
Acoustic Wave Propagation in Fluids With Coupled Chemical Reactions

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SUMMARY

This investigation presents a hydroacoustic theory which accounts for sound absorption and dispersion in a multicomponent mixture of reacting fluids (assuming a set of first-order acoustic equations without diffusion) such that several coupled reactions can occur simultaneously. General results are obtained in the form of a biquadratic characteristic equation (called the Kirchhoff-Langevin equation) for the complex propagation variable $\chi = -(\alpha + i\omega/c)$ in which α is the attenuation coefficient, c is the phase speed of the progressive wave and ω is the angular frequency. Computer simulations of sound absorption spectra have been made for three different chemical systems each comprised of two-step chemical reactions using physico-chemical data available in the literature. The chemical systems studied include: 1) water-dioxane, 2) aqueous solutions of glycine and 3) cobalt polyphosphate mixtures. Explicit comparisons are made between the exact biquadratic characteristic solution and the approximate equation (sometimes referred to as a Debye equation) previously applied to interpret the experimental data for the chemical reaction contribution to the absorption versus frequency. The relative chemical reaction and classical viscothermal contributions to the sound absorption are also presented. Several discrepancies that can arise when estimating thermodynamic data (chemical reaction heats or volume changes) for multistep chemical reaction systems when making dilute solution or constant density assumptions are discussed.

LIST OF SYMBOLS

A_j	Chemical affinity of j th reaction [ML^2T^{-2}]
A_{ij}	Coefficient of change of affinity of i th reaction with degree-of-advancement variable [$M \text{ mol}^{-1}$]
a_α	Activity of α th - component [1]
B_p^w	Frequency-dependent isothermal coefficient of expansion [1]
B_θ^w	Frequency-dependent isobaric coefficient of expansion [1]
c_o, c	Reference and frequency-dependent speeds of sound respectively [LT^{-1}]
c_p, c_p^e	Instantaneous and equilibrium heat capacities at constant pressure [$L^2 T^{-2}\theta$]
c_α	Mass concentration of constituent α [ML^{-3}]
c_v, c_v^e	Instantaneous and equilibrium heat capacities at constant volume [$L^2 T^{-2}\theta$]
C_α	Chemical constituent α [1]
C_p^w	Frequency-dependent heat capacity [1]
$C_{p\sigma}^w$	Frequency-dependent heat capacity for σ th orthonormal reaction [1]
C_α	Chemical constituent α [1]
f	Frequency of sound wave [T^{-1}]
G_{ij}	Matrix coefficients of kinetics equations [T^{-1}]
h_σ	Heat of σ th reaction at constant temperature and pressure [$H\text{-mol}^{-1}$]
H_σ	Heat of σ th orthonormal reaction [$H \text{ mol}^{-1}$]
J_{ij}	Symmetrized matrix coefficients of kinetics equations [T^{-1}]
n	Number of constituents [1]
k	Wave number [L^{-1}]
K_σ	Equilibrium constant of σ th reaction [1]
K_o	Bulk viscosity [$ML^{-1} T^{-1}$]
k_σ^F, k_σ^R	Forward and reverse reaction rate coefficients respectively of σ th reaction [$\text{mol M}^{-1} T^{-1}$]

k_{θ}	Thermal conductivity of mixture [MLT ⁻³ θ ⁻¹]
m_{α}	Molar density of α th constituent [mol (of α) L ⁻³]
M_a	Molecular weight of α th component [mol (of α) M ⁻¹]
M_e	Molecular weight of equilibrium mixture [M mol ⁻¹]
p, p_0, p^a	Thermodynamic, thermostatic and acoustic pressures respectively [ML ⁻¹ T ⁻²]
r	Number of reactions [1]
R	Number of independent reactions [1]
R^{\dagger}	Universal gas constant [ML ² T ⁻² θ ⁻¹ mol ⁻¹]
s	Specific entropy [H M ⁻¹ θ ⁻¹]
$S_{\sigma\alpha}$	Signed stoichiometric numbers [1]
S_{σ}	Sum of signed stoichiometric numbers of σ th reaction [1]
t	Time variable [T]
v_x, v_{x0}, v^a	Total, static and acoustic velocities in x-direction [LT ⁻¹]
v	Specific volume of equilibrium mixture [L ³ M ⁻¹]
v_{σ}	Volumetric change of σ th reaction at constant temperature and pressure [L ³ mol ⁻¹]
V_{σ}	Volumetric change of σ th orthonormal mode at constant temperature and pressure [L ³ mol ⁻¹]
\underline{x}, x_i	Position vector and components [L]
X_{α}	Mole-fraction of α -constituent
X	Frequency number [1]
Y	Thermoviscous number [1]
Z_{σ}	Extent-of-reaction of σ th orthonormal reaction
α	Absorption coefficient [L ⁻¹]
$\beta_{\theta}, \beta_{\theta}^e$	Instantaneous and equilibrium isobaric coefficients of thermal expansion [θ ⁻¹]

β_p, β_p^e	Instantaneous and equilibrium isothermal coefficients of compressibility [$T^2M^{-1}L^{-1}$]
γ_α	Activity coefficient of α th chemical components [1]
$\gamma = c_p/c_v$	Ratio of instantaneous heat capacities
δ_{ij}	Kronecker delta symbol [1]
ϵ	Specific internal energy [L^2T^{-2}]
ζ, ζ_σ	Degree-of-advancement vector and σ^{th} component [$\text{mol } M^{-1}$]
$+e$ ζ_σ	Reaction velocity at equilibrium [$\text{mol } M^{-1} T^{-1}$]
η_0	Shear viscosity [$ML^{-1} T^{-1}$]
$\theta, \theta_0, \theta^a$	Absolute equilibrium and acoustic temperature respectively [θ]
λ	Wavelength of acoustic wave [L]
λ_σ	Eigenvalue of σ th reaction [T^{-1}]
μ_α	Chemical potential of α th component [$L^2T^{-2}\text{mol}^{-1}$]
ρ	Density of equilibrium mixture [ML^{-3}]
τ_ρ, τ_ρ^*	Relaxation times of ρ th reaction at constant (p, θ) and (s, p) respectively [T]
χ	Complex propagation coefficient [L^{-1}]
ω	Angular frequency [T^{-1}]
$\underline{\omega}, \omega_\alpha$	Molar concentration vector and α th component [$\text{mol } M^{-1}$]
ω	Total molar concentration of mixture
$+ \underline{\omega}, \omega_\alpha^+$	Molar production vector and α th component [$\text{mol } M^{-1} T^{-1}$]
Ω_σ	Dimensionless chemical relaxation time of σ th reaction [1]

[] = 'dimensions of ' ; M = mass (g), L = length (cm),
T = time (sec), θ = absolute temperature ($^{\circ}K$),
H = heat (cal), mol = g mole

I. INTRODUCTION

Sound absorption and dispersion are directly dependent upon the properties of the transmitting material and are attributed to various dissipative mechanisms; that is, those that contribute to an increase of the entropy. In particular, ultrasound measurements have provided useful estimates of kinetic and thermodynamic parameters of fast reactions in gases and liquids which complement other traditional chemical kinetic measurement techniques.¹⁻⁹

Combined with an historical outline of classical linearized acoustic theory, Truesdell has given an exact theoretical description for the spatial attenuation and phase velocity of a one-dimensional, forced harmonic plane wave in a Newtonian viscous, linear heat-conducting (or Fourier), single-component fluid.¹⁰ Several investigations have extended the viscothermal sound absorption and dispersion problem for a fluid with a single chemical reaction or a binary set of reactions in a nonconducting fluid and have presented analytical solutions.¹¹⁻¹⁴ Recently, the Newtonian viscothermal problem of acoustics has been solved for the case of chemically reacting fluids with an arbitrary finite number of coupled reactions by Margulies and Schwarz.¹⁵ Our theoretical results for a multireaction system differed somewhat from previously reported work and it is appropriate to compare the different methods numerically. For example, in the analysis it was necessary to use certain transformations; that is, a reaction sequence orthonormalization to obtain an approximate formula for the absorption from the exact biquadratic solution that has the simple form:

$$\frac{\alpha}{f^2} = \sum_{\phi=1}^R \frac{N_{\phi}}{1 + (\omega\tau_{\phi})^2} + N_0 \quad (1)$$

Previous investigators have only examined the linearized kinetic equations to obtain a nonunique coordinate transformation.

Experimental data are more easily analyzed by using simple functional formulas such as Eq. (1). However, the range of validity of these approximations, particularly the viscous term, has not been examined in any great detail. This paper reports some calculations that were made in order to determine the magnitude of the various errors in these approximations and also to compare the different theoretical methods.

In this paper we present calculations of the sound absorption α and sound speed c as functions of frequency for three chemical systems. These fluids are interpreted in terms of a perturbation of a two-step chemical reaction mechanism from a state of strong equilibrium.

The paper is arranged as follows. First, we discuss some background information and acoustic theory. Next, the linearized partial differential equations of acoustics (both hydrodynamic and chemical kinetic) and the modified Kirchhoff-Langevin solution are summarized. Then, chemical kinetic equations and transformations pertinent to a relatively general two-step mechanism are provided. Finally, applications of the theory to three chemical reaction examples are presented.

II. ACOUSTIC THEORY FOR A REACTING FLUID MIXTURE

Given a semi-infinite continuous fluid medium initially at rest, the y, z plane of fluid is oscillated harmonically in the x -direction with frequency ω as shown pictorially in Fig. 1. This displacement of the plane boundary and resulting longitudinal wave motion within the fluid is assumed to be infinitesimal. The wave amplitude progressively diminishes with transmission distance as the mechanical energy which is imparted by the boundary surface is dynamically converted into thermal energy. This analysis assumes that the actual motion should be sufficiently well approximated by the exact solutions to the first-order field equations of the mixture, in which all nonlinear terms are omitted, and moreover, all coefficients are evaluated at their uniform equilibrium reference values.

The total value of each variable, I , in the list of system variables chosen to define this one-dimensional perturbed motion is decomposed into an equilibrium (static) and time-dependent incremental acoustic contribution.

$$I \left(\begin{array}{c} \text{Total} \\ \text{Variable} \end{array} \right) = I_0 \left(\begin{array}{c} \text{Static} \\ \text{Variable} \end{array} \right) + I^a \left(\begin{array}{c} \text{Acoustic} \\ \text{Variable} \end{array} \right)$$

Furthermore, each acoustic variable, I^a , such as pressure p^a , temperature θ^a , or velocity v^a is represented as a damped sinusoidal progressive wave by

$$I^a = \text{Re} \{ I_0^a \exp(\chi x + i\omega t) \} \quad (2)$$

$\chi = -(\alpha + i k)$ is the complex propagation variable where α is the spatial absorption coefficient and k is the magnitude of the wave number vector perpendicular to surfaces of constant phase. $k = \omega/c$ is the spatial analog of frequency and represents the number of wavecrests per unit length, or simply 2π multiplied by the reciprocal of wavelength in this one-dimensional problem.

