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THE APPLICATION OF ULTRASOUND ABSORPTION TO REACTION KINETICS

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CONTENTS

A. INTRODUCTION

The realm of relaxation techniques and their application to solution reaction kinetics is a relatively recent development[1,2] although progress has been explosive since their initial introduction. Historically one would place the methods applied to the study of solutions and solution properties prior to the middle 1950's in the category of vintage or classical techniques. For clarity, studies of the thermodynamic and mass transport properties of dissolved solutes would be included among those methods[3]. Our definition should not be considered vindictive since many very able scientists continue to apply these methods and the breadth of study continues to expand even if only slowly. The current emphasis is on more precision and the accumulation of new data, and in particular we would compliment those involved in the measurement of ΔC_p^0 data. These data contain additional information on solute–solvent interactions over and above the information gleaned from other thermodynamic parameters.

Anyone involved in relaxation methods is probably prejudiced by the exciting prospects this new area has to offer, but it will become increasingly apparent, on further exposure, how heavily the interpretation of kinetic results leans upon equilibrium data. As a consequence the two approaches to the same challenging problem will always be complementary.

At the time the relaxation methods were conceived the development of classical experiments and theories of solutions had reached an impasse. The apex of the theoretical development was reached with the Debye–Hückel theory of interionic attraction[3] and the empirical extensions to it[4]. Based solely upon electrostatics and the model of the solvent as a continuous dielectric, 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. These differences in equilibrium behavior were rationalized to some degree as data on the heat and entropy changes which contribute to the free energy of the equilibrium reaction were accumulated[4]. This represents the state of the art of classical methods then and indeed even now.

The advent of relaxation methods provided a new dimension to equilibrium studies in that, as the resolution of the time scale of the experiment was improved, the analysis of the progress of the reaction toward equilibrium became a tangible experiment. The proposed mechanism[5] for the convergence of ions to contact distances in solution primarily encompasses diffusion but more importantly at shorter separation distances it brings into focus the regions of ionic solvation where, due to ionic electrostriction, the solvent can no longer be thought of as a continuum. Regions of concentric potential wells enveloping the central ion, and whose minima correspond with the formation of a number of stable ion-pairs, punctuate the monotonic increase in coulombic energy of attraction expected from the continuum model. These ion-pairs are in a steady state kinetically, and thermodynamically all structural forms contribute to the complete energy picture.

As a result the conventional way of representing equilibria and equilibrium constants is no longer adequate and in terms of the mechanism a more exact representation is to write the equilibria as

$$M^{n+} + L^{y-} \rightleftharpoons \sum_{i=0}^{i} (MS_iL)^{(n-y)+} \qquad (1)$$

where S_i are solvent molecules, in all probability located between the metal M and the ligand L, and the overall equilibrium constants as

$$K_c = \frac{\left[\sum_{i=0}^{i} (\mathrm{MS}_i\mathrm{L})^{(n-y)+}\right]}{[\mathrm{M}^{n+}][\mathrm{L}^{y-}]} \qquad (2)$$

respectively. From a complete kinetic analysis the quantitative concentration distribution of species $(\mathrm{MS}_i\mathrm{L})^{(n-y)+}$ can conceivably be calculated. With this information in our possession we have learned considerably more about ion solvation and the competitive reaction which is complex formation, as well as the structural nature of the predominant species. Variations in overall equilibrium constants for reactions involving ions of the same charge types may then be reconciled, at least in some instances, simply by differences in ion-pair distributions.

These few ideas or objectives form the foundation from which we will describe the application of sound absorption as a kinetic tool. Other relaxation methods[1,2] are not discussed but the quality and the merits of the sound absorption results must bear comparison with results from these other methods. Examples chosen to illustrate the potential of the method are almost exclusively metal complexation reactions since they represent the area of greatest activity. A number of excellent reviews[6,7], chapters[1,2,8,9] and articles[10–12] have covered the theories behind the physically induced disturbance of a chemical equilibrium and its delayed relaxation to the final conditions. For completeness the theory behind the sound absorption perturbation method is dealt with briefly, and the reader is referred to these more extensive reviews for corroborative details.

B. GENERAL PRINCIPLES OF RELAXATION METHODS

(i) Introduction

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 reaction lags behind[1,2]. In the ultrasonic technique the parameter (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 magnitude of these rates determine the applicability of a particular relaxation technique and frequently more than one technique is required for a complete analysis. Unlike flash photolysis[2] the disturbance is small and is a compromise between a displacement which is large enough to be observed and recorded yet small enough that the mathematics can be reduced to linear equations.

(ii) Relaxation time

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

$$-\frac{dx}{dt} = k_{\text{eff}}\, x \tag{3}$$

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 equilibrium is re-established.

On integration eqn. (3) gives

$$\frac{x}{x_0} = e^{-k_{\text{eff}}\, t} \tag{4}$$

where x_0 is the magnitude of the instantaneous displacement. When $k_{\text{eff}}t = 1$, x becomes equal to x_0/e and the time taken to reach this equality is defined as the relaxation time, τ. Once the relaxation time can be measured, the effective rate constant is given by

$$k_{\text{eff}} = \tau^{-1}\ (\text{sec}^{-1}) \tag{5}$$

The analytical form of k_{eff} contains contributions from the forward and backward rate constants and depends upon the molecularity of both steps. Examples[1] are given in Table 1. The implication that the reactions proceed in a single step is inherent to these examples. k_{eff} increases in complexity if either (*a*) the overall reaction is multistep (Sect. C), or (*b*) the reaction involves ions whose concentrations contribute substantially to the ionic strength of the electrolyte solution.

It remains now to show the relationship between τ and the frequency of the periodic perturbation of the chemical equilibrium brought about by the progressive sound wave. It is apparent from eqn. (5) that for a displacement to occur τ^{-1} and the frequency of oscillation must be comparable in magnitude.

(iii) Relaxation time–sound absorption equations

The time scale of the ultrasonic instrumentation is wide, 10^{-4}–10^{-10} sec, but several techniques are necessary to embrace the entire range: resonance (0.1–50 kHz); interferometry or reverberation (50 kHz–2 MHz); optical method (Debye–Sears) (1–100 MHz); pulse method (5–500 MHz), recently extended with a special technique[13] to 2000 MHz; and Brillouin scattering[14] (~ 10^{10}–10^{11} Hz). All but the last two are thoroughly described in ref. 1. Rarely are all techniques available to one investigator, which leads to the usual frustrations in collating available experimental data for a complete interpretation of a multistep mechanism for which the characteristic relaxation times are widely separated. A more serious limitation to the method frequently is the identification of the equilibrium responding to the perturbation. Most assignments are made after a carefully planned process of elimination.

The attenuation of a sound wave passing through a fluid, whatever the mechanism of absorption, in terms of the amplitude level[6] is related exponentially to the distance travelled, d, by

$$P = P_0 e^{-\alpha d} \tag{6}$$

TABLE 1

Expanded forms of effective rate constants k_{eff}

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

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

where P_0 is the initial amplitude and P the amplitude at distance d (cm). Here α, in neper/cm, is the absorption coefficient, and is the experimentally measured quantity from which relaxation times are eventually determined. A somewhat elementary derivation of the relationship between α and τ follows.

Equation (3) 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 independent of time. If the perturbation is sinusoidal in nature then the equilibrium value will vary in phase with it (curve (b), Fig. 1) around the mean value ((a), Fig. 1). Call this variation $\bar{y}$

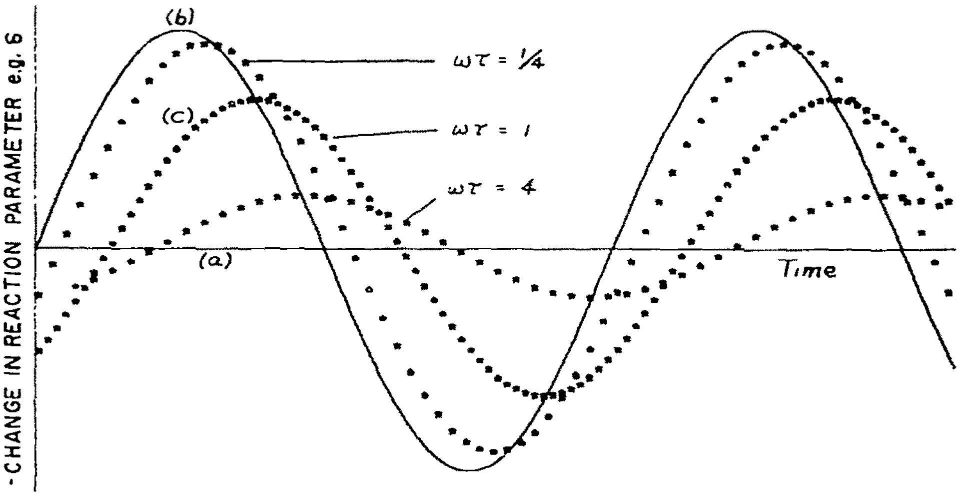

Fig. 1. Periodic disturbance of chemical equilibrium by external parameter; (a) τ much longer than period of oscillation (zero displacement); (b) τ much shorter than period of oscillation (in-phase displacement); (c) broken lines – τ comparable to period of oscillation (energy dissipation).

and let it be equal to $(\bar{x}-x_e)$, where $\bar{x}$ is the equilibrium value at time t. Similarly if the variation with perturbation of the actual concentration difference $(x-x_e)$ is defined as y then the revised form of eqn. (3) can be shown to be[2]

$$\tau \frac{dy}{dt} + y = \bar{y} \tag{7}$$

Suppose the ultrasonic frequency f is $\omega/2\pi$ and the amplitude of the wave is p, then the oscillatory variation in $\bar{y}$ is given by $\bar{y} = p \sin \omega t$. On substitution into eqn. (7) this gives the response to sinusoidal perturbation as

$$\tau \frac{dy}{dt} + y = p \sin \omega t \tag{8}$$

The solution to this differential equation in the steady state is

$$y = \left(\frac{1}{1+\omega^2\tau^2}\right) p \sin \omega t - \left(\frac{\omega\tau}{1+\omega^2\tau^2}\right) p \cos \omega t \tag{9}$$

Graphical representations of this equation are shown as broken lines in Fig. 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 out-of-phase second term, so the dissipation of energy is proportional to $\{\omega\tau/(1+\omega^2\tau^2)\}$. This expression has a maximum value of $\frac{1}{2}$ when $\omega\tau = 1$, which locates the characteristic or relaxation frequency ($\omega_R = 2\pi f_R$) when the plot of absorption versus frequency is a maximum. The relaxation time is therefore given by $\tau^{-1} = 2\pi f_R$. Curves (a) and (b) in Fig. 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

$$(\alpha_{chem}\lambda) = 2(\alpha_{chem}\lambda)_R \left\{\frac{\omega\tau}{1+\omega^2\tau^2}\right\} \tag{10}$$

where $(\alpha_{chem}\lambda)_R$ is the maximum chemical absorption per wavelength at $\omega\tau = 1$. Using this last equality, eqn. (10) can be revised to read

$$(\alpha_{chem}\lambda) = 2(\alpha_{chem}\lambda)_R \left\{\frac{f/f_R}{1+(f/f_R)^2}\right\} \tag{11}$$

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

$$\frac{\alpha_T}{f^2} = \frac{A}{\{1 + (f/f_R)^2\}} + B \tag{12}$$

where $A = 2(\alpha_{\text{chem}}\lambda)_R/cf_R$ and c is the velocity of sound, usually considered to be the same in solution and pure solvent. B is a constant term which includes solvent absorption and contributions from chemical 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 absorptions by the solvent and by chemical relaxations. The graphical representations of eqns. (11) and (12) versus frequency for single relaxations are given in Fig. 2. f_R corresponds to the frequency of the maximum in curve (a), eqn. (11) and with the frequency of maximum inflection, curve (b), eqn. (12).

