KINETICS AND THERMODYNAMICS OF LANTHANIDE SULFATE ASSOCIATION IN DEUTERIUM OXIDE

By

MICHAEL MARION FARROW

Bachelor of Arts

Western State College of Colorado

Gunnison, Colorado

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Thesis Approved:

N W Purdie
Thesis Adviser

J. Paul Devlin

Tom E. Moore

H. Olin Spivey

D. D. Durham
Dean of the Graduate College

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GLOSSARY OF SYMBOLS

$\mathring{a}$	distance of closest approach
A	constant of Debye-Hückel equation
$\mathring{A}$	ångstrom
A^{m-}	generalized ligand
B	constant of Debye-Hückel equation
B'	sound absorption due to solvent
C	capacitance
C_o	analytical salt concentration
C_{eq}	equivalent concentration
D	Demal (concentration standard for conductance)
e	protonic charge
f	frequency in cycles per second
f_R	frequency of maximum absorption
F	formality
G^o	Gibbs free energy
$G^{\ddagger}$	free energy of activation
H_t	enthalpy of transfer
$H^{\ddagger}$	enthalpy of activation
$\bar{H}_s$	partial molar enthalpy of solution
Hz	hertz (equivalent to cycles per second)
k	Boltzmann's constant
k_{ij}	rate constant
k_f	overall forward rate constant
k_b	overall backward rate constant
k_{ex}	solvent exchange rate
K	equilibrium constant

GLOSSARY OF SYMBOLS (Continued)

K_T	thermodynamic equilibrium constant
$K_{cond.}$	conditional concentration constant
Ln^{3+}	generalized lanthanide ion
m	molality
M	molarity
M^{n+}	generalized metal ion
N	Avogadro's number
p	amplitude of sound wave
q	Bjerrum distance
r	ionic separation distance
R	resistance
$\bar{S}_s$	partial molar entropy of solution
S	generalized solvent molecule
t	time
T	temperature
v	velocity
z_i	charge on ion i
[ ]	concentration in moles per liter
α_T	total absorption coefficient of solution
α_s	absorption coefficient of water
α_{chem}	absorption coefficient due to chemical relaxation
β	degree of association
γ_i	activity coefficient of ion i
Δ	generalized change in parameter
ε	macroscopic dielectric constant
η	viscosity
θ	concentration factor [eqn. 2.16]
κ	specific conductance
Λ	equivalent conductance of salt solution
Λ^o	zero concentration equivalent conductance

GLOSSARY OF SYMBOLS (Continued)

Λ_{exp}	experimental equivalent conductance
λ	wavelength
λ_i^o	limiting conductance of ith ion
μ	ionic strength
π	ratio of circumference of a circle to its diameter
π_f	activity coefficient quotient
τ	relaxation time
$\Phi(C)$	concentration factor [eqn. 4.13]
ω	angular frequency in radians

CHAPTER I

INTRODUCTION

The formation of ion-pairs and complexes in solutions of electrolytes is an area of physical chemistry in which considerable development has occurred in the last thirty years. Much of the recent impetus has come from the development of new physical methods for studying the thermodynamic and kinetic properties of solutions. These new methods have provided much of the needed additional information required for the detailed study of the factors involved in ion association.

In order to describe a system thermodynamically, it is necessary to have a detailed knowledge of the species present in a solution. New ions or uncharged molecules resulting from interactions in solution will affect the thermodynamic parameters of the solution, and a description involving only the unassociated constituent ions will not be adequate. There are many difficulties in the analysis of a system as complex as a solution, but a concerted effort is being made to solve the numerous problems.

One area of special interest in the description of solutions is the study of the formation of metal ion complexes and the manner in which these complexes are formed and interconverted. In solutions this process is most often a matter of the replacement of one coordinated ligand by another. The substitution of a ligand in the inner coordination sphere (leaving group) by another ligan (entering group) is the fundamental reaction in metal ion solution chemistry. All discussions of metal complex formation are dependent upon a knowledge of the dynamics of these processes.

Thermodynamic Background

The acceptance of the Debye-Hückel theory of interionic attraction has permitted a satisfactory interpretation of the thermodynamic behavior of very dilute solutions of electrolytes (1). In these solutions the ions are sufficiently far apart that the interionic effects are essentially electrostatic in nature. However, at higher concentrations when the ions are closer together, the approximations used in the development of the Debye-Hückel theory are no longer valid. It can be shown that the attraction force between ions of opposite charge may be considerably larger than the thermal energy which attempts to maintain random orientation of the ions (2). Thus ions in more concentrated solutions may not be considered as simple point charges in a dielectric continuum. If the attractive force is great enough, an actual bond may be formed between ions and a new species formed in the solution. Although the equilibrium is a dynamic equilibrium and not a static one, the result is that there exists an appreciable concentration of the ion-pair at any given instant.

Ion association in a solution of an electrolyte, M_mA_n, may be expressed by the equilibrium:

$$M^{n+} + A^{m-} \rightleftarrows MA^{(n-m)+} \tag{1.1}$$

If the solution is dilute enough that the activity of the solvent remains constant, then the thermodynamic association constant is related to the activities of the species in the solution by the Equation

$$K = \frac{[MA^{(n-m)+}]}{[M^{n+}][A^{m-}]} \tag{1.2}$$

where the brackets enclose the activities of the species.

The Debye-Hückel theory makes certain assumptions that clearly will not remain valid as the concentration increases. Among these are that the central ion sees its surroundings in the form of a smoothed-out charge density not as discrete charges; no ion-pairs are formed; only long-range coulombic forces are involved in ion-ion interaction; and the only role the solvent plays is to provide a dielectric continuum (3). The applicability of this theory to solutions is valid only long as the assumptions represent an approximation of the actual conditions in the solution. As the concentration increases ions will approach each other so that the charge density will not be smooth. Furthermore, if the solvent has a dipole moment, as many do, the ion will interact with the dipole and may actually be bound to the ions. This ion-dipole interaction will not be important (in most cases) to the thermodynamic properties of very dilute solutions, but if the ions interact, the solvent molecules bound to the ion may interfere.

In 1926 Bjerrum was the first to recognize the possibility of ion-pair formation in solution and proposed that the deviations from the Debye-Hückel theory could be accounted for on this basis. From purely electrostatic considerations he obtained the expression for a thermodynamic equilibrium constant for the formation of a single ion-pair as (1)

$$K = \frac{4\pi N}{1000} \int_{a}^{q} \exp \left[\frac{-z_{+} z_{-} e^{2}}{\varepsilon r k T}\right] r^{2} dr \qquad (1.3)$$

where N is Avogadro's number, q is the interaction limit, $\mathring{a}$ is the distance of closest approach of the ions, ε is the dielectric constant of the bulk solvent, z_i is the ionic charge of the i-th ion, r is the distance of separation of the two ions center-to-center, k is the Boltzmann constant, and T is the temperature of the solution in degrees Kelvin. Although this equation was developed from consideration of the factors that will determine the formation of ion-pairs, it uses the simplest model possible. The ions are considered to be rigid spheres in a continuous dielectric medium and all ion-solvent interactions are discounted. In order to evaluate the integral, Bjerrum found it necessary to impose a cut-off on the limits at r = q, and this was justified by arguing that only short-range coulombic interactions lead to ion-pair formation and ions separated at distances of $r > q$ are more appropriately considered as free ions. In the Bjerrum equation the value of $\mathring{a}$ is not necessarily that separation which places the ions in contact. Later theories are either very complex mathematically (4,5) or only consider ions in contact as forming ion-pairs (6,7) and are no more satisfactory for many purposes than is the Bjerrum equation (2).

At the time the relaxation methods were conceived, the development of classical experiments and theories of solutions were at an impasse. The development of the Debye-Hückel theory and the extensions to it were unable to explain electrolytic solutions in detail (1). Based solely upon electrostatics and the model of the solvent as a dielectric continuum, the relative simplicity of the model failed to account for differences in equilibrium behavior of reactions which involved ions of the same charge type, and restricted its application to relatively dilute solutions.

Kinetic Background

During the Second World War, as sonar was undergoing development, it was discovered that the seawater attenuated the propagated sound wave more than could be accounted for by theoretical predictions (8). Attempts were made to vary the sonar pulse frequency and achieve a longer range of detection. These attempts were unsuccessful as there appeared to be multiple absorption maxima at different frequencies. After the war, the application of ultrasonic tools to electrolyte solutions opened a new field to investigation, and ultrasonic relaxation processes were noticed and recorded but no definite interpretation proposed. It was necessary to wait for the work of Eigen and his school (9) for the interpretation of the ultrasonic spectra of electrolyte solutions as well as the introduction of new relaxation methods which has stimulated the recent fundamental advances in the theory of electrolytic solutions.

The advent of relaxation methods provided a new dimension to equilibrium studies in that, as the time resolution of the experiment was improved, the analysis of the progress of the reaction toward equilibrium became a tangible experiment. The multiple relaxations of seawater have been attributed to the divalent metal sulfates forming ion-pairs, and a new model of the structure of solutions developed to account for the multiple relaxations observed. Experimental results suggest that more than one type of ion-pair is formed as the constituent ions approach one another, in contrast with the more classical interpretation of only one ion-pair. As the ions converge to contact distances in solution, the process is primarily diffusion. More importantly, at shorter separation distances, there is a region of ionic solvation where, due to ion electrostriction, the solvent can no longer be thought of as a continuum. Regions of concentric potential wells enveloping the central ion, whose minima correspond to the formation of a number of stable ion-pairs, disrupt the monotonic increase of coulombic energy of attraction expected from the continuum model. A description of the proposed overall mechanism follows.

General Mechanism

The generalized elementary reaction to be considered is described by the equation

$$M + L \underset{k_b}{\overset{k_f}{\rightleftarrows}} ML \tag{1.4}$$

This reaction proceeds in competition with solvent exchange

$$MS + S^* \overset{k_{ex}}{\rightleftarrows} MS^* + S \tag{1.5}$$

The solvent is of paramount importance, and each ion has a characteristic rate of substitution. The observed rate law for the formation of ML (10) is

$$\frac{d[ML]}{dt} = k_f[M][L] - k_b[ML] \tag{1.6}$$

in the absence of competing chemical equilibrium, exclusive of solvent exchange; k_f is the observed overall effective forward rate constant for a reaction which may involve a number of steps, only one of which is rate determining. k_b is the overall backward rate constant. One step will involve the exchange of coordinated water(s). $k_f[M][L]$ then does not necessarily represent the structure of the activated complex nor the molecularity of the forward rate-controlling step. Based upon comparative kinetic studies done by varying M and L, activation energy, and non-kinetic considerations (10), three types of mechanisms are possible which are equally compatible with the rate law: (1) dissociative, D, (2) associative, A, and (3) interchange, I; the last having tendencies toward either dissociative interchange, I_d (non-limiting D), or associative interchange, I_a (non-limiting A).

In the D mechanism the rate-controlling step is cleavage of the metal water bond to produce a transition state of reduced coordination number. Confirmation of this mechanism is sought in equality between the rate of solvent exchange calculated from the rate of complex formation and k_{ex} measured experimentally (11) by ^{17}O nmr. k_f might also be expected to be independent of the nature of the entering ligand. A further test more recently proposed (12) is that a linear relationship between the free energy of activation $\Delta G^{\ddagger}$ and ΔG^{o} for a particular metal with a series of ligands is indicative of the D mechanism. A, on the other hand, will involve an activated complex of increased coordination and ultimate confirmation comes from k_f values which, for a given cation, are ligand dependent. This is believed to be the only true test for an associative mechanism (13). The interchange mechanism is a concerted exchange between water in the first coordination sphere and ligand in the second coordination sphere (14). Since the mechanism is not limiting like the other two it is impractical to describe the coordination number of the activated complex. Ligand dependence might be anticipated but to a lesser degree than in A. Distinction between I_d and D mechanisms could be difficult, if at all meaningful, since experimental error in k_f may conceal any differences between the directly measured and the calculated k_{ex}. To date it is perhaps fair to say that the dissociative, or if preferred, the I_d mechanism is the one most frequently encountered in complex formation reactions. Substitution into square- planar metal complexes appears to be the sole province for associative mechanisms (10).

The Ion-Pairing Mechanism

After considerable deliberation, the multi-relaxations observed acoustically were correlated with a multistep complex formation mechanism (15) attributed to Diebler and Eigen. A three-step mechanism was postulated to account for the relaxation spectra and the search has gone on for three distinct relaxations (16,17,18). The mechanism describes the approach of the ions from infinite separation to contact distances in steps controlled by (a) ion diffusion until the ions, with coordination spheres intact, are in contact (8,19,20), (b) desolvation of the anion to form an outer ion-pair, and (c) desolvation of the cation to form a contact ion-pair. These steps in order of decreasing relaxation frequency are

$$M^{m+}_{(aq)} + A^{a-}_{(aq)} \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} [M^{m+}\ O^{H}_{H}\ O^{H}_{H}\ A^{a-}]\ (aq) \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} [M^{m+}\ O^{H}_{H}\ A^{a-}]\ (aq)$$

$$\underset{k_{43}}{\overset{k_{34}}{\rightleftarrows}} [M^{m+}A^{a-}\ (aq)]$$

where the k_{ij} values ($j = i + 1$) represent the specific rate constants. The individual equilibrium constants are then defined as $K_{ij} = k_{ij}/k_{ji}$ for each of the consecutive steps.

The expression for the overall thermodynamic formation constant, Eq. (1.2), must be revised and now is related to the individual step-wise ion-pair formation constants by the following expression (neglecting charges, $W = H_2O$)

$$K = \frac{[MW_2A] + [MWA] + [MA]}{[M]\,[A]} \tag{1.7}$$

$$= \frac{[MW_2A]}{[M][A]}\{1 + \frac{[MWA]}{[MW_2A]} + \frac{[MA]}{[MWA]} \cdot \frac{[MWA]}{[MW_2A]}\}$$

$$K = K_{12}\,[1 + K_{23} + K_{23}K_{34}] \tag{1.8}$$

As a consequence, if the assigned mechanism is correct, the structure and molar distribution of the complex species present in the solution can not be identified from the overall formation constant. The only route to the evaluation of the individual equilibrium constants is by kinetic investigations. Typically these equilibria are established very rapidly and are accessible to relaxation technique.

Research on fast reactions in solution has developed rapidly in the years since fast kinetic methods have become available. Rates of reaction of the alkali metals (21,22) alkaline earths (21,23), and transition metal ions (21,24) with various ligands have been extensively studied. It is generally observed that the ions of these groups which have a noble gas electronic configuration show a linear rate dependence with inverse cation radius, but a similar relationship for the transition metal ions exists only after the ligand-field stabilization corrections have been made. In practically every case the role of water exchange is paramount to ligand substitution. Chemically the lanthanides may be compared to both the transition metal ions and the alkaline earth ions, but the relative unimportance of the ligand-field stabilization energy (LFSE) in the lanthanides (10) indicates a closer resemblance to the latter. It might be expected that a linear rate dependance with inverse cation radius would be apparent in the lanthanides but this is not the case (25). In the case where the entering group is murexide (26), sulfate (27-29), anthranilate (30,31), or oxalate (32), a sufficient number of the ions of lanthanide series have been studied to attempt an analysis of the rate dependence. The dependence is similar for all four cases showing a maximum rate of complexation for the ions in the middle of the series. Ultrasonic measurement of rates of complexation for the lanthanide sulfates (27-29) compare favorably with the rate of water exchange obtained by ^{17}O nmr line broadening for Gd^{3+} in perchlorate medium (33). These rates are generally about one order of magnitude greater than those for other systems studied by other techniques and under differing ionic strengths. Since these other ligands may be considered to be bidentate ligands a direct comparison may not be justified.

