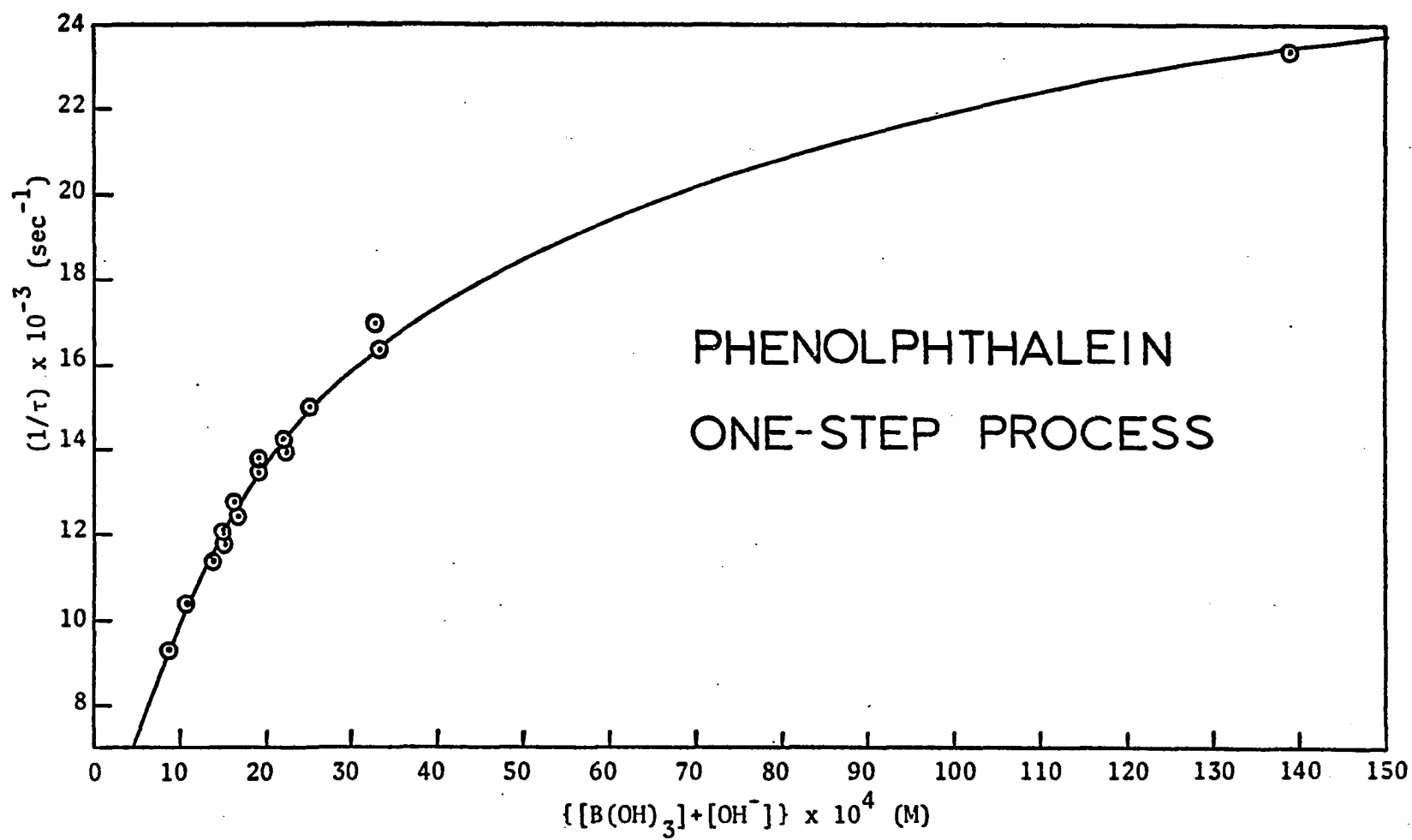


Figure 4-7

Table 4-9: $(1/\tau)$ vs. $\{[\text{OH}^-] + [\text{B}(\text{OH})_3]\} / \{K_{21} + [\text{OH}^-] + [\text{B}(\text{OH})_3]\}$ of two-step process of aqueous boric acid system with Thymol Blue as the indicator.

At: $K_{12} = 6.1177 \times 10^2 \text{ M}^{-1}$; $K_{\text{overall}} = 5.8072 \times 10^4 \text{ M}^{-1}$

Note: $4.4 \times 10^{-4} \text{ M} = (1x)$

$C_{\text{B}(\text{OH})_3}$:	pH:	$(1/\tau) \times 10^{-3} \text{ (sec}^{-1}\text{)}$:	$\frac{[\text{OH}^-] + [\text{B}(\text{OH})_3]}{K_{21} + [\text{OH}^-] + [\text{B}(\text{OH})_3]}$:
(2x)	8.57	7.987	0.3076
(2.5x)	8.55	8.799	0.3586
(3x)	8.63	10.14	0.3934
"	8.56	9.952	0.4005
(3.5x)	8.60	10.86	0.4338
(4x)	8.51	11.80	0.4756
"	8.53	11.93	0.4737
"	8.56	12.00	0.4708
(4.5x)	8.55	12.41	0.5012
"	8.53	12.29	0.5031
(5x)	8.51	13.08	0.5312
"	8.53	13.17	0.5294
"	8.50	12.79	0.5321
(6x)	8.50	14.21	0.5770
"	8.51	14.45	0.5761
(8x)	8.52	16.06	0.6435
"	8.51	15.78	0.6443
(10x)	8.50	17.08	0.6944
(14x)	8.50	19.04	0.7608
(20x)	8.50	20.35	0.8196

Slope (k_2) = $(2.44 \pm 0.03) \times 10^4 \text{ sec}^{-1}$

Intercept (k_{-2}) = $(2.57 \pm 1.9) \times 10^2 \text{ sec}^{-1}$

K_{12} (calc'd) = $6.12 \times 10^2 \text{ M}^{-1}$

K_{23} (calc'd) = 9.49×10

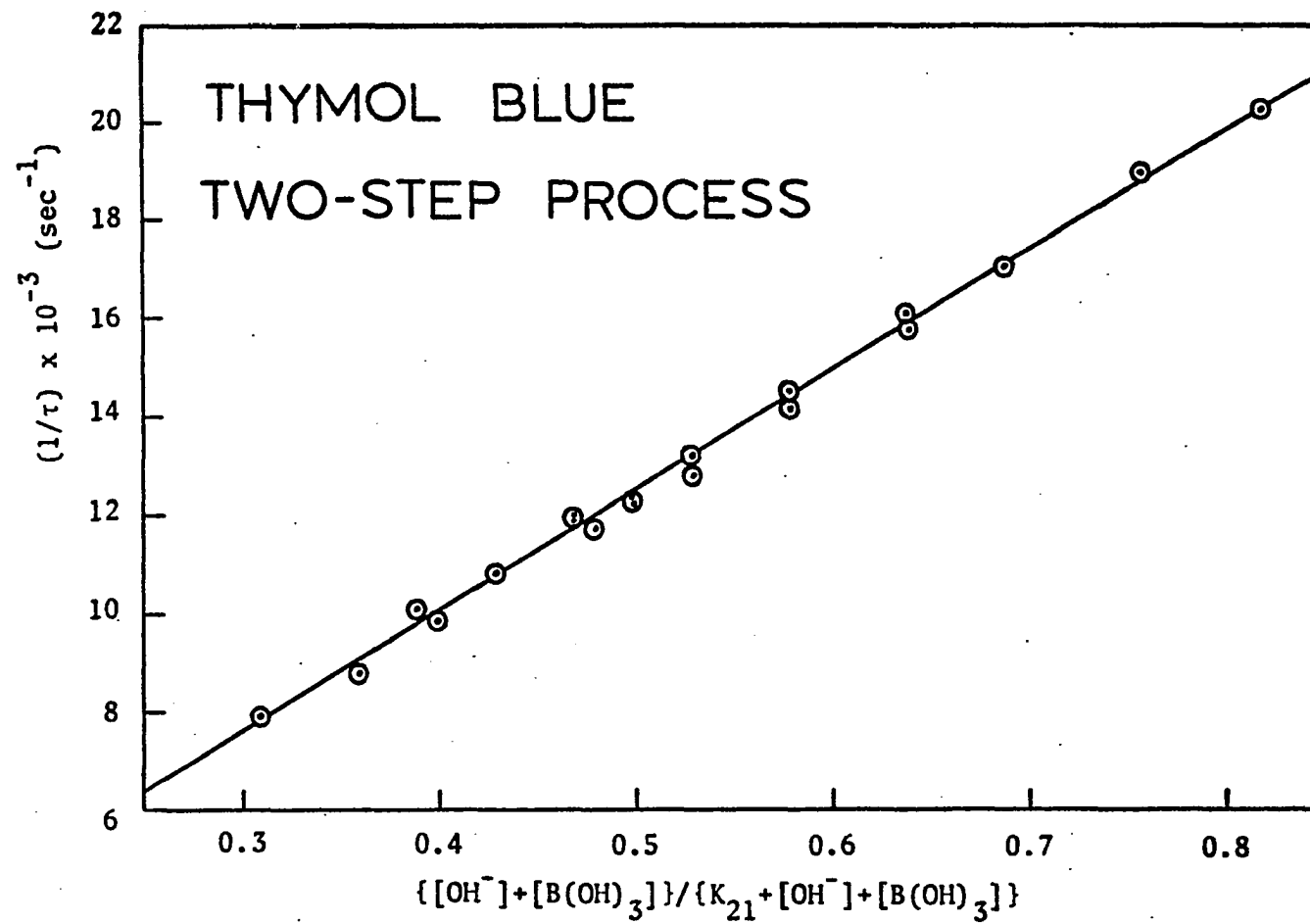


Figure 4-8

Table 4-10: $(1/\tau)$ vs. $\{[\text{OH}^-] + [\text{B}(\text{OH})_3]\} / \{K_{21} + [\text{OH}^-] + [\text{B}(\text{OH})_3]\}$ of two-step process of aqueous boric acid system with Phenol Red as the indicator.

At: $K_{12} = 5.5739 \times 10^2 \text{ M}^{-1}$; $K_{\text{overall}} = 5.8072 \times 10^4 \text{ M}^{-1}$

Note: $4.4 \times 10^{-4} \text{ M} = (1x)$

$C_{\text{B}(\text{OH})_3}$:	pH:	$(1/\tau) \times 10^{-3} \text{ (sec}^{-1}\text{)}:$	$\frac{[\text{OH}^-] + [\text{B}(\text{OH})_3]}{K_{21} + [\text{OH}^-] + [\text{B}(\text{OH})_3]}:$
(0.85x)	7.56	4.721	0.1697
(1.5x)	7.55	7.025	0.2650
"	7.54	6.918	0.2651
(2x)	7.54	8.322	0.3247
(2.5x)	7.53	9.748	0.3755
(3x)	7.52	10.84	0.4193
(3.5x)	7.52	11.85	0.4572
"	7.51	11.83	0.4573
(4.5x)	7.50	13.24	0.5201
"	7.49	13.33	0.5202
(5.5x)	7.51	14.65	0.5697
"	7.52	14.97	0.5696
(7x)	7.52	16.15	0.6275
(10x)	7.49	17.97	0.7067
(18x)	7.51	20.81	0.8125
(50x)	7.50	23.90	0.9233
"	7.49	23.53	0.9233

Slope (k_2) = $(2.53 \pm 0.02) \times 10^4 \text{ sec}^{-1}$

Intercept (k_{-2}) = $(2.43 \pm 0.91) \times 10^2 \text{ sec}^{-1}$

$K_{12} \text{ (calc'd)} = 5.58 \times 10^2 \text{ M}^{-1}$

$K_{23} \text{ (calc'd)} = 1.04 \times 10^2$

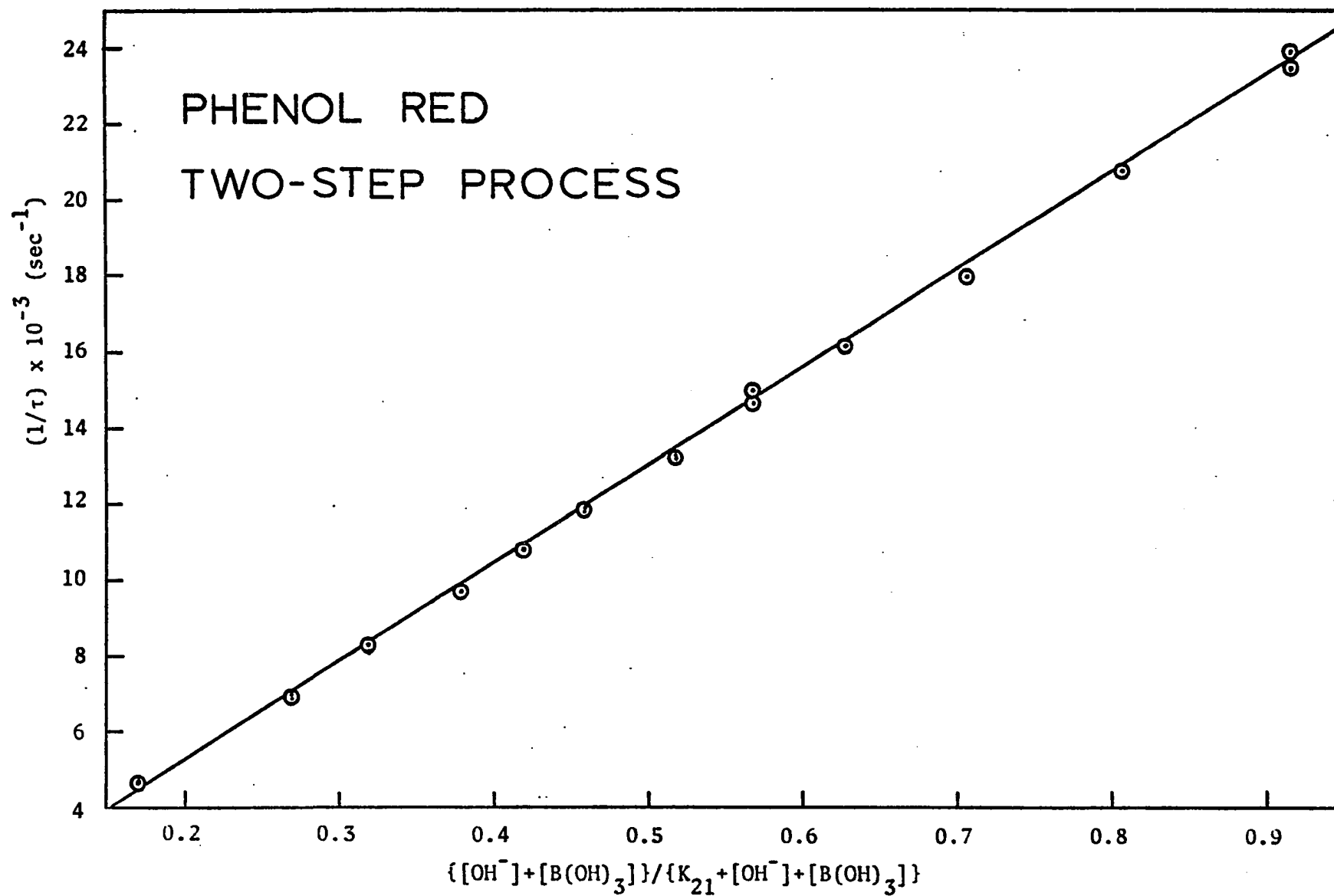


Figure 4-9

Table 4-11: $(1/\tau)$ vs. $\{[\text{OH}^-] + [\text{B}(\text{OH})_3]\} / \{K_{21} + [\text{OH}^-] + [\text{B}(\text{OH})_3]\}$ of two-step process of aqueous boric acid system with Cresol Red as the indicator.

At: $K_{12} = 5.8854 \times 10^2 \text{ M}^{-1}$; $K_{\text{overall}} = 5.8072 \times 10^4 \text{ M}^{-1}$

Note: $4.4 \times 10^{-4} \text{ M} = (1x)$

$C_{\text{B}(\text{OH})_3}$:	pH:	$(1/\tau) \times 10^{-3} \text{ (sec}^{-1}\text{)}$:	$\frac{[\text{OH}^-] + [\text{B}(\text{OH})_3]}{K_{21} + [\text{OH}^-] + [\text{B}(\text{OH})_3]}$:
(2x)	8.08	8.593	0.3264
(2.5x)	8.06	9.700	0.3778
"	8.03	9.173	0.3788
(3x)	8.02	10.53	0.4228
(3.5x)	8.02	11.60	0.4608
"	8.01	11.39	0.4611
(4.5x)	7.99	13.24	0.5244
"	8.00	12.99	0.5241
(5.5x)	8.00	14.35	0.5737
(6x)	7.92	14.97	0.5971
"	7.98	15.23	0.5955
(8x)	8.07	16.44	0.6597
(12x)	8.02	18.40	0.7454
(50x)	8.00	23.03	0.9244

Slope (k_2) = $(2.46 \pm 0.04) \times 10^4 \text{ sec}^{-1}$

Intercept (k_{-2}) = $(2.49 \pm 2.0) \times 10^2 \text{ sec}^{-1}$

K_{12} (calc'd) = $5.88 \times 10^2 \text{ M}^{-1}$

K_{23} (calc'd) = 9.87×10

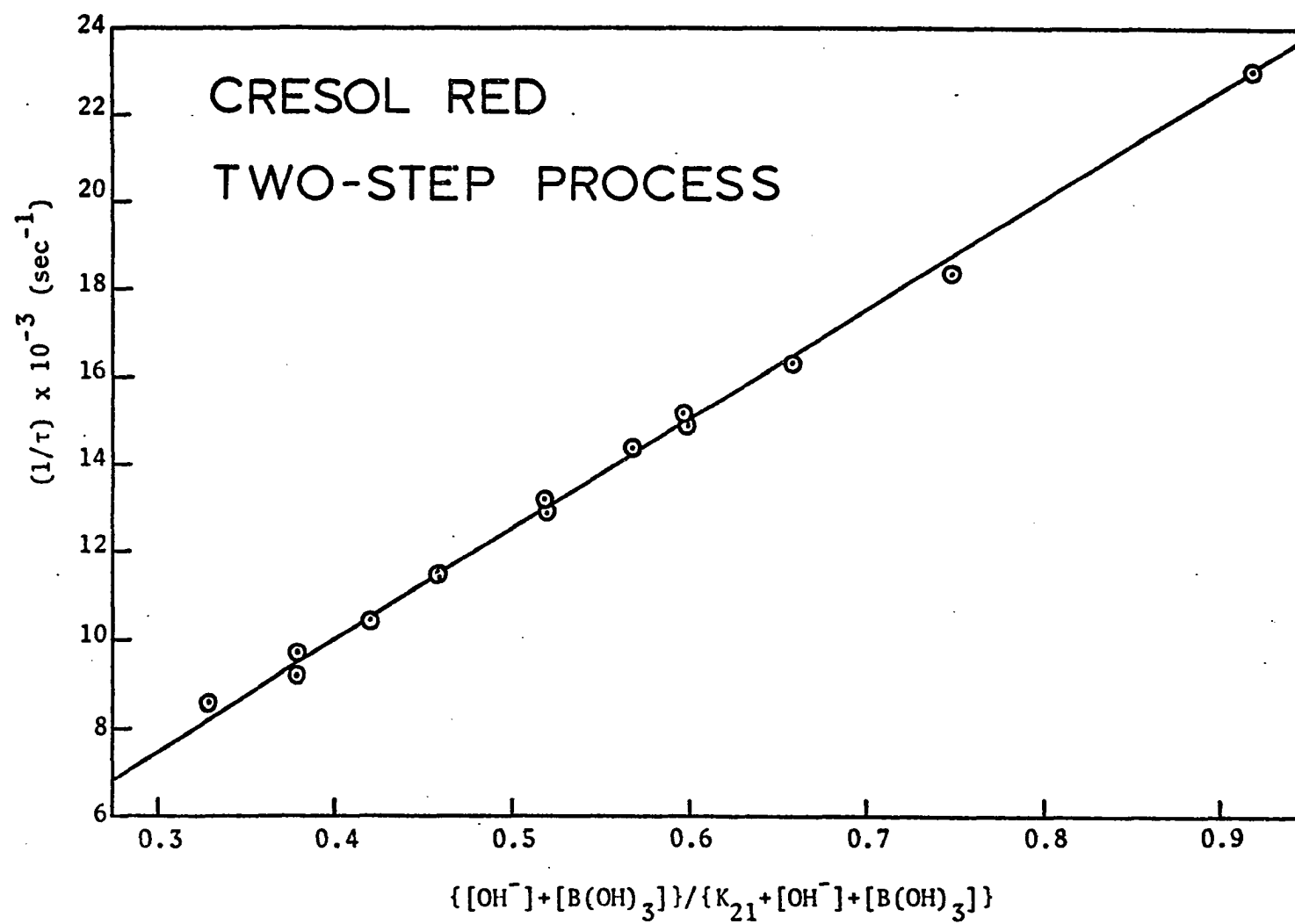


Figure 4-10

Table 4-12: $(1/\tau)$ vs. $\{[\text{OH}^-] + [\text{B}(\text{OH})_3]\} / \{K_{21} + [\text{OH}^-] + [\text{B}(\text{OH})_3]\}$ of two-step process of aqueous boric acid system with Phenolphthalein as the indicator.

At: $K_{12} = 5.6503 \times 10^2 \text{ M}^{-1}$; $K_{\text{overall}} = 5.8072 \times 10^4 \text{ M}^{-1}$
 Note: $4.4 \times 10^{-4} \text{ M} = (1x)$

$C_{\text{B}(\text{OH})_3}$:	pH:	$(1/\tau) \times 10^{-3} \text{ (sec}^{-1}\text{)}:$	$\frac{[\text{OH}^-] + [\text{B}(\text{OH})_3]}{K_{21} + [\text{OH}^-] + [\text{B}(\text{OH})_3]} :$
(3.5x)	9.10	9.343	0.3367
(4x)	9.03	10.35	0.3815
(5x)	9.01	11.37	0.4390
(5.5x)	9.02	12.14	0.4604
"	9.01	11.81	0.4625
"	9.00	12.03	0.4646
(6x)	8.99	12.37	0.4882
"	9.00	12.79	0.4861
(7x)	9.01	13.60	0.5223
"	9.00	13.75	0.5244
(8x)	9.00	14.21	0.5574
"	8.99	14.03	0.5595
(9x)	9.00	14.97	0.5861
(12x)	9.00	16.43	0.6535
"	9.02	17.02	0.6497
(50x)	9.00	23.45	0.8869

Slope (k_2) = $(2.55 \pm 0.07) \times 10^4 \text{ sec}^{-1}$

Intercept (k_{-2}) = $(2.48 \pm 3.9) \times 10^2 \text{ sec}^{-1}$

K_{12} (calc'd) = $5.65 \times 10^2 \text{ M}^{-1}$

K_{23} (calc'd) = 1.03×10^2

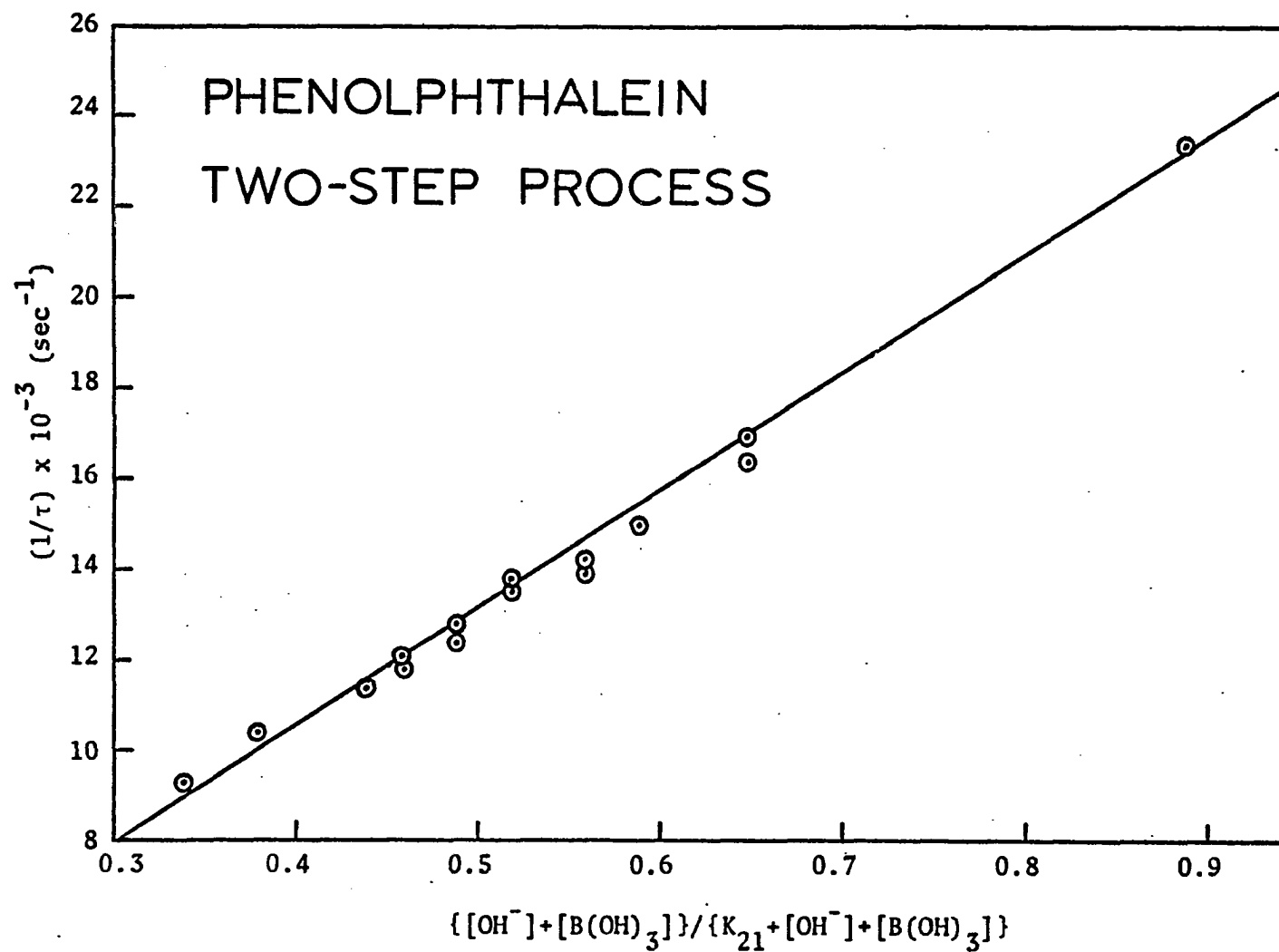


Figure 4-11

a trial-and-error repetition calculation has been used to evaluate the correct equilibrium constant values. Once the correct slope value has been evaluated, the forward rate constant can be determined from the slope and the backward rate constant can be obtained from the intercept. The equilibrium constant can then be checked using $K_{eq} = k_f/k_b$ relationship.

3. Determination of the Reaction Mechanism:

The result of plotting $(1/\tau)$ versus concentration terms indicates that for the assumed one-step process the line obtained is a curve, whereas for the two-step reaction assumed, it is a straight line. Therefore, it is clear that the reaction mechanism can be expressed better by a two-step reaction mechanism.

Usually the first step reaction is an ion pairing process. Such a reaction is normally a diffusion controlled reaction, and can, thus, be assigned a forward rate constant of the order of $10^{10} \text{ M}^{-1}\text{sec}^{-1}$. Therefore, k_1 has been assumed to have the value of $1.35 \times 10^{10} \text{ M}^{-1}\text{sec}^{-1}$. Under this assumption, the corresponding relaxation times for the first step reaction, τ_1 , have been calculated. They are shown in Tables 4-13 through 4-16.

B. Boric Acid Related Systems:

1. Aqueous Boric Acid-NaCl System:

The NaCl concentration has been adjusted at 0.1 M; 0.4 M;

Table 4-13: τ_1 and f_{r1} values of the first-step reaction of aqueous boric acid system in the two-step process with Thymol Blue as the indicator.

At: $K_{12} = 6.1177 \times 10^2 \text{ M}^{-1}$; $K_{\text{overall}} = 5.8072 \times 10^4 \text{ M}^{-1}$

(expt.)		(calc'd)	
τ_2 (μsec):	$\{[\text{B}(\text{OH})_3] + [\text{OH}^-]\} \times 10^4 \text{ (M)}:$	τ_1 (μsec):	f_{r1} (MHz):
125.2 $\pm$ 1.4	7.262	0.0314	5.07
113.7 $\pm$ 3.6	9.140	0.0291	5.47
98.65 $\pm$ 0.74	10.60	0.0275	5.79
100.5 $\pm$ 0.19	10.92	0.0272	5.85
92.05 $\pm$ 0.99	12.52	0.0257	6.19
84.78 $\pm$ 0.58	14.82	0.0238	6.69
83.82 $\pm$ 0.43	14.71	0.0238	6.69
83.32 $\pm$ 0.14	14.55	0.0240	6.63
80.60 $\pm$ 0.41	16.42	0.0226	7.04
81.39 $\pm$ 0.18	16.55	0.0225	7.07
76.43 $\pm$ 0.58	18.52	0.0212	7.51
75.92 $\pm$ 1.7	18.38	0.0213	7.47
78.20 $\pm$ 0.36	18.59	0.0212	7.51
70.39 $\pm$ 0.55	22.30	0.0192	8.29
69.19 $\pm$ 1.1	22.22	0.0192	8.29
62.25 $\pm$ 0.83	29.51	0.0162	9.82
63.37 $\pm$ 0.59	29.61	0.0161	9.89
58.56 $\pm$ 0.46	37.14	0.0138	11.5
52.53 $\pm$ 0.64	51.99	0.0108	14.7
49.14 $\pm$ 0.49	74.26	0.0082	19.4

Assume $k_1 = 1.35 \times 10^{10} \text{ sec}^{-1} \text{ M}^{-1}$,

then $k_{-1} = k_1/K_{12} = 2.21 \times 10^7 \text{ sec}^{-1}$.

Table 4-14: τ_1 and f_{r1} values of the first-step reaction of aqueous boric acid system in the two-step process with Phenol Red as the indicator.

At: $K_{12} = 5.5739 \times 10^2 \text{ M}^{-1}$; $K_{\text{overall}} = 5.8072 \times 10^4 \text{ M}^{-1}$

(expt.)		(calc'd)	
τ_2 (μsec):	$\{[\text{B}(\text{OH})_3] + [\text{OH}^-]\} \times 10^4 \text{ (M)}$:	τ_1 (μsec):	f_{r1} (MHz):
211.8 $\pm$ 9.5	3.666	0.0343	4.64
142.3 $\pm$ 6.6	6.469	0.0303	5.25
144.6 $\pm$ 3.4	6.472	0.0303	5.25
120.2 $\pm$ 6.9	8.628	0.0279	5.70
102.6 $\pm$ 1.6	10.79	0.0258	6.17
92.24 $\pm$ 0.56	12.95	0.0240	6.63
84.38 $\pm$ 0.65	15.11	0.0224	7.11
84.52 $\pm$ 0.89	15.12	0.0224	7.11
75.55 $\pm$ 1.1	19.44	0.0198	8.04
75.02 $\pm$ 0.37	19.45	0.0198	8.04
68.24 $\pm$ 0.71	23.75	0.0178	8.94
66.80 $\pm$ 0.05	23.74	0.0178	8.94
61.91 $\pm$ 1.4	30.22	0.0154	10.3
55.66 $\pm$ 0.98	43.22	0.0121	13.2
48.06 $\pm$ 0.27	77.73	0.0077	20.7
41.84 $\pm$ 1.3	215.9	0.0032	49.7
42.50 $\pm$ 0.93	216.1	0.0032	49.7

Assume $k_1 = 1.35 \times 10^{10} \text{ sec}^{-1} \text{ M}^{-1}$,

then $k_{-1} = k_1 / K_{12} = 2.42 \times 10^7 \text{ sec}^{-1}$.

Table 4-15: τ_1 and f_{r1} values of the first-step reaction of aqueous boric acid system in the two-step process with Cresol Red as the indicator.

At: $K_{12} = 5.8854 \times 10^2 \text{ M}^{-1}$; $K_{\text{overall}} = 5.8072 \times 10^4 \text{ M}^{-1}$

(expt.)		(calc'd)	
τ_2 (μsec):	$\{[\text{B}(\text{OH})_3] + [\text{OH}^-]\} \times 10^4 \text{ (M)}:$	τ_1 (μsec):	f_{r1} (MHz):
116.4 $\pm$ 8.1	8.232	0.0294	5.41
103.1 $\pm$ 1.9	10.32	0.0271	5.87
109.0 $\pm$ 1.8	10.36	0.0271	5.87
95.00 $\pm$ 0.49	12.45	0.0252	6.32
86.24 $\pm$ 1.0	14.52	0.0235	6.77
87.82 $\pm$ 0.53	14.54	0.0235	6.77
75.53 $\pm$ 0.50	18.74	0.0207	7.69
76.99 $\pm$ 1.2	18.71	0.0207	7.69
69.68 $\pm$ 0.63	22.87	0.0186	8.56
66.82 $\pm$ 0.71	25.18	0.0176	9.04
65.66 $\pm$ 0.79	25.01	0.0176	9.04
60.83 $\pm$ 0.61	32.94	0.0148	10.8
54.33 $\pm$ 0.84	49.75	0.0111	14.3
43.43 $\pm$ 0.77	207.8	0.0033	48.2

Assume $k_1 = 1.35 \times 10^{10} \text{ sec}^{-1} \text{ M}^{-1}$,

then $k_{-1} = k_1 / K_{12} = 2.29 \times 10^7 \text{ sec}^{-1}$.

Table 4-16: τ_1 and f_{r1} values of the first-step reaction of aqueous boric acid system in the two-step process with Phenolphthalein as the indicator.