A. Hydrodynamic Equations

For waves propagating in the x -direction into a fluid mixture initially at rest with a uniform equilibrium state the hydrodynamic equations for a Newtonian viscous fluid with Fourier heat conduction may be written in terms of the acoustic variables as follows:

$$-\beta_\theta \frac{\partial \theta^a}{\partial t} + \beta_p \frac{\partial p^a}{\partial t} - \rho_0 v_j \frac{\partial v_j^a}{\partial t} + \frac{\partial v^a}{\partial x} = 0 \quad (3)$$

$$\rho_0 \frac{\partial v^a}{\partial t} + \frac{\partial p^a}{\partial x} - \left(\frac{4}{3} \eta_0 + K_0 \right) \frac{\partial^2 v^a}{\partial x^2} = 0 \quad (4)$$

$$\rho_0 c_p \frac{\partial \theta^a}{\partial t} - \theta_0 \beta_\theta \frac{\partial p^a}{\partial t} + \rho_0 h_j \frac{\partial \xi_j^a}{\partial t} - k_\theta \frac{\partial^2 \theta^a}{\partial x^2} = 0 \quad (5)$$

$j = 1, 2, \dots R$ reactions.

These equations represent the linearized balances of total mixture mass, linear momentum and energy when diffusion and radiation supply can be omitted. Definitions for these variables and their units may be found in the nomenclature section. Repeated indices should be summed except when they are printed as bold subscripts (or underlined).

B. Stoichiometry and Chemical Kinetic Equations

Here, we consider a general reaction scheme composed of an arbitrary finite number of elementary reaction steps, say r , involving $\alpha = 1, 2, \dots n$ constituents C_α . This may be expressed by

$$\sum_{\alpha=1}^n S_{\rho\alpha} C_\alpha = 0 \quad \rho = 1, 2, \dots r \quad (6)$$

where the positive values of the stoichiometric coefficients $S_{\rho\alpha}$ correspond to the reaction products while negative values correspond to reactants. Also, by convention, a neutral species such as an inert solvent is assigned a stoichiometric number of zero. Let the rank of the stoichiometric matrix be denoted by $R \leq r$. This determines the possible number of independent reactions of the system. As a consequence, the total collection of reaction sequences may be completely represented by a selected subset of R reactions. It is noted that the number of "independent reactions" determines the calculated number of relaxation times.¹⁵

In order to express the composition changes during the progress of a reaction in a nondiffusing mixture, it is convenient to define the degree of advancement such that

$$\frac{w}{\alpha} - \frac{w^e}{\alpha} = \xi_\rho S_{\rho\alpha} \quad \begin{array}{l} \alpha = 1, 2, \dots n \\ \rho = 1, 2, \dots R \end{array} \quad (7)$$

where w_α^e is a reference molar density, say at equilibrium.¹⁶ A concise mathematical treatment of the stoichiometry of reacting materials has been given and provides a natural means for introducing the reaction velocities¹⁷ and gives a proof of the Law of Definite Proportions.¹⁸ This is briefly discussed below starting with an assertion that the atomic substances making up the mixture of constituents are indestructable which may be expressed by the equation

$$\sum_{q=1}^n T_{\alpha'}^q \frac{c_q}{M_q} = 0 \quad \alpha' = 1, 2, \dots U \text{ elements} \quad (8)$$

$T_{\alpha'}^q$ represents the number of moles of atomic substance α' in one mole of the q^{th} constituent. Also, note that if we multiply by $W_{\alpha'}$, the atomic weight of α' , and sum then Eq. (8) obtains

$$\sum_{q=1}^n c_q = 0 \quad \text{since} \quad M_q = \sum_{\alpha'=1}^U T_{\alpha'}^q W_{\alpha'}$$

Moreover, Eq. (8) establishes the following relationships among the n mass supplies

$$c_q = \rho M_q \sum_{\phi=1}^{n-\kappa} S_{q\phi} \zeta_{\phi}^+ \quad (9)$$

$$w_q = \sum_{\phi=1}^{n-\kappa} S_{q\phi} \zeta_{\phi}^+$$

where the stoichiometric matrix $[S_{q\phi}]$ is any $n \times (n-\kappa)$ matrix of rank $(n-\kappa) \equiv R$ such that

$$\sum_{q=1}^n T_{\alpha'}^q S_{q\phi} = 0; \quad \phi = 1, 2, \dots, (n-\kappa) \quad \alpha' = 1, 2, \dots, U \quad (10)$$

and $\kappa = \text{rank} [T_{\alpha'}^q] \leq \text{minimum}(n, U)$. ζ_{ϕ}^+ is interpreted as a reaction velocity or rate. If Eq. (10) is multiplied by $W_{\alpha'}$ and summed over α'

$$\sum_{\alpha'=1}^U \sum_{q=1}^n T_{\alpha'}^q W_{\alpha'} S_{q\phi} = \sum_{q=1}^n M_q S_{q\phi} = 0 \quad (11)$$

This latter expression corresponds to the notion that the $(n-\kappa)$ reaction equations are balanced. Neither the stoichiometric matrix nor the reaction velocities are unique; however, the maximum number of linearly independent chemical reactions possible in the mixture is unique. In our acoustic and applied chemical kinetic analysis the reactions are assumed in advance. Therefore this defines the elements of the stoichiometric matrix to within a nonzero constant.

The equations of mass balance for species α (i.e., sometimes called the partial mass balance equations for the mixture) may be written as

$$\dot{w}_q = \dot{w}_q^+ = \sum_{\phi=1}^R S_{q\phi} \dot{\zeta}_\phi \quad q = 1, 2, \dots, n$$

or alternatively

$$\dot{\zeta}_\phi = \dot{\zeta}_\phi^+ \quad \phi = 1, 2, \dots, R \quad (12)$$

which gives the composition of the mixture constituents versus time. Assuming a polynomial mass-action form for the kinetics constitutive relation the chemical kinetic (or partial mass balance) equations become:

$$\dot{\zeta}_j = \dot{\zeta}_j^+ = k_j^F(\theta, p) \prod_{\alpha=1}^n a_\alpha^{S_{\alpha j}^-} - k_j^R(\theta, p) \prod_{\alpha=1}^n a_\alpha^{S_{\alpha j}^+} \quad (13)$$

$$j = 1, 2, \dots, R$$

$S_{\alpha j}^-$ and $S_{\alpha j}^+$ denote the positive stoichiometric constants for the reactants and products, respectively.

Further, a linearized version of the above equation can be derived for small departures from a state of strong equilibrium.

$$\frac{\dot{\zeta}_j}{\zeta_j^e} = \left[\frac{\partial(\bar{A}_j/R^\dagger\theta)^e}{\partial\theta} \right] \theta^a + \left[\frac{\partial(\bar{A}_j/R^\dagger\theta)^e}{\partial p} \right] p^a + \left[\frac{\partial(\bar{A}_j/R^\dagger\theta)^e}{\partial\zeta_\ell} \right] \zeta_\ell^a \quad (14)$$

where

$$\zeta_j^e = k_j^F \prod_{\alpha=1}^n (a_\alpha^e)^{S_{\alpha j}^-} = k_j^R \prod_{\alpha=1}^n (a_\alpha^e)^{S_{\alpha j}^+}$$

$$S_{\alpha j} = (S_{\alpha j}^- - S_{\alpha j}^+)$$

$$\left[\frac{\partial(\bar{A}_j/R^\dagger\theta)^e}{\partial\theta} \right] = \frac{h_j}{R^\dagger\theta_0^2} ; \left[\frac{\partial(\bar{A}_j/R^\dagger\theta)^e}{\partial p} \right] = - \frac{v_j}{R^\dagger\theta_0}$$

$$- \left[\frac{\partial(\bar{A}_j/R^\dagger\theta)^e}{\partial\zeta_\ell} \right] \equiv A_{j\ell} = M_e \left[\sum_{\alpha=1}^n \frac{(S_{j\alpha} S_{\ell\alpha})}{x_\alpha^e} - S_j S_\ell \right] + NI$$

$$NI \equiv M_e^{-1} S_{j\alpha} \frac{\partial}{\partial \zeta_{j\alpha}} (\ln \gamma_\alpha)$$

$a_\alpha = \gamma_\alpha X_\alpha$ is the activity of component α (with γ_α the activity coefficient of α). For ideal systems $\gamma_\alpha = 1$ and the non-ideal terms, N.I., are identically zero.

Equation (14) is a system of coupled linear differential equations of first order in ζ_j^a . For $\theta^a = p^a = 0$ and for a single reaction (i.e., $j=1$), a chemical relaxation time towards equilibrium can be defined as

$$\frac{1}{\tau_1} = \frac{\zeta_1^+}{R^+ \theta_0} \left(\frac{\partial \bar{A}_1}{\partial \zeta_1} \right)^e$$

such that $\dot{\zeta}_1^a = -\frac{1}{\tau_1} \zeta_1^a$

When considering multistep reaction systems each chemical relaxation time rather than corresponding to an isolated reaction step corresponds to a "normal mode" of the chemical system. Also, for a system at constant $\{p, \theta\}$ the kinetics equations become

$$\dot{\zeta}_j^a = -G_{j\ell} \zeta_\ell^a$$

where $G_{j\ell} = \zeta_j^+ A_{j\ell}^e$ and the matrix \underline{G} is not necessarily symmetric.

A coordinate transformation of the linearized kinetic equations (at constant θ and p) is introduced at this point in the analysis in order to separate the differential equations into disjoint, independent equations. Let

$$\zeta_j^a = (\zeta_j^e)^{\frac{1}{2}} \zeta_j^a$$

Then Eq. (14) becomes

$$\dot{\zeta}_j^a = -J_{j\ell} \zeta_\ell^a \tag{15}$$

where $J_{j\ell} \equiv (\zeta_j^e)^{\frac{1}{2}} A_{j\ell}^e (\zeta_\ell^e)^{\frac{1}{2}} = J_{\ell j}$

Now it is convenient to define:

$$\xi_{j\sigma}^a = M_{j\sigma} Z_\sigma \quad ; \quad j, \sigma = 1, 2, \dots, R$$

such that

$$\dot{Z}_\ell = - (M_{\ell j}^{-1} J_{jk} M_{k\sigma}) Z_\sigma \quad (16)$$

$$\dot{Z}_\ell = - D_{\ell\sigma} Z_\sigma = - \lambda_\sigma Z_\sigma$$

and $\underline{M}^{-1} \underline{J} \underline{M} = \underline{D}$ is diagonal. Its elements are formed from the eigenvalues $\{\lambda_\sigma\}$ $\sigma = 1, 2, \dots, R$ obtained from $\det (\lambda_\sigma \delta_{\sigma k} - J_{\sigma k}) = 0$.

