



Studies of Metal Complex-Halide Exchange Equilibria.

by

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B.Sc. (hons) University of Adelaide, 1971.

Thesis presented for the degree of

Doctor of Philosophy.

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November, 1975.

This thesis contains no material previously submitted for a degree or diploma in any University, and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference is made in the text.

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November, 1975.

ACKNOWLEDGEMENTS

I wish to thank my supervisor Dr. S.F. Lincoln for continued help and advice concerning the work contained in this thesis. I am also indebted to Professor D.R. Stranks for providing much helpful discussion and criticism on the broad-line work and the electrostatic model. I also gratefully acknowledge Prof. H. Strehlow for kindly sending a listing of the original electrostatic energy computer program. I must also thank Mr Evan Williams for his valuable assistance on the operation of the Brucker HX90E N.m.r. spectrometer and for his help with computing. I am grateful for some more specific advice from Mr. Murray Peake on matrices and their inversions. I also thank the Australian Research Grants Committee and the Commonwealth Postgraduate Award Committee for support. Finally I must thank Mrs. D.A. Crozier for typing the first four chapters of this manuscript and Miss Kathy Whittall for typing the last chapter.

Summary

The introduction to this thesis reviews the past work concerned with halides exchanging on cation-halide complexes with specific emphasis on those studies in which rate parameters for such exchange processes are derived (Chapter 1).

Chapter 2 describes broad-line n.m.r. investigations of group(III)-tetrachloro complexes:

The equilibria between gallium(III) species were investigated by ^{71}Ga n.m.r., and the chloride exchange rates determined by ^{35}Cl n.m.r. for solutions of 11.0 and 7.00M chloride concentrations, in which the ratio $[\text{HCl}]:[\text{LiCl}]$ was varied over a wide range. The chloride exchange dynamics are rationalized in terms of an associative exchange of chloride on $[\text{GaCl}_4]^-$. In 11M HCl: $k'_{\text{ex}}(298\text{K}) = (164 \pm 8) \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$; $\Delta H^\ddagger = 30.1 \pm 1.5 \text{ kJ mol}^{-1}$; and $\Delta S^\ddagger = -44 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$. The parameters describing chloride exchange on indium(III), determined as above are: $k(298\text{K}) = (8.8 \pm 0.4) \times 10^6 \text{ s}^{-1}$, $\Delta H^\ddagger = 45.7 \pm 2.3 \text{ kJ mol}^{-1}$, and $\Delta S^\ddagger = 42 \pm 8 \text{ J K}^{-1} \text{ mol}^{-1}$; and $k(298\text{K}) = (2.0 \pm 0.1) \times 10^6 \text{ s}^{-1}$, $\Delta H^\ddagger = 37.7 \pm 1.9 \text{ kJ mol}^{-1}$, and $\Delta S^\ddagger = 3 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$ in 10.95 and 7.00M aqueous HCl respectively, calculated from the observed exchange rate - $k_{\text{ex}} 4[\text{InCl}_4(\text{H}_2\text{O})_2^-]$. For thallium(III) lower limits of $k_{\text{ex}}(219) = 1.6 \times 10^6 \text{ s}^{-1}$ and $1.3 \times 10^6 \text{ s}^{-1}$ were obtained in 10.95 and 7.00M aqueous HCl respectively, where $[\text{TlCl}_6]^{3-}$ is assumed to be the exchanging species. For zinc(II), the lower limit of $k_{\text{ex}}(235\text{K}) = 1.92 \times 10^5 \text{ s}^{-1}$ was obtained in 11.8M HCl, where $[\text{ZnCl}_4(\text{H}_2\text{O})_2]^{2-}$ is assumed to be the exchanging species

For both aluminium(III) and beryllium(II) no chloride exchange broadening was observed.

In chapter 3, theoretical calculations of the electrostatic energies of the gallium(III)-halide complexes with Born hydration terms included (assuming an electrostatic model) also suggest that the associative pathway provides the most probable exchange mechanism. An activation energy of 83 kJ mol^{-1} is calculated for this pathway, as opposed to 273 kJ mol^{-1} for the dissociative pathway. It is also shown that for such an associative mechanism, there is a decrease in the activation energy for chloride exchange on the tetrachloro species, as the cation radius increases.

Chapter 4 contains high resolution ^{19}F n.m.r. work in which the quartet resulting from ^{19}F (spin 1/2) coupling with ^7Be (spin 3/2), is observed to collapse with increasing temperature; this collapse is governed by a chemically controlled relaxation process, and so activation parameters can be obtained. Solutions used for measurements contain $4.5\text{M } [\text{F}^-]$ with the $[\text{Be}^{2+}]$ ranging from 0.25 to 0.9M. The data fits a two term rate equation and the proposed mechanism thus involves two reaction pathways contributing to the observed rate. A dissociative pathway with $k_1(298\text{K}) = 69 \pm 3 \text{ s}^{-1}$, $\Delta H^\ddagger = 29.9 \pm 3.0 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -110 \pm 10 \text{ J K}^{-1} \text{ mol}^{-1}$; and for the associative pathway involving a fluoride bridged intermediate, $k_2(298\text{K}) = (1.6 \pm 0.5) \times 10^3 \text{ l M}^{-1} \text{ s}^{-1}$, $\Delta H^\ddagger = 26.2 \pm 3.0 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -96 \pm 9 \text{ J K}^{-1} \text{ mol}^{-1}$. Electrostatic energy calculations for the $\text{Be}^{2+}/\text{F}^-$ system, similar to those carried out on $\text{Ga}^{3+}/\text{Cl}^-$ structures

in Chapter 3 are also included, and electrostatic energy values for structures presented, and theoretical mechanisms compared.

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CHAPTER 1

INTRODUCTION



INTRODUCTION

The halide exchange on a complex cation species in solution results in no net change in the free energy of the system; it has this characteristic in common with the more general solvent exchange reactions in solution. As a consequence of being at thermodynamic equilibrium, only first order rate constants are directly derived from exchange studies of the sort:



where M is the metal cation and X is the halide. The asterisk simply describes an artificial distinction between halides. Such a reaction *could* be studied by the classical method of creating a trivial net chemical reaction by isotopically labelling the halide, if the system is inert. This method has, in fact, been used to observe chloride exchange on platinum(IV)¹ and molybdenum(III)². However, in labile systems, this sort of reaction is much more conveniently studied using nuclear magnetic resonance (n.m.r.) and recognizing that n.m.r. line-shapes can be modified where dynamic molecular processes are involved; such processes may include the exchange of nuclei between chemically inequivalent sites, as above. Thus, if the nucleus is involved in some reversible chemical process which takes place in a time comparable with its relaxation time, a change in line shape will be effected. For the chloride, bromide, and iodide - nuclei that possess a quadrupolar moment - it is therefore possible to follow fast chemical processes that are comparable with the rapid relaxation times of these halides. The

special case of fluoride is considered further below.

Since these halide nuclei *do* produce broad signals, there has been little work published as a consequence of the difficulty involved in detection and resolution of the signals. Masudu³ measured the ³⁵Cl chemical shifts and relaxation time for the series SiCl₄, TiCl₄, CrO₂Cl₂ and VOCl₃, in what is probably the earliest use of n.m.r. in this study. Some of the earliest and most basic work involving n.m.r. studies of halogen exchange, was that done by Hertz⁴ in which the complex equilibria of Br⁻ with Hg²⁺, Zn²⁺ and Cd²⁺ were studied. Use was made of the fact that both chloride and bromide exist as the isotopes ³⁵Cl, ³⁷Cl and ⁷⁹Br, ⁸¹Br, to take comparative measurements of the line widths of each isotope and to consequently establish the value of T_{2B}τ_B where T_{2B} refers to the Transverse relaxation time in the bound site and τ_B is the correlation time for the halide in this state. Rate constants for the equilibria of the type:



were therefore calculated, and the resulting values for equilibrium constants enabled estimates of the proportions of the various species M²⁺, [MX]⁺, [MX₂], [MX₃]⁻ and [MX₄]²⁻ to be made. The orders of magnitude of the pseudo first order rates of this rapid reaction were given as $\approx 10^6 - 10^7 \text{ sec}^{-1}$. Such calculations did not yield activation parameters for the actual halide exchange between the free state and the complex species.

(i) Halide Exchange on Paramagnetic Species

First reports of actual n.m.r. studies of the kinetics of direct halide exchange between bulk solvent environment and coordinated complex, appeared in the work of Zeltman and Morgan⁵, with their comparison of the aqua and chloro exchange for Fe(III) solutions, by observing ¹⁷O and ³⁵Cl resonances. They observed that the transverse relaxation for each species was controlled by the rate of chemical exchange of H₂O or Cl⁻ at the low temperature range, by the relaxation rate due to electron nuclear spin interaction at high temperatures, and by both processes in the intermediate range. This system could be analysed by using the Swift and Connick model⁶ to fit the experimental data with a theoretical curve. The curve of best fit gave the activation parameters for exchange. In a similar manner, the same workers investigated the aqua and chloro exchange for oxovanadium(IV)⁷ and cobalt(II)⁸ in aqueous hydrochloric acid solutions. Lincoln, Aprile, Dodgen and Hunt⁹ measured both aqua and chloro exchange in aqueous solutions containing nickel(II). The difficulty, both for this system and for those investigated by Zeltman and Morgan, is in determining the nature of the exchanging species. The aqua:chloro ratio for the complexes is difficult to unambiguously determine. Such systems represent an intermediate step between the pure solvent exchange n.m.r. studies described by Langford and Stengle¹⁰ and the halide exchange on tetrahedral halide complexes about which so little is known. Such a clear cut system in comparison to the above would appear to be the chloride exchange on the tetrachloro-cobalt(II) complex.