More recently an attempt has been made to account for the variation of the rate constants by assigning the variation to a change in the degree of hydrogen bonding in the solvated lanthanide ions across the series. In a study of the association reaction of the lanthanide ions with anthranilate in two solvent media, H_2O and D_2O, a large solvent isotope effect was found (31), from a ratio of k_f $(H_2O)/k_f$ (D_2O) for lanthanum of 1:1 to a high at samarium of 6.3:1 and 6.9:1.1 at ytterbium.

These rates were determined by T-jump at 0.2 M ionic strength. A later study of the neodymium sulfate reaction by ultrasonic techniques (34) indicated again that the degree of hydrogen bonding might account for the variation in rate constants. The results of the latter study might be questioned as the thermodynamic formation constant was not determined by an independent method and in fact the ratio of the rate constants determined, $k_{34}(H_2O)/k_{34}(D_2O) = 2.37$, is approximately the same as the ratio of the formation constants, $K(H_2O)/K(D_2O) = 2.27$.

It is obvious from this resume of experimental results that rates of substitution and mechanisms have attracted most interest. Little information is yet available on molar distribution ratios.

The Solvent Media

Water is thought to have considerable structure throughout its liquid range and especially at common laboratory temperatures. There is considerable evidence for this structure (35) including calculations based on the "flickering cluster" model of Frank-Wen (36) done by Nemethy and Scheraga which assigns discrete energy levels to water molecules depending on their degree of hydrogen bonding. This model is capable of reproducing the thermodynamic properties for water from 0 to 100°C. The current models consider water to be composed of a variety of small polymeric species in rapid equilibrium with each other and monomeric water. These molecules in their clusters are held together by hydrogen bonds whose geometric energetic requirements are assumed to be sharply defined (35). Heavy water is considered to have much the same structure, indeed even more, as the strength of the deuterium bond is stronger than the hydrogen bond (35). A general rule in comparing H_2O to D_2O is that between 0° and 35°C D_2O is more structured than H_2O. The commonly assumed corollary that D_2O at one temperature behaves like H_2O at a lower temperature, is not necessarily exact.

When an electrolyte is added to water some of the structure is apparently lost which partially compensates for the normal types of electrostriction of water molecules close to the ions. Frank and Evans (37) have attributed this effect to the development of a transition zone between the well regulated geometric pattern of the first hydrated layer and the highly structured but less ordered region of the bulk of the solvent. When salts are added to heavy water (D_2O) there is an even greater loss of structure as would be expected. The evidence for this loss in structure is noted in larger negative values of $\Delta\bar{H}_s$ and $\Delta\bar{S}_s$, the partial molar enthalpy and entropy of solution respectively. Swain and Bader (38) noted the effects of salts on the broad infrared bands assigned to hindered rotation (libration) of water. They have shown that this could be closely correlated with the corresponding heats of transfer for the salts from H_2O to D_2O (ΔH_t^o). Assuming tetracoordinated water molecules and that the only difference between light and heavy water (as between ice and liquid water) is in their librational freedom, the entire solvent isotope effect can be ascribed to the change in the librational freedom of the four water molecules replaced as the ions are transferred from H_2O to D_2O.

Statement of the Problem

This study was undertaken in an attempt to further clarify the mechanism of the complex formation reaction in aqueous solution, and in particular the reaction of the trivalent lanthanide ions with the sulfate ion and the effect of the solvent medium on the reaction parameters. Experimentally the work has consisted of three major parts: (1) a conductimetric study of the free energy of complexation of the 1:1 lanthanide sulfates in deuterium oxide, (2) a kinetic study to determine if a solvent isotope effect (SIE) is apparent in the dynamics of the reaction, and (3) a study of the dynamics of the reaction at constant ionic strength. The developments and the pertinence of this investigation to the properties of the aqueous lanthanide ions are discussed in the following sections.

CHAPTER II

GENERAL THEORY OF RELAXATION METHODS

The general principle of relaxation methods is that some parameter which affects a chemical equilibrium (pressure, temperature, electric field) is changed so rapidly that the chemical reaction lags behind. In the ultrasonic technique the parameter (both temperature and pressure together) is varied periodically, as opposed to a transient disturbance (T-jump, P-jump, etc.). The effect of the periodic perturbation is felt in chemical reactions which establish equilibrium very rapidly. All relaxation methods are restricted in application to reversible reactions and the rates measured are those near equilibrium.

The response of a chemical equilibrium to an imposed perturbation is characterized by a relaxation time, τ. This time can be defined from the generalized first order rate equation

$$-\frac{dx}{dt} = k_{eff}x \tag{2.1}$$

where x is the extent of the displacement from the equilibrium value of reactant x_e at time t and k_{eff} the overall effective rate constant with which the equilibrium is re-established. On integtation Eq. (2.1) gives

$$\frac{x}{x_o} = e^{-k_{eff}t} \tag{2.2}$$

where x_o is the magnitude of the instantaneous displacement. When

$k_{eff}t = 1$, x becomes equal to x_o/e and the time taken to reach this equality is defined as the relaxation time, τ (39). Once the relaxation time is known, the effective rate constant is given by

$$k_{eff} = \tau^{-1} (\text{sec})^{-1} \tag{2.3}$$

The analytical form of k_{eff} contains contributions from the forward and backward rate constants and depends upon the molecularity of both steps.

The experimental objective is to measure the relaxation time, τ. Table II contains some typical expanded forms of the effective rate constants, k_{eff} (40). For ionic reactions in particular, the rate constants usually include concentration-dependent terms, primarily as a result of electrostatic interactions with other ions in the system, and increase in complexity because of induced changes in the ionic strength.

TABLE I

EXPANDED FORMS OF EFFECTIVE RATE CONSTANTS k_{eff}

	Stoichiometric Equilibrium	$k_{eff} = \tau^{-1}$
(1)	$A \underset{k_b}{\overset{k_f}{\rightleftarrows}} B$	$[k_f + k_b]$
(2)	$A + B \underset{k_b}{\overset{k_f}{\rightleftarrows}} AB$	$[k_f(\bar{A}+\bar{B}) + k_b]$
(3)	$A + B \underset{k_b}{\overset{k_f}{\rightleftarrows}} C + D$	$[k_f(\bar{A}+\bar{B}) + k_b(\bar{C}+\bar{D})]$
(4)	$2A \underset{k_b}{\overset{k_f}{\rightleftarrows}} A_2$	$[4k_f\bar{A} + k_b]$

$\bar{A}$, $\bar{B}$, etc. refer to equilibrium concentration. Whether these are initial or final equilibrium conditions depends upon the nature of the perturbation, forced oscillatory or transition.

Transient Relaxation Methods

In some relaxation methods the perturbation is not periodic in nature, but rather a single displacement from equilibrium. For example, the T-jump experiment consists of altering the temperature of the solution in a few microseconds by dischraging a high-voltage capacitor through the solution. If the complexation equilibrium is enthalpy dependent (or if any reaction coupled to the complexation is enthalpy dependent), the equilibrium will shift. Because the RC product (R is electrical resistance; C, capacitance) must be kept low (8) since RC/2 is the time constant of the temperature rise, an inert electrolyte (like $KClO_4$) is added to the solution to lower its resistance. In this case, use of electrical conductance as the sensor device for monitoring the charge would be a poor choice. A sensor device commonly used is the optical density of the solution (19). If the color of the solution does not change appreciably in some region of the visible or uv spectrum upon change of the ionization of the complex, a suitable indicator may be added to the solution coupling its dissociation with the dissociation of the ligand and the metal complex. The resulting information from the experiment is a signal relating the change in the optical density (and therefore the ionization of the complex, since the response of the indicator is much faster than the complexation reaction) with time. This signal is amplified and displayed on an oscilliscope and recorded permanently by making a photographic record. τ^{-1} is obtained from the photograph by determining the time it takes the concentration to fall to 1/e of its original value. The time resolution of the experiment is such that individual complexation equilibria can not be determined, instead the overall formation rates are determined in the form of forward and reverse, k_f and k_b, rate constants (8).

Forced Oscillatory Relaxation Methods

The attenuation of a sound wave passing through a fluid, for any type of absorption process, in terms of the amplitude level is related to the path length, d, by the Equation (41)

$$P = P_o e^{-\alpha d} \tag{2.4}$$

where P_o is the initial amplitude and P is the amplitude at d(cm), and α, in neper/cm, is the absorption coefficient. The quantity α is determined experimentally and is related to the relaxation time as follows.

Eq. (2.1) describes the response of the chemical equilibrium to the displacement in terms of a first order rate constant, provided the equilibrium value x_e is time independent. If the perturbation is sinusoidal in nature then the equilibrium value will vary in phase with it (curve b, Figure 1) around the mean value (curve a, Figure 1). If this variation is $\bar{y}$ and equal to $(\bar{x} - x_e)$ where $\bar{x}$ is the equilibrium value at time t, and similarly if the variation with the perturbation of the actual concentration difference $(x - x_e)$ is defined as y then the revised form of Eq. (2.1) can be shown to be (19)

$$\tau(\frac{dv}{dt}) + y = \bar{y} \tag{2.5}$$

If the ultrasonic fequency f is $\frac{\omega}{2\pi}$ and the amplitude of the wave is p, then the oscillatory variation in $\bar{y}$ is given by $\bar{y} = p \sin \omega t$ which on substitution into Eq. (2.5) gives the response to the sinusoidal perturbation to be

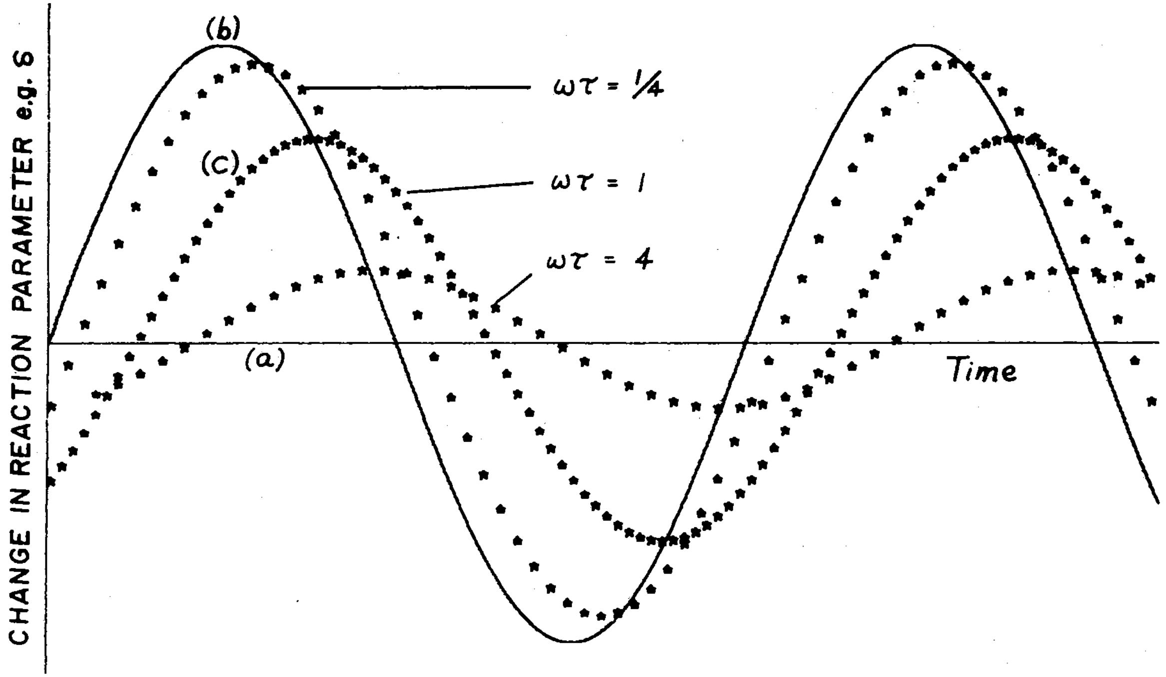

Figure 1. Periodic Disturbance of Chemical Equilibrium by External Parameter (a) τ Much Longer Than Period of Oscillation (Zero Displacement), (b) τ Much Shorter Than Period of Oscillation (In-Phase Displacement), (c) Broken Lines τ Comparable to Period of Oscillation (Energy Dissipation)

$$(\frac{dv}{dt}) + y = p \sin \omega t \qquad (2.6)$$

The solution to this equation in the steady state is

$$y = (\frac{1}{1 + \omega^2\tau^2})p \sin \omega t - (\frac{\omega\tau}{1 + \omega^2\tau^2})p \cos \omega t \qquad (2.7)$$

Graphical representations of this equation are shown as broken lines in Figure 1 for various values of $\omega\tau$. The first term gives the harmonic variation of y in phase with $\bar{y} = p \sin \omega t$. Absorption of power (the damped oscillations) arises from the second term, so the dissipation of energy is proportional to $(\omega\tau/[1 + \omega^2\tau^2])$. This expression has a maximum value of 1/2 when $\omega\tau = 1$ which locates the characteristic or relaxation frequency ($\omega_R = 2\pi f_R$) when the absorption is a maximum as a function of frequency. The relaxation time is therefore given by $\tau^{-1} = 2\pi f_R$. Lines a and b in Figure 1 correspond to the variation in y when τ is much longer than the period of oscillation (essentially zero displacement) and much shorter than the period of oscillation (in phase with it) respectively. Any other τ produces a lag in response.

In the absence of a chemical relaxation the absorption coefficient α increases with the square of the frequency as a function of frequency i.e., α/f^2 = constant. Consequently an expression for absorption which does maximize with increasing frequency is introduced. This is $(\alpha_{chem}\lambda)$, a dimensionless absorption coefficient for the chemical relaxation which is normalized with respect to frequency and called the absorption coefficient per wavelength or per cycle. The resultant equation for a single chemical relaxation then becomes

$$(\alpha_{chem}\lambda) = 2(\alpha_{chem}\lambda)_R \frac{\omega\tau}{1 + \omega^2\tau^2} \qquad (2.8)$$

where $(\alpha_{chem}\lambda)_R$ is the maximum chemical absorption per wavelength at $\omega\tau = 1$. Using this last equality, Eq. (2.8) can be revised to read

$$(\alpha_{chem}\lambda) = 2(\alpha_{chem}\lambda)_R \{\frac{f/f_R}{1 + (f/f_R)^2}\} \qquad (2.9)$$

An alternative representation of a chemical relaxation, this time in a solution where the solvent makes a contribution to the total absorption α_T, is (2.8)

$$\frac{\alpha T}{f^2} = \frac{A}{(1 + [f/f_R]^2)} + B \qquad (2.10)$$

where $A = 2(\alpha_{chem}\lambda)_R/cf_R$ and c is the velocity of sound usually considered to be the same in the solution and the solvent. B is a constant term which includes the classical solvent absorption and contributions from relaxations which are characterized by higher values of f_R. α_T, the total experimentally measured absorption coefficient, is usually taken to be the linear sum of the solvent absorption and the absorption by chemical relaxation. The graphical representations of Equations (2.9) and (2.10) as a function of frequency for a single relaxation are given in Figure 2. f_R corresponds with the frequency of the maximum in curve (a), Eq. (2.9) and with the frequency of maximum inflection, curve (b), Eq. (2.10).