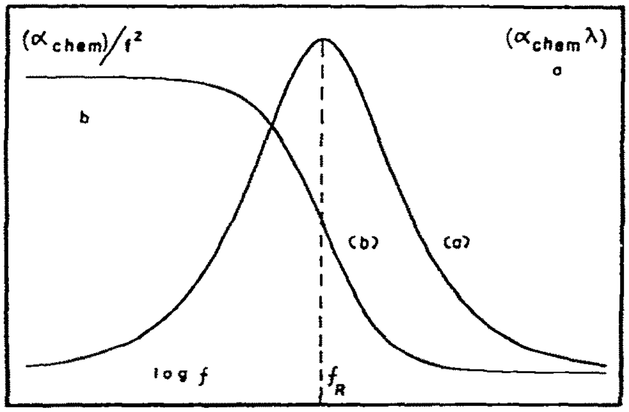

Fig. 2. Graphical representations of experimental single relaxation curves described by (a) eqn. (11) and (b) eqn. (12).

From the term in braces in eqn. (11) it can be shown that a single chemical relaxation extends over one decade in the frequency range. For example, if f_R = 5 MHz, then $(\alpha_{\text{chem}}\lambda)$ has the same value at 0.5 MHz and at 50 MHz. As a result the resolution of f_R is relatively poor. Plots of $(\alpha_{\text{chem}}\lambda)$ versus frequency must also be made as log–log plots to preserve the symmetry of the curves (Fig. 2).

Multiple chemical 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,

$$(\alpha_{\text{chem}}\lambda) = \sum_{i=1}^{i} \left[\frac{2(\alpha_{\text{chem}}\lambda)_{R,i}\,(f/f_{R,i})}{\{1 + (f/f_{R,i})^2\}}\right] \tag{13}$$

or

$$\frac{\alpha_T}{f^2} = \sum_{i=1}^{i} \left[\frac{A_i}{\{1 + (f/f_{R,i})^2\}} \right] + B \tag{14}$$

The experimental error in α_T and the uncertainty about how many single relaxations are present compounds the problem of fitting the experimental data to an equation which has $2i$ or $(2i + 1)$ parameters, eqns. (13) and (14) respectively. We will return to this problem later in the discussion of high-frequency, ~ 10^9 Hz, data (Sect. D).

If in a multiple-step equilibrium reaction, e.g. metal complex formation, the relaxation times are distinct, i.e. $\tau_i \geqslant 2\tau_{i+1}$, and the number of relaxation frequencies is equal to the number of steps, then the rate constants, forward and back, for each step i are directly related to the $f_{R,i}$ according to eqn. (5). Frequently, however, the number of relaxation times observed is less than the proposed number of steps. (Remember the mechanism is proposed before the analysis is attempted.) Accordingly the direct relationship between stepwise rate constants and $f_{R,i}$ breaks down and the mathematical analysis becomes so much more complex as to be intractable[8] unless justifiable simplifying assumptions are made. This subject is returned to at length in Sect. C, dealing with reaction mechanisms (p. 200). It is perhaps becoming clear that the interpretation of acoustic data in terms of rate constants and reaction mechanisms is complex even to the point of being subjective.

(iv) Absorption amplitude

Besides the kinetic data which can be derived from the dependence of relaxation frequencies on concentration (see expressions for k_{eff} in Table 1), the magnitude of $(\alpha_{\text{chem}}\lambda)$ can be interpreted in terms of the thermodynamic properties of the equilibrium perturbed.

Sound waves are propagated adiabatically, giving rise to small periodic fluctuations of temperature and pressure in the fluid. In an unstructured solvent, energy is dissipated only by the shearing motion of the compressional wave and through thermal conduction by the solvent. The loss in energy is described by eqn. (6). These mechanisms of energy dissipation are described as classical and give rise to the classical absorption coefficient α_{CL}, which can be calculated theoretically[15] using the Stokes–Navier equations. Solute or solvent equilibria which are sensitive to temperature and pressure and whose relaxation times are comparable with the periodic time will be perturbed and will lag behind the ultrasonic vibrations, absorbing energy in the process. In water the experimentally measured absorption coefficient α_S is approximately three times the theoretical value α_{CL} and the difference is attributed to a structural relaxation[16] characterized by a very high f_R. Attenuation caused by displacement of a solute equilibrium reaction with f_R in the proper frequency range will be in excess of that due to the solvent and is given by $\alpha_{\text{chem}} = (\alpha_T - \alpha_S)$. At frequencies below f_R for this particular solute equilibrium relaxation, energy will be dissipated in order to perturb it and all faster relaxations, whereas at frequencies above f_R only the faster equilibria will be affected. Coupling between successive relaxations is an ever-present possibility.

(v) Thermodynamics of sound absorption: the magnitude of $(\alpha_{chem}\lambda)_R$

Factors which affect the magnitude of $(\alpha_{\mathrm{chem}}\lambda)_\mathrm{R}$ are the nature of the solvent, the temperature, and for a solute equilibrium the mole fractions of the species participating. In the full mathematical analysis it is further shown[15] that $(\alpha_{\mathrm{chem}}\lambda)_\mathrm{R}$ depends upon the relaxational contribution to the adiabatic compressibility β so that

$$2(\alpha_{\mathrm{chem}}\lambda)_\mathrm{R} = \pi\frac{\Delta\beta}{\beta_0} \tag{15}$$

where $\Delta\beta$ is the difference between the adiabatic compressibilities at zero frequency β_0 and infinite frequency β_∞. $\Delta\beta/\beta_0$ is frequently referred to as the relaxation strength[15] which on further expansion is given by

$$\frac{\Delta\beta}{\beta_0} = \frac{(\gamma_0-1)}{C_{\mathrm{p}\infty}}\left[1-\frac{\Delta V^0\,C_{\mathrm{p}0}}{\Delta H^0\,V\theta_0}\right]^2\Delta' C_\mathrm{p} \tag{16}$$

where γ_0 is the ratio of specific heats at zero frequency, $C_{\mathrm{p}0}$ and $C_{\mathrm{p}\infty}$ are the heat capacities at zero and infinite frequencies respectively and $\Delta' C_\mathrm{p}$ their difference, and ΔV^0 and ΔH^0 are volume and enthalpy changes in the reaction. θ_0 is the coefficient of thermal expansion at zero frequency. In water, where there is no appreciable temperature effect ($\theta_0 \simeq 0$), eqn. (16) reduces to

$$\frac{\Delta\beta}{\beta_0} = \frac{T}{V}\left(\frac{\Delta V^0}{\Delta H^0}\right)^2\Delta' C_\mathrm{p} \tag{17}$$

from which it will be seen that $(\alpha_{\mathrm{chem}}\lambda)_\mathrm{R}$ provides the information necessary to calculate the volume change of the reaction, but not necessarily the sign of the volume change since it appears to the second power in the equation. Not apparent in eqn. (17) is the dependence of $(\alpha_{\mathrm{chem}}\lambda)_\mathrm{R}$ on the mole fraction distribution of reactants and products. On further expansion this can be shown[8] to be given by the general expression

$$\frac{\Delta\beta}{\beta_0} = \frac{(\Delta V^0)^2}{\beta_0 RT}K_\mathrm{c}\frac{\partial\theta}{\partial K_\mathrm{c}} \tag{18}$$

where θ is the extent of the reaction and K_c is the overall equilibrium constant. The solution of $K_\mathrm{c}(\partial\theta/\partial K_\mathrm{c})$ then depends upon the particular reaction under investigation.

In summary, the ultrasonic absorption relaxation technique offers two useful pieces of information: (*a*) the kinetics of the reaction, although it must be emphasized that the mechanism must first be assumed, and (*b*) the volume change associated with the particular equilibrium reaction perturbed. This last is particularly true when water is the solvent. In non-aqueous solvents where the condition of an approximately zero coefficient of thermal expansion is not strictly adhered to, ΔV^0 is more difficult to obtain[15].

C. MECHANISMS OF COMPLEX FORMATION

(i) Introduction

Since the original application of ultrasound absorption as a kinetic tool was the interpretation of the excess sound absorption in seawater as being due to the equilibrium reaction in which the $MgSO_4$ ion pair is formed[17–19], it is not surprising that the principal emphasis since then has remained in the area of the kinetics of complex formation.

The vast majority of rate studies of this type of reaction have been carried out in water[20]. In the process of complexation one or more water molecules is replaced by a ligand in what is effectively a competitive substitution reaction. If contact is made between metal and ligand these water molecules will have originated from the first coordination sphere of the metal ion[21]. Residence times of water molecules in the first coordination sphere, expressable as the inverse of the pseudo-first-order rate constant for water exchange[22] from the bulk solvent, k_{ex}, are significant in describing the lability of the ion to ligand substitution[23]. The residence times depend upon the identity of the cation and are known to vary over several orders of magnitude[24]. Where residence times are relatively long, $\geqslant$ 1 sec, reactions with ligands are amenable to study by the more classical kinetic methods (including flow techniques) in which mixing times are short compared to the half-life of the reaction[2]. Currently accepted kinetic mechanisms for complex formation, for the most part, have evolved from the very extensive classical studies[20]. An important point to remember is that although relaxation methods have made the study of faster reactions a reality, the basic mechanisms, if sound, should apply to all reactions regardless of the rate. With this in mind it is instructive to review these prescribed mechanisms before introducing the ramifications which result from the newer experimental data.

(ii) General mechanism

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

$$M + L \underset{k_b}{\overset{k_f}{\rightleftharpoons}} ML \qquad (19)$$

(no attempt is made at this point to distinguish between a unidentate and chelating ligand). In the absence of competing equilibria (e.g. hydrolysis etc.) the observed rate law[20] for the formation of ML is

$$d[ML]/dt = k_f[M][L] - k_b[ML] \qquad (20)$$

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 performed by varying M and L, from activation energies and from non-kinetic considerations[20], three types of mechanisms are described which are equally compatible with the rate law[24,25]: (1) dissociative, D; (2) associative, A; and (3) interchange, I. The last has tendencies toward either dissociative interchange I_d (non-limiting D) or associative interchange I_a (non-limiting A).

Without resorting to specific illustrations, for which the reader is referred to more exhaustive treatises[20,23,24], the mechanistic labels are descriptive of the fundamental differences in the structures of the activated complexes. 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 (Sect. D) and k_{ex} measured independently[22], e.g. 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[26], is that a linear relationship between the free energy of activation $\Delta G^{\ddagger}$ and ΔG^0 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[27]. The interchange mechanism is a concerted exchange between water in the first coordination sphere and ligand in the second coordination sphere[24]. 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[20,28].