At: $K_{12} = 5.6503 \times 10^2 \text{ M}^{-1}$; $K_{\text{overall}} = 5.8072 \times 10^4 \text{ M}^{-1}$

(expt.)		(calc'd)	
τ_2 (μsec):	$\{[\text{B}(\text{OH})_3] + [\text{OH}^-]\} \times 10^4 \text{ (M)}:$	τ_1 (μsec):	f_{r1} (MHz):
107.0 $\pm$ 0.69	8.986	0.0278	5.73
96.59 $\pm$ 0.80	10.92	0.0259	6.15
87.95 $\pm$ 0.43	13.85	0.0235	6.77
82.35 $\pm$ 0.30	15.10	0.0226	7.04
84.65 $\pm$ 0.16	15.23	0.0225	7.07
83.15 $\pm$ 1.5	15.36	0.0224	7.11
80.82 $\pm$ 0.33	16.88	0.0214	7.44
78.19 $\pm$ 1.0	16.74	0.0215	7.40
73.55 $\pm$ 0.26	19.35	0.0200	7.96
72.70 $\pm$ 0.10	19.52	0.0199	8.00
70.39 $\pm$ 1.3	22.29	0.0185	8.60
71.26 $\pm$ 0.02	22.48	0.0184	8.65
66.80 $\pm$ 1.0	25.06	0.0173	9.20
60.87 $\pm$ 0.51	33.38	0.0145	11.0
58.74 $\pm$ 0.84	32.82	0.0147	10.8
42.65 $\pm$ 1.9	138.8	0.0047	33.9

Assume $k_1 = 1.35 \times 10^{10} \text{ sec}^{-1} \text{ M}^{-1}$,

then $k_{-1} = k_1 / K_{12} = 2.39 \times 10^7 \text{ sec}^{-1}$.

0.7 M; and 1.0 M at each boric acid concentration. The relaxation times obtained indicate that there is no significant change in τ values at various sodium chloride concentrations. This means that no detectable effect of ionic strength on the boric acid reaction rate has been observed. The effect of sodium ion concentration on the coupled reaction of boric acid-sodium ion is also too small to be measured using temperature-jump technique.

2. Aqueous Boric Acid-MgCl₂ System:

At each boric acid concentration, three different MgCl₂ concentrations have been studied. The results show that the magnitude of the relaxation time is nearly the same, and not affected by MgCl₂ concentration. This means that the coupled reaction between B(OH)₄⁻ ion and Mg⁺² ion is very weak, and the effect of Mg⁺² ion on the reaction is too small to be measured.

3. Aqueous Boric Acid-CaCl₂ System:

Three different CaCl₂ concentrations have been used at each given concentration of boric acid. The results indicate that no detectable effect of CaCl₂ concentrations on the relaxation times can be observed.

Table 4-17: The relaxation times and the relaxation frequencies of aqueous boric acid-NaCl system.

Indicator: [Cresol Red] = 2×10^{-5} M

$\lambda_{\max} = 572$ nm

$C_{B(OH)_3}$ (M):	C_{NaCl} (M):	pH:	τ (μ sec):	f_r (KHz):
1.98×10^{-3} (4.5x)	0.1	8.03	74.4 ± 1.4	2.14
"	0.4	8.00	73.7 ± 1.4	2.16
"	0.7	8.02	77.1 ± 2.9	2.06
"	1.0	7.96	74.7 ± 2.7	2.13
2.64×10^{-3} (6x)	0.1	8.00	65.3 ± 2.5	2.44
"	0.4	7.96	65.2 ± 2.9	2.44
"	0.7	7.99	65.2 ± 2.9	2.44
"	1.0	8.07	62.9 ± 2.3	2.53
4.4×10^{-3} (10x)	0.1	8.03	56.5 ± 1.9	2.82
"	0.4	8.03	55.3 ± 1.3	2.88
"	0.7	8.00	55.5 ± 2.1	2.87
"	1.0	8.04	55.1 ± 0.96	2.89

Note: $C_{B(OH)_3} = 4.4 \times 10^{-4}$ M = (1x)

Table 4-18: The relaxation times and the relaxation frequencies of aqueous boric acid-MgCl₂ system.

Indicator: [Cresol Red] = 2×10^{-5} M

Inert Electrolyte: [NaCl] = 0.5 M; $\lambda_{\max} = 572$ nm

$C_{B(OH)_3}$ (M):	MgCl ₂ (M):	pH:	τ (μ sec):	f_r (KHz):
1.32×10^{-3} (3x)	0.05 (1x)	8.00	82.8 $\pm$ 1.5	1.92
"	0.25 (5x)	7.97	82.9 $\pm$ 2.0	1.92
"	0.50 (10x)	8.02	83.9 $\pm$ 3.5	1.90
0.0132 (30x)	0.05 (1x)	7.96	35.5 $\pm$ 3.1	4.48
"	0.25 (5x)	8.10	30.9 $\pm$ 2.0	5.15
"	0.50 (10x)	8.03	32.3 $\pm$ 2.2	4.93

Note: $C_{B(OH)_3} = 4.4 \times 10^{-4}$ M = (1x); $C_{MgCl_2} = 0.05$ M = (1x)

Table 4-19: The relaxation times and the relaxation frequencies of aqueous boric acid-CaCl₂ system.

Indicator: [Cresol Red] = 2×10^{-5} M

Inert Electrolyte: [NaCl] = 0.5 M; $\lambda_{\max} = 572$ nm

$C_{B(OH)_3}$ (M):	CaCl ₂ (M):	pH:	τ (μ sec):	f_r (KHz):
8.8×10^{-4} (2x)	0.01 (1x)	8.04	130 $\pm$ 7.2	1.22
"	0.05 (5x)	8.04	117 $\pm$ 9.7	1.36
"	0.10 (10x)	8.04	124 $\pm$ 5.6	1.28
8.8×10^{-3} (20x)	0.01 (1x)	8.07	46.0 $\pm$ 2.9	3.46
"	0.05 (5x)	8.09	45.1 $\pm$ 2.2	3.53
"	0.10 (10x)	7.95	43.6 $\pm$ 2.3	3.65

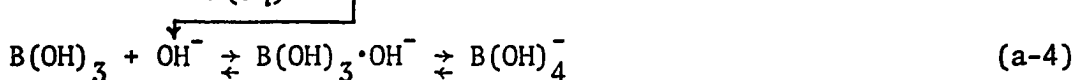
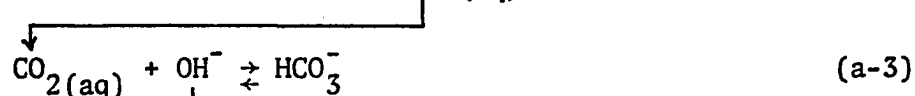
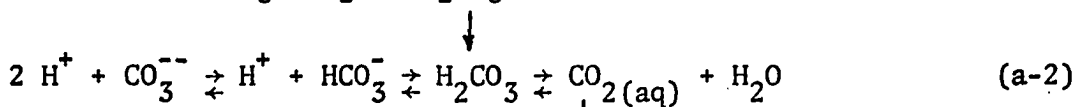
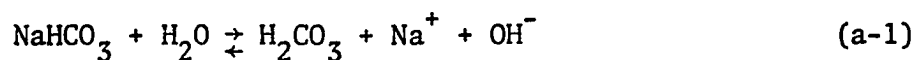
Note: $C_{B(OH)_3} = 4.4 \times 10^{-4}$ M = (1x); $C_{CaCl_2} = 0.01$ M = (1x)

4. Aqueous Boric Acid-NaHCO₃ System:

It has been noticed that on changing the concentration of boric acid or sodium bicarbonate, no definite pattern of change of τ values can be found for this system. The two most probable reasons for such a random distribution of the relaxation times are the following.

a. Overlapping relaxation times:

For the boric acid-sodium bicarbonate system, the main coupled reactions can be described by:



The forward rate constant of reaction (a-3) is $1.4 \times 10^4 \text{ sec}^{-1} \text{M}^{-1} \times 10^9$ which is the same order of magnitude as that of the second-step reaction rate in the two-step boric acid process described by reaction (a-4). Therefore, the relaxation times of these two reactions are not well separated. As a consequence, the relaxation time of the boric acid system matches with that of the sodium bicarbonate system and results in an overlapped relaxation spectrum.

b. Change of the CO₂(aq) concentration in solution:

At the moment of applying the temperature-jump, the sudden electrical discharge through the sample solution may cause some of

the dissolved CO_2 gas to be expelled out of the solution. Thus, the concentration of carbon dioxide in the solution is decreased. This decrease in $\text{CO}_{2(\text{aq})}$ concentration will, in turn, affect the equilibrium concentrations of all other species in the solution. Since the relaxation times are dependent on the species concentrations, this unusual change of the species concentrations will result in irregular variation of the relaxation times.

5. Aqueous Boric Acid-Seawater System (without NaHCO_3):

The relaxation times at various boric acid concentrations have been studied in the seawater medium with no NaHCO_3 . The results show that, generally, τ values will decrease upon increasing the boric acid concentration. Since the seawater itself has a certain relaxation reaction, and the τ values obtained for this boric acid-seawater system are different from that obtained for boric acid in fresh water system, some possible coupled reactions between boric acid and seawater components must exist.

6. Aqueous Boric Acid-Seawater System (with NaHCO_3):

For this reaction system, no definite pattern of change of the relaxation times can be found. The implication is that the reaction mechanisms involved may have several reaction steps which are coupled between boric acid-carbonate-seawater components, and their relaxation times overlap.

Table 4-20: The relaxation times and the relaxation frequencies of aqueous boric acid- NaHCO_3 system.

Indicator: [Cresol Red] = 2×10^{-5} M

Inert Electrolyte: [NaCl] = 0.5 M

$\lambda_{\text{max}} = 572$ nm

$C_{\text{B(OH)}_3}$ (M):	NaHCO_3 :	pH:	τ (μsec):	f_r (KHz):
0.0 (0x)	(1x)	9.03	139 ± 9.3	1.14
"	(10x)	8.22	365 ± 120	0.436
4.4×10^{-4} (1x)	(1x)	8.10	100 ± 7.4	1.58
"	(10x)	8.03	101 ± 4.1	1.58
"	(100x)	8.12	168 ± 16	0.950
2.2×10^{-3} (5x)	(1x)	8.38	65.3 ± 10	2.44
4.4×10^{-3} (10x)	(1x)	7.99	228 ± 10	0.698
"	(10x)	8.47	139 ± 16	1.14
"	(100x)	8.03	122 ± 13	1.31
8.8×10^{-3} (20x)	(1x)	8.00	69.0 ± 12	2.31
"	(10x)	8.37	177 ± 36	0.897

Note: $C_{\text{B(OH)}_3} = 4.4 \times 10^{-4}$ M = (1x); $C_{\text{NaHCO}_3} = 2.3328 \times 10^{-3}$ M = (1x)

Table 4-21: The relaxation times and the relaxation frequencies of aqueous boric acid-seawater (without NaHCO_3) system.

Indicator: [Cresol Red] = 2×10^{-5} M

$\lambda_{\text{max}} = 572$ nm

$C_{\text{B(OH)}_3}$ (M):	pH:	τ (μsec):	f_r (KHz):
0.0 (0x)	8.04	132 $\pm$ 13	1.20
8.8×10^{-4} (2x)	8.31	52.2 $\pm$ 2.9	3.05
2.2×10^{-3} (5x)	8.03	87.0 $\pm$ 26	1.83
4.4×10^{-3} (10x)	8.00	56.9 $\pm$ 11	2.80
6.6×10^{-3} (15x)	8.01	70.7 $\pm$ 7.2	2.25
8.8×10^{-3} (20x)	8.04	65.1 $\pm$ 10	2.44
0.0132 (30x)	7.78	63.8 $\pm$ 14	2.50

Note: $C_{\text{B(OH)}_3} = 4.4 \times 10^{-4}$ M = (1x)

Table 4-22: The relaxation times and the relaxation frequencies of aqueous boric acid-seawater (with NaHCO_3) system.

Indicator: [Cresol Red] = 2×10^{-5} M

$\lambda_{\text{max}} = 572$ nm; $[\text{NaHCO}_3] = 2.3328 \times 10^{-3}$ M (1x)

$C_{\text{B(OH)}_3}$ (M):	pH:	τ (μsec):	f_r (KHz):
0.0 (0x)	8.43	125 $\pm$ 31	1.28
4.4×10^{-4} (1x)	8.50	243 $\pm$ 34	0.654
8.8×10^{-4} (2x)	8.25	59.5 $\pm$ 3.3	2.68
2.2×10^{-3} (5x)	8.11	105 $\pm$ 18	1.51
4.4×10^{-3} (10x)	8.17	254 $\pm$ 28	0.627
6.6×10^{-3} (15x)	8.02	124 $\pm$ 15	1.29
8.8×10^{-3} (20x)	8.01	61.2 $\pm$ 17	2.60
0.0132 (30x)	7.85	156 $\pm$ 8.1	1.02

Note: $C_{\text{B(OH)}_3} = 4.4 \times 10^{-4}$ M = (1x)

Table 4-23: Summary of the various parameters obtained for the two-step boric acid reaction.

①	②	③
$B(OH)_3 + OH^- \rightleftharpoons B(OH)_3 \cdot OH^- \rightleftharpoons B(OH)_4^-$		
$k_{12} = 1.35 \times 10^{10} \text{ sec}^{-1} M^{-1}$		
$k_{21} = 2.33 \times 10^7 \text{ sec}^{-1}$		
$K_{12} = (5.81 \pm 0.19) \times 10^2 M^{-1}$		
$\Delta G_{12}^\circ = -3.77 \pm 0.02 \text{ Kcal/mole}$		
$k_{23} = (2.50 \pm 0.05) \times 10^4 \text{ sec}^{-1}$		
$k_{32} = (2.49 \pm 0.04) \times 10^2 \text{ sec}^{-1}$		
$K_{23} = (1.00 \pm 0.03) \times 10^2$		
$\Delta G_{23}^\circ = -2.73 \pm 0.02 \text{ Kcal/mole}$		
$K_{\text{overall}} = 5.81 \times 10^4 M^{-1}$		
$\Delta G_{\text{overall}}^\circ = -6.50 \text{ Kcal/mole}$		
$\Delta H_{\text{overall}}^\circ = -10.12 \pm 0.08 \text{ Kcal/mole}^{53}$		
$\Delta S_{\text{overall}}^\circ = -12.18 \pm 0.27 \text{ cal/deg} \cdot \text{mole}^{53}$		
$\Delta C_{p,\text{overall}}^\circ = 6.7 \pm 2.1 \text{ cal/deg} \cdot \text{mole}^{53}$		

Note: k = rate constant

K = equilibrium constant

ΔG° = free energy change of the reaction

ΔH° = enthalpy change of the reaction

ΔS° = entropy change of the reaction

ΔC_p° = constant pressure heat capacity change of the reaction

V. SUMMARY AND CONCLUSIONS:

The theoretical calculations have shown that no ultrasonic relaxation spectra should be detected experimentally for the aqueous boric acid system, the aqueous boric acid-sodium borate system, and the aqueous boric acid-polyborate system. This has been proven by actual ultrasonic absorption measurements.

The results obtained from the temperature-jump experiments indicate that there is a two-step reaction mechanism involved in the reaction of boric acid with the hydroxide ion to form the B(OH)_4^- ion. The reaction rate of the first step is much faster than that of the second step. The relaxation frequencies corresponding to the first step reaction have been evaluated to be from 5 MHz to 50 MHz. Although this frequency range is experimentally available, the excess sound absorption value is very small due to a very small value of ΔV_1° . For the second step reaction, although the magnitude of ΔV_2° value is greater, the relaxation frequencies calculated are only several KHz which is too low and experimentally impractical. Therefore, from the temperature-jump results, it can also be said that no relaxation spectrum due to the two-step boric acid reaction should be detected by the ultrasonic absorption method.

For the boric acid related systems, no effects of NaCl, MgCl₂, and CaCl₂ additions on the relaxation times have been observed. So it can be said that there is no measurable ionic strength effect on the boric acid reaction rate, and that the coupled reactions between boric acid-sodium ion, boric acid-magnesium ion, and boric acid-calcium ion are too weak to be measured. The results also indicate that there might exist some possible coupled reactions between boric acid and other seawater components. The reaction mechanisms involved in both the boric acid-carbonate system and the boric acid-carbonate-seawater system are very complicated and probably consist of several reaction steps with overlapping relaxation times. When dealing with such complicated reaction mechanisms, the temperature-jump method becomes quite impractical, and only qualitative analyses can be made. No quantitative results can be derived.

Because the sea is a multi-component system, it is author's suggestion that to understand seawater kinetics both the thermodynamics and kinetics of the various sub-systems involved must be studied. The influence of temperature and pressure on these sub-systems should also be investigated. Especially important and of great interest is the study of these sub-systems at low temperatures and under high pressures. Seawater has an average temperature of 3°C and a maximum pressure of near 1000 atmospheres. After each sub-system has been thoroughly studied and understood, combinations of sub-systems can be investigated for interactive effects. Finally, the resolution of many of the experimental techniques employed should also be improved.

With continuing advances in electronic techniques, these improvements can be expected in the near future.

APPENDIX A:

Computer Program 1

```

C      CALCULATION OF CONCENTRATIONS OF VARIOUS SPECIES FOR BORIC ACID AND
C      POLYBORATE SYSTEM
C      (H+)=C1
C      C(B(OH)3)=C2
C      (B(OH)3)=C3
C      (B(OH)4-)=C4
C      (B2(OH)7-)=C5
C      (B3O3(OH)4-)=C6
C      (B3O3(OH)5-2)=C7
C      (B4O5(OH)4-2)=C8
C      (B5O6(OH)4-)=C9
C      (OH-)=C10
C      EKW=EQUILIBRIUM CONSTANT OF WATER
C      EK1=EQUILIBRIUM CONSTANT OF REACTION I
C      N=NUMBER OF TOTAL ANALYTICAL CONCENTRATIONS OF BORIC ACID READ IN
C      M=NUMBER OF TOTAL PH VALUES READ IN
C      PRCNTI=PERCENTAGE OF TOTAL ANALYTICAL CONCENTRATION OF BORIC ACID
C      CONVERTED INTO SPECIES CI
C      REAL*8 MEANS 'DOUBLE PRECISION'
C      IMPLICIT REAL*8 (A-H,O-Z,$)
C      REAL*8 DABS,DLOG10
C      READ(5,1) EKW,EK1,EK2,EK3
1  FORMAT(4(D10.3))
C      READ(5,2) EK4,EK5,EK6
2  FORMAT(3(D10.3))
C      READ(5,30) N
30 FORMAT(I5)
C      READ(5,30)M
C      DO 99 K=1,M
C      READ(5,3)C1
3  FORMAT(D10.3)
C      DO 99 J=1,N
C      READ(5,3)C2
C      C10=EKW/C1
C      A=(5.*EK1*EK2*EK3*EK4*EK5*EK6)/C1
C      B=(4.*EK1*EK2*EK3*EK4*EK5*C10)/C1
C      C=((3.*EK1*EK2*EK3)+(3.*EK1*EK2*EK3*EK4*C10))/C1
C      D=(2.*EK1*EK2)/C1
C      E=1.0+(EK1/C1)
C      F=0.0-C2
C      WRITE(6,13)
13 FORMAT('1','-----
C-----
C')
C      WRITE(6,6)
6  FORMAT('0')
C      WRITE(6,6)

```

```

WRITE(6,4)
4 FORMAT(' ', 'CONCENTRATIONS OF VARIOUS SPECIES,   MOLES/LITER   ;',
CT63, 'PERCENTAGE OF TOTAL ANALYTICAL CONCENTRATION')
WRITE(6,19)
19 FORMAT(' ', T63, 'OF BORIC ACID CONVERTED,   %')
WRITE(6,6)
PH=-DLOG10(C1)
WRITE(6,21)PH
21 FORMAT(' ', 'T=25C,P=1ATM,PH=', F4.1)
WRITE(6,22) C2
22 FORMAT(' ', 'C(B(OH)3)=' ,D10.3)
WRITE(6,6)
C EVALUATION OF ROOTS OF EQUATIONS
ACCU=1.D-12
X=C2
WRITE(6,6)
WRITE(6,7) X
7 FORMAT(' ', 'X=', F15.7)
12 XN=(X)-(((A*(X**5)))+(B*(X**4)))+(C*(X**3)))+(D*(X**2)))+(E*X)+F)/((
C5.*A*(X**4)))+(4.*B*(X**3)))+(3.*C*(X**2)))+(2.*D*X)+E))
WRITE(6,8) XN
8 FORMAT(' ', 'XN=', F15.7)
IF(DABS(XN-X).LE.ACCU) GO TO 9
X=XN
GO TO 12
C CALCULATION OF CONCENTRATIONS OF VARIOUS SPECIES
9 C3=XN
C4=(EK1*C3)/C1
C5=(EK1*EK2*(C3**2))/C1
C6=(EK1*EK2*EK3*(C3**3))/C1
C7=(EK1*EK2*EK3*EK4*C10*(C3**3))/C1
C8=(EK1*EK2*EK3*EK4*EK5*C10*(C3**4))/C1
C9=(EK1*EK2*EK3*EK4*EK5*EK6*(C3**5))/C1
C CALCULATION OF PERCENTAGE OF TOTAL ANALYTICAL CONCENTRATION OF BORIC ACID
C CONVERTED INTO EACH SPECIES
PRCNT3=(C3/C2)*100.
PRCNT4=(C4/C2)*100.
PRCNT5=((2.*C5)/C2)*100.
PRCNT6=((3.*C6)/C2)*100.
PRCNT7=((3.*C7)/C2)*100.
PRCNT8=((4.*C8)/C2)*100.
PRCNT9=((5.*C9)/C2)*100.
WRITE(6,10)C3,PRCNT3
10 FORMAT(' ', ' (B(OH)3)=' ,D15.7,T63, ' (B(OH)3)=' ,D15.7)
WRITE(6,11) C4,PRCNT4
11 FORMAT(' ', ' (B(OH)4-)= ' ,D15.7,T63, ' (B(OH)4-)= ' ,D15.7)
WRITE(6,14) C5,PRCNT5
14 FORMAT(' ', ' (B2(OH)7-)= ' ,D15.7,T63, ' (B2(OH)7-)= ' ,D15.7)
WRITE(6,15) C6,PRCNT6
15 FORMAT(' ', ' (B3O3(OH)4-)= ' ,D15.7,T63, ' (B3O3(OH)4-)= ' ,D15.7)
WRITE(6,16) C7,PRCNT7
16 FORMAT(' ', ' (B3O3(OH)5-2)= ' ,D15.7,T63, ' (B3O3(OH)5-2)= ' ,D15.7)
WRITE(6,17) C8,PRCNT8

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```

17 FORMAT(' ', '(B405(OH)4-2)=' ,D15.7,T63, '(B405(OH)4-2)=' ,D15.7)
   WRITE(6,18) C9,PRCNT9
18 FORMAT(' ', '(B506(OH)4-)= ' ,D15.7,T63, '(B506(OH)4-)= ' ,D15.7)
   WRITE(6,6)
   WRITE(6,6)
   WRITE(6,5)
5  FORMAT(' ', '-----
C-----
C')
   WRITE(6,6)
99 CONTINUE
   STOP
   END

```

APPENDIX B:

Computer Program 2

```

C      ULTRASONIC RELAXATION SPECTRA FOR BORIC ACID SYSTEM
C      T=25C, P=1ATM
C      C(1)=(H+)
C      C(2)=(B(OH)3)
C      C(3)=(B(OH)4-)
C      C(4)=C(B(OH)3)
C      PRCNT1=PERCENTAGE OF TOTAL ANALYTICAL CONCENTRATION OF BORIC ACID
C      CONVERTED INTO SPECIES C(I)
C      EK=EQUILIBRIUM CONSTANT
C      RKF=FORWARD RATE CONSTANT
C      RKB=BACKWARD RATE CONSTANT
C      DELTAV=VOLUME CHANGE OF THE REACTION
C      DELTAH=ENTHALPY CHANGE OF THE REACTION
C      TAU=THE RELAXATION TIME
C      FRLX=THE RELAXATION FREQUENCY
C      M=TOTAL NUMBER OF 'ANALYTICAL CONCENTRATION SETS' READ IN
C      'REAL*8' MEANS 'DOUBLE PRECISION'
C      IMPLICIT REAL*8 (A-H,O-Z,$)
C      REAL*8 C(4),EK,RKF,RKB,DELTAV,DELTAH,TAU,FRLX,DLOG10,XMOLAR
C      REAL*8 SIGMA,XMUMAX,V,Y
C      READ(5,1) EK
1  FORMAT(D10.3)
C      READ(5,2) RKF
2  FORMAT(D15.5)
C      READ(5,1) DELTAV
C      READ(5,1) DELTAH
C      READ(5,30) M
30 FORMAT(I5)
C      DO 99 K=1,M
C      READ(5,3) C(1),C(4)
3  FORMAT(2D16.9)
C      PART I.--CALCULATE VARIOUS SPECIES CONCENTRATIONS
C      C(3)=(C(4))/((EK*C(1))+1.)
C      C(2)=C(4)-C(3)
C      CALCULATE PERCENTAGE OF TOTAL ANALYTICAL CONCENTRATION OF BORIC ACID
C      CONVERTED INTO EACH SPECIES
C      PRCNT2=(C(2)/C(4))*100.
C      PRCNT3=(C(3)/C(4))*100.
C      PART II.--CALCULATE ULTRASONIC RELAXATION SPECTRA
C      CALCULATE RKB
C      RKB=(RKF*C(1)*C(3))/C(2)
C      CALCULATE NORMAL MODE REACTION PARAMETERS
C      THETA=2.0661D-04
C      TEMP=298.15
C      BETA=0.463662D-04
C      CP=17.994
C      RR=82.0567

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```

VBAR=18.048
VEL=1.5D+05
C   CALCULATE RELAXATION TIME
    TAU=(1.)/((RKF*(C(1)+C(3)))+RKB)
C   CALCULATE RELAXATION FREQUENCY
    FRLX=(1.)/(2.*3.1416*TAU)
C   CALCULATE MAXIMUM ABSORPTION OF RELAXATION PEAK
    SIGMA=(1./C(1))+(1./C(3))+(1./C(2))
    XMUMAX=(3.1416*((DELTAV-((VBAR*THETA/CP)*DELTAH))**2))/(1000.*BETA
C*RR*TEMP*SIGMA)
    V=DLOG10(XMUMAX)
    Y=XMUMAX*(1.D+17)/(FRLX*VEL)
C   CALCULATE TOTAL BORIC ACID CONCENTRATION
C   (FOR CHECKING PURPOSE)
    XMOLAR=C(2)+C(3)
    WRITE(6,4)
4   FORMAT('1','-----
C-----
C')
    WRITE(6,5)
5   FORMAT('0')
    WRITE(6,5)
    WRITE(6,6)
6   FORMAT(' ','CONCENTRATIONS OF VARIOUS SPECIES,  MOLES/LITER  ;',
CT63,'PERCENTAGE OF TOTAL ANALYTICAL CONCENTRATION')
    WRITE(6,7)
7   FORMAT(' ','T63,'OF BORIC ACID CONVERTED,  %')
    WRITE(6,5)
    PH=-DLOG10(C(1))
    WRITE(6,8) PH
8   FORMAT(' ','AT T=25C,',3X,'P=1ATM,',3X,'PH=',F4.1)
    WRITE(6,9)C(4)
9   FORMAT(' ','C(B(OH)3)=' ,D15.7)
    WRITE(6,5)
    WRITE(6,5)
    WRITE(6,10)C(2),PRCNT2
10  FORMAT(' ','(B(OH)3)=' ,D15.7,T63,'(B(OH)3)=' ,D15.7)
    WRITE(6,11)C(3),PRCNT3
11  FORMAT(' ','(B(OH)4-)=' ,D15.7,T63,'(B(OH)4-)=' ,D15.7)
    WRITE(6,5)
    WRITE(6,12)
12  FORMAT(' ','DELTAV,  ML/MOLE')
    WRITE(6,5)
    WRITE(6,13)DELTAV
13  FORMAT(' ',D15.5)
    WRITE(6,5)
    WRITE(6,14)
14  FORMAT(' ','DELTAH,  CAL/MOLE')
    WRITE(6,5)
    WRITE(6,13)DELTAH
    WRITE(6,5)
    WRITE(6,16)
16  FORMAT(' ','RATE CONSTANTS')

```

```

WRITE(6,5)
WRITE(6,15)RKF,RKB
15 FORMAT(' ','RKF=',D15.5,5X,'RKB=',D15.5)
WRITE(6,5)
WRITE(6,17)
17 FORMAT(' ','EQUILIBRIUM CONSTANT')
WRITE(6,5)
WRITE(6,18)EK
18 FORMAT(' ','EK=',D15.5)
WRITE(6,19)
19 FORMAT('1','NORMAL MODE REACTION PARAMETERS')
WRITE(6,20)PH,XMOLAR
20 FORMAT(' ','AT P=1ATM,',3X,'T=25C,',3X,'PH=',F4.1,3X,'C(B(OH)3)=',
CD12.5)
WRITE(6,5)
WRITE(6,21)
21 FORMAT(' ','RELAXATION TIME, SEC')
WRITE(6,5)
WRITE(6,22)TAU
22 FORMAT(' ',D12.5)
WRITE(6,5)
WRITE(6,23)
23 FORMAT(' ','RELAXATION FREQUENCY, HZ')
WRITE(6,5)
WRITE(6,22)FRLX
WRITE(6,5)
WRITE(6,24)
24 FORMAT(' ','MAX SOUND ABSORPTION OF RELAXATION PEAK, MU(MAX)')
WRITE(6,5)
WRITE(6,22)XMUMAX
WRITE(6,5)
WRITE(6,25)
25 FORMAT(' ','LOG MU(MAX)')
WRITE(6,5)
WRITE(6,26)V
26 FORMAT(' ',F10.3)
WRITE(6,5)
WRITE(6,27)
27 FORMAT(' ','AMPLITUDE*(10**17)')
WRITE(6,5)
WRITE(6,28)Y
28 FORMAT(' ',D14.7)
WRITE(6,5)
WRITE(6,5)
WRITE(6,29)
29 FORMAT(' ','-----
C-----
C')
99 CONTINUE
STOP
END

```


APPENDIX C:

Computer Program 3

```

C      ULTRASONIC RELAXATION SPECTRA FOR BORIC ACID AND SODIUM BORATE SYSTEM
C      T=25C, P=1ATM
C      C(1)=(H+)
C      C(2)=(B(OH)3)
C      C(3)=(B(OH)4-)
C      C(4)=(NAB(OH)4)
C      C(5)=(NA+)
C      C(6)=C(B(OH)3)
C      C(7)=C(NA)
C      PRCNTI=PERCENTAGE OF TOTAL ANALYTICAL CONCENTRATION OF BORIC ACID
C      CONVERTED INTO SPECIES C(I)
C      EKI=EQUILIBRIUM CONSTANT FOR REACTION I
C      RKF(J)=FORWARD RATE CONSTANT FOR REACTION J
C      RKB(J)=BACKWARD RATE CONSTANT FOR REACTION J
C      DELTAV(J)=VOLUME CHANGE OF THE J-TH REACTION
C      DELTAH(J)=ENTHALPY CHANGE OF THE J-TH REACTION
C      RATE(I)=THE EXCHANGE RATE OF REACTION(I)
C      D(I)=THE I-TH PRINCIPAL SUB-DETERMINANT OF THE G DETERMINANT
C      TAU(I)=THE RELAXATION TIME OF REACTION(I)
C      FRLX(I)=THE RELAXATION FREQUENCY OF REACTION(I)
C      M=TOTAL NUMBER OF 'ANALYTICAL CONCENTRATION SETS' READ IN
C      'REAL*8' MEANS 'DOUBLE PRECISION'
C      IMPLICIT REAL*8 (A-H,O-Z,$)
C      REAL*8 C(7),EK1,EK2,RKF(2),RKB(2),DELTAV(2),DELTAH(2),RATE(2)
C      REAL*8 D(2),TAU(2),FRLX(2),DLOG10,XMOLAR,SIGMA(2),XMUMAX(2)
C      REAL*8 V(2),Y(2),XLAMDA(2),SODIUM,DSQRT
C      PART I.--CALCULATE VARIOUS SPECIES CONCENTRATIONS
C      READ(5,2)EK1,EK2
C      2 FORMAT(2(D10.3))
C      READ(5,17)DELTAV
C      17 FORMAT(2D10.3)
C      READ(5,17)DELTAH
C      READ(5,18)RKF(1),RKF(2)
C      18 FORMAT(2D15.5)
C      READ(5,43)M
C      43 FORMAT(I5)
C      DO 99 K=1,M
C      READ(5,1)C(1),C(6),C(7)
C      1 FORMAT(3D10.3)
C      A=(EK2*EK1*C(1))+(EK2)
C      B=(EK1*C(1))+(1.)+(EK2*C(7))-(C(6)*EK2)
C      E=-C(6)
C      EVALUATION OF ROOTS OF EQUATION
C      X1=(B**2)-(4.*A*E)
C      X2=DSQRT(X1)
C      X=(-B)-(X2))/(2.*A)
C      ZERO=0.0

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```

      IF(X.LT.ZERO)GO TO 14
      IF(X.GT.C(6))GO TO 14
C    CALCULATE VARIOUS SPECIES CONCENTRATIONS
      C(3)=X
15   C(2)=EK1*C(1)*C(3)
      C(5)=(C(7))/((1.)+(EK2*C(3)))
      C(4)=C(7)-C(5)
C    CALCULATE PERCENTAGE OF TOTAL ANALYTICAL CONCENTRATION OF BORIC ACID
C    CONVERTED INTO EACH SPECIES
      PRCNT2=(C(2)/C(6))*100.
      PRCNT3=(C(3)/C(6))*100.
      PRCNT4=(C(4)/C(6))*100.
      WRITE(6,7)
7    FORMAT('1','-----
C-----
C')
      WRITE(6,8)
8    FORMAT('0')
      WRITE(6,8)
      WRITE(6,9)
9    FORMAT(' ','CONCENTRATIONS OF VARIOUS SPECIES,  MOLES/LITER  ;',
CT63,'PERCENTAGE OF TOTAL ANALYTICAL CONCENTRATION')
      WRITE(6,10)
10   FORMAT(' ','T63,'OF BORIC ACID CONVERTED,  %')
      WRITE(6,8)
      PH=-DLOG10(C(1))
      WRITE(6,11)PH
11   FORMAT(' ','AT T=25C,',3X,'P=1ATM,',3X,'PH=',F4.1)
      WRITE(6,12)C(6)
12   FORMAT(' ','C(B(OH)3)=' ,D15.7)
      WRITE(6,13)C(7)
13   FORMAT(' ','C(NA)=' ,D15.7)
      WRITE(6,8)
      WRITE(6,8)
      WRITE(6,3)C(2),PRCNT2
3    FORMAT(' ','(B(OH)3)=' ,D15.7,T63,'(B(OH)3)=' ,D15.7)
      WRITE(6,4)C(3),PRCNT3
4    FORMAT(' ','(B(OH)4-)=' ,D15.7,T63,'(B(OH)4-)=' ,D15.7)
      WRITE(6,5)C(4),PRCNT4
5    FORMAT(' ','(NAB(OH)4)=' ,D15.7,T63,'(NAB(OH)4)=' ,D15.7)
      WRITE(6,6)C(5)
6    FORMAT(' ','(NA+)=' ,D15.7)
      WRITE(6,8)
      GO TO 16
14   XX=(((-B)+(X2))/(2.*A)
      C(3)=XX
      GO TO 15
C    PART II.--CALCULATE ULTRASONIC RELAXATION SPECTRA
16   WRITE(6,19)
19   FORMAT(' ','DELTAV,  ML/MOLE')
      WRITE(6,8)
      WRITE(6,20)DELTAV
20   FORMAT(' ',2(D15.5,3X))

