

THE UNIVERSITY OF MARYLAND

DEPARTMENT OF CHEMISTRY

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ULTRASONIC ABSORPTION STUDY OF TERTIARY BUTYL ALCOHOL IN CYCLOHEXANE

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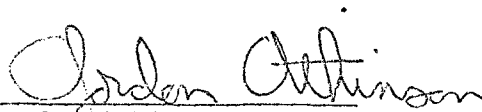
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ABSTRACT

Title of Thesis: Ultrasonic Absorption Study of Tertiary Butyl Alcohol
in Cyclohexane

Frank Garland, Doctor of Philosophy, 1968

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The ultrasonic absorption technique was used to study the self-association of t-butyl alcohol in cyclohexane at 5°C, 10°C, and 15°C. The absorption data were interpreted in terms of a single relaxation and characteristic time constants of the association process were found. It was concluded from the variation of the time constants with concentration of alcohol that the relaxation is due to perturbation of a monomer-dimer equilibrium. The association and dissociation rate constants, respectively, are: $5. \times 10^8 \text{ l}\cdot\text{mole}^{-1}\cdot\text{sec}^{-1}$ and $0.6 \times 10^8 \text{ sec}^{-1}$ at 5°C; $6.0 \times 10^8 \text{ l}\cdot\text{mole}^{-1}\cdot\text{sec}^{-1}$ and $0.89 \times 10^8 \text{ sec}^{-1}$ at 10°C; and $6.1 \times 10^8 \text{ l}\cdot\text{mole}^{-1}\cdot\text{sec}^{-1}$ and $1.2 \times 10^8 \text{ sec}^{-1}$ at 15°C. The equilibrium constants at these temperatures are 8.5, 6.8, and 4.9, respectively. The enthalpy of association was found to be $-7.0 \text{ kcal}\cdot\text{mole}^{-1}$ of dimer; the activation energies of association and dissociation were found to be $3.9 \text{ kcal}\cdot\text{mole}^{-1}$ and $10.9 \text{ kcal}\cdot\text{mole}^{-1}$ respectively. The method used to calculate the time constants from the absorption data is discussed.

ULTRASONIC STUDY OF TERTIARY BUTYL ALCOHOL
IN CYCLOHEXANE

by
Frank Garland

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I. INTRODUCTION

Hydrogen bonding has long been used to explain anomalous physical and chemical properties of many substances. An early example is the proposal made in 1920 by Latimer and Rodebush that the unique properties of water can be explained by H-bonding interactions.¹ Numerous methods have been used to detect and measure the hydrogen bond, resulting in information on the equilibrium constant and energy of forming H-bonded complexes, and on the structure of such complexes. Until the recent introduction of experimental methods known as relaxation techniques, no data on the rates of H-bonding interactions were available due to the extreme rapidity of the reactions involved. The ultrasonic technique, developed by Eigen, Lamb and others, affords a method of measuring these rates. In order to apply this technique to the measurement of hydrogen bonding rates, ultrasonic absorption spectra of dilute solutions of t-butyl alcohol in cyclohexane were measured.

A. Hydrogen Bonded Alcohol Polymers

Basic studies of the hydrogen bond have been done on systems involving alcohols. A thorough review of the literature to 1960 is found in the monograph of Pimentel and McClellan.² Most workers agree that solutions of alcohols in non-polar solvents consist of a variety of H-bonded polymers. Investigations such as those of G. von Elbe³ and H. Van Hess et al⁴ have established that 4-6 kcal·mole⁻¹ is needed to break a hydrogen bond in such solutions. Liddel and Becker;⁵ Davis, Pitzer, and Rao;⁶

Singh and Rao;⁷ and others^{4,8,9} have used infrared spectroscopy, nuclear magnetic resonance, and other methods on solutions of methanol, ethanol, 2-propanol, and t-butyl alcohol in inert solvents. The general conclusion of these workers is that dimers are a principal, if not the only, polymeric species in dilute solutions. Other authors disagree, finding evidence that trimers or tetramers are the predominant species.¹⁰⁻¹² Those who conclude that the dimer is a major constituent disagree on whether it is cyclic having two hydrogen bonds, or an open structure having one H-bond. Boud et al,⁹ in a cryoscopic and molecular polarization study of benzene solutions of n- and t-butyl alcohols, explained the results of their dilute solutions in terms of a monomer-dimer equilibrium, the dimer existing in an open form with the hydrogen bond linear with the bridging-OH group. H. Van Hess et al⁴ studied ethanol/n-heptane and ethanol/toluene mixtures and concluded that the dimeric polymer was cyclic. Association equilibrium constants for this type of system are scarce. A survey of results has been compiled by Pimentel and McClellan.^{2a}

B. Relaxation Technique

Classically, the kinetics of a reaction are studied by following the concentration of one or more of the reacting species with time. Methods of this type are limited by the rate at which the reactants can be mixed. Relaxation techniques can be used to study reactions which proceed too fast to be studied by conventional means. The general principle of these techniques is that some external parameter affecting a chemical equilibrium is changed suddenly. The finite time required by the reaction to attain the new equilibrium conditions is then used to calculate the forward and

reverse rate constants.

The "jump" methods use a single displacement of temperature, pressure, or electric field, after which the reaction is followed as it approaches the new equilibrium conditions. In the ultrasonic technique, a sound wave is used to change the equilibrium conditions in a sinusoidal fashion. If the sound frequency is high enough, the reaction will be unable to keep up with the rapidly changing equilibrium conditions. The lag in the attainment of equilibrium causes a change in the sound absorbed by the solution, and from this change a "characteristic frequency" of the reaction can be calculated (discussed in Chapter II). In all of these methods the displacement of the reaction from equilibrium is kept small so that the approach of a given reactant to equilibrium can be described by a first-order equation, regardless of the complexity of the rate expression of that reactant. Under this restriction the reaction, at specified temperature, pressure, and equilibrium concentration can be characterized by a time constant. In ultrasonics this constant is directly related to the characteristic frequency and leads to evaluation of the rate constants of the reaction (Chapter II).

Sound techniques have been used to study a variety of equilibrium reactions. The most common application is ion pair association in water. Proton transfer, hydrolysis reactions, and the rates of association and dissociation of weak acids and bases have also been studied. Ultrasonic absorption has been used to investigate rotational isomerism in pure liquids. Rate constants cannot be obtained since the equilibria are first-order in both directions; however, the characteristic frequency, and in certain cases the activation energies, of transformation between rotational

isomers can be measured. Hydrogen bonding studies have been done on the dimerization of benzoic and acetic acids in low dielectric solvents.

Various experimental methods for acoustic investigation of relaxation cover a wide range of sound frequencies. A review of these methods is given by Eigen and de Maeyer.¹³ The technique used here is described in Chapter III.

The approach of determining the characteristic frequency of a reaction from changes in the sound absorption of the solution make it desirable to cover as wide a frequency range as possible. First, the absorption curve characterizing a relaxational process is quite broad, covering a full decade in frequency. Secondly, if the process is not a single reaction, but consists of several coupled steps, it may be necessary to cover several decades in order to completely describe the mechanism. Unfortunately, it is not possible to cover more than about a decade and a half on a single piece of equipment. In this work, the equipment used proved capable of making sound absorption measurements over the range 15 to 130 MHz on the system studied. This range, though limited, was adequate to characterize the relaxation curves observed.

C. A Statement of Purpose

Present knowledge of H-bonding kinetics is extremely limited. The goal of this work is to provide an experimental and mathematical technique by which, under certain conditions, reactions involving the hydrogen bond may be studied. It is first necessary to construct absorption-measuring apparatus, the design of which takes into account the particular properties of most organic systems, namely, their very high acoustic absorption

and their volatility. Alcohol solutions in which several polymeric species are formed result in multiple, probably overlapping, relaxation curves which at the present time cannot be unambiguously analyzed. It is therefore desirable to pick a system in which one type of polymer predominates over all others. There is some evidence that small amounts of t-butyl alcohol in an inert solvent form a single polymeric species, although there is not complete agreement on what this species is. For this reason dilute solutions (< 0.26 molar) of this alcohol in cyclohexane were studied at three different temperatures. Musa and Eisner¹¹ have done sound absorption measurements, with a different experimental method than is used here, on this system. Their method of calculation and their results are compared with this work.

II. THEORY

A. Introduction

If the equilibrium conditions of a molecular process are changed instantaneously, a finite time is required for the system to regain equilibrium. Relaxation methods are techniques which use the lag in the attainment of equilibrium to study the molecular process involved. Chemical reactions too fast to be followed by other means can be studied by rapidly changing some parameter, such as temperature or pressure, affecting a chemical equilibrium. Either the concentration of one of the reacting species, or some other property affected by the time lag, is recorded as the reaction attempts to regain equilibrium. The ultrasonic technique uses an adiabatic sound wave to cause local fluctuations in pressure and temperature. Reactions having a volume or enthalpy change are in general affected by the sound wave. The rate at which the reacting system approaches equilibrium depends on the concentrations of the species involved and the rate constants. Under certain conditions this rate can be expressed in terms of a characteristic time constant (part B). By considering the response of the reacting species to the sound wave, the time constant can be related to the experimentally measurable amplitude absorption coefficient and to the time dependent (or relaxational) compressibility (part C). After expressing the relaxational compressibility as a function of thermodynamic parameters, an equation is obtained expressing the absorption coefficient in terms of the sound frequency and the time

constant (part D). The time constant can be obtained from the frequency dependence of the absorption coefficient. From the concentration dependence of the time constant (part E), the rate constants and equilibrium constant of the reaction may be calculated.

B. Chemical Relaxation

The rate of approach of the i th reacting species of a chemical equilibrium is proportional to the difference between the actual and equilibrium concentrations of i (denoted C_i and C_{ie} , respectively) providing the displacements from equilibrium are very small:^{13a,14a}

$$-\frac{dC_i}{dt} \propto (C_i - C_{ie}) ,$$

which can be written:

$$-\frac{dC_i}{dt} = \frac{C_i - C_{ie}}{\tau} , \quad (2.1)$$

where τ has the units of time. τ is a time constant characteristic of the reaction at a specified temperature, pressure, and C_{ie} , and is called the relaxation time. τ is independent of the actual concentration of i , C_i , as long as the displacements from equilibrium are small.

If a sound wave is used as the perturbation, C_{ie} varies sinusoidally about its mean, say C_{io} . The value of C_{io} is determined by external temperature and pressure. If we define

$$X_i = C_i - C_{io} \quad \text{and} \quad X_{ie} = C_{ie} - C_{io} , \quad (2.1a)$$

then equation (2.1) can be written:

$$-\frac{dC_i}{dt} = -\frac{dX_i}{dt} = \frac{X_i - X_{ie}}{\tau} . \quad (2.2)$$

X_{ie} , like C_{ie} , varies sinusoidally with time and is described by the function

$$X_{ie} = p \sin(\omega t - \phi) . \quad (2.3)$$

p is the amplitude of the oscillations and ω is the angular frequency.

Equation (2.3) can be written in the complex form,

$$X_{ie} = p e^{j\omega t} . \quad (2.4)$$

The time dependent behavior of X_i as a function of frequency can be seen by solving the differential equation (2.2) with X_{ie} given by (2.4). The result is

$$X_i = \left(\frac{1}{1 + j\omega\tau} \right) X_{ie} = \sigma X_{ie} . \quad (2.4a)$$

Separating real and imaginary parts of σ gives

$$X_i = \left[\frac{1}{1 + \omega^2\tau^2} - j \frac{\omega\tau}{1 + \omega^2\tau^2} \right] X_{ie} \quad (2.5)$$

When the period of the oscillation is long compared to the relaxation time (i.e., "low frequencies"); that is when $1/\omega \gg \tau$, then

$$\frac{1}{1 + \omega^2\tau^2} \rightarrow 1 \quad \text{and} \quad \frac{\omega\tau}{1 + \omega^2\tau^2} \rightarrow 0 .$$

So that (2.5) becomes $X_i \approx X_{ie}$.

In other words, under this condition the actual concentration of i at any instant is determined by the equilibrium conditions at that instant. When $\tau \gg 1/\omega$, then

$$\frac{1}{1 + \omega^2 \tau^2} \rightarrow 0 \quad \text{and} \quad \frac{\omega \tau}{1 + \omega^2 \tau^2} \rightarrow 0.$$

At high frequencies, therefore, X_i ceases to oscillate at all.

C. The Absorption Coefficient

If no energy is absorbed from a pressure wave passing through a medium, the wave can be represented by:

$$p = p_0 e^{j\omega(t - n\lambda/C_0)} \quad (2.6)$$

where λ is the wavelength, C_0 the phase velocity, and t the total time necessary for the wave to travel x cm from the sound source. p_0 is the amplitude of the wave. If the wave perturbs an equilibrium process, then the amplitude of the wave diminishes with distance due to the energy lost by the wave in performing the work. The amplitude x cm from the source is:^{13b}

$$p_0 e^{-\alpha x},$$

where α is a constant whose magnitude depends on the amount of energy lost per cm of travel. α is called the amplitude absorption coefficient. When relaxation occurs, then, the pressure wave is described by:

$$p = p_0 e^{j\omega(t - n\lambda/C_0) - \alpha x}$$

or
$$p = p_o e^{j\omega[t-x(1/c_o + \alpha/j\omega)]} , \quad (2.7)$$

since when n is large $n\lambda \approx x$.

The term

$$\left(\frac{1}{c_o} + \frac{\alpha}{j\omega} \right) \quad (2.8)$$

represents the inverse of the velocity when absorption due to a perturbation takes place.

The velocity of an adiabatic pressure wave is given by:¹⁵

$$\frac{1}{c^2} = \beta \rho \quad (2.9)$$

where ρ is the density and β the adiabatic compressibility of the medium.