From the term in brackets in Eq. (2.9) it can be shown that a single chemical relaxation extends over one decade in the frequency range, e.g., if $f_R = 5$ MHz, then $(\alpha_{chem}\lambda)$ has the same value at 0.5 MHz and 50 MHz. As a result the resolution of f_R is relatively poor. Plots of $(\alpha_{chem}\lambda)$

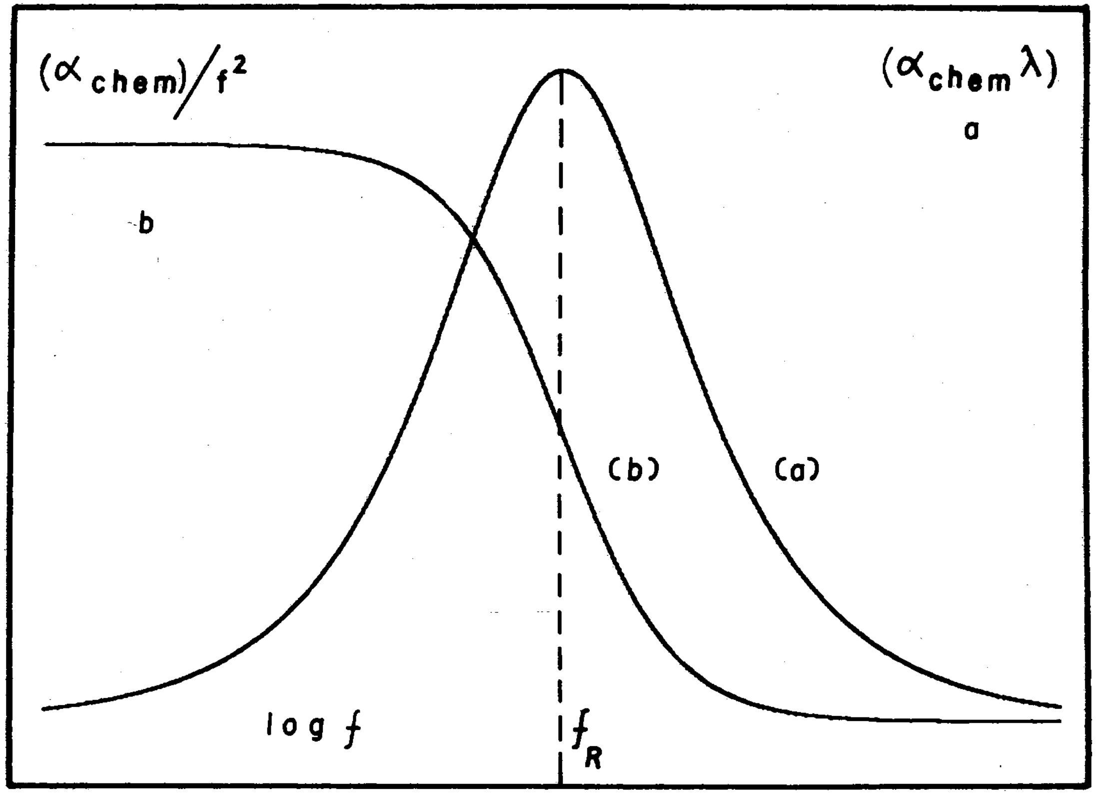

Figure 2. Graphical Representations of Experimental Single Relaxation Curves Described by (a) Eq. (2.8) and (b) Eq. (2.9)

versus frequency must be made as log-log plots to preserve the symmetry of the curves. Multiple relaxations are distinguishable as single relaxations only if the successive f_R values differ by at least a factor of two, a situation not too frequently encountered in practice. In that case the experimental data would be fitted to a multiple relaxation equation which is the simple sum of terms for the appropriate number of single relaxations (40).

Correlation Between Relaxation Times and Stepwise Rate Constants

Consider the two-step reaction:

$$\underset{(1)}{A^+ + B^-} \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} \underset{(2)}{AB} \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} \underset{(3)}{C} \qquad (2.11)$$

Eigen and deMaeyer (9) have demonstrated the correlation between relaxation times τ_i, the rate constants, and the concentration variables for such a mechanism. It can be shown (9) that the relaxation times are given by

$$\tau^{-1}_{I,II} = 1/2\ [\Sigma k \pm (\Sigma k^2 - 4\pi k)^{1/2}] \qquad (2.12)$$

where the positive sign corresponds to τ^{-1}_{I}, the negati-e to τ^{-1}_{II}, and $\Sigma k = (k'_{12} + k_{21} + k_{23} + k_{32})$ and $\pi k = k'_{12}(k_{23} + k_{32}) + k_{21}k_{32}$. k'_{12} is a bimolecular rate constant which includes an activity coefficient quotient to account for ionic atmosphere effects on the reactant ions.

Since chemical processes proceed with descrete time constants, the rate equations may be separated (9). If step 1 is diffusion controlled, as it would be for outer ion-pair formation, then k_{21}, $k_{21} >> k_{23}$, k_{32} in which case the separate rate equations reduce to

$$\tau_{I}^{-1} = 2\pi f_{R}(I) = k'_{12} + k_{21} \tag{2.13}$$

and

$$\tau_{II}^{-1} = 2\pi f_{R(II)} = \left(\frac{k'_{12}}{k'_{12} + k_{21}}\right) k_{23} + k_{32} \tag{2.14}$$

Here τ_{I} is independent of the other step but τ_{II} has to account for the faster equilibrium shift which must accompany the second step. By analogy for the addition of a third step (9), and a third relaxation time the correlation is given by

$$\tau_{III}^{-1} = 2\pi f_{R(III)} = \left(\frac{k'_{23}}{k_{23} + k_{32}}\right) k_{34} + k_{43} \tag{2.15}$$

where k'_{23} is the first term of Equation 26 and the simplifying assumption that $k_{12},k_{21} >> k_{23},k_{32} >> k_{34},k_{43}$ is used.

The overall rate expression is second order, and the only second order rate constant in the multistep mechanism is $k_{12} = k_{12}^{o}\,\theta$ where θ is the concentration function in moles/liter. The general expression for θ is (28)

$$\theta = \pi_{f} C_{o} \left\{[\bar{A}] + [\bar{B}] + [\bar{B}] \left(\frac{\partial \ln \pi_{f}}{\partial \ln \beta}\right)_{C_{o}}\right\} \tag{2.16}$$

where C_{o} is the analytical salt concentration, the bars represent equilibrium concentrations, β is the degree of association of the salt calculated from the overall equilibrium constant measured under the conditions of the kinetic experiment, π_f is the activity coefficient quotient which depends on the stoichiometry of the salt and the complex, and the partial derivative accounts for the change in the activity coefficeints on perturbation.

It should be emphasized that the stepwise rate constants, k_{ij} and k_{ji}, are determined by the ultrasonic technique and the overall rate constants, k_f and k_b, by the temperature (and pressure) jump techniques. One of the difficulties in the correlation is that u may differ between the methods.

Correlation Between Transient Methods and Acoustics

From the steady state kinetic analysis (8), the overall rate constants may be related to the individual rates by the following equations

$$k_f = \frac{K'_{12}k_{23}k_{34}}{k_{32} + k_{34}} \qquad k_b = \frac{k_{43}k_{32}}{k_{32} + k_{34}} \tag{2.17}$$

The overall forward rate constants from techniques other than acoustics are frequently written as $k_f = K_o k_{34}$ where K_o is the constant for a rapid preequilibrium step which if it can be calculated allows a comparison between k_{34} and the rate of solvent exchange, k_{ex}, for the purpose of mechanistic assignment. Herein lies a serious problem in that K_o (or indeed $K_{12}K_{23}$) cannot be calculated with confidence and usually these values are estimated from theoretical equations to establish an order of magnitude value. At the present it is not yet possible to measure these very high frequency reactions by acoustical means, although this eventuality is anticipated by some workers in the field.

Equation (2.17) is the relationship which correlates the overall and stepwise rate constants. The Bjerrum equation can be used to calculate the outer ion-pair association constant K''_{12} which where necessary must be corrected for the ionic strength conditions of the experiment such that $K''_{12} = K_{12}\pi_f$. Rewriting Eq. (2.17) in the new terms it becomes

$$k = \frac{K_{12}\pi_f \, k_{23}k_{34}}{k_{32} + k_{34}} \qquad (2.18)$$

To simplify the interpretation an assumption can be made regarding the relative magnitudes of the constants k_{32} and k_{34}. It is reasonable to assume that $k_{32} \simeq k_{34}$ (8) in which case $k_f = 1/2\ [K_{12}\pi_f K_{23} k_{34}]$.

The quantity $K_{12}\pi_f K_{23}$ should be consistant with theoretical predictions if the mechanistic result is correct. An exact comparison would require independent relaxation studies on the same metal-ligand system at the same conditions of temperature and ionic strength. So far this has not been attempted.

CHAPTER III

INSTRUMENTATION AND PROCEDURES

The Conductivity Apparatus

There are several methods available to measure the conductance of an electrolyte in aqueous solution. Of these methods, the a.c. audio frequency technique is less susceptible to polarization effects at the electrodes, and more capable of precise measurement. For this reason, the system chosen for this study was an a.c. conductivity apparatus operated at 1000 Hz.

The Conductivity Bridge

The bridge used in this study was a Leeds and Northrup (Model 4666) electrolytic conductivity bridge with the audio signal supplied by a General Radio audio oscillator (Type 1311-A) operated at 1000 Hz and 10 volts peak-to-peak. The detector circuit consisted of a General Radio tuned amplifier and null detector (Type 1232-A) and a Tektronix oscilloscope (Type 561-A equipped with Type 2B67 time base and Type 3A72 plug-in unit). When the 60 kohm range of the bridge was insufficient to balance the high resistance of the conductivity cell or when the capacitive reactance was greater than could be compensated for by the internal capacitors of the bridge, balance was achieved by connecting to the bridge a decade resistor (General Radio Type 1432-Q) and a decade polystyrene capacitor (General Radio Type 1419-A).

The Conductivity Cell

A dilution type conductivity cell with grey platinum electrodes was immersed in a thermostated bath containing light paraffin oil and connected to the conductance bridge with 12 gauge copper wire. The bath temperature was regulated by a Thermistemp temperature controller (Model 71) and monitored by a Beckman thermometer which had been calibrated against a NBS standardized thermocouple. The bath was maintained at 25 ± 0.001°C with no observable drift for the duration of the experiment.

The cell constant was measured using the standards of Jones and Bradshaw (43). Three solutions each of 0.1D and 0.01D KCl were prepared and multiple measurements of the resistance made. Using the values for the specific conductivities of 0.012856 int. ohm^{-1} cm^{-1} for the 0.1D KCl solution and 0.0014087 int. ohm^{-1} cm^{-1} for the 0.01D KCl solution, the cell constant was found to be 0.41687 cm^{-1}.

Experimental Procedure

A weighed amount of the solvent was introduced into the clean dry cell. The cell was sealed and placed in the thermostated bath and allowed to equilibrate, which required about twenty minutes. After equilibration, the resistance was measured in the following manner. The amplified signal from the bridge was used to drive the vertical amplifier of the oscilloscope and a signal from the input transformer on the bridge was used to drive the horizontal amplifier of the oscilloscope. The resulting trace on the oscilloscope was a Lissajous figure when the reactance of the cell was not in balance with the reactance of the bridge. This trace was reduced to a horizontal line trace as the bridge was adjusted to a balanced condition. The measurement was retained if the balance was stable to within 0.001 ohms for a period of ten minutes. The resistance value obtained was used to calculate the specific conductance of the solvent (specific conductance = cell constant/measured resistance) which was the value used in the remainder of the experiment. Weighed aliquots of the stock solution were added in succession to the cell from a weight buret and the resistance measurements repeated for each addition as described above.

The Ultrasonic Apparatus

The ultrasonic absorption technique can be applied to a broad range of relaxation times, from 10^{-4} to 10^{-10} seconds, but the instrumentation varies depending on the particular time scale to be studied. For the pulse method, due to mechanical and electronic limitations, the range is limited to 10^{-6} to 10^{-10} seconds. The instrument used in this study was limited to operating in the range from 5 MHz to 65 MHz.

The Electronic System

A block diagram of the apparatus is shown in Figure 3. A pair of square wave pulses are supplied by a pulse generator with a repetition rate of 60 pulses per second. The time separation of the two pulses was not permanently fixed and could be changed by means of a variable delay line. The first pulse was used to drive the transducer system and the second pulse was used as a standard for comparison purposes. After leaving the pulse generator, the first pulse was amplified from 23 volts to 500 volts amplitude by the pulse amplifier. This signal was then sent to the transmitter which modulated the pulse. The signal from the transmitter, which was now about 150 volts peak-to-peak, was fed into a

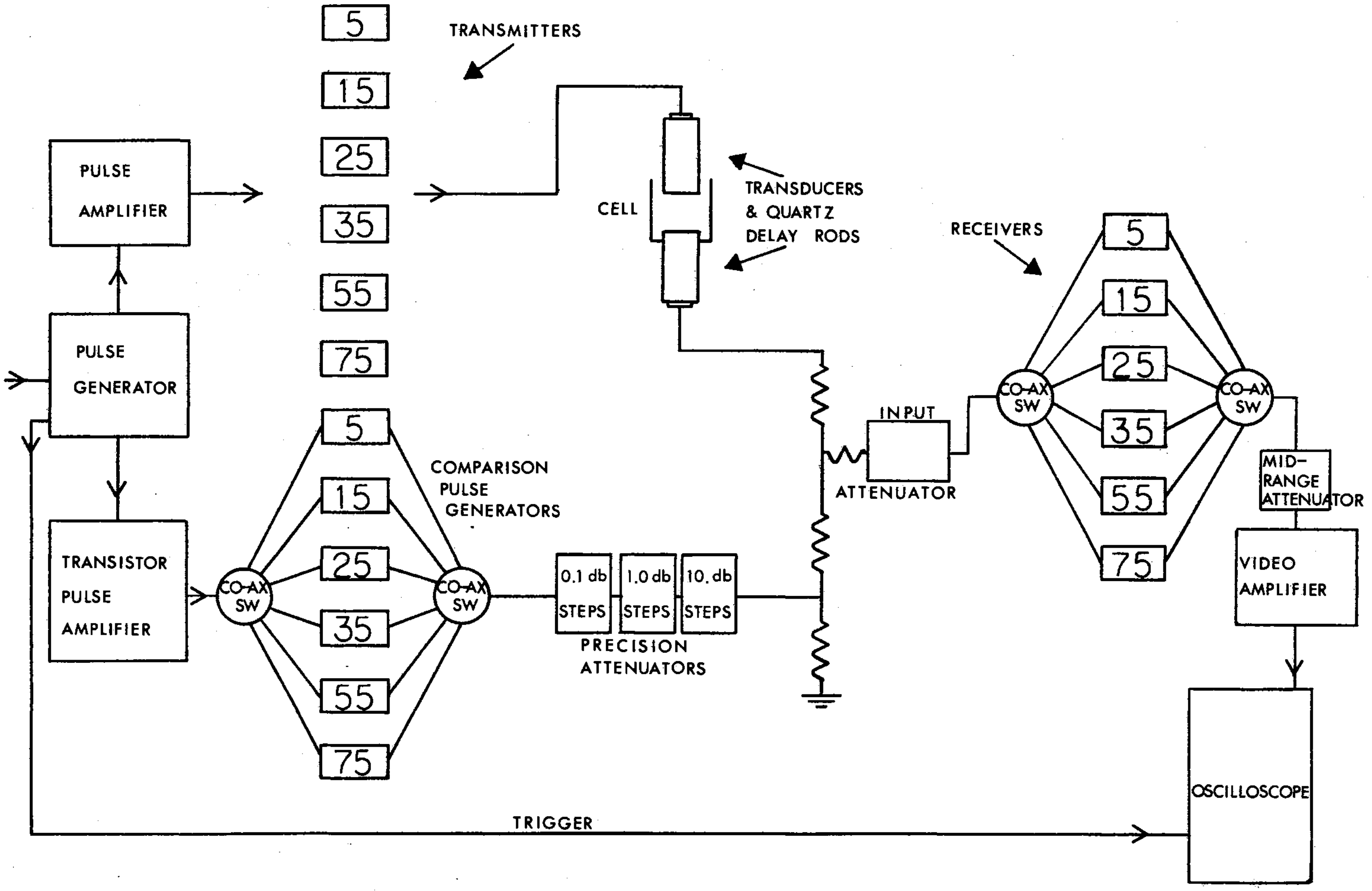

Figure 3. Block Diagram of Electrical System

circuit of about 75 ohms impedance. This final circuit contains the crystal transducer which oscillates at the frequency of the modulation on the pulse. The second pulse is amplified by the transistor pulse amplifier and modulated by the comparison pulse oscillator. The signal is then passed through a set of precision attenuators. The output from the receiver transducer of the mechanical system is combined with the output from the attenuators in a passive adder circuit. The combined signal pair drives a narrow-band, high gain amplifier. The amplified signal was then demodulated by the video amplifier and displayed on an oscilloscope (Tektronix 536 with Type L plug-in unit for fast rise time display).