```

```

WRITE(6,8)
WRITE(6,21)
21 FORMAT(' ','DELTAH,    CAL/MOLE')
WRITE(6,8)
WRITE(6,20)DELTAH
WRITE(6,8)
C   CALCULATE RKB(I)
RKB(1)=(RKF(1)*C(1)*C(3))/C(2)
RKB(2)=(RKF(2)*C(5)*C(3))/C(4)
WRITE(6,22)
22 FORMAT(' ','T5','I=',T19,'RKF(I)=',T38,'RKB(I)=')
WRITE(6,8)
DO 23 I=1,2
23 WRITE(6,24) I,RKF(I),RKB(I)
24 FORMAT(' ','I5,4X,D15.5,4X,D15.5)
WRITE(6,8)
WRITE(6,41)
41 FORMAT(' ','EQUILIBRIUM CONSTANTS')
WRITE(6,8)
WRITE(6,42)EK1,EK2
42 FORMAT(' ','EK1=',D15.5,3X,'EK2=',D15.5)
C   CALCULATE TOTAL BORIC ACID CONCENTRATION
C   (FOR CHECKING PURPOSE)
XMOLAR=C(2)+C(3)+C(4)
C   CALCULATE TOTAL SODIUM CONCENTRATION
C   (FOR CHECKING PURPOSE)
SODIUM=C(5)+C(4)
THETA=2.0661D-04
TEMP=298.15
BETA=0.463662D-04
CP=17.994
RR=82.0567
VBAR=18.048
VEL=1.5D+05
C   CALCULATE EXCHANGE RATE OF REACTION(I)
RATE(1)=RKF(1)*C(1)*C(3)
RATE(2)=RKF(2)*C(5)*C(3)
C   CALCULATE ELEMENTS OF G DETERMINANT
G11=(1./C(1))+(1./C(3))+(1./C(2))
G12=1./C(3)
G21=G12
G22=(1./C(5))+(1./C(3))+(1./C(4))
C   CALCULATE VALUES OF EACH D DETERMINANT
DZERO=1.0
D(1)=G11
D(2)=(G11*G22)-(G12*G21)
XLAMDA(1)=(RATE(1)*D(1))/DZERO
XLAMDA(2)=(RATE(2)*D(2))/D(1)
DO 25 I=1,2
25 TAU(I)=1./XLAMDA(I)
DO 26 I=1,2
26 FRLX(I)=1./(2.*3.1416*TAU(I))
C   CALCULATE NORMAL MODE REACTION PARAMETERS

```

```

WRITE(6,27)
27 FORMAT('1','NORMAL MODE REACTION PARAMETERS')
WRITE(6,28) PH,XMOLAR,SODIUM
28 FORMAT(' ','AT P=1ATM,',3X,'T=25C,',3X,'PH=',F4.1,3X,'C(B(OH)3)=',
CD12.5,3X,'C(NA)=' ,D12.5)
WRITE(6,8)
WRITE(6,29)
29 FORMAT(' ','RELAXATION TIMES, SEC')
WRITE(6,8)
WRITE(6,30) (TAU(I),I=1,2)
30 FORMAT(' ',2(D12.5,3X))
WRITE(6,8)
WRITE(6,31)
31 FORMAT(' ','RELAXATION FREQUENCIES, HZ')
WRITE(6,8)
WRITE(6,30) (FRLX(I),I=1,2)
SIGMA(1)=(1./C(1))+(1./C(3))+(1./C(2))
SIGMA(2)=(1./C(5))+(1./C(3))+(1./C(4))
C CALCULATE THE AMPLITUDE OF RELAXATION PEAK
DO 32 I=1,2
32 XMUMAX(I)=(3.1416*((DELTA V(I)-((VBAR*THETA/CP)*DELTA H(I)))**2))
C/(1000.*BETA*RR*TEMP*SIGMA(I))
WRITE(6,8)
WRITE(6,33)
33 FORMAT(' ','MAX SOUND ABSORPTION OF RELAXATION PEAK, MU(MAX)')
WRITE(6,8)
WRITE(6,30) (XMUMAX(I),I=1,2)
WRITE(6,8)
DO 34 I=1,2
34 V(I)=DLOG10(XMUMAX(I))
WRITE(6,35)
35 FORMAT(' ','LOG MU(MAX)')
WRITE(6,8)
WRITE(6,36) (V(I),I=1,2)
36 FORMAT(' ',2(F10.3,2X))
DO 37 I=1,2
37 Y(I)=XMUMAX(I)*(1.D+17)/(FRLX(I)*VEL)
WRITE(6,8)
WRITE(6,38)
38 FORMAT(' ','AMPLITUDE*(10**17)')
WRITE(6,8)
WRITE(6,39) (Y(I),I=1,2)
39 FORMAT(' ',2(D14.7,3X))
WRITE(6,8)
WRITE(6,8)
WRITE(6,40)
40 FORMAT(' ','-----
C-----
C')
99 CONTINUE
STOP
END

```

APPENDIX D:

Computer Program 4

```

C      ULTRASONIC RELAXATION SPECTRA FOR BORIC ACID AND SODIUM BORATE SYSTEM
C      T=25C,P=1ATM
C      INPUT
C      N=NUMBER OF STATES
C      C(1)=(H+)
C      C(2)=(B(OH)3)
C      C(3)=(B(OH)4-)
C      C(4)=(NAB(OH)4)
C      C(5)=(NA+)
C      RKF(J)=FORWARD RATE CONSTANTS FOR PROCESS J
C      RKB(J)=BACKWARD RATE CONSTANTS FOR PROCESS J
C      DELTAV(J)=VOLUME CHANGE OF THE J-TH REACTION
C      DELTAH(J)=ENTHALPY CHANGE OF THE J-TH REACTION
C      IMPLICIT REAL*8 (A-H,O-Z,$)
C      DIMENSION FR(2),XMUMAX(2),DELTAV(2),DELTAH(2),LA(4),MA(4)
C      'REAL*8' MEANS 'DOUBLE PRECISION'
C      REAL*8 RKF(2),RKB(2),C(5),V(2),EV(4),SIGMA(4),XMOLAR,CNA
C      REAL*8 QNORM,A(4,4),G(4,4),Q(4,4),A2(10),R(16)
C      REAL*8 EVALUE(4),GINV(4,4),B(4,4),DABS,DSQRT,D,DLOG10
C      N=4
C      NN=N*N
C      M=N+((N*N-N)/2)
C      READ(5,155)DELTAV
155  FORMAT(2D10.3)
C      READ(5,155)DELTAH
C      READ(5,2)(RKF(I),I=1,2)
2    FORMAT(2D15.5)
C      WRITE(6,156)
156  FORMAT('1','DELTAV,    ML/MOLE')
C      WRITE(6,5)
C      WRITE(6,157)DELTAV
157  FORMAT(' ',2(D10.3,2X))
C      WRITE(6,158)
158  FORMAT(' ','DELTAH,    CAL/MOLE')
C      WRITE(6,5)
C      WRITE(6,157)DELTAH
C      READ(5,1)(C(I),I=1,5)
1    FORMAT(5D15.5)
C      CALCULATE PH VALUE
C      PH=-DLOG10(C(1))
C      CALCULATE RKB(I)
C      RKB(1)=(RKF(1)*C(1)*C(3))/C(2)
C      RKB(2)=(RKF(2)*C(5)*C(3))/C(4)
C      WRITE(6,5)
C      WRITE(6,7)
7    FORMAT(' ',T5,'I=',T22,'C(I)=')
C      WRITE(6,5)

```

```

      DO 8 I=1,5
      8 WRITE(6,9)I,C(I)
      9 FORMAT(' ',I5,5X,D15.5)
      WRITE(6,6)
      6 FORMAT('1',T5,'I=',T19,'RKF(I)=',T38,'RKB(I)=')
      WRITE(6,5)
      DO 98 I=1,2
      98 WRITE(6,99)I,RKF(I),RKB(I)
      99 FORMAT(' ',I5,4X,D15.5,4X,D15.5)
C      CALCULATE TOTAL BORIC ACID CONCENTRATION
      XMOLAR=C(2)+C(3)+C(4)
      WRITE(6,5)
      WRITE(6,150)
      150 FORMAT(' ', 'TOTAL BORIC ACID CONCENTRATION,      MOLES/LITER')
      WRITE(6,5)
      WRITE(6,151)XMOLAR
      151 FORMAT(' ',D12.5)
C      CALCULATE TOTAL SODIUM CONCENTRATION
      CNA=C(4)+C(5)
      WRITE(6,5)
      WRITE(6,152)
      152 FORMAT(' ', 'TOTAL SODIUM CONCENTRATION,      MOLES/LITER')
      WRITE(6,5)
      WRITE(6,151)CNA
      THETA=2.0661D-04
      TEMP=298.15
      BETA=0.463662D-04
      CP=17.994
      RR=82.0567
      VBAR=18.048
      VEL=1.5D+05
C      CALCULATE ELEMENTS OF 'A MATRIX'
      DO 20 I=1,4
      DO 20 J=1,4
      A(I,J)=0.0
      20 G(I,J)=0.0
      A(1,1)=(-RKF(1)*C(1))- (RKF(1)*C(3))
      A(1,2)=RKB(1)
      A(1,3)=-RKF(1)*C(1)
      A(2,1)=(RKF(1)*C(1))+(RKF(1)*C(3))
      A(2,2)=-RKB(1)
      A(2,3)=RKF(1)*C(1)
      A(3,1)=-RKF(2)*C(5)
      A(3,3)=(-RKF(2)*C(5))- (RKF(2)*C(3))
      A(3,4)=RKB(2)
      A(4,1)=RKF(2)*C(5)
      A(4,3)=(RKF(2)*C(5))+(RKF(2)*C(3))
      A(4,4)=-RKB(2)
      WRITE(6,4)
      4 FORMAT('1','A MATRIX      (UNSYMMETRIC COEFFICIENT MATRIX)')
      WRITE(6,5)
      5 FORMAT('0')
      DO 62 I=1,4

```

```

62 WRITE(6,3) (A(I,J),J=1,4)
3 FORMAT(' ',4(D12.5,3X))
WRITE(6,5)
C   CALCULATE ELEMENTS OF 'G MATRIX'
G(1,1)=(1./C(1))+(1./C(3))
G(1,3)=1./C(3)
G(2,2)=1./C(2)
G(3,1)=G(1,3)
G(3,3)=(1./C(5))+(1./C(3))
G(4,4)=1./C(4)
WRITE(6,63)
63 FORMAT('1','G MATRIX')
WRITE(6,5)
DO 61 J=1,4
61 WRITE(6,3) (G(J,I),I=1,4)
WRITE(6,5)
C   CALCULATE EIGEN VALUES OF G MATRIX AND THE CORRESPONDING EIGEN VECTORS
CALL EIGEN (G,Q,N,NN,M,A2,R)
C   REARRANGE THE ORDER OF EIGEN VALUES AND THE CORRESPONDING EIGEN VECTORS
DO 100 I=1,N
D=1.D+75
DO 100 J=1,N
IF(DABS(1.-Q(J,I)).GT.D) GO TO 100
D=DABS(1.-Q(J,I))
LA(I)=J
100 CONTINUE
DO 101 I=1,N
LB=LA(I)
EV(LB)=G(I,I)
DO 101 J=1,N
101 GINV(J,LB)=Q(J,I)
DO 105 I=1,N
G(I,I)=EV(I)
DO 106 J=1,N
106 Q(J,I)=GINV(J,I)
105 CONTINUE
WRITE(6,64)
64 FORMAT('1','EIGEN VALUES OF G MATRIX')
WRITE(6,5)
WRITE(6,3) (G(I,I),I=1,4)
WRITE(6,5)
WRITE(6,65)
65 FORMAT(' ','EIGEN VECTORS OF G MATRIX')
WRITE(6,5)
DO 68 I=1,4
68 WRITE(6,3) (Q(I,J),J=1,4)
WRITE(6,5)
C   CALCULATE T MATRIX
DO 107 I=1,N
107 RKB(I)=DSQRT(G(I,I))
DO 108 I=1,N
DO 108 J=1,N
G(I,J)=Q(I,J)/RKB(J)

```

```

108 GINV(I,J)=G(I,J)
    WRITE(6,109)
109 FORMAT('1','T MATRIX    (TRANSFORMATION MATRIX)')
    WRITE(6,110)
110 FORMAT('0')
    DO 112 I=1,4
112 WRITE(6,3) (GINV(I,J),J=1,4)
    WRITE(6,5)
    D=0.0
C    D IS DETERMINANT VALUE OF GINV
C    CALCULATE INVERSE OF T MATRIX
    CALL MINV(GINV,R,N,NN,D,LA,MA)
    WRITE(6,5)
    WRITE(6,114)
114 FORMAT('1','INVERSE OF T MATRIX')
    WRITE(6,5)
    DO 115 I=1,4
115 WRITE(6,3) (GINV(I,J),J=1,4)
    WRITE(6,5)
C    WRITE OUT DETERMINANT VALUE OF GINV
    WRITE(6,5)
    WRITE(6,142)
142 FORMAT(' ','DETERMINANT VALUE OF TINV')
    WRITE(6,5)
    WRITE(6,141)D
141 FORMAT(' ','D=',D15.5)
C    CALCULATE B MATRIX
    DO 201 I=1,N
    DO 201 J=1,N
    B(I,J)=0.0
    DO 201 K=1,N
201 B(I,J)=B(I,J)+A(I,K)*G(K,J)
    DO 203 I=1,N
    DO 203 J=1,N
    A(I,J)=B(I,J)
203 B(I,J)=0.0
    DO 204 I=1,N
    DO 204 J=1,N
    DO 204 K=1,N
204 B(I,J)=B(I,J)+GINV(I,K)*A(K,J)
    WRITE(6,206)
206 FORMAT('1','B MATRIX    (SYMMETRIC COEFFICIENT MATRIX)')
    WRITE(6,5)
    DO 207 I=1,4
207 WRITE(6,3) (B(I,J),J=1,4)
    WRITE(6,5)
C    CALCULATE EIGEN VALUES OF B MATRIX AND THE CORRESPONDING EIGEN VECTORS
    CALL EIGEN(B,Q,N,NN,M,A2,R)
    DO 212 I=1,N
212 EVALU(I)=B(I,I)
    WRITE(6,208)
208 FORMAT('1','EIGEN VALUES OF B MATRIX')
    WRITE(6,5)

```



```

        WRITE(6,3) (EVALUE(I),I=1,4)
        WRITE(6,5)
        WRITE(6,209)
209  FORMAT(' ','EIGEN VECTORS OF B MATRIX')
        WRITE(6,5)
        DO 210 I=1,4
210  WRITE(6,3) (Q(I,J),J=1,4)
        WRITE(6,5)
C    CALCULATE EIGEN VECTORS OF A MATRIX
        DO 300 I=1,N
        DO 300 J=1,N
300  A(I,J)=0.0
        DO 306 I=1,N
        DO 306 J=1,N
        DO 306 K=1,N
306  A(I,J)=A(I,J)+G(I,K)*Q(K,J)
        DO 301 I=1,N
        DO 301 J=1,N
301  Q(I,J)=A(I,J)
        WRITE(6,302)
302  FORMAT('1','EIGEN VECTORS OF A MATRIX')
        WRITE(6,5)
        DO 303 I=1,4
303  WRITE(6,3) (Q(I,J),J=1,4)
        WRITE(6,5)
C    CHECK EIGENVECTOR SUMS
        DO 304 J=1,N
        EV(J)=0.0
        DO 304 I=1,N
304  EV(J)=EV(J)+Q(I,J)
        WRITE(6,5)
        WRITE(6,305)
305  FORMAT(' ','CHECKING EIGENVECTOR SUMS')
        WRITE(6,5)
        WRITE(6,3) (EV(J),J=1,4)
        WRITE(6,5)
C    CALCULATE NORMALIZED EIGEN VECTORS TO A MATRIX
        EV(1)=C(1)+C(3)
        EV(2)=C(2)
        EV(3)=C(5)+C(3)
        EV(4)=C(4)
        DO 401 I=1,N
        QNORM=0.D+00
        SIGMA(I)=0.D+00
        DO 402 J=1,N
        IF(DABS(Q(J,I)).GT.QNORM) QNORM=DABS(Q(J,I))
402  CONTINUE
        DO 401 J=1,N
        Q(J,I)=Q(J,I)/QNORM
401  SIGMA(I)=SIGMA(I)+Q(J,I)**2/EV(J)
        WRITE(6,404)
404  FORMAT('1','NORMALIZED EIGENVECTORS TO A MATRIX')
        WRITE(6,5)

```

```

      DO 405 J=1,4
405  WRITE(6,3) (Q(J,I),I=1,4)
      WRITE(6,5)
C    CHECK EIGENVECTOR SUMS
      DO 406 J=1,N
      EV(J)=0.0
      DO 406 I=1,N
406  EV(J)=EV(J)+Q(I,J)
      WRITE(6,5)
      WRITE(6,407)
407  FORMAT('1','CHECKING EIGENVECTOR SUMS')
      WRITE(6,5)
      WRITE(6,3) (EV(J),J=1,4)
      WRITE(6,5)
      WRITE(6,408)
408  FORMAT(' ','SIGMA,  LITERS/MOLE')
      WRITE(6,5)
      WRITE(6,3) (SIGMA(I),I=1,4)
      WRITE(6,5)
C    CALCULATE NORMAL MODE REACTION PARAMETERS
      NR=2
      DO 503 I=1,NR
403  FR(I)=-EVALUE(I)/6.2832
      WRITE(6,500)
400  FORMAT('1','NORMAL MODE REACTION PARAMETERS')
      WRITE(6,909) PH,XMOLAR,CNA
409  FORMAT(' ','AT P=1ATM, T=25C',3X,'PH=',F3.1,3X,'CB(OH)3=',D12.5,
      C3X,'CNA=',D12.5)
      WRITE(6,5)
      WRITE(6,501)
401  FORMAT(' ','RELAX FREQS,  HZ')
      WRITE(6,5)
      WRITE(6,502) (FR(I),I=1,2)
402  FORMAT(' ',2(D12.5,3X))
C    CALCULATE DELTAV(I)
      DO 600 I=1,NR
      XMUMAX(I)=0.0
      V(1)=Q(2,I)
      V(2)=Q(4,I)
      DO 600 J=1,NR
400  XMUMAX(I)=XMUMAX(I)+V(J)*DELTAV(J)
      DO 601 I=1,NR
401  DELTAV(I)=XMUMAX(I)
      WRITE(6,5)
      WRITE(6,602)
402  FORMAT(' ','DELTA V,  ML/MOLE')
      WRITE(6,5)
      WRITE(6,603) (DELTAV(I),I=1,2)
403  FORMAT(' ',2(F10.3,2X))
C    CALCULATE DELTAH(J)
      DO 250 I=1,NR
      XMUMAX(I)=0.0
      V(1)=Q(2,I)

```

```

      V(2)=Q(4,I)
      DO 250 J=1,NR
250  XMUMAX(I)=XMUMAX(I)+V(J)*DELTAH(J)
      DO 251 I=1,NR
251  DELTAH(I)=XMUMAX(I)
      WRITE(6,5)
      WRITE(6,252)
252  FORMAT(' ','DELTA H,    CAL/MOLE')
      WRITE(6,5)
      WRITE(6,903) (DELTAH(I),I=1,2)
903  FORMAT(' ',2(D12.5,3X))
C    CALCULATE LOG MU(MAX)
      DO 253 I=1,NR
      XMUMAX(I)=3.1416*(DELTAV(I)-THETA*VBAR*DELTAH(I)/CP)**2/
      C(1000.*SIGMA(I)*BETA*RR*TEMP)
253  V(I)=DLOG10(XMUMAX(I))
      WRITE(6,5)
      WRITE(6,254)
254  FORMAT(' ','LOG MU(MAX)')
      WRITE(6,5)
      WRITE(6,603) (V(I),I=1,2)
C    CALCULATE AMPL*(10**17)
      DO 257 I=1,NR
257  V(I)=XMUMAX(I)*(1.D+17)/(FR(I)*VEL)
      WRITE(6,5)
      WRITE(6,255)
255  FORMAT(' ','AMPL*(10**17)')
      WRITE(6,5)
      WRITE(6,256) (V(I),I=1,2)
256  FORMAT(' ',2(D14.7,2X))
      STOP
      END

```

```

      SUBROUTINE EIGEN(AA,QQ,N,NN,M,A,R)
      IMPLICIT REAL*8 (A-H,O-Z,$)
      REAL*8 AA(4,4),QQ(4,4),A(10),R(16),ANORM,ANRMX,THR
      CX,Y,SINX,SINX2,COSX,COSX2,SINCS,RANGE,DSQRT,DABS
      IJ=0
      DO 1 J=1,N
      DO 1 I=1,J
      IJ=IJ+1
1  A(IJ)=AA(I,J)
      MV=0
5  RANGE=1.0D-12
      IF(MV-1) 10,25,10
10  IQ=-N
      DO 20 J=1,N
      IQ=IQ+N
      DO 20 I=1,N
      IJ=IJ+I
      R(IJ)=0.0
      IF(I-J) 20,15,20

```

```

15 R(IJ)=1.0
20 CONTINUE
25 ANORM=0.0
   DO 35 I=1,N
   DO 35 J=1,N
   IF(I-J) 30,35,30
30 IA=I+(J-J-J)/2
   ANORM=ANORM+A(IA)*A(IA)
35 CONTINUE
   IF(ANORM) 165,165,40
40 ANORM=1.414*DSQRT(ANORM)
   ANRMX=ANORM*RANGE/FLOAT(N)
   IND=0
   THR=ANORM
45 THR=THR/FLOAT(N)
50 L=1
55 M=L+1
60 MQ=(M*M-M)/2
   LQ=(L*L-L)/2
   LM=L+MQ
62 IF(DABS(A(LM))-THR) 130,65,65
65 IND=1
   LL=L+LQ
   MM=M+MQ
   X=0.5*(A(LL)-A(MM))
68 Y=-A(LM)/DSQRT(A(LM)*A(LM)+X*X)
   IF(X) 70,75,75
70 Y=-Y
75 SINX=Y/DSQRT(2.0*(1.0+(DSQRT(1.0-Y*Y))))
   SINX2=SINX*SINX
78 COSX=DSQRT(1.0-SINX2)
   COSX2=COSX*COSX
   SINCS=SINX*COSX
   ILQ=N*(L-1)
   IMQ=N*(M-1)
   DO 125 I=1,N
   IQ=(I*I-I)/2
   IF(I-L) 80,115,80
80 IF(I-M) 85,115,90
85 IM=I+MQ
   GO TO 95
90 IM=M+IQ
95 IF(I-L) 100,105,105
100 IL=I+LQ
   GO TO 110
105 IL=L+IQ
110 X=A(IL)*COSX-A(IM)*SINX
   A(IM)=A(IL)*SINX+A(IM)*COSX
   A(IL)=X
115 IF(MV-1) 120,125,120
120 ILR=ILQ+I
   IMR=IMQ+I
   X=R(ILR)*COSX-R(IMR)*SINX

```

```

      R(IMR)=R(ILR)*SINX+R(IMR)*COSX
      R(ILR)=X
125  CONTINUE
      X=2.0*A(LM)*SINCS
      Y=A(LL)*COSX2+A(MM)*SINX2-X
      X=A(LL)*SINX2+A(MM)*COSX2+X
      A(LM)=(A(LL)-A(MM))*SINCS+A(LM)*(COSX2-SINX2)
      A(LL)=Y
      A(MM)=X
130  IF(M-N) 135,140,135
135  M=M+1
      GO TO 60
140  IF(L-(N-1)) 145,150,145
145  L=L+1
      GO TO 55
150  IF(IND-1) 160,155,160
155  IND=0
      GO TO 50
160  IF(THR-ANRMX) 165,165,45
165  IQ=-N
      DO 185 I=1,N
      IQ=IQ+N
      LL=I+(I*I-I)/2
      JQ=N*(I-2)
      DO 185 J=I,N
      JQ=JQ+N
      MM=J+(J*J-J)/2
      IF(A(LL)-A(MM)) 170,185,185
170  X=A(LL)
      A(LL)=A(MM)
      A(MM)=X
      IF(MV-1) 175,185,175
175  DO 180 K=1,N
      ILR=IQ+K
      IMR=JQ+K
      X=R(ILR)
      R(ILR)=R(IMR)
180  R(IMR)=X
185  CONTINUE
      K=0
      IJ=0
      DO 190 L=1,N
      J=N-L+1
      K=K+L
      AA(J,J)=A(K)
      DO 190 I=1,N
      IJ=IJ+1
190  QQ(I,J)=R(IJ)
      RETURN
      END

```

SUBROUTINE MINV(AA,A,N,NN,D,L,M)

```

      IMPLICIT REAL*8 (A-H,O-Z,$)
      DIMENSION L(4),M(4)
      REAL*8 A(16),AA(4,4),D,BIGA,HOLD,DABS
      IZZ=0
      DO 5 I=1,N
      DO 5 J=1,N
      IZZ=IZZ+1
5  A(IZZ)=AA(J,I)
      D=1.0
      NK=-N
      DO 80 K=1,N
      NK=NK+N
      L(K)=K
      M(K)=K
      KK=NK+K
      BIGA=A(KK)
      DO 20 J=K,N
      IZ=N*(J-1)
      DO 20 I=K,N
      IJ=IZ+I
10  IF(DABS(BIGA)-DABS(A(IJ))) 15,20,20
15  BIGA=A(IJ)
      L(K)=I
      M(K)=J
20  CONTINUE
      J=L(K)
      IF(J-K) 35,35,25
25  KI=K-N
      DO 30 I=1,N
      KI=KI+N
      HOLD=-A(KI)
      JI=KI-K+J
      A(KI)=A(JI)
30  A(JI)=HOLD
35  I=M(K)
      IF(I-K) 45,45,38
38  JP=N*(I-1)
      DO 40 J=1,N
      JK=NK+J
      JI=JP+J
      HOLD=-A(JK)
      A(JK)=A(JI)
40  A(JI)=HOLD
45  IF(BIGA) 48,46,48
46  D=0.0
      RETURN
48  DO 55 I=1,N
      IF(I-K) 50,55,50
50  IK=NK+I
      A(IK)=A(IK)/(-BIGA)
55  CONTINUE
      DO 65 I=1,N
      IK=NK+I

```

```

        HOLD=A(IK)
        IJ=I-N
        DO 65 J=1,N
            IJ=IJ+N
            IF(I-K) 60,65,60
60      IF(J-K) 62,65,62
62      KJ=IJ-I+K
        A(IJ)=HOLD*A(KJ)+A(IJ)
65      CONTINUE
        KJ=K-N
        DO 75 J=1,N
            KJ=KJ+N
            IF(J-K) 70,75,70
70      A(KJ)=A(KJ)/BIGA
75      CONTINUE
        D=D*BIGA
        A(KK)=1.0/BIGA
80      CONTINUE
        K=N
100     K=(K-1)
        IF(K) 150,150,105
105     I=L(K)
        IF(I-K) 120,120,108
108     JQ=N*(K-1)
        JR=N*(I-1)
        DO 110 J=1,N
            JK=JQ+J
            HOLD=A(JK)
            JI=JR+J
            A(JK)=-A(JI)
110     A(JI)=HOLD
120     J=M(K)
        IF(J-K) 100,100,125
125     KI=K-N
        DO 130 I=1,N
            KI=KI+N
            HOLD=A(KI)
            JI=KI-K+J
            A(KI)=-A(JI)
130     A(JI)=HOLD
        GO TO 100
150     CONTINUE
        IZZ=0
        DO 160 I=1,N
            DO 160 J=1,N
                IZZ=IZZ+1
160     AA(J,I)=A(IZZ)
        RETURN
        END

```

APPENDIX E:

Computer Program 5

```

C      ULTRASONIC RELAXATION SPECTRA FOR BORIC ACID AND POLYBORATE  SYSTEM
C      T=25C, P=1ATM
C      C(1)=(H+)
C      C(2)=(B(OH)3)
C      C(3)=(B(OH)4-)
C      C(4)=(B2(OH)7-)
C      C(5)=(B3O3(OH)4-)
C      C(6)=(B3O3(OH)5-2)
C      C(7)=(B4O5(OH)4-2)
C      C(8)=(B5O6(OH)4-)
C      C(9)=(OH-)
C      RKF(J)=FORWARD RATE CONSTANTS FOR PROCESS J
C      RKB(J)=BACKWARD RATE CONSTANTS FOR PROCESS J
C      DELTAV(J)=VOLUME CHANGE OF THE J-TH REACTION
C      DELTAH(J)=ENTHALPY CHANGE OF THE J-TH REACTION
C      RATE(I)=THE EXCHANGE RATE OF REACTION(I)
C      D(I)=THE I-TH PRINCIPAL SUB-DETERMINANT OF THE G DETERMINANT
C      TAU(I)=THE RELAXATION TIME OF REACTION(I)
C      FRLX(I)=THE RELAXATION FREQUENCY OF REACTION(I)
C      M=TOTAL NUMBER OF 'SPECIES CONCENTRATION SETS' READ IN
C      'REAL*8' MEANS 'DOUBLE PRECISION'
      IMPLICIT REAL*8 (A-H,O-Z,$)
      REAL*8 DELTAV(6),DELTAH(6),RKF(6),RKB(6),C(9),XMOLAR,DLOG10
      REAL*8 SIGMA(6),XMUMAX(6),V(6),Y(6),TAU(6),FRLX(6),RATE(6),D(6)
      REAL*8 XLAMDA(6)
      READ(5,155)DELTAV
155  FORMAT(6D10.3)
      READ(5,155)DELTAH
      READ(5,2)(RKF(I),I=1,6)
      2  FORMAT(3D15.5)
      READ(5,18)M
18  FORMAT(I5)
      DO 19 K=1,M
      WRITE(6,16)
16  FORMAT('1','-----')
      C-----
      C')
      WRITE(6,5)
      5  FORMAT('0')
      WRITE(6,5)
      WRITE(6,156)
156  FORMAT(' ','DELTAV,  ML/MOLE')
      WRITE(6,5)
      WRITE(6,157)DELTAV
157  FORMAT(' ',6(D15.5,3X))
      WRITE(6,5)
      WRITE(6,158)

```



```

158 FORMAT(' ', 'DELTAH,    CAL/MOLE')
    WRITE(6,5)
    WRITE(6,157)DELTAH
    READ(5,1) (C(I), I=1,5)
1  FORMAT(5D15.5)
    READ(5,11) (C(I), I=6,9)
11  FORMAT(4D15.5)
C   CALCULATE PH VALUE
    PH=-DLOG10(C(1))
    C(9)=(1.0D-14)/C(1)
C   CALCULATE RKB(I)
    RKB(1)=(RKF(1)*C(2))/(C(1)*C(3))
    RKB(2)=(RKF(2)*C(3)*C(2))/C(4)
    RKB(3)=(RKF(3)*C(4)*C(2))/C(5)
    RKB(4)=(RKF(4)*C(5)*C(9))/C(6)
    RKB(5)=(RKF(5)*C(6)*C(2))/C(7)
    RKB(6)=(RKF(6)*C(7)*C(2))/(C(8)*C(9))
    WRITE(6,5)
    WRITE(6,7)
7  FORMAT(' ', T5, 'I=', T22, 'C(I)=')
    WRITE(6,5)
    DO 8 I=1,9
8  WRITE(6,9) I, C(I)
9  FORMAT(' ', I5, 5X, D15.5)
    WRITE(6,5)
    WRITE(6,6)
6  FORMAT(' ', T5, 'I=', T19, 'RKF(I)=', T38, 'RKB(I)=')
    WRITE(6,5)
    DO 98 I=1,6
98  WRITE(6,99) I, RKF(I), RKB(I)
99  FORMAT(' ', I5, 4X, D15.5, 4X, D15.5)
C   CALCULATE TOTAL BORIC ACID CONCENTRATION
    XMOLAR=C(2)+C(3)+(2.*C(4))+(3.*C(5))+(3.*C(6))+(4.*C(7))+(5.*C(8))
    WRITE(6,5)
    WRITE(6,150)
150 FORMAT(' ', 'TOTAL BORIC ACID CONCENTRATION,    MOLES/LITER')
    WRITE(6,5)
    WRITE(6,151)XMOLAR
151 FORMAT(' ', D12.5)
    THETA=2.0661D-04
    TEMP=298.15
    BETA=0.463662D-04
    CP=17.994
    RR=82.0567
    VBAR=18.048
    VEL=1.5D+05
C   CALCULATE EXCHANGE RATE OF REACTION(I)
    RATE(1)=RKF(1)*C(2)
    RATE(2)=RKF(2)*C(3)*C(2)
    RATE(3)=RKF(3)*C(4)*C(2)
    RATE(4)=RKF(4)*C(5)*C(9)
    RATE(5)=RKF(5)*C(6)*C(2)
    RATE(6)=RKF(6)*C(7)*C(2)