Gentzler, Stengle and Langford¹¹ examined the exchange as a function of pyridine concentration. For the simple $[\text{CoCl}_4]^{2-}$ in the absence of pyridine, the Cl^- exchange is too slow to affect the n.m.r. signal width. Apparently with the addition of pyridine, a $[\text{CoCl}_3\text{py}]^-$ species is formed - a much more labile species towards chloride exchange.

(ii) Halide Exchange on Diamagnetic Species

The above exchange systems have all been concerned with a paramagnetic nuclear spin relaxation mechanism. This represents only one limiting case for the more general Swift and Connick formulation of the 2 site exchange. Most work with diamagnetic species has concentrated less on the actual rates of exchange of the halide ligands, because of the experimental difficulties involved, and more on the elucidation of the equilibrium constants for the various complex aqua-halo-diamagnetic species. Because of this emphasis, the halide exchange rates are less well known, but the nature of the species in solution is more certain. Halide broad-line n.m.r. can therefore be employed with more confidence.

Gallium(III) aqua and chloro species have been investigated by n.m.r.^{12,13}, Raman^{14,15} and X-ray¹⁶ studies, and the stoichiometry of $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{GaCl}_4]^-$ well established. The equilibria between aqua-chloro-gallium(III) species were demonstrated in 1965 by Akitt, Greenwood and Storr¹⁷, using ^{71}Ga n.m.r. In the same year the chloride complexes of thallium(III) in aqueous solution, were investigated by Spiro¹⁸, using Raman spectroscopy. At about the same time Cannon and Richards¹⁹, by

using ^{115}In n.m.r. *did* include estimates of exchange rates for



where X = F, Cl, Br, I.

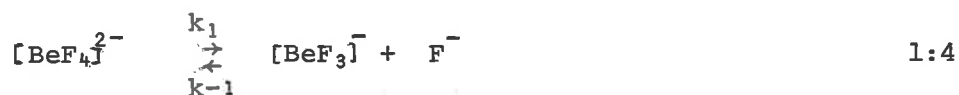
This was achieved by observing the exchange broadenings of the ^{115}In peak. A calculation of the exchange rate for $[\text{InCl}_4]^-/\text{Cl}^-$ was also attempted, although the authors realised a hydrated indium(III) exchanging species would be more likely: namely $[\text{InCl}_4(\text{H}_2\text{O})_2]^-$. Dobud, Lee and Tuck²⁰ have studied the nature of the halogen species in mixed water, alcohol solutions, using radiochemical methods with special attention being given to Au(III), In(III) and Ga(III). Similar work, concerning the elucidation of the equilibrium constants for the complex aqua, chloro and bromo complexes has been carried out by recent workers²¹⁻²⁴. Recent studies employing indium-115 n.m.r. have been made by Fratiello, Davis, Peak and Schuster²⁵ and by Haraguchi, Fuwa and Fujiwara²⁶. Both groups investigated the nature of the indium(III)-halogen species, but the latter group's results are more relevant, in that line widths were used along with the chemical shifts to elucidate the chemical equilibria and the *chemical exchange* of indium(III)-halogen complexes in HCl, HBr and HI aqueous solution. The broad-line n.m.r. work contained in this thesis, examines the chloride exchange processes on diamagnetic cations (Ga^{3+} , In^{3+} , Tl^{3+} , Zn^{2+}). The Swift and Connick equation for the two site exchange with quadrupolar relaxation was used in calculating exchange rates. Bromide exchange studies were excluded for experimental reasons described in Chapter 5.

(iii) Fluoride Exchange

The basic difference between fluoride and the rest of the halides is that fluorine, with a spin of $1/2$, and possessing no quadrupolar moment, is a suitable nucleus to observe with the high resolution spectrometer; the ^{19}F resonance displays a similar character to the proton resonance. Tetrafluoroberyllate(II) ion in excess fluoride, was chosen for study, since it is one of the few simple fluoro-cation complexes stable and labile in aqueous solution. It was possible to obtain clear sets of experimental ^{19}F spectra showing the collapse of the quartet produced by fluorine, with a spin of $1/2$, coupling with the beryllium spin of $3/2$. To these spectra, were matched theoretical curves (developed for this study - see chpt. 4) simulating the collapse of the quartet, and accurate activation parameters were obtained.

Other n.m.r. studies of beryllium fluoride complexes have not been that extensive. Leane and Richards²⁷ and Blink and Levstek²⁸ have investigated using *p.m.r.*, $(\text{NH}_4)_2\text{BeF}_4$ in the solid state. Early reports on the spectra of aqueous BeF_2 solutions by Gutowsky and Hoffmann²⁹ were included as part of their survey on fluoride molecule chemical shifts. The quadruplet(quartet) ^{19}F signal was initially resolved by Francis and Lawrenson³⁰ in a qualitative ^{19}F study of ammonium tetrafluoroberyllate solutions. The temperature dependence of the ^{19}F quartet was briefly noted by Kotz, Schaeffer and Clouse and the spectra illustrating the collapse of the quartet for $[\text{BeF}_4]^{2-}$ and $[\text{BeF}_3]^-$ is reproduced³¹. Feeney, Haque, Reeves and Yue³² extended this ^{19}F study of $[\text{BeF}_4]^{2-}$ to include an

equilibrium constant determination ($K_c = (8.0 \pm 2.0) \times 10^{-2} \text{ mol. l}^{-1}$) for the dissociation reaction:



Rate constants for reaction schemes involving F^- exchanging on $[\text{BeF}_4]^{2-}$ and $[\text{BeF}_3]^-$ were also calculated by the line width method which is not strictly accurate. In a similar study Baldwin³³ calculated by line width methods, limits to the rate of fluoride exchange between beryllium-fluoride complexes and free F^- . And so, the work contained in this thesis, includes a *rigorous* analysis of the F^- exchange on $[\text{BeF}_4]^{2-}$, to yield reliable rate parameters.

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CHAPTER 2

BROAD-LINE N.M.R. STUDY OF CHLORIDE-CATION EXCHANGE SYSTEMS

BROAD-LINE N.M.R. STUDY OF CHLORIDE-CATION EXCHANGE SYSTEMS

Theory

Nuclear magnetic resonance measurements of the ^{35}Cl nucleus give a resonance signal of wide line width in comparison to signals from ^1H and ^{19}F nuclei. The chlorine nucleus, together with bromine and iodine, has an electric quadrupolar moment (their nuclear spins are $>\frac{1}{2}$) which results in the chlorine nuclei experiencing a fluctuating electric field gradient from adjacent nuclei. As a result of experiencing this dynamic field gradient, the precessing ^{35}Cl nuclei are relaxed from one spin state to another with greater ease. Because there *is* a fluctuating electric field gradient, the actual ^{35}Cl resonance frequency is less well defined and the signal produced is very broad. The ground state nuclear spins of halogen nuclei and of the proton and deuteron are shown in table 2:1 together with other nuclear properties.

The transverse relaxation time T_2 is related to the width (W) of the resonance signal at half height by the expression:

$$T_2 = 2/(W\gamma) \qquad 2:1$$

where W has units of Tesla

T_2 has units of seconds

γ is the magnetogyric ratio. For ^{35}Cl the value of γ is $2620 \times 10^4 \text{ rad. T}^{-1}\text{s}^{-1}$.

Broad-line n.m.r. measurements of the ^{35}Cl nucleus thus enable the

Table 2:1

Isotope	Natural abundance %	Resonance freq/MHz at 1T field	Sensitivity at const.field rel. to H=1.000	Ground State nuclear spin (h)	Nuclear elec. quad.moment/ barns (e x 10 ⁻²⁴ cm ²)
¹ H	99.985	42.5759	1.000	1/2	0
² D	0.015	6.53566	9.65 x 10 ⁻³	1	2.77 x 10 ⁻³
¹⁹ F	100.00	40.055	0.833	1/2	0
³⁵ Cl	75.53	4.1717	4.70 x 10 ⁻³	3/2	-7.89 x 10 ⁻²
³⁷ Cl	24.47	3.472	2.71 x 10 ⁻³	3/2	-6.21 x 10 ⁻²
⁷⁹ Br	50.54	10.667	7.86 x 10 ⁻²	3/2	0.33
⁸¹ Br	49.46	11.498	9.85 x 10 ⁻²	3/2	0.28
¹²⁷ I	100.00	8.5183	9.34 x 10 ⁻²	5/2	-0.69

Nuclear Properties of naturally-occurring halogen isotopes compared with hydrogen.¹

transverse relaxation time for this nucleus to be determined. When the ^{35}Cl nucleus alters its magnetic environment, it experiences a different transverse relaxation time. If the ^{35}Cl exchanges onto a diamagnetic cation in solution, it will change its environment from that of the bulk solvent to that of the first coordination sphere of the cation. Since the chemical bond itself can produce a large electric field gradient, the electric quadrupole moment of the ^{35}Cl nucleus couples with this. The stationary ^{35}Cl nucleus can now be thought of as being surrounded by a rotating electric field gradient coupled to its own quadrupolar moment. This results in the ^{35}Cl nucleus experiencing a fluctuating electric field which can more efficiently relax it. The broadening of the bulk ^{35}Cl signal produced by this relaxation, is proportional to the mole fraction (P_M) of coordinated chloride for rapid exchange processes where $P_M < 0.1$ and in this situation the bulk signal only, will be observed for the exchange process.