The Mechanical System

The mechanical system used was that described by Fay (44). It consists of three parallel stainless steel platforms anchored to a stainless steel back. On the lower platform is positioned a table, fastened by a spring through the center and two spin-off nuts on either side. The table is supported by three adjustable leveling feet, and is also a chuck into which the quartz delay rod is inserted. The electrical contacts with the rod are made through either side of the chuck and through the bottom by a leaf assembly. Externally, the connection to the electronic system is made through a BNC connector mounted on the side of the table. The center platform is equipped with a movable chuck (with electrical connections through the sides and base) tensioned by springs. The upper platform has a micrometer attached to it and mounted directly above the upper chuck. The micrometer moves the upper chuck via an intermediate stainless steel ball; the motion of the micrometer is against the tension of the springs and provides a calibrated vertical motion of the receiver transducer.

The Transducer Assembly

Two delay rods of spectrosil B grade fused quartz were obtained from Thermal Syndicates Ltd., England. The emitter and lower delay rod was manufactured to the following specifications: length, 80 ± 1.0 mm; diameter, 30 ± 0.5 mm, with one end ground to a taper with a semi-angle of 5°. This tapered end was fitted into a ground glass joint on the lower part of a water jacket and formed the bottom of the absorption cell. The detector delay rod was prepared to the following specifications: length, 80 mm ± 1 mm, diameter, 20 mm ± 0.5 mm. Both cylinders had end faces optically flat to 1/4 the wavelength of green light and parallel to within 6 seconds of arc.

Each rod was plated with platinum on one end for a length of about 30 mm by application of Liquid Bright Platinum (DuPont #7447) and heating to 700°C. The plating was considered acceptable if the resistance between the face and side was approximately 1 ohm. The piezoelectric transducer elements were X-cut quartz crystals with a fundamental resonant frequency of 5000 KHz with a tolerance of 70 KHz (Marconi's W. T. Co., Ltd.). The crystals were attached to the delay rods using hot paraffin wax and the crystals were "rung-in" until there was less than 20 db of loss as measured by the electronic system operating on common transmit-receive mode. The outer face of the crystal was plated with liquid silver conducting paint to achieve electrical contact.

Experimental Procedure

The solution under study was placed in the thermostated cell and sealed with a Plexiglas cap equipped with latex rubber seals. The delay rods were made parallel by adjusting the lower table until the transmitted pulse displayed on the oscilloscope was maximized. This procedure was carried out at minimum separation of the delay rods so that all subsequent operations would be removing a thermally stable rod from the solution rather than introducing a cold rod to the solution. The transmitter pulse was tuned to a maximum amplitude as displayed on the oscilloscope. To insure that the comparison pulse generator was operating at the same frequency as the transmitter circuit, the comparison pulse and the transmitted pulse were overalpped by adjusting the time delay in the comparison pulse circuit and adjusting the comparison pulse oscillator until a common frequency was obtained and "beating" of the two signals occurred. The operating frequency was then measured by supplying a radio propagated continuous wave (c.w.) to the receivers from a signal generator (Eico, Model 315) powering a loop antenna encircling the receiver circuits. The exact frequency of the c.w. signal was monitored by a frequency counter (ElDorado, Model 1615) in the antenna circuit and the operating frequency noted when the oscilloscope once again displayed "beating" of the pulses. As it was not possible to measure the precise separation of the delay rods, the total sound absorbed, in decibels, was measured as a function of the change in separation, in centimeters, of the delay rods.

CHAPTER IV

EXPERIMENTAL AND TREATMENT OF THE DATA

Solutions for Conductivity

Reagent grade potassium chloride (Baker Analyzed) was dried at 300° C and 1 micron pressure for 48 hours. The Demal solutions used to obtain the cell constant were prepared from the fried KCl and conductivity water. The conductivity water was steam-distillate passed through a 2 meter column containing Research Grade Rexyn 300 (H-OH)(Fisher Certified Reagent) mixed bed deionizing resin and trace organics were removed by further passage over a 1 meter long column of activated charcoal. The water was stored under a stream of dry nitrogen gas to purge dissolved carbon dioxide. The specific conductivity of the water was always 9.9×10^{-7} mho cm^{-1} or better for the duration of the study.

Deuterium oxide of 99.9 w/w % quality was obtained from Stohler Isotope Chemicals, Inc. The initial measurement of the conductance of the D_2O indicated the presence of ionic impurities which were reduced by fractional distillation under a stream of dry nitrogen gas. The distillation apparatus was purged with dry nitrogen for 48 hours before the D_2O was introduced and only the middle fraction of the distillate was retained and stored in the manner described above for H_2O. The D_2O was periodicially checked by measuring the velocity of sound at ultrasonic frequencies (45) and was never observed to exceed 0.5 mole percent. The specific conductivity of the D_2O was always 2.3×10^{-6} mho cm^{-1} or better after distillation.

Commercially available lanthanide sulfates (American Potash and Chemical Corp.) were found to contain sufficient free sulfuric acid that the literature values for equivalent conductance in water could not be reproduced. After recrystallizing the salts from water with absolute ethanol and repeating the measurements, the agreement was excellent (Figure 3). Prior to preparing the solutions, all salts were dried at $70^{o}C$ and at 1 micron pressure for 72 hours to remove as much of the water of hydration as possible. The equivalent weight of each of the salts was determined by cation exchange on columns prepared from Dowex 50W-X4 resin (Baker Analyzed Reagent) and titration of the eluant acid with standard potassium hydroxide solution. It was determined that the salts retained one or two water molecules per formula weight of the salt and that this amount of H_2O would not significantly effect the isotopic composition of the resulting solution. Stock solutions, approximately 10^{-2} N in concentration, were prepared by weight and corrected from molality to normality using the equivalent weights determined by titration and the densities of H_2O and D_2O of 0.9970 gm/ml and 1.1044 gm/ml respectively.

Conductivity Data

In the association reaction of a lanthanide ion with a sulfate ion, there are at least three species of major thermodynamic importance present at equilibrium in dilute aqueous solution: Ln^{3+}, SO_4^{2-}, and the associated ion-pair, $LnSO_4^{+}$. In order to describe the system thermodynamically, it is necessary to have a knowledge of the activity of each of the ions.

The thermodynamic formation constant for the lanthanide sulfate complex is given by

$$K = \frac{[LnSO_4^+]}{[Ln^{3+}][SO_4^{2-}]} \; \frac{\gamma_1}{\gamma_3\gamma_2} = \frac{\beta}{m(2-\beta)(3-\beta)} \; \frac{1}{\gamma_1^{12}} \qquad (4.1)$$

where m is the molar concentration, β is the degree of association, and γ_i is the activity coefficient of the i-th ion. For a dilute solution, the activity coefficient may be calculated by using a modified form of the Debye-Hückel equation suggested by Davies (2)

$$-\log \gamma_1 = A \left\{ \frac{\mu^{1/2}}{1 + B \overset{o}{a} \mu^{1/2}} - 0.3\ \mu \right\} \qquad (4.2)$$

where $\mu = (15m - 6\beta m)$ is the ionic strength, $\overset{o}{a}$ is the distance of closest approach. A and B are defined by the following equations:

$$A = \left(\frac{2\pi N}{1000}\right)^{1/2} \cdot \frac{e^3}{2.303\ k^{3/2}} \cdot \frac{1}{(\epsilon T)^{3/2}} = \frac{1.8246 \times 10^6}{(\epsilon T)^{3/2}} \; \frac{1^{1/2} ({}^{o}K)^{3/2}}{mole^{1/2}}$$

$$B = {\frac{8\ Ne^{2}}{1000\ k}}^{1/2} \cdot \frac{1}{(\epsilon T)^{1/2}} = \frac{50.29 \times 10^8}{(\epsilon T)^{1/2}} \; \frac{1^{1/2} ({}^{o}K)^{1/2}}{cm\ mole^{1/2}}$$

where N is Avogadro's number, e is the protonic charge (equal but opposite in sign to the electronic charge), k is Boltzmann's constant, ϵ is the bulk dielectric constant of the solvent, and T is the temperature in degrees Kelvin.

The denominator of the Davies equation was empirically modified to include the variable parameter $\overset{o}{a}$, identified with the Bjerrum distance of closest approach. In the original form of the Davies equation, the product $B\mathring{a}$ is taken as being equal to 1 for univalent symmetrical electrolytes. It is known that a trivalent ion will have a larger region of interaction (2) than a univalent ion especially in the case of the interaction of a trivalent ion with a divalent ion. To be consistent with the previous kinetic studies, the value of $\mathring{a}$ is set equal to 8.86 Å, the sum of the ionic crystal radii plus two water molecule diameters. In any case, the over-all analysis proved to be relatively insensitive to the choice of $\mathring{a}$.

A solution of a lathanide sulfate salt in water may be treated conductimetrically as a mixture of the uni-bivalent salt $(LnSO_4)_2SO_4$ at equivalent concentration βm, and the tri-bivalent salt $Ln_2(SO_4)_3$ at equivalent concentration (6m - 3βm). The conductance of each component may be calculated from the summation of the Onsager equations for both the cation and the anion, and with the universal constants inserted (2)):

$$\Lambda = \Lambda^o - \left[\frac{2.801 \times 10^6 \; z_1 z_2 q}{(\epsilon T)^{3/2}(1 + q^{1/2})} + \frac{41.25 \; (z_1 + z_2)}{\eta(\epsilon T)^{1/2}}\right] \mu^{1/2} \qquad (4.3)$$

where

$$q = \frac{z_1 z_2 \; (\Lambda_1^o + \Lambda_2^o)}{(z_1 + z_2)(z_2\Lambda_1^o + z_1\Lambda_2^o)}$$

and

$$\mu = 1/2 \; (m_1 z_1^2 + m_2 z_2^2)$$

Here Λ is the equivalent conductance of the salt considered, Λ^o is its zero concentration equivalent conductance, T is the absolute temperature,

η the viscosity of the solvent, z_1 and z_2 are the charges carried by the cation and anion, Λ_1^o and Λ_2^o their zero concentration equivalent conductance, and m_1 and m_2 their concentrations in moles per liter.

All terms of order higher than the limiting square root terms have been truncated and the error introduced in Λ_i is absorbed in K. The degree of association may then be calculated by applying the mixture rule and solving the Equation (2)

$$\Lambda_{exp} = \frac{\alpha}{6}\Lambda'_{1,2} + \frac{6 - 3\beta}{6}\Lambda_{3,2} \tag{4.4}$$

where Λ_{exp} is the experimentally measured equivalent conductance obtained by the following equation (Table II)

$$\Lambda_{exp} = \frac{1000\ \kappa_{soln}}{c_{eq}} \qquad \kappa_{soln} = \frac{\text{cell constant}}{\text{resistance}} \tag{4.5}$$

where κ is the specific conductance of the solution corrected for the specific conductance of the pure solvent and c_{eq} is the concentration in equivalents per liter.

A difficulty arises in that a knowledge of the limiting conductance of the associated ion-pair, $\lambda^o_{LnSO_4^+}$, is not available by direct experimental measurement. Several values have been assigned on an empirical basis, varying from 23.2 to 40 conductance units (46,47). An arbitrary value for $\lambda^o_{LnSO_4^+}$, was chosen and a formation constant calculated by a standard iterative technique. To do this a computer program was developed which calculated a value for K at each concentration, using the initial guess for the value of $\lambda^o_{LnSO_4^+}$, and the standard deviation obtained. The initial guess for the limiting mobility of the ion-pair

TABLE II

EQUIVALENT CONDUCTANCES IN Mho. Cm^{-1} IN H_2O AND D_2O AT 25°

La(D_2O)	10^4N	Pr(D_2O)	10^4N	Sm(D_2O)	10^4N
78.38	5.177	68.58	9.070	92.11	1.634
72.30	7.383	63.46	12.55	84.72	2.965
68.78	9.070	61.27	14.44	78.13	4.705
63.66	12.37	56.14	19.91	75.19	6.012
57.44	18.49	52.05	27.01	71.42	7.131
51.47	27.50	38.61	80.40	68.36	8.481
46.31	41.46	36.81	95.20	66.53	9.411
41.57	62.57	35.48	110.8	62.90	11.67
				57.97	15.79
				52.77	22.25
				46.36	35.73

Dy(D_2O)	10^4N	Yb(D_2O)	10^4N	Lu(D_2O)	10^4N
77.13	5.574	95.25	2.073	85.94	3.369
69.56	8.691	80.17	5.539	70.48	9.395
66.83	10.20	76.28	7.035	67.23	11.59
61.58	14.20	71.54	9.391	63.93	14.39
59.53	16.21	68.85	11.13	62.01	16.33
57.40	18.71	65.17	13.87	60.24	18.37
55.67	21.02	57.32	23.14	57.60	21.99
53.41	24.67	53.38	30.67	51.30	34.70
50.96	29.52	49.55	40.98	49.44	40.11
46.56	41.67	47.20	49.40	46.47	51.03
43.05	56.20			44.76	59.05
				42.62	71.18

Sm(H_2O)	10^4N	Lu(H_2O)	10^4N
117.2	1.925	123.5	1.285
100.3	4.551	106.5	3.997
91.22	6.956	97.16	6.593
85.74	8.987	90.02	9.344
80.62	11.52	86.18	11.50
75.41	14.94	82.44	14.01
68.78	21.16	78.07	17.72
62.28	30.65	71.95	24.70
55.71	46.49	64.58	37.83
52.89	56.35	58.30	56.24
		53.98	75.72

was then increased incrementally and the calculations repeated. The criterion for the best fit of Eq. (4.3) to the experimental curve was that the standard deviation (SD) be a minimum and therefore the variation of the formation constant with concentration minimized. Figure 4 illustrates an abbreviated set of iterations for $Lu_2(SO_4)_3$ in which the variation of the formation constant is plotted as a function of ionic strength. The values of $\lambda^o_{LnSO_4^+}$ which give the best fit for all salts in H_2O are considerably less than those used previously. However, at $\mu = 0$ the agreement in K for any salt using either value of $\lambda^o_{LnSO_4^+}$ is reasonably good. The physical justification for using the value 23.2 for $\lambda^o_{LnSO_4^+}$ was that the charge on the ion-pair is one third that of the free metal ion ($\lambda^o_{La^{3+}} = 69.6$ mho cm^2 $equiv.^{-1}$), and therefore the complex should be no more than one third as mobile as is the metal ion. However, this assumption presumes a spherical ion-pair, an improbable geometry. Thus, the mobility of the complex would be expected to be lower than the values previously used.