The reciprocals of the elements of the diagonal matrix represent the relaxation times of the reaction (i.e., $\tau_\sigma = \frac{1}{\lambda_\sigma}$). It can be shown that:

- (1) both the eigenvalues of the matrix \underline{G} and \underline{J} are the same;
- (2) the matrix \underline{M} needs to be orthogonal (i.e., $\underline{M}^{-1} = \underline{M}^T$) as previously shown to obtain sound absorption formulas similar to Eq. (1) for practical application.¹⁵
- (3) different relaxation times may be defined according to the particular set of independent variables used. For example, equivalent relaxation times can be defined with $\{\theta, s\}$ held fixed where s is the specific entropy.

C. First-Order Acoustic Equations

The linearized Eqs. (3, 4, 5 and 14) explicitly written for a two independent reaction mechanism are

$$-\frac{\partial \theta^a}{\partial t} + \beta_{p,\zeta} \frac{\partial p^a}{\partial t} - \rho_0 [V_1 \dot{Z}_1 + V_2 \dot{Z}_2] + \frac{\partial v^a}{\partial x} = 0 \quad (17)$$

$$\rho_0 \frac{\partial v^a}{\partial t} + \frac{\partial p^a}{\partial x} - (K_0 + \frac{4}{3} \eta_0) \frac{\partial^2 v^a}{\partial x^2} = 0 \quad (18)$$

$$\rho_0 c_{p,\zeta} \frac{\partial \theta^a}{\partial t} - \theta_0 \beta_{\theta,\zeta} \frac{\partial p^a}{\partial t} + \rho_0 [H_1 \dot{Z}_1 + H_2 \dot{Z}_2] - k_\theta \frac{\partial^2 \theta^a}{\partial x^2} = 0 \quad (19)$$

$$\dot{Z}_1 + \frac{H_1}{R^\dagger \theta_0^2} \theta^a + \frac{V_1}{R^\dagger \theta_0} p^a + \lambda_1 Z_1 = 0 \quad (20)$$

$$\dot{Z}_2 + \frac{H_2}{R^\dagger \theta_0^2} \theta^a + \frac{V_2}{R^\dagger \theta_0} p^a + \lambda_2 Z_2 = 0 \quad (21)$$

These equations constitute a set of first-order hydroacoustic equations for infinitesimal sound waves propagating in the x-direction. These equations admit damped harmonic waves of the form of Eq. (2) where $I^a = \{ \theta^a, p^a, v^a, Z_1, Z_2 \}$. For nontrivial χ solutions, the determinant of the matrix of the coefficients, given in partitioned form below, must be identically zero.

$$\det \begin{pmatrix} \underline{\underline{A}} & \underline{\underline{B}} \\ \underline{\underline{C}} & \underline{\underline{\Delta}} \end{pmatrix} = 0 = \det \left(\underline{\underline{A}} - \underline{\underline{B}} \underline{\underline{\Delta}}^{-1} \underline{\underline{C}} \right) \quad (22)$$

where

$$\underline{\underline{A}} = \begin{pmatrix} -i\omega\beta_\theta & i\omega\beta_p & \chi \\ 0 & \chi & i\rho\omega - (K_0 + \frac{4}{3}\eta_0)\chi^2 \\ (i\omega\rho c_p - k_\theta\chi^2) - i\omega\theta_0\beta_\theta & 0 & 0 \end{pmatrix}$$

$$\underline{\underline{B}} = \begin{pmatrix} -i\omega\rho_0 V_1 & -i\omega\rho_0 V_2 \\ 0 & 0 \\ i\omega\rho_0 H_1 & i\omega\rho_0 H_2 \end{pmatrix} \quad \underline{\underline{\Delta}} = \begin{pmatrix} 1 + i\omega\tau_1 & 0 \\ 0 & 1 + i\omega\tau_2 \end{pmatrix}$$

$$\underline{\underline{C}} = \begin{pmatrix} \frac{H_1}{R^\dagger \theta_0^2} & \frac{V_1}{R^\dagger \theta_0} & 0 \\ \frac{H_2}{R^\dagger \theta_0^2} & \frac{V_2}{R^\dagger \theta_0} & 0 \end{pmatrix}$$

D. Modified Kirchhoff-Langevin Equation

In general, a complex-valued biquadratic algebraic equation for χ is obtained. This may be expressed in terms of dimensionless parameters as follows:

$$\left(\frac{X}{k_0}\right)^4 [iXY (i\gamma X B_p^w + 1)] + \left(\frac{X}{k_0}\right)^2 [C_p^w + i\gamma X (C_p^w B_p^w - \frac{\gamma-1}{\gamma} (B_p^w)^2 + \gamma B_p^w)] + \gamma [C_p^w B_p^w - \frac{\gamma-1}{\gamma} (B_p^w)^2] = 0 \quad (23)$$

where $k_0 = \omega/c_0$

$$X = \omega \left(\frac{4}{3} \eta_0 + K_0 \right) / \rho c_0^2 \quad \text{Frequency Number}$$

$$Y = k_\theta / \left(\frac{4}{3} \eta_0 + K_0 \right) c_p \quad \text{Thermoviscous Number}$$

$$\Omega_\sigma = \tau_\sigma \omega \quad \text{Reaction Frequency Number}$$

and

$$\gamma = c_p / c_v \quad \text{Ratio of Specific Heats}$$

Also,

$$C_p^w = 1 + \sum_{\sigma=1}^R \frac{\Delta C_{p\sigma}}{1 + i\omega \tau_\sigma} ; \quad \Delta C_{p\sigma} = \frac{H_\sigma^2 \tau_\sigma}{c_p R^\dagger \theta_0^2}$$

$$B_\theta^w = 1 + \sum_{\sigma=1}^R \frac{\Delta B_{\theta\sigma}}{1 + i\omega \tau_\sigma} ; \quad \Delta B_{\theta\sigma} = \frac{H_\sigma V_\sigma \tau_\sigma}{v \beta_\theta R^\dagger \theta_0^2}$$

$$B_p^w = 1 + \sum_{\sigma=1}^R \frac{\Delta B_{p\sigma}}{1 + i\omega \tau_\sigma} ; \quad \Delta B_{p\sigma} = \frac{V_\sigma \tau_\sigma}{v \beta_p R^\dagger \theta_0}$$

$$H_p = (\zeta_\sigma^e)^{\frac{1}{2}} M_{\sigma p} h_\sigma ; \quad V_p = (\zeta_\sigma^e)^{\frac{1}{2}} M_{\sigma p} v_\sigma$$

For the cases of 1) a single-component nonreacting fluid and 2) a fluid mixture with a single elementary reaction the algebraic equations correspond to the results of Truesdell¹⁰ and Mazo¹¹, respectively. In the case of a nondiffusive,

nonreacting system ($B_p^w \rightarrow 1$, $C_p^w \rightarrow 1$, $B_\theta^w \rightarrow 1$) the classical Kirchhoff-Langevin equation is obtained.

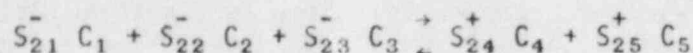
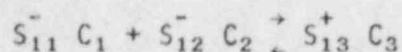
$$\left(\frac{\chi}{k_0}\right)^4 [iXY (1 + i\gamma X) + \left(\frac{\chi}{k_0}\right)^2 (1 + iX(1+\gamma Y))] + 1 = 0$$

The propagation constant χ can be determined by solving the complex algebraic equation numerically. Two of the four values of χ are unphysical (negative values of α) and the other two correspond to type I and type II waves respectively. The type I waves are chosen to correspond to the classical theories. The type II waves are found to have very large attenuation and have not been observed experimentally.

III. COUPLED CHEMICAL REACTIONS

A. Kinetic Equations and Relaxation Times

The ideas and formulas in the previous section will be specialized to the case of two independent coupled chemical reactions and later used in the illustrative acoustic perturbation examples. Consider the two-step reaction mechanism



where C_α represents chemical species $\alpha = 1, 5$ and $S_{\rho\alpha}^-$ and $S_{\rho\alpha}^+$ denote the positive stoichiometric constants for the reactants and products, respectively. The stoichiometric matrix $S_{\rho\alpha}$ for this relatively general two-step mechanism becomes:

$$S_{\rho\alpha} = \begin{pmatrix} -S_{11}^- & -S_{12}^- & S_{13}^+ & 0 & 0 \\ -S_{21}^- & -S_{22}^- & -S_{23}^- & S_{24}^+ & S_{25}^+ \end{pmatrix} \quad (24)$$

The Rank ($S_{\rho\alpha}$) in Eq. (24) equals two (i.e., $R=2$) corresponding to two independent reactions and

$$S_\rho = \sum_{\alpha=1}^5 S_{\rho\alpha} \quad \text{obtains}$$

$$S_1 = (-S_{11}^- \quad -S_{12}^- \quad +S_{13}^+)$$

$$S_2 = (-S_{21}^- \quad -S_{22}^- \quad -S_{23}^- \quad +S_{24}^+ \quad +S_{25}^+)$$

The linearized kinetic equations (at $\theta^a = p^a = 0$) for this two independent reaction example are written

$$\begin{pmatrix} \dot{\zeta}_1^a \\ \dot{\zeta}_2^a \end{pmatrix} = \begin{pmatrix} \zeta_1^e & A_{11} & \zeta_1^e & A_{12} \\ \zeta_2^e & A_{21} & \zeta_2^e & A_{22} \end{pmatrix} \begin{pmatrix} \zeta_1^a \\ \zeta_2^a \end{pmatrix} \quad (25)$$