The line width (W_A) of this broadened bulk signal will be:

$$W_A = 2/(T_{2A}\gamma) \quad 2:2$$

where W_A has units of Tesla and T_{2A} is the transverse relaxation time (in seconds) for the broadened ^{35}Cl bulk signal.

The actual broadening ($W - W_A$) of the bulk signal is related to the induced transverse relaxation by:^{2,3}

$$T_{2ex} = 2 \times (\gamma\Delta)^{-1} \quad 2:3$$

where $\Delta = W - W_A$ 2:4

γ is as defined above. T_{2ex} is the derived transverse relaxation time for a ^{35}Cl nucleus in the process of exchanging onto and off the first coordination sphere of a metal ion.

From a consideration of the phenomenological Bloch equations for a nucleus in more than one site, Swift and Connick² have shown that for the above two site system in dilute solution:

$$T_{2ex} = \frac{\tau_M}{P_M} \left[\frac{(T_{2M}^{-1} + \tau_M^{-1})^2 + \Delta\omega_M^2}{T_{2M}^{-2} + (T_{2M}\tau_M)^{-1} + \Delta\omega_M^2} \right] \quad 2:5$$

where: T_{2M} is the transverse relaxation time of the Cl^- coordinated to the metal ion.

τ_M is the mean lifetime for the exchange of a Cl^- onto the cation.

$\Delta\omega_M$ is the difference in chemical shift of the coordinated Cl^- with the bulk Cl^- in solution.

P_M is the mole fraction of Coordinated Cl^- to total Cl^- .

In the systems examined, the cations were diamagnetic, and no chemical shifts were observed (limit of detection ca. 20ppm) for the sample bulk Cl^- compared with the solvent reference Cl^- . Relaxation occurs as described above, by coupling of the electric field gradient (eq) of the chemical bond, with the electric quadrupole (eQ). For this type of system, equation 2:5 simplifies into two different limiting cases.

- a) At low temperature the broadening is a direct function of the rate at which halide exchanges, since relaxation by T_{2M} is fast.

$$1/T_{2M}^2 \gg \Delta\omega_M^2, 1/\tau_M^2; 1/T_{2ex} = P_M/\tau_M \quad 2:6$$

- b) At high temperatures, the exchange rate is so rapid that relaxation effects are determined by the actual quadrupolar relaxation process.

$$1/(T_{2M}\tau_M) \gg 1/T_{2M}^2, \Delta\omega_M^2; 1/T_{2ex} = P_M/T_{2M} \quad 2:7$$

Therefore when measurements are taken over a large temperature range:

$$T_{2ex} = \tau_M/P_M + T_{2M}/P_M \quad 2:8$$

Now T_{2M} is controlled by the quadrupolar relaxation process,³

$$\text{viz. } T_{2M}^{-1} = (1 + \frac{\tilde{\eta}^2}{3}) (\frac{e^2 Qq}{\hbar})^2 \tau_c \quad 2:9$$

where eq and eQ are defined above as the electric field gradient and the electric quadrupole moment respectively.

$\tilde{\eta}$ is the nuclear quadrupole resonance parameter, which is here assumed $\ll 1$ (the case for CCl_4 and C_6H_5Cl)⁴ in the absence of a value determined for the system under study.

τ_c is the *correlation time* for the quadrupole induced relaxation process.

$\hbar$ is (Plank's constant)/ 2π

Equation 2:8 now becomes:

$$T_{2ex} = \tau_M / P_M + \frac{\hbar^2 (e^2 Qq)^{-2} (1 + \frac{\tilde{\eta}^2}{3})^{-1}}{P_M \tau_c} \quad 2:10$$

This equation has defined the situation for the two site exchange process and is used to fit a theoretical curve to the experimental points obtained by measuring values of T_{2ex} over a large temperature range (213K to 333K). The equation is a curve, as the chemical exchange term predominates at low temperature whereas the quadrupole term does at high temperature, with intermediate temperatures representing a balance in these terms to produce a curve.

Activation parameters can be derived from equation 2:10. The correlation time τ_M is simply the reciprocal of the first order rate constant. Thus, assuming a transition state model:

$$\begin{aligned} k_{ex} &= \tau^{-1} \\ &= \frac{k_b T}{h} \exp(-\Delta H^\# / RT + \Delta S^\# / R) \end{aligned} \quad 2:11$$

k_b is the Boltzmann Constant

h is Plank's Constant

R is the gas constant

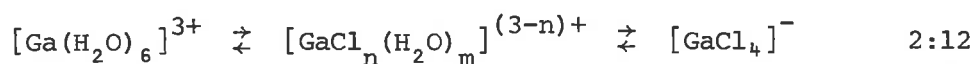
A plot of $\log (T_{2ex} \times P_M)$ against reciprocal temperature gives the rate constant at 298K and activation parameters, when the low temperature reaction rate component of the curve is considered. Similarly, activation parameters for the quadrupolar processes can be gained from the high temperature component of the curve.

(i) Chloride Exchange on Gallium(III)

RESULTS AND DATA TREATMENT

⁷¹Ga N.m.r. Studies.

The first series of ³⁵Cl n.m.r. measurements involved the chloride changing environment from bulk Cl⁻ to the gallium(III) species. Measurement of the ⁷¹Ga n.m.r. spectra were therefore made since information concerning the type of gallium(III) species in solution can be derived from the nature of the spectra. The equilibrium in aqueous gallium(III)-chloride solutions was established by Raman^{5,6} and n.m.r.⁷ studies and is the following:



(where n varies from 1 to 4)

The ⁷¹Ga nucleus with a spin of 3/2, will be relaxed *most* efficiently when it is surrounded by an asymmetric electric field gradient. When the gallium(III) is in a symmetrical environment however, it will experience an overall electric field gradient of zero since the vector sum of the individual gradients will be zero if symmetry exists. Consequently [GaCl₄]⁻, a symmetrical species, will have a sharp ⁷¹Ga peak which is downfield relative to the broader [Ga(H₂O)₆]³⁺ peak. The actual chemical shift is a result of the chlorides deshielding the gallium(III) nucleus, by decreasing the electron density around the nucleus, and thus causing the gallium(III) in [GaCl₄]⁻ to resonate downfield relative to the gallium(III) species of lower chloride coordination number.

^{71}Ga measurements were made on solutions of $[\text{H}^+]/[\text{Li}^+]$ and $[\text{Cl}^-]$ values corresponding to the solutions used for ^{35}Cl studies, however the $[\text{Ga}^{3+}]$ value was increased in order to obtain a better signal (see table 2:2). Results for 11M $[\text{Cl}^-]$ solutions (shown in Fig. 2:1) display a single, narrow peak 240 ± 10 ppm downfield from the $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$, for all acid concentrations (which compares with 257 ± 5 ppm for $[\text{GaCl}_4]^-$ of an earlier study⁷). It is therefore concluded that the predominant species in these solutions is $[\text{GaCl}_4]^-$. The discrepancy in shift values could occur because the gallium(III) concentrations are different for the two studies; it has been shown⁷ that the ^{71}Ga shift for $[\text{GaCl}_4]^-$ does vary by as much as 60 ppm together with line width variation, as the environment is varied.

The three 7M $[\text{Cl}^-]$ solutions each display a peak which corresponds to a $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$ peak and in the case of the 5.5 and 3.5M $[\text{H}^+]$ solutions, a downfield peak is also observed. The disappearance of the downfield peak with decrease in the acid content corresponds to a shift in equation 2:12 to the left; i.e. favouring the formation of the higher aqua-gallium (III) species. The variation in the width of the downfield peak results from rapid environmental averaging of $[\text{GaCl}_4]^-$ with lower chloro species, but the constant $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$ peak at each acid concentration indicates that such an averaging process does not include the hexaaqua species, which must be exchanging relatively slowly with the species to the right in equation 2:12. It has already been shown that these equilibria can be affected by addition of extra chloride in the form of MgCl_2 , to acid chloride solutions of gallium(III).⁷

Table 2:2

Composition of Solutions for ^{71}Ga n.m.r. Studies.