β is defined by:^{14b}

$$\beta = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S . \quad (2.10)$$

The affinity A and extent of reaction ξ are introduced from the expression for the Gibbs free energy:

$$dG = -SdT + VdP - Ad\xi ,$$

where
$$A = - \sum_i \nu_i \mu_i , \quad (2.10a)$$

and
$$d\xi = dn_i / \nu_i . \quad (2.10b)$$

ν_i , μ_i , and n_i are the stoichiometric coefficient, chemical potential,

and mole number, respectively, of component i of a reaction. Considering the volume as a function of P and ξ , the partial in (2.10) may be expanded to give:

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,\xi} - \frac{1}{V}\left(\frac{\partial V}{\partial \xi}\right)_{S,P}\left(\frac{\partial \xi}{\partial P}\right)_S \quad (2.11)$$

The first term on the right side represents the value of β at extremely high frequencies where, as we have seen, the concentration of the reacting species becomes constant. The term is usually denoted by β_∞ and called the residual compressibility.^{13c} The value of the remaining term decreases from a static value at low frequency to zero at very high frequencies, where ξ does not respond at all to the adiabatic pressure wave. This term may be denoted $\delta\beta$ and called the excess or relaxational compressibility. Equation (2.11) can therefore be written:

$$\beta = \beta_\infty + \delta\beta \quad (2.12)$$

Consider for a moment the adiabatic compressibility of a system in which ξ is in phase with the instantaneous equilibrium conditions at all frequencies; i.e., $A = 0$. Equation (2.10) then becomes:

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,A} \quad (2.12a)$$

Expanding in the same way as (2.10):

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,\xi} - \frac{1}{V}\left(\frac{\partial V}{\partial \xi}\right)_{S,P}\left(\frac{\partial \xi}{\partial P}\right)_{S,A} \quad (2.12b)$$

The first term is identical with β_∞ above. The second, which is constant

at all frequencies, may be denoted by $\delta\beta_e$. If (2.4a) is written in terms of ξ , we have:

$$\xi = \sigma \xi_e .$$

It follows that: $\left(\frac{\partial \xi}{\partial P}\right)_S = \sigma \left(\frac{\partial \xi_e}{\partial P}\right)_S = \sigma \left(\frac{\partial \xi}{\partial P}\right)_{S,A} .$

Substituting this expression into the definition of $\delta\beta$:

$$\delta\beta = - \frac{1}{V} \left(\frac{\partial V}{\partial \xi}\right)_{S,P} \left(\frac{\partial \xi}{\partial P}\right)_{S,A} \sigma$$

or
$$\delta\beta = \delta\beta_e \sigma .$$

(2.12) can now be written:

$$\beta = \beta_\infty + \delta\beta_e \sigma ,$$

Substitution into (2.9) yields:

$$\frac{1}{c^2} = (\beta_\infty + \sigma \delta\beta_e) \rho . \quad (2.13)$$

(2.13) gives the velocity of an adiabatic sound wave when a relaxational process occurs and is identical to the velocity of (2.8). Separating the real and imaginary parts of (2.13) yields:

$$\frac{1}{c^2} = \left[\frac{\beta_\infty \rho + \delta\beta_e \rho + \beta_\infty \rho \omega^2 \tau^2}{1 + \omega^2 \tau^2} \right] - j \left[\frac{\delta\beta_e \rho \omega \tau}{1 + \omega^2 \tau^2} \right] . \quad (2.14)$$

Squaring (2.8):

$$\frac{1}{c^2} = \left[\frac{1}{c_o} - \frac{\alpha^2}{\omega^2} \right] - j \left[\frac{2\alpha}{c_o \omega} \right] . \quad (2.15)$$

Equating the imaginary parts of (2.14) and (2.15):

$$\frac{2\alpha}{c_o \omega} = \delta\beta_e \cdot \rho \cdot \frac{\omega\tau}{1 + \omega^2\tau^2} . \quad (2.16)$$

D. The Absorption Coefficient and Thermodynamics

The relaxational part of the adiabatic compressibility, $\delta\beta_e$, can be expressed as a function of measurable thermodynamic quantities. The method of obtaining the desired expression is to define certain thermodynamic coefficients in terms of partial derivatives. The definitions of these coefficients can be split into residual and relaxational parts. The resulting expressions can be combined with the definition of $\delta\beta_e$ arising from (2.12b):

$$\delta\beta_e = - \frac{1}{V} \left(\frac{\partial V}{\partial \xi} \right)_{S,P} \left(\frac{\partial \xi}{\partial P} \right)_{S,A} , \quad (2.17)$$

to give:

$$\delta\beta_e = \frac{V(\gamma - 1)\beta}{C_{P\infty}RT^2 \sum_i (v_i^2/c_i)} \left(\Delta H - \frac{C_P \Delta V}{V\theta} \right)^2 . \quad (2.37)$$

The symbols are defined below. Principal sources for this chapter are given by references 13, 14, 19 and 20.

First, we shall obtain expressions for the partials to be used in the derivation of (2.37) from the definitions of the coefficients and

their residual and excess parts. Second, two needed thermodynamic equations will be derived. In the third section, we shall combine the results of the first two to obtain (2.37). In the last section we shall relate $\delta\beta_e$ to the absorption parameter, α/f^2 .

(1) Thermodynamic Coefficients. The constant volume and constant pressure heat capacities, and the thermal coefficient of expansion are defined as follows:^{14b}

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V, \quad (2.19)$$

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P, \quad (2.20)$$

$$\theta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P. \quad (2.21)$$

E, H, S, T, V, and P have their usual meaning. By considering the extensive variable of the partial derivatives in (2.19) through (2.21) as functions of T and ξ , the partials may be expanded in the same way the partial of (2.10) was to obtain (2.11). We then define the residual (indexed ∞) and relaxational (designated δC_{Pe} , e.g.) parts of the coefficients defined by (2.19) through (2.21), as was done for the adiabatic compressibility, at constant A, in part C. We then have:^{14b}

$$C_{V\infty} = T \left(\frac{\partial S}{\partial T} \right)_{V,\xi}, \quad (2.22)$$

$$\delta C_{Ve} = T \left(\frac{\partial S}{\partial \xi} \right)_{V,T} \left(\frac{\partial \xi}{\partial T} \right)_{V,A}; \quad (2.23)$$

$$C_{P\infty} = T \left(\frac{\partial S}{\partial T} \right)_{P,\xi}, \quad (2.24)$$

$$\delta C_{Pe} = T \left(\frac{\partial S}{\partial \xi} \right)_{P,T} \left(\frac{\partial \xi}{\partial T} \right)_{P,A} ; \quad (2.25)$$

$$\theta_{\infty} = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P,\xi} , \quad (2.26)$$

$$\delta \theta_e = \frac{1}{V} \left(\frac{\partial V}{\partial \xi} \right)_{P,T} \left(\frac{\partial \xi}{\partial T} \right)_{P,A} . \quad (2.27)$$

The volume and enthalpy change of the reaction may be defined by:^{14b}

$$\Delta V = \left(\frac{\partial V}{\partial \xi} \right)_{P,T} , \quad (2.28)$$

$$\Delta H = \left(\frac{\partial H}{\partial \xi} \right)_{P,T} = T \left(\frac{\partial S}{\partial \xi} \right)_{P,T} \quad (2.29)$$

Other needed expressions are obtained from combinations of the above.

(2.29) and (2.25) may be combined to give:

$$\left(\frac{\partial \xi}{\partial T} \right)_{P,A} = \frac{\delta C_{Pe}}{\Delta H} . \quad (2.30)$$

A useful expression for $(\partial \xi / \partial P)_{T,A}$ may be obtained by using the Maxwell relation:^{16a}

$$\left(\frac{\partial V}{\partial T} \right)_P = - \left(\frac{\partial S}{\partial P} \right)_T ,$$

to rewrite the definition of θ , (2.21), as

$$\theta = - \frac{1}{V} \left(\frac{\partial S}{\partial P} \right)_{T,A} .$$

Expanding $(\partial S/\partial P)_{T,A}$ in the usual way and identifying θ_∞ and $\delta\theta_e$ with the resulting terms, we obtain:

$$\delta\theta_e = - \frac{1}{V} \left(\frac{\partial S}{\partial \xi} \right)_{T,P} \left(\frac{\partial \xi}{\partial P} \right)_{T,A}$$

Substituting from (2.29) and rearranging gives:

$$\left(\frac{\partial \xi}{\partial P} \right)_{T,A} = - \frac{TV \delta\theta_e}{\Delta H} .$$

It will be convenient to express the partials to be used in terms of the same excess quantity. We therefore obtain a relation between $\delta\theta_e$ and δC_{Pe} . Substitution of (2.28) into (2.27) yields:

$$\left(\frac{\partial \xi}{\partial T} \right)_{P,A} = \frac{V \delta\theta_e}{\Delta V} .$$

This may be combined with (2.30) to give:

$$\delta\theta_e = \frac{\Delta V \delta C_{Pe}}{V \Delta H} .$$

The above expression for $(\partial \xi/\partial P)_{T,A}$ can therefore be written as:

$$\left(\frac{\partial \xi}{\partial P} \right)_{T,A} = - \frac{T \Delta V \delta C_{Pe}}{\Delta H^2} \quad (2.31)$$

(2) Derivations. It is necessary to express the excess quantity δC_{Pe} , which will appear in $\delta\beta_e$ by means of (2.30) and (2.31), in terms of thermodynamic quantities. Eigen has indicated how this can be done.^{13d} We start with a transformation formula:¹⁷

$$\left(\frac{\partial \xi}{\partial T}\right)_{P,A} = -\left(\frac{\partial \xi}{\partial A}\right)_{P,T} \left(\frac{\partial A}{\partial T}\right)_{P,\xi} ,$$

and a Maxwell relation:^{16a}

$$\left(\frac{\partial A}{\partial T}\right)_{P,\xi} = \left(\frac{\partial S}{\partial \xi}\right)_{P,T} ,$$

to obtain:

$$\left(\frac{\partial \xi}{\partial T}\right)_{P,A} = -\left(\frac{\partial \xi}{\partial A}\right)_{P,T} \left(\frac{\partial S}{\partial \xi}\right)_{P,T} .$$

We then substitute for $(\partial \xi / \partial T)_{P,A}$ from (2.30), and for $(\partial S / \partial \xi)_{P,T}$ from (2.29) to obtain, upon rearrangement:

$$\delta C_{Pe} = - \frac{\Delta H^2}{T(\partial A / \partial \xi)_{P,T}} .$$

A was defined by (2.10a):

$$A = - \sum_i v_i \mu_i ,$$

where v_i is the stoichiometric coefficient of the i th species in a reaction, and μ_i is the chemical potential of i , defined by:

$$\mu_i = \mu_i^{\circ} + RT \ln a_i .$$

μ_i° is the potential at defined standard conditions and a_i is the activity of i . The definition of A can therefore be written

$$A = - \sum_i \nu_i \mu_i^0 - RT \sum_i \nu_i \ln a_i .$$

Taking the partial of A with respect to ξ at constant P and T:

$$\left(\frac{\partial A}{\partial \xi} \right)_{P,T} = - RT \sum_i \nu_i \left(\frac{\partial \ln a_i}{\partial \xi} \right)_{P,T} .$$

If we restrict ourselves to dilute solutions, then the definition of $\partial \xi$ can be written:

$$\partial \xi = \left(\frac{\partial n_i}{\nu_i} \right) = \left(\frac{\partial C_i}{\nu_i} \right)_V ,$$

where C_i is the molar concentration of i. If, in addition, we consider cases in which the activity coefficient is unity, then

$$\left(\frac{\partial \ln a_i}{\partial \xi} \right) = \frac{\nu_i}{V a_i} \left(\frac{\partial a_i}{\partial C_i} \right) = \frac{\nu_i}{C_i V} ,$$

and $(\partial A / \partial \xi)_{P,T}$ becomes:

$$\left(\frac{\partial A}{\partial \xi} \right)_{P,T} = - \frac{RT}{V} \sum_i (\nu_i^2 / C_i) .$$

The expression for δC_{Pe} is therefore:

$$\delta C_{Pe} = \frac{V \Delta H^2}{RT^2 \sum_i (\nu_i^2 / C_i)} . \quad (2.32)$$

We shall also use the relationship:

$$\gamma - 1 = \frac{TV\theta^2}{C_P\beta} \quad (2.33)$$

where $\gamma = C_P/C_V$. This expression may be derived from the relation between enthalpy and internal energy:^{16b}

$$dH = dE + VdP + PdV.$$

Taking the partial with respect to T at constant P:

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P.$$

Expanding the partial $(\partial E/\partial T)_P$ in terms of T and V yields:

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P.$$

$(\partial E/\partial T)_V$ is the constant volume heat capacity, (2.19). From:

$$\partial E = T \partial S - P \partial V,$$

we can write:

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P,$$

so that $(\partial E/\partial T)_P$ becomes:

$$\left(\frac{\partial E}{\partial T}\right)_P = C_V + \left[T\left(\frac{\partial S}{\partial V}\right)_T - P\right]\left(\frac{\partial V}{\partial T}\right)_P.$$

This equation may be substituted into the $(\partial H/\partial T)_P$ expression above to give:

$$C_P - C_V = T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial V} \right)_T \cdot V\theta ,$$

where we substitute for $(\partial V/\partial T)_P$ from (2.21). $(\partial S/\partial V)_T$ can be expanded using two basic transformation formulas:¹⁷

$$\begin{aligned} \left(\frac{\partial S}{\partial V} \right)_T &= - \left(\frac{\partial S}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial S}{\partial T} \right)_V \left(\frac{\partial T}{\partial P} \right)_S \left(\frac{\partial P}{\partial V} \right)_S \\ &= \left(\frac{\partial S}{\partial T} \right)_V \left(\frac{\partial T}{\partial S} \right)_P \left(\frac{\partial S}{\partial P} \right)_T \left(\frac{\partial P}{\partial V} \right)_S . \end{aligned}$$

We may substitute $-(\partial V/\partial T)_P$ for $(\partial S/\partial P)_T$, according to the Maxwell formulas.^{18a} Using the definitions (2.19), (2.20), (2.21), and (2.12a) of C_V , C_P , θ , and β , respectively, we obtain for $(\partial S/\partial V)_T$:

$$\left(\frac{\partial S}{\partial V} \right)_T = \frac{C_V \theta}{C_P \beta} .$$

The difference between the heat capacities can therefore be written as:

$$C_P - C_V = \frac{TV\theta^2 C_V}{C_P \beta} ,$$

or:

$$\gamma - 1 = \frac{TV\theta^2}{C_P \beta} . \quad (2.33)$$

(3) The Relaxational Compressibility, $\delta\beta_e$. From (2.12b), $\delta\beta_e$ is defined by:

$$\delta\beta_e = - \frac{1}{V} \left(\frac{\partial V}{\partial \xi} \right)_{S,P} \left(\frac{\partial \xi}{\partial P} \right)_{S,A} . \quad (2.17)$$

We shall take each of the partials of (2.17) and, using some of the above relations, express them in terms of thermodynamic quantities.

(a) $(\partial V/\partial \xi)_{S,P}$. This partial may be expanded in terms of T and ξ :¹⁷

$$\left(\frac{\partial V}{\partial \xi}\right)_{S,P} = \left(\frac{\partial V}{\partial \xi}\right)_{T,P} + \left(\frac{\partial V}{\partial T}\right)_{P,\xi} \left(\frac{\partial T}{\partial \xi}\right)_{P,S} .$$

We may substitute for $(\partial V/\partial \xi)_{T,P}$ and $(\partial V/\partial T)_{P,\xi}$ from (2.28) and (2.26) respectively:

$$\left(\frac{\partial V}{\partial \xi}\right)_{S,P} = \Delta V + v\theta_{\infty} \left(\frac{\partial T}{\partial \xi}\right)_{P,S} .$$

The remaining partial, $(\partial T/\partial \xi)_{P,S}$, can be expressed:

$$\left(\frac{\partial T}{\partial \xi}\right)_{P,S} = - \left(\frac{\partial T}{\partial S}\right)_{P,\xi} \left(\frac{\partial S}{\partial \xi}\right)_{T,P} .$$

We may substitute for these partial derivatives from (2.24) and (2.29) respectively to obtain:

$$\left(\frac{\partial T}{\partial \xi}\right)_{P,S} = - \frac{\Delta H}{C_{P\infty}} .$$

$(\partial V/\partial \xi)_{S,P}$, upon rearrangement, now becomes:

$$\left(\frac{\partial V}{\partial \xi}\right)_{S,P} = V \Delta H \left(\frac{\Delta V}{V \Delta H} - \frac{\theta_{\infty}}{C_{P\infty}} \right) . \quad (2.34)$$

(b) $(\partial \xi/\partial P)_{S,A}$. We can expand $(\partial \xi/\partial P)_{S,A}$ just as we did $(\partial V/\partial \xi)_{S,P}$, obtaining:

$$\left(\frac{\partial \xi}{\partial P}\right)_{S,A} = \left(\frac{\partial \xi}{\partial P}\right)_{T,A} + \left(\frac{\partial \xi}{\partial T}\right)_{P,A} \left(\frac{\partial T}{\partial P}\right)_{S,A} .$$

Expressions for $(\partial \xi / \partial P)_{T,A}$ and $(\partial \xi / \partial T)_{P,A}$ have already been derived, equations (2.31) and (2.30) respectively. $(\partial T / \partial P)_{S,A}$ may be written:

$$\left(\frac{\partial T}{\partial P}\right)_{S,A} = - \left(\frac{\partial T}{\partial S}\right)_{P,A} \left(\frac{\partial S}{\partial P}\right)_{T,A} .$$