Using the mass-action kinetics constitutive relation and assuming an ideal mixture (e.g., $\gamma_\alpha = 1$; $\alpha = 1, 5$) further defines the kinetics problem:

$$\zeta_1^+ = k_1^F(\theta, p)(X_1)S_{11}^-(X_2)S_{12}^- = k_1^R(\theta, p)(X_3)S_{13}^+$$

$$\zeta_2^+ = k_2^F(\theta, p)(X_1)S_{21}^-(X_2)S_{22}^-(X_3)S_{23}^- = k_2^R(\theta, p)(X_4)S_{24}^+(X_5)S_{25}^+$$

$$A_{11} = \left[\frac{(S_{11}^-)^2}{X_1} + \frac{(S_{12}^-)^2}{X_2} + \frac{(S_{13}^-)^2}{X_3} - (S_1)^2 \right]$$

$$A_{12} = A_{21} = \left[\frac{(S_{11}^-)(S_{21}^-)}{X_1} + \frac{(S_{12}^-)(S_{22}^-)}{X_2} + \frac{(S_{13}^-)(S_{23}^-)}{X_3} - (S_1)(S_2) \right]$$

$$A_{22} = \left[\frac{(S_{21}^-)^2}{X_1} + \frac{(S_{22}^-)^2}{X_2} + \frac{(S_{23}^-)^2}{X_3} + \frac{(S_{24}^+)^2}{X_4} + \frac{(S_{25}^+)^2}{X_5} - (S_2)^2 \right]$$

Also, Eq. (15) gives the transformed reaction velocities

$$\begin{pmatrix} \dot{\xi}_1 \\ \dot{\xi}_2 \end{pmatrix} = - \begin{pmatrix} J_{11} & J_{12} \\ J_{21} & J_{22} \end{pmatrix} \begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix} \quad (26)$$

where an orthogonal matrix \underline{M} is used to diagonalize \underline{J} .

$$J_{11} = \zeta_1^+ A_{11}$$

$$J_{12} = J_{21} = (\zeta_1^+ \zeta_2^+)^{1/2} A_{12}$$

$$J_{22} = \zeta_2^+ A_{22}$$

The relaxation times are computed from

$$\det \begin{pmatrix} J_{11} - \lambda & J_{12} \\ J_{21} & J_{22} - \lambda \end{pmatrix} = 0$$

$$\lambda_1, \lambda_2 = \frac{1}{2} \{ \text{tr } \underline{J} \pm [(\text{tr } \underline{J})^2 - 4 \det \underline{J}]^{1/2} \} \quad (27)$$

or

$$= \frac{1}{2} \text{tr } \underline{J} \{ 1 \pm [1 - 4 (\det \underline{J} / (\text{tr } \underline{J})^2)] \}$$

where $\lambda_1 = \frac{1}{\tau_1}$; $\lambda_2 = \frac{1}{\tau_2}$; $\text{tr } \underline{J} = \lambda_1 + \lambda_2$ and $\det \underline{J} = \lambda_1 \lambda_2$.

The chemical system relaxation times, in general, are not simply related to the individual relaxation times, say τ_{11} and τ_{22} , if it were possible to set up the equilibria in each reaction (steps one and two) in isolation. Let

$$\frac{1}{\tau_{11}} \equiv - \zeta_1^+ A_{11}$$

$$\frac{1}{\tau_{22}} \equiv - \zeta_2^+ A_{22}$$

For $\frac{4 \det \underline{J}}{(\text{tr } \underline{J})^2} \ll 1$ or when the relaxation times are well separated

$$\frac{1}{\tau_1} \approx \text{tr } \underline{J} = \frac{1}{\tau_{11}} + \frac{1}{\tau_{22}}$$

$$\frac{1}{\tau_2} \approx - \frac{\det \underline{J}}{\text{tr } \underline{J}}$$

and the first overall relaxation time is equal to the single very short time.

Now,

$$\begin{pmatrix} \xi_1^a \\ \xi_2^a \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} Z_1 \\ Z_2 \end{pmatrix}$$

The components of \underline{M} for a two reaction case are obtained from

$$\frac{M_{11}}{M_{21}} = \frac{J_{12}}{\lambda_1 - J_{11}} = \frac{\lambda_1 - J_{22}}{J_{21}}$$

and
$$\frac{M_{12}}{M_{22}} = \frac{J_{12}}{\lambda_2 - J_{11}} = \frac{\lambda_2 - J_{22}}{J_{21}}$$

When conditions of orthonormality (e.g., $M_{11}^2 + M_{21}^2 = 1$ and $M_{12}^2 + M_{22}^2 = 1$) are used, the orthogonal transformation matrix becomes

$$\underline{M} = \begin{pmatrix} \left[\frac{J_{12}^2}{(\lambda_1 - J_{11})^2 + J_{12}^2} \right]^{1/2} & - \left[\frac{J_{12}^2}{(\lambda_2 - J_{11})^2 + J_{12}^2} \right]^{1/2} & = M_{21} \\ \left[\frac{(\lambda_1 - J_{11})^2}{(\lambda_1 - J_{11})^2 + J_{12}^2} \right]^{1/2} & \left[\frac{(\lambda_2 - J_{11})^2}{J_{12}^2 + (\lambda_2 - J_{11})^2} \right]^{1/2} & = M_{11} \end{pmatrix}$$

B. Calculated Results

Estimates of the absorption or sound speed versus frequency may be directly calculated given that all the physicochemical parameters that define the materials under study are known. Alternatively, measured absorption data, for example, when combined with data available in the literature for some of the parameters can be used to quantify unknown parameters associated with fast reactions (such as kinetic and thermodynamic information). To this end, simple formulas and direct relationships such as given by Eq. (1) are sought for fitting the data from experimental measurements.

N_α ($\alpha > 0$) in Eq. (1) is proportional to Q_α^2 which is a linear combination of the heat of reaction and the volumetric change for the orthonormal reaction sequence. Our relations between the normalized reactions and the proposed two-step reaction sequences are given as:

$$Q_1 = (\xi_1^e)^{1/2} M_{11} q_1 + (\xi_2^e)^{1/2} M_{21} q_2 \quad (28)$$

$$Q_2 = (\zeta_1^e)^{\frac{1}{2}} M_{21} q_1 + (\zeta_2^e)^{\frac{1}{2}} M_{22} q_2$$

where $q_\sigma = h_\sigma - \left(\frac{c_p \rho_0}{\beta_\theta}\right) v_\sigma$; $\sigma = 1, 2$

Further, our approach obtains

$$N_\alpha = \frac{2\pi^2 \rho_0 c_0}{R^\dagger \theta_0} \tau_\alpha^* \left(v_\alpha - \frac{\beta_\theta}{\rho_0 c_p} H_\alpha \right)^2 \quad (29)$$

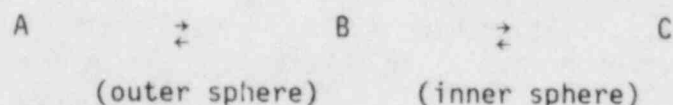
It is noted that this relation differs from other investigators because of the transformations required in the acoustics equations to obtain the simple approximate forms given by Eq. (1). For the single reaction case the comparison is exact. We remark that the theoretical derivation used by others did not explicitly use the balance of mass, linear momentum and energy for acoustical wave propagation and was obtained in a heuristic manner.

We wrote a computer program to calculate the absorption and speed of sound by the "direct" method, which requires all the physical property data. The results of calculations for three chemical systems including cobalt polyphosphate mixtures, aqueous solutions of glycine, and water/dioxane are discussed in the following sections.

1. Cobalt Polyphosphate Mixtures

The technique of ultrasonic absorption has been used to study counterion site binding for polysalt solutions such as cobalt polyphosphate. Arguments were made that 1) the absorption mechanism is analogous to Eigen's ion-pair formation in simple electrolyte solutions³ and 2) a fraction of the ions were condensed according to Manning's theory for polyelectrolytes.¹⁹

The model considers ion-pairs exhibiting three states of hydration that were in equilibrium relative to the two reaction sequence:



State A corresponds to the hydration shells of the polyion site and the counterion in contact without overlapping; State B consists of relatively unaffected counterions and partially dehydrated polyion sites and State C consists of the hydration shells of both the counterions and the polyion sites being modified.

Zana and Tondre^{20,21} have examined the divalent cobalt polyphosphate system in some detail using density, nuclear magnetic resonance and ultrasonic measurements. They assumed 1) that the ultrasonic absorption due to chemical reactions is only affected by the condensed counter-ions and not by the mobile ions; 2) the ultrasonic absorption is determined primarily by volumetric changes and not by

the heats of reaction; 3) the fraction (f_m) of condensed counter-ions can be calculated from the work of Manning

$$f_m M_A^0 = M_A^e + M_B^e + M_C^e$$

and is independent of the polyion concentration provided it is not too large; 4) the excess absorption due to the above described chemical processes can be separated from other effects by subtracting the absorption using TMA (tetramethylammonium) as the counterion; and 5) the forward rate for the second reaction ($B \rightleftharpoons C$) which relates to the exchange of water molecules from the inner hydration sheath of the ion and bulk water is close to that of any small ligand and is given by $1.333 \times 10^5 \text{ mol g}^{-1} \text{ sec}^{-1}$.

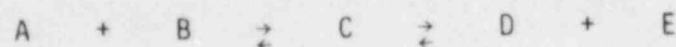
In our calculations, we have made certain assumptions: 1) the degree of polymerization is not important provided that it is large enough ($P_w > 500$); 2) the equivalent monomer molecular weight is 108.43; and the solutions are sufficiently dilute such that the values for the physical properties are close to pure solvent (water). Refer to Table 1 for a list of physical property data used in the calculations.

We remark that the approximate calculation of α (cobalt polyphosphate)/ f^2 minus $\alpha(\text{TMA}^+ \text{PP})/f^2$ differs from the exact by less than 1 percent which is well within experimental error. The relaxation frequencies did not change over the concentration range (0.068 N to 0.125 N) examined. (Refer to Fig. 2).

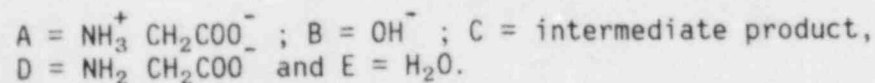
The relative contributions to the absorption per wavelength ($\alpha\lambda$ curve) are shown in Fig. 3. The viscous contribution is less than the chemical reaction contribution at low frequencies but dominates at higher frequencies. The first reaction is fast and corresponds to the second peak while the second reaction is slower (first peak). The relaxation frequencies are about a factor of ten apart. Approximately 1/5th of the second reaction peak is contributed by the first reaction. Total $[(\alpha\lambda)_1 + (\alpha\lambda)_2]$ maxima may not correspond directly to the relaxation frequencies even in this well separated case. The reaction volume changes are estimated to be approximately equal to the normal reaction changes. Zana and Tondre reported reaction volume changes of approximately 22.9 and 4.4 $\text{cm}^3 \text{ mol}^{-1}$ for reactions one and two, respectively. Our data-fit and interpretation (using the orthonormalized approach) gives 20.98 and 5.26 $\text{cm}^3 \text{ mol}^{-1}$ for the volume changes associated with the first and second reaction.