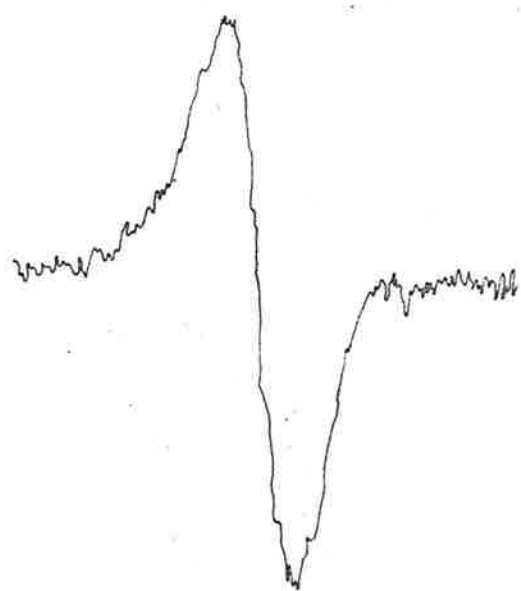
Soln.	$[\text{Ga}^{3+}] \text{ M}$	$[\text{H}^+] \text{ M}^a$	$[\text{Li}^+] \text{ M}^b$	$[\text{Cl}^-]_{\text{total}} \text{ M}$
i	0.50	9.5	0	11.00
ii	0.50	4.5	5.00	11.00
iii	0.50	1.00	8.50	11.00
iv	0.25	0.50	9.75	11.00
v	0.50	5.50	0	7.00
vi	0.50	3.50	2.00	7.00
vii	0.25	0.60	5.70	7.00

a, b formal hydrochloric acid and lithium chloride concentrations respectively.

Figure 2:1

^{71}Ga N.m.r. spectra of gallium(III) - chloride solutions. All solutions are stoichiometrically 0.5M in GaCl_3 except (vii) which is 0.25M, and the hydrochloric acid and lithium chloride concentrations are respectively (i) 9.50 and 0, (v) 5.50 and 0, (vi) 3.50 and 2.00 and (vii) 0.60 and 5.65M.

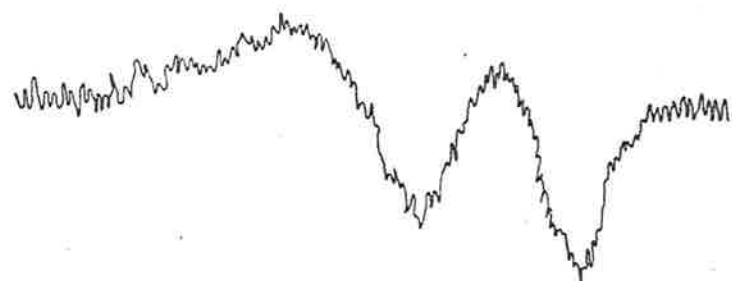
(i)



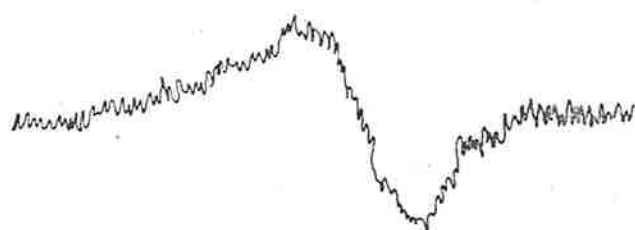
(v)



(vi)



(vii)



PPM

0

1

200

400

³⁵Cl N.m.r. Studies.

Results from the ⁷¹Ga n.m.r. study, as well as the ⁷¹Ga work of Akitt *et al*⁷, and Raman studies^{5,6}, demonstrate that in HCl solutions of 11M concentration the gallium(III) exists in solution as a tetra-chlorogallate(III) species. Therefore in determining rate constants for the chloride exchange on gallium(III), it was assumed that the coordination number is 4. Measurements of the chloride exchange rate on [GaCl₄]⁻ were carried out using ³⁵Cl n.m.r. spectroscopy for chloride concentrations of 11 and 7M. Gallium(III) concentration was varied between 0.10 - 0.30M and 0.05 - 0.15M for the two chloride concentrations respectively. The bulk ³⁵Cl resonance signal widths were broadened in the expected manner by the addition of the gallium(III) and advantage was taken of the proportionality between this broadening and the gallium(III) concentration, to produce reasonably broad sample signals relative to the reference, for all temperatures. This ensures that the error in broadening is kept low. It matters only that the mole fraction of coordinated chloride(P_M) is kept less than about² 0.1.

A plot of log P_M^T_{2ex} against reciprocal temperature for all solutions (see tables 2:3 and 2:4) shows the typical temperature dependence expected from equation 2:10. These curves (fig.2:2 & 2:3) are therefore all consistent with an environmental averaging occurring between the bulk and coordinated chloride sites. The use of equation 2:10 in the analysis of results is supported for solutions viii - xiv by the lack of any chemical shift of bulk ³⁵Cl (limit of detection *ca.* 20 ppm) from the ³⁵Cl

Table 2:3

³⁵Cl n.m.r. Kinetic Data and Solution Compositions 11.00M

total [Chloride] solutions.^a

Soln.	[H ⁺] M	[Li ⁺] M	10 ⁻⁴ k _{ex} (298K) ^b s ⁻¹	10 ⁻³ k' _{ex} (298) ^c M ⁻¹ s ⁻¹	ΔH [#] kJ mol ⁻¹
viii	9.80-10.70	0	180 ± 9	164 ± 8	30.1 ± 1.5
ix	5.80- 6.70	4.00	97 ± 5	88 ± 5	16.3 ± 1.0
x	3.00- 3.7	7.00	83 ± 4	75 ± 4	16.7 ± 1.0
xi	0.40- 0.70	10.00	250 ± 1.0	227 ± 1.0	19.7 ± 1.0

	ΔS ^{#b} J mol ⁻¹ K ⁻¹	ΔS ^{#c} J mol ⁻¹ K ⁻¹	10 ¹² τ _c (298K) s ⁻¹	E _Q kJ mol ⁻¹
viii	-24±5	-44±5	16±2	17.6±1.5
ix	-76±4	-96±4	24±2	23.5±1
x	-76±4	-96±4	24±2	23.4±1
xi	-56±3	-76±3	30±2	26.7±1

^a The total [chloride] was adjusted to 11.00M and 7.00M respectively with hydrochloric acid and gallium(III) chloride solution as described, in the experimental section.

^b Calculated from the pseudo first order rate expression,
Rate = k_{ex} 4[GaCl₄⁻].

^c Calculated from the pseudo second order rate expression,
Rate = k'_{ex} 4[GaCl₄⁻][Cl⁻].

Table 2:4

^{35}Cl n.m.r. Kinetic Data and Solution Compositions.

7.00M total $[\text{chloride}]^-$ solutions^a

Soln.	$[\text{H}^+]$	$[\text{Li}^+]$	$10^{-3}k_{\text{ex}}(298\text{K})^b$	E_a
	M	M	s^{-1}	kJ mol^{-1}
xii	6.28	0	430 ± 30	28.9 ± 1.5
xiii	3.28	3.00	47 ± 3	43.9 ± 2.0
xiv	0.28	6.00	11 ± 0.5	51.0 ± 2.0

^a The total $[\text{chloride}]$ was adjusted to 11.00M and 7.00M respectively with hydrochloric acid and gallium(III) chloride solution as described, in the experimental section.

^b Calculated from the pseudo first order rate expression,

$$\text{Rate} = k_{\text{ex}} 4[\text{GaCl}_4^-].$$

Figure 2:2

^{35}Cl N.m.r. $\text{P}_{\text{M}}\text{T}_{2\text{ex}}$ data for 11M total chloride solutions (viii) (o) and (x) (●). (____), Best fit of data to Swift and Connick two-site equation (eqn. 2:10). The hydrochloric acid and lithium chloride concentrations for the solutions are respectively (viii) 9.80 - 10.70 and 0, and (x) 3.00 - 3.70 and 7.00M.