The one distinctive feature of the ultrasound absorption technique which sets it apart from almost all other kinetic techniques is that the overall effective forward rate constant, k_f, is not measured experimentally. After considerable deliberation the multi-relaxations observed acoustically were correlated with a multistep complex formation mechanism[5] attributed to Diebler and Eigen (DE). A three-step mechanism was postulated to account for the relaxation spectra and three distinct relaxations have since been sought[29–31]. For reasons given in Sect. B, a one-to-one correlation is not mandatory. Numerous workers since DE have satisfactorily treated the data in terms of a two-step mechanism[32–34]. 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[2,8,35]; (*b*) desolvation of the anion to form an outer ion-pair, and (*c*) desolvation of the cation to form a contact ion-pair in order of decreasing relaxation frequencies according to

$$\text{(I)}\quad \mathrm{M(aq)} + \mathrm{L(aq)} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{MW_M W_L L} \tag{21a}$$

$$\text{(II)}\quad \mathrm{MW_M W_L L} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \mathrm{MW_M L} + \mathrm{W_L} \tag{21b}$$

$$\text{(III)} \quad \mathrm{MW_M L} \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} \mathrm{ML} + \mathrm{W_M} \tag{21c}$$

The discussion of diffusion-controlled reactions is not one of the principal objectives of this review. Excellent descriptions can be found in a number of articles[2,8,35] and the reader is referred to these for information.

In Sect. E the kinetic equations in terms of relaxation times are specifically described and critically evaluated for the lanthanide series of complexes. We propose now to show the connection between the rate constants in this mechanism and k_f in eqn. (20).

(iii) Correlation between overall and stepwise mechanisms

First of all the equilibrium constant for the reaction given in eqn. (20) is $K_c = k_f/k_b$. In eqn. (21) the ions are in equilibrium with all three structural ion-pairs of eqn. (2)

$$K_c = \frac{\{[\mathrm{MW_M W_L L}] + [\mathrm{MW_M L}] + [\mathrm{ML}]\}}{[\mathrm{M}]\,[\mathrm{L}]} \tag{22}$$

By introducing stepwise equilibrium constants $K'_{12} = k'_{12}/k_{21}$, etc., K_c can be shown to be given by $K_c = K'_{12}(1 + K_{23} + K_{23}K_{34})$, where the prime indicates an activity coefficient dependence on K_{12}. A complete steady-state analysis of eqn. (21) has been described by Petrucci and co-workers[36] for a two-step mechanism. This is readily extended to the three-step mechanism and the resultant rate law for the formation of ML is

$$\frac{\mathrm{d[ML]}}{\mathrm{d}t} = \frac{K'_{12}k_{23}k_{34}}{k_{32}+k_{34}}\,[\mathrm{M}]\,[\mathrm{L}] - \frac{k_{43}k_{32}}{k_{32}+k_{34}}\,[\mathrm{ML}] \tag{23}$$

if the assumption that $k_{21} \gg k_{23}$ made in the two-step treatment is retained[36]. Comparing eqn. (20) with eqn. (23) it is seen that

$$k_f = \frac{K'_{12}k_{23}k_{34}}{k_{32}+k_{34}} \quad \text{and} \quad k_b = \frac{k_{43}k_{32}}{k_{32}+k_{34}} \tag{24}$$

Under the circumstances that $k_{32} \gg k_{34}$, $k_f = K'_{12}K_{23}k_{34}$ and $k_b = k_{43}$. If the reverse holds then $k_f = K'_{12}k_{23}$ and $k_b = K_{34}k_{32}$.

Overall forward rate constants from techniques other than acoustics are frequently written as $k_f = K_0 k_{34}$, where K_0 is the constant for a rapid pre-equilibrium step, which, if it can be calculated, allows a comparison between k_{34} and k_{ex} for the purpose of mechanistic assignment. Herein lies a serious problem in that K_0 or indeed $K'_{12}K_{23}$ cannot be calculated with confidence. Usually resort is made to theoretical equations[37,38] to establish an order of magnitude value (for a comparative critique of the theories see ref. 36). It is the hope of those involved in acoustic measurements that higher-frequency techniques will eventually permit the experimental determination of K'_{12} and K_{23} from observed relaxation frequencies.

It will be pointed out in a later section (Sect. E) that the assumptions made about the relative magnitudes of competitive rate constants in arriving at the final equations for k_f and k_b are also contestable[36]. This further complicates bringing the complete interpretation to a satisfactory conclusion.

We will have occasion later to call upon a four-step mechanism of which the last step involves ring closure by a chelating ligand[39,40]. The appropriate equations for k_f and k_b, which contain the prior assumptions that $k_{21} \gg k_{23}$ and $k_{32} \gg k_{34}$, become

$$k_f = \frac{K'_{12}K_{23}k_{34}k_{45}}{k_{43}+k_{45}} \quad \text{and} \quad k_b = \frac{k_{43}k_{54}}{k_{43}+k_{45}} \tag{25}$$

which reduce to $k_f = K'_{12}K_{23}K_{34}k_{45}$ and $k_b = k_{54}$, if $k_{43} \gg k_{45}$. Prior restrictions on the validity of pre-equilibrium constants and comparative magnitudes of rate constants still hold.

This section has been written at some length to allow us easy reference when the results from acoustic studies of the lanthanide complexes are critically compared with results from other relaxation methods (Sect. E).

D. APPLICATIONS OF SOUND ABSORPTION TO SOLUTION KINETICS

This section is devoted to a general review of those systems already examined by sound absorption methods. The following section deals specifically with the rare-earth series of trivalent ions. Figure 3 summarizes the frequency ranges, the experimental technique, and the metal ions which form complexes with relaxation frequencies, within the limits of each range and technique.

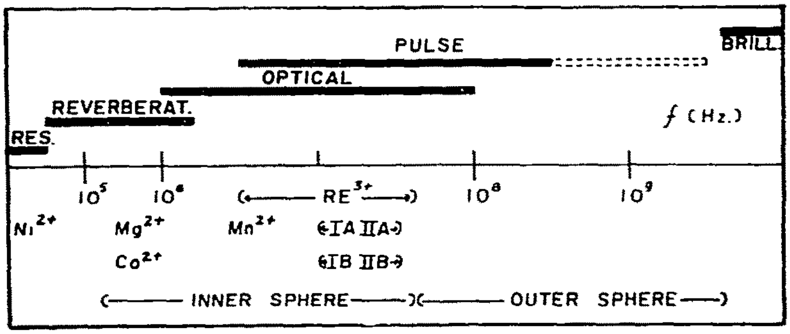

Fig. 3. Experimental frequency ranges of acoustic methods and the ions amenable to study within each range.

(i) Classification of ions

Metal ions have been classified into groups (Table 2) according to how rapidly their complexes are formed, expressed in terms of first-order substitution rate constants[41].

TABLE 2

Classification of metal ions according to rates of substitution

	First-order rate constant (sec^{-1})	Metal ions
Class I	$k \gtrsim 10^8$	IA, IIA (except Be^{2+}, Mg^{2+}), IIB
Class II	$10^4 \lesssim k \lesssim 10^8$	First transition series (M^{2+}), lanthanides, Mg^{2+}
Class III	$1 \lesssim k \lesssim 10^4$	Be^{2+}, IIIB, first transition series (V^{3+}, Mn^{3+}, Fe^{3+})
Class IV	$k \lesssim 1$	Cr^{3+}, Co^{3+}, Pt^{2+}, Pt^{4+}

Members of Classes I and II can be studied by sound absorption methods, but only Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} of the first transition series. The borderline between I and II is vague but unimportant to what follows and will not therefore be pursued. Examples from each group within the Classes will be considered but not in any preferred sequence.

(ii) Divalent metal sulfates

The systems which have attracted most attention are the $MgSO_4$ and $MnSO_4$ complexation reactions in both aqueous and non-aqueous solvents[11,12,17–19,29–34,42–46]. Formation constants for both metal monosulfates are equal[47] and in terms of the adequacy of the classical model of solutions in describing association of electrolytes of the same charge type these salts would not be an exception to it (Sect. A). Discrete solute–solvent interactions are apparently different, however, because the heats and entropies of complexation differ[47]; $\Delta H^0 = 5.7$ kcal.mole^{-1} and 3.4 kcal.mole^{-1} and $\Delta S^0 = 31.0$ cal.mole^{-1}.deg^{-1} and 22.6 cal.mole^{-1}.deg^{-1} for $MgSO_4$ and $MnSO_4$ respectively. Compensating changes in K_{23} and K_{34}, for example, could account for the fact that K_c is constant, and the concomitant difference in mole fraction distributions could account for the variation in ΔH^0 and ΔS^0, if the stepwise values for each are of opposite sign. Such a criterion has already been used to distinguish between predominantly inner- and predominantly outer-sphere complexes[48,49].

Figure 4 is an up-to-date compilation of all the acoustic data for 0.1 M $MnSO_4$ at temperatures around 25°C. At various intervals the incomplete and eventually the complete data set have been analyzed both in terms of a two-step and a three-step mechanism. With the exception of two isolated instances[29,30] in which a relaxation was reported with a maximum frequency around 35–50 MHz, two absorption maxima are identifiable. The third (35–50 MHz), which would have made the spectrum consistent with a one-to-one correlation between relaxation times and reaction steps, was challenged[50,51] and in view of the new data should perhaps no longer be considered to be real. For one thing the "relaxation" did not extend over a decade in frequency (see eqn. (11)). The remaining two relaxations have maximum absorptions around 400–600 MHz (relaxation is very broad) and 3–6 MHz. Other sulfates included with $MnSO_4$ and $MgSO_4$ in some of the above references showed the same broad high-frequency relaxation which led to its being attributed to Steps I and II, or to Step II alone in the multistep mechanism, eqn. (21). The lower-frequency relax-

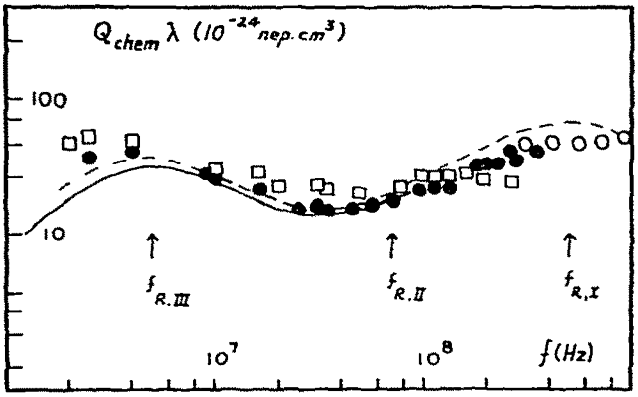

Fig. 4. Only most recent data shown for clarity: □, ref. 30; ○, ref. 32; ●, ref. 45; ---, ref. 34; ——, ref. 44. Frequencies indicated are approximate and chosen to illustrate the three-step DE mechanism.

ation was therefore attributed to Step III and the assignment was endorsed by the dependence of this frequency on the identity of the central cation[11,32,52]. Among results for other sulfates one will find evidence for relaxations in the low kHz range and a "relaxation" at 12 MHz for $MgSO_4$ (ref. 31) analogous to the intermediate one observed in $MnSO_4$.

Before data in the 10^3 MHz or GHz frequency range were gathered the high-frequency relaxation was located at as low as 200 MHz. The availability of GHz data has stimulated some conflict in the interpretation of this broad high-frequency relaxation which is indicative of closely coupled multiple relaxations. Two interpretations, equal in merit, are described in the literature. It is difficult to decide upon the right interpretation because the data used are in considerable error (~ 25% in α_T) and assignments are made beginning with an assumed mechanism (quite the reverse situation from the usual procedure in which the kinetic equation is used to arrive at a probable mechanism).