Since the purpose of this study was to make comparisons between thermodynamic formation constants obtained in two solvent media, it was thought advisable to repeat a dilution study in H_2O that the data may be compared with those of Spedding and Jaffe (46)(Figure 5) as well as to complete the study of the lanthanide series by obtaining data on lutetium sulfate. Since no value for the limiting conductance of lutetium (III) is available from the literature, the computer program was modified to calculate by iteration a value for $\lambda^o_{Lu^{3+}}$.

For such a calculation to succeed, it was necessary to estimate the value for $\lambda^o_{Lu^{3+}}$ before determining the mobility of the $LuSO_4^+$ complex. In the case of lutetium the former value was first estimated from a

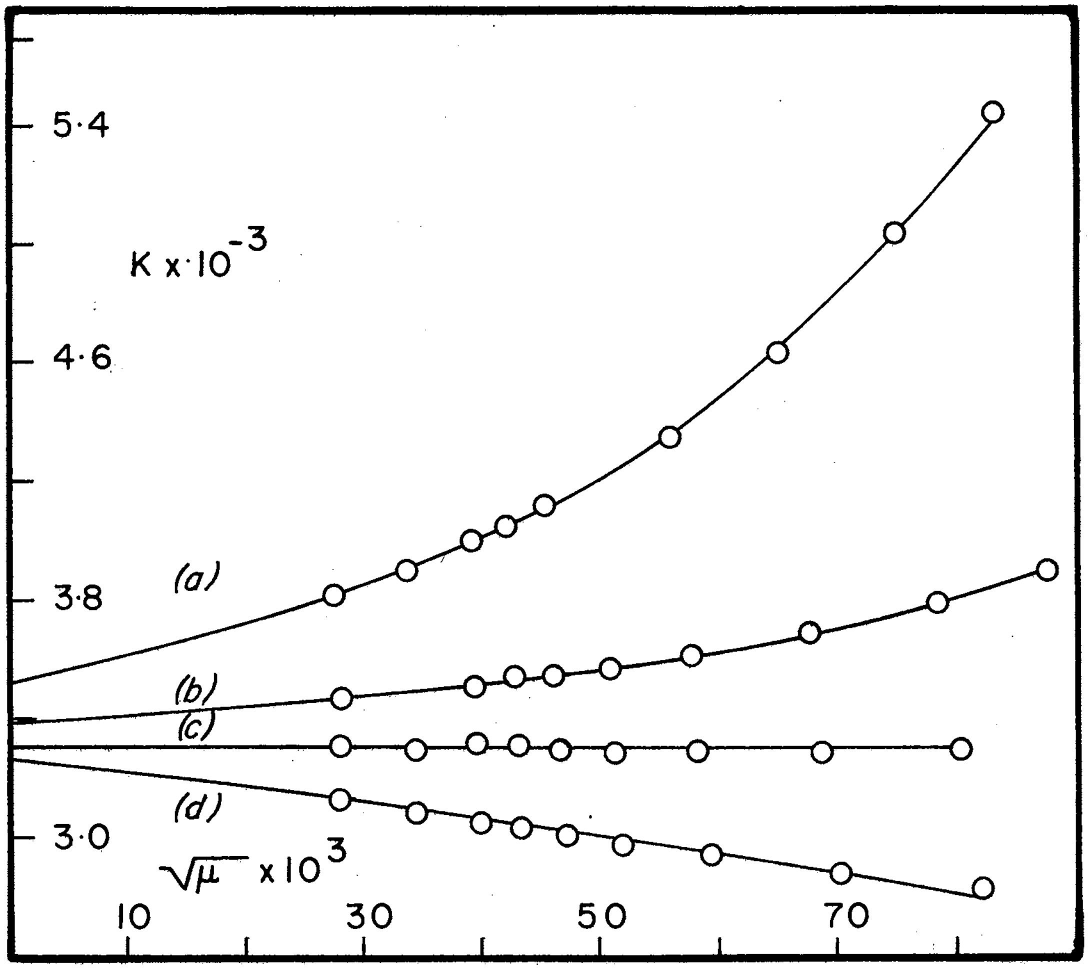

Figure 4. Calculated Formation Constant K Versus the Square Root of the Ionic Strength μ as a Function of $\lambda^{o}_{LnSO_4^+}$ for $Lu_2(SO_4)_3$ in H_2O; a) 40; (b) 23.2; (c) 13.2; d) 10

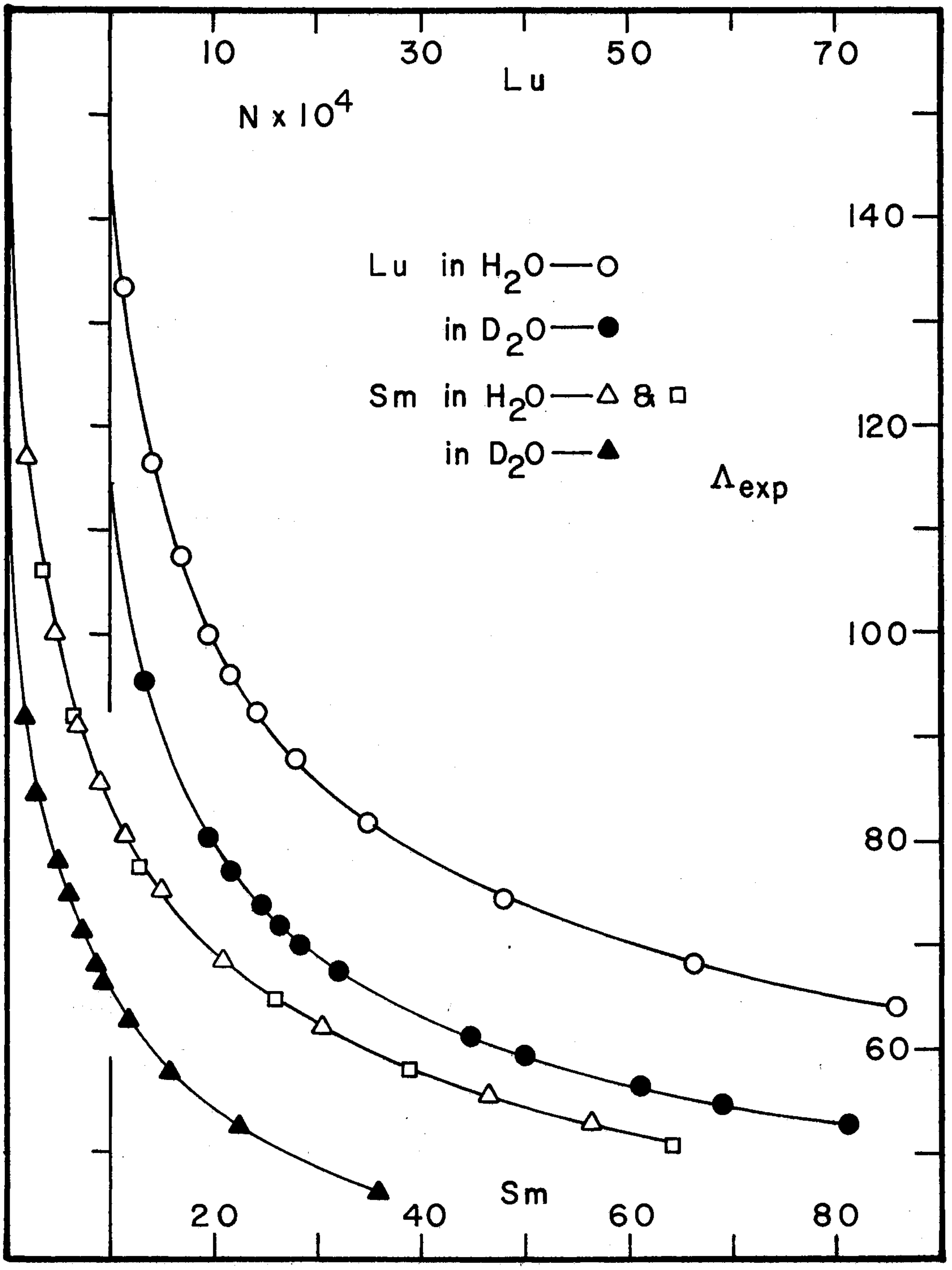

Figure 5. Experimental Equivalent Conductances Versus Normality for $Sm_2(SO_4)_3$: ⊙ Present Data in H_2O; ⊡ Data From Ref. 46; ● Present Data in D_2O; and $Lu_2(SO_4)_3$: △ Data in H_2O; ▲ Data in D_2O

linear extrapolation of the limiting conductances of the trivalent ions of the lanthanide series. A value for $\lambda^o_{LuSO_4^+}$ was subsequently found by minimizing the SD as before. Using this value for $\lambda^o_{LuSO_4^+}$, the computer program was recycled by incrementing $\lambda^o_{Lu^{3+}}$ until the SD was again minimized. The results of this series of calculations indicated that such a procedure was in fact successful and the value of $\lambda^o_{Lu^{3+}}$ that minimized the SD was 64.7 mho cm^2 $equiv.^{-1}$ which was approximately the value expected from extrapolation.

Although more than one minimum in the standard deviation could be obtained depending on the value estimated for $\lambda^o_{Lu^{3+}}$, it was found that the final SD was smaller if the initial estimate was chosen to be about 80% of the expected value and the computer program allowed to cycle by incrementing up to the final value. In every case, the SD reported is the smallest obtained. Table III includes the values for the formation constants determined by this method for the equivalent conductances obtained in this study and, for comparison, those recalculated from Spedding and Jaffe's data (46) using this treatment. Also included in the table is a recent value for $EuSO_4^+$ formation obtained by differential uv spectrophotometry (48).

The success of this approach in determining both a reasonable value for the limiting conductance of the lutetium ion and the formation constant for the system indicated that, provided a value for the limiting conductance of the sulfate ion could be assigned, the measurement of the limiting conductance of $\lambda^o_{Ln^{3+}}$ in D_2O would not be necessary in order to arrive at a value for the formation constants in D_2O.

From available experimental data on the limiting conductances of various univalent cations and anions in D_2O, including the polyatomic

TABLE III

FORMATION CONSTANTS AND EQUIVALENT CONDUCTANCE PARAMETERS

$(D_2O)\ \lambda^o(SO_4^{\ 2-}) = 64.2$ MHO. CM ^{2} EQUIV^{-1}

Ion	$\Lambda_{o(1,2)}$	$\Lambda_{o(3,2)}$	$\lambda^o(LnSO_4^{\ +})$	$\lambda^o_{Ln^{3+}}$	$Kx10^{-3}$	S.D.
La	72.0	120.3	7.8	56.1	4.69	23
Pr	72.4	118.9	8.2	54.7	4.63	126
Sm	71.4	117.8	7.2	53.6	4.82	100
Dy	70.8	117.5	6.6	53.3	4.26	29
Yb	73.9	117.1	9.7	52.9	3.57	92
Lu	73.7	114.5	9.5	50.3	3.50	15
$(H_2O)^a\ \lambda^o(SO_4^{\ 2-}) = 79.8$ mho. cm.^{2} equiv^{-1}						
La	91.3	149.5	11.5	69.7	4.43	129
Ce	92.5	149.5	12.7	69.7	4.69	46
Pr	91.3	149.5	11.5	69.7	4.70	57
Nd	92.3	149.5	12.5	69.7	4.76	45
Sm[b]	89.8	148.5	10.0	68.7	4.78	12
Gd	91.9	147.4	12.1	67.6	4.72	39
Ho	92.8	146.3	13.0	66.5	3.95	187
Er	92.8	145.9	13.0	66.1	3.79	63
Yb	90.3	145.2	10.5	65.4	3.26	49
Lu	93.0	144.5	13.2	64.7	3.31	20
Eu[c]					4.69	

[a] Present analysis of data of reference 46.

[b] Present data combined with data from reference 46.

[c] From U.V. Spectral Analysis, reference 48.

anion nitrate (49), it is apparent that the ionic mobility in D_2O is approximately 80% of the value in H_2O. On considering the Stokes equation

$$V = \frac{F}{(6\pi\eta r)} \tag{4.6}$$

where V is the particle velocity in cm/sec, F is the force in dynes, r is the radius of the spherical particle, and η is the viscosity of the medium, this is not an unexpected result as the viscosity of H_2O is about 80% of the viscosity of D_2O. Although this equation is not really applicable to small particles, a value of $\lambda^o_{SO_4^{2-}}$ equal to 80% of the limiting conductance in H_2O is a useful approximation. Such an approximation would also seem justifiable for determining the limiting conductance of the lanthanide ions, but these values were not fixed. Instead they were used as variable parameters in the calculation. In this way the variation of the limiting conductance with atomic number would not be an artifact of the calculational method.

The calculations were carried out on the equivalent conductances obtained in D_2O using the method described above for lutetium, and a value of $\lambda^o_{SO_4^{2-},D_2O}$ = 64.2 mho cm^2 equiv.$^{-1}$ ($\lambda^o_{SO_4^{2-},H_2O}$ = 79.8 mho cm^2 equiv.$^{-1}$). In all cases the initial estimate used for $\lambda^o_{Ln^{3+},D_2O}$ was chosen to be about 75% of the corresponding limiting mobility in water. No attempt was made to force a trend of decreasing mobility with increasing atomic number. In addition, various initial estimates were used, ranging from 50% of the water value to 90% of the water value and no lower final SD was ever obtained.

Although the value for $\lambda^o_{LnSO_4^+,D_2O}$ seems realistic, the 80% correspondence between the two solvents is not good. Because of this lack of agreement and since $\lambda^{o}_{LnSO_4^+}$ is used only as a fitting parameter, no physical significance can be attached to these values.

Solutions for Kinetics

All solutions used in the kinetic study were prepared using salts and solvents treated as described above for the conductivity study. Approximately 20 ml of each solution was prepared by weighing both salt and solvent into small erlenmyer flasks which were then sealed with rubber serum stoppers. The solutions were stored in a dessicator until the measurements were made. These solutions were not recycled by distillation nor were they mixed with new D_2O as the opportunity for isotopic exchange was considered to be too great during the measurement and transfer to and from the ultrasonic absorption apparatus, although velocity measurements indicated no significant exchange before and during the measurement.

The solutions for the constant ionic strength study were prepared in a similar manner except that the solvent was 0.75 and 0.50 F $NaClO_4$ (G. Frederick Smith Chemical Co.) and delivered by a transfer pipet and not weighed. The concentration range and ionic strength of the medium was restricted by a marked decrease in the solubility of the samarium sulfate.