2. Aqueous Solutions of Glycine

Zinov'ev et al.²² have reported their measurements of aqueous solutions of glycine (0.53 moles liter⁻¹; pH 10-13) for temperatures 15° to 30°C, in the frequency range 0.5-1200 MHz. The data were analyzed on the basis of a proton transfer reaction of the form:



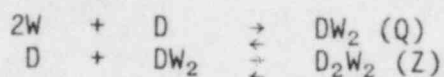
where



This proposed mechanism is consistent with the two-relaxation shape of the absorption spectrum. Previous investigations have identified a single acoustic relaxation (dependent on pH) and Appelgate postulated a two-step reaction to explain the estimated single reaction volume change.²³⁻²⁵ Data were fit to the approximate formula given by Eq. (1). We have applied our calculation procedure to Zinov'ev et al.'s data for 25°C using values for physical properties listed in Table 1. See Figs. 4 and 5. The rate constants reported were used but adjusted for M_e and a slightly different value for the classical absorption was used. Our calculated results for the reaction volume changes are 25.07 and -0.444 $\text{cm}^3\text{mol}^{-1}$ for reactions one and two, respectively. The first reaction volume change corresponds almost exactly to that of Zinov'ev et al. (e.g., is within experimental measurement); however, the second reaction volume estimate is about a factor of five different (in comparison to their estimate of -2 $\text{cm}^3\text{mol}^{-1}$). This discrepancy in the second reaction volume change which results from the orthonormal transformation occurs even for this case when the relaxation times are well-separated.

3. Water-Dioxane

Hammes and Knoche²⁶ reported their acoustic experiments for the water-p-dioxane system and interpreted their absorption data by postulating the coupled independent two-reaction system



The authors used a "trial-and-error" method to calculate the coefficients in Eq. (1) with the relation

$$N_\phi = 2\pi^2 \rho c_0 \tau_\phi^* \Gamma_\phi Q_\phi^2 / R^\dagger \theta$$

where $\Gamma_1 = [vM_e (4/\chi_W^e + 1/\chi_D^e + 1/\chi_Q^e - 4)^{-1}]$,

$$\Gamma_2 = \{vM_e [1/\chi_Z^e + 1/\chi_D^e + (a_{12}/a_{11})/\chi_D^e + 1/\chi_Q^e - (a_{12}/a_{11})/\chi_Q^e - (2a_{12}/a_{11} + 1)]\}^{-1}$$

and $Q_\phi = V_\phi - (\beta_\theta/\rho c_p) H_\phi$

There appears to be a basic difference in the theoretical results. It is noted that Hammes and Knoche only examined the linearized kinetics equations to obtain a nonunique normal-coordinate transformation. This is not the same transformation needed to obtain Eq. (1) from the formal theory.

Hammes and Knoche²⁶ obtained

$$H_1 = -h_1 \tag{30}$$

$$H_2 = - (a_{12}/a_{11}) h_1 - h_2$$

and similarly for the volumetric change. Here the H_β 's and h_β 's correspond to the heats of reaction for the normalized reactions and the proposed reaction sequences, respectively.

$$a_{11} = -\bar{k}_1^F (X_W^e)^2 - 4\bar{k}_1^F X_W^e X_D^e - \bar{k}_1^R + 4\bar{k}_1^F (X_W^e)^2 (X_D^e)$$

and

$$a_{12} = \bar{k}_1^F (X_W^e)^2 (1-2 X_D^e) - \bar{k}_1^F$$

where the \bar{k} 's correspond to the reported kinetics constants of Hammes and Knoche. We also remark that our kinetic constitutive relation ζ_ρ (the molar production term for the ρ th reaction) is in terms of the degree-of-advancement variables ζ_ρ where $w_\alpha - w_\alpha^e = \sum_{\rho=1}^p S_{\rho\alpha} \zeta_\rho$ (w_α is the molar concentration-moles of α/g of solution). The consequence is that the reaction rate constants used by Hammes and Knoche differ from ours by the factor M_e (the molecular weight of the mixture at equilibrium) which is concentration dependent.

The parameters for the exact calculation were obtained by: 1) choosing k_1^F (or k_1^R) and k_2^F (or k_2^R) and using the values of Hammes and Knoche for the equilibrium constants (K_1 and K_2) in order to obtain eigenvalues of the two reactions that matched the experimental data; 2) choosing values for the q_i (or linear combination of heat and volume change) for the actual reactions to fit the absorption-frequency data so that the calculated values of N_j matched the measured values; and 3) selecting a value for the bulk viscosity of the mixture to match the experimental data at high frequencies where the viscous contribution to the absorption dominates. The other physical property data are listed in Table 3 for $\theta_0 = 25^\circ\text{C}$ and $X_W^0 = 0.62$. Using these parameters, the absorption was computed with the exact formulas and is shown in Fig. 6 compared to the results of the approximate formula. The values are only about 2% higher, and within the error of experiments. The contributions for each reaction and the viscous and thermal effects are shown in order to indicate their relative magnitude (Fig. 7). It is obvious that the viscous term is not small compared to the reactive terms over the entire range of frequencies. We remark that the approximate formula for the viscous term is valid at frequencies such that $\omega_\rho \gg 1$.¹⁵ From these calculations it is not possible to determine if the difference between the exact and the approximate values is due to the viscous approximation or the chemical approximation. Because the criteria for the chemical approximation are satisfied and the error decreases at high frequencies where the viscous term dominates, we attribute the difference to the nonlinear viscous contribution at low frequencies.

Assuming values for the normal heats of reaction reported by Hammes and Knoche (i.e., ± 1000 and ± 300 cal mol⁻¹ for reactions one and two, respectively) which neglects any volume change contribution, the individual reaction heats would be calculated according to them by Eq. (30). Their results give approximately the same value for the heat for the first reaction while the estimate for the second reaction heat differs somewhat. This discrepancy is partly due to the normalization of the transformation \underline{J} used to separate the chemical kinetic equations. Our calculated results for the individual reaction heats are ± 1010 and ∓ 215 cal mol⁻¹ for the first and second reaction, respectively. It is noted that the signs of the heat (or volume) changes for two independent reactions occur as (+, -) or (-, +) pairs corresponding to our choice of $\det \underline{M} = 1$. The pairs (+, +) or (-, -) would correspond to the transformation having the property that its determinant equals negative one. Also, it is noted that our reaction rate constants are slightly different than Hammes and Knoche, even though the equilibrium constants and eigenvalues are the same.

CONCLUSION

The absorption and speed of sound have been calculated for three different chemical systems by the "direct" method which requires all the physical property data, in addition to, the approximate formula for the absorption - sometimes referred to as a Debye equation. The assumptions needed to obtain the approximate formula are¹⁵ 1) viscous, thermal and diffusive effects are negligible 2) either a dilute solution or $S_{\sigma} = 0$ 3) $\alpha \ll k$ and an ideal solution.

Furthermore, the transformation must be orthonormal (i.e., $\underline{M} \underline{M}^T = \underline{I}$; $\underline{M}^{-1} = \underline{M}^T$) where $\det \underline{M} = \pm 1$.

The exact calculation and interpretation of the sound absorption spectra for the chemical systems examined can provide different estimates of thermodynamic reaction parameters compared to the approximate formula, especially for estimates of thermodynamic parameters associated with the second reaction. In general, the calculated results depend explicitly upon the orthonormal transformation \underline{M} . Our examples indicate that the approximate formula gives estimates of thermodynamic parameters for the first reaction which closely agree with those derived from the exact calculation. However, the calculated second reaction volume (or heat) change appears to be sensitive to the orthonormal transformation used even in dilute cases where the chemical relaxation times are well separated.

Furthermore, assuming that the viscous term can be decoupled from the kinetics by a linear subtraction is not necessarily valid as shown in Fig. 7 and previously discussed. The practical consequence of a large viscous contribution is the loss of sensitivity of the acoustic data for determining the kinetics contribution. All in all, ultrasound measurements provide extremely valuable information on the thermodynamics and chemical kinetics of fast reactions in solutions. Approximate formulas for predicting and attributing sound absorption and dispersion due to chemical reactions must be shown to be quantitatively valid.

Table 1: Physical Property Data For Cobalt-Polyphosphate Mixture (0.125N)