```

C CALCULATE ELEMENTS OF G DETERMINANT

G11=(1./C(2))+(1./C(1))+(1./C(3))
G12=(1./C(2))-(1./C(3))
G13=1./C(2)
G14=0.0
G15=1./C(2)
G16=1./C(2)
G21=G12
G22=(1./C(3))+(1./C(2))+(1./C(4))
G23=(1./C(2))-(1./C(4))
G24=0.0
G25=1./C(2)
G26=1./C(2)
G31=G13
G32=G23
G33=(1./C(4))+(1./C(2))+(1./C(5))
G34=-1./C(5)
G35=1./C(2)
G36=1./C(2)
G41=G14
G42=G24
G43=G34
G44=(1./C(5))+(1./C(9))+(1./C(6))
G45=-1./C(6)
G46=-1./C(9)
G51=G15
G52=G25
G53=G35
G54=G45
G55=(1./C(6))+(1./C(2))+(1./C(7))
G56=(1./C(2))-(1./C(7))
G61=G16
G62=G26
G63=G36
G64=G46
G65=G56
G66=(1./C(7))+(1./C(2))+(1./C(8))+(1./C(9))
S1=(G22*G33*G44)+(G23*G34*G42)+(G24*G43*G32)
C-(G24*G33*G42)-(G23*G32*G44)-(G22*G43*G34)
S2=(G21*G33*G44)+(G23*G34*G41)+(G24*G43*G31)
C-(G24*G33*G41)-(G23*G31*G44)-(G21*G43*G34)
S3=(G21*G32*G44)+(G22*G34*G41)+(G24*G42*G31)
C-(G24*G32*G41)-(G22*G31*G44)-(G21*G42*G34)
S4=(G21*G32*G43)+(G22*G33*G41)+(G23*G42*G31)
C-(G23*G32*G41)-(G22*G31*G43)-(G21*G42*G33)
S5=(G33*G44*G55)+(G34*G45*G53)+(G35*G54*G43)
C-(G35*G44*G53)-(G34*G43*G55)-(G33*G54*G45)
S6=(G32*G44*G55)+(G34*G45*G52)+(G35*G54*G42)
C-(G35*G44*G52)-(G34*G42*G55)-(G32*G54*G45)
S7=(G32*G43*G55)+(G33*G45*G52)+(G35*G53*G42)
C-(G35*G43*G52)-(G33*G42*G55)-(G32*G53*G45)
S8=(G32*G43*G54)+(G33*G44*G52)+(G34*G53*G42)
C-(G34*G43*G52)-(G33*G42*G54)-(G32*G53*G44)

$S9 = (G33 * G44 * G55) + (G34 * G45 * G53) + (G35 * G54 * G43)$
 $C - (G35 * G44 * G53) - (G34 * G43 * G55) - (G33 * G54 * G45)$
 $S10 = (G31 * G44 * G55) + (G34 * G45 * G51) + (G35 * G54 * G41)$
 $C - (G35 * G44 * G51) - (G34 * G41 * G55) - (G31 * G54 * G45)$
 $S11 = (G31 * G43 * G55) + (G33 * G45 * G51) + (G35 * G53 * G41)$
 $C - (G35 * G43 * G51) - (G33 * G41 * G55) - (G31 * G53 * G45)$
 $S12 = (G31 * G43 * G54) + (G33 * G44 * G51) + (G34 * G53 * G41)$
 $C - (G34 * G43 * G51) - (G33 * G41 * G54) - (G31 * G53 * G44)$
 $S13 = (G32 * G44 * G55) + (G34 * G45 * G52) + (G35 * G54 * G42)$
 $C - (G35 * G44 * G52) - (G34 * G42 * G55) - (G32 * G54 * G45)$
 $S14 = (G31 * G44 * G55) + (G34 * G45 * G51) + (G35 * G54 * G41)$
 $C - (G35 * G44 * G51) - (G34 * G41 * G55) - (G31 * G54 * G45)$
 $S15 = (G31 * G42 * G55) + (G32 * G45 * G51) + (G35 * G52 * G41)$
 $C - (G35 * G42 * G51) - (G32 * G41 * G55) - (G31 * G52 * G45)$
 $S16 = (G31 * G42 * G54) + (G32 * G44 * G51) + (G34 * G52 * G41)$
 $C - (G34 * G42 * G51) - (G32 * G41 * G54) - (G31 * G52 * G44)$
 $S17 = (G32 * G43 * G55) + (G33 * G45 * G52) + (G35 * G53 * G42)$
 $C - (G35 * G43 * G52) - (G33 * G42 * G55) - (G32 * G53 * G45)$
 $S18 = (G31 * G43 * G55) + (G33 * G45 * G51) + (G35 * G53 * G41)$
 $C - (G35 * G43 * G51) - (G33 * G41 * G55) - (G31 * G53 * G45)$
 $S19 = (G31 * G42 * G55) + (G32 * G45 * G51) + (G35 * G52 * G41)$
 $C - (G35 * G42 * G51) - (G32 * G41 * G55) - (G31 * G52 * G45)$
 $S20 = (G31 * G42 * G53) + (G32 * G43 * G51) + (G33 * G52 * G41)$
 $C - (G33 * G42 * G51) - (G32 * G41 * G53) - (G31 * G52 * G43)$
 $S21 = (G44 * G55 * G66) + (G45 * G56 * G64) + (G46 * G65 * G54)$
 $C - (G46 * G55 * G64) - (G45 * G54 * G66) - (G44 * G65 * G56)$
 $S22 = (G43 * G55 * G66) + (G45 * G56 * G63) + (G46 * G65 * G53)$
 $C - (G46 * G55 * G63) - (G45 * G53 * G66) - (G43 * G65 * G56)$
 $S23 = (G43 * G54 * G66) + (G44 * G56 * G63) + (G46 * G64 * G53)$
 $C - (G46 * G54 * G63) - (G44 * G53 * G66) - (G43 * G64 * G56)$
 $S24 = (G43 * G54 * G65) + (G44 * G55 * G63) + (G45 * G64 * G53)$
 $C - (G45 * G54 * G63) - (G44 * G53 * G65) - (G43 * G64 * G55)$
 $S25 = (G44 * G55 * G66) + (G45 * G56 * G64) + (G46 * G65 * G54)$
 $C - (G46 * G55 * G64) - (G45 * G54 * G66) - (G44 * G65 * G56)$
 $S26 = (G42 * G55 * G66) + (G45 * G56 * G62) + (G46 * G65 * G52)$
 $C - (G46 * G55 * G62) - (G45 * G52 * G66) - (G42 * G65 * G56)$
 $S27 = (G42 * G54 * G66) + (G44 * G56 * G62) + (G46 * G64 * G52)$
 $C - (G46 * G54 * G62) - (G44 * G52 * G66) - (G42 * G64 * G56)$
 $S28 = (G42 * G54 * G65) + (G44 * G55 * G62) + (G45 * G64 * G52)$
 $C - (G45 * G54 * G62) - (G44 * G52 * G65) - (G42 * G64 * G55)$
 $S29 = (G43 * G55 * G66) + (G45 * G56 * G63) + (G46 * G65 * G53)$
 $C - (G46 * G55 * G63) - (G45 * G53 * G66) - (G43 * G65 * G56)$
 $S30 = (G42 * G55 * G66) + (G45 * G56 * G62) + (G46 * G65 * G52)$
 $C - (G46 * G55 * G62) - (G45 * G52 * G66) - (G42 * G65 * G56)$
 $S31 = (G42 * G53 * G66) + (G43 * G56 * G62) + (G46 * G63 * G52)$
 $C - (G46 * G53 * G62) - (G43 * G52 * G66) - (G42 * G63 * G56)$
 $S32 = (G42 * G53 * G65) + (G43 * G55 * G62) + (G45 * G63 * G52)$
 $C - (G45 * G53 * G62) - (G43 * G52 * G65) - (G42 * G63 * G55)$
 $S33 = (G43 * G54 * G66) + (G44 * G56 * G63) + (G46 * G64 * G53)$
 $C - (G46 * G54 * G63) - (G44 * G53 * G66) - (G43 * G64 * G56)$
 $S34 = (G42 * G54 * G66) + (G44 * G56 * G62) + (G46 * G64 * G52)$
 $C - (G46 * G54 * G62) - (G44 * G52 * G66) - (G42 * G64 * G56)$
 $S35 = (G42 * G53 * G66) + (G43 * G56 * G62) + (G46 * G63 * G52)$
 $C - (G46 * G53 * G62) - (G43 * G52 * G66) - (G42 * G63 * G56)$

$S36 = (G42 * G53 * G64) + (G43 * G54 * G62) + (G44 * G63 * G52)$
 $C - (G44 * G53 * G62) - (G43 * G52 * G64) - (G42 * G63 * G54)$
 $S37 = (G43 * G54 * G65) + (G44 * G55 * G63) + (G45 * G64 * G53)$
 $C - (G45 * G54 * G63) - (G44 * G53 * G65) - (G43 * G64 * G55)$
 $S38 = (G42 * G54 * G65) + (G44 * G55 * G62) + (G45 * G64 * G52)$
 $C - (G45 * G54 * G62) - (G44 * G52 * G65) - (G42 * G64 * G55)$
 $S39 = (G42 * G53 * G65) + (G43 * G55 * G62) + (G45 * G63 * G52)$
 $C - (G45 * G53 * G62) - (G43 * G52 * G65) - (G42 * G63 * G55)$
 $S40 = (G42 * G53 * G64) + (G43 * G54 * G62) + (G44 * G63 * G52)$
 $C - (G44 * G53 * G62) - (G43 * G52 * G64) - (G42 * G63 * G54)$
 $S41 = (G44 * G55 * G66) + (G45 * G56 * G64) + (G46 * G65 * G54)$
 $C - (G46 * G55 * G64) - (G45 * G54 * G66) - (G44 * G65 * G56)$
 $S42 = (G43 * G55 * G66) + (G45 * G56 * G63) + (G46 * G65 * G53)$
 $C - (G46 * G55 * G63) - (G45 * G53 * G66) - (G43 * G65 * G56)$
 $S43 = (G43 * G54 * G66) + (G44 * G56 * G63) + (G46 * G64 * G53)$
 $C - (G46 * G54 * G63) - (G44 * G53 * G66) - (G43 * G64 * G56)$
 $S44 = (G43 * G54 * G65) + (G44 * G55 * G63) + (G45 * G64 * G53)$
 $C - (G45 * G54 * G63) - (G44 * G53 * G65) - (G43 * G64 * G55)$
 $S45 = (G44 * G55 * G66) + (G45 * G56 * G64) + (G46 * G65 * G54)$
 $C - (G46 * G55 * G64) - (G45 * G54 * G66) - (G44 * G65 * G56)$
 $S46 = (G41 * G55 * G66) + (G45 * G56 * G61) + (G46 * G65 * G51)$
 $C - (G46 * G55 * G61) - (G45 * G51 * G66) - (G41 * G65 * G56)$
 $S47 = (G41 * G54 * G66) + (G44 * G56 * G61) + (G46 * G64 * G51)$
 $C - (G46 * G54 * G61) - (G44 * G51 * G66) - (G41 * G64 * G56)$
 $S48 = (G41 * G54 * G65) + (G44 * G55 * G61) + (G45 * G64 * G51)$
 $C - (G45 * G54 * G61) - (G44 * G51 * G65) - (G41 * G64 * G55)$
 $S49 = (G43 * G55 * G66) + (G45 * G56 * G63) + (G46 * G65 * G53)$
 $C - (G46 * G55 * G63) - (G45 * G53 * G66) - (G43 * G65 * G56)$
 $S50 = (G41 * G55 * G66) + (G45 * G56 * G61) + (G46 * G65 * G51)$
 $C - (G46 * G55 * G61) - (G45 * G51 * G66) - (G41 * G65 * G56)$
 $S51 = (G41 * G53 * G66) + (G43 * G56 * G61) + (G46 * G63 * G51)$
 $C - (G46 * G53 * G61) - (G43 * G51 * G66) - (G41 * G63 * G56)$
 $S52 = (G41 * G53 * G65) + (G43 * G55 * G61) + (G45 * G63 * G51)$
 $C - (G45 * G53 * G61) - (G43 * G51 * G65) - (G41 * G63 * G55)$
 $S53 = (G43 * G54 * G66) + (G44 * G56 * G63) + (G46 * G64 * G53)$
 $C - (G46 * G54 * G63) - (G44 * G53 * G66) - (G43 * G64 * G56)$
 $S54 = (G41 * G54 * G66) + (G44 * G56 * G61) + (G46 * G64 * G51)$
 $C - (G46 * G54 * G61) - (G44 * G51 * G66) - (G41 * G64 * G56)$
 $S55 = (G41 * G53 * G66) + (G43 * G56 * G61) + (G46 * G63 * G51)$
 $C - (G46 * G53 * G61) - (G43 * G51 * G66) - (G41 * G63 * G56)$
 $S56 = (G41 * G53 * G64) + (G43 * G54 * G61) + (G44 * G63 * G51)$
 $C - (G44 * G53 * G61) - (G43 * G51 * G64) - (G41 * G63 * G54)$
 $S57 = (G43 * G54 * G65) + (G44 * G55 * G63) + (G45 * G64 * G53)$
 $C - (G45 * G54 * G63) - (G44 * G53 * G65) - (G43 * G64 * G55)$
 $S58 = (G41 * G54 * G65) + (G44 * G55 * G61) + (G45 * G64 * G51)$
 $C - (G45 * G54 * G61) - (G44 * G51 * G65) - (G41 * G64 * G55)$
 $S59 = (G41 * G53 * G65) + (G43 * G55 * G61) + (G45 * G63 * G51)$
 $C - (G45 * G53 * G61) - (G43 * G51 * G65) - (G41 * G63 * G55)$
 $S60 = (G41 * G53 * G64) + (G43 * G54 * G61) + (G44 * G63 * G51)$
 $C - (G44 * G53 * G61) - (G43 * G51 * G64) - (G41 * G63 * G54)$
 $S61 = (G44 * G55 * G66) + (G45 * G56 * G64) + (G46 * G65 * G54)$
 $C - (G46 * G55 * G64) - (G45 * G54 * G66) - (G44 * G65 * G56)$
 $S62 = (G42 * G55 * G66) + (G45 * G56 * G62) + (G46 * G65 * G52)$

C- (G46*G55*G62) - (G45*G52*G66) - (G42*G65*G56)
 S63= (G42*G54*G66) + (G44*G56*G62) + (G46*G64*G52)
 C- (G46*G54*G62) - (G44*G52*G66) - (G42*G64*G56)
 S64= (G42*G54*G65) + (G44*G55*G62) + (G45*G64*G52)
 C- (G45*G54*G62) - (G44*G52*G65) - (G42*G64*G55)
 S65= (G44*G55*G66) + (G45*G56*G64) + (G46*G65*G54)
 C- (G46*G55*G64) - (G45*G54*G66) - (G44*G65*G56)
 S66= (G41*G55*G66) + (G45*G56*G61) + (G46*G65*G51)
 C- (G46*G55*G61) - (G45*G51*G66) - (G41*G65*G56)
 S67= (G41*G54*G66) + (G44*G56*G61) + (G46*G64*G51)
 C- (G46*G54*G61) - (G44*G51*G66) - (G41*G64*G56)
 S68= (G41*G54*G65) + (G44*G55*G61) + (G45*G64*G51)
 C- (G45*G54*G61) - (G44*G51*G65) - (G41*G64*G55)
 S69= (G42*G55*G66) + (G45*G56*G62) + (G46*G65*G52)
 C- (G46*G55*G62) - (G45*G52*G66) - (G42*G65*G56)
 S70= (G41*G55*G66) + (G45*G56*G61) + (G46*G65*G51)
 C- (G46*G55*G61) - (G45*G51*G66) - (G41*G65*G56)
 S71= (G41*G52*G66) + (G42*G56*G61) + (G46*G62*G51)
 C- (G46*G52*G61) - (G42*G51*G66) - (G41*G62*G56)
 S72= (G41*G52*G65) + (G42*G55*G61) + (G45*G62*G51)
 C- (G45*G52*G61) - (G42*G51*G65) - (G41*G62*G55)
 S73= (G42*G54*G66) + (G44*G56*G62) + (G46*G64*G52)
 C- (G46*G54*G62) - (G44*G52*G66) - (G42*G64*G56)
 S74= (G41*G54*G66) + (G44*G56*G61) + (G46*G64*G51)
 C- (G46*G54*G61) - (G44*G51*G66) - (G41*G64*G56)
 S75= (G41*G52*G66) + (G42*G56*G61) + (G46*G62*G51)
 C- (G46*G52*G61) - (G42*G51*G66) - (G41*G62*G56)
 S76= (G41*G52*G64) + (G42*G54*G61) + (G44*G62*G51)
 C- (G44*G52*G61) - (G42*G51*G64) - (G41*G62*G54)
 S77= (G42*G54*G65) + (G44*G55*G62) + (G45*G64*G52)
 C- (G45*G54*G62) - (G44*G52*G65) - (G42*G64*G55)
 S78= (G41*G54*G65) + (G44*G55*G61) + (G45*G64*G51)
 C- (G45*G54*G61) - (G44*G51*G65) - (G41*G64*G55)
 S79= (G41*G52*G65) + (G42*G55*G61) + (G45*G62*G51)
 C- (G45*G52*G61) - (G42*G51*G65) - (G41*G62*G55)
 S80= (G41*G52*G64) + (G42*G54*G61) + (G44*G62*G51)
 C- (G44*G52*G61) - (G42*G51*G64) - (G41*G62*G54)
 S81= (G43*G55*G66) + (G45*G56*G63) + (G46*G65*G53)
 C- (G46*G55*G63) - (G45*G53*G66) - (G43*G65*G56)
 S82= (G42*G55*G66) + (G45*G56*G62) + (G46*G65*G52)
 C- (G46*G55*G62) - (G45*G52*G66) - (G42*G65*G56)
 S83= (G42*G53*G66) + (G43*G56*G62) + (G46*G63*G52)
 C- (G46*G53*G62) - (G43*G52*G66) - (G42*G63*G56)
 S84= (G42*G53*G65) + (G43*G55*G62) + (G45*G63*G52)
 C- (G45*G53*G62) - (G43*G52*G65) - (G42*G63*G55)
 S85= (G43*G55*G66) + (G45*G56*G63) + (G46*G65*G53)
 C- (G46*G55*G63) - (G45*G53*G66) - (G43*G65*G56)
 S86= (G41*G55*G66) + (G45*G56*G61) + (G46*G65*G51)
 C- (G46*G55*G61) - (G45*G51*G66) - (G41*G65*G56)
 S87= (G41*G53*G66) + (G43*G56*G61) + (G46*G63*G51)
 C- (G46*G53*G61) - (G43*G51*G66) - (G41*G63*G56)
 S88= (G41*G53*G65) + (G43*G55*G61) + (G45*G63*G51)
 C- (G45*G53*G61) - (G43*G51*G65) - (G41*G63*G55)

$S89 = (G42 * G55 * G66) + (G45 * G56 * G62) + (G46 * G65 * G52)$
 $C - (G46 * G55 * G62) - (G45 * G52 * G66) - (G42 * G65 * G56)$
 $S90 = (G41 * G55 * G66) + (G45 * G56 * G61) + (G46 * G65 * G51)$
 $C - (G46 * G55 * G61) - (G45 * G51 * G66) - (G41 * G65 * G56)$
 $S91 = (G41 * G52 * G66) + (G42 * G56 * G61) + (G46 * G62 * G51)$
 $C - (G46 * G52 * G61) - (G42 * G51 * G66) - (G41 * G62 * G56)$
 $S92 = (G41 * G52 * G65) + (G42 * G55 * G61) + (G45 * G62 * G51)$
 $C - (G45 * G52 * G61) - (G42 * G51 * G65) - (G41 * G62 * G55)$
 $S93 = (G42 * G53 * G66) + (G43 * G56 * G62) + (G46 * G63 * G52)$
 $C - (G46 * G53 * G62) - (G43 * G52 * G66) - (G42 * G63 * G56)$
 $S94 = (G41 * G53 * G66) + (G43 * G56 * G61) + (G46 * G63 * G51)$
 $C - (G46 * G53 * G61) - (G43 * G51 * G66) - (G41 * G63 * G56)$
 $S95 = (G41 * G52 * G66) + (G42 * G56 * G61) + (G46 * G62 * G51)$
 $C - (G46 * G52 * G61) - (G42 * G51 * G66) - (G41 * G62 * G56)$
 $S96 = (G41 * G52 * G63) + (G42 * G53 * G61) + (G43 * G62 * G51)$
 $C - (G43 * G52 * G61) - (G42 * G51 * G63) - (G41 * G62 * G53)$
 $S97 = (G42 * G53 * G65) + (G43 * G55 * G62) + (G45 * G63 * G52)$
 $C - (G45 * G53 * G62) - (G43 * G52 * G65) - (G42 * G63 * G55)$
 $S98 = (G41 * G53 * G65) + (G43 * G55 * G61) + (G45 * G63 * G51)$
 $C - (G45 * G53 * G61) - (G43 * G51 * G65) - (G41 * G63 * G55)$
 $S99 = (G41 * G52 * G65) + (G42 * G55 * G61) + (G45 * G62 * G51)$
 $C - (G45 * G52 * G61) - (G42 * G51 * G65) - (G41 * G62 * G55)$
 $S100 = (G41 * G52 * G63) + (G42 * G53 * G61) + (G43 * G62 * G51)$
 $C - (G43 * G52 * G61) - (G42 * G51 * G63) - (G41 * G62 * G53)$
 $S101 = (G43 * G54 * G66) + (G44 * G56 * G63) + (G46 * G64 * G53)$
 $C - (G46 * G54 * G63) - (G44 * G53 * G66) - (G43 * G64 * G56)$
 $S102 = (G42 * G54 * G66) + (G44 * G56 * G62) + (G46 * G64 * G52)$
 $C - (G46 * G54 * G62) - (G44 * G52 * G66) - (G42 * G64 * G56)$
 $S103 = (G42 * G53 * G66) + (G43 * G56 * G62) + (G46 * G63 * G52)$
 $C - (G46 * G53 * G62) - (G43 * G52 * G66) - (G42 * G63 * G56)$
 $S104 = (G42 * G53 * G64) + (G43 * G54 * G62) + (G44 * G63 * G52)$
 $C - (G44 * G53 * G62) - (G43 * G52 * G64) - (G42 * G63 * G54)$
 $S105 = (G43 * G54 * G66) + (G44 * G56 * G63) + (G46 * G64 * G53)$
 $C - (G46 * G54 * G63) - (G44 * G53 * G66) - (G43 * G64 * G56)$
 $S106 = (G41 * G54 * G66) + (G44 * G56 * G61) + (G46 * G64 * G51)$
 $C - (G46 * G54 * G61) - (G44 * G51 * G66) - (G41 * G64 * G56)$
 $S107 = (G41 * G53 * G66) + (G43 * G56 * G61) + (G46 * G63 * G51)$
 $C - (G46 * G53 * G61) - (G43 * G51 * G66) - (G41 * G63 * G56)$
 $S108 = (G41 * G53 * G64) + (G43 * G54 * G61) + (G44 * G63 * G51)$
 $C - (G44 * G53 * G61) - (G43 * G51 * G64) - (G41 * G63 * G54)$
 $S109 = (G42 * G54 * G66) + (G44 * G56 * G62) + (G46 * G64 * G52)$
 $C - (G46 * G54 * G62) - (G44 * G52 * G66) - (G42 * G64 * G56)$
 $S110 = (G41 * G54 * G66) + (G44 * G56 * G61) + (G46 * G64 * G51)$
 $C - (G46 * G54 * G61) - (G44 * G51 * G66) - (G41 * G64 * G56)$
 $S111 = (G41 * G52 * G66) + (G42 * G56 * G61) + (G46 * G62 * G51)$
 $C - (G46 * G52 * G61) - (G42 * G51 * G66) - (G41 * G62 * G56)$
 $S112 = (G41 * G52 * G64) + (G42 * G54 * G61) + (G44 * G62 * G51)$
 $C - (G44 * G52 * G61) - (G42 * G51 * G64) - (G41 * G62 * G54)$
 $S113 = (G42 * G53 * G66) + (G43 * G56 * G62) + (G46 * G63 * G52)$
 $C - (G46 * G53 * G62) - (G43 * G52 * G66) - (G42 * G63 * G56)$
 $S114 = (G41 * G53 * G66) + (G43 * G56 * G61) + (G46 * G63 * G51)$
 $C - (G46 * G53 * G61) - (G43 * G51 * G66) - (G41 * G63 * G56)$
 $S115 = (G41 * G52 * G66) + (G42 * G56 * G61) + (G46 * G62 * G51)$

C- (G46*G52*G61) - (G42*G51*G66) - (G41*G62*G56)
 S116= (G41*G52*G63) + (G42*G53*G61) + (G43*G62*G51)
 C- (G43*G52*G61) - (G42*G51*G63) - (G41*G62*G53)
 S117= (G42*G53*G64) + (G43*G54*G62) + (G44*G63*G52)
 C- (G44*G53*G62) - (G43*G52*G64) - (G42*G63*G54)
 S118= (G41*G53*G64) + (G43*G54*G61) + (G44*G63*G51)
 C- (G44*G53*G61) - (G43*G51*G64) - (G41*G63*G54)
 S119= (G41*G52*G64) + (G42*G54*G61) + (G44*G62*G51)
 C- (G44*G52*G61) - (G42*G51*G64) - (G41*G62*G54)
 S120= (G41*G52*G63) + (G42*G53*G61) + (G43*G62*G51)
 C- (G43*G52*G61) - (G42*G51*G63) - (G41*G62*G53)
 S121= (G43*G54*G65) + (G44*G55*G63) + (G45*G64*G53)
 C- (G45*G54*G63) - (G44*G53*G65) - (G43*G64*G55)
 S122= (G42*G54*G65) + (G44*G55*G62) + (G45*G64*G52)
 C- (G45*G54*G62) - (G44*G52*G65) - (G42*G64*G55)
 S123= (G42*G53*G65) + (G43*G55*G62) + (G45*G63*G52)
 C- (G45*G53*G62) - (G43*G52*G65) - (G42*G63*G55)
 S124= (G43*G54*G65) + (G44*G55*G63) + (G45*G64*G53)
 C- (G45*G54*G63) - (G44*G53*G65) - (G43*G64*G55)
 S125= (G41*G54*G65) + (G44*G55*G61) + (G45*G64*G51)
 C- (G45*G54*G61) - (G44*G51*G65) - (G41*G64*G55)
 S126= (G41*G53*G65) + (G43*G55*G61) + (G45*G63*G51)
 C- (G45*G53*G61) - (G43*G51*G65) - (G41*G63*G55)
 S127= (G41*G53*G64) + (G43*G54*G61) + (G44*G63*G51)
 C- (G44*G53*G61) - (G43*G51*G64) - (G41*G63*G54)
 S128= (G42*G54*G65) + (G44*G55*G62) + (G45*G64*G52)
 C- (G45*G54*G62) - (G44*G52*G65) - (G42*G64*G55)
 S129= (G41*G54*G65) + (G44*G55*G61) + (G45*G64*G51)
 C- (G45*G54*G61) - (G44*G51*G65) - (G41*G64*G55)
 S130= (G41*G52*G65) + (G42*G55*G61) + (G45*G62*G51)
 C- (G45*G52*G61) - (G42*G51*G65) - (G41*G62*G55)
 S131= (G41*G52*G64) + (G42*G54*G61) + (G44*G62*G51)
 C- (G44*G52*G61) - (G42*G51*G64) - (G41*G62*G54)
 S132= (G42*G53*G65) + (G43*G55*G62) + (G45*G63*G52)
 C- (G45*G53*G62) - (G43*G52*G65) - (G42*G63*G55)
 S133= (G41*G53*G65) + (G43*G55*G61) + (G45*G63*G51)
 C- (G45*G53*G61) - (G43*G51*G65) - (G41*G63*G55)
 S134= (G41*G52*G65) + (G42*G55*G61) + (G45*G62*G51)
 C- (G45*G52*G61) - (G42*G51*G65) - (G41*G62*G55)
 S135= (G41*G52*G63) + (G42*G53*G61) + (G43*G62*G51)
 C- (G43*G52*G61) - (G42*G51*G63) - (G41*G62*G53)
 S136= (G42*G53*G64) + (G43*G54*G62) + (G44*G63*G52)
 C- (G44*G53*G62) - (G43*G52*G64) - (G42*G63*G54)
 S137= (G41*G53*G64) + (G43*G54*G61) + (G44*G63*G51)
 C- (G44*G53*G61) - (G43*G51*G64) - (G41*G63*G54)
 S138= (G41*G52*G64) + (G42*G54*G61) + (G44*G62*G51)
 C- (G44*G52*G61) - (G42*G51*G64) - (G41*G62*G54)
 S139= (G41*G52*G63) + (G42*G53*G61) + (G43*G62*G51)
 C- (G43*G52*G61) - (G42*G51*G63) - (G41*G62*G53)
 S140= (G32*G43*G54) + (G33*G44*G52) + (G34*G53*G42)
 C- (G34*G43*G52) - (G33*G42*G54) - (G32*G53*G44)
 S141= (G31*G43*G54) + (G33*G44*G51) + (G34*G53*G41)
 C- (G34*G43*G51) - (G33*G41*G54) - (G31*G53*G44)

$S142 = (G31 * G42 * G54) + (G32 * G44 * G51) + (G34 * G52 * G41)$
 $C - (G34 * G42 * G51) - (G32 * G41 * G54) - (G31 * G52 * G44)$
 $S143 = (G31 * G42 * G53) + (G32 * G43 * G51) + (G33 * G52 * G41)$
 $C - (G33 * G42 * G51) - (G32 * G41 * G53) - (G31 * G52 * G43)$
 $A1 = (G22 * S5) - (G23 * S6) + (G24 * S7) - (G25 * S8)$
 $A2 = (G21 * S9) - (G23 * S10) + (G24 * S11) - (G25 * S12)$
 $A3 = (G21 * S13) - (G22 * S14) + (G24 * S15) - (G25 * S16)$
 $A4 = (G21 * S17) - (G22 * S18) + (G23 * S19) - (G25 * S20)$
 $A5 = (G21 * S140) - (G22 * S141) + (G23 * S142) - (G24 * S143)$
 $A6 = (G33 * S21) - (G34 * S22) + (G35 * S23) - (G36 * S24)$
 $A7 = (G32 * S25) - (G34 * S26) + (G35 * S27) - (G36 * S28)$
 $A8 = (G32 * S29) - (G33 * S30) + (G35 * S31) - (G36 * S32)$
 $A9 = (G32 * S33) - (G33 * S34) + (G34 * S35) - (G36 * S36)$
 $A10 = (G32 * S37) - (G33 * S38) + (G34 * S39) - (G35 * S40)$
 $A11 = (G33 * S41) - (G34 * S42) + (G35 * S43) - (G36 * S44)$
 $A12 = (G31 * S45) - (G34 * S46) + (G35 * S47) - (G36 * S48)$
 $A13 = (G31 * S49) - (G33 * S50) + (G35 * S51) - (G36 * S52)$
 $A14 = (G31 * S53) - (G33 * S54) + (G34 * S55) - (G36 * S56)$
 $A15 = (G31 * S57) - (G33 * S58) + (G34 * S59) - (G35 * S60)$
 $A16 = (G32 * S61) - (G34 * S62) + (G35 * S63) - (G36 * S64)$
 $A17 = (G31 * S65) - (G34 * S66) + (G35 * S67) - (G36 * S68)$
 $A18 = (G31 * S69) - (G32 * S70) + (G35 * S71) - (G36 * S72)$
 $A19 = (G31 * S73) - (G32 * S74) + (G34 * S75) - (G36 * S76)$
 $A20 = (G31 * S77) - (G32 * S78) + (G34 * S79) - (G35 * S80)$
 $A21 = (G32 * S81) - (G33 * S82) + (G35 * S83) - (G36 * S84)$
 $A22 = (G31 * S85) - (G33 * S86) + (G35 * S87) - (G36 * S88)$
 $A23 = (G31 * S89) - (G32 * S90) + (G35 * S91) - (G36 * S92)$
 $A24 = (G31 * S93) - (G32 * S94) + (G33 * S95) - (G36 * S96)$
 $A25 = (G31 * S97) - (G32 * S98) + (G33 * S99) - (G35 * S100)$
 $A26 = (G32 * S101) - (G33 * S102) + (G34 * S103) - (G36 * S104)$
 $A27 = (G31 * S105) - (G33 * S106) + (G34 * S107) - (G36 * S108)$
 $A28 = (G31 * S109) - (G32 * S110) + (G34 * S111) - (G36 * S112)$
 $A29 = (G31 * S113) - (G32 * S114) + (G33 * S115) - (G36 * S116)$
 $A30 = (G31 * S117) - (G32 * S118) + (G33 * S119) - (G34 * S120)$
 $A31 = (G32 * S121) - (G33 * S122) + (G34 * S123) - (G35 * S124)$
 $A32 = (G31 * S124) - (G33 * S125) + (G34 * S126) - (G35 * S127)$
 $A33 = (G31 * S128) - (G32 * S129) + (G34 * S130) - (G35 * S131)$
 $A34 = (G31 * S132) - (G32 * S133) + (G33 * S134) - (G35 * S135)$
 $A35 = (G31 * S136) - (G32 * S137) + (G33 * S138) - (G34 * S139)$
 $B1 = (G22 * A6) - (G23 * A7) + (G24 * A8) - (G25 * A9) + (G26 * A10)$
 $B2 = (G21 * A11) - (G23 * A12) + (G24 * A13) - (G25 * A14) + (G26 * A15)$
 $B3 = (G21 * A16) - (G22 * A17) + (G24 * A18) - (G25 * A19) + (G26 * A20)$
 $B4 = (G21 * A21) - (G22 * A22) + (G23 * A23) - (G25 * A24) + (G26 * A25)$
 $B5 = (G21 * A26) - (G22 * A27) + (G23 * A28) - (G24 * A29) + (G26 * A30)$
 $B6 = (G21 * A31) - (G22 * A32) + (G23 * A33) - (G24 * A34) + (G25 * A35)$
C CALCULATE VALUES OF EACH D DETERMINANT
 $DZERO = 1.0$
 $D(1) = G11$
 $D(2) = (G11 * G22) - (G12 * G21)$
 $D(3) = (G11 * G22 * G33) + (G12 * G23 * G31) + (G13 * G32 * G21)$
 $C - (G13 * G22 * G31) - (G12 * G21 * G33) - (G11 * G32 * G23)$
 $D(4) = (G11 * S1) - (G12 * S2) + (G12 * S3) - (G14 * S4)$
 $D(5) = (G11 * A1) - (G12 * A2) + (G13 * A3) - (G14 * A4) + (G15 * A5)$


```

D(6)=(G11*B1)-(G12*B2)+(G13*B3)-(G14*B4)+(G15*B5)-(G16*B6)
XLAMDA(1)=(RATE(1)*D(1))/DZERO
XLAMDA(2)=(RATE(2)*D(2))/D(1)
XLAMDA(3)=(RATE(3)*D(3))/D(2)
XLAMDA(4)=(RATE(4)*D(4))/D(3)
XLAMDA(5)=(RATE(5)*D(5))/D(4)
XLAMDA(6)=(RATE(6)*D(6))/D(5)
DO 3 I=1,6
3 TAU(I)=1./XLAMDA(I)
DO 12 I=1,6
12 FRLX(I)=1./(2.*3.1416*TAU(I))
C   CALCULATE NORMAL MODE REACTION PARAMETERS
WRITE(6,500)
500 FORMAT('1','NORMAL MODE REACTION PARAMETERS')
WRITE(6,909)PH,XMOLAR
909 FORMAT(' ','AT P=1ATM,',3X,'T=25C,',3X,'PH=',F4.1,3X,'CB(OH)3=',
CD12.5)
WRITE(6,5)
WRITE(6,4)
4 FORMAT(' ','RELAXATION TIMES, SEC')
WRITE(6,5)
WRITE(6,502)(TAU(I),I=1,6)
WRITE(6,5)
WRITE(6,501)
501 FORMAT(' ','RELAXATION FREQUENCIES, HZ')
WRITE(6,5)
WRITE(6,502)(FRLX(I),I=1,6)
502 FORMAT(' ',6(D12.5,3X))
SIGMA(1)=(1./C(2))+(1./C(1))+(1./C(3))
SIGMA(2)=(1./C(3))+(1./C(2))+(1./C(4))
SIGMA(3)=(1./C(4))+(1./C(2))+(1./C(5))
SIGMA(4)=(1./C(5))+(1./C(9))+(1./C(6))
SIGMA(5)=(1./C(6))+(1./C(2))+(1./C(7))
SIGMA(6)=(1./C(7))+(1./C(2))+(1./C(8))+(1./C(9))
C   CALCULATE THE AMPLITUDE OF RELAXATION PEAK
DO 10 I=1,6
10 XMUMAX(I)=(3.1416*((DELTAV(I)-((VBAR*THETA/CP)*DELTAH(I)))**2))
C/(1000.*BETA*RR*TEMP*SIGMA(I))
WRITE(6,5)
WRITE(6,13)
13 FORMAT(' ','MAX SOUND ABSORPTION OF RELAXATION PEAK, MU(MAX)')
WRITE(6,5)
WRITE(6,502)(XMUMAX(I),I=1,6)
WRITE(6,5)
DO 14 I=1,6
14 V(I)=DLOG10(XMUMAX(I))
WRITE(6,15)
15 FORMAT(' ','LOG MU(MAX)')
WRITE(6,5)
WRITE(6,603)(V(I),I=1,6)
603 FORMAT(' ',6(F10.3,2X))
DO 257 I=1,6
257 Y(I)=XMUMAX(I)*(1.D+17)/(FRLX(I)*VEL)