Since $(\partial S / \partial P)_T = -(\partial V / \partial T)_P$, ^{16a} then:

$$\left(\frac{\partial T}{\partial P}\right)_{S,A} = \left(\frac{\partial T}{\partial S}\right)_{P,A} \left(\frac{\partial V}{\partial T}\right)_{P,A} .$$

We may use the definitions of C_P and θ [equations (2.20) and (2.21) respectively] to obtain:

$$\left(\frac{\partial T}{\partial P}\right)_{S,A} = \frac{TV\theta}{C_P}$$

Substituting this result, (2.30), and (2.31) into the above $(\partial \xi / \partial P)_{S,A}$ expression, we get:

$$\left(\frac{\partial \xi}{\partial P}\right)_{S,A} = - \frac{T \Delta V \delta C_{Pe}}{\Delta H^2} + \frac{\delta C_{Pe}}{\Delta H} \cdot \frac{TV\theta}{C_P} ,$$

or

$$\left(\frac{\partial \xi}{\partial P}\right)_{S,A} = - \frac{TV \delta C_{Pe}}{\Delta H} \left(\frac{\Delta V}{V \Delta H} - \frac{\theta}{C_P} \right) . \quad (2.35)$$

(2.34) and (2.35) may be substituted for the partials in the $\delta \beta_e$ definition, equation (2.17), to give:

$$\delta\beta_e = TV \delta C_{Pe} \left(\frac{\Delta V}{V \Delta H} - \frac{\theta}{C_P} \right) \left(\frac{\Delta V}{V \Delta H} - \frac{\theta_\infty}{C_{P\infty}} \right) .$$

The parentheses can be combined:

$$\delta\beta_e = \frac{\theta^2 TV \delta C_{Pe}}{C_P C_{P\infty}} \left(\frac{\Delta V C_P}{\theta V \Delta H} - 1 \right)^2 \quad (2.36)$$

The desired expression for $\delta\beta_e$ can now be obtained by substituting the two relationships derived in (2) [equations (2.32) and (2.33)] into (2.36), which gives:

$$\delta\beta_e = \frac{V(\gamma - 1)\beta \Delta H^2}{C_{P\infty} RT^2 \sum (v_i^2 / C_i)} \left(\frac{C_P \Delta V}{\theta V \Delta H} - 1 \right)^2$$

or

$$\delta\beta_e = \frac{V(\gamma - 1)\beta}{C_{P\infty} RT^2 \sum (v_i^2 / C_i)} \left(\frac{C_P \Delta V}{\theta V} - \Delta H \right)^2 . \quad (2.37)$$

(4) A definitive expression for the absorption coefficient may now be obtained by substituting (2.37) into (2.16):

$$\frac{\alpha'}{\omega} = \left[\frac{V(\gamma - 1)\beta \rho C_o}{2C_{P\infty} RT^2 \sum (v_i^2 / C_i)} \left(\frac{C_P \Delta V}{\theta V} - \Delta H \right)^2 \right] \left(\frac{\omega \tau}{1 + \omega^2 \tau^2} \right) . \quad (2.38)$$

α'/ω is the absorption per cycle due to the chemical relaxation. At a specific temperature, pressure, and equilibrium concentration, C_{io} , the terms in the brackets will be constant, providing our original assumption

of small displacements from equilibrium holds true. By calculating α'/ω at different values of $\omega\tau$, one can see that this absorption function maximizes at $\omega\tau = 1$. The frequency, in Hz, at which this occurs is called the relaxation frequency; and since $\omega = 2\pi f$, then:

$$\tau = \frac{1}{2\pi f_c} \quad (2.39)$$

where f_c is the relaxation frequency.

If we substitute $\omega = 2\pi f$ and (2.39) into (2.38); and if we designate all of the terms of (2.38) that are constant at a given P, T, and C_{i0} as A, then we obtain:

$$\frac{\alpha'}{f^2} = \frac{A}{1 + (f/f_c)^2} \quad (2.40)$$

where the absorption parameter α/f^2 has units of $\text{sec}^2 \cdot \text{cm}^{-1}$, and A is given by:

$$A = \frac{\pi(\gamma - 1)\rho\beta C_o V}{f_c C_{P0} RT^2 \sum (v_i^2/C_i)} \left(\frac{C_P \Delta V}{\theta V} - \Delta H \right)^2 \quad (2.40a)$$

Litovitz¹⁸ has shown that pure liquids give rise to absorption due to shear viscosity (η_s):

$$\alpha_\eta = \frac{2\pi^2}{\rho C_o^3} \cdot \frac{4}{3} \eta_s \cdot f^2, \quad (2.41)$$

and thermal conductivity (κ):

$$\alpha_n = \frac{2\pi^2}{\rho C_o^3} (\gamma - 1) \frac{n}{C_P} \cdot f^2 \quad (2.42)$$

The parameter α/f^2 of a liquid obeying (2.41) and (2.42) does not change with frequency and may be designated by the constant B (at a given T and P). The total α/f^2 of a dilute solution in which a single chemical relaxation takes place is therefore:

$$\frac{\alpha}{f^2} = \frac{A}{1 + (f/f_c)^2} + B \quad (2.43)$$

where:

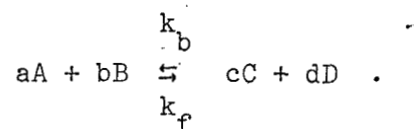
$$B = \frac{2\pi^2}{\rho C_o^3} \left[\frac{4}{3} \eta_s + (\gamma - 1) \frac{n}{C_P} \right]$$

B may also include absorption due to additional chemical relaxations occurring at much higher frequencies. The absorption of a liquid arising from shear viscosity and thermal conductivity is affected by the presence of a solute. B is therefore concentration-dependent. Equation (2.43) holds at constant (external) temperature, pressure, and equilibrium concentrations; we assume small displacements from these externally determined equilibrium conditions. The solution we study is dilute; the activity coefficients of the reacting species are assumed unity.³² (2.43) will be used to evaluate f_c , and therefore τ .

If α/f^2 is plotted against $\log f$, assuming arbitrary values of A, B, and f_c , it is seen that α/f^2 decreases from a low frequency value of $A + B$ through an inflection point (at $f = f_c$) to a high frequency value of B.

E. Kinetics

In this part we shall obtain a generalized expression for the relaxation time as a function of concentrations and rate constants. We start by considering the reaction:



If the condition of small displacements from equilibrium is imposed, then from (2.2) we have:

$$-\frac{dC_A}{dt} = -\frac{dX_A}{dt} = \frac{X_A - X_{Ae}}{\tau} \quad (2.44)$$

C_A is the concentration of A; X_A and X_{Ae} have the same definitions that X_i and X_{ie} had in part B. The general rate equation for this reaction is:

$$-\frac{1}{a} \frac{dC_A}{dt} = k_f C_A^a C_B^b - k_b C_C^c C_D^d \quad (2.45)$$

Combining the definitions of X_i and X_{ie} [equations (2.1a)], we have:

$$C_i = X_i + C_{ie} - X_{ie}$$

Substitution of expressions of this type, in terms of A, B, C, and D, yields:

$$\begin{aligned} -\frac{1}{a} \frac{dC_A}{dt} = & k_f (C_{Ae} + X_A - X_{Ae})^a (C_{Be} + X_B - X_{Be})^b \\ & - k_b (C_{Ce} + X_C - X_{Ce})^c (C_{De} + X_D - X_{De})^d \end{aligned}$$

Expanding each parenthesis gives

$$C_{Ae}^a + aC_{Ae}^{a-1}(X_A - X_{Ae}) + \dots + (X_A - X_{Ae})^a,$$

and analogous expressions for the other components. Since the displacements from equilibrium are small, higher order terms in $(X_A - X_{Ae})$ will be negligible compared with the first two terms. If the higher order terms of each expansion are dropped, the rate expression becomes:

$$\begin{aligned} -\frac{1}{a} \frac{dC_A}{dt} = & k_f [C_{Ae}^a + aC_{Ae}^{a-1}(X_A - X_{Ae})] [C_{Be}^b + bC_{Be}^{b-1}(X_B - X_{Be})] \\ & - k_b [C_{Ce}^c + cC_{Ce}^{c-1}(X_C - X_{Ce})] [C_{De}^d + dC_{De}^{d-1}(X_D - X_{De})]. \end{aligned}$$

Now:
$$\frac{X_A - X_{Ae}}{a} = \frac{X_B - X_{Be}}{b} = -\frac{X_C - X_{Ce}}{c} = -\frac{X_D - X_{De}}{d}.$$

We can therefore substitute $(X_A - X_{Ae})$ for each of the analogous differences of the other reacting species. If this is done, and if terms containing $(X_A - X_{Ae})^2$ are dropped when the brackets are multiplied out, we obtain:

$$\begin{aligned} -\frac{1}{a} \frac{dC_A}{dt} = & k_f \left[C_{Ae}^a C_{Be}^b + a^2 C_{Ae}^{a-1} C_{Be}^b \cdot \frac{X_A - X_{Ae}}{a} \right. \\ & \left. + b^2 C_{Ae}^a C_{Be}^{b-1} \cdot \frac{X_A - X_{Ae}}{a} \right] \\ & - k_b \left[C_{Ce}^c C_{De}^d - c^2 C_{Ce}^{c-1} C_{De}^d \cdot \frac{X_A - X_{Ae}}{a} \right. \\ & \left. - d^2 C_{Ce}^c C_{De}^{d-1} \cdot \frac{X_A - X_{Ae}}{a} \right] \end{aligned}$$

At equilibrium, (2.45) becomes:

$$0 = k_f C_{Ae}^a C_{Be}^b - k_f C_{Ce}^c C_{De}^d .$$

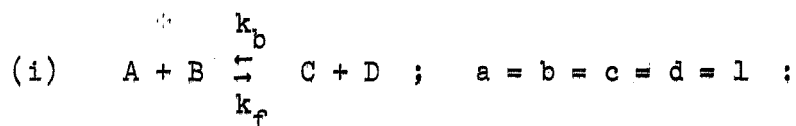
The rate equation can therefore be written:

$$-\frac{dC_A}{dt} = \left[k_f \left(a^2 C_{Ae}^{a-1} C_{Be}^b + b^2 C_{Ae}^a C_{Be}^{b-1} \right) + k_f \left(c^2 C_{Ce}^{c-1} C_{De}^d - d^2 C_{Ce}^c C_{De}^{d-1} \right) \right] \cdot (X_A - X_{Ae}) .$$

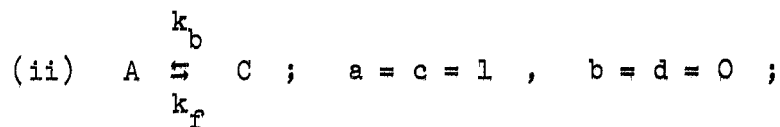
Equating this result with (2.44), we obtain a generalized equation for τ :

$$\tau^{-1} = k_f \left(a^2 C_{Ae}^{a-1} C_{Be}^b + b^2 C_{Ae}^a C_{Be}^{b-1} \right) + k_b \left(c^2 C_{Ce}^{c-1} C_{De}^d + d^2 C_{Ce}^c C_{De}^{d-1} \right) \quad (2.46)$$

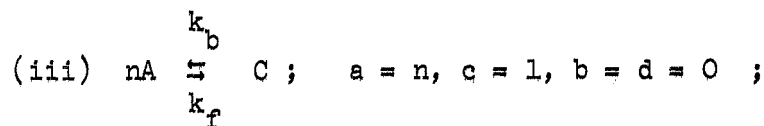
Specific examples of the concentration dependence of τ are given below.



$$\tau^{-1} = k_f (C_{Ae} + C_{Be}) + k_b (C_{Ce} + C_{De}) .$$



$$\tau^{-1} = k_f + k_b .$$



$$\tau^{-1} = n^2 k_f C_{Ae}^{n-1} + k_b . \quad (2.47)$$

III. EXPERIMENTAL

A. Introduction

The ultrasonic absorption spectra of the solutions were obtained by measuring the absorption coefficient α at a series of frequencies between 10 MHz and 130 MHz. At a given frequency, α was obtained by measuring the change in intensity of the ultrasonic waves as a function of the distance between a source and a detector, placed in the solution. Piezoelectric transducers (quartz crystals) were used to generate and detect the sound waves. The pulse technique,^{13,21} in which short pulses of sound are passed through the solution, was used. The electronic equipment used in the absorption measurement is described below. The measurement of the frequency of the sound wave, and the preparation of the solutions are also described.

B. The Cell

The cell design (Fig. 1) is basically that of Warren Slie,²² to whom the author is indebted. The cell was originally designed for high pressure absorption measurements and has several features, described below, considered necessary for work on volatile, highly absorbing systems.

The transducers²³ used to transmit and detect the sound waves are matched to vibrate at the same fundamental frequency by having them cut to the same thickness, since it is this property which controls the fundamental frequency of this type of crystal. The crystals are cut, ground, and optically polished so that higher harmonics of the fundamental are

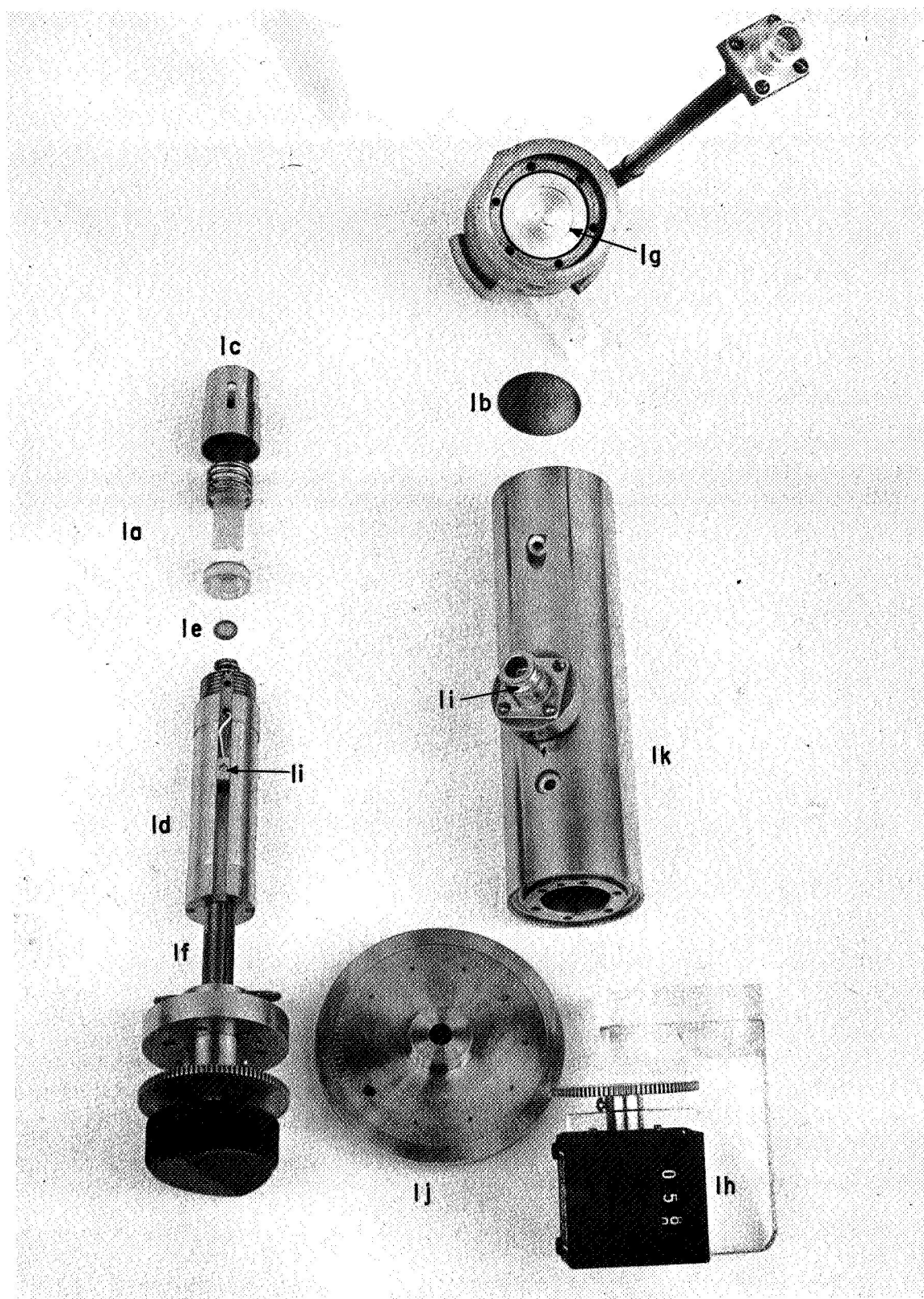


Fig. 1 ULTRASONIC ABSORPTION CELL

Legend to Fig. 1

- 1a. Quartz delay line.
- 1b. Receiving crystal.
- 1c. Transmitting crystal/delay line holder.
- 1d. Piston.
- 1e. Transmitting crystal.
- 1f. Micrometer screw.
- 1g. Receiving crystal contact.
- 1h. Counter.
- 1i. Electric lead for transmitting crystal.
- 1j. Circular dial.
- 1k. Cylinder.

also excited; they are chrome-gold plated for electrical contact.