Calculation

$$f_m \text{ (bound fraction)} = 0.86$$

$$\theta_0 = 298.16 \text{ } ^\circ\text{K}$$

$$\rho_0 = 0.997 \text{ g cm}^{-3}$$

$$\beta_\theta = 0.000257 \text{ } ^\circ\text{K}^{-1}$$

$$c_p = 0.99828 \text{ cal g}^{-1} \text{ } ^\circ\text{K}^{-1}$$

$$c_v = 0.9878 \text{ cal g}^{-1} \text{ } ^\circ\text{K}^{-1}$$

$$\eta_0 = 0.0100 \text{ P}$$

$$k_0 = 0.0266 \text{ P}$$

$$c_0 = 1.497 \times 10^5 \text{ cm sec}^{-1}$$

$$N_1 = 107.0 \times 10^{-17} \text{ cm}^{-1} \text{ sec}^2$$

$$N_2 = 1445 \times 10^{-17} \text{ cm}^{-1} \text{ sec}^2$$

$$N_0 = 24.7 \times 10^{-17} \text{ cm}^{-1} \text{ sec}^2$$

$$k_1^F = .273 \times 10^7 \text{ mol g}^{-1} \text{ sec}^{-1}$$

$$k_1^R = .00455 \times 10^7 \text{ mol g}^{-1} \text{ sec}^{-1}$$

$$k_2^F = .00950 \times 10^7 \text{ mol g}^{-1} \text{ sec}^{-1}$$

$$k_2^R = .01583 \times 10^7 \text{ mol g}^{-1} \text{ sec}^{-1}$$

$$K_1 = 60.$$

$$K_2 = 0.6$$

$$\tau_1 = 1.982 \times 10^{-8} \text{ sec}$$

$$\tau_2 = 2.188 \times 10^{-7} \text{ sec}$$

$$v_1 = 20.98 \text{ cm}^3 \text{ mol}^{-1}$$

$$v_2 = 5.26 \text{ cm}^3 \text{ mol}^{-1}$$

Table 2: Physical Property Data For Aqueous Glycine Solution

$\text{pH}_{\text{max}} = 11.6$	$m_B^0 = 5.2$	$\text{mol } \ell^{-1}$
$\theta_0 = 298.16 \text{ } ^\circ\text{K}$	$m_A^0 = 5.2$	$\text{mol } \ell^{-1}$
$\rho_0 = .997 \text{ g cm}^{-3}$	$K_1 = 1.7 \times 10^5$	
$\beta_\theta = .000257 \text{ } ^\circ\text{K}^{-1}$	$K_2 = 10.4$	
$c_p = .99828 \text{ cal g}^{-1} \text{ } ^\circ\text{K}^{-1}$	$k_1^F = .472 \times 10^{11} \text{ mol g}^{-1} \text{ sec}^{-1}$	
	$\bar{k}_1^F = 1.7 \times 10^{10} \text{ } \ell \text{ mol}^{-1} \text{ sec}^{-1}$	
$c_v = .98784 \text{ cal gm}^{-1} \text{ } ^\circ\text{K}^{-1}$	$k_1^R = .5 \times 10^6 \text{ mol g}^{-1} \text{ sec}^{-1}$	
	$\bar{k}_1^R = 10. \times 10^6 \text{ sec}^{-1}$	
$k_\theta = 1.4 \times 10^{-3} \text{ cal cm sec}^{-1} \text{ } ^\circ\text{K}^{-1}$	$k_2^F = .317 \times 10^6 \text{ mol g}^{-1} \text{ sec}^{-1}$	
	$\bar{k}_2^F = 5.7 \times 10^6 \text{ sec}^{-1}$	
$\eta_0 = .008904 \text{ P}$	$k_2^R = .333 \times 10^5 \text{ mol g}^{-1} \text{ sec}^{-1}$	
	$\bar{k}_2^R = 0.6 \times 10^6 \text{ sec}^{-1}$	
$K_0 = .0237 \text{ P}$	$v_1 = 25.07 \text{ cm}^3 \text{ mol}^{-1}$	
$M_e = 18.61 \text{ g mol}^{-1}$	$v_2 = -.444 \text{ cm}^3 \text{ mol}^{-1}$	
$c_0 = 1523 \text{ m sec}^{-1}$	$\tau_1 = 5.7 \times 10^{-9} \text{ sec}$	
$c_0 (\text{H}_2\text{O}) = 1496.7 \text{ m sec}^{-1}$		
$N_1 = 100 \times 10^{-17} \text{ cm}^{-1} \text{ sec}^2$	$\tau_2 = 1.5 \times 10^{-7} \text{ sec}$	
$N_2 = 270 \times 10^{-17} \text{ cm}^{-1} \text{ sec}^2$		
$N_0 = 23 \times 10^{-17} \text{ cm}^{-1} \text{ sec}^2$		

M_A	M_B	M_C	M_D	M_E	glycine
79.11	17.	96.11	79.11	18.00	80.11

Table 3: Physical Property Data For Water-Dioxane Mixture

Quantity/Value	Source
$x_W^0 = 0.62$ (25% water; 75% dioxane)	
$\theta_0 = 298.16$ °K	
$c_0 = 1.48 \times 10^5$ cm sec ⁻¹	Atkinson et al. (Table III) ²⁷
$\rho_0 = 1.0361$ g cm ⁻³	Atkinson et al. (Table III) ²⁷
$c_p = 2.6$ joules g ⁻¹ °K ⁻¹	Stellard and Amis ²⁸
$= .621$ ergs g ⁻¹ °K ⁻¹	
$\gamma = 1.18671$	Calculation: $\gamma = 1 + \theta_0 \beta_{\theta}^2 c_0^2 / c_p$
$k_{\theta} = 8.628 \times 10^{-4}$ °K ⁻¹ cal cm sec ⁻¹	Atkinson, et al. (Table III)
$\eta_0 = 0.02$ P	Emel'yanov et al. ²⁹ (adjusted for temperature)
$K_0 = 0.0503$ P	Chosen to obt in $(\alpha/f^2)_{\nu} N_0$
$k_1^F = 150 \times 10^5$ mols g ⁻¹ sec ⁻¹	K_0/η_0^{\sim} value for pure water
$\bar{k}_1^F = 140 \times 10^7$ sec ⁻¹	
$k_1^R = 30 \times 10^5$ mol g ⁻¹ sec ⁻¹	
$\bar{k}_1^R = 28 \times 10^7$ sec ⁻¹	Hammes and Knoche ²⁶
$k_2^F = 24 \times 10^5$ mol g ⁻¹ sec ⁻¹	
$\bar{k}_2^F = 15 \times 10^7$ sec ⁻¹	
$k_2^R = 16 \times 10^5$ mol g ⁻¹ sec ⁻¹	
$\bar{k}_2^R = 10 \times 10^7$ sec ⁻¹	
$\lambda_1 = 7 \times 10^8$ sec ⁻¹	Hammes and Knoche ²⁶
$\lambda_2 = 1.9 \times 10^8$ sec ⁻¹	

Table 3. (Continued)

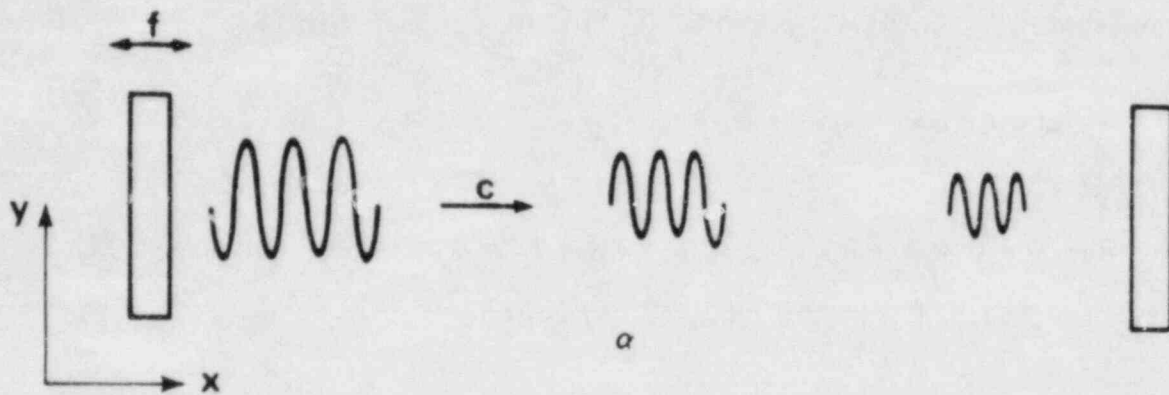
K_1	= 5	Hammes and Knoche ²⁶
K_2	= 1.5	
N_1	= $30 \times 10^{-17} \text{ cm}^{-1} \text{ sec}^2$	Hammes and Knoche ²⁶
N_2	= $12 \times 10^{-17} \text{ cm}^{-1} \text{ sec}^2$	
N_0	= $47 \times 10^{-17} \text{ cm}^{-1} \text{ sec}^2$	

*Atkinson et al. lists $6.338 \text{ joules g}^{-1} \text{ } ^\circ\text{K}^{-1}$ for $X_{iV}^0 = 0.5$ which differs from Morcom and Smith's listed value for the excess heat capacity and Stallard and Amis' value of $2.25 \text{ joule g}^{-1} \text{ } ^\circ\text{K}^{-1}$ at 40°C .

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$$I = I_0 \exp \left[-\underbrace{\left(\alpha + \frac{i\omega}{c} \right)}_{\chi} x + i\omega t \right]$$

- $\chi =$ Complex Propagation Constant
- $\alpha =$ Attenuation coefficient
- $\omega =$ Angular Frequency ($= 2 \pi f$)
- $c =$ Sound Speed

Figure 1: Monochromatic Forced Plane Sound Waves of Infinitesimal Amplitude Propagating Through A Fluid