Kinetic Data

In the evaluation of specific rate constants the usual procedure is to measure the ultrasonic absorption, $\alpha\lambda$, over the frequency range of interest. Since the solvent also absorbs some of the energy of the sound wave, a correction is made for this by assuming additivity of the chemical absorption, $\alpha_{chem}\lambda$, and the solvent absorption, $\alpha_s\lambda$. The frequency of maximum chemical absorption is assigned by various means. In this study two methods were used. The first method was to apply Equation (2.9)

$$(\alpha_{chem}\lambda) = 2(\alpha_{chem}\lambda)_R \left\{\frac{f/f_R}{1 + (f/f_R)^2}\right\} \tag{2.9}$$

at two experimental frequencies and solve the resulting equation for f_R. If this is done at all experimental frequencies, by pairs, and the results averaged, the results are not smoothed as they may be by other methods. The second method of determining the relaxation frequency was by a non-linear, weighted, least squares technique. In this particular case, a computer program was written which operated in the following manner: (1) a ten by ten array was established using initial estimates of the minimum and maximum values for $(\alpha_{chem}\lambda)_R$ and f_R; (2) a value of $(\alpha_{chem}\lambda)^i_{calc}$ was calculated at each of the 100 grid points from the equation

$$(\alpha_{chem}\lambda)^i_{calc} = \frac{2(\alpha_{chem}\lambda)_R\, f_i/f_R}{1 + f_i^2/f_R^2} \tag{4.7}$$

where f_i is the frequency of experimental measurement, the sum of the variance of each $\alpha_{chem}\lambda$ from the calculated value was obtained from the equation

$$S^2 = \frac{1}{n} \sum_{i=1}^{6} [(\alpha_{chem}\lambda)^i_{exp} - (\alpha_{chem}\lambda)^i_{calc}]^2 \cdot W_i \tag{4.8}$$

where n is the number of experimental data points and W_i is the weighting coefficient; (3) the array was then searched for the minimum value of S^2; (4) a new array established using the values which gave the minimum S^2 and new minimum and maximum values for f_R and $(\alpha_{chem}\lambda)_R$ (obtained by incrementing these new f_R and $(\alpha_{chem}\lambda)_R$ values appropriately) and repeating the above procedure a number of times (in most cases 7). The final values represent the best fit of the experimental values to a single relaxation curve and were presented along with a value of S. The weighting coefficients were obtained by analyzing the expected error in the measurement at each frequency. The results of both calculational methods were in good agreement and either was determined to be an adequate method of analysis.

High frequency relaxation studies (50,51) indicate that another relaxation occurs in the range 400 to 600 MHz and this is sufficiently separated from those in the 10 to 60 MHz range that there will be no interference from the former at the lower range. For this reason the spectra were interpreted as single relaxations (Figure 6). The same three-step mechanism assumed in H_2O previously (28,42) was adopted for consistency.

Once the relaxation frequencies for a number of solutions with differing salt concentrations are known, it is the possible to evaluate the step-wise rate constants. This is discussed specifically for the trivalent lanthanide sulfates for which the association reaction is written as

$$\underset{(2C_o-\beta)}{Ln^{3+}} + \underset{(3C_o-\beta)}{SO_4^{2-}} \rightleftarrows \underset{\beta C_o}{LnSO_4^+} \qquad (4.9)$$

TABLE IV

EXCESS ABSORPTION ($\alpha_{CHEM}\lambda \times 10^3$) DB AS A FUNCTION OF FREQUENCY

		f (MHz)					
	10^3C_o	5.2	15.4	25.5	36.1	56.0	66.5
				D_2O			
Pr	25.17	28.62	51.17	47.77	41.80	33.04	30.33
	19.79	25.90	37.84	37.73	32.91	26.12	23.71
	14.97	22.44	32.05	30.30	25.35	20.94	18.72
	9.92	17.71	21.40	20.93	17.68	14.02	12.68
	6.96	10.34	16.09	15.63	14.13	10.80	8.66
Sm	19.82	19.26	43.86	55.37	56.74	54.00	46.85
	14.94	16.62	34.49	41.88	44.78	40.40	33.68
	10.46	8.97	24.07	31.28	31.61	27.40	24.99
	7.40	7.60	20.50	24.20	24.80	20.20	19.40
Gd	15.22	15.77	39.40	44.76	44.24	37.25	33.76
	7.79	10.41	18.96	23.09	22.05	18.51	16.71
	3.26	5.67	9.15	10.53	10.04	6.93	4.27
Dy	24.45	26.08	43.88	43.50	36.19	28.57	27.59
	20.13	21.64	37.53	36.16	30.82	26.55	23.62
	14.28	17.07	27.72	26.49	22.87	18.54	18.73

TABLE V

RELAXATION FREQUENCIES AND CONCENTRATION DATA

Ion	$C_o \times 10^3$,F	$\theta(C) \times 10^3$,F	$2\Pi f_{III}$ (MHz)	RMS
		— H_2O[a] —		
Pr	14.70[a]	6.23	128 ± 8	1.1
	9.76[a]	5.07	122 ± 7	0.73
	5.38[a]	3.58	122 ± 7	1.3
	2.69	2.29	100 ± 5	0.20
	1.34	1.43	80 ± 8	0.09
Nd	15.26[a]	6.36	155 ± 4	0.95
	9.61[a]	5.04	147 ± 4	0.62
	5.08[a]	3.46	142 ± 10	0.72
Sm	18.51	6.91	236 ± 5	0.14
	9.76[a]	5.10	228 ± 5	0.04
	4.88[a]	3.38	214 ± 7	0.03
Eu	15.02	6.33	255 ± 6	0.82
	9.80[a]	5.11	249 ± 6	
	5.00[a]	3.44	230 ± 7	0.54
Gd	15.28	6.38	211 ± 5	0.89
	9.45	5.01	202 ± 5	
	4.73	3.31	196 ± 5	
	2.36	2.10	173 ± 7	
Tb	9.88	5.11	148 ± 5	
	4.99[a]	3.42	133 ± 7	
	2.50	2.18	128 ± 7	
Dy	15.17[a]	6.30	117 ± 5	
	9.70[a]	5.03	114 ± 5	
	6.50[a]	4.00	105 ± 8	
Ho	10.80[a]	5.30	72 ± 10	
	5.40[a]	3.56	69 ± 10	
	2.70	2.29	69 ± 12	
		— D_2O —		
Pr	25.17	7.46	119 ± 5	0.12
	19.79	6.99	121 ± 5	0.14
	14.97	6.26	112 ± 5	0.12
	9.92	5.10	116 ± 5	0.12
	6.96	4.17	105 ± 6	0.06
	5.18	3.49	112 ± 8	0.03
	3.02	2.46	96 ± 8	0.02

TABLE V (Continued)

Ion	$C_o \times 10^3$,F	$\theta(C) \times 10^3$,F	$2\Pi f_{III}$ (MHz)	RMS
Sm	19.82	7.01	212 ± 5	0.80
	14.94	6.26	205 ± 5	0.82
	10.46	5.25	208 ± 5	0.26
	7.40	4.33	196 ± 5	0.31
Gd	15.22	6.30	180 ± 5	0.65
	7.79	4.45	179 ± 8	0.31
	3.26	2.59	150 ± 10	0.63
Dy	24.45	7.37	126 ± 7	1.1
	20.13	6.99	123 ± 7	1.0
	14.28	6.08	123 ± 7	1.1

[a] Data from reference 47.

[b] RMS calculated for only those experiments done on present equipment. Other data taken from ref. a.

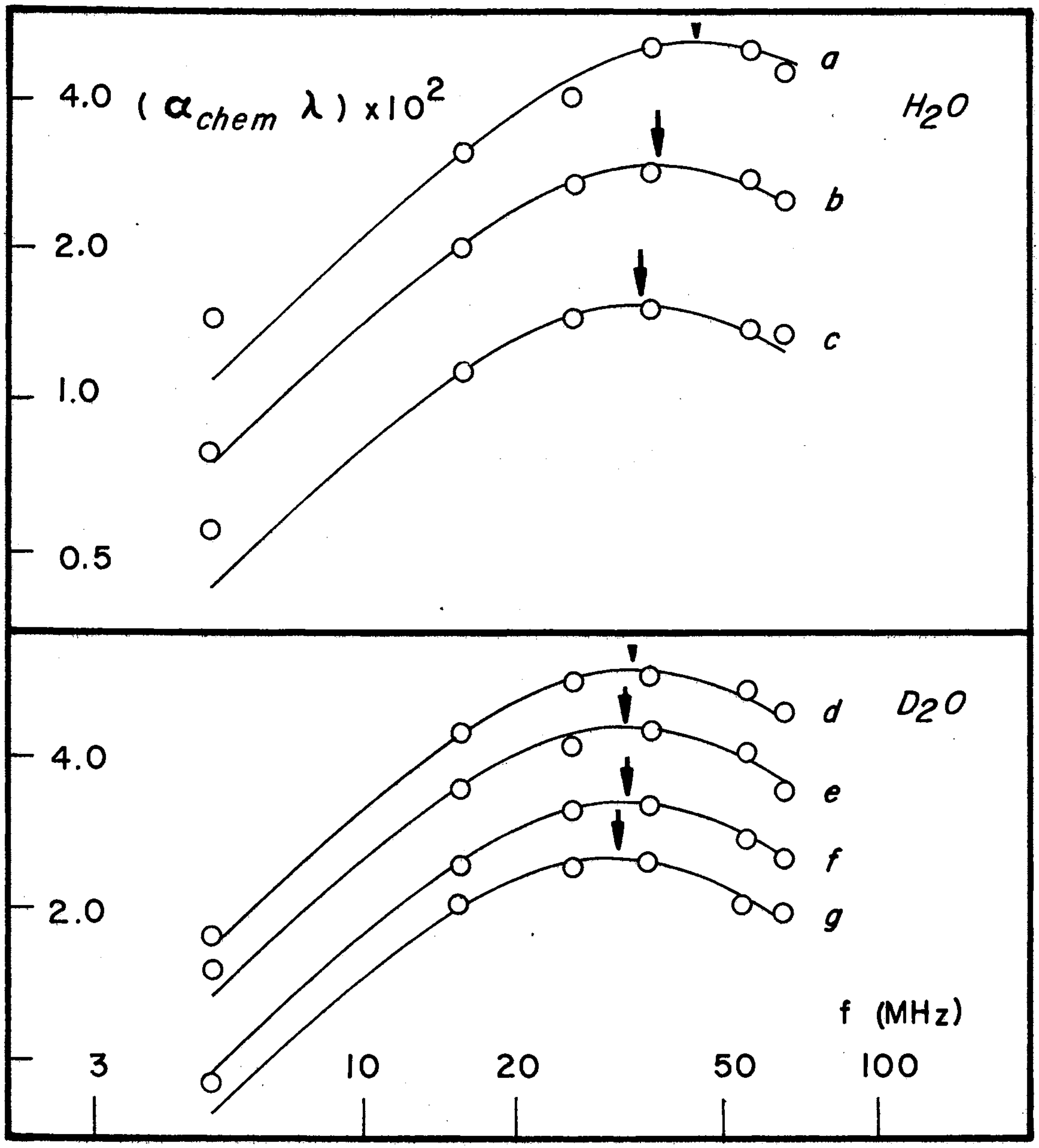

Figure 6. Chemical Absorption Versus Frequency for $Sm_2(SO_4)_3$ Solutions in H_2O and D_2O for (a) 18.51x10^{-3}F, (b) 9.76x10^{-3}F, (c) 5.08x10^{-3}F, (d) 19.82x10^{-3}F, (e) 14.94x10^{-3}F, (g) 7.40x10^{-3}F. Solid lines are calculated single relaxation curves the arrows indicating the relaxation frequencies f_{III}

Substitution into Equations (2.13-2.15) gives

$$\tau_I^{-1} = 2\pi f_R = k_{12}^{o}\ \theta + k_{21} \tag{4.10}$$

$$\tau_{II}^{-1} = 2\pi f_R = \left[\frac{\theta}{\theta + (K_{12})^{-1}}\right] k_{23} + k_{32} \tag{4.11}$$

$$\tau_{III}^{-1} = 2\pi f_R = \left[\frac{\theta}{(K_{12}K_{23})^{-1} + (1 + K_{23}^{-1})\theta}\right] k_{34} + k_{43} \tag{4.12}$$

$$= \phi\ k_{34} + k_{43} \tag{4.13}$$

where $K_{12} = k_{12}^{o}/k_{21}$ and $K_{23} = k_{23}/k_{32}$ and

$$\theta = \pi_f C_o\ [5 - 4\beta + (3 - 2\beta)(\frac{\ln\pi_f}{\ln\beta})_{C_o}] \tag{4.14}$$

where $\pi_f = \gamma_1/\gamma_3\gamma_2$ and γ_i is the activity coefficient of the i-th ion.

The solution of these equations for k_{34} and k_{43} present considerable difficulty. Among these are how to evaluate K_{12} since τ_I and τ_{II} are not observed, the activity coefficients, and the partial derivative term. In addition, there is a problem of more practical importance, is the concentration dependence of τ_{III} large enough that the variation in τ_{III} is greater than the experimental error in its determination?

The equilibrium constant for the first step is calculated from the Bjerrum equation (Eq. 1.3)(for the very good reason that K_{12} does not pass through a minimum with increasing distance of closest approach (38)). For the lanthanide sulfates, the value of K_{12} is about 440 at $\mu \rightarrow 0$ using $\mathring{a} = 8.86\mathring{A}$ (Table III). The activity coefficients are calculated from the Davies equation (Eq. 4.2) in the same manner as the values used in the conductance study.

The concentration function in Equation (4.13), ϕ, may not be determined until a value of K_{23} is assigned. Generally this is left as a variable parameter and used to fit Equation (4.13) to the expression

$$K = K_{12} (1 + K_{23} + K_{23}K_{34}) \qquad (4.15)$$

where $K_{34} = k_{34}/k_{43}$. The fit may be made by a reiterative calculation (44), but in the iteration process a graphical solution to equation is necessary. Figure 7 describes the variation of ϕ with analytical concentration of a lanthanide sulfate. It is apparent that ϕ is relatively insensitive to the variation of the analytical concentration even for a reasonably wide concentration span. It would seem that a reasonable solution to the difficulty would be to lower the concentration so that the values lie in the region of greatest change for the function ϕ. Unfortunately the error in the absorption measurements at low concentration are so great as to preclude this solution. Likewise, it is obvious that measurements at higher concentrations will not improve the precision of the analysis. Using typical values of k_{34} and k_{43} and the calculated values of ϕ, the anticipated frequency range can be shown to be around 3-4 MHz. If a conservative error in $f_{R(III)}$ is used, about ± 1 MHz, it is apparent that the linear plot of $2\pi f_{R(III)}$ versus ϕ will often result in a negative intercept (42) because of the very long extrapolation to zero. Figure 8 shows a typical result of the calculation. Although this is not the result of a direct graphical solution, it can be seen that a long extrapolation is necessary to evaluate the rate constants (the slope of the line is k_{34} and the zero intercept is k_{43}). The reiterative calculation may be avoided by the appropriate combination of