A sound wave of frequency f [$f = (2n - 1)f_0$, where f_0 equals the fundamental frequency of the crystal] is produced by exciting the transmitting crystal with an rf pulse of the same frequency. This crystal is bonded to a quartz rod or acoustic delay line (1-a, Fig. 1) with an extremely thin coating of "Nonaq" (Fischer, Cat. No. 14-633), care being taken that no air is between the transducer and the rod.

The pulse of sound travels through the delay line into the solution and is detected by the second crystal (1-b), which converts the sound waves back into an rf signal. The amount of the sound energy received at the detecting crystal actually converted into rf signal is quite small, most of the sound wave being reflected back towards the sending crystal. The delay line is largely transparent (acoustically), so the sound pulse reflects off the transmitting crystal, travels again through the delay line and solution to the receiving crystal, and is again reflected. The rf signals resulting from the successive echoes of the sound pulse reaching the detecting transducer appear on an oscilloscope as a series of narrow spikes. The height of successive spikes decreases exponentially.

The function of the delay line is to prevent stray electric impulses from being received.^{13e} It also serves to separate successive echoes, the importance of which is seen in the electronics section.

The principal mechanical functions of the cell are to vary the path length between the two crystals and to measure this variation accurately. This is done by a piston and cylinder arrangement, shown in Fig. 1. The transmitting crystal-delay line assembly is held in a crystal holder (1-c) which screws onto the piston (1-d). The micrometer screw, which is fixed

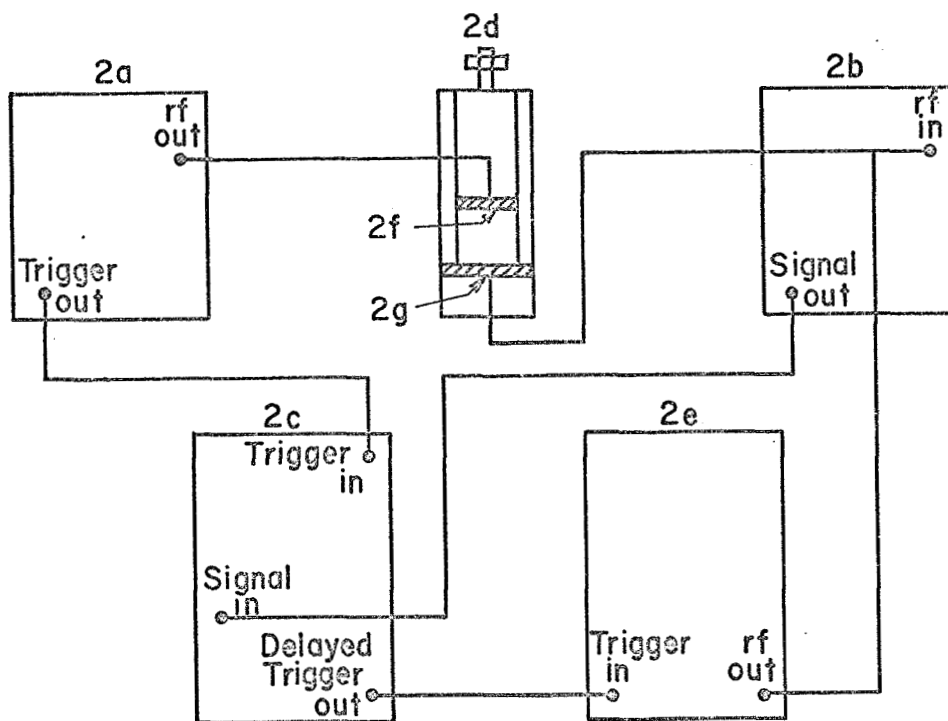
vertically with respect to the cell, threads into the top of the piston. The piston is prevented from rotating about its axis by a key and channel arrangement, so that rotating the micrometer screw moves the piston up or down. A counter and circular dial count revolutions (and fractions thereof) of the micrometer screw. This is easily converted into centimeters of piston travel since the screw has forty threads per inch.

Two important features of this cell design are (1) the leveling of the crystals and (2) sealing of the solution from the atmosphere. The surfaces of the transmitting and receiving crystals must be parallel to each other or the distances recorded on the micrometer will be in error. In this cell this is accomplished by accurate machining of the surfaces supporting the transducers. These surfaces were the bottom of the piston and of the cylinder. The high acoustic absorption (up to $\alpha = 34 \text{ cm}^{-1}$) of the system measured meant that the use of leveling screws, a device used in some cell designs to level the crystals by mechanically changing the position of one crystal with respect to the other, would have been very difficult at the higher frequencies.

The second feature mentioned above is necessary to prevent (1) evaporation of the solution and (2) absorption of moisture by the solution. The loading of the solution into the cell is accomplished by a syringe fitting snugly into a hole bored through the cell wall. Before filling the cell is purged with dry nitrogen.

C. The Electronics

A block diagram of the electronic circuit is shown in Fig. 2. The rf signal from a pulsed oscillator (2-a) is used to excite the transmitting



LEGEND :

- 2a. ARENBERG PG-650C PULSED OSCILLATOR
- 2b. NAVY MODEL RDO RECEIVER
- 2c. TETRONIX 545A OSCILLOSCOPE
- 2d. ULTRASONIC ABSORPTION CELL
- 2e. HEWLETT-PACKARD 608D VHF SIGNAL GENERATOR
- 2f. TRANSMITTING CRYSTAL
- 2g. RECEIVING CRYSTAL

Fig. 2 BLOCK DIAGRAM OF ULTRASONIC ABSORPTION APPARATUS.

crystal. The rf signal from the receiving crystal is fed into an amplifier (2-b) and displayed on an oscilloscope (2-c) as the exponentially decreasing series of spikes described earlier. Attenuation measurements are made by comparing the change in height of the first spike of the cell signal with an equal change in height of a pulse produced by a signal generator. This pulse, the comparator signal, consists of a single spike and can be accurately attenuated. The height of the cell signal is changed by increasing or decreasing the distance between the crystals. The coefficient α is obtained from the slope of a plot of distances, in centimeters, versus corresponding attenuation, in decibels. The units of α are converted from $\text{db}\cdot\text{cm}^{-1}$ to cm^{-1} by dividing by 8.686.^{13b}

An Arenberg PG-650C high power, pulsed oscillator is used to excite the sending crystal. The oscillator was modified to be used over the range 8-220 MHz. The pulses are 3-5 μsec long.

It is necessary that the pulser, signal generator and receiver be tuned to the same frequency. In addition, the pulses from the oscillator and the signal generator, as well as the sweep of the scope, must be synchronized. To accomplish this the pulse generator triggers itself, the oscilloscope, and the signal generator. To enable the comparator pulse to be moved relative to the cell signal, the triggering voltage to the signal generator is fed through a variable trigger delay. This is used to prevent the comparator spike from overlapping one of the spikes of the cell signal. The delay line separates the latter enough so that the comparator pulse can be placed between the first and second spikes of the cell signal.

At higher frequencies it is necessary to use a Weinschel DS-109H double-stub tuner between the oscillator and the transmitting crystal to

optimize energy transfer to the crystal. At the lowest frequencies, 15-25 MHz, an attenuator is used to prevent overloading the sending crystal.

The output of the receiving crystal is amplified by a Navy model RDO receiver and displayed on a Tektronix 545A oscilloscope. The receiver has a range of 38 to 1000 MHz, which is extended down to approximately 10 MHz by use of a plug-in preamplifier designed for this purpose. The RDO has a measured sensitivity of 8-9 μ volts at 50 MHz, decreasing steadily to 45-50 μ volts at 150 MHz. This decreasing sensitivity proved to be the principal barrier to measuring at higher frequencies.

The signal generator producing the comparator signal is a Hewlett-Packard 608D VHF generator. The frequency at which the absorption measurement was made is measured on a Gertsch FM-3 VHF frequency meter. This is done by (1) beating the continuous-wave output of the signal generator against the cell signal to resonance using the oscilloscope, (2) determining the resulting frequency of the generator with the Gertsch FM-3. The measurement was found to be reproducible within several kilocycles.

D. Materials

Cyclohexane was distilled from P_2O_5 , passed through a 45 cm x 3.5 cm column of Linde 4A molecular sieve into a vessel without exposure to the air. The vessel was designed so that solvent could be transferred to volumetric flasks with very brief contact with the air. The t-Butanol was handled the same way, except that it was distilled from CaO. It was necessary to warm the apparatus slightly to prevent freezing of the alcohol. The solutions were made up by weight and injected into the cell with a syringe, as mentioned before.

IV. RESULTS

A. Introduction

Absorption measurements of solutions of t-butyl alcohol in cyclohexane were carried out to clarify the association behavior and, if possible, to obtain the rate constants involved. Measurements were taken at three (or four) concentrations, at each temperature to determine the concentration dependence of the relaxation time τ , thus enabling the rate constants and equilibrium constant to be evaluated. From the temperature dependence of these three parameters the enthalpy change of the reaction and the activation energies of the association and dissociation processes can be calculated from the van't Hoff^{16c} and Arrhenius^{21a} expressions, respectively. Measurements were made at 5°, 10°, and 15°C; the concentrations ranged from 0.1 to 0.25 molar.

f_c , hence τ , was calculated from the absorption data by means of equation (2.43).

B. The Initial Data

The attenuation, which is recorded in terms of power ratios and has the unit of decibels, is a linear function of distance. The slope of a plot of these quantities gives the absorption of the solution in decibels/cm. In order to obtain α , the pressure amplitude absorption coefficient, the value of the absorption in db/cm must be divided by 8.686.^{13b} The recorded data were processed using a computer technique (see Appendix A).

The slope of each attenuation-distance set was calculated by a least squares method. The results of three such series were averaged for each value of α . At higher frequencies, where the uncertainty becomes larger, four or five determinations were made. The standard deviation of α was calculated from:

$$\frac{1}{n-1} \sum_{i=1}^n (\alpha_i - \bar{\alpha})^2 = \frac{1}{n-1} \left[\sum_{i=1}^n \alpha_i^2 - \frac{(\sum_{i=1}^n \alpha_i)^2}{n} \right] .$$

n is the number of determinations of α , $\bar{\alpha}$ is the mean value. The uncertainty in the frequency is negligible compared to that in the absorption coefficient. The quantity α/f^2 was calculated from the mean and from the measured frequency.

Since pure cyclohexane has no relaxation up to 200 MHz,^{14c} α/f^2 should be constant over the frequency range used. The precision of the measurements of the cell was tested by determining α/f^2 from 25 to 125 MHz, at 25°C. These results are shown in Table I. The precision is seen to be excellent. The average value of $198.8 \times 10^{-17} \text{ sec}^2 \cdot \text{cm}^{-1}$ compares well with literature values of $192 \times 10^{-17} \text{ sec}^2 \cdot \text{cm}^{-1}$,^{14c} and $200 \times 10^{-17} \text{ sec}^2 \cdot \text{cm}^{-1}$,¹¹ the latter at 27°C. Measured α/f^2 values of the pure solvent at 10°C and 15°C are shown in Table II.

Absorption measurements of solutions of t-butanol in cyclohexane are given in Tables III through XII.

Table I. Measured Absorption of Cyclohexane at 25°C

f, MHz	α , cm ⁻¹	Standard deviation of α	$\alpha/f^2 \times 10^{17}$ cm ² ·sec ⁻¹
25.031	1.241	0.0031	198.1
35.165	2.458	0.0075	198.8
45.148	4.051	0.0274	198.7
65.210	8.406	0.2830	197.7
85.280	14.47	0.4089	199.0
115.192	26.26	0.1432	197.9
125.288	31.67	0.1323	201.8

Table II. Measured Absorption of Cyclohexane

T, °C	$\alpha/f^2 \times 10^{17}$ cm ² ·sec ⁻¹
10.	179.
15.	187.
25.	199.

Table III. Measured Absorption of 0.151 Molar t-Butyl Alcohol in Cyclohexane at 5°C

f, MHz	α , cm ⁻¹	Standard deviation of α	$\alpha/f^2 \times 10^{17}$ sec ² .cm ⁻¹
15.099	0.9558	0.0158	419.2
25.141	2.247	0.0335	355.5
35.173	3.722	0.0369	300.9
45.176	5.375	0.0542	263.4
55.196	7.274	0.0120	238.8
65.230	9.538	0.1174	224.2
75.344	11.90	0.2300	209.6
105.284	21.07	0.4119	190.1

Table IV. Measured Absorption of 0.199 Molar t-Butyl Alcohol in Cyclohexane at 5°C

f, MHz	α , cm ⁻¹	Standard deviation of α	$\alpha/f^2 \times 10^{17}$ sec ² .cm ⁻¹
15.460	1.016	0.0032	424.9
25.079	2.332	0.0047	370.8
35.169	4.023	0.0091	325.3
45.228	5.748	0.0331	281.0
55.212	7.908	0.0691	259.4
65.224	10.01	0.0340	235.3
75.220	12.78	0.0505	225.9
85.360	15.42	0.0580	211.6
105.284	21.33	0.0824	192.5
125.272	31.11	0.1224	198.2

Table V. Measured Absorption of 0.246 Molar t-Butyl Alcohol
in Cyclohexane at 5°C

f, MHz	α , cm ⁻¹	Standard deviation in α	$\alpha/f^2 \times 10^{17}$ sec ² ·cm ⁻¹
15.460	1.021	0.0035	427.2
25.141	2.350	0.0250	371.8
35.145	4.110	0.0163	332.7
45.214	6.054	0.0235	296.1
55.204	8.139	0.0316	267.1
65.392	10.63	0.0921	248.6
75.276	13.20	0.0601	233.0
85.348	16.10	0.0508	221.1
95.312	19.28	0.0266	212.2
105.272	21.80	0.0364	196.7

Table VI. Measured Absorption of 0.150 Molar t-Butyl Alcohol
in Cyclohexane at 10°C

f, MHz	α , cm ⁻¹	Standard deviation in α	$\alpha/f^2 \times 10^{17}$ sec ² ·cm ⁻¹
15.076	0.8808	0.0184	387.5
25.077	2.181	0.0097	346.8
35.112	3.875	0.0500	314.3
45.176	5.746	0.0363	281.5
55.180	7.803	0.0221	256.3
65.262	10.05	0.1056	236.0
75.286	12.24	0.1768	216.0
85.332	15.46	0.1528	212.4
95.288	18.76	0.2800	206.6
105.256	21.64	0.1665	195.4