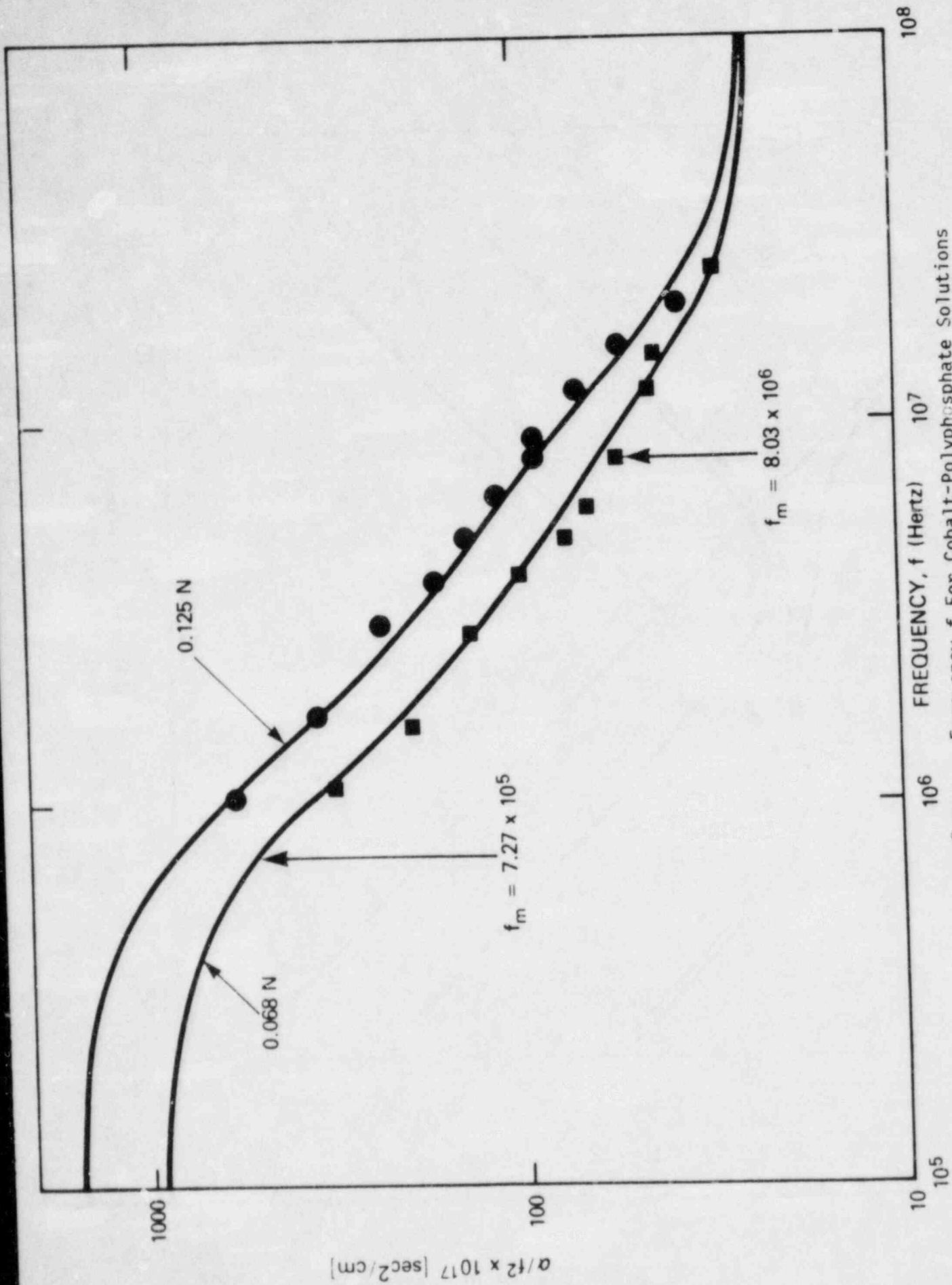


Figure 2: Plots of α/f^2 Versus Frequency f For Cobalt-Polyphosphate Solutions

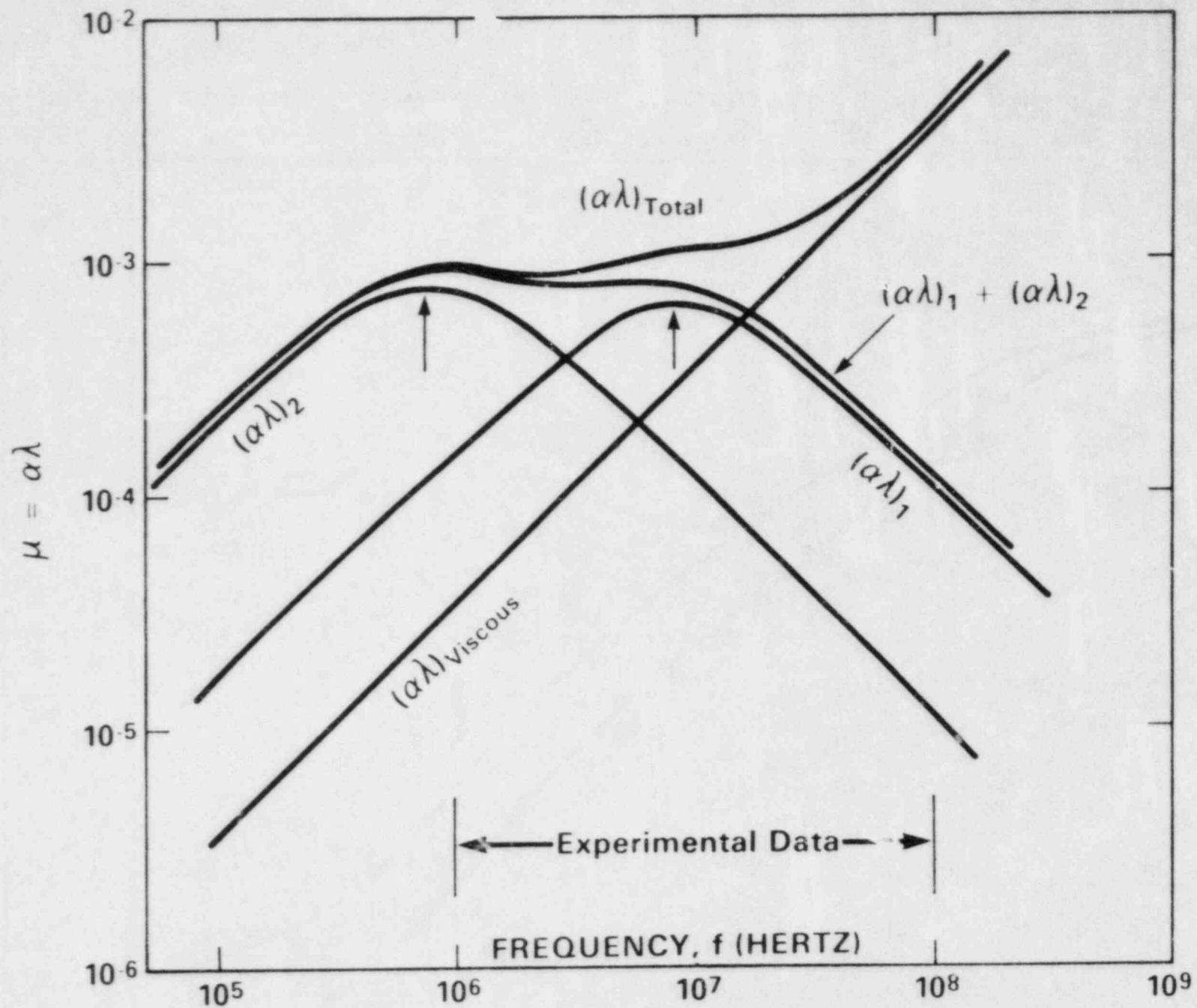


Figure 3: Absorption per Wavelength Versus Frequency f for 0.125 Normal Cobalt-Polyphosphate Solution