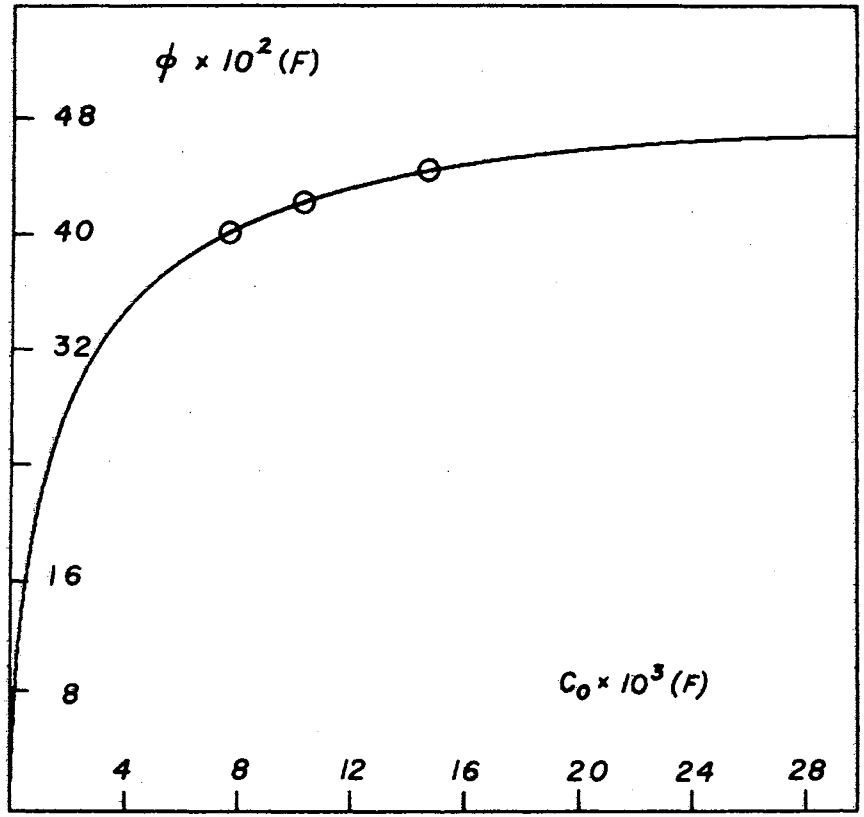

Figure 7. Plot of Frequency Dependent Concentration Variable ϕ Versus the Analytical Salt Concentration C_o for $Sm_2(SO_4)_3$ in Water. Open circles are typical experimental values

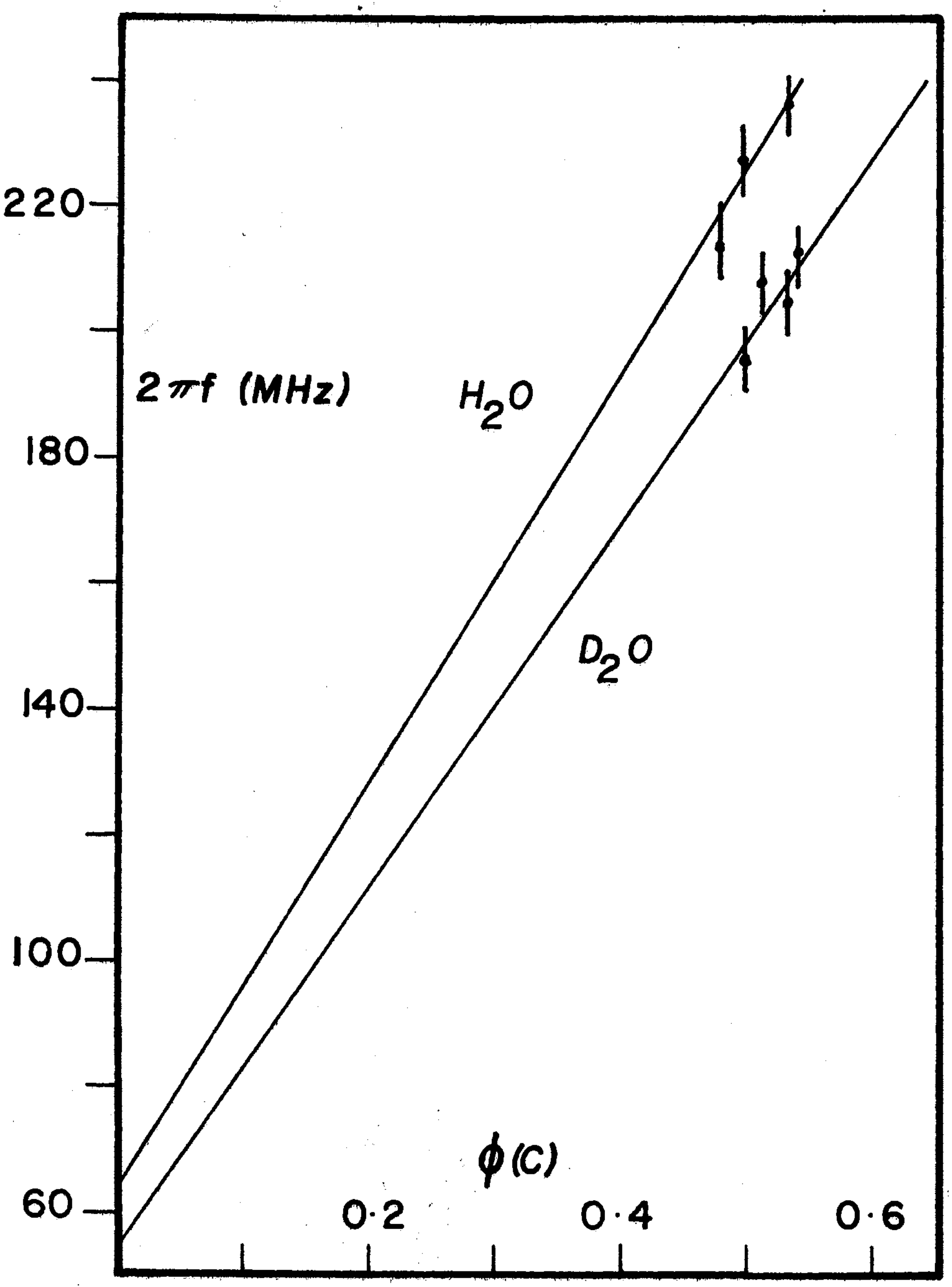

Figure 8. The Graphical Solution of Eq. (4.13) for $Sm_2(SO_4)_3$ in H_2O and D_2O. Solid lines correspond with the values of k_{34} and k_{43} from the solution of Eq. (4.16)

Eq. (4.13), the equation for the overall formation constant, Eq. (4.15), and the expression for ϕ. A two parameter equation is obtained:

$$2\pi f_{R(III)} = \left[\frac{(1 + K\theta)}{1 + K_{12}\,[K_{23} + 1]\theta}\right] k_{43} \tag{4.16}$$

which, on substituting two values of $2\pi f_{R(III)}$ and θ, yields K_{23} and k_{43} on simultaneous solution. k_{34} is determined by substituting the values of K_{23} and k_{43} into equation. Figure 8 was constructed using rate constants calculated by this method.

For this study a computer program was written which incorporated the above equations and solved them for each pair of data points. The derivative term was evaluated by the same method used previously (44)

$$\left(\frac{\ln \pi_f}{\ln \beta}\right)_{C_o} = 0.509\,[(Z_{M^{3+}}^{2}) + (Z_{L^{2-}}^{2}) - (Z_{ML^{+}}^{2})] \times \frac{1}{(2\mu^{1/2}(1+B\overset{o}{a}\mu^{1/2})^{2}-0.3\mu)(1-\beta)C_o} \tag{4.17}$$

the values of β and μ being obtained by standard iterative procedures. The individual rate constants determined for each data point pair were averaged to obtain the remaining unknowns. The results of these calculations are shown in Table VI.

In the case of the constant ionic strength study, Tables VII, VIII, IX, the calculational procedure was somewhat simplified in that the derivative term (Eq. 4.17) vanishes and the term θ reduces to

$$\theta = (5 - 2\beta)C_o \tag{4.18}$$

θ may then be determined from the conditional formation constant. Figure 9 shows the variation of pK_{cond} with μ. Since the functional relation-

TABLE VI

RATE CONSTANTS AND STEPWISE ASSOCIATION CONSTANTS

Ion	$k_{34} \times 10^{-8}$ sec^{-1}	$k_{43} \times 10^{-7}$ sec^{-1}	K_{12}	K_{23}	K_{34}	$K_c \times 10^{-3}$
			H_2O			
Pr	2.1	2.8	432	1.0	7.5	4.17
Nd	2.3	4.0	433	1.3	5.9	4.35
Sm	3.3	6.3	436	1.5	5.3	4.55
Eu	3.4	6.7	437	1.5	5.1	4.55
Gd	2.8	5.7	437	1.6	4.9	4.55
Tb	1.9	4.4	439	1.7	4.2	4.32
Dy	1.3	3.9	440	1.9	3.3	4.08
Ho	1.0	2.5	441	1.5	4.1	3.85
			D_2O			
Pr	1.5	3.0	432	1.6	5.0	4.63
Sm	2.9	5.4	436	1.6	5.4	4.82
Gd	2.9	4.3	437	1.2	6.8	4.55
Dy	1.3	4.4	440	2.2	2.9	4.24

TABLE VII

EXCESS ABSORPTION ($\alpha_{CHEM}\lambda \times 10^3$) DB AS A FUNCTION OF FREQUENCY

	f(MHz)					
$C_o \times 10^3$	5.0	15.30	25.40	35.40	56.00	66.00
		$Sm_2(SO_4)_3$ in 0.5 M $NaClO_4$				
9.31	9.30	17.93	22.32	20.23	15.70	15.20
18.53	15.68	32.34	40.83	40.08	35.03	29.60
22.05	18.26	43.57	48.31	50.84	43.97	43.94
		$Sm_2(SO_4)_3$ in 0.75 M $NaClO_4$				
10.00	12.19	13.78	17.10	17.27	12.88	11.67
12.52	12.72	21.81	24.93	23.74	19.05	17.17
15.09	12.30	28.02	32.18	31.40	24.20	23.47

TABLE VIII

RELAXATION FREQUENCIES AND CONCENTRATION DATA FOR $Sm_2(SO_4)_3$ AT CONSTANT IONIC STRENGTH

$C_o \times 10^3$	$\theta(C) \times 10^2$	$2\pi f_{III}$ (MHz)	RMS
0.5 M $NaClO_4$			
9.31	2.54	166.75	0.4799
18.53	4.12	188.43	0.5902
22.05	4.65	192.89	1.3906
0.75 M $NaClO_4$			
10.00	3.18	157.08	1.0007
12.5 2	3.75	159.65	0.5345
15.09	4.30	168.89	0.2961

TABLE IX

RATE CONSTANTS AND STEP-WISE ASSOCIATION CONSTANTS FOR $Sm_2(SO_4)_3$ AS A FUNCTION OF IONIC STRENGTH

$k_{34} \times 10^{-8}$	$k_{43} \times 10^{-7}$	K_{12}	K_{23}	K_{34}	K_c
		0.75 M $NaClO_4$			
2.5	9.9	4.0	2.6	2.6	40.
		0.50 M $NaClO_4$			
2.4	9.6	7.5	2.6	2.6	76.
		$\mu \rightarrow 0$			
3.3	6.3	436.	1.5	5.3	4400

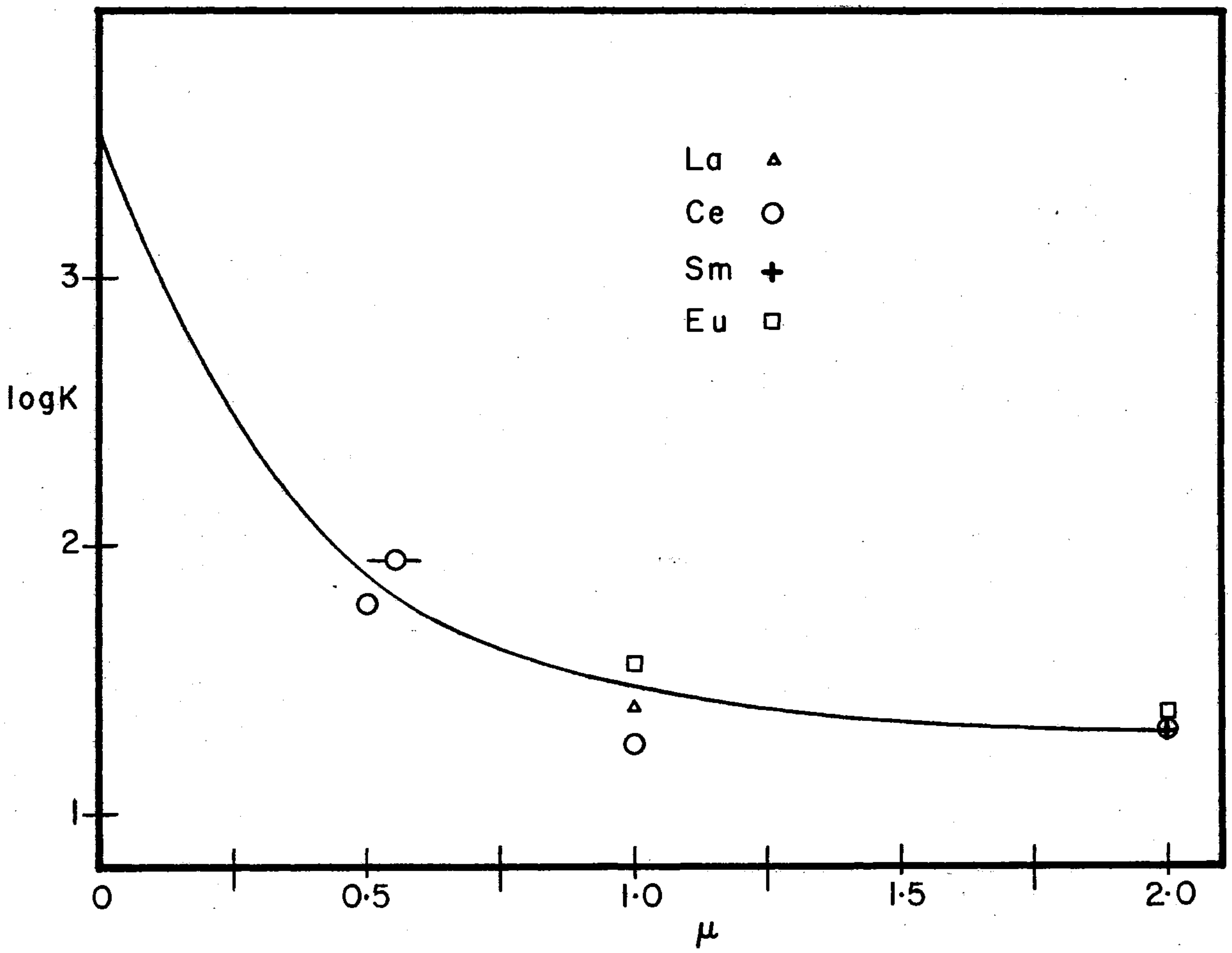

Figure 9. Variation of $K_{LnSO_4^+}$ With Ionic Strength

ship between K_{cond} and μ is not known, a monotonically decreasing function (with increasing ionic strength) was assumed and the line drawn arbitrarily. $Sm_2(SO_4)_3$ has not been studied at more than two different ionic strengths ($\mu \rightarrow 0$, and $u = 2.0$ m) so that the intermediate values are those for $Ce_2(SO_4)_3$ (53). It was assumed that no large variation in K_{cond} for the two salts would occur since no large change in K_{thermo} was seen. The values of pK_{cond} were taken directly from the graph.

K'_{12} was determined as follows:

$$K_{conditional} = K_{thermodynamic}\ \pi_f \tag{4.19}$$

and

$$K''_{12} = K_{12}\ (\mu \rightarrow 0)\ \pi_f \tag{4.20}$$

then

$$\frac{K_{cond}}{K''_{12}} = \frac{K_T \pi_f}{K_{12}\ (\mu \rightarrow 0)\ \pi_f} \tag{4.21}$$

so that

$$K''_{12} = \frac{K_{12}\ (\mu \rightarrow 0)\ K_{cond}}{K_T} \tag{4.22}$$

Table IX is the rate constant data for $Sm_2(SO_4)_3$ at constant ionic strengths of 0.5 M and 0.75 M ($NaClO_4$). Since the formation constants were calculated from potentiometric data measured in $NaClO_4$ media (53), no correction was made for $NaSO_4^-$.