Table VII. Measured Absorption of 0.198 Molar t-Butyl Alcohol
in Cyclohexane at 10°C

f, MHz	α , cm ⁻¹	Standard deviation of α	$\alpha/f^2 \times 10^{17}$ sec ² ·cm ⁻¹
15.460	0.9503	0.0075	397.6
25.086	2.293	0.0160	364.4
35.177	4.105	0.0355	331.7
45.180	6.001	0.0420	294.0
55.172	8.230	0.1116	270.4
65.160	10.88	0.1347	256.2
85.332	16.51	0.1128	226.7
105.288	22.78	0.0705	205.5
125.244	29.49	0.4219	188.0

Table VIII. Measured Absorption of 0.245 Molar t-Butyl Alcohol
in Cyclohexane at 10°C

f, MHz	α , cm ⁻¹	Standard deviation of α	$\alpha/f^2 \times 10^{17}$ sec ² ·cm ⁻¹
15.460	0.9236	0.0009	386.4
25.001	2.263	0.0009	362.1
35.001	4.150	0.0118	338.8
45.168	6.255	0.0263	306.6
55.186	8.643	0.0954	283.8
65.152	11.36	0.0645	267.7
75.254	14.22	0.0982	251.1
85.284	17.33	0.0776	238.3
95.296	20.32	0.3996	223.7
105.260	24.05	0.2162	217.1
125.212	32.32	0.4315	206.2

Table IX. Measured Absorption of 0.101 Molar t-Butyl Alcohol
in Cyclohexane at 15°C

f, MHz	α , cm ⁻¹	Standard Deviation of α	$\alpha/f^2 \times 10^{17}$ sec ² ·cm ⁻¹
17.502	0.9632	0.0043	314.4
22.517	1.514	0.0081	298.7
29.430	2.527	0.0349	291.8
48.680	5.836	0.0102	246.3
68.302	10.32	0.0642	221.3
87.924	15.83	0.1948	204.7
107.620	23.31	0.3582	201.2
127.372	31.69	0.5931	195.3

Table X. Measured Absorption of 0.149 Molar t-Butyl Alcohol
in Cyclohexane at 15°C

f, MHz	α , cm ⁻¹	Standard deviation of α	$\alpha/f^2 \times 10^{17}$ sec ² ·cm ⁻¹
25.217	2.118	0.0147	333.1
35.222	3.820	0.0338	307.9
45.162	5.823	0.0050	285.5
55.146	8.092	0.0816	266.1
65.202	10.70	0.1381	251.7
75.254	13.66	0.0771	241.2
85.272	16.52	0.2215	227.2
95.268	19.81	0.2073	218.2
105.234	23.64	0.3745	212.9

Table XI. Measured Absorption of 0.197 Molar t-Butyl Alcohol
in Cyclohexane at 15°C

f, MHz	α , cm ⁻¹	Standard deviation of α	$\alpha/f^2 \times 10^{17}$ sec ² ·cm ⁻¹
25.064	2.153	0.0042	342.8
35.103	4.028	0.0686	326.9
45.168	6.096	0.0057	298.8
55.172	8.426	0.0568	276.8
65.180	11.44	0.1468	269.2
75.262	14.01	0.0793	247.3
85.304	17.56	0.1617	241.4
95.276	20.53	0.2517	226.2
105.236	24.65	0.1512	222.6
125.240	33.53	0.4112	213.8

Table XII. Measured Absorption of 0.243 Molar t-Butyl Alcohol
in Cyclohexane at 15°C

f, MHz	α , cm ⁻¹	Standard deviation of α	$\alpha/f^2 \times 10^{17}$ sec ² ·cm ⁻¹
25.096	2.125	0.0129	337.4
35.134	3.960	0.0369	320.8
45.232	6.249	0.0103	305.4
55.176	8.722	0.0146	286.5
65.214	11.67	0.0534	274.3
75.300	14.80	0.0996	261.0
85.304	18.26	0.3762	250.9
105.236	26.12	0.6687	235.8

C. Calculation of τ

The relaxation time was determined from the data by means of a least squares method. Since:

$$\frac{\alpha}{f^2} = \frac{A}{1 + (f/f_c)^2} + B \quad (4.1)$$

is not linear in f_c , a method described by R. Kay²⁵ was used. From:

$$\frac{\alpha}{f^2} = f(A, B, f_c) \quad ,$$

we can write the total differential as:

$$\Delta y = \frac{\partial y}{\partial A} \Delta A + \frac{\partial y}{\partial B} \Delta B + \frac{\partial y}{\partial f_c} \Delta f_c \quad ,$$

where $y \equiv \alpha/f^2$. We now have an equation linear in the unknowns ΔA , ΔB , and Δf_c . Δy is defined as the difference between the measured and calculated values of α/f^2 . The latter are calculated from (4.1) using estimates of A , B , and f_c . A theoretical curve is fitted to the data by minimizing $\sum \Delta y^2$, the sum of Δy^2 over the data points. The three normal equations are obtained by differentiating $\sum \Delta y^2$ with respect to each of the constants to be fitted. The normal equations are:

$$\sum \left(\Delta y \cdot \frac{\partial y}{\partial A} \right) = \sum \left(\frac{\partial y}{\partial A} \right)^2 \Delta A + \sum \left(\frac{\partial y}{\partial A} \cdot \frac{\partial y}{\partial B} \right) \Delta B + \sum \left(\frac{\partial y}{\partial A} \cdot \frac{\partial y}{\partial f_c} \right) \Delta f_c \quad ,$$

$$\sum \left(\Delta y \cdot \frac{\partial y}{\partial B} \right) = \sum \left(\frac{\partial y}{\partial B} \cdot \frac{\partial y}{\partial A} \right) \Delta A + \sum \left(\frac{\partial y}{\partial B} \right)^2 \Delta B + \sum \left(\frac{\partial y}{\partial B} \cdot \frac{\partial y}{\partial f_c} \right) \Delta f_c \quad ,$$

$$\sum \left(\Delta y \cdot \frac{\partial y}{\partial f_c} \right) = \sum \left(\frac{\partial y}{\partial f_c} \cdot \frac{\partial y}{\partial A} \right) \Delta A + \sum \left(\frac{\partial y}{\partial f_c} \cdot \frac{\partial y}{\partial B} \right) \Delta B + \sum \left(\frac{\partial y}{\partial f_c} \right)^2 \Delta f_c ,$$

where:

$$\begin{aligned} \partial y / \partial A &= 1 / [1 + (f/f_c)^2] , \\ \partial y / \partial B &= 1 , \\ \partial y / \partial f_c &= 2A f_c f^2 / [(f_c^2 + f^2)] . \end{aligned}$$

The procedure, then, is to estimate values of A, B, and f_c from a plot of α/f^2 versus $\log f$. These estimates are used to calculate the theoretical curve and the partials $\partial y / \partial A$, $\partial y / \partial B$ and $\partial y / \partial f_c$. The sums in the normal equations are calculated, and the resulting expressions solved for ΔA , ΔB and Δf_c . These quantities are used to correct the initial estimates of the three constants. The variance of the fit was calculated from:^{24b}

$$\sqrt{\frac{\sum \Delta y^2}{n - 3}} ,$$

where n is the number of data points used. The process was iterated until the variance was constant to five digits. The standard error in the final values of A, B, and f_c was calculated from:^{24b}

$$\sqrt{\frac{DA}{D} \cdot \frac{\sum \Delta y^2}{n - 3}} , \quad \sqrt{\frac{DB}{D} \cdot \frac{\sum \Delta y^2}{n - 3}} , \quad \sqrt{\frac{Df_c}{D} \cdot \frac{\sum \Delta y^2}{n - 3}} ,$$

respectively. D is the determinant of the normal equations, and DA, DB, and Df_c are the minor determinants of the diagonal terms of ΔA , ΔB , and Δf_c , respectively, of D.

The results are shown in Table XIII. τ is calculated from f_c using

(2.39). Shown also is the standard error of f_c . Figures 3, 4 and 5 are plots of α/f^2 versus $\log f$. The points are measured data; the curves are calculated as described above.

Table XIII. Calculated Values of f_c and τ

Temperature	Concentration, moles/liter	Relaxation Frequency, MHz	Relaxation Time $\times 10^9$, sec
5°C	0.151	30.5 ± 0.6	5.22
	0.199	35.1 ± 1.6	4.53
	0.246	39.6 ± 1.7	4.02
10°C	0.150	42.6 ± 1.7	3.74
	0.198	48.4 ± 2.1	3.29
	0.245	53.6 ± 3.1	2.97
15°C	0.101	42.8 ± 3.6	3.72
	0.149	52.9 ± 2.1	3.01
	0.197	57.4 ± 3.1	2.78
	0.243	65.0 ± 2.1	2.45

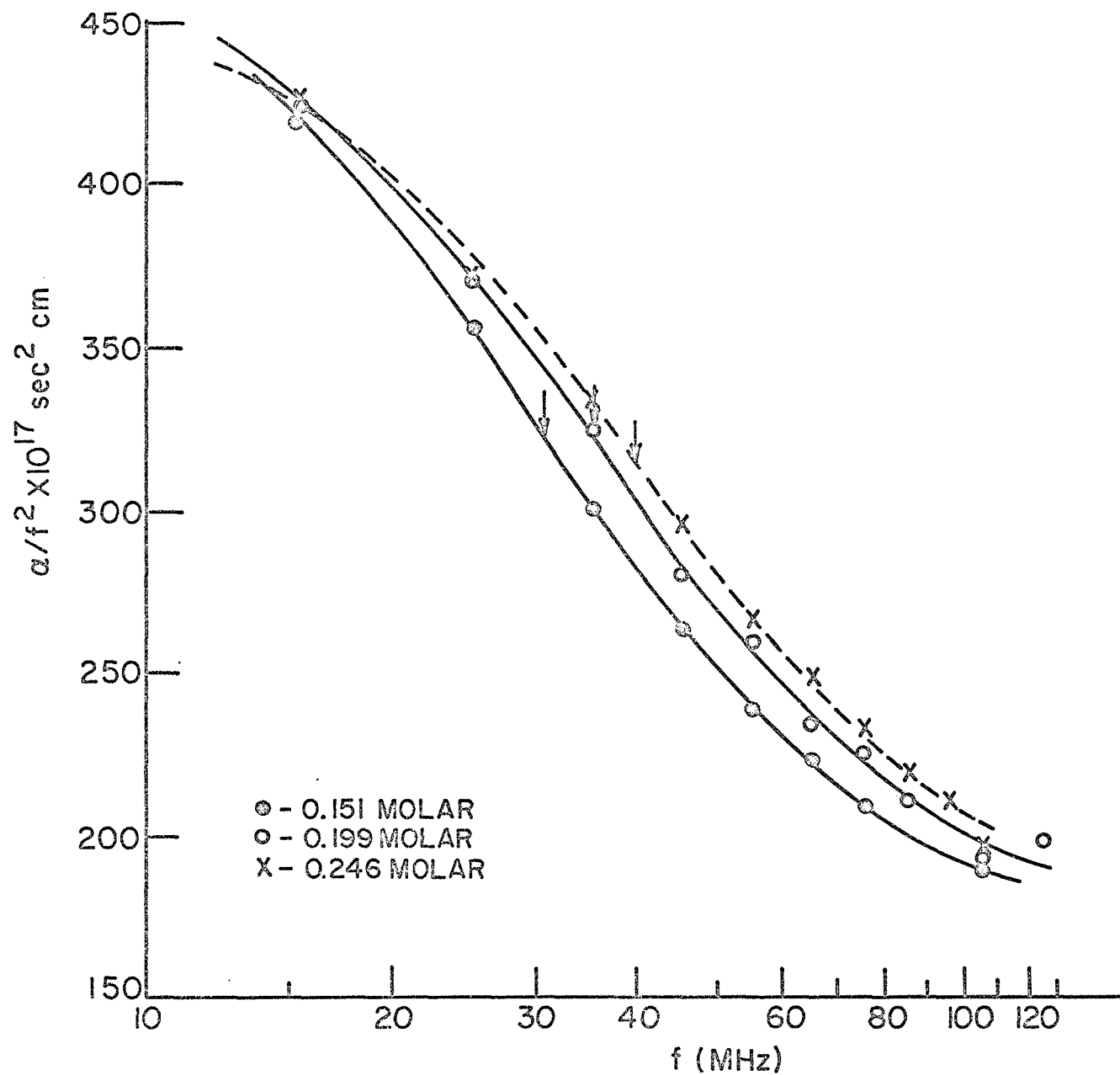


Fig. 3 α/f^2 vs LOG f of t -BUTYL ALCOHOL IN CYCLOHEXANE, 5°C

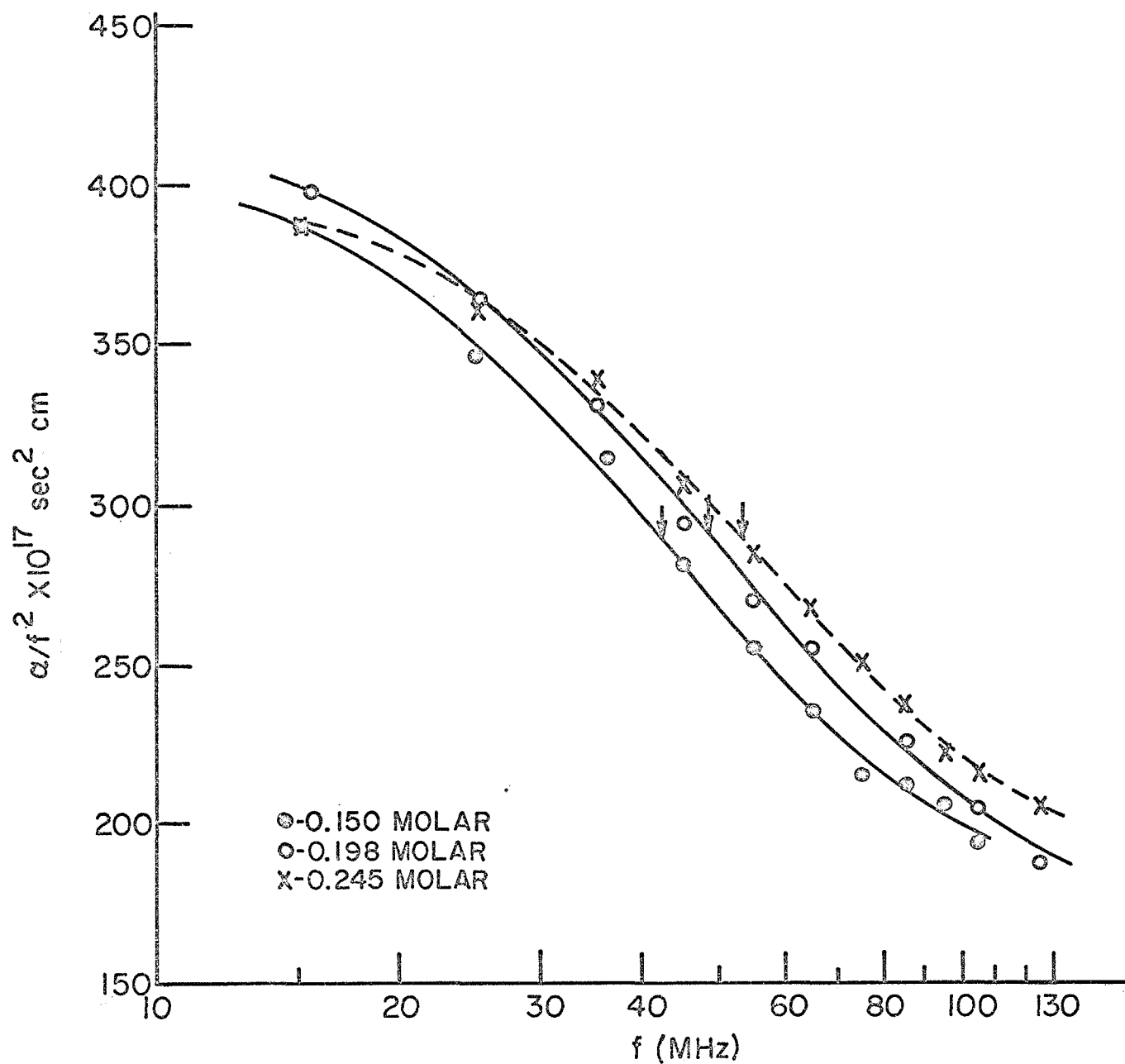


Fig. 4 α/f^2 vs LOG f of *t*-BUTYL ALCOHOL IN CYCLOHEXANE, 10°C.