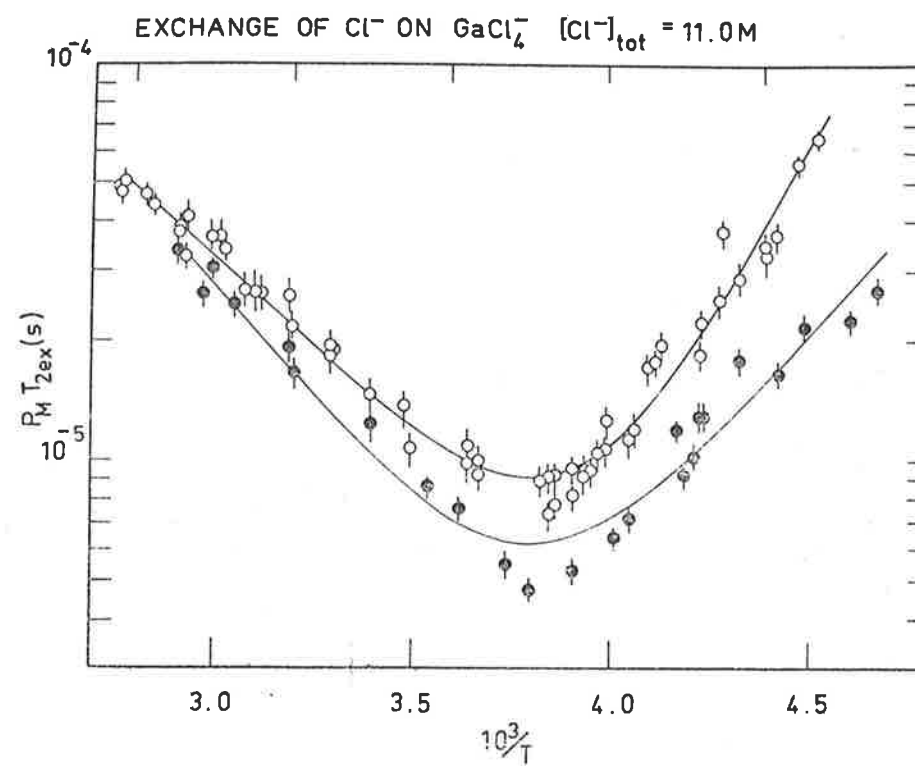
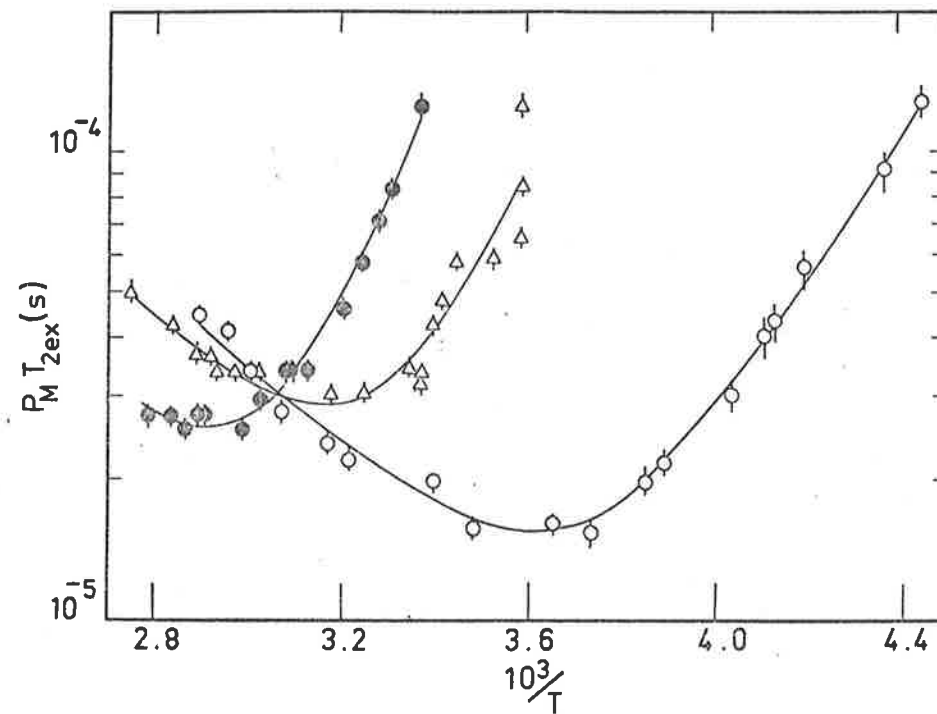


Figure 2:3

^{35}Cl N.m.r. $P_{M-2ex}T_2$ data for 7M total chloride solutions (xii) (o), (xiii) (Δ), and (xiv) ($\bullet$). (____), Best fit of the data to equation 2:10, the Swift and Connick two-site equation.

The hydrochloric acid and lithium chloride concentrations for the solutions are respectively (xii) 6.28 and 0, (xiii) 3.28 and 3.00 and (xiv) 0.28 and 6.00M.

EXCHANGE OF Cl^- ON GaCl_4^- $[\text{Cl}^-]_{\text{tot}} = 7.0\text{M}$



resonance in reference solutions. Evidence for the quadrupolar mechanism for ^{35}Cl relaxation was also found when the spectrometer frequency was halved from 4.17MHz to 2.085MHz. A constant value of $T_{2\text{ex}}$ (294K) for solution (viii) was obtained, rather than a change in the rate of relaxation on frequency change, which would occur if there was a shift dependent relaxation mechanism in operation.

The rate of exchange is given by equation 2:13:

$$\text{rate} = k_{\text{ex}} [\text{GaCl}_4^-] \quad 2:13$$

with rate parameters being derived from the low temperature component of the curve. The results for 11M $[\text{Cl}^-]$ are presented in table 2:3. A value for τ_c is calculated from the high temperature component of the 11M $[\text{Cl}^-]$ curves assuming a value for e^2Qqh^{-1} of 32.2MHz (the value obtained from $\text{Ga}^+[\text{GaCl}_4]^-$ data.⁸ The associated activation energy (E_q) for the quadrupolar relaxation, is also calculated directly from the gradient of the high temperature curve component. These E_q values are larger than values obtained for pure CCl_4 and TiCl_4 .⁹ However, they would appear to be similar to reported values for metal complexes in solution.¹⁰ The higher value could reflect some modification in the molecule tumbling process, as a result of solvation and such a modification could also account for the differing τ_c values for solutions viii - xi.

The activation energy calculation for the 7M $[\text{Cl}^-]$ system (table 2:4) assumed a coordination number of 4 chlorides around the gallium(III)

for the purpose of comparison, even though in these solutions the actual species type is in doubt. The distribution of T_{2ex} values obtained over the temperature range however, indicates that the two site exchange process is still in operation and that the use of equation 2:10 is valid. Bulk chloride is relaxing on a single gallium(III) species, for each $[H^+]/[Li^+]$ ratio despite the obvious differences between the data sets characterizing each of the three solutions. Values of $\Delta H^\ddagger$ for the 7M chloride exchange process are not calculated because of the likely possibility that such values will also contain enthalpy components resulting from the equilibria between low chloro content gallium(III) species present in solutions of this $[Cl^-]$.

DISCUSSION

Equation 2:12 defines the equilibrium between the gallium(III) chloro species and it should be realised that chloride exchange between the bulk and coordinated state is possible for each chloro species. However, *only* those exchange processes which occur at a sufficient rate - which is consistent with the use of equation 2:8 and 2:10 - induce observable ^{35}Cl relaxation of the free chloride ion.

It can be seen from the diagrams of the curves of $\log P_M T_{2ex}$ versus reciprocal temperature, that the maximum accurately detectable value of $T_{2ex} \approx 3 \times 10^{-3}s$ and since the maximum allowable value for $P_M \approx 0.1$, $P_M T_{2ex} \approx 3 \times 10^{-4}s$ is the maximum observable value of $\tau_M = k_{ex}^{-1}$ when the first term to the right of equation 2:10 predominates. This discussion

is necessarily restricted to those exchange processes detected through such ^{35}Cl relaxation. Examination of table 2:4 shows that for the 7M chloride exchange on gallium(III), the rate constants k_{ex} (298K) decrease simultaneously with a shift in the equilibrium 2:12, to the left. It is also evident that the k_{ex} values obtained for 11M chloride solutions (table 2:3) are greater than those analogous 7M chloride results. This situation is consistent with the exchange of a chloride on $[\text{GaCl}_4]^-$, being the most predominant form of free chloride relaxation in 11M and 7M solutions. The following arguments develop this reasoning in detail.

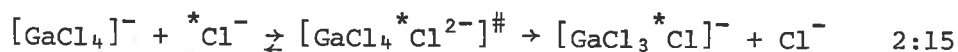
11M Chloride Exchange.

For the four solutions, the exchange process of chloride on $[\text{GaCl}_4]^-$ is characterized by a large, negative entropy of activation. In general, for the exchange of chloride, two limiting reaction mechanisms can be postulated:

The dissociative D scheme -



The associative A scheme -



Very approximate theoretical values of $\Delta S^\ddagger$ can be derived for these two mechanisms, by assuming that the two cases are purely electrostatic

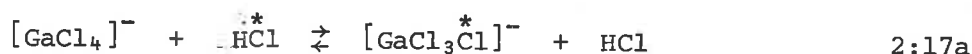
in nature and thus using the Born equation for ions of charge z and radii r interacting across a dielectric medium of dielectric constant D , namely:¹¹

$$\Delta S = \frac{z^2}{2Dr} \left(\frac{\partial D}{\partial T} \right) \quad 2:16$$

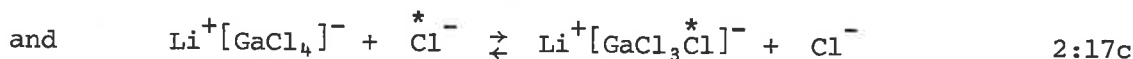
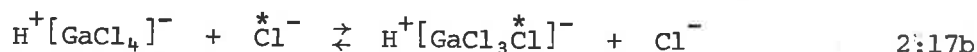
At 298K it is assumed that $(\partial D/\partial T) = -0.0046$ (value for water) and $r_{\text{Ga}^{3+}} = 0.62\text{\AA}$ and $r_{\text{Cl}^-} = 1.81\text{\AA}$. Thus, for the D process, the electrostatic contribution $\Delta S_{\text{el}}^{\#} = -13 \text{ J K}^{-1}\text{mol}^{-1}$. For the A process, $\Delta S_{\text{el}}^{\#} = -5 \text{ J K}^{-1}\text{mol}^{-1}$. A further term which defines the entropy due to the species themselves, rather than the entropy of the coordinated species, must also be considered. This is the so called cratic entropy¹¹ and for the D process it is $+33 \text{ J K}^{-1}\text{mol}^{-1}$. For the A process it is $-33 \text{ J K}^{-1}\text{mol}^{-1}$. Thus, for the overall entropy, the two contributions are added. For the limiting D reaction $\Delta S^{\#} = +33 - 13 = +20 \text{ J K}^{-1}\text{mol}^{-1}$ whilst for the A reaction $\Delta S^{\#} = -33 - 5 = -38 \text{ J K}^{-1}\text{mol}^{-1}$. Now since the observed values for the entropy vary from -24 to $-76 \text{ J K}^{-1}\text{mol}^{-1}$, it is reasonable to reject the wholly dissociative mechanism. The above calculation does not consider more specific effects of solvent on solute. It is assumed however, that non-electrostatic chloride-solvent interaction will be present in both ground and transition state for the two postulated mechanisms. The entropy term contributed by the solvent interaction should thus be constant for the two energy states, so that the sign of $\Delta S^{\#}$ for the D mechanism as calculated, using the Born model, is unlikely to be reversed. The D type mechanism is therefore excluded from sub-

sequent discussion.