```

```

WRITE(6,5)
WRITE(6,255)
255 FORMAT(' ','AMPLITUDE*(10**17)')
WRITE(6,5)
WRITE(6,256)(Y(I),I=1,6)
256 FORMAT(' ',6(D14.7,3X))
WRITE(6,5)
WRITE(6,5)
WRITE(6,17)
17 FORMAT(' ','-----
C-----
C')
19 CONTINUE
STOP
END

```

APPENDIX F:

Computer Program 6

```

C    CALCULATION OF RELAXATION SPECTRA, MU(CHEM), FOR BORIC ACID
C    AND POLYBORATE SYSTEM
C    T=25C, P=1ATM
C    F=SCANNING FREQUENCIES
C    FRELXI=RELAXATION FREQUENCY OF REACTION I
C    XMUMXI=MAXIMUM SOUND ABSORPTION OF REACTION I
C    XMUCHE=EXCESS SOUND ABSORPTION DUE TO CHEMICAL REACTIONS
DO 99 J=1,14
  READ(5,8)CBORIC,PH
8  FORMAT(E12.3,F4.1)
  WRITE(6,4)
  WRITE(6,9)
9  FORMAT(' ', '-----')
  C-----
  C')
  WRITE(6,4)
4  FORMAT('0')
  WRITE(6,3)CBORIC,PH
3  FORMAT(' ', 'CB(OH)3=',E12.3,3X,'PH=',F4.1)
  WRITE(6,4)
  WRITE(6,5)
5  FORMAT(' ', 'F=',T15,'MU(CHEM)=',T32,'LOG F=',T43,'LOG MU(CHEM)=')
  WRITE(6,4)
  READ(5,1)XMUMX1,XMUMX2,XMUMX3,XMUMX4,XMUMX5,XMUMX6
1  FORMAT(6E12.4)
  READ(5,1)FRELX1,FRELX2,FRELX3,FRELX4,FRELX5,FRELX6
  DO 7 I=1,16
    READ(5,2)F
2  FORMAT(E10.1)
    A1=F/FRELX1
    CHEM1=(2.*XMUMX1*A1)/(1.+(A1**2))
    A2=F/FRELX2
    CHEM2=(2.*XMUMX2*A2)/(1.+(A2**2))
    A3=F/FRELX3
    CHEM3=(2.*XMUMX3*A3)/(1.+(A3**2))
    A4=F/FRELX4
    CHEM4=(2.*XMUMX4*A4)/(1.+(A4**2))
    A5=F/FRELX5
    CHEM5=(2.*XMUMX5*A5)/(1.+(A5**2))
    A6=F/FRELX6
    CHEM6=(2.*XMUMX6*A6)/(1.+(A6**2))
    XMUCHE=CHEM1+CHEM2+CHEM3+CHEM4+CHEM5+CHEM6
    B=ALOG10(F)
    C=ALOG10(XMUCHE)
    WRITE(6,6)F,XMUCHE,B,C
6  FORMAT(' ',E8.1,T15,E12.5,T32,F4.1,T43,F7.3)
7  CONTINUE
99 CONTINUE
  STOP
  END

```

APPENDIX G:

Computer Program 7

```

C    LINEAR LEAST SQUARES FIT
C    X(I),Y(I)=EXPERIMENTAL DATA POINTS READ IN
C    W(I)=WEIGHTING FACTORS
C    YCALC(I)=CALCULATED Y(I) VALUES FROM THE THEORETICAL STRAIGHT
C    LINE EQUATION
C    NN=TOTAL NUMBER OF DATA SETS READ IN
C    FREQ=FREQUENCY USED IN MEASUREMENT
C    N=NUMBER OF DATA POINTS PER SET
C    NW=FLAG SIGNALS
C    A1=SLOPE
C    AZ=INTERCEPT
C    SA1=STANDARD DEVIATION OF A1
C    SAZ=STANDARD DEVIATION OF AZ
C    STD=STANDARD DEVIATION OF THE ENTIRE FIT
C    DIMENSION X(10),Y(10),W(10),YCALC(10)
C    READ(5,18)NN
18  FORMAT(I5)
C    DO 40 K=1,NN
C    READ(5,5)FREQ
5   FORMAT(I5)
C    READ(5,19)N,NW
19  FORMAT(2I5)
C    READ(5,29)(X(I),Y(I),I=1,N)
29  FORMAT(8F10.4)
C    IF(NW) 1,1,2
1   DO 10 I=1,N
10  W(I)=1.0
C    GO TO 3
2   DO 20 I=1,N
20  W(I)=1.0/Y(I)
3   CALL LLS(W,X,Y,N,A1,AZ,SA1,SAZ,STD)
C    DO 30 I=1,N
30  YCALC(I)=(X(I)*A1)+(AZ)
C    WRITE(6,6)FREQ
6   FORMAT('1','FREQUENCY USED IN THE MEASUREMENT=',I4,2X,'MHZ')
C    WRITE(6,4)
4   FORMAT('0')
C    WRITE(6,9)
9   FORMAT(' ',T3,'I=',T12,'CM(I)=',T28,'DB(I)=',T45,'W(I)=',T61,'DB(C
CALC)(I)=')
C    WRITE(6,4)
C    WRITE(6,39)(I,X(I),Y(I),W(I),YCALC(I),I=1,N)
39  FORMAT(' ',T3,I2,T12,F8.6,T28,F9.6,T45,F8.6,T61,F9.6)
C    WRITE(6,4)
C    WRITE(6,49)N
49  FORMAT(' ', 'NUMBER OF POINTS=',I5)
C    WRITE(6,4)

```

```

WRITE(6,50)AZ,SAZ
50 FORMAT(' ','INTERCEPT=',E14.4,5X,'STANDARD DEVIATION=',E16.4)
WRITE(6,4)
WRITE(6,51)A1,SA1
51 FORMAT(' ','SLOPE(OR ALPHA)=',E18.4,5X,'STANDARD DEVIATION=',E12.4
C)
WRITE(6,4)
40 WRITE(6,52)STD
52 FORMAT(' ','OVERALL STANDARD DEVIATION OF THE FIT=',E14.4)
STOP
END

```

```

SUBROUTINE LLS(W,X,Y,N,A1,AZ,SA1,SAZ,STD)
DIMENSION W(N),X(N),Y(N)
WW=0.0
WX=0.0
WY=0.0
WXY=0.0
WXX=0.0
WYY=0.0
DO 10 I=1,N
AW=W(I)
AX=X(I)
AY=Y(I)
WW=WW+AW
WX=(WX)+(AW*AX)
WY=(WY)+(AW*AY)
WXY=(WXY)+(AW*AX*AY)
WXX=(WXX)+(AW*AX*AX)
10 WYY=(WYY)+(AW*AY*AY)
DENOM=(WW*WXX)-(WX*WX)
A1=((WW*WXY)-(WX*WY))/DENOM
AZ=((WXX*WY)-(WX*WXY))/DENOM
VSUM=0.0
DO 20 I=1,N
20 VSUM=VSUM+(Y(I)-AZ-(A1*X(I)))**2
SS=VSUM/(N-2)
STD=SQRT(SS)
SA1=SQRT(SS*WW/DENOM)
SAZ=SQRT((SS/WW)*(1.0+((WX*WX)/DENOM)))
RETURN
END

```

APPENDIX H:

Computer Program 8

```

C      CALCULATION OF RELAXATION SPECTRA, MU(CHEM), FOR BORIC ACID
C      AND SODIUM BORATE SYSTEM
C      T=25C, P=1ATM
C      F=SCANNING FREQUENCIES
C      FRELXI=RELAXATION FREQUENCY OF REACTION I
C      XMUMXI=MAXIMUM SOUND ABSORPTION OF REACTION I
C      XMUCHE=TOTAL EXCESS SOUND ABSORPTION DUE TO CHEMICAL RELAXATION REACTIONS
DO 99 J=1,19
  READ(5,8)CBORIC,CNA,PH
8  FORMAT(E12.3,F5.2,F4.1)
  WRITE(6,4)
  WRITE(6,9)
9  FORMAT(' ', '-----
C-----
C')
  WRITE(6,4)
4  FORMAT('0')
  WRITE(6,3)CBORIC,CNA,PH
3  FORMAT(' ', 'CB(OH)3=', E12.3, 3X, 'CNA=', F5.2, 3X, 'PH=', F4.1)
  WRITE(6,4)
  WRITE(6,5)
5  FORMAT(' ', 'F=', T15, 'MU(CHEM)=', T32, 'LOG F=', T43, 'LOG MU(CHEM)=')
  WRITE(6,4)
  READ(5,1)XMUMX1,XMUMX2
1  FORMAT(2E12.4)
  READ(5,1)FRELX1,FRELX2
  DO 7 I=1,16
    READ(5,2)F
2  FORMAT(E10.1)
    A1=F/FRELX1
    CHEM1=(2.*XMUMX1*A1)/(1.+(A1**2))
    A2=F/FRELX2
    CHEM2=(2.*XMUMX2*A2)/(1.+(A2**2))
    XMUCHE=CHEM1+CHEM2
    B=ALOG10(F)
    C=ALOG10(XMUCHE)
    WRITE(6,6)F,XMUCHE,B,C
6  FORMAT(' ', E8.1, T15, E12.5, T32, F4.1, T43, F7.3)
7  CONTINUE
99 CONTINUE
  STOP
  END

```

APPENDIX I:

Computer Program 9

```

C      CALCULATION OF RELAXATION SPECTRA, MU(CHEM), FOR BORIC ACID SYSTEM
C      T=25C, P=1ATM
C      F=SCANNING FREQUENCIES
C      FRELX=RELAXATION FREQUENCY OF THE REACTION
C      XMUMX=MAXIMUM SOUND ABSORPTION OF THE REACTION
C      XMUCHE=TOTAL EXCESS SOUND ABSORPTION DUE TO CHEMICAL RELAXATION
      DO 99 J=1,4
        READ(5,8)CBORIC,PH,DELTAV
      8  FORMAT(E12.3,F4.1,E10.2)
        WRITE(6,4)
        WRITE(6,9)
      9  FORMAT(' ', '-----'
C-----
C')
        WRITE(6,4)
      4  FORMAT('0')
        WRITE(6,3)CBORIC,PH,DELTAV
      3  FORMAT(' ', 'CB(OH)3=', E12.3, 3X, 'PH=', F4.1, 3X, 'DELTA V=', F6.2)
        WRITE(6,4)
        WRITE(6,5)
      5  FORMAT(' ', 'F=', T15, 'MU(CHEM)=', T32, 'LOG F=', T43, 'LOG MU(CHEM)=')
        WRITE(6,4)
        READ(5,1)XMUMX
      1  FORMAT(E12.4)
        READ(5,1)FRELX
        DO 7 I=1,16
          READ(5,2)F
        2  FORMAT(E10.1)
          A=F/FRELX
          XMUCHE=(2.*XMUMX*A)/(1.+(A**2))
          B=ALOG10(F)
          C=ALOG10(XMUCHE)
          WRITE(6,6)F, XMUCHE, B, C
        6  FORMAT(' ', E8.1, T15, E12.5, T32, F4.1, T43, F7.3)
        7  CONTINUE
      99 CONTINUE
        STOP
        END

```

APPENDIX J:

Computer Program 10

```

C    CALCULATION OF KF, KB, AND KEQ OF ONE-STEP REACTION OF
C    AQUEOUS BORIC ACID SYSTEM
C    CBOH3(I)=TOTAL BORIC ACID CONCENTRATION OF EXPT(I)
C    EK=EQUILIBRIUM CONSTANT
C    OH(I)=SOLUTION PH OF EXPT(I)
C    TAU(I)=RELAXATION TIME OF EXPT(I)
C    X(I),Y(I)=DATA POINTS FOR LINEAR LEAST SQUARES FIT
C    W(I)=WEIGHTING FACTORS
C    N=NUMBER OF DATA POINTS USED
C    A1=SLOPE
C    AZ=INTERCEPT
C    SA1=STANDARD DEVIATION OF A1
C    SAZ=STANDARD DEVIATION OF AZ
C    STD=STANDARD DEVIATION OF THE ENTIRE FIT
C    DIMENSION CBOH3(30),OH(30),TAU(30),X(30),Y(30),W(30),BOH3(30)
C    READ(5,1) EK
1    FORMAT(E12.4)
C    WRITE(6,2) EK
2    FORMAT('1','EK(ASSUMED VALUE)=' ,E15.5)
C    WRITE(6,3)
3    FORMAT('0')
C    READ(5,4)N
4    FORMAT(I5)
C    READ(5,5) (CBOH3(I),OH(I),TAU(I),I=1,N)
5    FORMAT(E12.4,E12.4,E15.4)
C    DO 6 I=1,N
C    Y(I)=1./TAU(I)
6    W(I)=1.0
11   DO 7 I=1,N
C    BOH3(I)=CBOH3(I)/(1.+(EK*OH(I)))
7    X(I)=BOH3(I)+OH(I)
C    CALL LLS(W,X,Y,N,A1,AZ,SA1,SAZ,STD)
C    XEK=A1/AZ
C    WRITE(6,8)A1,AZ,XEK
8    FORMAT(' ','A1=' ,E18.5,5X,'AZ=' ,E18.5,5X,'EK(CALCULATED)=' ,E15.5)
C    ZERO=0.0
C    REFA1=A1-ZERO
C    REFAZ=AZ-ZERO
C    IF(REFA1.GT.ZERO) GO TO 17
C    GO TO 10
17   IF(REFAZ.GT.ZERO) GO TO 18
C    GO TO 10
18   DIFF=XEK-EK
C    DIFFAB=ABS(DIFF)
C    DFALOW=1.0E-08
C    IF(DIFFAB.GT.DFALOW) GO TO 9

```



```

      GO TO 10
9    EK=XEK
      GO TO 11
10   WRITE(6,3)
      WRITE(6,12)AZ,SAZ
12   FORMAT(' ','INTERCEPT (OR RKB)=' ,E15.5,5X,'STANDARD DEVIATION=' ,E1
C6.5)
      WRITE(6,3)
      WRITE(6,13)A1,SA1
13   FORMAT(' ','SLOPE (OR RKF)=' ,E18.5,5X,'STANDARD DEVIATION=' ,E15.5)
      WRITE(6,3)
      WRITE(6,14)STD
14   FORMAT(' ','OVERALL STANDARD DEVIATION OF THE FIT=' ,E15.5)
      WRITE(6,3)
      WRITE(6,15)XEK
15   FORMAT(' ','EK=' ,E15.5)
      STOP
      END

```

SUBROUTINE LLS(W,X,Y,N,A1,AZ,SA1,SAZ,STD)

(same as that shown in computer program 7)

APPENDIX K:

Computer Program 11

```

C    CALCULATION OF K2,K-2,K12,AND K23 OF TWO-STEP REACTION OF
C    AQUEOUS BORIC ACID SYSTEM
C    TWO-STEP PROCESS (TAU USED AS TAU 2)
C    CBOH3(I)=TOTAL BORIC ACID CONCENTRATION OF EXPT(I)
C    EK12=EQUILIBRIUM CONSTANT OF FIRST STEP REACTION
C    OH(I)=SOLUTION PH OF EXPT(I)
C    EKT=TOTAL EQUILIBRIUM CONSTANT OF THE TWO-STEP PROCESS
C    TAU(I)=RELAXATION TIME OF EXPT(I)
C    X(I),Y(I)=DATA POINTS FOR LINEAR LEAST SQUARES FIT
C    W(I)=WEIGHTING FACTORS
C    N=NUMBER OF DATA POINTS USED
C    A1=SLOPE
C    AZ=INTERCEPT
C    SA1=STANDARD DEVIATION OF A1
C    SAZ=STANDARD DEVIATION OF AZ
C    STD=STANDARD DEVIATION OF THE ENTIRE FIT
C    DIMENSION CBOH3(100),OH(100),TAU(100),X(100),Y(100),W(100),BOH3(10
C0)
      DO 99 NSET=1,4
      READ(5,1)EK12,EKT
1    FORMAT(2E12.4)
      WRITE(6,16)EK12
16   FORMAT('1','EK12(ASSUMED VALUE)=' ,E15.5)
      WRITE(6,9)
9    FORMAT('0')
      READ(5,2)N
2    FORMAT(I5)
      READ(5,3)(CBOH3(I),OH(I),TAU(I),I=1,N)
3    FORMAT(E12.4,E12.4,E15.4)
      DO 14 I=1,N
      Y(I)=1./TAU(I)
14   W(I)=1.0
6    EK21=1./EK12
      DO 4 I=1,N
      BOH3(I)=CBOH3(I)/(1.+(EK12*OH(I))+(EKT*OH(I)))
4    X(I)=(OH(I)+BOH3(I))/(EK21+OH(I)+BOH3(I))
      CALL LLS(W,X,Y,N,A1,AZ,SA1,SAZ,STD)
      XEK23=A1/AZ
      XEK12=EKT/XEK23
      WRITE(6,15)A1,AZ,XEK12
15   FORMAT(' ','A1=' ,E18.5,5X,'AZ=' ,E18.5,5X,'EK12(CALCULATED)=' ,E15.5
C)
7    WRITE(6,9)
      WRITE(6,8)AZ,SAZ
8    FORMAT(' ','INTERCEPT (OR RK-2)=' ,E15.5,5X,'STANDARD DEVIATION=' ,E
C16.5)

```

```

WRITE(6,9)
WRITE(6,10)A1,SA1
10 FORMAT(' ','SLOPE (OR RK2)=' ,E18.5,5X,'STANDARD DEVIATION=' ,E15.5)
WRITE(6,9)
WRITE(6,11)STD
11 FORMAT(' ','OVERALL STANDARD DEVIATION OF THE FIT=' ,E15.5)
WRITE(6,9)
WRITE(6,12)XEK23
12 FORMAT(' ','EK23=' ,E15.5)
WRITE(6,9)
WRITE(6,13)XEK12
13 FORMAT(' ','EK12=' ,E15.5)
READ(5,20)M
20 FORMAT(I5)
WRITE(6,9)
WRITE(6,19)M
19 FORMAT(' ','DATA SET NUMBER=' ,I5)
99 CONTINUE
STOP
END

```

SUBROUTINE LLS(W,X,Y,N,A1,AZ,SA1,SAZ,STD)

(same as that shown in computer program 7)

APPENDIX L:

Various Tables of Part I

Table 1-1: The Effect of pH and ΔV° Values on the Relaxation Frequency, Maximum Sound Absorption, Excess Sound Absorption, and Relx. Amplitude Values of the Boric Acid System at Total Boric Acid Concentration of 4.4×10^{-4} M

PH:	ΔV° : (ml/mole)	f_r : (Hz)	$\mu_{\max}$: (nepers)	α' : (dB/cm)	(Amp1.x10 ¹⁷)/2: (sec ² /cm) (nepers)
3.0	20	2.1486×10^6	3.0311×10^{-10}	3.7712×10^{-8}	9.4050×10^{-5}
	30	"	6.6679×10^{-10}	8.2961×10^{-8}	2.0689×10^{-4}
	35.45	"	9.2459×10^{-10}	1.1504×10^{-7}	2.8688×10^{-4}
	40	"	1.1720×10^{-9}	1.4582×10^{-7}	3.6365×10^{-4}
3.5	20	6.7945×10^5	9.5852×10^{-10}	3.7713×10^{-8}	9.4050×10^{-4}
	30	"	2.1086×10^{-9}	8.2962×10^{-8}	2.0689×10^{-3}
	35.45	"	2.9238×10^{-9}	1.1504×10^{-7}	2.8688×10^{-3}
	40	"	3.7062×10^{-9}	1.4582×10^{-7}	3.6365×10^{-3}
4.0	20	2.1487×10^5	3.0310×10^{-9}	3.7713×10^{-8}	9.4044×10^{-3}
	30	"	6.6677×10^{-9}	8.2962×10^{-8}	2.0688×10^{-2}
	35.45	"	9.2455×10^{-9}	1.1504×10^{-7}	2.8686×10^{-2}
	40	"	1.1720×10^{-8}	1.4582×10^{-7}	3.6363×10^{-2}
4.5	20	6.7963×10^4	9.5825×10^{-9}	3.7712×10^{-8}	9.3997×10^{-2}
	30	"	2.1080×10^{-8}	8.2961×10^{-8}	2.0678×10^{-1}
	35.45	"	2.9229×10^{-8}	1.1503×10^{-7}	2.8672×10^{-1}
	40	"	3.7051×10^{-8}	1.4581×10^{-7}	3.6345×10^{-1}
5.0	20	2.1542×10^4	3.0231×10^{-8}	3.7711×10^{-8}	9.3555×10^{-1}
	30	"	6.6502×10^{-8}	8.2956×10^{-8}	2.0581
	35.45	"	9.2212×10^{-8}	1.1503×10^{-7}	2.8537
	40	"	1.1689×10^{-7}	1.4581×10^{-7}	3.6174

Table 1-1 (continued)

pH:	ΔV° :	f_r :	$\mu_{\max}$:	α' :	$(\text{Amp1.} \times 10^{17})/2$:
5.5	20	6.9693×10^3	9.3431×10^{-8}	3.7706×10^{-8}	8.9375
	30	"	2.0553×10^{-7}	8.2946×10^{-8}	1.9661×10
	35.45	"	2.8499×10^{-7}	1.1501×10^{-7}	2.7262×10
	40	"	3.6126×10^{-7}	1.4579×10^{-7}	3.4557×10
6.0	20	2.6985×10^3	2.4120×10^{-7}	3.7690×10^{-8}	5.9589×10
	30	"	5.3060×10^{-7}	8.2912×10^{-8}	1.3108×10^2
	35.45	"	7.3574×10^{-7}	1.1497×10^{-7}	1.8176×10^2
	40	"	9.3262×10^{-7}	1.4573×10^{-7}	2.3040×10^2
6.5	20	2.4136×10^3	2.6934×10^{-7}	3.7644×10^{-8}	7.4394×10
	30	"	5.9249×10^{-7}	8.2808×10^{-8}	1.6365×10^2
	35.45	"	8.2156×10^{-7}	1.1482×10^{-7}	2.2693×10^2
	40	"	1.0414×10^{-6}	1.4555×10^{-7}	2.8765×10^2
7.0	20	5.6744×10^3	1.1411×10^{-7}	3.7495×10^{-8}	1.3406×10
	30	"	2.5102×10^{-7}	8.2482×10^{-8}	2.9492×10
	35.45	"	3.4807×10^{-7}	1.1437×10^{-7}	4.0893×10
	40	"	4.4121×10^{-7}	1.4498×10^{-7}	5.1836×10
7.5	20	1.7117×10^4	3.7362×10^{-8}	3.7033×10^{-8}	1.4551
	30	"	8.2189×10^{-8}	8.1465×10^{-8}	3.2011
	35.45	"	1.1396×10^{-7}	1.1296×10^{-7}	4.4386
	40	"	1.4446×10^{-7}	1.4319×10^{-7}	5.6264
8.0	20	5.1910×10^4	1.1858×10^{-8}	3.5644×10^{-8}	1.5228×10^{-1}
	30	"	2.6084×10^{-8}	7.8407×10^{-8}	3.3500×10^{-1}
	35.45	"	3.6169×10^{-8}	1.0872×10^{-7}	4.6451×10^{-1}
	40	"	4.5848×10^{-8}	1.3782×10^{-7}	5.8882×10^{-1}

Table 1-1 (continued)

pH:	ΔV° :	f_r :	$\mu_{\max}$:	α' :	$(\text{Amp} \cdot 10^{17})/2$:
8.5	20	1.4668×10^5	3.7511×10^{-9}	3.1861×10^{-8}	1.7049×10^{-2}
	30	"	8.2518×10^{-9}	7.0089×10^{-8}	3.7504×10^{-2}
	35.45	"	1.1442×10^{-8}	9.7185×10^{-8}	5.2004×10^{-2}
	40	"	1.4504×10^{-8}	1.2319×10^{-7}	6.5920×10^{-2}
9.0	20	3.4731×10^5	1.1863×10^{-9}	2.3858×10^{-8}	2.2770×10^{-3}
	30	"	2.6096×10^{-9}	5.2483×10^{-8}	5.0090×10^{-3}
	35.45	"	3.6185×10^{-9}	7.2774×10^{-8}	6.9456×10^{-3}
	40	"	4.5868×10^{-9}	9.2248×10^{-8}	8.8043×10^{-3}
9.5	20	6.1208×10^5	3.7513×10^{-10}	1.3296×10^{-8}	4.0859×10^{-4}
	30	"	8.2522×10^{-10}	2.9249×10^{-8}	8.9882×10^{-4}
	35.45	"	1.1443×10^{-9}	4.0558×10^{-8}	1.2463×10^{-3}
	40	"	1.4505×10^{-9}	5.1411×10^{-8}	1.5798×10^{-3}
10.0	20	8.0650×10^5	1.1863×10^{-10}	5.5402×10^{-9}	9.8059×10^{-5}
	30	"	2.6096×10^{-10}	1.2187×10^{-8}	2.1571×10^{-4}
	35.45	"	3.6185×10^{-10}	1.6899×10^{-8}	2.9911×10^{-4}
	40	"	4.5868×10^{-10}	2.1421×10^{-8}	3.7915×10^{-4}
10.5	20	8.9656×10^5	3.7513×10^{-11}	1.9476×10^{-9}	2.7894×10^{-5}
	30	"	8.2522×10^{-11}	4.2843×10^{-9}	6.1362×10^{-5}
	35.45	"	1.1443×10^{-10}	5.9408×10^{-9}	8.5086×10^{-5}
	40	"	1.4505×10^{-10}	7.5305×10^{-9}	1.0785×10^{-4}
11.0	20	9.2938×10^5	1.1863×10^{-11}	6.3843×10^{-10}	8.5095×10^{-6}
	30	"	2.6096×10^{-11}	1.4044×10^{-9}	1.8719×10^{-5}
	35.45	"	3.6185×10^{-11}	1.9474×10^{-9}	2.5956×10^{-5}
	40	"	4.5868×10^{-11}	2.4685×10^{-9}	3.2902×10^{-5}

Table 1-1 (continued)

pH:	ΔV° :	f_r :	$\mu_{\max}$:	α' :	$(\text{Ampl.} \times 10^{17})/2$:
11.5	20	9.4026×10^5	3.7513×10^{-12}	2.0425×10^{-10}	2.6598×10^{-6}
	30	"	8.2522×10^{-12}	4.4931×10^{-10}	5.8510×10^{-6}
	35.45	"	1.1443×10^{-11}	6.2304×10^{-10}	8.1131×10^{-6}
	40	"	1.4505×10^{-11}	7.8976×10^{-10}	1.0284×10^{-5}
12.0	20	9.4375×10^5	1.1863×10^{-12}	6.4831×10^{-11}	8.3798×10^{-7}
	30	"	2.6096×10^{-12}	1.4261×10^{-10}	1.8434×10^{-6}
	35.45	"	3.6185×10^{-12}	1.9775×10^{-10}	2.5561×10^{-6}
	40	"	4.5868×10^{-12}	2.5067×10^{-10}	3.2401×10^{-6}

Table 1-2: The Effect of pH Values on the Relaxation Frequency, Maximum Sound Absorption, Excess Sound Absorption, and Relx. Amplitude Values of Boric Acid System at Total Boric Acid Concentration of 4.4×10^{-3} M

PH:	f_r :	$\mu_{\max}$:	α' :	$(\text{Ampl.} \times 10^{17})/2$:
	(Hz)	(nepers)	(dB/cm)	$(\text{sec}^2/\text{cm})(\text{nepers})$
3.0	2.1486×10^6	9.2458×10^{-9}	1.1503×10^{-6}	2.8688×10^{-3}
4.0	2.1491×10^5	9.2434×10^{-8}	1.1503×10^{-6}	2.8673×10^{-1}
5.0	2.2036×10^4	9.0145×10^{-7}	1.1503×10^{-6}	2.7272×10
6.0	7.6366×10^3	2.5998×10^{-6}	1.1497×10^{-6}	2.2696×10^2
7.0	5.4799×10^4	3.6042×10^{-7}	1.1437×10^{-6}	4.3848
8.0	5.1889×10^5	3.6183×10^{-8}	1.0872×10^{-6}	4.6488×10^{-2}
9.0	3.4731×10^6	3.6185×10^{-9}	7.2774×10^{-7}	6.9457×10^{-4}

Table 1-2 (continued)

pH:	f_r :	$\mu_{\max}$:	α' :	$(\text{Ampl.} \times 10^{17})/2$:
10.0	8.0650×10^6	3.6185×10^{-10}	1.6899×10^{-7}	2.9911×10^{-5}
11.0	9.2937×10^6	3.6185×10^{-11}	1.9474×10^{-8}	2.5957×10^{-6}
12.0	9.4375×10^6	3.6185×10^{-12}	1.9775×10^{-9}	2.5561×10^{-7}

Table 1-3: The Effect of pH Values on the Relaxation Frequency, Maximum Sound Absorption, Excess Sound Absorption, and Relx. Amplitude Values of Boric Acid System at Total Boric Acid Concentration of 0.01 M

pH:	f_r :	$\mu_{\max}$:	α' :	$(\text{Ampl.} \times 10^{17})/2$:
	(Hz)	(nepers)	(dB/cm)	(sec^2/cm) (nepers)
3.0	2.1486×10^6	2.1013×10^{-8}	2.6144×10^{-6}	6.5200×10^{-3}
4.0	2.1498×10^5	2.1001×10^{-7}	2.6144×10^{-6}	6.5124×10^{-1}
5.0	2.2735×10^4	1.9858×10^{-6}	2.6143×10^{-6}	5.8230×10
6.0	1.4620×10^4	3.0864×10^{-6}	2.6129×10^{-6}	1.4074×10^2
7.0	1.2427×10^5	3.6122×10^{-7}	2.5994×10^{-6}	1.9379
8.0	1.1793×10^6	3.6184×10^{-8}	2.4710×10^{-6}	2.0456×10^{-2}
9.0	7.8934×10^6	3.6185×10^{-9}	1.6539×10^{-6}	3.0561×10^{-4}
10.0	1.8330×10^7	3.6185×10^{-10}	3.8408×10^{-7}	1.3161×10^{-5}
11.0	2.1122×10^7	3.6185×10^{-11}	4.4258×10^{-8}	1.1421×10^{-6}
12.0	2.1449×10^7	3.6185×10^{-12}	4.4943×10^{-9}	1.1247×10^{-7}

Table 1-4: The Effect of pH Values on the Relaxation Frequency,
Maximum Sound Absorption, Excess Sound Absorption, and
Relx. Amplitude Values of Boric Acid System at Total
Boric Acid Concentration of 0.025 M

pH:	f_r : (Hz)	μ_{max} : (nepers)	α' : (dB/cm)	$(\text{Ampl.} \times 10^{17})/2$: (sec^2/cm) (nepers)
3.0	2.1486×10^6	5.2533×10^{-8}	6.5361×10^{-6}	1.6300×10^{-2}
4.0	2.1517×10^5	5.2457×10^{-7}	6.5360×10^{-6}	1.6253
5.0	2.4606×10^4	4.5869×10^{-6}	6.5357×10^{-6}	1.2427×10^2
6.0	3.3325×10^4	3.3851×10^{-6}	6.5324×10^{-6}	6.7718x10
7.0	3.1035×10^5	3.6160×10^{-7}	6.4984×10^{-6}	7.7676×10^{-1}
8.0	2.9481×10^6	3.6185×10^{-8}	6.1773×10^{-6}	8.1825×10^{-3}
9.0	1.9734×10^7	3.6185×10^{-9}	4.1350×10^{-6}	1.2225×10^{-4}
10.0	4.5824×10^7	3.6185×10^{-10}	9.6017×10^{-7}	5.2644×10^{-6}
11.0	5.2805×10^7	3.6185×10^{-11}	1.1065×10^{-7}	4.5683×10^{-7}
12.0	5.3622×10^7	3.6185×10^{-12}	1.1236×10^{-8}	4.4987×10^{-8}

Table 1-5: The Effect of pH Values on the f_r , $\mu_{\max}$, α' , and Ampl.