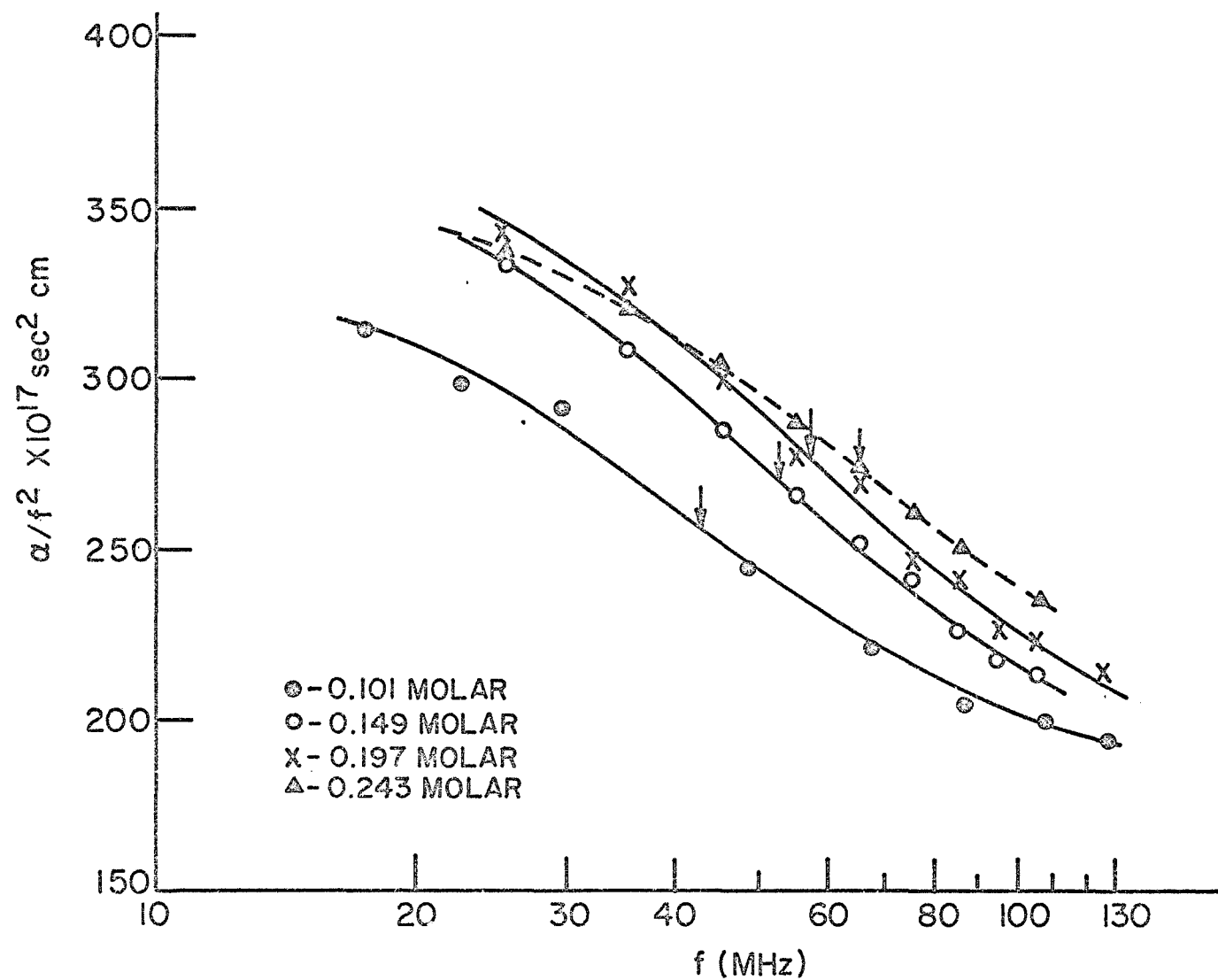


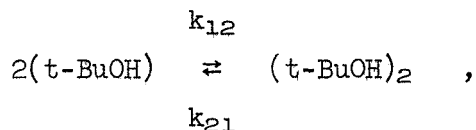
Fig. 5 α/f^2 vs LOG f of t-BUTYL ALCOHOL IN CYCLOHEXANE, 15°C.

V. DISCUSSION

A. Interpretation

In order to analyze the data and to interpret the relaxation time in terms of a physical process, it is necessary to assume some model. The relaxation process is interpreted in terms of self-association of the alcohol. Various models of association are considered: monomer-dimer, monomer-polymer, dimer-tetramer, and multistep processes. The monomer-dimer model is found most consistent with the data.

1. Monomer-Dimer. For the reaction:



the association equilibrium constant is given by:

$$K_A = \frac{k_{12}}{k_{21}} = \frac{C_2}{C_1^2} ,$$

k_{12} and k_{21} are the association and dissociation rate constants, C_1 and C_2 are the molar concentrations of monomer and dimer respectively. Activity coefficients are taken to be unity. This supposes that deviations from ideality are entirely due to the self-association process, an assumption supported by Prigogine.³² In this case, (2.47) becomes:

$$\tau^{-1} = 4k_{12}C_1 + k_{21} . \quad (5.1)$$

We can express the relaxation time in terms of total concentration of

alcohol, C_A , rather than in terms of monomer. If it is assumed that all of the alcohol is present either as monomer or dimer, then:

$$C_A = C_1 + 2C_2 \quad .$$

If $C_2 = K_A C_1^2$ is substituted into this expression and the result solved for C_1 , we obtain as the positive root:

$$C_1 = -\frac{k_{21}}{4k_{12}} + \frac{k_{21}\sqrt{1 + 8K_A C_A}}{4k_{12}} \quad . \quad (5.2)$$

Substitution of this expression for C_1 into (5.1) and squaring yields:

$$\tau^{-2} = 8k_{12}k_{21}C_A + k_{21}^2 \quad . \quad (5.3)$$

Figure 6 shows τ^{-2} plotted against total alcohol concentration at 5°, 10°, and 15°C. From the linearity of the plots it was concluded that the relaxation is due to the monomer-dimer equilibrium. The errors in τ^{-2} are calculated from the standard errors of the characteristic frequency, f_c , shown in Table XIII. The uncertainty of C_A is negligible compared with that of τ^{-2} .

k_{21} is calculated from the intercept of the plots. k_{12} and K_A are obtained by dividing the slope by $8k_{21}$ and $8k_{21}^2$ respectively. τ^{-2} vs C_A at 5°C passes through the origin within experimental error, so that it is not possible to calculate the rate constants directly at this temperature. The equilibrium constant found at 10°C and the value of ΔH calculated in part B are used to calculate K_A at 5°C. The rate constants are then calculated from K_A and the slope of τ^{-2} vs C_A . The activation energy of the dissociation rate, ΔH_{21}^* , is calculated from k_{21} at 10° and

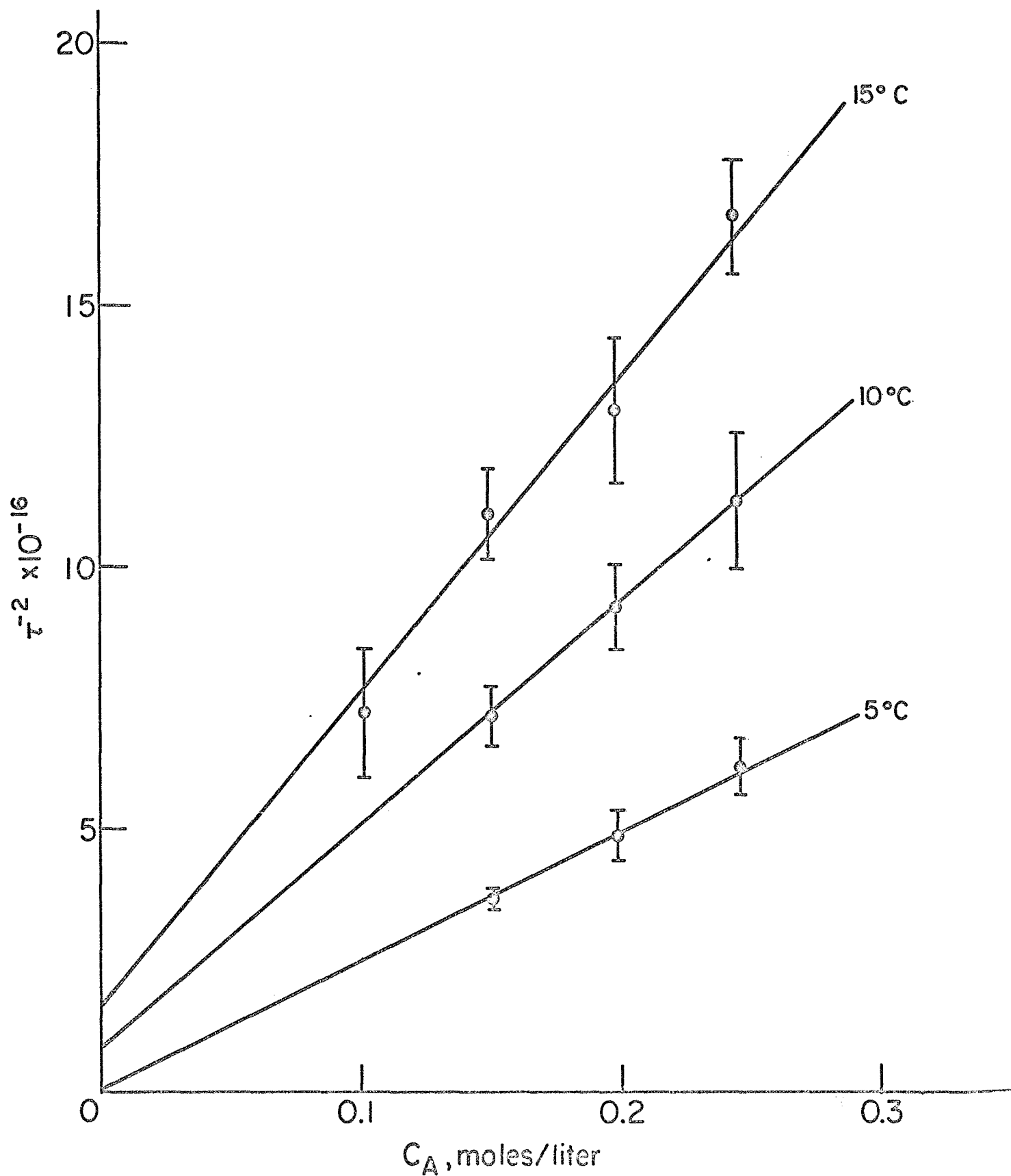
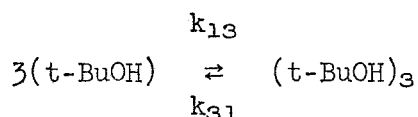


Fig. 6 τ^{-2} vs CONCENTRATION FOR t-BUTANOL IN CYCLOHEXANE.

15°C using the Arrhenius expression. The activation energy of the association rate is not calculated directly since k_{12} varies so little with temperature. These results are shown in Table XIV. The maximum error of the results is extremely large. The range of values of k_{21} at each temperature can be calculated from the minimum and maximum possible intercepts of lines drawn within the standard deviations of τ^{-2} . If we restrict ourselves to positive values of k_{21} , the ranges are zero to $1 \times 10^8 \text{ sec}^{-1}$, 2.0×10^8 , and 1.8×10^8 at 5°, 10°, and 15°C respectively. The minimum possible values of k_{12} and K_A at these three temperatures are therefore: $2.4 \times 10^8 \text{ l}\cdot\text{mole}^{-1}\cdot\text{sec}^{-1}$ and $2.4 \text{ l}\cdot\text{mole}^{-1}$ at 5°C; 1.5×10^8 and 0.71 at 10°C; and 3.4×10^8 and 1.9 at 15°C. The results shown in Table XIV are obtained from the best straight lines drawn through the data points.

2. Monomer-Polymer. Monomer-Trimer equilibrium is described by the reaction:



where the equilibrium constant is given by:

$$K_A = \frac{k_{13}}{k_{31}} = \frac{C_3}{C_1^3} .$$

k_{13} and k_{31} again are the rate constants involved, C_3 and C_1 the molar concentrations of trimer and monomer, respectively. For this equilibrium, equation (2.47) becomes:

$$\tau^{-1} = 9k_{13}C_1 + k_{31} . \quad (5.4)$$

Table XIV. Results for t-Butyl Alcohol in Cyclohexane

	$\frac{k_{21}}{k_{12}}$	$\frac{k_{12} \times 10^{-8}}{1 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}}$	$\frac{k_{21} \times 10^{-8}}{\text{sec}^{-1}}$
	$2(t\text{-BuOH}) \rightleftharpoons (t\text{-BuOH}), K_A = k_{12}/k_{21}$		
	K_A $1 \cdot \text{mole}^{-1}$	$k_{12} \times 10^{-8}$ $1 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$	$k_{21} \times 10^{-8}$ sec^{-1}
5°C	8.5 ^{a/}	5. ^{b/}	0.6 ^{b/}
10°C	6.8	6.0	0.89
15°C	4.9	6.1	1.2

Enthalpy, Activation Energies:

$$\Delta H = -7.0 \text{ kcal} \cdot \text{mole}^{-1} \cdot \text{c/}$$

$$\Delta H_{21}^* = 10.9 \text{ kcal} \cdot \text{mole}^{-1} \cdot \text{d/}$$

$$\Delta H_{12}^* = 3.9 \text{ kcal} \cdot \text{mole}^{-1} \cdot \text{e/}$$

^{a/} Calculated from $\Delta H = -7.0$ and $K_A = 6.8$ (10°C)

^{b/} Calculated from $K_A = 8.5$ and slope of τ^{-2} vs C_A at 5°C.

^{c/} Calculated according to eq. (5.6) in Part B.

^{d/} Calculated from values of k_{21} at 10° and 15°C.

^{e/} Calculated from ΔH and ΔH_{21}^* .

As before, we can write:

$$C_A = C_1 + 3C_3 \quad .$$

Substituting for C_3 from the equilibrium constant gives:

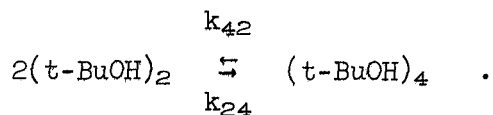
$$C_A = C_1 + 3K_A C_1^3 \quad . \quad (5.5)$$

Rather than solve this result explicitly for C_1 , an iterative procedure is followed. First, a value of K_A is assumed. Equation (5.5) is then solved for C_1 by trial and error. The rate constants are calculated from the slope and intercept of a plot of τ^{-1} vs C_1 , according to (5.4). An improved K_A is calculated, and the process is iterated. It was found that the plots became distinctly curved as the iteration proceeded, making the calculation of the rate constants progressively less exact. The curvature was more pronounced at the higher temperatures.