One interpretation treats the broad relaxation in terms of one solute equilibrium relaxation and a constant non-relaxational solvent contribution α_{nr}/f^2 which is only slightly greater than the low-frequency value for the solvent[33,34,52]. Steps I and II in the mechanism are combined to interpret the single relaxation. Including the lowest-frequency relaxation, eqn. (21) is fitted to the experimental data using four parameters and in one instance α_{nr}/f^2 is varied over reasonable limits[52]. Jackopin and Yeager[34] have observed that if α_{nr}/f^2 is only 3% greater than the low-frequency value for the solvent the theoretical fit with experiment is excellent and there is no need to involve three steps. The second analysis is made in terms of two solute equilibrium relaxations (Steps I and II) and an ion-atmosphere relaxational contribution[32,44]. Seven parameters are needed to fit eqn. (14) to the experimental data. Typical values are given in Table 3 for $CuSO_4$ and $MnSO_4$. Data for other salts are also available[33,34,52]. Technology must be advanced to the point that the quality of the data is improved, in order to resolve this controversy.

One consistent conclusion from all the studies is that the lowest-frequency relaxation is due to contact ion-pair formation. Rate constants for this step and for water exchange, and successive equilibrium constants are given in Table 4 for a number of divalent cations.

TABLE 3

Analyses of multiple relaxation spectra involving high-frequency data (eqn. (14))

Solution	Concn. (*M*)	$A_I \times 10^{17}$ (sec^2.cm^{-1})	f_I (MHz)	$A_{II} \times 10^{17}$ (sec^2.cm^{-1})	f_{II} (MHz)	$A_{III} \times 10^{17}$ (sec^2.cm^{-1})	f_{III} (MHz)	$B_\infty \times 10^{17}$ [c] (sec^2.cm^{-1})	$B_0 \times 10^{17}$ [c] (sec^2.cm^{-1})	Ref.
$CuSO_4$ [a]	0.2	(3.1×10^{-17}; 282 MHz)						24.1	22.0	33
$CuSO_4$ [a]	0.1	($19 \pm 3 \times 10^{-17}$; 340 ± 80 MHz)				6 ± 4	36 ± 30	25.4 ± 1.3	22.0	52 [b]
$CuSO_4$	0.1	1.6	3000	9.0	220			22.2	21.7	32 [b]
$MnSO_4$ [a]	0.1	(7.1×10^{-17}; 266 MHz)				370	4.91	21.86	21.7	34
$MnSO_4$	2.0	120	260	8	50	3100	2.3	var	21.7	44

[a] Analyzed as only two relaxations.

[b] A number of other ions besides Cu^{II} are included.

[c] B_∞ is the α_{nr}/f^2 value given to the solvent at very high frequencies. B_0 is the $\alpha_{solvent}/f^2$ regularly reported at lower frequencies.

TABLE 4

Kinetic analyses of the multiple relaxation spectra of divalent metal monosulfate complexes

Ion	K_{12}	K_{23}	k_{34} (sec^{-1})	E_a (ref. 44) (kcal.mole^{-1})	k_{43} (sec^{-1})	K_{34}	k_{ex} (ref. 22) (sec^{-1})	$E_a(\text{ex})$ (ref. 22) (kcal.mole^{-1})	Ref.
Mg	50	3.3	1.4×10^5	7	8.6×10^5	0.16	~ 14 (ref. 54)		52
	20	4.8	8×10^5		2.7×10^5	0.29			44
Mn	50	3.0	3.6×10^6	7	2.2×10^7	0.16	2.5×10^7	8	52
	52	0.36	4.8×10^7		1.4×10^7	3.4			30
			4×10^6		2×10^7	0.2			11
			2×10^7		2×10^7	1.0			34
	100	1	4×10^6		3×10^7	0.13			33
	20	4.7	2.2×10^7		2×10^7	1.1			44
Co	45	5	4×10^5	7.9	2.2×10^6	0.17	1×10^6	8	52
			2×10^5		2.5×10^6	0.08			11
Ni	45	4.2	9.3×10^3	9.5	5.6×10^4	0.17	3×10^4	12	52
			1.5×10^4		10^5	0.15			11
Cu	41	4.7	1.4×10^7	5.6	8.6×10^7	0.17	2×10^8	5	52
			$>10^7$		20×10^7 (?)				11
	(100)		7×10^8		7×10^8	1.0			53
Zn	41	3.4	1.1×10^7	6.8	6.8×10^7	0.17			52
			$>10^7$		$>10^8$				11
	100	1	3×10^7		1.5×10^8	0.2			33

Discrepancies in particular numbers for the same cation are representative of the present state of flux of the analysis. We venture to suggest that the mechanism is dissociative (perhaps even I_d) for these ions because comparisons between k_{34} (or k_{23} for two-step) and k_{ex}, where available, are fair, as are the corresponding energies of activation, Table 4. Nickel(II) especially has been shown to follow the D reaction path from studies on a wide variety of ligands[27]. There is a need for more temperature dependence data.

Where K_{12} and K_{23} have been calculated the values are, of course, alike for all divalent cations. Because of this limitation it is futile even to begin to explain variations in thermodynamic properties in terms of dissimilar mole fraction distributions. The indication is that the most predominant structure is the MW_MW_LL ion-pair (Table 4). Once again the need is for more accurate high-frequency absorption data so that K_{12} and K_{23} can be obtained from the rate constant ratios.

Volume changes ΔV_{ij} involved with the stepwise equilibria are another subject of contention. Eigen and Tamm[11,44] in their interpretations for both $MgSO_4$ and $MnSO_4$ had to use volume changes of opposite sign for the successive steps ΔV_{ij} so that the summation would approximate to the total observed ΔV_T^0 obtained by the pressure dependence study of the overall equilibrium constant[55,56]. Other values of ΔV_{ij} are also available[30,42,43]. We favor Jackopin and Yeager's argument[34] for $MnSO_4$ that the sign of ΔV_{ij} will be consistently positive, when the reaction is written as a formation process, since as the ions converge to form a complex of reduced charge, electrostriction of the solvent by the ions will be progressively relieved (Table 5).

TABLE 5

Volume changes associated with the formation of $MnSO_4$ and $MgSO_4$ complexes [a]

Ion	ΔV_{12} (ml.mole^{-1})	ΔV_{23} (ml.mole^{-1})	ΔV_{34} (ml.mole^{-1})	ΔV_T (kinetic) (ml.mole^{-1})	ΔV_T^0 (thermodynamic) (ml.mole^{-1})	Ref.
Mg	+18.0	−13.2	+3.5	8.3	7.3 ± 0.4 (ref. 55)	44
Mg	0	+ 14.0	+3.0	17.0		11
Mn	+18.3	−13.3	+3.5	8.5	7.4 (ref. 56)	44
Mn	(+9)		+2.0	11.0		34

[a] For further details of the calculation see Sect. E.

While on the subject of volume changes we would like to digress somewhat to point out that the effect of applied pressure on equilibrium and rate constants is an intriguing and very promising avenue of research. Considerable expertise in high pressure techniques is essential to embark on such a program. Such techniques have been described in detail for sound absorption measurements in the MHz frequency range[57]. One goal of such a study is to be able to determine the overall volume change accompanying the equilibrium according to the equation

$$\left[\left(\frac{\partial \ln K_c}{\partial P}\right)_T\right] = -\Delta V_T/RT \qquad (26)$$

By analogy the pressure dependence of the rate constant gives the volume of activation, e.g. $\Delta V^{\ddagger}_{34}$, and the nature of the transition state is brought into focus. Carnevale and Litovitz[58] combined sound absorption and high-pressure techniques in an elegant study of the pressure dependence of the rate of ionization of aqueous ammonia. The volume of activation at one atmosphere pressure was found to be equal in magnitude to the overall volume change for the reaction $\Delta V^0_T = -28.5$ ml/mole. Consequently the structure of the transition state must bear a close resemblance to the product, i.e. the ionized form of the base. The utility of this approach in confirming the mechanism of complex formation should be obvious.

Extension of this work to metal complexation reactions is, however, thwarted by a serious deficiency in equilibrium constant data from work done under high pressures. The effect of pressure on sound velocity and absorption coefficients is well documented[57], but only two salts have been examined this far, $MgSO_4$ (ref. 42) and $MnSO_4$ (ref. 43). Results are a little disappointing in that the relaxation frequencies are relatively insensitive to pressure. Nevertheless some consolation is obtained from the fact that measurements were made at only one or two frequencies and these at values lower than the relaxation frequency observed at one atmosphere.

One other study on $MnSO_4$ was carried out over the frequency range 9–75 MHz but at 60°C, so the results cannot be compared with other data[59].

(iii) Other systems involving transition metals

Other related areas of interest which involve divalent and trivalent transition metal ions are slowly developing. Attention has been given to the formation of outer-sphere complexes where the cation is fully coordinated by ammonia or amines and is inert to ligand substitution[60], e.g. $Co(NH_3)_6{}^{3+}$. The sound spectra through 200 MHz bear a striking resemblance to those of aquated ions which are labile to substitution, confirming the prior assignment of the higher relaxation frequency to outer ion-pair formation. Rates approach diffusion control but the activation energies are not reported. $Cu(en)_2{}^{2+}$ would be labile to substitution if the overall ion coordination were octahedral, the two axial positions being occupied by water molecules. This has apparently been confirmed[33]. Studies have also begun in non-aqueous–aqueous mixtures, e.g. ethylene glycol–water[45,53], dioxan–water[9,46], methanol–water[9]. Where the non-aqueous component does not form stable complexes with the cation the results are similar to those in pure water. The independence of the rate of formation on the mole fraction of ethylene glycol[45] is taken to mean that the cation is preferentially solvated by water. Such is the case for $MnSO_4$ and $ZnSO_4$ (ref. 45) but not for $CuSO_4$ (ref. 53). Finally the outer-sphere complexation of a number of divalent cations with *m*-benzenedisulfonates in methanol has been studied[61]. Volume changes correspond to the elimination of one methanol molecule and the activation energy is equal to the one for viscous flow. The rate is diffusion-controlled.

Data from complexation reactions in heavy water could contribute to our understanding of the mechanism in that if hydrogen bonding is involved a ligand dependence might be observed and manifest itself in a solvent isotope effect on the rate constant. This was part of the subject of an early publication on $MnSO_4$ complexation[29]. Relaxation frequencies were seen to be identical and the topic was not pursued. As frequently happens the subject has been re-opened, this time with reference to the rare-earth monosulfate complexation reactions. This discussion is deferred until the next section.

(iv) Remaining members of Classes I and II

Interest in the remaining ions has been neither so thorough nor so repetitive. These are relatively more easily disposed of in concluding this section.

For cadmium and mercury(II) the chloro complexes have been studied by sound absorption and the rates of formation appear to be relatively insensitive to the number of coordinated chloride ions[23,63]. No data on water exchange rates are available but for Cd^{2+} the monosulfate[23] and monoacetate[64] complexes (other divalent transition metals included) are formed at the same rate as the chloro complexes, $k \geqslant 10^8$ sec^{-1}. The indication is that the mechanism is dissociative.