CHAPTER V

DISCUSSION

The purpose of this study was to investigate the complexation reaction of the lanthanide sulfates. The presence or absence of a solvent isotope effect (SIE) in the reaction is critical to the understanding of the mechanism. The lack of a SIE would support a rate controlling dissociative step in the general Eigen mechanism. The constant ionic strength study was undertaken in an attempt to resolve the discrepancy which exists between rate constants measured by the ultrasonic technique are those determined by transient methods by conducting the acoustic studies in a high salt media. Since the error in the overall equilibrium constants determined kinetically is greater than that in conventional methods, K_T was measured by an independent, non-kinetic method for the lanthanide sulfate salts in D_2O.

All of the variations in the thermodynamic formation constants for complex formation of the lanthanide series with various ligands can be grouped in three ways (53). The first and simplest is a monotonic increase in K_T which is easily explained in terms of an electrostatic model. The remaining two groups are less regular and K_T either increases to a plateau value around Gd^{3+}, group two, or increases to a maximum at the same ion with a subsequent decrease, group three. The sulfate series of complexes in water fall into group three. The increase in K_T over the light lanthanides is shallow (Figure 10). Earlier K_T data from

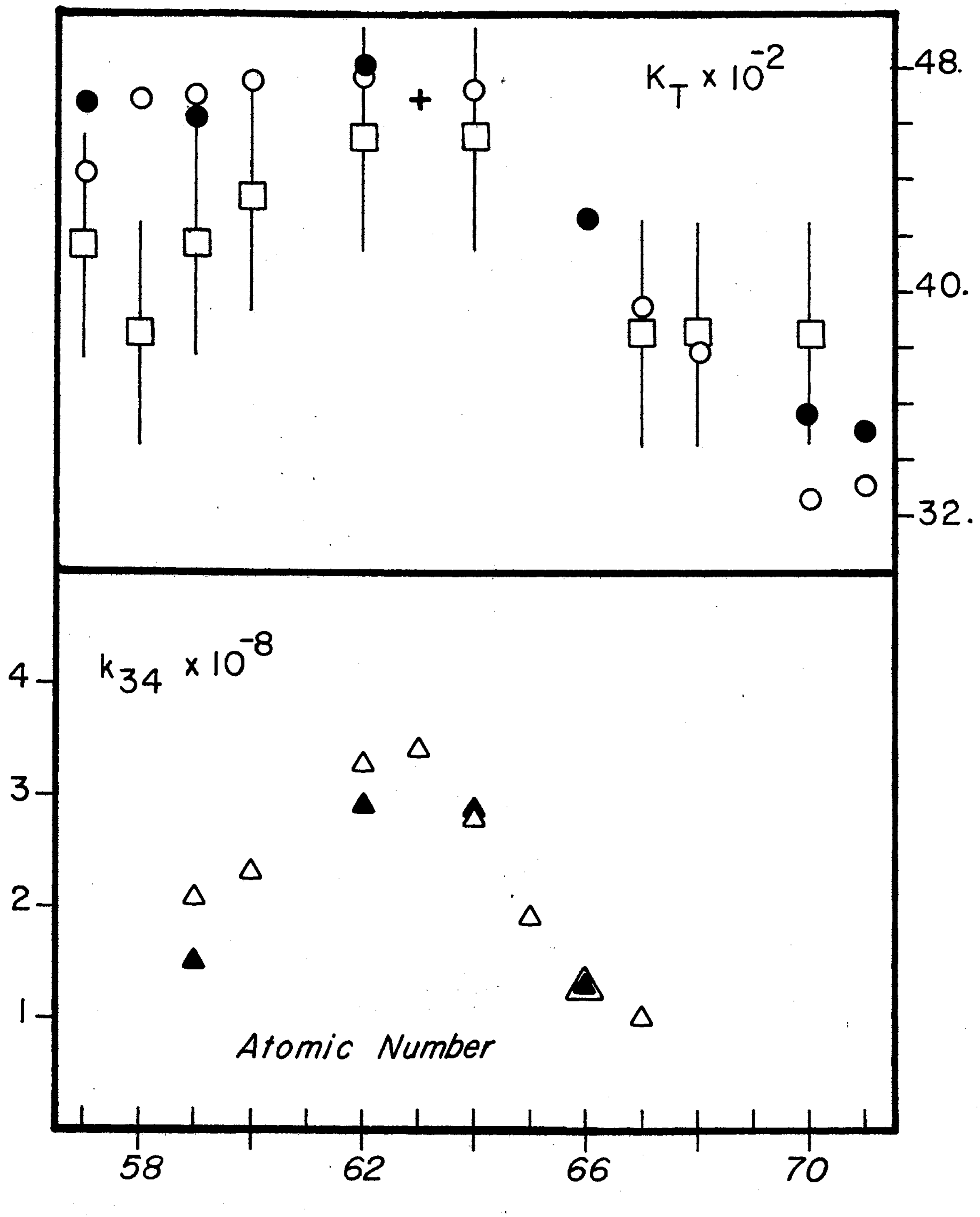

Figure 10. K_T Vs. Atomic Number for $LnSO_4^+$: O H_2O Data From Ref. 46 and This Work; □ Ref. 46; ● D_2O; + Ref. 48; k_{34} Vs. Atomic Number; Δ H_2O Recalculated From Ref. 44; ▲ D_2O

Spedding and Jaffe (46) for these members were low which exaggerated the increase in K_T. Recalculation of their data and a comparison with the present results leaves only $CeSO_4^+$ formation outside the proposed error of ± 10% from both conductance studies. This study is the first reported for any lanthanide complex in heavy water done by non-kinetic methods. The change of solvent produced no significant variation in the trend of K_T with atomic number from that observed in water. By coincidence all of the ligands for which a kinetic study has been done fall into group three.

The interpretation of this trend in thermodynamic parameters could have a significant bearing upon the mechanistic discussion. From a kinetic study of the complete series of sulfate complexes (Figure 10) the variation in k_{34} with atomic number is seen to be exactly analogous to the variation in K_T. The possibility exists however that the rate constant variation is not due to the same reason suggested by thermodynamists but is indicative of a change in mechanism between the light and heavy members of the series.

In order to explain the departure of K_T from the purely electrostatic dependence on atomic number, several factors have been considered. Among these are ligand field stabilization effects (LFSE), steric effects, changes in the coordination number of the cation, changes in the degree of hydrogen bonding in the first hydration sphere of the cation, and differences in the coordinating ability of the ligands. LFSE are an unlikely possibility since the enthalpy of complex formation show both stabilization and destabilization relative to those for La^{3+}, Gd^{3+}, and Lu^{3+} (first, middle, and last members of the series) for which ligand field stabilization effects would be zero (54), (but see also (25)).

Steric and ligand coordinating abilities can probably also be dismissed as relatively unimportant since the irregularity always occurs around Gd^{3+} and the change is never abrupt. The remaining effects of importance are the change in the degree of hydrogen bonding and the coordination number change across the series.

If the degree of hydrogen bonding is involved, then an isotope effect should be noticed in the formation constants in D_2O as the strength of the deuterium bond differs from the strength of the hdyrogen bond by about 0.3 kcal/mole (55). In both previous studies of the lanthanide ion association reaction in D_2O (34,35), such an isotope effect was found in K_T. However, the formation constant was not determined independently but was used as a fitting parameter in the kinetic analysis. The results of this current study do not support the previous result in that, within experimental error, the formation constants of the lanthanide sulfates in D_2O were the same as those in H_2O. From this analysis it would appear that the only reasonable explanation of the variation in K_T of the second and third types is that of the coordination number change and this is the most generally accepted thermodynamic interpretation.

Although the error in the determination of K_T is probably within the limits set by Spedding and Jaffe (46), there were some approximations made which should be explained. Since the limiting conductance of the complex ion, $LnSO_4^+$, is not accessible to experimental measurement, and since in this study they were actually used as a fitting parameter, the true value will be distorted by the calculational procedure and the error may be propagated to K_T. Also excluded was higher complex formation, e.g., $Ln(SO_4)_2^-$. Although the formation of further complexes is a possibility, the concentration range used in this study was thought to be low enough that only a very limited error in the formation constant is introduced by this approximation.

No attempt should be made to generalize the lack of a SIE found in this study and infer that all complex formation reactions are without a possible SIE. Indeed there in fact may be a small secondary isotope effect in sulfate complexation that is undetectable over the error. If the complexation reaction involves a weak acid such as N_3^-, $C_2O_4^{2-}$, or others (35), the isotope effect on the ionization of the acid may effect the formation constant of any complex formed. The only generalization that should be applied to the results of this study is that HSO_4^- and cation hydrolysis do not complicate the reaction as either of these would involve a primary isotope effect and thus would cause a significant change in the formation constant.

The result of the present kinetic study also show no SIE. In the two previous studies (30,34) where a kinetic isotope effect was found (in addition to an isotope effect in the thermodynamic formation constant) the results were interpreted to be caused by a mechanistic change. However, in the anthranilate study (30), the possibility of a SIE for the reaction of the indicator used to follow the reaction in the T-jump experiment was not discussed, nor was the effect of the possible complex formation of the metal with the indicator (methyl red). Since both of these reactions involve the breaking of a hydrogen (deuterium) bond, the possibility of a large primary isotope effect is high. This SIE for the indicator would definitely effect the results of the kinetic analysis because the reaction cannot be followed directly and so is coupled to an indicator ionization

$$HIn \rightleftarrows In^- + H^+$$

and the variation of the optical density of the solution that is followed spectrophotometrically is not that contributed by the reaction products, but that of the indicator ionization. In the second study (34), the formation constant for $NdSO_4^+$ was not determined by independent, non-kinetic means and is probably grossly unreliable and that unreliability transmitted to the rate constants. There is no experimental justification at this time to argue in favor of a change from a dissociative (D) mechanism. However, the absence of a SIE on k_{34}, coupled the constancy observed between k_{34} and k_{ex} and $\Delta H_{34}^{\ddagger}$ and $\Delta H_{ex}^{\ddagger}$ (33) there is good reason to believe that the mechanism in D for all ions of the series.

It has been noted that the variation of k_f with atomic number through the lanthanide series is similar to the variation of k_{34} for the same ions, at least with some ligands (8). It would be interesting to compare the rate constants determined acoustically with those from T-jump experiments. Unfortunately the solution conditions are such that a comparison cannot be made directly. For this reason the study of samarium sulfate was undertaken at constant ionic strength in this work.

The results from the constant ionic strength study indicate a small decrease in k_{34} as well as a somewhat larger increase in k_{43}. From theory one would expect the rate constant for the forward reaction to decrease as the ionic strength increases in accordance with the Bronsted-Debye-Hückel equations (56) and conversely, the reverse rate to increase with increasing ionic strength.

Unfortunately, assuming the validity of the Eigen dissociative mechanism, these results do not resolve the discrepancy in the calculated rate constants and rate constants measured by differing techniques. For a comparison between the measured k_f by transient methods and the calculated k_f from acoustics the lack of agreement is unequivocal: for samarium with murexide, $k_f = 9.6 \times 10^7$ (57), with anthranilate $k_f = 6.3 \times 10^7$ (30), and with oxalate $k_f = 8.2 \times 10^7$ (32) (all with the units M^{-1} sec^{-1}). If Equation (2.18) is applied to the ultrasonically measured rates, assuming $k_{32} = k_{34}$

$$k_f = \frac{K''_{12}K_{23}k_{34}}{2}$$

then the calculated k_f for samarium sulfate (using data from Table IX) is 1.3×10^9, 2.3×10^9, and 1.1×10^{10} (all M^{-1} sec^{-1}) at $u = 0.75$, 0.5, and $\to 0$ respectively. These values should agree to within experimental error if the same mechanism applies to all ligands since a) K''_{12} is calculated from Bjerrum's equation and should be the same at least for sulfate and oxalate; b) K_{23} should not change over two orders of magnitude as the interaction is primarily electrostatic in origin and between similar charge types the variation should be small; c) from the D mechanism, k_{34} is thought to be characteristic of the metal and equal to the water exchange rate, k_{ex}.

The discrepancy might be resolved if the mechanistic assignment is different for some ligand types. All of the ligands whose reaction rates are slow enough to be studied by T-jump also show the probability of polydentate binding to the metal. If a four step chelation mechanism is postulated with the slow step being ring-closure, the discrepancy between measured rates and calculated rates could be resolved.

The rates fail to compare because $K''_{12}K_{23}/2 > 1$. If this term was less than one then k_f would be greater than or equal to k_{34}. Assuming a chelation mechanism with k_{45} rate controlling, then

$$k_f = \frac{K''_{12}K_{23}K_{34}k_{45}}{2} \quad \text{and } k_b = k_{54}$$

There should now be a correspondence between k_f and k_{45}. If $K''_{12}K_{23}K_{34}/2$ is also greater than one, then k_{45} is very small which would indicate that the relaxation frequency of this fourth step is almost at the lower limit of the pulse sound absorption method. So far no "probable" chelating ligands have been studied acoustically and the order of magnitude for k_{45} is unavailable.

Conclusions and Suggestions for Further Work

Although the present work supports the D mechanism, it in no way proves the correctness of the mechanism unequivocally. The results of the constant ionic strength study indicate the differences between pressure and temperature jump analysis and ultrasonic absorption analysis are not due to a dependence of the rate controlling step on the ionic strength of the medium. The only possible cause of the variation in the measured k_f from P- and T-jump method and the k_f calculated from ultrasonic measurements is that the reactions slow enough to observe by the slower methods are not proceeding by the same mechanism as are the faster (ultrasonic) reactions. This different mechanism might involve a fourth step in which the ligand chelates the cation. In order to study the slower reactions, the ultrasonic method must be improved in accuracy at the lower frequencies and the low frequency absorption spectra measured. If a relaxation is detected the controversy might be resolved and the Eigen mechanism would receive more support. In addition, if the high frequency ultrasonic absorption (up to the Ghz range) could be obtained with sufficient accuracy to assign a relaxation frequency (or frequencies) to the first and/or the second step, the dissociative Eigen mechanism could be confirmed.

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VITA

Michael Marion Farrow

Candidate for the Degree of

Doctor of Philosophy

Thesis: KINETICS AND THERMODYNAMICS OF LANTHANIDE SULFATE ASSOCIATION IN DEUTERIUM OXIDE

Major Field: Chemistry

Biographical:

Personal Data: The author was born in Boulder, Colorado, June 17, 1943, the son of Mason L. and Elizabeth C. Farrow.

Education: The author attended Sacred Heart School in Boulder and Regis High School in Denver before graduating from Boulder High School in June, 1961. He attended Mesa Jr. College in Grand Junction, Colorado, from 1961 to 1963 and the University of Colorado in Boulder, Colorado, from 1963 to 1966. From 1967 to 1969 he attended Western State College of Colorado in Gunnison, Colorado, and obtained a Bachelor of Arts degree in Chemistry and Physics in May, 1969. He entered the graduate college of Oklahoma State University in September, 1969, and completed the requirements for the Doctor of Philosophy degree in May, 1973.

Professional Experience: The author has served in the following capacities: Laboratory instructor, Western State College, 1968-1969; NDEA Graduate Research Fellow, Oklahoma State University, 1969-1972; Graduate Teaching Assistant in Chemistry Department, 1969-1973.

Professional Societies: The author is a member of the American Chemical Society and Phi Lambda Epsilon, National Honorary Chemical Society.