It is concluded that the excess absorption in the frequency range measured is due to a single relaxation and that there are no additional relaxations arising from the self-association of the alcohol at frequencies higher than those measured. These conclusions will be discussed in part D. The lack of multiple relaxation is taken as evidence that the self-association takes place in one step, involving a single equilibrium. This result supports the dimer case since the formation of a trimer from three monomers by a one-step process seems unlikely in such dilute solutions.

For the above two reasons, the monomer-trimer model was discounted. Equilibria involving higher polymers, e.g., monomer-tetramer, were not considered. The τ^{-1} vs C_1 plots would have greater curvature than the monomer-trimer case; the formation of a tetramer from four monomers by a one-step process seems impossible at the concentrations used.

3. Dimer-Tetramer. Another possibility, which is kinetically indistinguishable from the monomer-dimer case, is the association of dimers to form tetramers:

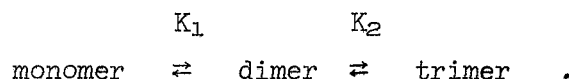


Assuming, as before, that all of the alcohol is present as the two species considered, the equations take the same form as in the monomer-dimer case. The concentration dependence of τ is therefore given by:

$$\tau^{-2} = 8k_{42}k_{24}C_A + k_{42}^2 .$$

This possibility, and any other not including monomers, is discounted as the only association process since there is considerable evidence that monomers are present in appreciable quantities in dilute solutions of t-butyl alcohol in non-polar solvents.^{5,9,27}

4. Multistep Processes. One may consider a two-step process such as:



There is no reason to suppose that K_2 would cause a relaxation and K_1 would not, since both steps involve the same kind of reaction. In general we would expect K_1 to be as fast or faster than K_2 . Since a single relaxation is observed in and above the frequency range measured, this relaxation would be due to the fastest step of a multistep association process. Thus it is not possible to explain the observed relaxation in terms of a dimer-trimer or dimer-tetramer equilibrium preceded by a monomer-dimer equilibrium, the latter in order to explain the observed presence of monomers.

Since K_2 might be considerably slower than K_1 , it is possible that the observed relaxation is due to K_1 with K_2 occurring at much lower frequencies. This possibility cannot be eliminated without investigating the lower frequency range. In this case equation (5.3), which assumes that only monomers and dimers are present, is not valid. If K_1 and K_2 are far enough apart (time-wise) so that no direct coupling occurs, the degree to which the data fit (5.3) depends on the amount of polymers, other than dimers, that are present. Thus the fact that the data fit (5.3) indicates that higher polymers are not present in large enough amounts to cause large errors in the kinetic results.

B. Calculation of ΔH

The enthalpy of dimerization can be calculated independently of the kinetic results. Fitting the data to:

$$\frac{\alpha}{f^2} = \frac{A}{1 + (f/f_c)^2} + B \quad ,$$

yields values of A and B, shown together with calculated standard errors, in Table XV. A is given by equation (2.40a);

$$A = \frac{\pi(\gamma - 1)\rho\beta C_o V}{f_c C_{P\infty} RT^2 \sum (v_i^2 / C_i)} \left(\frac{C_P \Delta V}{\theta V} - \Delta H \right)^2 \quad .$$

The volume change of dimerization must be very small in non-polar solvents such as cyclohexane. If we assume that $\Delta V = 0$, and if we substitute $\beta\rho = 1/C_o^2$ [equation (2.9)] into the above, we obtain, for ΔH^2 :

Table XV. Values of the Constants A and B calculated by fitting the Data to $\alpha/f^2 = A/[1 + (f/f_c)^2] + B$

T, °C	C _A mole·l ⁻¹	A x 10 ¹⁷ , sec ² ·cm ⁻¹	B x 10 ¹⁷ , sec ² ·cm ⁻¹
5°C	.151	316.7 ± 2.7	165.5 ± 5.0
	.199	306.0 ± 6.8	168.9 ± 8.1
	.246	296.4 ± 5.4	166.6 ± 8.6
10°C	.150	254.9 ± 4.1	160.3 ± 6.9
	.198	262.3 ± 5.1	158.5 ± 8.3
	.245	240.9 ± 6.0	168.3 ± 12.0
15°C	.101	159.7 ± 4.8	177.6 ± 6.5
	.149	194.7 ± 2.6	173.8 ± 6.3
	.197	199.3 ± 4.9	177.1 ± 7.3
	.243	171.9 ± 2.5	188.0 ± 4.0

$$\Delta H^2 = \frac{A f_c C_{P\infty} RT^2 C_o \sum (\nu_i^2 / C_i)}{\pi(\gamma - 1)V} \quad (5.6)$$

Table XVI shows the data to be used in equation (5.6). The calculation is done at 15°C. The decrease in ΔH with increasing concentration is probably due to the use of data of pure cyclohexane. The value of ΔH is taken as $-7.0 \text{ kcal}\cdot\text{mole}^{-1}$ of dimer. This result agrees well with the value of $-10 \text{ kcal}\cdot\text{mole}^{-1}$ estimated from the values of K_A at 10 and 15°C, considering the very large uncertainty involved. The activation energy of the association rate is calculated from ΔH_{21}^* and the enthalpy change obtained here; both of these results are shown in Table XIV.

The possible error introduced by assuming that the volume change of the association process is zero may be calculated. If ΔV were as large as $-3 \text{ ml}\cdot\text{mole}^{-1}$, for example, then:

$$\frac{C_P \Delta V}{\theta V} = -0.8 \text{ kcal}\cdot\text{mole}^{-1} \quad .$$

C. Literature Results

Liddel and Becker⁵ studied the infrared spectra of several simple alcohols in CCl_4 , concluding that cyclic dimers are formed. For *t*-butyl alcohol they obtain an equilibrium constant of approximately $1.2 \text{ l}\cdot\text{mole}^{-1}$ at 15°C and an enthalpy change of $-4.8 \pm 1.1 \text{ kcal}\cdot\text{mole}^{-1}$ of dimer. This value is lower than that expected for the formation of two hydrogen bonds (4-6 $\text{kcal}\cdot\text{mole}^{-1}$ per bond). The authors suggest that the enthalpy change of a monomer cyclic dimer equilibrium may be lower than that of an open dimer since both H bonds of a cyclic dimer are nonlinear. The corresponding

Table XVI. Data used in Calculating ΔH from A at 15°C

C_A m.liter ⁻¹	$\sum \left(\frac{v_i^2}{C_i} \right) = \left(\frac{4}{C_1} + \frac{1}{C_2} \right)^{a/}$ ml.mole ⁻¹	$f_c^{b/}$ Hz	$A^{b/}$ sec ² .cm ⁻¹	$-\Delta H$ kcal.mole ⁻¹
0.101	116. x 10 ³	42.8 x 10 ⁸	159.7 x 10 ⁻¹⁷	6.9
.149	78.6	52.9	194.7	7.0
.197	60.4	57.4	199.3	6.5
.243	50.4	65.0	171.9	5.8

The following values are for pure cyclohexane.

$$C_{P\infty} \cong C_P = 36.8 \text{ cal.mole}^{-1}.\text{deg}^{-1}.\underline{c/}$$

$$C_O = 1.295 \times 10^5 \text{ cm.sec}^{-1}.\underline{d/}$$

$$\tau = 288.15^\circ\text{K.}$$

$$\gamma-1 = 0.385.\underline{e/}$$

$$V = 108 \text{ ml.mole}^{-1}.$$

$$\theta = 1.208 \text{ deg}^{-1}.\underline{c/}$$

a/ Calculated from $K_A = 4.9 \text{ l.mole}^{-1}$, $k_{12} = 6.1 \times 10^8 \text{ l.mole}^{-1}.\text{sec}^{-1}$ and

$k_{21} = 1.2 \times 10^8 \text{ sec}^{-1}$, using eq. (5.2).

b/ Experimental results of this work.

c/ J. Timmermans, ref. 28.

d/ Experimentally determined by the method described in ref. 29.

e/ Calculated using eq. (2.33).

results of this work are $K_A = 4.9 \text{ l}\cdot\text{mole}^{-1}$ and $\Delta H = -7.0 \text{ kcal}\cdot\text{mole}^{-1}$.

There are very few ultrasonic kinetic investigations on systems similar to the one studied here. Maier and Rudolf²⁶ studied dilute solutions of benzoic acid in CCl_4 , where dimers are known to form. The procedure used by these workers is quite different from that used here and depends on there being a very high degree of association. The results obtained at 15°C are: $k_{12} = 4.2 \times 10^9 \text{ l}\cdot\text{mole}^{-1}\cdot\text{sec}^{-1}$, $k_{21} = 3.3 \times 10^5 \text{ sec}^{-1}$, $K_A = 1300 \text{ l}\cdot\text{mole}^{-1}$, $\Delta H = -10.5 \text{ kcal}\cdot\text{mole}^{-1}$, $\Delta H_{12}^* = 3.3 \text{ kcal}\cdot\text{mole}^{-1}$, and $\Delta H_{21}^* = 13.8 \text{ kcal}\cdot\text{mole}^{-1}$. Hammes and Spivey³⁰ have studied the H-bond dimerization of 2-pyridone in three different solvent systems. Their results in 1,4-dioxane at 13°C are: $k_{12} = 1.7 \times 10^9 \text{ l}\cdot\text{mole}^{-1}\cdot\text{sec}^{-1}$, $k_{21} = 0.9 \times 10^8 \text{ sec}^{-1}$, $K_A = 19$, $\Delta H_{12}^* = 3.4 \text{ kcal}\cdot\text{mole}^{-1}$. The symbols have the same meaning as in this work. The comparable results of the t-butanol/cyclohexane system are given in Table XIV. The rate constant and activation energy of the association reaction of all three systems are in the range expected for a diffusion-controlled rate.^{13,27} The lower value of k_{21} for t-butanol may be due to some degree of steric hindrance in the self-association of the alcohol.

Musa and Eisner¹¹ have used an ultrasonic absorption technique to study the kinetics of t-butanol in cyclohexane. Evaluating their results on the basis of a single relaxation, these workers conclude that a monomer-tetramer equilibrium is responsible for the observed excess absorption. The method used by Musa and Eisner to calculate the relaxation frequency from absorption data is different from that used here and will be discussed in detail in part D. It will be shown that their method of calculating the relaxation frequency is questionable. Since values of f_c and not

experimental absorption data are listed, it is not possible to determine whether their data is at variance with our monomer-dimer interpretation.

Musa and Eisner's results were reanalyzed by Goodman,³¹ who interpreted their results in terms of a monomer-dimer equilibrium, supposing that the activity coefficients of the reactants is not unity. Regardless of the validity of Goodman's analysis, we do not feel it is justified in this case. Both Musa and Eisner, and Goodman use partial pressure data obtained by Prigogine.³² Prigogine, however, concludes that in the concentration range considered here, deviations from ideality may be attributed entirely to intermolecular complexes of the alcohol. It should be noted that both Musa and Eisner and Goodman mistakenly use Prigogine's data obtained at 21° and apply it without correction at 27°C. The interpretation we use is that deviations from ideality apart from the monomer-dimer equilibrium are negligible. This is of course consistent with Prigogine's conclusion.

D. Method of Calculation

It is instructive to discuss the method used to calculate the relaxation frequencies in this work and compare it with the method used by Musa and Eisner. We shall also mention the calculations of Hammes and Spivey.

1. Method of Musa and Eisner. These workers also used the α/f^2 equation (2.43) to analyze their data. Using $\omega\tau$ for f/f_c , (2.43) can be rearranged to:

$$\frac{1}{\alpha/f^2 - B} = \frac{1}{A} + \frac{\tau^2}{A} \omega^2 \quad . \quad (5.7)$$

If the constant B can be calculated, one may plot $(\alpha/f^2 - B)^{-1}$ versus ω^2 , obtaining $1/A$ as the intercept and τ^2/A as the slope. The value of A calculated from the intercept is used to calculate τ from the slope. The background absorption B is concentration dependent. In order to obtain B , Musa and Eisner used a scheme originating in the paper of Maier and Rudolf.²⁶ The change in absorption with concentration is measured at a temperature at which the excess absorption is found to disappear. By assuming that the concentration dependence of B is independent of temperature, the value of B can be found for any dilute concentration of solute at a given temperature from the α/f^2 of the pure solvent at that temperature. Maier and Rudolf state that they could determine the concentration dependence of B to about 25%. Furthermore, there is no guarantee that this dependence is temperature independent, as these authors find.

An attempt was made to analyze the 5°C data using (5.7). It is found that the high frequency values of $(\alpha/f^2 - B)^{-1}$, where the difference $\alpha/f^2 - B$ becomes very small, are extremely sensitive to the value of B used. The relaxation times calculated from the slope and intercept of a plot of $(\alpha/f^2 - B)^{-1}$ could not be determined with enough precision to be used in the calculation of the rate constants.

2. Method of Hammes and Spivey. These authors improve on the calculation of Musa and Eisner by using a weighted, least squares technique on a slightly rearranged form of equation (5.7). Values of the background absorption giving the minimum standard deviations in τ were taken as the correct values. The authors find that values of B calculated in this way do not differ significantly from the absorption (α/f^2) of the pure solvent. An attempt to analyze the t-butanol/cyclohexane data using pure solvent

absorption values was not successful. The B values obtained from the fit (Table XV) differ by 2 to 10% from the measured absorption of cyclohexane (Table II).

3. Method of Calculation Used in This Work. The method used here to evaluate the data has several important advantages over that used by Musa and Eisner. The data, consisting of values of α/f^2 as a function of frequency, are used to calculate directly a theoretical, single-relaxation curve. It can be determined whether the relaxation curve is due to the perturbation of a single equilibrium from how well the data fit the theoretical curve over the frequency range measured. Figures 1, 2 and 3 show the plotted data and the fitted theoretical curves. In all cases the fits are quite close. It is therefore concluded that the excess absorption is due to a single relaxation. This important result is necessary if the data are to be interpreted in terms of a one-step monomer-dimer equilibrium. Furthermore, the fitted values of the background absorption B, shown in Table XIV, are below the absorption of the pure solvent at the same temperature. This is a strong indication that no chemical relaxation occurs at higher frequencies.

A second big advantage is that the resulting τ 's do not depend on a previously derived value of B, the calculation of which necessarily involves assumptions. In addition, it is possible to calculate the uncertainty of the relaxation times from the closeness of the fit.

E. Conclusion

Dilute solutions of t-butyl alcohol in cyclohexane were studied by the ultrasonic absorption technique, with the conclusion that the relaxation observed is single and is due to perturbation of a monomer-dimer equilibrium. The association and dissociation rate constants are found to be: $5 \times 10^8 \text{ l}\cdot\text{mole}^{-1}\cdot\text{sec}^{-1}$ and $0.6 \times 10^8 \text{ sec}^{-1}$ at 5°C ; $6.0 \times 10^8 \text{ l}\cdot\text{mole}^{-1}\cdot\text{sec}^{-1}$ and $0.89 \times 10^8 \text{ sec}^{-1}$ at 10°C ; and $6.1 \times 10^8 \text{ l}\cdot\text{mole}^{-1}\cdot\text{sec}^{-1}$ and $1.2 \times 10^8 \text{ sec}^{-1}$ at 15°C . Association equilibrium constants of 8.5, 6.8, and $4.9 \text{ l}\cdot\text{mole}^{-1}$ were calculated at 5° , 10° , and 15°C . The activation energy of dissociation, ΔH_{21}^* , was calculated from values of the appropriate rate constant at 10° and 15°C ; the result is $10.9 \text{ kcal}\cdot\text{mole}^{-1}$. The enthalpy of the equilibrium was calculated to be $-7.0 \text{ kcal}\cdot\text{mole}^{-1}$ of dimer. This value is reasonably consistent with that estimated from the equilibrium constant at 10° and 15°C . The activation energy of association, calculated from ΔH_{21}^* and ΔH to be $3.9 \text{ kcal}\cdot\text{mole}^{-1}$, is about what one would expect for a diffusion controlled process.