Values of Boric Acid & Sodium Borate System(I) at

$$C_{B(OH)_3} = 4.4 \times 10^{-4} \text{ M and } C_{Na} = 0.1 \text{ M}$$

PH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	α' : (dB/cm)	$(\text{Ampl.} \times 10^{17})/2$: (sec^2/cm) (nepers)
3.0	2.1486×10^6	9.2459×10^{-10}	1.1504×10^{-7}	2.8688×10^{-4}
	3.3925×10^9	1.3127×10^{-16}	2.3010×10^{-7}	2.5796×10^{-14}
4.0	2.1487×10^5	9.2455×10^{-9}	1.1504×10^{-7}	2.8686×10^{-2}
	3.3925×10^9	1.3127×10^{-15}	2.3033×10^{-7}	2.5796×10^{-13}
5.0	2.1542×10^4	9.2212×10^{-8}	1.1503×10^{-7}	2.8537
	3.3930×10^9	1.3126×10^{-14}	2.3263×10^{-7}	2.5791×10^{-12}
6.0	2.6985×10^3	7.3572×10^{-7}	1.1496×10^{-7}	1.8176×10^2
	3.4319×10^9	1.3119×10^{-13}	2.5600×10^{-7}	2.5484×10^{-11}
7.0	5.6726×10^3	3.4806×10^{-7}	1.1433×10^{-7}	4.0906x10
	3.5786×10^9	1.3047×10^{-12}	4.9903×10^{-7}	2.4306×10^{-10}
8.0	5.1748×10^4	3.6169×10^{-8}	1.0838×10^{-7}	4.6597×10^{-1}
	3.5858×10^9	1.2368×10^{-11}	2.7849×10^{-6}	2.2993×10^{-9}
9.0	3.4019×10^5	3.6185×10^{-9}	7.1282×10^{-8}	7.0910×10^{-3}
	3.5862×10^9	8.1328×10^{-11}	1.7032×10^{-5}	1.5119×10^{-8}
10.0	7.6911×10^5	3.6185×10^{-10}	1.6119×10^{-8}	3.1365×10^{-4}
	3.5865×10^9	1.8383×10^{-10}	3.8210×10^{-5}	3.4170×10^{-8}
11.0	8.8007×10^5	3.6185×10^{-11}	1.8493×10^{-9}	2.7411×10^{-5}
	3.5866×10^9	2.1034×10^{-10}	4.3689×10^{-5}	3.9097×10^{-8}
12.0	8.9296×10^5	3.6185×10^{-12}	1.9260×10^{-10}	2.7015×10^{-6}
	3.5866×10^9	2.1342×10^{-10}	4.4325×10^{-5}	3.9669×10^{-8}

Table 1-6: The Effect of pH and ΔV_2^0 Values on the f_r , $\mu_{\max}$, α' , and
 Ampl. Values of Boric Acid & Sodium Borate System(I) at
 $C_{B(OH)_3} = 4.4 \times 10^{-4}$ M and $C_{Na} = 0.48$ M

pH:	ΔV_2^0 :	f_r :	$\mu_{\max}$:	α' :	(Ampl. $\times 10^{17}$)/2:
	(ml/mole)	(Hz)	(nepers)	(dB/cm)	(sec ² /cm) (nepers)
3.0	0.04	2.1486×10^6	9.2459×10^{-10}	1.1504×10^{-7}	2.8688×10^{-4}
		3.3925×10^9	5.2294×10^{-16}	2.3017×10^{-7}	1.0276×10^{-13}
	1.0	2.1486×10^6	9.2459×10^{-10}	1.1504×10^{-7}	2.8688×10^{-4}
		3.3925×10^9	1.5774×10^{-13}	2.6106×10^{-7}	3.0999×10^{-11}
	5.0	2.1486×10^6	9.2459×10^{-10}	1.1504×10^{-7}	2.8688×10^{-4}
		3.3925×10^9	3.8289×10^{-12}	9.8225×10^{-7}	7.5243×10^{-10}
4.0	0.04	2.1487×10^5	9.2455×10^{-9}	1.1504×10^{-7}	2.8686×10^{-2}
		3.3925×10^9	5.2293×10^{-15}	2.3110×10^{-7}	1.0276×10^{-12}
	1.0	2.1487×10^5	9.2455×10^{-9}	1.1504×10^{-7}	2.8686×10^{-2}
		3.3925×10^9	1.5774×10^{-12}	5.3995×10^{-7}	3.0998×10^{-10}
	5.0	2.1487×10^5	9.2455×10^{-9}	1.1504×10^{-7}	2.8686×10^{-2}
		3.3925×10^9	3.8289×10^{-11}	7.7519×10^{-6}	7.5242×10^{-9}
5.0	0.04	2.1542×10^4	9.2211×10^{-8}	1.1503×10^{-7}	2.8537
		3.3949×10^9	5.2290×10^{-14}	2.4033×10^{-7}	1.0268×10^{-11}
	1.0	2.1542×10^4	9.2211×10^{-8}	1.1503×10^{-7}	2.8537
		3.3949×10^9	1.5773×10^{-11}	3.3308×10^{-6}	3.0974×10^{-9}
	5.0	2.1542×10^4	9.2211×10^{-8}	1.1503×10^{-7}	2.8537
		3.3949×10^9	3.8286×10^{-10}	7.5495×10^{-5}	7.5184×10^{-8}
6.0	0.04	2.6984×10^3	7.3565×10^{-7}	1.1495×10^{-7}	1.8175×10^2
		3.5816×10^9	5.2255×10^{-13}	3.3827×10^{-7}	9.7265×10^{-11}
	1.0	2.6984×10^3	7.3565×10^{-7}	1.1495×10^{-7}	1.8175×10^2
		3.5816×10^9	1.5763×10^{-10}	3.2922×10^{-5}	2.9340×10^{-8}

Table 1-6 (continued)

pH:	ΔV_2° :	f_r :	$\mu_{\max}$:	α' :	(Ampl. $\times 10^{17}$)/2:
	5.0	2.6984×10^3 3.5816×10^9	7.3565×10^{-7} 3.8261×10^{-9}	1.1495×10^{-7} 7.9376×10^{-4}	1.8175×10^2 7.1217×10^{-7}
7.0	0.04	5.6658×10^3 4.2855×10^9	3.4805×10^{-7} 5.1910×10^{-12}	1.1419×10^{-7} 1.5166×10^{-6}	4.0953×10 8.0752×10^{-10}
	1.0	5.6658×10^3 4.2855×10^9	3.4805×10^{-7} 1.5659×10^{-9}	1.1419×10^{-7} 3.8882×10^{-4}	4.0953×10 2.4359×10^{-7}
	5.0	5.6658×10^3 4.2855×10^9	3.4805×10^{-7} 3.8008×10^{-8}	1.1419×10^{-7} 9.4323×10^{-3}	4.0953×10 5.9127×10^{-6}
8.0	0.04	5.1142×10^4 4.3203×10^9	3.6169×10^{-8} 4.8691×10^{-11}	1.0711×10^{-7} 1.2395×10^{-5}	4.7148×10^{-1} 7.5135×10^{-9}
	1.0	5.1142×10^4 4.3203×10^9	3.6169×10^{-8} 1.4688×10^{-8}	1.0711×10^{-7} 3.6748×10^{-3}	4.7148×10^{-1} 2.2665×10^{-6}
	5.0	5.1142×10^4 4.3203×10^9	3.6169×10^{-8} 3.5652×10^{-7}	1.0714×10^{-7} 8.9192×10^{-2}	4.7148×10^{-1} 5.5014×10^{-5}
9.0	0.04	3.1559×10^5 4.3209×10^9	3.6185×10^{-9} 3.0057×10^{-10}	6.6128×10^{-8} 7.5338×10^{-5}	7.6437×10^{-3} 4.6375×10^{-8}
	1.0	3.1559×10^5 4.3209×10^9	3.6185×10^{-9} 9.0667×10^{-8}	6.6369×10^{-8} 2.2686×10^{-2}	7.6437×10^{-3} 1.3989×10^{-5}
	5.0	3.1559×10^5 4.3209×10^9	3.6185×10^{-9} 2.2008×10^{-6}	7.2002×10^{-8} 5.5066×10^{-1}	7.6437×10^{-3} 3.3955×10^{-4}
10.0	0.04	6.5390×10^5 4.3211×10^9	3.6185×10^{-10} 6.2269×10^{-10}	1.3709×10^{-8} 1.5584×10^{-4}	3.6891×10^{-4} 9.6069×10^{-8}
	1.0	6.5390×10^5 4.3211×10^9	3.6185×10^{-10} 1.8783×10^{-7}	1.5854×10^{-8} 4.6999×10^{-2}	3.6891×10^{-4} 2.8979×10^{-5}
	5.0	6.5390×10^5 4.3211×10^9	3.6185×10^{-10} 4.5593×10^{-6}	6.5951×10^{-8} 1.1408	3.6891×10^{-4} 7.0341×10^{-4}

Table 1-6 (continued)

pH:	ΔV_2° :	f_r :	$\mu_{\max}$:	α' :	$(\text{Amp1.} \times 10^{17})/2$:
11.0	0.04	7.3242×10^5	3.6185×10^{-11}	1.5447×10^{-9}	3.2937×10^{-5}
		4.3212×10^9	6.9743×10^{-10}	1.7452×10^{-4}	1.0760×10^{-7}
	1.0	7.3242×10^5	3.6185×10^{-11}	4.5594×10^{-9}	3.2937×10^{-5}
		4.3212×10^9	2.1038×10^{-7}	5.2643×10^{-2}	3.2457×10^{-5}
	5.0	7.3242×10^5	3.6185×10^{-11}	7.4953×10^{-8}	3.2937×10^{-5}
		4.3212×10^9	5.1066×10^{-6}	1.2778	7.8784×10^{-4}
12.0	0.04	7.4132×10^5	3.6185×10^{-12}	1.6573×10^{-10}	3.2541×10^{-6}
		4.3212×10^9	7.0591×10^{-10}	1.7664×10^{-4}	1.0891×10^{-7}
	1.0	7.4132×10^5	3.6185×10^{-12}	3.2917×10^{-9}	3.2541×10^{-6}
		4.3212×10^9	2.1294×10^{-7}	5.3283×10^{-2}	3.2852×10^{-5}
	5.0	7.4132×10^5	3.6185×10^{-12}	7.6282×10^{-8}	3.2541×10^{-6}
		4.3212×10^9	5.1686×10^{-6}	1.2933	7.9741×10^{-4}

Table 1-7: The Effect of pH Values on the f_r , $\mu_{\max}$, α' , and Amp1.
 Values of Boric Acid & Sodium Borate System(I) at
 $C_{\text{B(OH)}_3} = 4.4 \times 10^{-4} \text{ M}$ and $C_{\text{Na}} = 0.8 \text{ M}$

pH:	f_r :	$\mu_{\max}$:	α' :	$(\text{Amp1.} \times 10^{17})/2$:
	(Hz)	(nepers)	(dB/cm)	$(\text{sec}^2/\text{cm})(\text{nepers})$
3.0	2.1486×10^6	9.2459×10^{-10}	1.1504×10^{-7}	2.8688×10^{-4}
	3.3925×10^9	7.6238×10^{-16}	2.3022×10^{-7}	1.4982×10^{-13}
4.0	2.1487×10^5	9.2455×10^{-9}	1.1504×10^{-7}	2.8686×10^{-2}
	3.3926×10^9	7.6237×10^{-15}	2.3157×10^{-7}	1.4981×10^{-12}
5.0	2.1542×10^4	9.2210×10^{-8}	1.1503×10^{-7}	2.8536
	3.3965×10^9	7.6231×10^{-14}	2.4504×10^{-7}	1.4963×10^{-11}
6.0	2.6984×10^3	7.3558×10^{-7}	1.1494×10^{-7}	1.8174×10^2
	3.7077×10^9	7.6173×10^{-13}	3.9342×10^{-7}	1.3696×10^{-10}

Table 1-7 (continued)

pH:	f_r :	$\mu_{\max}$:	α' :	$(\text{Ampl.} \times 10^{17})/2$:
7.0	5.6601×10^3	3.4803×10^{-7}	1.1407×10^{-7}	4.0993×10
	4.8808×10^9	7.5598×10^{-12}	2.3648×10^{-6}	1.0326×10^{-9}
8.0	5.0643×10^4	3.6169×10^{-8}	1.0607×10^{-7}	4.7613×10^{-1}
	4.9389×10^9	7.0293×10^{-11}	2.0316×10^{-5}	9.4884×10^{-9}
9.0	2.9748×10^5	3.6185×10^{-9}	6.2333×10^{-8}	8.1091×10^{-3}
	4.9396×10^9	4.1305×10^{-10}	1.1827×10^{-4}	5.5747×10^{-8}
10.0	5.8065×10^5	3.6185×10^{-10}	1.2173×10^{-8}	4.1545×10^{-4}
	4.9398×10^9	8.0616×10^{-10}	2.3062×10^{-4}	1.0880×10^{-7}
11.0	6.4174×10^5	3.6185×10^{-11}	1.3533×10^{-9}	3.7590×10^{-5}
	4.9398×10^9	8.9096×10^{-10}	2.5486×10^{-4}	1.2024×10^{-7}
12.0	6.4857×10^5	3.6185×10^{-12}	1.4478×10^{-10}	3.7195×10^{-6}
	4.9398×10^9	9.0043×10^{-10}	2.5757×10^{-4}	1.2152×10^{-7}

Table 1-8: The Effect of pH Values on the f_r , $\mu_{\max}$, α' , and Ampl.
 Values of Boric Acid & Sodium Borate System(I) at
 $C_{B(OH)_3} = 4.4 \times 10^{-4}$ M and $C_{Na} = 1.0$ M

pH:	f_r :	$\mu_{\max}$:	α' :	$(\text{Ampl.} \times 10^{17})/2$:
	(Hz)	(nepers)	(dB/cm)	(sec ² /cm)(nepers)
3.0	2.1486×10^6	9.2459×10^{-10}	1.1504×10^{-7}	2.8688×10^{-4}
	3.3925×10^9	8.8377×10^{-16}	2.3025×10^{-7}	1.7367×10^{-13}
4.0	2.1487×10^5	9.2455×10^{-9}	1.1504×10^{-7}	2.8686×10^{-2}
	3.3926×10^9	8.8377×10^{-15}	2.3181×10^{-7}	1.7367×10^{-12}
5.0	2.1542×10^4	9.2209×10^{-8}	1.1502×10^{-7}	2.8536
	3.3975×10^9	8.8369×10^{-14}	2.4743×10^{-7}	1.7340×10^{-11}
6.0	2.6983×10^3	7.3554×10^{-7}	1.1493×10^{-7}	1.8173×10^2
	3.7865×10^9	8.8297×10^{-13}	4.2346×10^{-7}	1.5546×10^{-10}

Table 1-8 (continued)

pH:	f_r :	$\mu_{\max}$:	α' :	$(\text{Amp1.} \times 10^{17})/2$:
7.0	5.6565×10^3	3.4803×10^{-7}	1.1400×10^{-7}	4.1018×10
	5.2528×10^9	8.7579×10^{-12}	2.8919×10^{-6}	1.1115×10^{-9}
8.0	5.0336×10^4	3.6169×10^{-8}	1.0543×10^{-7}	4.7903×10^{-1}
	5.3254×10^9	8.0992×10^{-11}	2.5187×10^{-5}	1.0139×10^{-8}
9.0	2.8718×10^5	3.6185×10^{-9}	6.0175×10^{-8}	8.3999×10^{-3}
	5.3263×10^9	4.6225×10^{-10}	1.4269×10^{-4}	5.7857×10^{-8}
10.0	5.4266×10^5	3.6185×10^{-10}	1.1376×10^{-8}	4.4454×10^{-4}
	5.3264×10^9	8.7341×10^{-10}	2.6941×10^{-4}	1.0932×10^{-7}
11.0	5.9565×10^5	3.6185×10^{-11}	1.2555×10^{-9}	4.0499×10^{-5}
	5.3265×10^9	9.5868×10^{-10}	2.9569×10^{-4}	1.1999×10^{-7}
12.0	6.0153×10^5	3.6185×10^{-12}	1.3366×10^{-10}	4.0103×10^{-6}
	5.3265×10^9	9.6814×10^{-10}	2.9861×10^{-4}	1.2117×10^{-7}

Table 1-9: At $C_{B(OH)_3} = 4.4 \times 10^{-3}$ M and $C_{Na} = 0.1$ M

pH:	f_r :	$\mu_{\max}$:	α' :	$(\text{Amp1.} \times 10^{17})/2$:
3.0	2.1486×10^6	9.2458×10^{-9}	1.1503×10^{-6}	2.8688×10^{-3}
	3.3925×10^9	1.3127×10^{-15}	2.3009×10^{-6}	2.5796×10^{-13}
4.0	2.1491×10^5	9.2434×10^{-8}	1.1503×10^{-6}	2.8673×10^{-1}
	3.3926×10^9	1.3127×10^{-14}	2.3032×10^{-6}	2.5796×10^{-12}
5.0	2.2036×10^4	9.0145×10^{-7}	1.1503×10^{-6}	2.7272×10
	3.3973×10^9	1.3126×10^{-13}	2.3264×10^{-6}	2.5758×10^{-11}
6.0	7.6365×10^3	2.5998×10^{-6}	1.1496×10^{-6}	2.2696×10^2
	3.5315×10^9	1.3119×10^{-12}	2.5676×10^{-6}	2.4766×10^{-10}
7.0	5.4781×10^4	3.6042×10^{-7}	1.1433×10^{-6}	4.3862
	3.5852×10^9	1.3047×10^{-11}	4.9953×10^{-6}	2.4260×10^{-9}
8.0	5.1727×10^5	3.6183×10^{-8}	1.0838×10^{-6}	4.6633×10^{-2}
	3.5863×10^9	1.2365×10^{-10}	2.7846×10^{-5}	2.2985×10^{-8}

Table 1-9 (continued)

pH:	f_r :	$\mu_{\max}$:	α' :	$(\text{Amp1.} \times 10^{17})/2$:
9.0	3.4019×10^6	3.6185×10^{-9}	7.1312×10^{-7}	7.0911×10^{-4}
	3.5888×10^9	8.1204×10^{-10}	1.7018×10^{-4}	1.5085×10^{-7}
10.0	7.6917×10^6	3.6185×10^{-10}	1.6466×10^{-7}	3.1363×10^{-5}
	3.5924×10^9	1.8321×10^{-9}	3.8144×10^{-4}	3.3999×10^{-7}
11.0	8.8017×10^6	3.6185×10^{-11}	2.3674×10^{-8}	2.7408×10^{-6}
	3.5933×10^9	2.0953×10^{-9}	4.3602×10^{-4}	3.8873×10^{-7}
12.0	8.9306×10^6	3.6185×10^{-12}	7.3354×10^{-9}	2.7012×10^{-7}
	3.5935×10^9	2.1258×10^{-9}	4.4236×10^{-4}	3.9439×10^{-7}

Table 1-10: At $C_{B(OH)_3} = 4.4 \times 10^{-3}$ M and $C_{Na} = 0.48$ M

pH:	f_r :	$\mu_{\max}$:	α' :	$(\text{Amp1.} \times 10^{17})/2$:
3.0	2.1486×10^6	9.2458×10^{-9}	1.1503×10^{-6}	2.8688×10^{-3}
	3.3925×10^9	5.2294×10^{-15}	2.3017×10^{-6}	1.0276×10^{-12}
4.0	2.1491×10^5	9.2434×10^{-8}	1.1503×10^{-6}	2.8673×10^{-1}
	3.3927×10^9	5.2293×10^{-14}	2.3109×10^{-6}	1.0276×10^{-11}
5.0	2.2036×10^4	9.0143×10^{-7}	1.1503×10^{-6}	2.7271×10
	3.4157×10^9	5.2290×10^{-13}	2.4039×10^{-6}	1.0206×10^{-10}
6.0	7.6358×10^3	2.5997×10^{-6}	1.1495×10^{-6}	2.2698×10^2
	4.0595×10^9	5.2255×10^{-12}	3.5274×10^{-6}	8.5815×10^{-10}
7.0	5.4713×10^4	3.6042×10^{-7}	1.1419×10^{-6}	4.3916
	4.3171×10^9	5.1909×10^{-11}	1.5260×10^{-5}	8.0160×10^{-9}
8.0	5.1122×10^5	3.6183×10^{-8}	1.0711×10^{-6}	4.7186×10^{-2}
	4.3210×10^9	4.8682×10^{-10}	1.2395×10^{-4}	7.5110×10^{-8}
9.0	3.1561×10^6	3.6185×10^{-9}	6.6212×10^{-7}	7.6433×10^{-4}
	4.3228×10^9	3.0024×10^{-9}	7.5288×10^{-4}	4.6303×10^{-7}
10.0	6.5409×10^6	3.6185×10^{-10}	1.4417×10^{-7}	3.6881×10^{-5}
	4.3250×10^9	6.2135×10^{-9}	1.5564×10^{-3}	9.5777×10^{-7}

Table 1-10 (continued)

pH:	f_r :	$\mu_{\max}$:	α' :	$(\text{Amp1.} \times 10^{17})/2$:
11.0	7.3269×10^6	3.6185×10^{-11}	2.5353×10^{-8}	3.2924×10^{-6}
	4.3255×10^9	6.9578×10^{-9}	1.7428×10^{-3}	1.0724×10^{-6}
12.0	7.4160×10^6	3.6185×10^{-12}	1.1924×10^{-8}	3.2529×10^{-7}
	4.3255×10^9	7.0421×10^{-9}	1.7639×10^{-3}	1.0854×10^{-6}

Table 1-11: At $C_{B(OH)_3} = 4.4 \times 10^{-3}$ M and $C_{Na} = 0.8$ M

pH:	f_r :	$\mu_{\max}$:	α' :	$(\text{Amp1.} \times 10^{17})/2$:
3.0	2.1486×10^6	9.2458×10^{-9}	1.1503×10^{-6}	2.8688×10^{-3}
	3.3925×10^9	7.6238×10^{-15}	2.3022×10^{-6}	1.4982×10^{-12}
4.0	2.1491×10^5	9.2434×10^{-8}	1.1503×10^{-6}	2.8673×10^{-1}
	3.3929×10^9	7.6237×10^{-14}	2.3156×10^{-6}	1.4980×10^{-11}
5.0	2.2036×10^4	9.0143×10^{-7}	1.1503×10^{-6}	2.7271×10
	3.4311×10^9	7.6231×10^{-13}	2.4520×10^{-6}	1.4812×10^{-10}
6.0	7.6352×10^3	2.5996×10^{-6}	1.1494×10^{-6}	2.2699×10^2
	4.5042×10^9	7.6173×10^{-12}	4.2855×10^{-6}	1.1274×10^{-9}
7.0	5.4656×10^4	3.6042×10^{-7}	1.1407×10^{-6}	4.3962
	4.9334×10^9	7.5597×10^{-11}	2.3878×10^{-5}	1.0216×10^{-8}
8.0	5.0622×10^5	3.6183×10^{-8}	1.0607×10^{-6}	4.7651×10^{-2}
	4.9397×10^9	7.0281×10^{-10}	2.0315×10^{-4}	9.4853×10^{-8}
9.0	2.9751×10^6	3.6185×10^{-9}	6.2424×10^{-7}	8.1084×10^{-4}
	4.9409×10^9	4.1269×10^{-9}	1.1820×10^{-3}	5.5684×10^{-7}
10.0	5.8088×10^6	3.6185×10^{-10}	1.2808×10^{-7}	4.1529×10^{-5}
	4.9423×10^9	8.0494×10^{-9}	2.3039×10^{-3}	1.0858×10^{-6}
11.0	6.4205×10^6	3.6185×10^{-11}	2.2045×10^{-8}	3.7573×10^{-6}
	4.9426×10^9	8.8951×10^{-9}	2.5459×10^{-3}	1.1998×10^{-6}
12.0	6.4888×10^6	3.6185×10^{-12}	1.0228×10^{-8}	3.7177×10^{-7}
	4.9427×10^9	8.9895×10^{-9}	2.5729×10^{-3}	1.2125×10^{-6}

Table 1-12: The Effect of pH Values on the f_r , $\mu_{\max}$, α' , and Ampl.

Values of Boric Acid & Sodium Borate System(I) at

$C_{B(OH)_3} = 4.4 \times 10^{-3}$ M and $C_{Na} = 1.0$ M

pH:	f_r :	$\mu_{\max}$:	α' :	(Ampl. $\times 10^{17}$)/2:
3.0	2.1486×10^6	9.2458×10^{-9}	1.1503×10^{-6}	2.8688×10^{-3}
	3.3925×10^9	8.8377×10^{-15}	2.3024×10^{-6}	1.7367×10^{-12}
4.0	2.1491×10^5	9.2434×10^{-8}	1.1503×10^{-6}	2.8673×10^{-1}
	3.3930×10^9	8.8377×10^{-14}	2.3180×10^{-6}	1.7364×10^{-11}
5.0	2.2036×10^4	9.0142×10^{-7}	1.1502×10^{-6}	2.7271×10
	3.4408×10^9	8.8369×10^{-13}	2.4766×10^{-6}	1.7122×10^{-10}
6.0	7.6348×10^3	2.5996×10^{-6}	1.1493×10^{-6}	2.2699×10^2
	4.7820×10^9	8.8297×10^{-12}	4.7436×10^{-6}	1.2309×10^{-9}
7.0	5.4620×10^4	3.6042×10^{-7}	1.1400×10^{-6}	4.3991
	5.3186×10^9	8.7577×10^{-11}	2.9252×10^{-5}	1.0977×10^{-8}
8.0	5.0315×10^5	3.6183×10^{-8}	1.0542×10^{-6}	4.7942×10^{-2}
	5.3263×10^9	8.0980×10^{-10}	2.5187×10^{-4}	1.0136×10^{-7}
9.0	2.8721×10^6	3.6185×10^{-9}	6.0263×10^{-7}	8.3991×10^{-4}
	5.3273×10^9	4.6190×10^{-9}	1.4261×10^{-3}	5.7803×10^{-7}
10.0	5.4289×10^6	3.6185×10^{-10}	1.1934×10^{-7}	4.4435×10^{-5}
	5.3283×10^9	8.7234×10^{-9}	2.6918×10^{-3}	1.0914×10^{-6}
11.0	5.9596×10^6	3.6185×10^{-11}	1.9878×10^{-8}	4.0478×10^{-6}
	5.3285×10^9	9.5744×10^{-9}	2.9543×10^{-3}	1.1979×10^{-6}
12.0	6.0184×10^6	3.6185×10^{-12}	8.8727×10^{-9}	4.0083×10^{-7}
	5.3286×10^9	9.6687×10^{-9}	2.9834×10^{-3}	1.2097×10^{-6}

Table 1-13: The Effect of pH Values on the f_r , $\mu_{\max}$, α' , and Ampl.

Values of Boric Acid & Sodium Borate System(I) at

$C_{B(OH)_3} = 0.01 \text{ M}$ and $C_{Na} = 0.1 \text{ M}$

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	α' : (dB/cm)	(Ampl. $\times 10^{17}$)/2: (sec ² /cm)(nepers)
3.0	2.1486 $\times 10^6$ 3.3925 $\times 10^9$	2.1013 $\times 10^{-8}$ 2.9834 $\times 10^{-15}$	2.6144 $\times 10^{-6}$ 5.2294 $\times 10^{-6}$	6.5200 $\times 10^{-3}$ 5.8628 $\times 10^{-13}$
4.0	2.1498 $\times 10^5$ 3.3926 $\times 10^9$	2.1001 $\times 10^{-7}$ 2.9834 $\times 10^{-14}$	2.6144 $\times 10^{-6}$ 5.2346 $\times 10^{-6}$	6.5124 $\times 10^{-1}$ 5.8625 $\times 10^{-12}$
5.0	2.2735 $\times 10^4$ 3.4031 $\times 10^9$	1.9858 $\times 10^{-6}$ 2.9832 $\times 10^{-13}$	2.6143 $\times 10^{-6}$ 5.2874 $\times 10^{-6}$	5.8230 $\times 10$ 5.8441 $\times 10^{-11}$
6.0	1.4619 $\times 10^4$ 3.5575 $\times 10^9$	3.0864 $\times 10^{-6}$ 2.9816 $\times 10^{-12}$	2.6128 $\times 10^{-6}$ 5.8397 $\times 10^{-6}$	1.4074 $\times 10^2$ 5.5874 $\times 10^{-10}$
7.0	1.2423 $\times 10^5$ 3.5856 $\times 10^9$	3.6122 $\times 10^{-7}$ 2.9650 $\times 10^{-11}$	2.5985 $\times 10^{-6}$ 1.1353 $\times 10^{-5}$	1.9385 5.5128 $\times 10^{-9}$
8.0	1.1756 $\times 10^6$ 3.5869 $\times 10^9$	3.6184 $\times 10^{-8}$ 2.8092 $\times 10^{-10}$	2.4632 $\times 10^{-6}$ 6.3275 $\times 10^{-5}$	2.0520 $\times 10^{-2}$ 5.2213 $\times 10^{-8}$
9.0	7.7318 $\times 10^6$ 3.5924 $\times 10^9$	3.6185 $\times 10^{-9}$ 1.8416 $\times 10^{-9}$	1.6236 $\times 10^{-6}$ 3.8634 $\times 10^{-4}$	3.1200 $\times 10^{-4}$ 3.4175 $\times 10^{-7}$
10.0	1.7483 $\times 10^7$ 3.6007 $\times 10^9$	3.6185 $\times 10^{-10}$ 4.1439 $\times 10^{-9}$	4.0707 $\times 10^{-7}$ 8.6475 $\times 10^{-4}$	1.3798 $\times 10^{-5}$ 7.6724 $\times 10^{-7}$
11.0	2.0007 $\times 10^7$ 3.6029 $\times 10^9$	3.6185 $\times 10^{-11}$ 4.7361 $\times 10^{-9}$	1.0286 $\times 10^{-7}$ 9.8819 $\times 10^{-4}$	1.2057 $\times 10^{-6}$ 8.7637 $\times 10^{-7}$
12.0	2.0300 $\times 10^7$ 3.6031 $\times 10^9$	3.6185 $\times 10^{-12}$ 4.8048 $\times 10^{-9}$	6.7894 $\times 10^{-8}$ 1.0025 $\times 10^{-3}$	1.1883 $\times 10^{-7}$ 8.8901 $\times 10^{-7}$

Table 1-14: The Effect of pH Values on the f_r , $\mu_{\max}$, α' , and Ampl.

Values of Boric Acid & Sodium Borate System(I) at

$C_{B(OH)_3} = 0.01 \text{ M}$ and $C_{Na} = 0.48 \text{ M}$

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	α' : (dB/cm)	$(\text{Ampl.} \times 10^{17})/2$: (sec^2/cm) (nepers)
3.0	2.1486×10^6	2.1013×10^{-8}	2.6144×10^{-6}	6.5200×10^{-3}
	3.3925×10^9	1.1885×10^{-14}	5.2311×10^{-6}	2.3355×10^{-12}
4.0	2.1498×10^5	2.1001×10^{-7}	2.6144×10^{-6}	6.5124×10^{-1}
	3.3930×10^9	1.1885×10^{-13}	5.2521×10^{-6}	2.3351×10^{-11}
5.0	2.2735×10^4	1.9858×10^{-6}	2.6143×10^{-6}	5.8230×10
	3.4435×10^9	1.1884×10^{-12}	5.4656×10^{-6}	2.3008×10^{-10}
6.0	1.4618×10^4	3.0863×10^{-6}	2.6125×10^{-6}	1.4076×10^2
	4.1843×10^9	1.1876×10^{-11}	8.1025×10^{-6}	1.8922×10^{-9}
7.0	1.2407×10^5	3.6122×10^{-7}	2.5952×10^{-6}	1.9409
	4.3192×10^9	1.1797×10^{-10}	3.4696×10^{-5}	1.8209×10^{-8}
8.0	1.1618×10^6	3.6184×10^{-8}	2.4344×10^{-6}	2.0763×10^{-2}
	4.3214×10^9	1.1061×10^{-9}	2.8166×10^{-4}	1.7064×10^{-7}
9.0	7.1737×10^6	3.6185×10^{-9}	1.5125×10^{-6}	3.3627×10^{-4}
	4.3254×10^9	6.8128×10^{-9}	1.7094×10^{-3}	1.0500×10^{-6}
10.0	1.4872×10^7	3.6185×10^{-10}	3.9490×10^{-7}	1.6221×10^{-5}
	4.3304×10^9	1.4079×10^{-8}	3.5311×10^{-3}	2.1674×10^{-6}
11.0	1.6661×10^7	3.6185×10^{-11}	1.5188×10^{-7}	1.4479×10^{-6}
	4.3316×10^9	1.5760×10^{-8}	3.9531×10^{-3}	2.4256×10^{-6}
12.0	1.6864×10^7	3.6185×10^{-12}	1.2482×10^{-7}	1.4305×10^{-7}
	4.3317×10^9	1.5951×10^{-8}	4.0011×10^{-3}	2.4548×10^{-6}

Table 1-15: The Effect of pH Values on the f_r , $\mu_{\max}$, α' , and Ampl.