The only study to date of the IA metal ions was done using amino-polycarboxylates and tri-polyphosphate as ligands[65]. For comparison IIA elements were included. To summarize the results three points can be made: the rate of complexation with a particular ligand increases linearly with increasing cationic radius within a group; the rate of complexation for a particular cation decreases as the denticity of the ligand increases; when compared with results from simple ligands the first-order rate constant for substitution is apparently ligand-dependent, e.g. $CaCrO_4$ (ref. 11), $k = 5 \times 10^7$ sec^{-1}, CaIDA, $k = 3 \times 10^8$ sec^{-1}. This led to the conclusion that all Class I cations showed a ligand dependence in their complexation rates. In the light of the possibility that ring closure by a chelating ligand may become rate-controlling for these cations, that conclusion may not be totally true. On the other hand, where transition metals are involved it is known that the first substitution is rate-determining[40]. In this instance the directional influence of the first substituent could labilize the remaining coordinated waters to subsequent substitution. Directional influences are absent in ions with inert-gas configurations which could conceivably bring about a change in control. We will return to this point more fully in our discussion of the rare-earth complexes (Sect. E).

Results for the formation of a number of monoacetate complexes of divalent ions have been reported[9,64]. Those of Mg and Ca were studied with another objective in mind[66]. Heats and entropies of complexation differ but in such a way that, by self-compensation, the thermodynamic formation constants are equivalent[48]. From an ultrasonic absorption study it was hoped that the thermodynamic interpretation of the difference, $CaAc^+$ as inner-sphere ($\Delta H^0 = +0.91$ kcal/mole, $\Delta S^0 = 8.7$ cal/mole.deg) and $MgAc^+$ as predominantly outer-sphere ($\Delta H^0 = -1.52$ kcal/mole, $\Delta S^0 = 0.6$ cal/mole.deg) would be confirmed. No evidence for inner-sphere coordination was found for either salt. However, the volume changes at equimolar concentrations are completely different and could be related to the entropy changes via the Maxwell equation[67]

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

There would seem to be no direct and simple correlation between the sign of the enthalpy or entropy change and the nature of the predominant species, contrary to previous suggestions[48,49], since the energy changes involved in restructuring the solvent are a significant proportion of the whole.

The last group of ions which fall into the category of the Class I and II metal ions is the rare-earth series. This has been the principal activity in sound absorption studies in our group and we have chosen to lean on our personal experiences to describe in detail the data analysis and the assumptions which lead to its inherent limitations.

E. KINETICS OF RARE-EARTH (RE) COMPLEXATION REACTIONS

(i) Introduction

A kinetic study of the complexation of the RE^{III} ions was destined to arrive as the metals in the periodic table were systematically examined. Although the first results[68] appeared as late as 1965, there has been considerable activity since then. The ions are labile to substitution, even more than might have been expected by comparison with divalent ions of comparable size. Relaxation times for substitution fall within the time scales of pressure-jump, temperature-jump, and ultrasound absorption, all of which have been applied. Consequently overall and stepwise rate constants can be measured. A wide variety of ligands have been used including oxalate[69] and tartrate[70] (P-jump), murexide[68], anthranilate[71,72] and acetate[72] (T-jump), sulfate[73–80], nitrate[36,75,81,82] and acetate[83] (sound absorption), but only for two of these have the studies included all ions of the series (save Pm) plus yttrium[68,74,75].

It is tempting to relate the acoustic results with those from the other methods and from ^{17}O NMR[85–88] which we shall eventually try to do and which Petrucci has already done[36]. However, differences in experimental temperatures and medium ionic strengths between methods detract from the ultimate aim of the comparison, which is to gain more insight into the equilibrium constants for the more rapid association steps. One prominant issue common to all of the studies is that the variation in the rates of formation is not a simple function of the cationic radii or the atomic number. This is illustrated in Fig. 5, where most of the available data are compiled. Reasons to account for this kinetically unusual behavior (for the alkaline earths the dependence is a linear function[65]), have included a coordination number change for the RE ion somewhere in the middle of the series or a change in mechanistic control. Before we elaborate upon these topics for discussion we will describe in detail the intricacies of the analysis of acoustic data. We will use the RE sulfates as our particular example, and the three-step DE mechanism.

At present there are no data in the GHz frequency range for any of the RE sulfates. Observed relaxations fall in the range 10–50 MHz and vary with the cation[74–78]. At equimolar concentrations the relaxation frequency increases to a maximum at Sm–Eu–Gd and decreases again over the remainder of the series. For Y^{3+}, $f_R \leqslant 10$ MHz. Absorption amplitudes are much greater than those observed for divalent metal sulfates. As before, this relaxation is attributed to substitution of water by sulfate in the inner coordination sphere of the RE. In passing it is worth noting that for the monoacetate complexes[83] this low-frequency relaxation is independent of both the cation and the solution concentration. If the high-frequency relaxation(s) are representative of a diffusion-controlled step we might

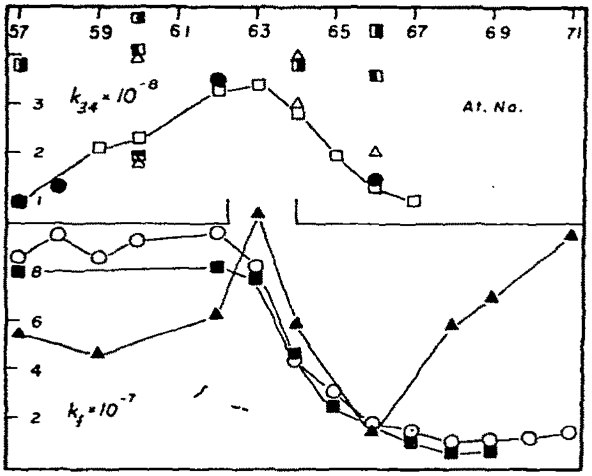

Fig. 5. Rate constants versus atomic number for RE series with the ligands ●, acetate; □, ◧, ◫, ▣, sulfate; △, nitrate; ○, murexide; ■, oxalate; ▲, anthranilate.

speculate that the additional charge on the RE ion would move this band to even higher frequencies and that there would be little coupling between it and the observed low-frequency relaxation. This is exceedingly important in allowing us to simplify the analysis although we are cognizant of the limitations adroitly spelled out by Petrucci[36].

(ii) Treatment of the data

Eigen and de Maeyer[1] have demonstrated the correlation between relaxation times τ_i, the rate constants, and concentration variables for a two-step overall mechanism of which eqns. (21a), (21b) can be used as an illustration. The roots of the secular determinant are

$$(\tau_{\rm I,II})^{-1} = \tfrac{1}{2}\{\Sigma k \pm (\Sigma k^2 - 4\Pi k)^{1/2}\} \qquad (27)$$

where the positive sign corresponds to $\tau_{\rm I}^{-1}$, the negative to $\tau_{\rm II}^{-1}$, 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 discrete time constants the rate equations (27) may be separated. If, for example, step I is diffusion-controlled an ordinarily acceptable assumption would be that $k'_{12}, k_{21} \gg k_{23}, k_{32}$, in which case the separate rate equations reduce to

$$\tau_{\rm I}^{-1} = 2\pi f_{\rm R(I)} = k'_{12} + k_{21} \qquad (28)$$

and

$$\tau_{\rm II}^{-1} = 2\pi f_{\rm R(II)} = \left(\frac{k'_{12}}{k'_{12} + k_{21}}\right) k_{23} + k_{32} \qquad (29)$$

Here $\tau_{\rm I}$ is independent of the other step but $\tau_{\rm II}$ has to account for the faster equilibrium shift which must accompany the second step. By analogy, for the addition of a third step[1], eqn. (21c), and a third relaxation time, the correlation is given by

$$\tau_{\rm III}^{-1} = 2\pi f_{\rm R(III)} = \left(\frac{k'_{23}}{k'_{23} + k_{32}}\right) k_{34} + k_{43} \qquad (30)$$

where k'_{23} is the first term of eqn. (29) and the simplifying assumption that $k'_{12}, k_{21} \gg k'_{23}, k_{32} \gg k_{34}, k_{43}$ is used.

We know from eqn. (19) that the overall rate equation is second-order. In the multistep mechanism the only second-order rate constant is $k'_{12} = k^0_{12}\theta$, where θ is the concentration variable in moles/liter. The general expression[1] for θ is

$$\theta = \Pi_{\rm f} C_0 \left\{[\overline{\rm M}] + [\overline{\rm L}] + [\overline{\rm L}]\left(\frac{\partial \ln \Pi_{\rm f}}{\partial \ln \delta}\right)_{C_0}\right\} \qquad (31)$$

where C_0 is the analytical salt concentration, the bars represent equilibrium concentrations, δ is the degree of association of the salt calculated from the overall equilibrium constant measured under the conditions of the kinetic experiment, $\Pi_{\rm f}$ is the activity coefficient quotient, which depends upon the stoichiometry of the salt and the complex, and the partial derivative accounts for the change in the activity coefficients on perturbation. This last term is absent when an excess of inert electrolyte is added to maintain constant ionic strength.

For the specific example of trivalent RE sulfates for which the association equilibrium reaction is written as

$$\underset{(2C_0-\delta)}{({\rm RE})^{3+}} + \underset{(3C_0-\delta)}{{\rm SO_4}^{2-}} \rightleftharpoons \underset{\delta C_0}{({\rm RE}){\rm SO_4}^{+}} \qquad (32)$$

substitution into eqns. (28)–(31) gives[75]

$$\tau_{\rm I}^{-1} = 2\pi f_{\rm R(I)} = k_{12}{}^0\theta + k_{21} \qquad (33)$$

$$\tau_{\rm II}^{-1} = 2\pi f_{\rm R(II)} = \left[\frac{\theta}{\theta + (K_{12})^{-1}}\right] k_{23} + k_{32} \qquad (34)$$

$$\tau_{\rm III}^{-1} = 2\pi f_{\rm R(III)} = \left[\frac{\theta}{(K_{12}K_{23})^{-1} + (1 + K_{23}{}^{-1})\,\theta}\right] k_{34} + k_{43} \qquad (35)$$

$$= \phi k_{34} + k_{43} \qquad (36)$$

where

$$K_{12} = \frac{k_{12}{}^{0}}{k_{21}} \quad \text{and} \quad K_{23} = \frac{k_{23}}{k_{32}}$$

and

$$\theta = \Pi_f C_0 \left\{ (5-4\delta) + (3-2\delta) \left(\frac{\partial \ln \Pi_f}{\partial \ln \delta} \right)_{C_0} \right\} \tag{37}$$

where $\Pi_f = \gamma_1 / \gamma_3 \gamma_2$, and γ_i is the activity coefficient of the ith ion.

Solving these equations to determine k_{34} and k_{43} presents considerable difficulties. Some workers feel they have lessened the problem by assuming a two-step mechanism, in which case eqn. (35) does not apply. Reasons for doing this were enumerated before in the discussion of high-frequency data. Essentially all that has been accomplished is the removal of K_{23} as a parameter, and k_{23} in the two-step mechanism then becomes equivalent to k_{34} in the three-step mechanism. The principal problems remain. Among these are: how to evaluate K_{12}, the activity coefficients, and the partial derivative; and whether the concentration dependence of τ_{III} is sufficiently large (eqn. (36)) that the variation in τ_{III} is greater than the experimental error in its determination. These will be dealt with in turn, but we must first examine objectively the validity of the assumption which permitted us to arrive at the separate rate equations, namely that the consecutive steps are discrete.