The method used to determine the kinetic data has several important advantages over others. First, it allows one to determine experimentally whether the assumption of a single relaxation is justified or not. If more than one relaxation is present, it is still possible to analyze the system provided one has the necessary equipment to carry out measurements over a very wide frequency range. Secondly, the method of obtaining the relaxation time from α/f^2 curves allows τ to be calculated without having to make assumptions about the background absorption. It also permits one to estimate the uncertainty in the relaxation times. The principal

disadvantage is that for a moderately high degree of association the intercept of the kinetic plot becomes too small for the rate constants to be calculated. This disadvantage can be overcome if one has access to the equilibrium constant either from another experimental technique or from the literature.

APPENDIX A

COMPUTER PROGRAM FOR CALCULATING THE ABSORPTION COEFFICIENT

```

$IBJOB
$IRFTE EGUS
      DIMENSION DB(20,200),ZL(20,200),S(200),SLP(200),AL(200),DIS(200),
1ALAM(200),FREQ(200),IQ(200),H(10),SIG(200)
      REAL LOGF(200)
      READ(5,9) ISFTS
1 CONTINUE
      READ(5,14) (H(I),I=1,10)
      WRITE(6,100) (H(I),I=1,10)
      READ(5,10) K,CF,VFL
      CF=.55156
      DO 20 I=1,200
      DO 21 J=1,20
21 ZL(J,I)=0.0
      S(I)=0.0
      SLP(I)=0.0
      AL(I)=0.0
      DIS(I)=0.0
      ALAM(I)=0.0
      FREQ(I)=0.0
      LOGF(I)=0.0
      IQ(I)=0.0
20 CONTINUE
      DO 40 J=1,K
      READ(5,13) IQ(J),N,FREQ(J)
      READ(5,11) (DB(I,J),I=1,N)
      READ(5,12) (ZL(I,J),I=1,11)
      IF(N.LE.11)GO TO 22
      READ(5,12) (ZL(I,J),I=12,20)
22 FREQ(J)=FREQ(J)*1.E6
      ZN=FLOAT(N)
      SLSQ=0.0
      SDBL=0.0
      SDB=0.0
      SL=0.0
      DO 50 I=1,N
      SDB=SDB+DB(I,J)
      SL=SL+ZL(I,J)
      SDBL=SDBL+DB(I,J)*ZL(I,J)
      SLSQ=SLSQ+ZL(I,J)**2
50 CONTINUE
      S(J)= (ZN*SDBL-SL*SDB)/(ZN*SLSQ-SL**2)
      BINT=(SDB*SLSQ-SL*SDBL)/(ZN*SLSQ-SL**2)
      D1=0.
      DO 30 I=1,N
30 DELY=DB(I,J)-(S(J)*ZL(I,J)+BINT)
      D1=D1+DELY**2
      D2=D1/FLOAT(N-2)
      SIGFIT=SQRT(D2)
      IF(IQ(J).NE.IQ(J-1)) WRITE(6,101)FREQ(J)
      WRITE(6,109)N
      WRITE(6,102) (DB(IA,J),IA=1,N)
      WRITE(6,104) (ZL(IA,J),IA=1,N)
      WRITE(6,103)S(J),SIGFIT

```

```

40 CONTINUE
M=0
DO 60 J=1,K
M1=M+1
ZM1=FLOAT(M+1)
M5=M+5
TSL=0.0
X1=0.
X2=0.
DO 70 I=M1,M5
FREQ(J)=FREQ(I)
IF(FREQ(J).LE.0.0) GO TO 72
LOGF(J)=ALOG10(ABS(FREQ(J)))
72 CONTINUE
M=I
ZM=FLOAT(I)
TSL=TSL+S(I)
X1=X1+S(I)
X2=X2+S(I)**2
70 IF((IQ(I+1)-IQ(I)).NE.0) GO TO 71
71 SLP(J)=TSL/(ZM-ZM1+1.)
SIG(J)=(X2-(X1**2/(ZM-ZM1+1.)))/(ZM-ZM1)
SIG(J)=SQRT(SIG(J))
JFUZZ=J-1
IF(SLP(J).EQ.0.0) GO TO 61
60 CONTINUE
61 DO 80 I=1,JFUZZ
AL(I)=SLP(I)/CF
DIS(I)=AL(I)/(FREQ(I)**2)
ALAM(I)=VEL/FREQ(I)
80 CONTINUE
WRITE(6,100) (H(I),I=1,10)
WRITE(6,105)
DO 310 I=1,JFUZZ
DIS(I)=DIS(I)*1.E17
310 WRITE(6,106) FREQ(I),LOGF(I),ALAM(I),SLP(I),SIG(I),AL(I),DIS(I)
WRITE(7,107)(AL(I),I=1,5)
WRITE(7,107)(AL(I),I=6,10)
WRITE(7,107)(AL(I),I=11,15)
WRITE(7,107)(AL(I),I=16,20)
WRITE(7,107)(AL(I),I=21,25)
WRITE(7,107)(ALAM(I),I=1,5)
WRITE(7,107)(ALAM(I),I=6,10)
WRITE(7,107)(ALAM(I),I=11,15)
WRITE(7,107)(ALAM(I),I=16,20)
WRITE(7,107)(ALAM(I),I=21,25)
WRITE(7,108)(FREQ(I),I=1,5)
WRITE(7,108)(FREQ(I),I=6,10)
WRITE(7,108)(FREQ(I),I=11,15)
WRITE(7,108)(FREQ(I),I=16,20)
WRITE(7,108)(FREQ(I),I=21,25)
ISETS=ISETS-1
IF(ISETS.GT.0) GO TO 1
9 FORMAT(I2)
10 FORMAT(I2,F6.3,F10.5)
11 FORMAT(16(F4.2,1X))
12 FORMAT(11(F6.4,1X))
13 FORMAT(212,F12.6)
14 FORMAT(10A6)

```

```

100 FORMAT(1H1,10A6)
101 FORMAT(1H0,11HFREQUENCY= , -6PF10.5,2HMC)
102 FORMAT(1H0,5X,13(3X,F5.2,1H,1)
103 FORMAT(1H0 ,6HSLOPE=F12.5,5X,27HSTANDARD DEVIATION OF FIT =F8.4)
104 FORMAT(1H ,5X,13(1X,F7.3,1H,))
105 FORMAT(1H0,5X,9HFREQ.(MC),10X,8HLOG FREQ,11X,10HLAMBDA(CM),12X,10H
1AVG. SLOPE,13X,5HALPHA,15X,10HALPHA/F**2/1H ,92X,4H*E17//)
106 FORMAT(1H0,4X, -6PF10.5,9X,0PF10.6,9X,0PE12.5,4X,0PF8.4,5H +/- ,0PF
18.5,5X,0PF12.5,9X,0PF9.3)
107 FORMAT(5E15.7)
108 FORMAT(5(-6PF10.4))
109 FORMAT(1H0,5X,1H(,12,1X, 7HPOINTS))
STOP
END
$DATA

```

APPENDIX B

COMPUTER PROGRAM FOR CALCULATING RELAXATION TIME FROM ABSORPTION DATA

```

$IRJOB
$IRETC LSTO      NODECK
      REAL AL(25), ALAM(25), F(25), D(1000), Y(500), X(500), H(10), SIG1(16)
      INTEGER MO(25)
      DEFDA(O,R)=(O**2)/(O**2+R**2)
      DEFDER(O,R,S)=(2.*(O*R))*(S**2)/((R**2+S**2)**2)
      DELY(O,R,S,T,U)=U-(O*R**2/(R**2+S**2)+T)
      DEFDP=1.
C      DEFDA=DERIVATIVE OF ALPHA/FREQ**2 W/R A
C      DELY=DIFFERENCE BETWEEN FITTED CURVE AND POINT
      CALL PLOTS(O,1000)
      CALL PLOTG(O.,-11.,-3)
      CALL PLOTG(O.,.5,-3)
      READ(5,13) ISETS
1  CONTINUE
      READ(5,9) (H(I),I=1,10)
      READ(5,14) (MO(I),I=1,25)
      READ(5,16) A,FR,R
      READ(5,13) N
      READ(5,11) (AL(I),I=1,5)
      READ(5,11) (AL(I),I=6,10)
      READ(5,11) (AL(I),I=11,15)
      READ(5,11) (AL(I),I=16,20)
      READ(5,11) (AL(I),I=21,25)
      READ(5,11) (ALAM(I),I=1,5)
      READ(5,11) (ALAM(I),I=6,10)
      READ(5,11) (ALAM(I),I=11,15)
      READ(5,11) (ALAM(I),I=16,20)
      READ(5,11) (ALAM(I),I=21,25)
      READ(5,12) (F(I),I=1,5)
      READ(5,12) (F(I),I=6,10)
      READ(5,12) (F(I),I=11,15)
      READ(5,12) (F(I),I=16,20)
      READ(5,12) (F(I),I=21,25)
      READ(5,17) YMIN,YDELT,XMIN,XDELT
      XDELT=XDELT*1.E6
      XMIN=XMIN*1.E6
      YMIN=YMIN*1.E-17
      YDELT=YDELT*1.E-17
      JA=0
      DO 520 IA=1,25
      Y(IA)=0.
      X(IA)=0.
      IF (MO(IA).EQ.0) GO TO 520
      JA=JA+1
      Y(JA)=(AL(IA)/F(IA)**2)*1.E5
      X(JA)=F(IA)
520 CONTINUE
      Y(N+2)=YDELT
      Y(N+1)=YMIN
      X(N+2)=XDELT
      X(N+1)=XMIN
      WRITE(6,102) (H(I),I=1,10)
      SIG1(1)=0.
      DO 60 IA=1,15

```

```

WRITE(6,107)IA
WRITE(6,106)A,FR,B
S1=0.
S2=0.
S3=0.
S4=0.
S5=0.
S6=0.
S7=0.
S8=0.
S9=0.
DO 40 I=1,N
S1=S1+DEDA(FR,X(I))**2
S2=S2+DEDA(FR,X(I))*DEDFR(A,FR,X(I))
S3=S3+DEDA(FR,X(I))*DEDB
S4=S4+DEDFR(A,FR,X(I))**2
S5=S5+DEDB*DEDFR(A,FR,X(I))
S6=S6+DEDB**2
S7=S7+DEDA(FR,X(I))*DELY(A,FR,X(I),B,Y(I))
S8=S8+DEDFR(A,FR,X(I))*DELY(A,FR,X(I),B,Y(I))
S9=S9+DEDB*DELY(A,FR,X(I),B,Y(I))
40 CONTINUE
DETD=(S1*(S4*S6-S5**2)-S2*(S2*S6-S3*S5))+S3*(S2*S5-S3*S4)
DETA=(S7*(S4*S6-S5**2)-S2*(S6*S8-S9*S5))+S3*(S8*S5-S9*S4)
DETER=(S1*(S9*S6-S9*S5)-S7*(S2*S6-S3*S5))+S3*(S9*S2-S3*S8)
DETR=(S1*(S9*S4-S5*S8)-S2*(S2*S9-S3*S8))+S7*(S2*S5-S3*S4)
DELTA=DETA/DETD
DELTFR=DETER/DETD
DELTB=DETR/DETD
A=A+DELTA
FR=FR+DELTFR
B=B+DELTB
DY1=0.
DO 80 I=1,N
DY=DELY(A,FR,X(I),B,Y(I))
DY1=DY1+DY**2
80 CONTINUE
N1=N-3
SIGFIT=DY1/FLOAT(N1)
SIG1(IA+1)=SIGFIT
DIFF=SIG1(IA+1)-SIG1(IA)
IF(IA.LT.5) GO TO 60
IF(DIFF.LT..0001) GO TO 61
60 CONTINUE
61 CONTINUE
WRITE(6,108)
WRITE(6,106) A,FR,B
WRITE(6,201)
DY1=0.
DO 70 I=1,N
DY=DELY(A,FR,X(I),B,Y(I))
WRITE(6,109) Y(I),X(I),DY
DY1=DY1+DY**2
70 CONTINUE
SIGA=((S4*S6-S5**2)/DETD)*SIGFIT
SIGFR=((S1*S6-S3**2)/DETD)*SIGFIT
SIGR=((S1*S4-S3**2)/DETD)*SIGFIT
SIGFIT=SQRT(SIGFIT)
SIGA=SQRT(SIGA)

```

```

SIGER=SQRT(SIGER)
SIGB=SQRT(SIGB)
WRITE(6,10) SIGFIT,SIGA,SIGER,SIGB
T=(1./(2.*(3.1416*FR)))*1.F-6
T1=(1./T**2)*1.F-16
T2=((8.*3.1416**2)*FR)*SIGER)*1.E-4
T3=T1-T2
T4=T1+T2
WRITE(6, 15) T,T1,T2,T3,T4
DO 140 I=1,N
Y(I)=Y(I)*1.E-17
140 X(I)=X(I)*1.F6
A=A*1.E-17
FR=FR*1.F6
B=B*1.F-17
CALL PLOTG(12.,0.,-3)
IF(YMIN.NE.0.) GO TO 141
CALL SCALE(Y,10.,N,1)
CALL SCALE(X,10.,N,1)
141 CONTINUE
CALL AXIS(0.,0.,23HALPHA OVER FREQ SQUARED,23,10.,90.,Y(N+1),Y(N+2
1))
CALL AXIS(0.,0.,8HFREQ(MC),-8,10.,0.,X(N+1),X(N+2))
CALL LINE(X,Y,N,1,-1,11)
CALL SYMBOL(1.,10.,,15,H,0.,60)
YMAX=10.*YDELT+YMIN
DO 160 I=1,50
X(I)=XMIN+(1.F6)*FLOAT(I)
Y(I)=((A*FR**2)/(FR**2+X(I)**2))+B
IF(Y(I).LT.YMAX) GO TO 161
160 CONTINUE
161 CONTINUE
DELT=XDELT/50.
XMAX=10.*XDELT+XMIN
DO 150 I=2,498
X(I)=X(I-1)+DELT
Y(I)=((A*FR**2)/(FR**2+X(I)**2))+B
J=I
IF(X(I).GE.XMAX) GO TO 151
IF(Y(I).LE.YMIN) GO TO 151
150 CONTINUE
151 CONTINUE
X(J+1)=XMIN
X(J+2)=XDELT
Y(J+1)=YMIN
Y(J+2)=YDELT
CALL LINE(X,Y,J,1,0,19)
1000 CONTINUE
ISETS=ISETS-1
IF(ISETS.GT.0) GO TO 1
CALL PLOTG(16.,3.,-3)
CALL PLOTG(0,0,999)
9 FORMAT(10A6)
10 FORMAT(1H ,26HSTANDARD DEVIATION OF FIT=F7.3//1H ,21HSTANDARD ERRO
1RS OF A=F8.4//1H ,19X,3HFR=,F8.4//1H ,19X,2HB=,F8.4)
11 FORMAT(5F15.7)
12 FORMAT(5F10.4)
13 FORMAT(I2)
14 FORMAT(25I1)

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15 FORMAT(1H0,4HTAU=E12.4,5X, 21H(1/TAU SQUARED)*E-16=F7.3,5H +/- F6
1.3,5X,9HRANGE IS F7.3,4H TO F7.3)
16 FORMAT(3F10.5)
17 FORMAT(4F10.5)
102 FORMAT(1H1,13A6)
106 FORMAT(1H0,5X,3HA= F8.2//1H ,5X,3HFR= F8.2//1H ,5X,3HR= F8.2)
107 FORMAT(10HOPASS NO. I2)
108 FORMAT(14HOFINAL VALUES )
109 FORMAT(1H ,5X,1H(,F8.2,1H,,F8.2,1H),5X,F9.3/30X,9H-----)
201 FORMAT(11HODEVIATIONS//)
STOP
END

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\$DATA

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