Values of Boric Acid & Sodium Borate System(I) at

$C_{B(OH)_3} = 0.01 \text{ M}$ and $C_{Na} = 0.8 \text{ M}$

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	α' : (dB/cm)	(Ampl. $\times 10^{17}$)/2: (sec ² /cm) (nepers)
3.0	2.1486 $\times 10^6$ 3.3925 $\times 10^9$	2.1013 $\times 10^{-8}$ 1.7327 $\times 10^{-14}$	2.6144 $\times 10^{-6}$ 5.2322 $\times 10^{-6}$	6.5200 $\times 10^{-3}$ 3.4049 $\times 10^{-12}$
4.0	2.1498 $\times 10^5$ 3.3934 $\times 10^9$	2.1001 $\times 10^{-7}$ 1.7327 $\times 10^{-13}$	2.6144 $\times 10^{-6}$ 5.2628 $\times 10^{-6}$	6.5124 $\times 10^{-1}$ 3.4040 $\times 10^{-11}$
5.0	2.2735 $\times 10^4$ 3.4775 $\times 10^9$	1.9857 $\times 10^{-6}$ 1.7325 $\times 10^{-12}$	2.6142 $\times 10^{-6}$ 5.5773 $\times 10^{-6}$	5.8229 $\times 10$ 3.3214 $\times 10^{-10}$
6.0	1.4617 $\times 10^4$ 4.7121 $\times 10^9$	3.0863 $\times 10^{-6}$ 1.7312 $\times 10^{-11}$	2.6123 $\times 10^{-6}$ 9.9484 $\times 10^{-6}$	1.4077 $\times 10^2$ 2.4493 $\times 10^{-9}$
7.0	1.2394 $\times 10^5$ 4.9369 $\times 10^9$	3.6122 $\times 10^{-7}$ 1.7181 $\times 10^{-10}$	2.5925 $\times 10^{-6}$ 5.4302 $\times 10^{-5}$	1.9429 2.3201 $\times 10^{-8}$
8.0	1.1505 $\times 10^6$ 4.9400 $\times 10^9$	3.6184 $\times 10^{-8}$ 1.5969 $\times 10^{-9}$	2.4107 $\times 10^{-6}$ 4.6163 $\times 10^{-4}$	2.0968 $\times 10^{-2}$ 2.1551 $\times 10^{-7}$
9.0	6.7626 $\times 10^6$ 4.9428 $\times 10^9$	3.6185 $\times 10^{-9}$ 9.3678 $\times 10^{-9}$	1.4270 $\times 10^{-6}$ 2.6841 $\times 10^{-3}$	3.5672 $\times 10^{-4}$ 1.2635 $\times 10^{-6}$
10.0	1.3209 $\times 10^7$ 4.9460 $\times 10^9$	3.6185 $\times 10^{-10}$ 1.8255 $\times 10^{-8}$	3.5136 $\times 10^{-7}$ 5.2289 $\times 10^{-3}$	1.8263 $\times 10^{-5}$ 2.4606 $\times 10^{-6}$
11.0	1.4602 $\times 10^7$ 4.9467 $\times 10^9$	3.6185 $\times 10^{-11}$ 2.0169 $\times 10^{-8}$	1.3128 $\times 10^{-7}$ 5.7774 $\times 10^{-3}$	1.6521 $\times 10^{-6}$ 2.7183 $\times 10^{-6}$
12.0	1.4757 $\times 10^7$ 4.9467 $\times 10^9$	3.6185 $\times 10^{-12}$ 2.0383 $\times 10^{-8}$	1.0701 $\times 10^{-7}$ 5.8387 $\times 10^{-3}$	1.6347 $\times 10^{-7}$ 2.7470 $\times 10^{-6}$

Table 1-16: The Effect of pH Values on the f_r , $\mu_{\max}$, α' , and Amp1.

Values of Boric Acid & Sodium Borate System(I) at

$C_{B(OH)_3} = 0.01 \text{ M}$ and $C_{Na} = 1.0 \text{ M}$

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	α' : (dB/cm)	$(\text{Amp1.} \times 10^{17})/2$: (sec^2/cm) (nepers)
3.0	2.1486×10^6 3.3925×10^9	2.1013×10^{-8} 2.0086×10^{-14}	2.6144×10^{-6} 5.2327×10^{-6}	6.5200×10^{-3} 3.9471×10^{-12}
4.0	2.1498×10^5 3.3936×10^9	2.1001×10^{-7} 2.0086×10^{-13}	2.6144×10^{-6} 5.2682×10^{-6}	6.5123×10^{-1} 3.9457×10^{-11}
5.0	2.2735×10^4 3.4987×10^9	1.9857×10^{-6} 2.0084×10^{-12}	2.6142×10^{-6} 5.6353×10^{-6}	5.8229×10 3.8269×10^{-10}
6.0	1.4616×10^4 5.0420×10^9	3.0863×10^{-6} 2.0067×10^{-11}	2.6121×10^{-6} 1.1083×10^{-5}	1.4077×10^2 2.6534×10^{-9}
7.0	1.2386×10^5 5.3229×10^9	3.6122×10^{-7} 1.9904×10^{-10}	2.5908×10^{-6} 6.6532×10^{-5}	1.9442 2.4928×10^{-8}
8.0	1.1435×10^6 5.3266×10^9	3.6184×10^{-8} 1.8401×10^{-9}	2.3960×10^{-6} 5.7236×10^{-4}	2.1095×10^{-2} 2.3030×10^{-7}
9.0	6.5286×10^6 5.3288×10^9	3.6185×10^{-9} 1.0487×10^{-8}	1.3777×10^{-6} 3.2387×10^{-3}	3.6950×10^{-4} 1.3119×10^{-6}
10.0	1.2346×10^7 5.3310×10^9	3.6185×10^{-10} 1.9791×10^{-8}	3.2423×10^{-7} 6.1100×10^{-3}	1.9540×10^{-5} 2.4750×10^{-6}
11.0	1.3554×10^7 5.3315×10^9	3.6185×10^{-11} 2.1720×10^{-8}	1.1508×10^{-7} 6.7057×10^{-3}	1.7798×10^{-6} 2.7159×10^{-6}
12.0	1.3688×10^7 5.3316×10^9	3.6185×10^{-12} 2.1934×10^{-8}	9.2136×10^{-8} 6.7718×10^{-3}	1.7623×10^{-7} 2.7426×10^{-6}

Table 1-17: The Effect of pH Values on the f_r , $\mu_{\max}$, α' , and Ampl.

Values of Boric Acid & Sodium Borate System(I) at

$C_{B(OH)_3} = 0.025 \text{ M}$ and $C_{Na} = 0.1 \text{ M}$

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	α' : (dB/cm)	$(\text{Ampl.} \times 10^{17})/2$: (sec^2/cm) (nepers)
3.0	2.1486×10^6	5.2533×10^{-8}	6.5361×10^{-6}	1.6300×10^{-2}
	3.3925×10^9	7.4585×10^{-15}	1.3074×10^{-5}	1.4657×10^{-12}
4.0	2.1517×10^5	5.2457×10^{-7}	6.5360×10^{-6}	1.6253
	3.3928×10^9	7.4585×10^{-14}	1.3087×10^{-5}	1.4656×10^{-11}
5.0	2.4606×10^4	4.5869×10^{-6}	6.5357×10^{-6}	1.2427×10^2
	3.4170×10^9	7.4581×10^{-13}	1.3219×10^{-5}	1.4551×10^{-10}
6.0	3.3324×10^4	3.3851×10^{-6}	6.5322×10^{-6}	6.7720x10
	3.5734×10^9	7.4538×10^{-12}	1.4607×10^{-5}	1.3906×10^{-9}
7.0	3.1024×10^5	3.6160×10^{-7}	6.4961×10^{-6}	7.7702×10^{-1}
	3.5860×10^9	7.4119×10^{-11}	2.8383×10^{-5}	1.3779×10^{-8}
8.0	2.9390×10^6	3.6185×10^{-8}	6.1584×10^{-6}	8.2081×10^{-3}
	3.5884×10^9	7.0169×10^{-10}	1.5812×10^{-4}	1.3036×10^{-7}
9.0	1.9331×10^7	3.6185×10^{-9}	4.1055×10^{-6}	1.2479×10^{-4}
	3.6023×10^9	4.5776×10^{-9}	9.6298×10^{-4}	8.4717×10^{-7}
10.0	4.3722×10^7	3.6185×10^{-10}	1.5411×10^{-6}	5.5174×10^{-6}
	3.6230×10^9	1.0229×10^{-8}	2.1478×10^{-3}	1.8821×10^{-6}
11.0	5.0038×10^7	3.6185×10^{-11}	1.0372×10^{-6}	4.8210×10^{-7}
	3.6284×10^9	1.1669×10^{-8}	2.4520×10^{-3}	2.1441×10^{-6}
12.0	5.0772×10^7	3.6185×10^{-12}	9.8415×10^{-7}	4.7513×10^{-8}
	3.6290×10^9	1.1836×10^{-8}	2.4873×10^{-3}	2.1744×10^{-6}

Table 1-18: The Effect of pH Values on the f_r , $\mu_{\max}$, α' , and Ampl.

Values of Boric Acid & Sodium Borate System(I) at

$C_{B(OH)_3} = 0.025 \text{ M}$ and $C_{Na} = 0.48 \text{ M}$

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	α' : (dB/cm)	$(\text{Ampl.} \times 10^{17})/2$: (sec^2/cm) (nepers)
3.0	2.1486×10^6	5.2533×10^{-8}	6.5361×10^{-6}	1.6300×10^{-2}
	3.3925×10^9	2.9712×10^{-14}	1.3078×10^{-5}	5.8388×10^{-12}
4.0	2.1517×10^5	5.2456×10^{-7}	6.5359×10^{-6}	1.6253
	3.3939×10^9	2.9712×10^{-13}	1.3130×10^{-5}	5.8365×10^{-11}
5.0	2.4606×10^4	4.5868×10^{-6}	6.5355×10^{-6}	1.2427×10^2
	3.5102×10^9	2.9710×10^{-12}	1.3675×10^{-5}	5.6426×10^{-10}
6.0	3.3320×10^4	3.3850×10^{-6}	6.5312×10^{-6}	6.7728x10
	4.2609×10^9	2.9690×10^{-11}	2.0388×10^{-5}	4.6454×10^{-9}
7.0	3.0986×10^5	3.6160×10^{-7}	6.4882×10^{-6}	7.7799×10^{-1}
	4.3203×10^9	2.9490×10^{-10}	8.6753×10^{-5}	4.5507×10^{-8}
8.0	2.9046×10^6	3.6185×10^{-8}	6.0868×10^{-6}	8.3053×10^{-3}
	4.3226×10^9	2.7633×10^{-9}	7.0385×10^{-4}	4.2618×10^{-7}
9.0	1.7939×10^7	3.6185×10^{-9}	3.9047×10^{-6}	1.3447×10^{-4}
	4.3324×10^9	1.6960×10^{-8}	4.2624×10^{-3}	2.6098×10^{-6}
10.0	3.7221×10^7	3.6185×10^{-10}	2.0689×10^{-6}	6.4810×10^{-6}
	4.3451×10^9	3.4910×10^{-8}	8.7853×10^{-3}	5.3562×10^{-6}
11.0	4.1710×10^7	3.6185×10^{-11}	1.8966×10^{-6}	5.7836×10^{-7}
	4.3481×10^9	3.9047×10^{-8}	9.8316×10^{-3}	5.9869×10^{-6}
12.0	4.2219×10^7	3.6185×10^{-12}	1.8846×10^{-6}	5.7139×10^{-8}
	4.3484×10^9	3.9516×10^{-8}	9.9502×10^{-3}	6.0583×10^{-6}

Table 1-19: The Effect of pH Values on the f_r , $\mu_{\max}$, α' , and Ampl.

Values of Boric Acid & Sodium Borate System(I) at

$C_{B(OH)_3} = 0.025 \text{ M}$ and $C_{Na} = 0.8 \text{ M}$

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	α' : (dB/cm)	$(\text{Ampl.} \times 10^{17})/2$: (sec^2/cm) (nepers)
3.0	2.1486×10^6 3.3925×10^9	5.2533×10^{-8} 4.3317×10^{-14}	6.5361×10^{-6} 1.3081×10^{-5}	1.6300×10^{-2} 8.5122×10^{-12}
4.0	2.1517×10^5 3.3948×10^9	5.2456×10^{-7} 4.3317×10^{-13}	6.5359×10^{-6} 1.3157×10^{-5}	1.6253 8.5066×10^{-11}
5.0	2.4606×10^4 3.5887×10^9	4.5868×10^{-6} 4.3313×10^{-12}	6.5355×10^{-6} 1.3971×10^{-5}	1.2427×10^2 8.0463×10^{-10}
6.0	3.3317×10^4 4.8397×10^9	3.3850×10^{-6} 4.3280×10^{-11}	6.5306×10^{-6} 2.5190×10^{-5}	6.7734×10 5.9617×10^{-9}
7.0	3.0953×10^5 4.9386×10^9	3.6160×10^{-7} 4.2949×10^{-10}	6.4813×10^{-6} 1.3579×10^{-4}	7.7880×10^{-1} 5.7978×10^{-8}
8.0	2.8762×10^6 4.9409×10^9	3.6185×10^{-8} 3.9899×10^{-9}	6.0274×10^{-6} 1.1536×10^{-3}	8.3871×10^{-3} 5.3835×10^{-7}
9.0	1.6913×10^7 4.9478×10^9	3.6185×10^{-9} 2.3342×10^{-8}	3.7002×10^{-6} 6.6948×10^{-3}	1.4263×10^{-4} 3.1451×10^{-6}
10.0	3.3071×10^7 4.9558×10^9	3.6185×10^{-10} 4.5375×10^{-8}	1.8526×10^{-6} 1.3023×10^{-2}	7.2945×10^{-6} 6.1040×10^{-6}
11.0	3.6569×10^7 4.9575×10^9	3.6185×10^{-11} 5.0112×10^{-8}	1.6421×10^{-6} 1.4386×10^{-2}	6.5966×10^{-7} 6.7388×10^{-6}
12.0	3.6961×10^7 4.9577×10^9	3.6185×10^{-12} 5.0641×10^{-8}	1.6238×10^{-6} 1.4538×10^{-2}	6.5268×10^{-8} 6.8096×10^{-6}

Table 1-20: The Effect of pH Values on the f_r , $\mu_{\max}$, α' , and Ampl.

Values of Boric Acid & Sodium Borate System(I) at

$C_{B(OH)_3} = 0.025 \text{ M}$ and $C_{Na} = 1.0 \text{ M}$

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	α' : (dB/cm)	$(\text{Ampl.} \times 10^{17})/2$: (sec^2/cm) (nepers)
3.0	2.1486×10^6	5.2533×10^{-8}	6.5361×10^{-6}	1.6300×10^{-2}
	3.3925×10^9	5.0214×10^{-14}	1.3082×10^{-5}	9.8676×10^{-12}
4.0	2.1517×10^5	5.2456×10^{-7}	6.5359×10^{-6}	1.6253
	3.3953×10^9	5.0214×10^{-13}	1.3171×10^{-5}	9.8595×10^{-11}
5.0	2.4606×10^4	4.5867×10^{-6}	6.5354×10^{-6}	1.2427×10^2
	3.6377×10^9	5.0210×10^{-12}	1.4128×10^{-5}	9.2017×10^{-10}
6.0	3.3315×10^4	3.3850×10^{-6}	6.5302×10^{-6}	6.7738x10
	5.2015×10^9	5.0168×10^{-11}	2.8171×10^{-5}	6.4299×10^{-9}
7.0	3.0933×10^5	3.6160×10^{-7}	6.4771×10^{-6}	7.7931×10^{-1}
	5.3250×10^9	4.9756×10^{-10}	1.6638×10^{-4}	6.2292×10^{-8}
8.0	2.8588×10^6	3.6185×10^{-8}	5.9910×10^{-6}	8.4383×10^{-3}
	5.3273×10^9	4.5975×10^{-9}	1.4302×10^{-3}	5.7534×10^{-7}
9.0	1.6329×10^7	3.6185×10^{-9}	3.5729×10^{-6}	1.4773×10^{-4}
	5.3326×10^9	2.6142×10^{-8}	8.0793×10^{-3}	3.2682×10^{-6}
10.0	3.0914×10^7	3.6185×10^{-10}	1.6688×10^{-6}	7.8034×10^{-6}
	5.3383×10^9	4.9248×10^{-8}	1.5225×10^{-2}	6.1503×10^{-6}
11.0	3.3951×10^7	3.6185×10^{-11}	1.4219×10^{-6}	7.1054×10^{-7}
	5.3395×10^9	5.4031×10^{-8}	1.6706×10^{-2}	6.7460×10^{-6}
12.0	3.4288×10^7	3.6185×10^{-12}	1.3984×10^{-6}	7.0355×10^{-8}
	5.3397×10^9	5.4561×10^{-8}	1.6871×10^{-2}	6.8120×10^{-6}

Table 1-21: The Effect of pH Values on the f_r , $\mu_{\max}$, α' , and Ampl.

Values of Boric Acid & Sodium Borate System(II) at

$C_{B(OH)_3} = 4.4 \times 10^{-4}$ M and $C_{Na} = 0.1$ M

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	α' : (dB/cm)	(Ampl. $\times 10^{17}$)/2: (sec ² /cm) (nepers)
3.0	2.1486×10^6 7.5389×10^2	9.2459×10^{-10} 1.3127×10^{-16}	1.1504×10^{-7} 2.8331×10^{-14}	2.8688×10^{-4} 1.1608×10^{-7}
4.0	2.1487×10^5 7.5389×10^2	9.2455×10^{-9} 1.3127×10^{-15}	1.1504×10^{-7} 2.8323×10^{-12}	2.8686×10^{-2} 1.1608×10^{-6}
5.0	2.1542×10^4 7.5400×10^2	9.2212×10^{-8} 1.3126×10^{-14}	1.1503×10^{-7} 2.8150×10^{-10}	2.8537 1.1606×10^{-5}
6.0	2.6985×10^3 7.6265×10^2	7.3572×10^{-7} 1.3119×10^{-13}	1.1496×10^{-7} 1.7007×10^{-8}	1.8176×10^2 1.1468×10^{-4}
7.0	5.6726×10^3 7.9524×10^2	3.4806×10^{-7} 1.3047×10^{-12}	1.1433×10^{-7} 4.4074×10^{-9}	4.0906x10 1.0938×10^{-3}
8.0	5.1748×10^4 7.9685×10^2	3.6169×10^{-8} 1.2368×10^{-11}	1.0838×10^{-7} 5.1958×10^{-11}	4.6597×10^{-1} 1.0347×10^{-2}
9.0	3.4019×10^5 7.9693×10^2	3.6185×10^{-9} 8.1328×10^{-11}	7.1289×10^{-8} 4.5354×10^{-12}	7.0910×10^{-3} 6.8034×10^{-2}
10.0	7.6911×10^5 7.9701×10^2	3.6185×10^{-10} 1.8383×10^{-10}	1.6133×10^{-8} 8.5188×10^{-12}	3.1365×10^{-4} 1.5377×10^{-1}
11.0	8.8007×10^5 7.9703×10^2	3.6185×10^{-11} 2.1034×10^{-10}	1.8635×10^{-9} 9.7109×10^{-12}	2.7411×10^{-5} 1.7594×10^{-1}
12.0	8.9296×10^5 7.9703×10^2	3.6185×10^{-12} 2.1342×10^{-10}	2.0681×10^{-10} 9.8503×10^{-12}	2.7015×10^{-6} 1.7851×10^{-1}

Table 1-22: The Effect of pH and ΔV_2° Values on the f_r , $\mu_{\max}$, α' , and
 Ampl. Values of Boric Acid & Sodium Borate System(II) at
 $C_{B(OH)_3} = 4.4 \times 10^{-4}$ M and $C_{Na} = 0.48$ M

pH:	ΔV_2° : (ml/mole) (Hz)	f_r : (Hz)	$\mu_{\max}$: (nepers)	α' : (dB/cm)	(Ampl. $\times 10^{17}$)/2: (sec ² /cm) (nepers)
3.0	0.04	2.1486×10^6	9.2459×10^{-10}	1.1504×10^{-7}	2.8688×10^{-4}
		7.5389×10^2	5.2294×10^{-16}	2.8348×10^{-14}	4.6243×10^{-7}
	1.0	2.1486×10^6	9.2459×10^{-10}	1.1504×10^{-7}	2.8688×10^{-4}
		7.5389×10^2	1.5774×10^{-13}	3.5211×10^{-14}	1.3949×10^{-4}
	5.0	2.1486×10^6	9.2459×10^{-10}	1.1504×10^{-7}	2.8688×10^{-4}
		7.5389×10^2	3.8289×10^{-12}	1.9548×10^{-13}	3.3859×10^{-3}
5.0	0.04	2.1542×10^4	9.2211×10^{-8}	1.1503×10^{-7}	2.8537
		7.5443×10^2	5.2290×10^{-14}	2.8182×10^{-10}	4.6207×10^{-5}
	1.0	2.1542×10^4	9.2211×10^{-8}	1.1503×10^{-7}	2.8537
		7.5443×10^2	1.5773×10^{-11}	2.8250×10^{-10}	1.3938×10^{-2}
	5.0	2.1542×10^4	9.2211×10^{-8}	1.1506×10^{-7}	2.8537
		7.5443×10^2	3.8286×10^{-10}	2.9854×10^{-10}	3.3833×10^{-1}
7.0	0.04	5.6658×10^3	3.4805×10^{-7}	1.1419×10^{-7}	4.0953x10
		9.5233×10^2	5.1910×10^{-12}	6.2753×10^{-9}	3.6339×10^{-3}
	1.0	5.6658×10^3	3.4805×10^{-7}	1.1436×10^{-7}	4.0953x10
		9.5233×10^2	1.5659×10^{-9}	6.3614×10^{-9}	1.0962
	5.0	5.6658×10^3	3.4805×10^{-7}	1.1827×10^{-7}	4.0953x10
		9.5233×10^2	3.8008×10^{-8}	8.3710×10^{-9}	2.6607x10
8.0	0.04	5.1142×10^4	3.6169×10^{-8}	1.0712×10^{-7}	4.7148×10^{-1}
		9.6008×10^2	4.8691×10^{-11}	7.8178×10^{-11}	3.3811×10^{-2}
	1.0	5.1142×10^4	3.6169×10^{-8}	1.0875×10^{-7}	4.7148×10^{-1}
		9.6008×10^2	1.4688×10^{-8}	8.9205×10^{-10}	1.0199x10
	5.0	5.1142×10^4	3.6169×10^{-8}	1.4674×10^{-7}	4.7148×10^{-1}
		9.6008×10^2	3.5652×10^{-7}	1.9896×10^{-8}	2.4756×10^2

Table 1-22 (continued)

pH:	ΔV_2° :	f_r :	$\mu_{\max}$:	α' :	$(\text{Ampl.} \times 10^{17})/2$:
10.0	0.04	6.5390×10^5	3.6185×10^{-10}	1.3771×10^{-8}	3.6891×10^{-4}
		9.6025×10^2	6.2269×10^{-10}	3.4684×10^{-11}	4.3231×10^{-1}
	1.0	6.5390×10^5	3.6185×10^{-10}	3.4590×10^{-8}	3.6891×10^{-4}
		9.6025×10^2	1.8783×10^{-7}	1.0444×10^{-8}	1.3041×10^2
	5.0	6.5390×10^5	3.6185×10^{-10}	5.2074×10^{-7}	3.6891×10^{-4}
		9.6025×10^2	4.5593×10^{-6}	2.5352×10^{-7}	3.1654×10^3
12.0	0.04	7.4132×10^5	3.6185×10^{-12}	2.3384×10^{-10}	3.2541×10^{-6}
		9.6026×10^2	7.0591×10^{-10}	3.9253×10^{-11}	4.9008×10^{-1}
	1.0	7.4132×10^5	3.6185×10^{-12}	2.3837×10^{-8}	3.2541×10^{-6}
		9.6026×10^2	2.1294×10^{-7}	1.1841×10^{-8}	1.4783×10^2
	5.0	7.4132×10^5	3.6185×10^{-12}	5.7496×10^{-7}	3.2541×10^{-6}
		9.6026×10^2	5.1686×10^{-6}	2.8740×10^{-7}	3.5883×10^3

Table 1-23: The Effect of pH Values on the f_r , $\mu_{\max}$, α' , and Ampl.

Values of Boric Acid & Sodium Borate System(II) at

$$C_{B(OH)_3} = 4.4 \times 10^{-4} \text{ M and } C_{Na} = 1.0 \text{ M}$$

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	α' : (dB/cm)	$(\text{Ampl.} \times 10^{17})/2$: (sec^2/cm) (nepers)
3.0	2.1486×10^6 7.5389×10^2	9.2459×10^{-10} 8.8377×10^{-16}	1.1504×10^{-7} 2.8363×10^{-14}	2.8688×10^{-4} 7.8152×10^{-7}
4.0	2.1487×10^5 7.5390×10^2	9.2455×10^{-9} 8.8377×10^{-15}	1.1504×10^{-7} 2.8327×10^{-12}	2.8686×10^{-2} 7.8150×10^{-6}
5.0	2.1542×10^4 7.5501×10^2	9.2209×10^{-8} 8.8369×10^{-14}	1.1502×10^{-7} 2.8224×10^{-10}	2.8536 7.8029×10^{-5}
6.0	2.6983×10^3 8.4144×10^2	7.3554×10^{-7} 8.8297×10^{-13}	1.1493×10^{-7} 2.0371×10^{-8}	1.8173×10^2 6.9957×10^{-4}
7.0	5.6565×10^3 1.1673×10^3	3.4803×10^{-7} 8.7579×10^{-12}	1.1400×10^{-7} 9.3134×10^{-9}	4.1018×10 5.0019×10^{-3}
8.0	5.0336×10^4 1.1834×10^3	3.6169×10^{-8} 8.0992×10^{-11}	1.0544×10^{-7} 1.2203×10^{-10}	4.7903×10^{-1} 4.5626×10^{-2}
9.0	2.8718×10^5 1.1836×10^3	3.6185×10^{-9} 4.6225×10^{-10}	6.0238×10^{-8} 3.3726×10^{-11}	8.3999×10^{-3} 2.6036×10^{-1}
10.0	5.4266×10^5 1.1837×10^3	3.6185×10^{-10} 8.7341×10^{-10}	1.1490×10^{-8} 5.9975×10^{-11}	4.4454×10^{-4} 4.9193×10^{-1}
11.0	5.9565×10^5 1.1837×10^3	3.6185×10^{-11} 9.5868×10^{-10}	1.3795×10^{-9} 6.5722×10^{-11}	4.0499×10^{-5} 5.3995×10^{-1}
12.0	6.0153×10^5 1.1837×10^3	3.6185×10^{-12} 9.6814×10^{-10}	2.5876×10^{-10} 6.6361×10^{-11}	4.0103×10^{-6} 5.4528×10^{-1}

Table 1-24: The Effect of pH Values on the f_r , $\mu_{\max}$, α' , and Ampl.

Values of Boric Acid & Sodium Borate System(II) at

$$C_{B(OH)_3} = 4.4 \times 10^{-3} \text{ M and } C_{Na} = 0.48 \text{ M}$$

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	α' : (dB/cm)	$(\text{Ampl.} \times 10^{17})/2$: (sec^2/cm) (nepers)
3.0	2.1486×10^6 7.5389×10^2	9.2458×10^{-9} 5.2294×10^{-15}	1.1503×10^{-6} 2.8347×10^{-13}	2.8688×10^{-3} 4.6243×10^{-6}
4.0	2.1491×10^5 7.5394×10^2	9.2434×10^{-8} 5.2293×10^{-14}	1.1503×10^{-6} 2.8316×10^{-11}	2.8673×10^{-1} 4.6240×10^{-5}
5.0	2.2036×10^4 7.5904×10^2	9.0143×10^{-7} 5.2290×10^{-13}	1.1503×10^{-6} 2.7263×10^{-9}	2.7271×10 4.5926×10^{-4}
6.0	7.6358×10^3 9.0212×10^2	2.5997×10^{-6} 5.2255×10^{-12}	1.1495×10^{-6} 3.1648×10^{-8}	2.2698×10^2 3.8617×10^{-3}
7.0	5.4713×10^4 9.5935×10^2	3.6042×10^{-7} 5.1909×10^{-11}	1.1419×10^{-6} 7.0482×10^{-10}	4.3916 3.6072×10^{-2}
8.0	5.1122×10^5 9.6022×10^2	3.6183×10^{-8} 4.8682×10^{-10}	1.0712×10^{-6} 3.4627×10^{-11}	4.7186×10^{-2} 3.3799×10^{-1}
9.0	3.1561×10^6 9.6061×10^2	3.6185×10^{-9} 3.0024×10^{-9}	6.6165×10^{-7} 1.6713×10^{-10}	7.6433×10^{-4} 2.0836
10.0	6.5409×10^6 9.6111×10^2	3.6185×10^{-10} 6.2135×10^{-9}	1.3775×10^{-7} 3.4582×10^{-10}	3.6881×10^{-5} 4.3099
11.0	7.3269×10^6 9.6122×10^2	3.6185×10^{-11} 6.9578×10^{-9}	1.6127×10^{-8} 3.8728×10^{-10}	3.2924×10^{-6} 4.8257
12.0	7.4160×10^6 9.6123×10^2	3.6185×10^{-12} 7.0421×10^{-9}	2.3379×10^{-9} 3.9197×10^{-10}	3.2529×10^{-7} 4.8841

Table 1-25: The Effect of pH Values on the f_r , $\mu_{\max}$, α' , and Ampl.

Values of Boric Acid & Sodium Borate System(II) at

$C_{B(OH)_3} = 0.01 \text{ M}$ and $C_{Na} = 0.48 \text{ M}$

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	α' : (dB/cm)	(Ampl. $\times 10^{17}$)/2: (sec ² /cm) (nepers)
3.0	2.1486×10^6 7.5389×10^2	2.1013×10^{-8} 1.1885×10^{-14}	2.6144×10^{-6} 6.4425×10^{-13}	6.5200×10^{-3} 1.0510×10^{-5}
4.0	2.1498×10^5 7.5401×10^2	2.1001×10^{-7} 1.1885×10^{-13}	2.6144×10^{-6} 6.4326×10^{-11}	6.5124×10^{-1} 1.0508×10^{-4}
5.0	2.2735×10^4 7.6522×10^2	1.9858×10^{-6} 1.1884×10^{-12}	2.6143×10^{-6} 5.9168×10^{-9}	5.8230×10 1.0353×10^{-3}
6.0	1.4618×10^4 9.2984×10^2	3.0863×10^{-6} 1.1876×10^{-11}	2.6125×10^{-6} 2.1056×10^{-8}	1.4076×10^2 8.5148×10^{-3}
7.0	1.2407×10^5 9.5982×10^2	3.6122×10^{-7} 1.1797×10^{-10}	2.5952×10^{-6} 3.1717×10^{-10}	1.9409 8.1940×10^{-2}
8.0	1.1618×10^6 9.6032×10^2	3.6184×10^{-8} 1.1061×10^{-9}	2.4344×10^{-6} 6.4835×10^{-11}	2.0763×10^{-2} 7.6788×10^{-1}
9.0	7.1737×10^6 9.6120×10^2	3.6185×10^{-9} 6.8128×10^{-9}	1.5039×10^{-6} 3.7925×10^{-10}	3.3627×10^{-4} 4.7252
10.0	1.4872×10^7 9.6232×10^2	3.6185×10^{-10} 1.4079×10^{-8}	3.1319×10^{-7} 7.8455×10^{-10}	1.6221×10^{-5} 9.7532
11.0	1.6661×10^7 9.6258×10^2	3.6185×10^{-11} 1.5760×10^{-8}	3.6668×10^{-8} 8.7846×10^{-10}	1.4479×10^{-6} 1.0915×10
12.0	1.6864×10^7 9.6261×10^2	3.6185×10^{-12} 1.5951×10^{-8}	5.3119×10^{-9} 8.8913×10^{-10}	1.4305×10^{-7} 1.1047×10

Table 1-26: The Effect of pH Values on the f_r , $\mu_{\max}$, α' , and Ampl.