If we allow the mechanism to be D, so that we can get an a priori estimate of k_{34}, then k_{34} should approximate to the value of k_{ex}. For Gd^{3+}, $k_{ex} = 9 \times 10^8$ sec^{-1} (ref. 85). Applying a statistical correction[85] for nine-coordination, $k_{ex} = 6 \times 10^8$ sec^{-1}. According to Petrucci's argument, if the forward and backward rate constants are calculated from the Smoluchowski[89] and Eigen[90] equations for diffusion-controlled reactions (steps I and II) the values obtained are 3.7×10^{10} l.mole^{-1} .sec^{-1} and 1.7×10^8 sec^{-1} (using a distance of closest approach $\mathring{a} = 5$ Å). Clearly the assumption that $k_{21} \gg k_{32} \gg k_{34}$ does not hold, in fact $k_{32} \simeq k_{34}$. We are faced with an ultimate dilemma that if the assumption is not made the equations are intractable[52], yet if it is made the analysis is inadequate. Under these circumstances one would normally accept the assumption as valid, proceed with the analysis, and look for consistency among the resultant k_{34} values for different ligands and a good comparison between k_{34} and k_{ex}. If the agreement is good then the analysis is at least compatible with a dissociative mechanism, although one could not say that it has been proved.

Let us return now to the evaluation of K_{12}, activity coefficients, and the partial derivative. K_{12} is usually calculated from theory using either the Fuoss[37] or Bjerrum[38] association expression. For the very good reason that K_{12} does not pass through a minimum[36] with increasing distance of closest approach $\mathring{a}$, the Bjerrum expression is preferred

$$K_{12} = \frac{4\Pi N \mathring{a}^3}{1000} b^3\, Q(b) \tag{38}$$

For definitions of b and $Q(b)$ see ref. 3. A typical estimate of $\mathring{a}$ for the three-step mechanism is a distance equal to the sum of ionic crystal radii plus two water molecule diameters: e.g. $\mathring{a} = 8.86$ Å for RE sulfates[75], which makes $K_{12} \simeq 440$. In the two-step mechanism $\mathring{a}$ is typically shorter by one water molecule diameter and $K_{12} \simeq 1100$. Because the chemical absorption is large for the RE sulfates, relatively dilute solutions can be used and the ionic strength is around the upper limit ($I \simeq 0.1\ M$) of the utility of the Davies extension[91] to the Debye–Hückel equation. This is not true for divalent metal sulfates where concentrations have to be $\geqslant 0.1\ M$. We, like many others, have used the Davies equation (39) to calculate γ_i and hence Π_f,

$$-\log \gamma_i = AZ_i^2 \left(\frac{\sqrt{I}}{1 + B\mathring{a}\sqrt{I}} - 0.3I \right) \tag{39}$$

where $A = 0.509$ and $B = 0.33 \times 10^8$ at 25°C and $I = 3C_0 + 12(1-\delta)C_0$. For consistency with the K_{12} calculation, the equation is modified by changing $\mathring{a}$ from 3 Å to $\mathring{a} = 8.86$ Å. The partial derivative is readily solved[3] by applying the chain rule

$$\begin{aligned} \left(\frac{\partial \ln \Pi_f}{\partial \ln \delta} \right)_{C_0} &= \frac{\partial \ln \Pi_f}{\partial I} \cdot \frac{\partial I}{\partial \ln \delta} \\ &= 0.509(Z_{M^{3+}}^2 + Z_{L^{2-}}^2 - Z_{ML^+}^2)^2 \times \\ &\qquad \frac{1}{(2I^{1/2}(1 + B\mathring{a}I^{1/2})^2 - 0.3I)(1-\delta)C_0} \end{aligned} \tag{40}$$

the values of δ and I required being obtained by standard reiterative calculations[4]. The resultant rate constants k_{34} and k_{43} are therefore subject to the assumptions made in choosing a value for $\mathring{a}$, and the applicability of the equations from the theoretical continuum model of solutions to a model which involves discrete steps.

So far no directions have been given as to how to calculate K_{23}. This parameter is usually left as a separate variable which must simultaneously fit eqn. (35) and the expression for the overall constant $K_c = K_{12}(1 + K_{23} + K_{23}K_{34})$. The fit can be made by a reiterative calculation[75]. However, in the reiteration eqn. (36) must be solved graphically. This is the weakest link in the calculation for the following reason. Equation (36) describes the linear variation of τ_{III}^{-1} with the concentration variable ϕ. Figure 6 shows the variation of ϕ with analytical concentration C_0 for a RE sulfate. The points on the curve correspond to actual experimental conditions[80]. It is apparent that although the span in concentration is reasonably wide, ϕ is relatively insensitive to it. Obviously ϕ is more sensitive at lower concentrations but the error in the measured α_T increases rapidly. Likewise there is no advantage to be gained in going to higher concentrations. Using typical values for k_{34} and k_{43} and calculated values of ϕ the anticipated experimental frequency range can be shown[80] to be around 3–4 MHz. If a conservative error in $f_{R(\text{III})}$ is ± 1 MHz it will become apparent that the linear plot of $2\pi f_{R(\text{III})}$ versus ϕ will often result in a negative intercept[76] because of the long extrapolation to ϕ equal to zero. Ironically a relaxation frequency which is independent of the concentration offers a simpler solution. Under these circumstances $k_{34}\,\phi \ll k_{43}$ and therefore $2\pi f_{R(\text{III})} \simeq k_{43}$. k_{34} can then be calculated from

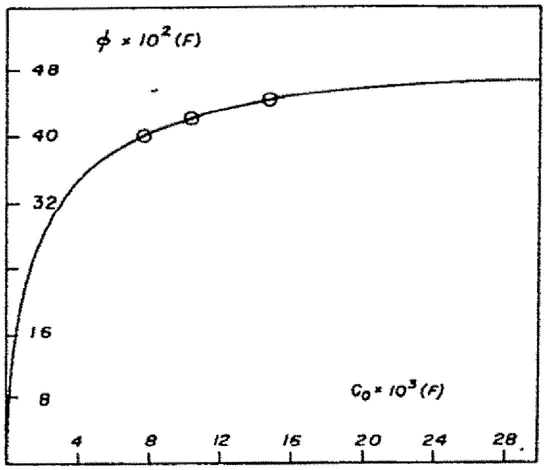

Fig. 6. Plot of frequency-dependent concentration variable ϕ versus the analytical salt concentration C_0 for $Sm_2(SO_4)_3$ in water. Open circles are typical experimental values.

the overall equilibrium constant, as was done for the RE monoacetate complexes[83]. An honest appraisal of the experimental error is crucial to the calculation of the rate constants.

The reiterative procedure can be avoided by the appropriate combination of eqn. (36), the equation for the overall constant, K_c, in terms of stepwise constants, and the expression for ϕ. A two-parameter linear equation is obtained[80].

$$2\pi f_{R(III)} = \left(\frac{(1 + K_c\theta)}{1 + K_{12}(K_{23} + 1)\theta}\right) k_{43} \tag{41}$$

which on substituting two values for $2\pi f_{R(III)}$ and θ yields K_{23} and k_{43} on simultaneous solution. Alternatively a plot of $2\pi f_{R(III)}$ versus the term in parentheses[79] will have a zero intercept when the right value of K_{23} is substituted. The forward rate constant is then given by $k_{34} = K_{34}k_{43}$. One advantage this method has over the reiterative method is that experimental errors in relaxation frequencies are more easily handled.

The methods used to obtain relaxation frequencies from the absorption curve for a single relaxation are many and varied. In the simplest method a template manufactured to fit eqn. (11) is superimposed on the experimental curve. No justifiable estimate of the error can be made using this method. A better approach is to rearrange eqn. (12) to read[92]

$$\frac{\alpha_{\text{chem}}}{f^2} = -\left[\frac{\alpha_{\text{chem}}}{f^2_{R(III)}}\right] + A \tag{42}$$

The plot of $(\alpha_{\text{chem}}/f^2)$ vs. (α_{chem}) is linear with slope $= -1/(f_{R(III)})^2$ and intercept A but it is linear only over the decade of frequency which includes the complete single relaxation. A least-squares fit to the data is complicated by the fact that deviation from linearity may be real and not due to experimental error. The procedure recently adopted by us[80] is to simultaneously solve eqn. (11) using all possible combinations of two data points and to express the error from the mean $f_{R(III)}$ in terms of an average deviation. The frequencies which correspond to the limits of the error and the mean frequency are then used in the solution of eqn. (41) to arrive at our error estimate for the rate constant. This is typically of the order of ± 20%.

(iii) Summary of acoustic studies

To compile all the data for all the ions in the series with the three ligands sulfate, nitrate and acetate would consume an inordinate amount of space. The most up-to-date values for k_{34} have already been given in Fig. 5. Assembled in Table 6 are the data for the three most commonly recurring ions in acoustic studies, Nd^{3+}, Gd^{3+} and Dy^{3+}.

All three ligands form inner-sphere or contact ion-pairs to varying extents, which is consistent with the projections from other kinetic[86, 87] and thermodynamic studies[93–95]. The sulfate complex, for example, is around 80% inner-sphere[94]. From an NMR study it is further proposed that nitrate and acetate may even behave as bidentate ligands[87]. Bidentate coordination was also suggested to explain changes in the infrared spectra of acetate on complexation[96], and thermodynamic studies strongly indicate the presence of both outer- and inner-coordinated nitrate[93, 97]. The chloride complex on the other hand is exclusively outer-sphere[94] and no evidence of an acoustic relaxation has been forthcoming. The monofluorides are predominantly inner-sphere in structure[98] but the insolubility of the RE fluorides prohibits their study by sound absorption methods.

For dysprosium and other RE monoacetates k_{43} was taken to be equal to $2\pi f_{R(III)}$ since the relaxation frequency ($f_{R(III)}$ = 5.9 MHz) was independent of changes in the cation and the salt concentration[83]. Results are given in Table 7 for two interpretations – the formation of a 1:1 complex with and without chelation. The chelation mechanism, in which ring closure was the rate-controlling step, was originally preferred. In the light of the revised sulfate[80] data, the most recent nitrate data[82], and the indication of possible interference from the bis-acetato complex equilibrium[84], a modified mechanism is no longer considered necessary.

RE nitrate absorption spectra have led to considerable controversy for two apparent reasons. Absorptions are neither as great as the corresponding sulfates nor are they similar in magnitude for all members of the RE series as they are for the sulfates. One will find interpretations in terms of a single relaxation[36, 81] as well as a double relaxation[75, 82]. The error in the relatively low absorption coefficients makes it difficult to decide in favor of one or the other. Add to this the great uncertainty in the overall formation constants, then the variation in the observed rate constants (particularly k_{43}) is more easily understood. For a mechanistic test we are more interested in comparing k_{34} values where, quite fortunately, the variation is more tolerable.