The variation of the activation parameters with change in the $[H^+]/[Li^+]$ ratio necessitates more subtle interpretation than does the *sign* of $\Delta S^\ddagger$. Table 2:3 shows a variation by only a factor of 3, for k_{ex} , but the enthalpy ($\Delta H^\ddagger$) and entropy ($\Delta S^\ddagger$) of activation display marked differences for the various solutions. It would appear that the kinetic variations are not due to significantly different bulk properties of HCl and LiCl solutions, which have similar osmotic and activity coefficients, and hydration numbers for the concentrations involved.¹² Nor, it seems, can the HCl molecule act, as in the reaction:



since the HCl molecular proportion, even in 10.5M HCl, is only 0.3%. Another possibility is cationic association with $[GaCl_4]^-$ giving two concurrent paths for the associative reaction:



Such a mechanism is incompatible with the constant values for the rate for solutions ix and x, compared with the large increase in k_{ex} for solutions viii and xi. It seems, therefore, that pathways which include a pre-equilibrium $H^+[GaCl_4]^-$ or $HCl[GaCl_4]^-$ species, are excluded from

consideration. This can be contrasted with the case for iron(III) chloride where the suggested mechanism¹³ for chloride exchange has an acid dependence of the form $k_{\text{ex}}^4 [\text{FeCl}_4^-] a_{\text{HCl}}$. Pathway (c) cannot be justified either, since it could be thought that increased $[\text{Li}^+]$ would decrease the activation energy for the exchange, by formation of the $\text{Li}^+[\text{GaCl}_4]^-$ species. The expected dependence is not observed.

Since the activation parameters *are* affected by changes in the H^+ and Li^+ concentrations, a more subtle interaction must be assumed; namely, that the ions have different influences upon the secondary coordination sphere of $[\text{GaCl}_4]^-$. There is, for the $[\text{GaCl}_4]^-$ system, an enthalpy-entropy balance, in which changes in the $\Delta H^\ddagger$ value are compensated by changes in the $\Delta S^\ddagger$ value. This process has also been observed for solvent exchange and ligand exchange reactions on a variety of metal ions,¹⁴ but the model proposed by Bennetto and Caldin¹⁴ to account for these dilute solution reactions can not be applied in the case of concentrated chloride solution. To explain the results, the HCl and LiCl interaction with the secondary solvation sphere must be different (even though their bulk solution properties are similar) and this interaction must affect the enthalpy-entropy balance for the associative exchange process so that the activation parameters will change as the solvent medium changes.

7M Chloride Exchange.

It has been shown that in 7M $[\text{Cl}^-]$ solutions of gallium(III), the aqua-chloro-gallium(III) species depends on the $[\text{H}^+]/[\text{Li}^+]$ ratio. It is

clearly shown from the ^{71}Ga data that a decrease in $[\text{H}^+]$ shifts the equilibria in equation 2:12 to the left. This shift cannot be caused by changes in the activity of water a_w , since this quantity remains virtually constant¹⁵ over the concentration range of the HCl-LiCl solutions. For the iron(III)-chloride exchange system it has been postulated that the 4 - coordinate $[\text{FeCl}_3(\text{OH}_2)]$ is preferred to $[\text{FeCl}_3(\text{OH}_2)_3]$ ¹³ in low a_w solutions. Equation 2:12 does incorporate this possibility as $[\text{GaCl}_3(\text{OH}_2)_3] \rightleftharpoons [\text{GaCl}_3(\text{OH}_2)]$ and the change in activity a_w in 7M and 11M chloride solutions could influence this equilibria.

It is possible that with gallium(III) existing in solution as several different species, relaxation of ^{35}Cl could occur as a consequence of exchange on lower chloro content species in addition to $[\text{GaCl}_4]^-$. The relaxation curves shown in fig. 2:3 however, are typical of those expected when ^{35}Cl relaxation occurs predominantly on a single species which, on the basis of the 11M data, is most likely to be $[\text{GaCl}_4]^-$. Thus it appears that whilst chloride exchange will occur on lower chloro species, the rate of such exchange is too small to induce significant ^{35}Cl relaxation of the free Cl^- species. (There is a possibility however, which should be noted, that in the fortuitous circumstance of a chloride exchanging on a lower chloro content species with a rate that is adequate to produce free ^{35}Cl relaxation, then it is unlikely that such a differing exchange process will be detected as a modification in the relaxation curve if the exchange processes are characterized by rates differing by not more than a factor of three, and by similar activation energies).

If the decrease in k_{ex} observed for the 7M solutions as $[\text{H}^+]$ decreases, is attributed predominantly to the concomitant decrease in $[\text{GaCl}_4^-]$, then as a first approximation, the rate of exchange k_{ex} for the 7M solutions can be equated to k_{ex} observed for the 11M chloride solution in which $[\text{GaCl}_4^-]$ is the predominant species. It now follows, since the observed first order rate constant is proportional to $[\text{GaCl}_4^-]$, that if $k_{\text{ex}} = 180 \times 10^4 \text{ s}^{-1}$ is chosen for the rate of exchange, then:

$$\frac{[\text{GaCl}_4^-]^{7\text{M}}}{[\text{GaCl}_4^-]^{11\text{M}}} = \frac{k_{\text{ex}}^{7\text{M}}}{180 \times 10^4} \quad 2:18$$

Thus, since the proportion of gallium(III) species existing as $[\text{GaCl}_4^-]$ in 11M media is assumed to be near 100%, then the above ratio is a measure of the proportion of $[\text{GaCl}_4^-]$ in each different acid solution for the 7M media. These mole fractions of gallium(III) existing as $[\text{GaCl}_4^-]$ are 0.239 (HCl = 6.28M), 0.026 (HCl = 3.28M, LiCl = 3.00M) and 0.0061 (HCl = 0.28M, LiCl = 6.00M). The relaxation curves can now be normalized, knowing the correct concentration of $[\text{GaCl}_4^-]$ rather than assuming that all gallium(III) is present as $[\text{GaCl}_4^-]$. The shift, however, of the curves along the horizontal temperature axis, gives a different high temperature component for each of the 7M solutions. A different tumbling time τ_c thus characterizes these solutions. $10^{12}\tau_c$ (298K) for the above solutions respectively is 6.1, 66 and 240s^{-1} .

The above estimates of $[\text{GaCl}_4^-]$ mole fractions, and qualitatively similar ones obtained from other 11M k_{ex} values, ignore variations in

activity of the chloride ion, but are consistent with the significant change in proportions of the chloro-gallium(III) complexes as revealed by ^{71}Ga n.m.r. measurements. The calculated τ_c values are of an order of magnitude expected from the l1M data and qualitatively indicate a definite decrease in the tumbling rate of $[\text{GaCl}_4]^-$ as $[\text{H}^+]$ decreases. This trend is also observed to a less obvious extent for the l1M solutions. It may be possible that an ion association is taking place between $[\text{GaCl}_4]^-$ and the lower aqua-chloro species, (probably $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$) and this becomes important as a factor in increasing τ_c as $[\text{H}^+]$ decreases in 7M solutions. This explanation however, is only a qualitative one and it is inappropriate to consider it in any further detail. The changing value of the activation energy for the chemical exchange in 7M chloride media probably results from the ΔH associated with the equilibria between aqua-chloro species in equation 2:12.

The associative mechanism as described by the examples of equations 2:17a, 2:17b and 2:17c is not completely unexpected for the $[\text{GaCl}_4]^-$ species, as there are a number of cases of this sort of mechanism operating in metal complexes where the maximum coordination number is not exhibited.¹⁶ Such exchange of chloride on $[\text{GaCl}_4]^-$ also becomes quite reasonable in view of the apparently associative solvent exchange and ligand substitution mechanisms observed¹⁷⁻²⁰ for $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Ga}(\text{DMF})_6]^{3+}$ systems. The greater lability of $[\text{GaCl}_4]^-$ (compared with the lower chloro complexes of gallium(III)) as suggested by the relaxation curves for 7M $[\text{Cl}^-]$, is consistent with similar trends observed in aqueous chloride solutions of iron(III)¹³, vanadium(III)²¹ and cobalt(II)²², and

also in the cobalt(II)-thiocyanate system²³. The tetrahedral iron(III) and cobalt(II) chloro and thiocyanato species have much greater rates of ligand exchange, than the hexa-aqua, aqua-thiocyanato and aqua-chloro octahedral species of those same cations. This effect is also clearly observed in the gallium(III) system. The chloride exchange on $[\text{GaCl}_4]^-$ proceeds at a rate of about 10^6 sec^{-1} (298K) but this rate drops to $1.8 \times 10^3 \text{ sec}^{-1}$ (298K) when a single water¹⁷ exchanges on the $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$ species. An explanation of this overall behaviour, presumes that the associative transition state is less energetically favourable for the sterically hindered octahedral species than for the tetrahedral species.