Values of Boric Acid & Sodium Borate System(II) at

$C_{B(OH)_3} = 0.025 \text{ M}$ and $C_{Na} = 0.48 \text{ M}$

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	α' : (dB/cm)	(Ampl. $\times 10^{17}$)/2: (sec ² /cm) (nepers)
3.0	2.1486×10^6	5.2533×10^{-8}	6.5361×10^{-6}	1.6300×10^{-2}
	7.5389×10^2	2.9712×10^{-14}	1.6106×10^{-12}	2.6275×10^{-5}
4.0	2.1517×10^5	5.2456×10^{-7}	6.5359×10^{-6}	1.6253
	7.5419×10^2	2.9712×10^{-13}	1.6061×10^{-10}	2.6264×10^{-4}
5.0	2.4606×10^4	4.5868×10^{-6}	6.5355×10^{-6}	1.2427×10^2
	7.8005×10^2	2.9710×10^{-12}	1.3123×10^{-8}	2.5392×10^{-3}
6.0	3.3320×10^4	3.3850×10^{-6}	6.5312×10^{-6}	6.7728x10
	9.4686×10^2	2.9690×10^{-11}	1.0541×10^{-8}	2.0904×10^{-2}
7.0	3.0986×10^5	3.6160×10^{-7}	6.4882×10^{-6}	7.7799×10^{-1}
	9.6006×10^2	2.9490×10^{-10}	1.4096×10^{-10}	2.0478×10^{-1}
8.0	2.9046×10^6	3.6185×10^{-8}	6.0865×10^{-6}	8.3053×10^{-3}
	9.6058×10^2	2.7633×10^{-9}	1.5504×10^{-10}	1.9178
9.0	1.7939×10^7	3.6185×10^{-9}	3.7607×10^{-6}	1.3447×10^{-4}
	9.6277×10^2	1.6960×10^{-8}	9.4556×10^{-10}	1.1744x10
10.0	3.7221×10^7	3.6185×10^{-10}	7.8382×10^{-7}	6.4811×10^{-6}
	9.6558×10^2	3.4910×10^{-8}	1.9519×10^{-9}	2.4103x10
11.0	4.1710×10^7	3.6185×10^{-11}	9.1767×10^{-8}	5.7836×10^{-7}
	9.6624×10^2	3.9047×10^{-8}	2.1847×10^{-9}	2.6941x10
12.0	4.2219×10^7	3.6185×10^{-12}	1.3269×10^{-8}	5.7139×10^{-8}
	9.6631×10^2	3.9516×10^{-8}	2.2111×10^{-9}	2.7262x10

Table 1-27: The Effect of pH Values on the f_r , $\mu_{\max}$, and Amplitude

Values of Boric Acid & Polyborate System at $C_{B(OH)_3} = 0.05 \text{ M}$

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	(Amp1.x10 ¹⁷)/2: (sec ² /cm) (nepers)
5.0	2.7727x10 ⁴	7.8319x10 ⁻⁶	1.8831x10 ²
	9.8517x10	5.1583x10 ⁻⁹	4.1674x10
	5.8864	1.3989x10 ⁻⁶	1.5843x10 ⁵
	1.2147x10 ²	5.7244x10 ⁻¹²	3.1418x10 ⁻²
	6.3916	8.1873x10 ⁻¹¹	8.5396
	2.0509x10 ⁻²	2.4615x10 ⁻¹⁰	8.0013x10 ³
6.0	6.4484x10 ⁴	3.3645x10 ⁻⁶	3.4784x10
	1.0206x10 ²	6.1473x10 ⁻⁸	4.0157x10 ²
	6.7058	1.3961x10 ⁻⁵	1.3879x10 ⁶
	1.7251x10 ²	4.7145x10 ⁻¹⁰	1.8219
	8.1647	8.1634x10 ⁻⁹	6.6657x10 ²
	2.0521x10 ⁻¹	1.3419x10 ⁻⁸	4.3597x10 ⁴
7.0	6.1799x10 ⁵	3.4794x10 ⁻⁷	3.7534x10 ⁻¹
	1.0219x10 ²	6.0391x10 ⁻⁷	3.9396x10 ³
	6.7442	1.3686x10 ⁻⁴	1.3529x10 ⁷
	4.6645x10 ²	1.7054x10 ⁻⁸	2.4379x10
	1.6077x10	7.9294x10 ⁻⁷	3.2881x10 ⁴
	2.0522	2.3935x10 ⁻⁷	7.7754x10 ⁴
8.0	5.6765x10 ⁶	3.4806x10 ⁻⁸	4.0877x10 ⁻³
	1.0204x10 ²	5.1068x10 ⁻⁶	3.3365x10 ⁴
	6.7673	1.1342x10 ⁻³	1.1173x10 ⁸
	2.6736x10 ³	2.3068x10 ⁻⁷	5.7520x10
	1.8773x10	6.0210x10 ⁻⁵	2.1382x10 ⁶
	2.0527x10	2.2862x10 ⁻⁶	7.4250x10 ⁴
9.0	3.3651x10 ⁷	3.4806x10 ⁻⁹	6.8955x10 ⁻⁵
	1.0151x10 ²	1.8039x10 ⁻⁵	1.1847x10 ⁵
	6.7159	3.4624x10 ⁻³	3.4370x10 ⁸
	5.4252x10 ³	2.3521x10 ⁻⁶	2.8903x10 ²

Table 1-27 (continued)

pH:	f_r :	$\mu_{\max}$:	$(\text{Amp1.} \times 10^{17})/2$:
10.0	1.3522x10	1.0563x10 ⁻³	5.2078x10 ⁷
	2.0519x10 ²	4.2262x10 ⁻⁶	1.3731x10 ⁴
	8.4672x10 ⁷	3.4806x10 ⁻¹⁰	2.7404x10 ⁻⁶
	1.0185x10 ²	1.1383x10 ⁻⁵	7.4506x10 ⁴
	6.1260	1.1472x10 ⁻³	1.2485x10 ⁸
	1.0259x10 ³	1.3335x10 ⁻⁵	8.6655x10 ³
	7.1646	7.8708x10 ⁻⁴	7.3238x10 ⁷
	2.0505x10 ³	4.8433x10 ⁻⁸	1.5747x10
11.0	1.0466x10 ⁸	3.4806x10 ⁻¹¹	2.2171x10 ⁻⁷
	1.0217x10 ²	1.7336x10 ⁻⁶	1.1312x10 ⁴
	5.6988	3.2218x10 ⁻⁵	3.7690x10 ⁶
	2.2739x10 ²	6.7615x10 ⁻⁷	1.9823x10 ³
	5.2546	2.5405x10 ⁻⁵	3.2233x10 ⁶
	2.0504x10 ⁴	1.3975x10 ⁻¹¹	4.5439x10 ⁻⁴
12.0	1.0715x10 ⁸	3.4806x10 ⁻¹²	2.1655x10 ⁻⁸
	1.0221x10 ²	1.8165x10 ⁻⁷	1.1848x10 ³
	5.6332	3.6873x10 ⁻⁷	4.3637x10 ⁴
	2.1568x10 ²	7.4406x10 ⁻⁹	2.2999x10
	5.0664	2.9409x10 ⁻⁷	3.8699x10 ⁴
	2.0504x10 ⁵	1.5721x10 ⁻¹⁵	5.1116x10 ⁻⁹

Table 1-28: The Effect of pH Values on the f_r , $\mu_{\max}$, and Amplitude

Values of Boric Acid & Polyborate System at $C_{B(OH)_3} = 0.1 \text{ M}$

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	$(\text{Amp} \cdot 10^{17})/2$: (sec^2/cm) (nepers)
5.0	3.3964×10^4	1.2786×10^{-5}	2.5096×10^2
	1.0095×10^2	2.3529×10^{-8}	1.5538×10^2
	7.2858	6.1838×10^{-6}	5.6583×10^5
	1.0143×10^2	3.9322×10^{-11}	2.5844×10^{-1}
	1.6734×10	7.4432×10^{-10}	2.9652×10
	2.0596×10^{-2}	1.9487×10^{-9}	6.3077×10^4
6.0	1.2667×10^5	3.4215×10^{-6}	1.8007×10
	1.0681×10^2	2.3439×10^{-7}	1.4629×10^3
	9.8137	6.1579×10^{-5}	4.1832×10^6
	4.0430×10^2	1.6010×10^{-9}	2.6399
	2.6086×10	7.3974×10^{-8}	1.8905×10^3
	2.0676×10^{-1}	3.2698×10^{-8}	1.0543×10^5
7.0	1.2216×10^6	3.4800×10^{-7}	1.8991×10^{-1}
	1.0684×10^2	2.2579×10^{-6}	1.4089×10^4
	9.8099	5.9096×10^{-4}	4.0161×10^7
	2.6628×10^3	2.3106×10^{-8}	5.7849
	3.4564×10	6.9620×10^{-6}	1.3428×10^5
	2.0682	3.5038×10^{-7}	1.1294×10^5
8.0	1.0382×10^7	3.4806×10^{-8}	2.2350×10^{-3}
	1.0585×10^2	1.6467×10^{-5}	1.0371×10^5
	9.3135	4.1751×10^{-3}	2.9886×10^8
	1.5636×10^4	2.4166×10^{-7}	1.0304×10
	3.1322×10	4.1684×10^{-4}	8.8722×10^6
	2.0691×10	3.4780×10^{-6}	1.1206×10^5

Table 1-28 (continued)

pH:	f_r :	$\mu_{\max}$:	$(\text{Amp1.} \times 10^{17})/2$:
9.0	5.2833×10^7	3.4806×10^{-9}	4.3919×10^{-5}
	1.0383×10^2	4.3474×10^{-5}	2.7913×10^5
	8.2601	9.5175×10^{-3}	7.6815×10^8
	2.0578×10^4	2.4161×10^{-6}	7.8275×10
	1.8791×10	4.6478×10^{-3}	1.6490×10^8
	2.0577×10^2	2.0056×10^{-5}	6.4977×10^4
10.0	1.4422×10^8	3.4806×10^{-10}	1.6089×10^{-6}
	1.0495×10^2	3.2048×10^{-5}	2.0357×10^5
	7.0353	4.4293×10^{-3}	4.1972×10^8
	4.4051×10^3	2.0888×10^{-5}	3.1611×10^3
	9.3962	5.0675×10^{-3}	3.5954×10^8
	2.0508×10^3	6.9305×10^{-7}	2.2529×10^2
11.0	2.0436×10^8	3.4806×10^{-11}	1.1354×10^{-7}
	1.0668×10^2	6.3307×10^{-6}	3.9562×10^4
	5.8931	2.2376×10^{-4}	2.5313×10^7
	5.1097×10^2	4.9457×10^{-6}	6.4526×10^3
	5.7995	3.3851×10^{-4}	3.8913×10^7
	2.0504×10^4	3.9673×10^{-10}	1.2899×10^{-2}
12.0	2.1379×10^8	3.4806×10^{-12}	1.0854×10^{-8}
	1.0696×10^2	6.9104×10^{-7}	4.3072×10^3
	5.6546	2.9048×10^{-6}	3.4247×10^5
	4.2774×10^2	5.9099×10^{-8}	9.2111×10
	5.1273	4.6117×10^{-6}	5.9963×10^5
	2.0504×10^5	4.9712×10^{-14}	1.6163×10^{-7}

Table 1-28 (continued)

pH:	f_r :	$\mu_{\max}$:	$(\text{Amp1.} \times 10^{17})/2$:
9.0	5.2833×10^7	3.4806×10^{-9}	4.3919×10^{-5}
	1.0383×10^2	4.3474×10^{-5}	2.7913×10^5
	8.2601	9.5175×10^{-3}	7.6815×10^8
	2.0578×10^4	2.4161×10^{-6}	7.8275×10
	1.8791×10	4.6478×10^{-3}	1.6490×10^8
	2.0577×10^2	2.0056×10^{-5}	6.4977×10^4
10.0	1.4422×10^8	3.4806×10^{-10}	1.6089×10^{-6}
	1.0495×10^2	3.2048×10^{-5}	2.0357×10^5
	7.0353	4.4293×10^{-3}	4.1972×10^8
	4.4051×10^3	2.0888×10^{-5}	3.1611×10^3
	9.3962	5.0675×10^{-3}	3.5954×10^8
	2.0508×10^3	6.9305×10^{-7}	2.2529×10^2
11.0	2.0436×10^8	3.4806×10^{-11}	1.1354×10^{-7}
	1.0668×10^2	6.3307×10^{-6}	3.9562×10^4
	5.8931	2.2376×10^{-4}	2.5313×10^7
	5.1097×10^2	4.9457×10^{-6}	6.4526×10^3
	5.7995	3.3851×10^{-4}	3.8913×10^7
	2.0504×10^4	3.9673×10^{-10}	1.2899×10^{-2}
12.0	2.1379×10^8	3.4806×10^{-12}	1.0854×10^{-8}
	1.0696×10^2	6.9104×10^{-7}	4.3072×10^3
	5.6546	2.9048×10^{-6}	3.4247×10^5
	4.2774×10^2	5.9099×10^{-8}	9.2111×10
	5.1273	4.6117×10^{-6}	5.9963×10^5
	2.0504×10^5	4.9712×10^{-14}	1.6163×10^{-7}

Table 1-29: The Effect of pH Values on the f_r , $\mu_{\max}$, and AmplitudeValues of Boric Acid & Polyborate System at $C_{B(OH)_3} = 0.2 \text{ M}$

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	(Ampl. $\times 10^{17}$)/2: (sec ² /cm) (nepers)
5.0	4.6428×10^4	1.8697×10^{-5}	2.6847×10^2
	1.0770×10^2	8.6322×10^{-8}	5.3436×10^2
	1.4715×10	2.6084×10^{-5}	1.1817×10^6
	1.6611×10^2	1.4771×10^{-10}	5.9280×10^{-1}
	9.3037×10	6.3818×10^{-9}	4.5729×10
	2.1493×10^{-2}	3.3999×10^{-9}	1.0546×10^5
6.0	2.4993×10^5	3.4506×10^{-6}	9.2043
	1.1625×10^2	8.5286×10^{-7}	4.8909×10^3
	2.0993×10	2.5733×10^{-4}	8.1722×10^6
	2.2321×10^3	2.2873×10^{-9}	6.8313×10^{-1}
	6.4718×10	6.2549×10^{-7}	6.4432×10^3
	2.1676×10^{-1}	3.5566×10^{-8}	1.0939×10^5
7.0	2.3373×10^6	3.4802×10^{-7}	9.9268×10^{-2}
	1.1543×10^2	7.6519×10^{-6}	4.4195×10^4
	1.9814×10	2.2796×10^{-3}	7.6697×10^7
	1.7814×10^4	2.4200×10^{-8}	9.0568×10^{-1}
	6.4196×10	5.2249×10^{-5}	5.4260×10^5
	2.1651	3.5726×10^{-7}	1.1001×10^5
8.0	1.6836×10^7	3.4806×10^{-8}	1.3783×10^{-3}
	1.1107×10^2	4.1267×10^{-5}	2.4769×10^5
	1.4890×10	1.1494×10^{-2}	5.1465×10^8
	6.6218×10^4	2.4339×10^{-7}	2.4504
	4.8029×10	1.8900×10^{-3}	2.6235×10^7
	2.1361×10	3.5673×10^{-6}	1.1133×10^5

Table 1-29 (continued)

pH:	f_r :	$\mu_{\max}$:	$(\text{Amp1.} \times 10^{17})/2$:
9.0	7.3945×10^7	3.4806×10^{-9}	3.1380×10^{-5}
	1.0639×10^2	8.3115×10^{-5}	5.2084×10^5
	1.0677x10	1.9700×10^{-2}	1.2300×10^9
	5.6151×10^4	2.4308×10^{-6}	2.8860×10
	2.4695x10	1.3447×10^{-2}	3.6302×10^8
	2.0721×10^2	3.1205×10^{-5}	1.0040×10^5
10.0	2.1481×10^8	3.4806×10^{-10}	1.0802×10^{-6}
	1.0863×10^2	6.8691×10^{-5}	4.2155×10^5
	8.6513	1.1496×10^{-2}	8.8587×10^8
	1.4060×10^4	2.3214×10^{-5}	1.1007×10^3
	1.2415x10	1.7671×10^{-2}	9.4890×10^8
	2.0518×10^3	5.0185×10^{-6}	1.6306×10^3
11.0	3.7720×10^8	3.4806×10^{-11}	6.1516×10^{-8}
	1.1449×10^2	2.0096×10^{-5}	1.1701×10^5
	6.4751	1.2462×10^{-3}	1.2831×10^8
	1.6139×10^3	2.8088×10^{-5}	1.1603×10^4
	7.0474	2.9784×10^{-3}	2.8175×10^8
	2.0504×10^4	8.4993×10^{-9}	2.7634×10^{-1}
12.0	4.2371×10^8	3.4806×10^{-12}	5.4763×10^{-9}
	1.1631×10^2	2.4963×10^{-6}	1.4309×10^4
	5.7306	2.2211×10^{-5}	2.5839×10^6
	1.1716×10^3	4.6000×10^{-7}	2.6176×10^2
	5.2596	6.7692×10^{-5}	8.5801×10^6
	2.0504×10^5	1.5201×10^{-12}	4.9425×10^{-6}

Table 1-30: The Effect of pH Values on the f_r , $\mu_{\max}$, and Amplitude

Values of Boric Acid & Polyborate System at $C_{B(OH)_3} = 0.3 \text{ M}$

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	$(\text{Amp} \cdot 10^{17})/2$: (sec^2/cm) (nepers)
5.0	5.8859×10^4	2.2099×10^{-5}	2.5031×10^2
	1.1560×10^2	1.7919×10^{-7}	1.0334×10^3
	2.8096×10	5.9672×10^{-5}	1.4159×10^6
	4.6626×10^2	2.0436×10^{-10}	2.9220×10^{-1}
	1.5709×10^2	2.2010×10^{-8}	9.3406×10
	2.3381×10^{-2}	3.5403×10^{-9}	1.0095×10^5
6.0	3.7019×10^5	3.4604×10^{-6}	6.2316
	1.2546×10^2	1.7437×10^{-6}	9.2661×10^3
	3.7132×10	5.7831×10^{-4}	1.0383×10^7
	7.0083×10^3	2.3908×10^{-9}	2.2743×10^{-1}
	9.7538×10	2.1006×10^{-6}	1.4358×10^4
	2.3529×10^{-1}	3.5726×10^{-8}	1.0123×10^5
7.0	3.2820×10^6	3.4803×10^{-7}	7.0695×10^{-2}
	1.2270×10^2	1.4195×10^{-5}	7.7125×10^4
	3.1958×10	4.5710×10^{-3}	9.5354×10^7
	4.9079×10^4	2.4323×10^{-8}	3.3039×10^{-1}
	8.8530×10	1.4799×10^{-4}	1.1144×10^6
	2.3261	3.5758×10^{-7}	1.0248×10^5
8.0	2.1058×10^7	3.4806×10^{-8}	1.1019×10^{-3}
	1.1449×10^2	6.2636×10^{-5}	3.6472×10^5
	1.9709×10	1.8243×10^{-2}	6.1710×10^8
	1.2945×10^5	2.4365×10^{-7}	1.2548
	5.8953×10	3.7714×10^{-3}	4.2648×10^7
	2.2181×10	3.5735×10^{-6}	1.0741×10^5

Table 1-30 (continued)

pH:	f_r :	$\mu_{\max}$:	$(\text{Amp1.} \times 10^{17})/2$:
9.0	8.7019×10^7	3.4806×10^{-9}	2.6665×10^{-5}
	1.0797×10^2	1.1342×10^{-4}	7.0032×10^5
	1.2531×10	2.7821×10^{-2}	1.4802×10^9
	9.1411×10^4	2.4341×10^{-6}	1.7752×10
	2.8450×10	2.2151×10^{-2}	5.1905×10^8
	2.0860×10^2	3.3587×10^{-5}	1.0734×10^5
10.0	2.5870×10^8	3.4806×10^{-10}	8.9693×10^{-7}
	1.1092×10^2	9.7576×10^{-5}	5.8647×10^5
	9.9271	1.7624×10^{-2}	1.1836×10^9
	2.4356×10^4	2.3704×10^{-5}	6.4882×10^2
	1.4510×10	2.9670×10^{-2}	1.3632×10^9
	2.0528×10^3	1.2445×10^{-5}	4.0418×10^3
11.0	5.1332×10^8	3.4806×10^{-11}	4.5204×10^{-8}
	1.2065×10^2	3.5318×10^{-5}	1.9516×10^5
	7.1189	2.8549×10^{-3}	2.6735×10^8
	3.1813×10^3	6.0243×10^{-5}	1.2625×10^4
	8.5123	7.4076×10^{-3}	5.8015×10^8
	2.0505×10^4	3.9668×10^{-8}	1.2897
12.0	6.2651×10^8	3.4806×10^{-12}	3.7037×10^{-9}
	1.2533×10^2	5.0645×10^{-6}	2.6939×10^4
	5.8387	7.0413×10^{-5}	8.0398×10^6
	2.2073×10^3	1.4864×10^{-6}	4.4893×10^2
	5.3877	2.9181×10^{-4}	3.6108×10^7
	2.0504×10^5	1.0744×10^{-11}	3.4932×10^{-5}

Table 1-31: The Effect of pH Values on the f_r , $\mu_{\max}$, and AmplitudeValues of Boric Acid & Polyborate System at $C_{B(OH)_3} = 0.4 \text{ M}$

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	$(\text{Ampl.} \times 10^{17})/2$: (sec^2/cm) (nepers)
5.0	7.1226×10^4	2.4305×10^{-5}	2.2750×10^2
	1.2402×10^2	2.9524×10^{-7}	1.5870×10^3
	4.6426×10	1.0670×10^{-4}	1.5322×10^6
	1.1442×10^3	2.2541×10^{-10}	1.3134×10^{-1}
	1.9704×10^2	5.2543×10^{-8}	1.7777×10^2
	2.6110×10^{-2}	3.5650×10^{-9}	9.1027×10^4
6.0	4.8510×10^5	3.4651×10^{-6}	4.7621
	1.3426×10^2	2.8061×10^{-6}	1.3934×10^4
	5.6394×10	1.0049×10^{-3}	1.1880×10^7
	1.5675×10^4	2.4176×10^{-9}	1.0282×10^{-1}
	1.2765×10^2	4.8047×10^{-6}	2.5094×10^4
	2.6097×10^{-1}	3.5753×10^{-8}	9.1333×10^4
7.0	4.0523×10^6	3.4804×10^{-7}	5.7257×10^{-2}
	1.2863×10^2	2.0643×10^{-5}	1.0699×10^5
	4.3934×10	7.0236×10^{-3}	1.0658×10^8
	9.2263×10^4	2.4356×10^{-8}	1.7599×10^{-1}
	1.0827×10^2	2.8161×10^{-4}	1.7340×10^6
	2.5213	3.5763×10^{-7}	9.4564×10^4
8.0	2.4175×10^7	3.4806×10^{-8}	9.5983×10^{-4}
	1.1701×10^2	8.0767×10^{-5}	4.6015×10^5
	2.3806×10	2.4213×10^{-2}	6.7805×10^8
	1.9577×10^5	2.4375×10^{-7}	8.3002×10^{-1}
	6.7041×10	5.7601×10^{-3}	5.7279×10^7
	2.3034×10	3.5751×10^{-6}	1.0347×10^5

Table 1-31 (continued)

pH:	f_r :	$\mu_{\max}$:	$(\text{Amp1.} \times 10^{17})/2$:
9.0	9.6707×10^7	3.4806×10^{-9}	2.3994×10^{-5}
	1.0914×10^2	1.3857×10^{-4}	8.4647×10^5
	1.4073x10	3.4720×10^{-2}	1.6447×10^9
	1.2541×10^5	2.4355×10^{-6}	1.2947x10
	3.1291x10	3.0422×10^{-2}	6.4815×10^8
	2.0989×10^2	3.4446×10^{-5}	1.0941×10^5
10.0	2.9099×10^8	3.4806×10^{-10}	7.9740×10^{-7}
	1.1260×10^2	1.2161×10^{-4}	7.2001×10^5
	1.0990x10	2.2956×10^{-2}	1.3926×10^9
	3.4531×10^4	2.3904×10^{-5}	4.6151×10^2
	1.6139x10	4.0143×10^{-2}	1.6582×10^9
	2.0537×10^3	2.1799×10^{-5}	7.0765×10^3
11.0	6.2153×10^8	3.4806×10^{-11}	3.7334×10^{-8}
	1.2554×10^2	4.9760×10^{-5}	2.6425×10^5
	7.7300	4.7008×10^{-3}	4.0541×10^8
	4.9809×10^3	8.9756×10^{-5}	1.2013×10^4
	1.0069x10	1.1907×10^{-2}	7.8840×10^8
	2.0505×10^4	1.0323×10^{-7}	3.3562
12.0	8.1981×10^8	3.4806×10^{-12}	2.8304×10^{-9}
	1.3394×10^2	8.1146×10^{-6}	4.0389×10^4
	5.9671	1.5457×10^{-4}	1.7269×10^7
	3.4042×10^3	3.3280×10^{-6}	6.5173×10^2
	5.5175	7.3190×10^{-4}	8.8434×10^7
	2.0504×10^5	4.1219×10^{-11}	1.3402×10^{-4}

Table 1-32: The Effect of pH Values on the f_r , $\mu_{\max}$, and Amplitude

Values of Boric Acid & Polyborate System at $C_{B(OH)_3} = 0.5 \text{ M}$

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	$(\text{Ampl.} \times 10^{17})/2$: (sec^2/cm) (nepers)
5.0	8.3477×10^4	2.5846×10^{-5}	2.0642×10^2
	1.3267×10^2	4.2892×10^{-7}	2.1553×10^3
	6.8624×10	1.6668×10^{-4}	1.6193×10^6
	2.3449×10^3	2.3400×10^{-10}	6.6527×10^{-2}
	2.2981×10^2	1.0249×10^{-7}	2.9733×10^2
	2.9614×10^{-2}	3.5718×10^{-9}	8.0408×10^4
6.0	5.9215×10^5	3.4679×10^{-6}	3.9043
	1.4245×10^2	3.9472×10^{-6}	1.8473×10^4
	7.7095×10	1.5078×10^{-3}	1.3039×10^7
	2.8482×10^4	2.4273×10^{-9}	5.6816×10^{-2}
	1.5532×10^2	8.8229×10^{-6}	3.7870×10^4
	2.9221×10^{-1}	3.5761×10^{-8}	8.1588×10^4
7.0	4.6798×10^6	3.4804×10^{-7}	4.9581×10^{-2}
	1.3346×10^2	2.6535×10^{-5}	1.3255×10^5
	5.4882×10	9.4086×10^{-3}	1.1429×10^8
	1.4203×10^5	2.4369×10^{-8}	1.1438×10^{-1}
	1.2433×10^2	4.3642×10^{-4}	2.3402×10^6
	2.7313	3.5765×10^{-7}	8.7297×10^4
8.0	2.6655×10^7	3.4806×10^{-8}	8.7052×10^{-4}
	1.1902×10^2	9.6532×10^{-5}	5.4069×10^5
	2.7375×10	2.9560×10^{-2}	7.1989×10^8
	2.6237×10^5	2.4379×10^{-7}	6.1946×10^{-1}
	7.3500×10	7.7641×10^{-3}	7.0423×10^7
	2.3891×10	3.5757×10^{-6}	9.9778×10^4

Table 1-32 (continued)

pH:	f_r :	$\mu_{\max}$:	$(\text{Amp}1.\times10^{17})/2$:
9.0	1.0450×10^8	3.4806×10^{-9}	2.2204×10^{-5}
	1.1008×10^2	1.6043×10^{-4}	9.7160×10^5
	1.5416×10	4.0810×10^{-2}	1.7648×10^9
	1.5821×10^5	2.4363×10^{-6}	1.0266×10
	3.3615×10	3.8270×10^{-2}	7.5898×10^8
	2.1111×10^2	3.4858×10^{-5}	1.1008×10^5
10.0	3.1862×10^8	3.4806×10^{-10}	7.3239×10^{-7}
	1.1395×10^2	1.4246×10^{-4}	8.3347×10^5
	1.1912×10	2.7710×10^{-2}	1.5508×10^9
	4.4469×10^4	2.4013×10^{-5}	3.5999×10^2
	1.7489×10	4.9304×10^{-2}	1.8794×10^9
	2.0545×10^3	3.2303×10^{-5}	1.0482×10^4
11.0	7.1033×10^8	3.4806×10^{-11}	3.2666×10^{-8}
	1.2955×10^2	6.2982×10^{-5}	3.2409×10^5
	8.2897	6.6018×10^{-3}	5.3093×10^8
	6.8928×10^3	1.1342×10^{-4}	1.0970×10^4
	1.1603×10	1.5889×10^{-2}	9.1294×10^8
	2.0505×10^4	2.0127×10^{-7}	6.5439
12.0	1.0023×10^9	3.4806×10^{-12}	2.3151×10^{-9}
	1.4206×10^2	1.1435×10^{-5}	5.3664×10^4
	6.1068	2.7662×10^{-4}	3.0198×10^7
	4.6693×10^3	6.0747×10^{-6}	8.6731×10^2
	5.6544	1.3490×10^{-3}	1.5905×10^8
	2.0504×10^5	1.1259×10^{-10}	3.6606×10^{-4}

Table 1-33: The Effect of pH Values on the f_r , $\mu_{\max}$, and Amplitude

Values of Boric Acid & Polyborate System at $C_{B(OH)_3} = 0.6 \text{ M}$

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	$(\text{Amp} \cdot 10^{17})/2$: (sec^2/cm) (nepers)
5.0	9.5543×10^4	2.6978×10^{-5}	1.8824×10^2
	1.4137×10^2	5.7547×10^{-7}	2.7138×10^3
	9.3695×10	2.3879×10^{-4}	1.6990×10^6
	4.1926×10^3	2.3800×10^{-10}	3.7845×10^{-2}
	2.6030×10^2	1.7563×10^{-7}	4.4982×10^2
	3.3844×10^{-2}	3.5743×10^{-9}	7.0408×10^4
6.0	6.8950×10^5	3.4697×10^{-6}	3.3548
	1.4990×10^2	5.0911×10^{-6}	2.2641×10^4
	9.7853×10	2.0534×10^{-3}	1.3990×10^7
	4.4972×10^4	2.4317×10^{-9}	3.6047×10^{-2}
	1.8035×10^2	1.4015×10^{-5}	5.1805×10^4
	3.2712×10^{-1}	3.5764×10^{-8}	7.2887×10^4
7.0	5.1995×10^6	3.4804×10^{-7}	4.4625×10^{-2}
	1.3746×10^2	3.1803×10^{-5}	1.5424×10^5
	6.4675×10	1.1647×10^{-2}	1.2006×10^8
	1.9475×10^5	2.4375×10^{-8}	8.3442×10^{-2}
	1.3762×10^2	6.0097×10^{-4}	2.9114×10^6
	2.9459	3.5766×10^{-7}	8.0938×10^4
8.0	2.8724×10^7	3.4806×10^{-8}	8.0782×10^{-4}
	1.2070×10^2	1.1054×10^{-4}	6.1058×10^5
	3.0550×10	3.4425×10^{-2}	7.5122×10^8
	3.2830×10^5	2.4382×10^{-7}	4.9512×10^{-1}
	7.8905×10	9.7515×10^{-3}	8.2391×10^7
	2.4744×10	3.5760×10^{-6}	9.6344×10^4

Table 1-33 (continued)

pH:	f_r :	$\mu_{\max}$:	$(\text{Amp}1.\times 10^{17})/2$:
9.0	1.1108×10^8	3.4806×10^{-9}	2.0889×10^{-5}
	1.1088×10^2	1.7997×10^{-4}	1.0821×10^6
	1.6618×10	4.6318×10^{-2}	1.8581×10^9
	1.8997×10^5	2.4368×10^{-6}	8.5513
	3.5605×10	4.5744×10^{-2}	8.5651×10^8
	2.1226×10^2	3.5092×10^{-5}	1.1021×10^5
10.0	3.3851×10^8	3.4806×10^{-10}	6.8546×10^{-7}
	1.1508×10^2	1.6103×10^{-4}	9.3290×10^5
	1.2735×10	3.2029×10^{-2}	1.6767×10^9
	5.4162×10^4	2.4080×10^{-5}	2.9640×10^2
	1.8651×10	5.7421×10^{-2}	2.0525×10^9
	2.0552×10^3	4.3437×10^{-5}	1.4090×10^4
11.0	7.8545×10^8	3.4806×10^{-11}	2.9542×10^{-8}
	1.3295×10^2	7.5040×10^{-5}	3.7628×10^5
	8.8002	8.4811×10^{-3}	6.4250×10^8
	8.8590×10^3	1.3178×10^{-4}	9.9165×10^3
	1.3066×10	1.9319×10^{-2}	9.8570×10^8
	2.0505×10^4	3.3271×10^{-7}	1.0817×10
12.0	1.1735×10^9	3.4806×10^{-12}	1.9773×10^{-9}
	1.4969×10^2	1.4878×10^{-5}	6.6262×10^4
	6.2517	4.3480×10^{-4}	4.6366×10^7
	5.9430×10^3	9.7352×10^{-6}	1.0921×10^3
	5.8028	2.0583×10^{-3}	2.3647×10^8
	2.0504×10^5	2.4771×10^{-10}	8.0540×10^{-4}

Table 1-34: The Effect of pH Values on the f_r , $\mu_{\max}$, and Amplitude
Values of Boric Acid & Polyborate System at $C_{B(OH)_3} = 1.0 \text{ M}$

pH:	f_r : (Hz)	$\mu_{\max}$: (nepers)	$(\text{Ampl.} \times 10^{17})/2$: (sec^2/cm) (nepers)
5.0	1.4014×10^5	2.9469×10^{-5}	1.4019×10^2
	1.7432×10^2	1.2094×10^{-6}	4.6252×10^3
	2.0588×10^2	6.1745×10^{-4}	1.9994×10^6
	1.9171×10^4	2.4246×10^{-10}	8.4313×10^{-3}
	3.7121×10^2	7.2943×10^{-7}	1.3100×10^3
	5.6313×10^{-2}	3.5763×10^{-9}	4.2338×10^4
6.0	9.8263×10^5	3.4730×10^{-6}	2.3562
	1.7235×10^2	9.0116×10^{-6}	3.4858×10^4
	1.6903×10^2	4.2040×10^{-3}	1.6581×10^7
	1.3038×10^5	2.4367×10^{-9}	1.2460×10^{-2}
	2.5541×10^2	4.1022×10^{-5}	1.0707×10^5
	4.7450×10^{-1}	3.5766×10^{-8}	5.0251×10^4
7.0	6.6477×10^6	3.4805×10^{-7}	3.4904×10^{-2}
	1.4860×10^2	4.8088×10^{-5}	2.1573×10^5
	9.4970x10	1.9142×10^{-2}	1.3437×10^8
	4.0687×10^5	2.4384×10^{-8}	3.9954×10^{-2}
	1.7464×10^2	1.2659×10^{-3}	4.8324×10^6
	3.7851	3.5766×10^{-7}	6.2995×10^4
8.0	3.4756×10^7	3.4806×10^{-8}	6.6762×10^{-4}
	1.2558×10^2	1.5555×10^{-4}	8.2577×10^5
	4.0776x10	5.0693×10^{-2}	8.2881×10^8
	5.8148×10^5	2.4387×10^{-7}	2.7959×10^{-1}
	9.4769x10	1.7391×10^{-2}	1.2234×10^8
	2.8093x10	3.5764×10^{-6}	8.4870×10^4

Table 1-34 (continued)

pH:	f_r :	$\mu_{\max}$:	$(\text{Amp1.} \times 10^{17})/2$:
9.0	1.3067×10^8	3.4806×10^{-9}	1.7758×10^{-5}
	1.1325×10^2	2.4328×10^{-4}	1.4353×10^6
	2.0558×10	6.4687×10^{-2}	2.0978×10^9
	3.0911×10^5	2.4377×10^{-6}	5.2575
	4.1696×10	7.2719×10^{-2}	1.1627×10^9
	2.1641×10^2	3.5462×10^{-5}	1.0924×10^5
10.0	4.0262×10^8	3.4806×10^{-10}	5.7632×10^{-7}
	1.1842×10^2	2.2138×10^{-4}	1.2463×10^6
	1.5411×10	4.6477×10^{-2}	2.0106×10^9
	9.0866×10^4	2.4206×10^{-5}	1.7760×10^2
	2.2219×10	8.2959×10^{-2}	2.4891×10^9
	2.0578×10^3	8.8509×10^{-5}	2.8675×10^4
11.0	1.0067×10^9	3.4806×10^{-11}	2.3050×10^{-8}
	1.4295×10^2	1.1464×10^{-4}	5.3464×10^5
	1.0478×10	1.5413×10^{-2}	9.8070×10^8
	1.6845×10^4	1.7371×10^{-4}	6.8745×10^3
	1.8097×10	2.9262×10^{-2}	1.0780×10^9
	2.0506×10^4	1.1503×10^{-6}	3.7398×10
12.0	1.7546×10^9	3.4806×10^{-12}	1.3225×10^{-9}
	1.7556×10^2	2.8359×10^{-5}	1.0769×10^5
	6.8193	1.3429×10^{-3}	1.3129×10^8
	1.0639×10^4	3.2239×10^{-5}	2.0202×10^3
	6.5546	4.7690×10^{-3}	4.8505×10^8
	2.0504×10^5	1.8510×10^{-9}	6.0184×10^{-3}

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