Considering k_{34} values alone the rates of complexation for a particular ion with the three ligands are compatible with a dissociative mechanism if the chelation mechanism for acetate[83] is rejected. For Gd^{3+} k_{34} is of the same order of magnitude as k_{ex} with perhaps an indication of some ligand assistance in removing water since $k_{34} < k_{ex}$. Enthalpies of activation for solvent exchange[85, 87] and complex formation[76] agree favorably for both Gd^{3+} and Dy^{3+}. A disturbing lack of correspondence is, however, found[87] be-

TABLE 6

Rate and equilibrium data for Nd^{3+}, Gd^{3+}, Dy^{3+} complexes at 25°C

Ligand	K_{12} (K_{13})	K_{23}	$k_{34} \times 10^{-8}$ (sec^{-1})	$k_{43} \times 10^{-7}$ (sec^{-1})	K_{34}	$K_c \times 10^{-3}$	$\Delta H^{\ddagger}_{34}$ (kcal.-mole^{-1})	Ref.
Neodymium								
Sulfate (H_2O)	358	1.0	4.1	16.0	2.5	3.65		73
	433	1.3	2.3	3.9	5.9	4.55	4–6	76, 80
	680	0.5	6.3	16.0	4.0	3.74		77
	(900)		1.9	4.8	4.0	4.37		78
Sulfate (D_2O)	(900)		0.8	7.1	1.1	1.92		79
Nitrate	(2.9)		1.8	3.6	5.0	0.017		82
	(6±3)		6.0	30.0	2±1	0.017		81
	(6±3)		4.0	29.0	1.4	0.017		36
Gadolinium ($k_{ex} \simeq 6 \times 10^8$ sec^{-1}, $\Delta H^{\ddagger}_{ex} = 3.0$ kcal.mole^{-1})[85]								
Sulfate (H_2O)	437	1.6	2.8	5.7	4.9	4.55	2–4	76, 80
	(200)		8.2	3.8	2.2	4.50		79
Sulfate (D_2O)	437	1.2	2.9	4.3	6.8	4.55		80
	(200)		6.9	0.7	10.0	18.9		79
Nitrate	(?)		3.0			0.017		82
	(4±2)		5.0	17.0	3±1	0.015		81
	(4±3)		4.0	15.0	2.6	0.017		36
Acetate	?			3.7				83
Dysprosium ($k_{ex} \simeq 0.3–2.6 \times 10^7$ sec^{-1}; $\Delta H^{\ddagger}_{ex} \not> 5$ kcal.mole^{-1})[87]								
Sulfate (H_2O)	358	1.0	3.6	8.1	4.5	4.22		73
	440	1.9	1.3	3.3	3.3	4.08	1–4	76, 80
	(1350)		0.9	4.5	2.0	4.10		79
Sulfate (D_2O)	440	1.2	1.3	4.4	2.9	4.24		80
	(1350)		1.3	0.3	4.3	58.0		79
Nitrate	(?)		2.0			< 0.0075		82
Acetate	(10)		1.4	3.7	3.7	0.047		83
Acetate[a]	10	3.0	0.09	3.7	0.23	0.047		83

[a] Treated as chelating mechanism.

tween k_{34} and k_{ex} for Dy^{3+}. The proponents of the idea of a change in mechanistic control in the series somewhere around Gd^{3+} might be encouraged by this discrepancy in the comparison. However, it is our feeling that such an abrupt change in k_{ex} (6×10^8 to 2×10^7 sec^{-1}) would be reflected in a sharp discontinuity in k_{34} and the overall formation constants as a function of atomic number. This is not observed and, like the authors[87], we prefer to think of $k_{ex} = 0.3–2.6 \times 10^7$ sec^{-1} as the lower limit for solvent exchange on the ions Tb^{3+}–Tm^{3+}.

Results for the kinetics of complexation of RE sulfates in D_2O are sharply contrasting[78–80].

In one study[78, 79] there is evidence for a distinct solvent isotope effect (SIE) which would argue in favor of a change in mechanism. In the other[80] no SIE is evident, a result which would endorse a dissociative mechanism. The conflict in the results can be traced to differences in overall formation constants measured in D_2O. In the former study the calculation of the formation constants was an integral part of the kinetic analysis while in the latter the precaution was taken to measure the formation constants in an independent conductimetric study[99]. Whereas K_c varies from 1920 (Nd) to 58,000 (Dy) from the kinetic interpretation, the values are essentially constant from the conductance work. The difference between 1920 and 58,000 is taken up in different K_{12} values, which is difficult to reconcile with theory[89]. Furthermore the ratio $k_{34}(H_2O)/k_{34}(D_2O)$, defined as the SIE on $NdSO_4^+$ formation, is exactly equal to the ratio of the formation constants. There would seem to be no reason to change our opinion from a dissociative mechanism for all RE ions on the strength of these results.

Within reasonable experimental limits k_{43} is constant for all RE ions with the same ligand. The difference in stability constants within the series is apparently a consequence of the small variation in k_{34} from metal to metal. Accordingly the reason chosen by thermodynamicists to explain the unusual variation of K_c with atomic number, i.e., a change in cation coordination number somewhere in the middle of the series[4, 97], would conceivably account for the analogous variation of k_{34} with atomic number.

(iv) Thermodynamic considerations: volume changes for complexation

The amplitude of a particular relaxation in a multi-relaxation spectrum will contain a contribution from each of the faster relaxing processes, the magnitude of which depends upon the degree of coupling between relaxations. From eqn. (18) it is obvious that the same condition holds for volume changes associated with the relaxation. For the three-step mechanism the relationship between observed volume changes ΔV_n and the individual volume changes ΔV_{ij} for the reaction step ij are given by the equations[7]

$$\Delta V_{\mathrm{I}} = \Delta V_{12} \tag{43}$$

$$\Delta V_{\mathrm{II}} = \Delta V_{23} + \left(\frac{k_{21}}{k'_{12} + k_{21}}\right) \Delta V_{12} \tag{44}$$

$$\Delta V_{\mathrm{III}} = \Delta V_{34} + \left(\frac{k'_{23}}{k'_{23} + k_{32}}\right) \Delta V_{\mathrm{II}} \tag{45}$$

Combining eqns. (15) and (18) and substituting a new symbol G_n^+ for $K(\partial\theta/\partial K)$, the general equation which relates ΔV_n to the relaxation amplitude can be derived[76]

$$(\Delta V_n)^2 = \frac{\beta_0 RT}{8.686\pi} \cdot \frac{2(\alpha_{\mathrm{chem}}\lambda)_{n,\mathrm{R}}}{C_0} \cdot \frac{1}{G_n^+} \tag{46}$$

where 8.686 is introduced to convert decibels to the c.g.s. units of nepers. At 25°C, $\beta_0 = 4.46 \times 10^{-11}$ cm^3/erg and on substitution the equation reduces to

$(\Delta V_n)^2 = 8.1 \times 10^{-2} (\alpha_{\mathrm{chem}}\lambda)_{n,\mathrm{R}}/C_0 G_n^+$. Included in the term G_n^+ are such functions as θ, Π_f, δ, the partial derivative $(\partial \ln \Pi_f)/(\partial \ln \delta)$, and stepwise equilibrium constants K_{ij}. The expansion of G_n^+ depends upon the stoichiometry of the salt and the complex and the step n of the multistep reaction identified with the relaxation. These are adequately described in the literature[7] and the reader is referred there for the complete details. At 25°C G_n^+ is usually in the order of 0.2.

It should be remembered that one must use one's intuition and judgment in deciding upon the sign of any or all volume changes. Unless three relaxations are identified the total volume change for the overall reaction ΔV_T cannot be calculated from acoustic data without making assumptions. One such assumption frequently used, for example[44], is that $\Delta V_{12} \simeq 0$ ml/mole, which means that no relaxation would be observed. More often ΔV_n is calculated and is compared with ΔV_T. Comparisons are severely limited, however, since little information is as yet available on ΔV_T for metal complexation reactions. The pressure dependence of formation constants[55, 56] at constant temperature and dilatometry[94] are the classical methods applicable to the determination of ΔV_T. In the few cases where comparisons can be made for RE salts the results are consistent with the multistep mechanism for complexation[94, 100]. For $LaSO_4^+$ $\Delta V_{III} = 19.1$ ml/mole and $\Delta V_T = 25.7$ ml/mole at a concentration of 8.8×10^{-3} F. No ΔV_T data are available for the other RE sulfates but a dependence of ΔV_{III} on atomic number[76] is observed which is similar to the dependence of K_c on the same variable. A rough estimate of ΔV_T in the series might then be made. Obviously the volume change for inner-coordination accounts for the majority of the total volume change when restructuring of the solvent is at its most pronounced. For $NdNO_3^{2+}$, Silber et al.[82] estimate ΔV_{II} (a two-step mechanism is used) to be 3.5 ml/mole. From dilatometry[94], values of ΔV_T for $CeNO_3^{2+}$ and $EuNO_3^{2+}$ are 3.4 and 4.2 ml/mole respectively so the volume change in Step I is perhaps negligible. The smaller volume change for inner-coordination of nitrate compared with sulfate is consistent with a reduced electrostatic attraction on complexation. Petrucci[36] on the other hand, assuming $\Delta V_{12} = 0$ ml/mole, obtained a value of 16 ml/mole for $NdNO_3^{2+}$. However, he admitted some concern over the validity of this calculation because of the uncertainty in the values used for K_{12} and K_{23} which results from the extreme uncertainty in K_c.

Much useful work remains to be done in the area of volume changes and particularly with respect to volumes of activation. We have really only taken the first small step. In the next section we try to evaluate the merits of the sound absorption results as they are compared with the results from other relaxation techniques.

F. RARE EARTH COMPLEXATION KINETICS

(i) A comparative appraisal of results in terms of a single mechanism

Let us begin by re-emphasizing the fact that stepwise rate constants, k_{ij} and k_{ji}, are determined by the sound absorption technique and overall rate constants, k_f and k_b, by temperature- and pressure-jump techniques. The objective of this section is to correlate these constants via the steady-state kinetic analysis (Sect. C). Since k_{34} is virtually constant for a given RE ion with the ligands sulfate, nitrate and acetate, and of the same order of magnitudes as k_{ex}, our modus operandi will be to consider this as the characteristic rate constant for substitution into the inner-coordination sphere of that particular RE ion and to use it as the basis for the comparison. Because of the relative similarities in the plots of k_f and k_{34} versus atomic number (Fig. 5), it would seem to be redundant to include more than one RE ion in developing the discussion. We have chosen the Dy^{3+} ion but for the following very special reason. Whereas k_{34} for the monosulfate[74, 75] series maximizes around Sm^{3+} there is a plateau in the k_f curves for the murexide[68] and oxalate[69] series which extends over the early members to Eu–Gd. Since this may be real we should perhaps use at least two ions for our comparison. One alternative suggestion we have, which might account for the difference, is that the chemical relaxation times for the early members are so close to the time constants for the T-jump[68] and P-jump[69] apparatus ($\tau \simeq 50$–60 μsec) that there is a "levelling effect" on k_f. Whether this is the case or not, the following discussion is restricted to Dy^{3+}.

That the comparison will not be easy can be seen from the information in Table 7. There is little correspondence between temperatures and the ionic strengths of the media, a consequence of the experimental conditions demanded for the method and/or the availability of overall formation constants respectively.

Now that the data from the other methods have been introduced we can begin by looking for similarities in the results, just as we did for the sound data. Within the limits of experimental error k_f is essentially constant for all ligands and apparently it is not too sensitive to temperature and ionic strength differences, which is something of a surprise. The two results for anthranilate[71, 72] give a $\Delta H_f^{\ddagger} = 4.4$ kcal/mole. Backward rate constants, k_b, on the other hand vary over four orders of magnitude. Differences in overall formation constants from ligand to ligand are therefore determined by the rate constant for the backward reaction. This is even more general than it appears from the limited data presented here. If one looks at the k_b data for all of the RE ions with one ligand, murexide[68] for example, the values are constant at $4.6 \pm 1.0 \times 10^3$ sec^{-1}. There is therefore a linear dependence of k_f on K_c, or in other words, both constants show an analogous variation with atomic number, a situation which has already been shown to exist in the results from sound absorption studies. Two results are given from the temperature-jump study on dysprosium acetate complexation, The second entry under acetate in Table 7 refers to the formation of the bis-acetato–metal complex[79]. k_b is again constant but the significant result is that second substitution appears to occur more rapidly, as is the case for divalent transition metal ions[40]. This could have considerable adverse bearing upon our ensuing discussion but it is important to remember that no steric requirement would be expected unless the acetate coordinates in a bidentate fashion.