(ii) Chloride Exchange on Indium(III) and Thallium(III)

RESULTS AND DATA TREATMENT

³⁵Cl N.m.r. Studies.

For convenience in observation of the trends between activation parameter values, the indium(III) and thallium(III) studies are grouped together. A comparison of activation parameters for the first four group III elements is considered further below. Plots of $\text{Log } MT_{2\text{ex}}$ (where M is the cation molarity) against reciprocal temperature, for 10.95 and 7M chloride exchange on 0.05, 0.15M and 0.1, 0.15M respective indium(III) concentrations, (see fig. 2:4) demonstrate that the ³⁵Cl relaxation occurs predominantly on one species. At low temperature τ_M (see eqn. 2:5 et seq.) predominates and at high temperature the quadrupolar term is most significant. Studies have shown that in indium(III) solutions with the above concentrations of chloride, the predominant species appears to be $[\text{InCl}_4(\text{H}_2\text{O})_2]^-$ ^{24,25} Chemical exchange parameters and the activation energy for the quadrupolar process E_q , are calculated assuming that there are 4 chlorides coordinated as in the species shown above. The first order rate equation is therefore given by equation 2:19:

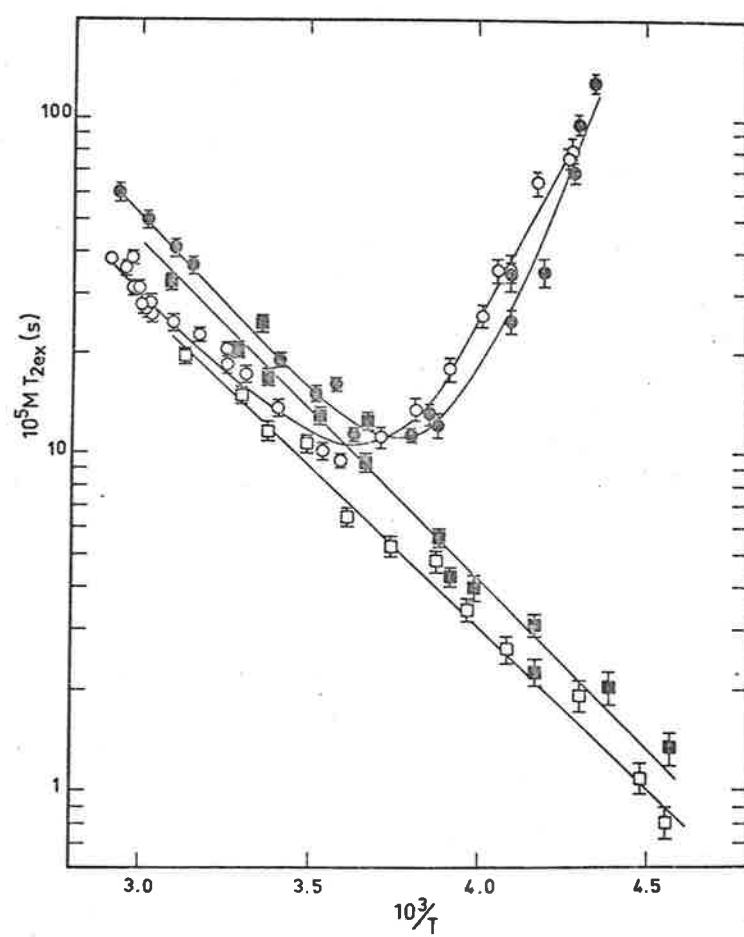
$$\text{Rate} = \tau_M^{-1} 4[\text{InCl}_4(\text{H}_2\text{O})_2]^- = k_{\text{ex}} 4[\text{InCl}_4(\text{H}_2\text{O})_2]^- \quad 2:19$$

Data on rate constants etc., does not lead to a knowledge of the stereochemistry of $[\text{InCl}_4(\text{H}_2\text{O})_2]^-$.

A plot of $\text{Log } MT_{2\text{ex}}$ against reciprocal temperature for solutions of 11M and 7M HCl with Tl³⁺ concentration 0.01, 0.04M and 0.005, 0.087,

Figure 2:4

^{35}Cl N.m.r. $\text{MT}_{2\text{ex}}$ data variation with $1/K$. The closed and open circles are datum points obtained in 10.95M and 7.00M hydrochloric acid respectively for the indium(III) system. The closed and open squares are datum points obtained in 11.00M and 7.00M hydrochloric acid respectively for the thallium(III) system. The solid curves represent the best fit of the Swift and Connick 2-site equation (2:10). $\text{MT}_{2\text{ex}}$ values were plotted rather than $P_{\text{MT}_{2\text{ex}}}$ since there is uncertainty about the actual chloride coordination number on thallium(III) and hence the value of the mole fraction (P_M).



0.019M respectively (see fig. 2:4) shows that the quadrupolar term dominates the curve for the entire temperature range. Because the curve has no contribution from the lower temperature rate controlled relaxation process, no actual values of kinetic activation parameters can be obtained. However, an upper limit for $\tau_M (= k_{ex}^{-1})$ can be evaluated (see table 2:5) by assuming that the lowest temperature MT_{2ex} datum points correspond to the point where the quadrupolar and kinetic terms, in equation 2:10 are equal in magnitude. The predominant species assumed responsible for relaxation is $[TlCl_6]^{3-}$.^{26,27} This gives a rate equation as follows:

$$\text{Rate} = \tau_M^{-1} 6[TlCl_6^{3-}] = k_{ex} 6[TlCl_6^{3-}] \quad 2:20$$

As there is some doubt as to the actual chloride coordination number, the lower limit for k_{ex} is also calculated assuming that $[TlCl_5]^{2-}$ is the predominant species. Therefore at 219K (lowest temperature recorded) $k_{ex} ([TlCl_5]^{2-}) \geq 1.9 \times 10^6 \text{ s}^{-1}$ and $1.6 \times 10^6 \text{ s}^{-1}$ in 11M and 7M hydrochloric acid respectively. Using the value of τ_c ($\sim 2 \times 10^{-11} \text{ s}$) obtained for the $[GaCl_4]^-$ system, approximate values for $e^2 Q q h^{-1}$ of 40M Hz and 37.5M Hz for indium(III) and thallium(III) respectively are obtained. These values have not, so far, been determined directly, but they are of the magnitude expected.²⁸

¹¹⁵In N.m.r. Studies.

As in the gallium(III) - chloride exchange system, a special 0.5M

Table 2:5

^{35}Cl n.m.r. Exchange Data for In^{3+} and Tl^{3+} .

M^{3+}	$[\text{HCl}]$ M	$10^{-4}k_{\text{ex}}$ (298K) s^{-1}	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ $\text{J mol}^{-1}\text{K}^{-1}$	E_Q kJ mol^{-1}
$^a\text{Ga}^{3+}$	11.00	$180 \pm 9 (15.4)^b$	30.1 ± 1.5	-24 ± 5	17.6 ± 1.5
In^{3+}	10.95	$884 \pm 44 (7.6)^b$	45.7 ± 2.3	42 ± 8	20.3 ± 1.5
In^{3+}	7.00	$203 \pm 10 (5.6)^b$	37.7 ± 1.9	3 ± 6	18.2 ± 1.3
Tl^{3+}	11.00	$\geq 160^b$	-	-	19.3 ± 1.5
Tl^{3+}	7.00	$\geq 130^b$	-	-	18.3 ± 1.1

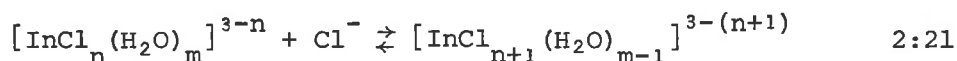
^{a} Data from table 2:3 - chloride exchange in this system is associative and characterized by: $\text{rate} = k'_{\text{ex}} 4[\text{GaCl}_4^-][\text{Cl}^-]$, but for comparison purposes the pseudo first order rate constant k_{ex} and $\Delta S^{\#}$ values are quoted.

^{b} at 219K.

$[\text{In}^{3+}]$ solution in 11M $[\text{Cl}^-]$ was prepared and the nuclear magnetic resonance of ^{115}In was observed in an attempt to elucidate the nature of the species in solution. Unfortunately, the signal turned out to be very weak at 0.5M $[\text{In}^{3+}]$. A solution of 2M $[\text{In}^{3+}]$ was tested using ^{115}In n.m.r., and a very broad signal could just be distinguished. The signal width was comparable with ^{71}Ga in 7M $[\text{Cl}^-]$ ($\approx 6 \times 10^{-5}\text{T}$) but the signal to noise ratio was so low that an adequate signal could not be obtained for reproduction. Extraction of this 2M $[\text{In}^{3+}]$ solution into ether and testing of the ether solution yielded a signal which was easily observable at normal settings; i.e. a signal was obtained that was similar to but slightly less intense than those observed for ^{71}Ga n.m.r. of 11M $[\text{Cl}^-]$ ($4.2 \times 10^{-5}\text{T}$).