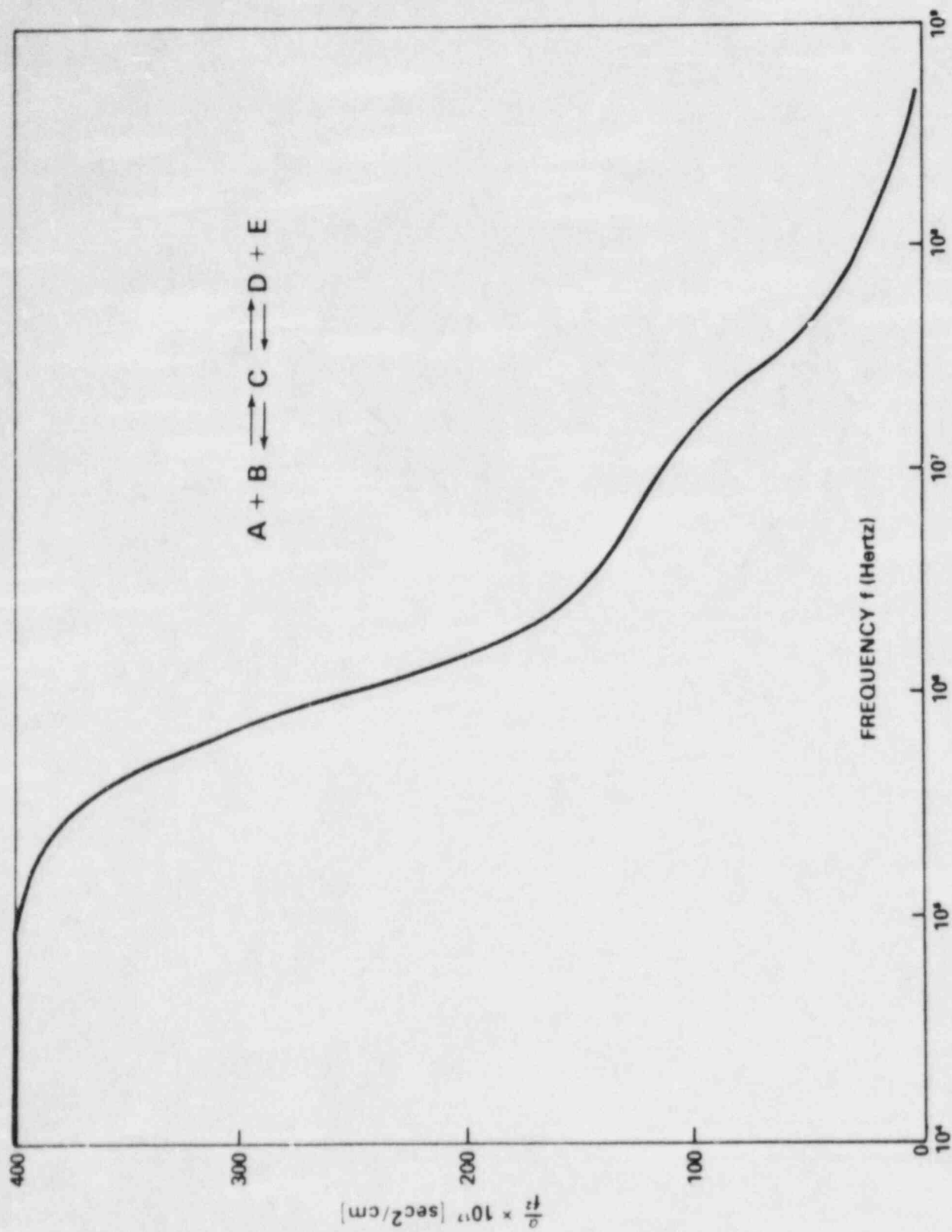


Figure 4: Plot of α/f^2 Versus Frequency f For Aqueous Solution of Glycine

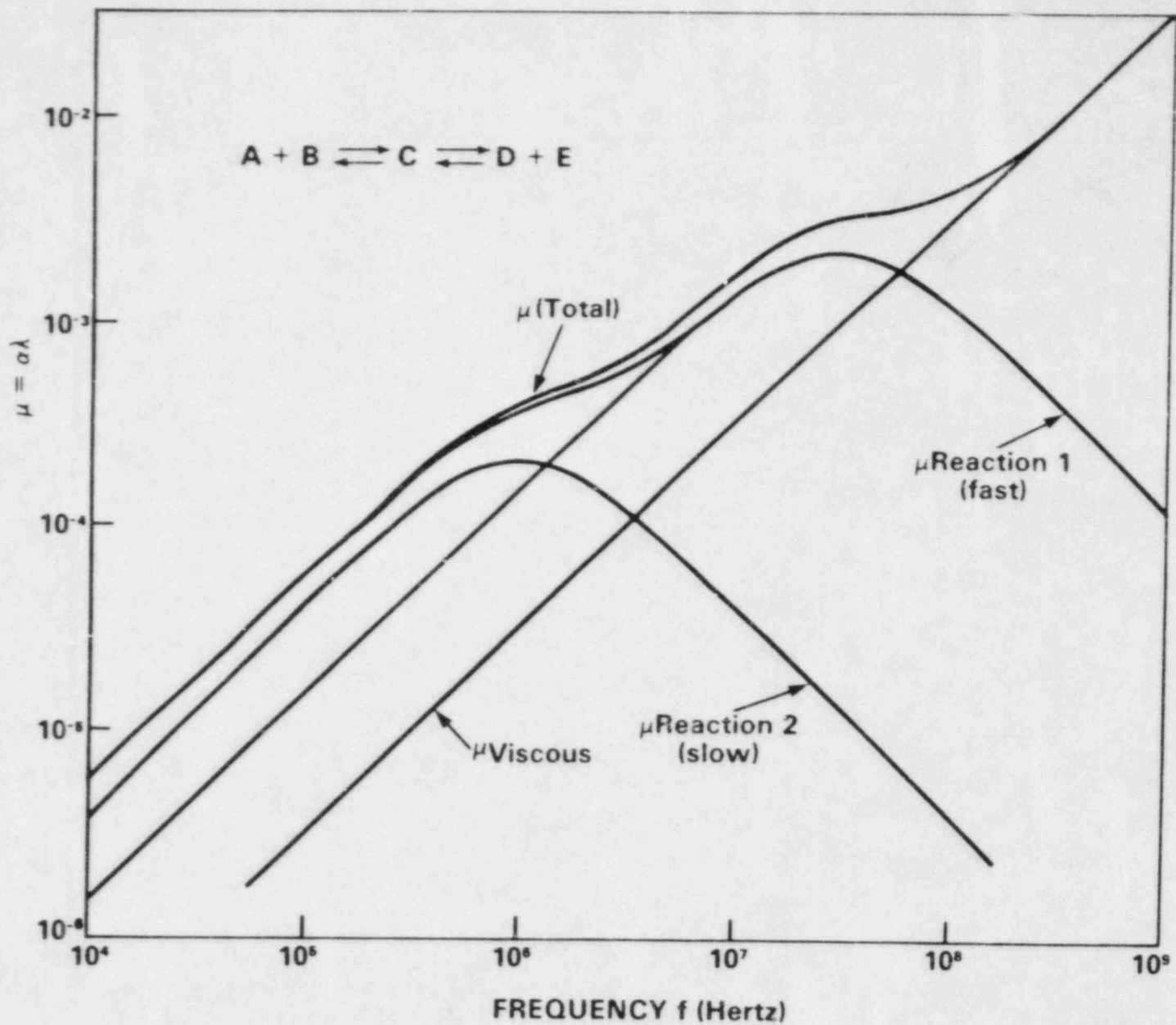


Figure 5: Absorption per Wavelength Versus Frequency f for Aqueous Glycine Solution

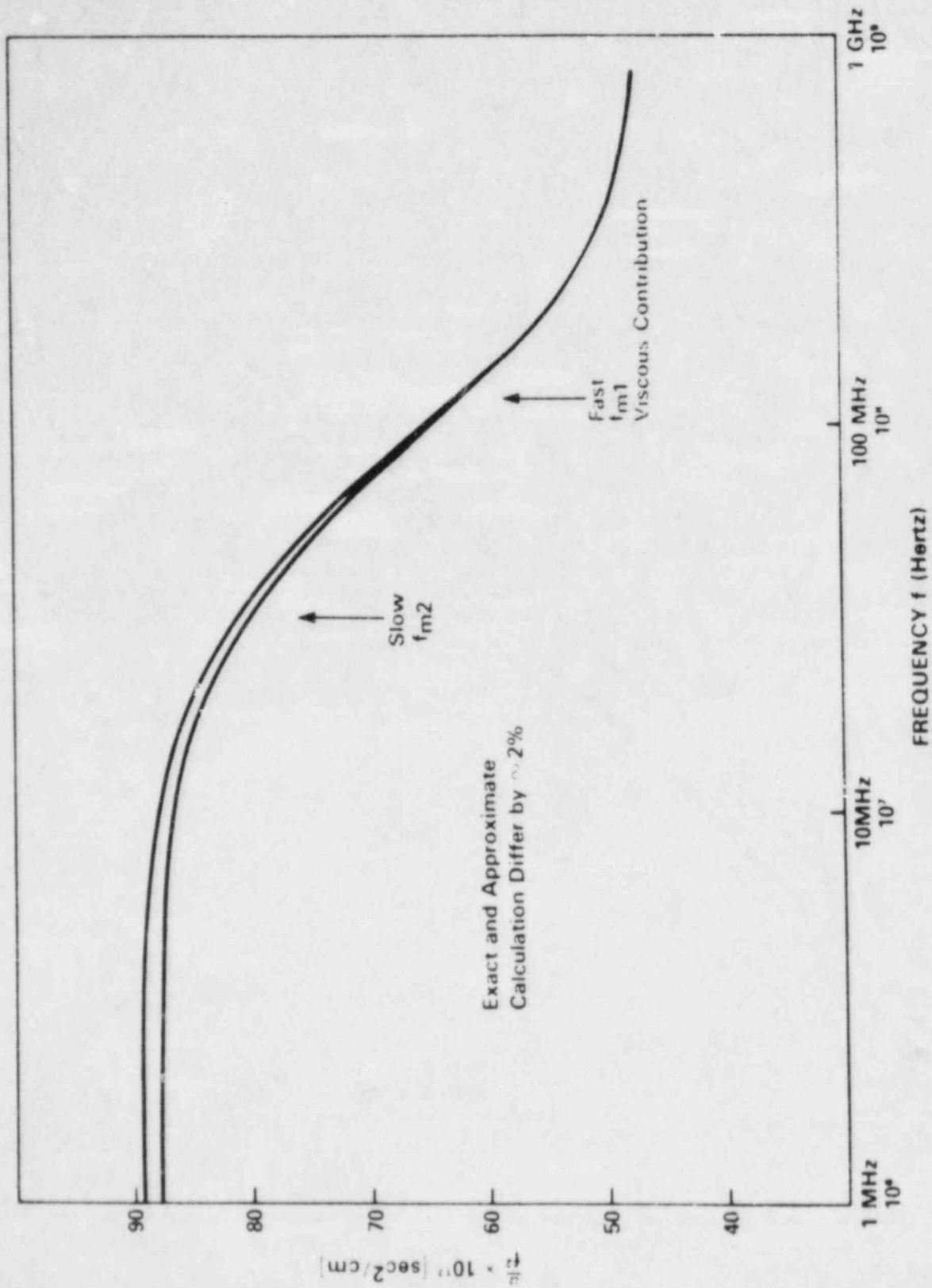


Figure 6: Exact and Approximate Calculation of α/f^2 Versus Frequency f For p-Dioxane Water Solution

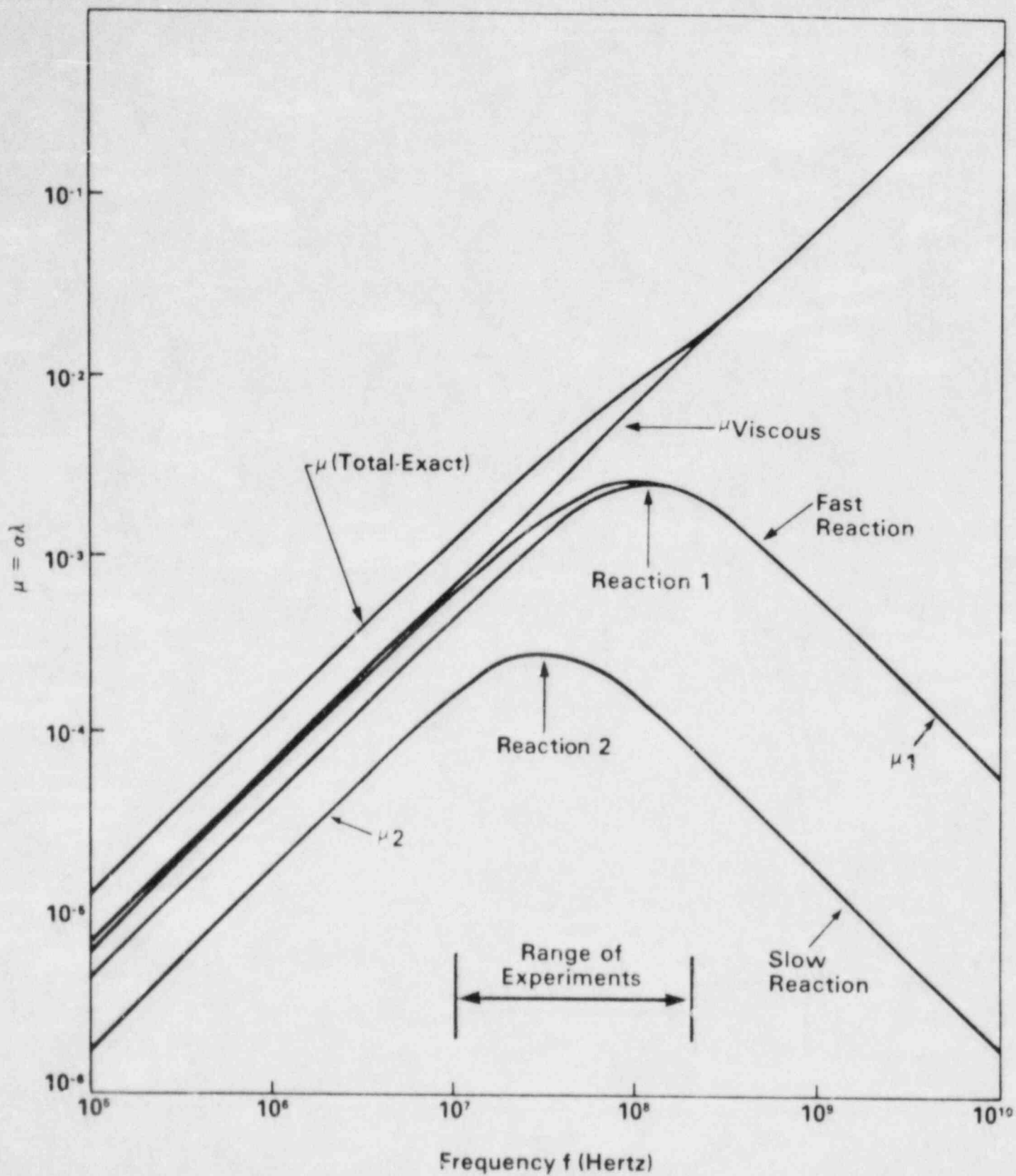


Figure 7: Absorption per Wavelength Versus Frequency f For p-Dioxane Water Solution

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16. ABSTRACT (200 words or less) <p>This report presents a hydroacoustic theory which accounts for sound absorption and dispersion in a multicomponent mixture of reacting fluids (assuming a set of first-order acoustic equations without diffusion) such that several coupled reactions can occur simultaneously. General results are obtained in the form of a biquadratic characteristic equation (called the Kirchhoff-Langevin equation) for the complex propagation variable $\chi = -(\alpha + i\omega/c)$ in which α is the attenuation coefficient, c is the phase speed of the progressive wave and ω is the angular frequency. Computer simulations of sound absorption spectra have been made for three different chemical systems each comprised of two-step chemical reactions using physico-chemical data available in the literature. The relative chemical reaction and classical viscothermal contributions to the sound absorption are also presented. Several discrepancies that can arise when interpreting ultrasonic measurements for estimating thermodynamic data (chemical reaction heats or volume changes) for multistep chemical reaction systems are discussed.</p>				8. (Leave blank)	
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ACOUSTIC WAVE PROPAGATION IN FLUIDS WITH COUPLED CHEMICAL REACTIONS

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