Equation (24), Sect. C, is the relationship from the steady-state kinetic analysis which will be used in our attempt to correlate overall and stepwise rate constants. The Bjerrum outer ion-pair association constant K_{12} must first be corrected for the ionic strength conditions of the experiment such that $K_{12}' = K_{12}\Pi_f$. Rewriting eqn. (24) in the new terms, it becomes

$$k_f = \frac{K_{12}\Pi_f k_{23} k_{34}}{k_{32}+k_{34}}$$

TABLE 7

Rate data for Dy^{III} complexation reactions

Ligand	Method	I (M)	T (°C)	$k_f \times 10^{-7}$ $(M^{-1}.sec^{-1})$	k_b (sec^{-1})	$k_{34} \times 10^{-8}$ (sec^{-1})	$k_{43} \times 10^{-7}$ (sec^{-1})	K_c	Ref.
Sulfate	SA	→ 0	25	3700		1.3	4.4	4.2×10^3	80
Nitrate	SA	var.	25			2.0		17	82
Murexide	T	0.1 KNO_3	12	1.7	2.8×10^3			6.1×10^3	68
Oxalate	P	→ 0	25	1.3	1.4			9.3×10^6	69
Anthranilate	T	0.2 $NaClO_4$	12.5	1.4	1.2×10^4			1.2×10^3	71
		0.2 $NaClO_4$	20	1.8	1.5×10^4			1.2×10^3	72
Acetate	T	?	8.5	1.1	1.9×10^4			$K_1 = 570$	79
Acetate	T	?	8.5	3.7	2.1×10^4			$\beta_2 = 1.8 \times 10^3$	79
Acetate	SA	2 $NaClO_4$	25			1.4	3.7	47	83

To simplify the interpretation an assumption can be made regarding the relative magnitudes of the constants k_{32} and k_{34}. From the discussions in Sect. E, a reasonable assumption would be that $k_{32} \simeq k_{34}$, in which case $k_f = \frac{1}{2}K_{12}\Pi_f K_{23}k_{34}$. For a 3:2 electrolyte (sulfate, oxalate) $K_{12} \simeq 440$ when $\mathring{a}$ is taken equal to 8.86 Å, and for the conditions of the oxalate experiment $\Pi_f = 0.02$. Using K_{23} and k_{34} from Table 7, the calculated k_f for dysprosium oxalate complex formation is $\sim 5.5 \times 10^8$ M^{-1}.sec^{-1}, or 40 times greater than the experimentally observed value. For 3:1 electrolytes (murexide, anthranilate) using $K_{12} = 10$ and $\Pi_f \simeq 0.2$, the calculated $k_f \simeq 1.5 \times 10^8$ M^{-1}.sec^{-1}, about an order of magnitude greater than the observed value. We must conclude that within the confines of this model and subject to the inadequacies of the acoustic interpretation there is no correlation between k_f and k_{34} obtained by independent relaxation methods.

An alternative model or mechanism is one which involves a chelation step. This is a perfectly reasonable possibility since murexide, anthranilate, oxalate and tartrate are bidentate ligands and, unlike the unidentate ligands where k_{43} may be considered constant, k_b is very dependent upon the identity of the ligand. This could be interpreted to mean that there is a variable steric restriction to dissociation. Revising eqn. (25), Sect. C, the appropriate relationship is given by $k_f = K_{12}\Pi_f K_{23}k_{34}k_{45}/(k_{43}+k_{45})$. If $k_{45} \gg k_{43}$ then the situation reverts to the argument of the previous model. If there is to be a correlation then k_{43} must be taken to be much greater than k_{45}, which makes ring-closure the rate-controlling step. This would be in accord with the decrease in rate constants as the denticity of the ligand increases, as was observed for the IA and IIA metal ions. But it would not be consistent with the faster second substitution step reported for the bis-acetato complex[79]. We can only surmise that just as there is steric hindrance to dissociation so there is a steric requirement to be met on ring-closure which would be absent when two unidentate acetates are coordinated.

Since k_{45} data are not available from sound absorption experiments the calculation must be reversed using the parameters given in Tables 6 and 7 and the Π_f values given above to calculate k_{45} for each ligand. The calculated values are 1.2×10^6 sec^{-1} (murexide), 1.3×10^6 sec^{-1} (anthranilate), and 4×10^5 sec^{-1} (oxalate). Some confirmation of the model might have been anticipated if k_{45} had turned out to be constant. That it did not may have some real significance. In fact the smallest chelate ring is made by oxalate, which may inspire greater steric hindrance. This is pure speculation however and we should perhaps rather admit that the chelation model has not been confirmed. All in all we are disenchanted by the first model since an order of magnitude difference in k_f calculated and observed cannot be reconciled; there is no justifiable reason for changing either k_{34} or K_{12} by a power of ten. A study which is long overdue is to take any of the potentially bidentate ligands and use it in a sound absorption study. Preliminary work which has been done on samarium anthranilate in our laboratory[101] has had to be suspended until the accuracy in the low-frequency range of the equipment can be improved. The results were encouraging in that the frequency maximum was much lower in the presence of anthranilate ion, e.g. 8 MHz vs. 38 MHz for the corresponding Sm salts.

Petrucci in his comparison[36] chose to do the reverse calculation so that k_f values might be compared. He too expressed some concern over the oxalate results, but we share the same feeling that the most effective comparison can be made if a chelation mechanism is adopted. It is perhaps informative in concluding this section to emphasize the point by calculating what k_f would be for the monosulfate complexation, in which chelation is not a factor. The value obtained for k_f for $DySO_4^+$ formation, assuming $k_{34} \gg k_{32}$, is $2.2 \times 10^9 M^{-1}.sec^{-1}$.

G. RARE EARTH COMPLEXATION EQUILIBRIA

In the two preceding sections we have at times labored the point that forward rate constants, be they overall or stepwise constants, vary with atomic number in a manner analogous to the variation of overall formation constants. This similarity was used as an argument against the possible interpretation of the trend in rate constants as being due to a change in mechanism. It is appropriate, therefore, in this brief section, that we enumerate some of the reasons which have brought us to believe that there is a coordination number change toward the middle of the series.

All the observed variations in K_c can be grouped in three ways[97]. The first and simplest is a monotonic increase in K_c which is readily explained in terms of an electrostatic model. The remaining two groups are less regular. K_c either increases to a plateau value around Gd^{3+}, group 2, or increases to a maximum at the same ion with a subsequent decrease in magnitude, group 3. Quite by accident all of the ligands for which a kinetic study has been done fall into the last group (e.g. murexide complexes, Fig. 7).

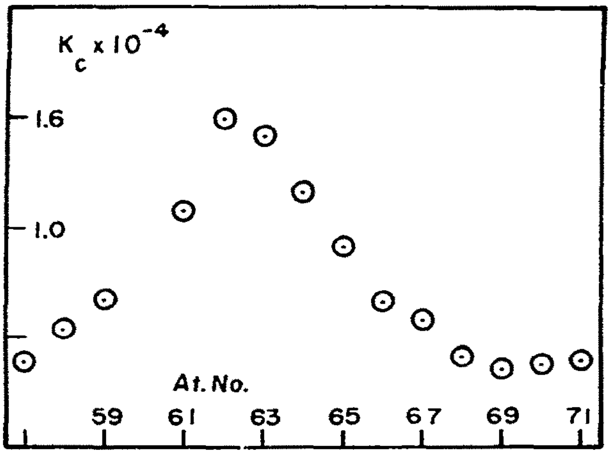

Fig. 7. Plot of K_c for RE–murexide complexes versus atomic number typical of the third type of relationship exhibited by all ligands studied kinetically.

In order to explain the departure from the monotonic electrostatic dependence, a number of factors have been considered. Included among these factors are ligand field stabilization effects, steric effects, changes in the coordination number of the RE cation, and differences in the coordinating abilities of the ligands. Ligand field effects are quickly disposed of as a possibility in that enthalpies of complexation show both stabilization and destabilization relative to those for La^{3+}, Gd^{3+} and Lu^{3+} for which LF effects would be zero[102] (but see ref. 103). Steric and ligand coordinating abilities can perhaps also be dismissed as relatively unimportant since the onset of the irregularity is always around Gd^{3+} and is never abrupt[4]. The remaining effect of importance is therefore the change in coordination number of the cation. Why it should not occur among those complexes in the first group may well be one of relative magnitude since the energy difference brought about by the change in coordination is only one term in the total energy picture.

Just as it cannot be said that it has been proved that the change in coordination number is the cause of the irregularity, neither can it be concluded that the absolute coordination number of any ion in the series is known. With a few exceptions the weight of experimental evidence would seem to lie in favor of this explanation and the most popular interpretation of the change in coordination number appears to be from nine, among the early, light RE, through a nine–eight statistical ratio in the middle, to eight-coordination among the heaviest RE ions[104]. The sources of the experimental support for this concept can be found in heats and entropies of complexation[4], conductance[49], electronic spectra[105], partial molar volumes[104, 106], entropies of solvation[107], and X-ray structural analyses[97]. Opposing this idea are the results from the determination of the entropies of the RE ions in aqueous solution, which give no indication of a coordination number change[108].

The kinetic results, we believe, are not definitive enough to be used in support of the conviction that a coordination number change will account for the irregularity. Perhaps our opinion would change if complexes from the other two groups were studied kinetically. At present however we prefer to think in terms of using this other evidence to assist us in making the decision that the variation in rate constants with atomic number is not a consequence of a change in mechanism.

H. CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

At present the results from kinetic studies in which the sound absorption technique is used are at the same time encouraging yet unsatisfactory. Much remains to be done and can be done using the techniques available. Inadequacies exist both experimentally and mathematically. The next important advance can be expected when the accuracy of the data is improved over the present available range, particularly at the low- and high-frequency limits. There is no way in which to escape the problem that a mechanism must first be assumed before a sound spectrum can be interpreted. However, we must feel encouraged that there is some semblance of a correlation between results from acoustics and the transient relaxation techniques.

Profitable pursuits which should be encouraged can be grouped into two categories. In the first we would favor an increase in activity in the study of solute equilibria in non-aqueous solvents. Much remains to be learned about the mechanisms of complexation reactions in these media and in particular in reference to outer ion-pair formations. The second category is of course aqueous solutions. It is firmly believed by many able solution chemists[109] that volume changes are more informative than enthalpy or entropy changes with regard to solute–solvent interactions. One should not overlook the significance of the volume of activation in giving us more information about the structure and solvation of the transition state. Some really definitive high-pressure studies are called for, hopefully in the relatively near future. Of more specific and immediate interest to us are the lanthanide complexation reactions. This group of ions offers the one real possibility for comparing results from different relaxation techniques. Serious consideration must be given to duplicating the systems for study by more than one technique, whatever the experimental difficulties. Over the short haul this could be one of the most gratifying developments in fast solution kinetics.

The contents of this review must not be considered exhaustive and we apologize to any of our colleagues and personal friends who might feel slighted by our omissions.

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