DISCUSSION

The k_{ex} for chloride exchange on indium(III) in 10.95M hydrochloric acid is shown in table 2:5. The k_{ex} for exchange of chloride on gallium (III) is shown for the purpose of comparison. For the indium(III) data, the species in solution at this chloride concentration is considered to be $[\text{InCl}_4(\text{H}_2\text{O})_2]^-$. The slightly lower k_{ex} value obtained in the 7M hydrochloric acid, is probably a consequence of the proportion of indium(III) existing as $[\text{InCl}_4(\text{H}_2\text{O})_2]^-$ decreasing for the 7M chloride medium. The chloride could also be exchanging on lower chloro species which are apparently less labile. The overall system is described, according to equilibrium studies,^{24,25} by the equilibria:



(where $m + n = 6$; $n \leq 3$)

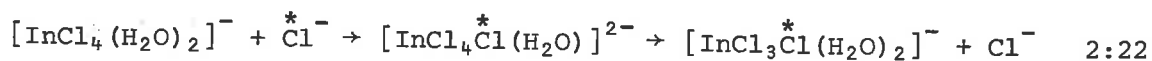
(A k_{ex}^* (298) of $7.45 \times 10^4 \text{ s}^{-1}$ in 2M chloride media calculated from the data of Cannon and Richards²⁹ indicates lower lability for lower chloro species. Such decreased rates of exchange on the lower chloride content species for indium(III) parallel the gallium(III) situation and similar trends are observed in the iron(III)¹³, vanadium(III)²¹, and cobalt(II)²² aqueous chloride systems). It is probable that the $\Delta H^\ddagger$ value observed in 7.00M hydrochloric acid contains contributions from the ΔH values typifying the above equilibrium. The nature of the 10.95M hydrochloric acid-indium(III) solutions, ensures that the $\Delta H^\ddagger$ value will be unlikely to contain any other enthalpy contributions, and can thus be interpreted more readily.

The actual magnitude of the $\Delta H^\ddagger$ value is large in the case of free chloride exchanging on $[\text{InCl}_4(\text{H}_2\text{O})_2]^-$ and, together with a more positive value for $\Delta S^\ddagger$ in comparison to the $[\text{GaCl}_4]^-$ system, suggests that there is a greater degree of bond breaking involved in the formation of the transition state, than is the case with chloride exchange on $[\text{GaCl}_4]^-$.

* These authors quote $k_{\text{ex}}(298\text{K}) = 3.74 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ in 2M chloride

for the exchange: $[\text{In}(\text{H}_2\text{O})_{6-x}\text{Cl}_3]^*^{3-x} + \text{Cl}^- \xrightleftharpoons{k_{\text{ex}}} [\text{In}(\text{H}_2\text{O})_{6-x}\text{Cl}_3]^*^{3-x} + \text{Cl}^-$

In the latter case the mechanism for exchange is thought to be completely associative. When the stereochemistry of the species involved is considered, the observations are not unexpected. Thus, the indium(III) is surrounded by 6 ligands which cause more steric hindrance towards increased coordination in the transition state than does $[\text{GaCl}_4]^-$ with only four chlorides and no aqua ligands surrounding the central cation. This does not eliminate the possibility that chloride exchange on $[\text{InCl}_4(\text{H}_2\text{O})_2]^-$ exhibits some associative character, but since it is not possible to reliably* assign the order of the chloride exchange rate on free chloride concentration, the degree of associative character remains uncertain. There is also a possibility of a sequential mechanism in addition to direct exchange of chloride on $[\text{InCl}_4(\text{H}_2\text{O})_2]^-$. The sequential mechanism is of the type:



This mechanism is indistinguishable from ordinary associative exchange, on the basis of the available equilibrium and kinetic data and cannot therefore be eliminated.

* The variation of k_{ex} in the 10.95M and 7.00M hydrochloric acid solution is consistent with a rate dependence upon $[\text{InCl}_4(\text{H}_2\text{O})_2]^-$ only or upon $[\text{InCl}_4(\text{H}_2\text{O})_2]^-$ and $[\text{Cl}^-]$. The K_4 values quoted for $[\text{InCl}_4(\text{H}_2\text{O})_2]^-$ vary considerably, and assignment of an order for $[\text{Cl}^-]$ is thus rendered doubtful value. There is also a considerable difference in a_w in 10.6M (0.256)³⁰ and (0.527)³⁰ hydrochloric acid, the effect of which upon k_{ex} is uncertain.

Observations of the ^{115}In nuclear magnetic resonance, did not yield conclusive evidence for the structure of the indium(III) species in solution. The quadrupolar moment of the ^{115}In , which is greater than that of ^{71}Ga ,¹ must have caused very efficient relaxation of the ^{115}In nucleus to occur in the asymmetric environment of the $[\text{InCl}_4(\text{H}_2\text{O})_2]^-$. (A very weak signal of width $>6 \times 10^{-5}\text{T}$ could just be distinguished above the noise level) N.m.r. measurement of an ether extract of the same solution, in which the indium(III) exists in a symmetric tetrahedral chloride environment, demonstrates the expected narrow intense signal type ($4.2 \times 10^{-5}\text{T}$.) characterizing a symmetrical environment.

In the case of thallium(III), the chloride exchange is rapid; in fact it has reached a rate such that over the entire temperature range, the chloride relaxation is dependent only on the quadrupolar process. Lower limits for k_{ex} have been determined for the 11M and 7M chloride concentrations assuming $[\text{TlCl}_6]^{3-}$ (or $[\text{TlCl}_5]^{2-}$). On the basis of a simple electrostatic model³¹ it might be anticipated that thallium(III) would have a greater lability towards exchange reactions than gallium(III) or indium(III), because it has the greatest radius and hence least charge density. On this basis the lability would increase with atomic radii in the sequence $\text{Ga}^{3+} < \text{In}^{3+} < \text{Tl}^{3+}$. Such a simple view will not suffice however, since for each cation the stereochemistry has to be considered and the actual lability will reflect both changes in the radius of the cation and the stoichiometry of the first coordination sphere. The predominant species in 11M $[\text{Cl}^-]$ changes on descending group (III), from $[\text{GaCl}_4]^-$ to $[\text{InCl}_4(\text{H}_2\text{O})_2]^-$ to $[\text{TlCl}_6]^{3-}$.

It must be with considerable caution that any mechanism for chloride exchange is postulated, with only lower limits of k_{ex} . There is evidence^{26,27} however, for preferential binding of two ligands in thallium (III) complexes and, coupled with electronic arguments,³² it suggests that $[\text{TlCl}_6]^{3-}$ may be tetragonally distorted. The 4 equatorial chloro ligands would be less strongly bound to the thallium(III) and therefore presumably more labile than the axial ligands. Of course there could be rapid reorientation of the tetragonal distortion, to produce an identical lability for all six ligands, as in the case of the copper(II) species.³³

No n.m.r. measurements could be attempted for ^{205}Tl in view of its possessing a resonance frequency of 24.57 MHz at 1 T, thus placing it outside of the range of operation of the probes; the highest frequency measurement possible with the interchangeable probes is 16 MHz at 1 T. (see experimental chapter) Also, the nucleus does not possess a quadrupolar moment and would not therefore be as definitive in the elucidation of likely complex structures as ^{71}Ga .

(iii) Chloride Exchange on Aluminium(III) and Beryllium(II)

Solutions of 1.0M aluminium(III) and 0.18M beryllium(II) in 11M HCl were examined using broadband ^{35}Cl n.m.r. In both cases, there was no exchange broadening of the bulk ^{35}Cl n.m.r. signal. It is concluded that the chloride exchange on the $[\text{AlCl}_4]^-$ species is retarded as a consequence of the large charge density on the aluminium(III) cation (it has the smallest radius of the group III cations) compared with the group (III) cations below it in the periodic table. The same simple electrostatic model can also explain the absence of exchange broadening of the bulk ^{35}Cl n.m.r. signal for beryllium(II). In this case, the surface charge density is greater than for the aluminium(III), despite the charge dropping to +2. This decrease in charge is more than compensated for by a decrease in cationic radius from $r_{\text{Al}^{3+}} = 0.5 \text{ \AA}$ to $r_{\text{Be}^{2+}} = 0.34 \text{ \AA}$. The beryllium(II) situation is complicated however, in that the species observed in aqueous solution is probably $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ - the tetrachloroberyllate(II) species being unstable in this environment.³⁴ Consequently if the beryllium(II) species is tetraaqua and offers no primary coordination site for chloride, then quadrupolar relaxation of the ^{35}Cl nucleus certainly cannot occur.

(iv) Chloride Exchange on Zinc(II)

RESULTS AND DATA TREATMENT

³⁵Cl Study.

A plot of $\log P_M^T \tau_{ex}$ versus reciprocal temperature, for solutions of 11.8M HCl with zinc(II) concentrations of 0.15M and 0.075M, produces a plot that, in common with the thallium(III) ³⁵Cl data, is dominated by the quadrupolar relaxation term. Because the lower temperature rate controlled relaxation process does not contribute to the curve, only an upper limit for τ_M ($= k_{ex}^{-1}$) can be evaluated; the assumption used, in common with thallium(III) results, is that the lowest temperature $P_M^T \tau_{ex}$ datum point corresponds to the point where the quadrupolar and kinetic terms in equation 2:10 are equal in magnitude. The complex zinc(II) species in HCl of the above concentration, is assumed to be the species $[ZnCl_4(H_2O)_2]^{2-}$. Evidence for such a species in solutions of this concentration comes from Raman studies.³⁵ A rate equation as follows is therefore used:

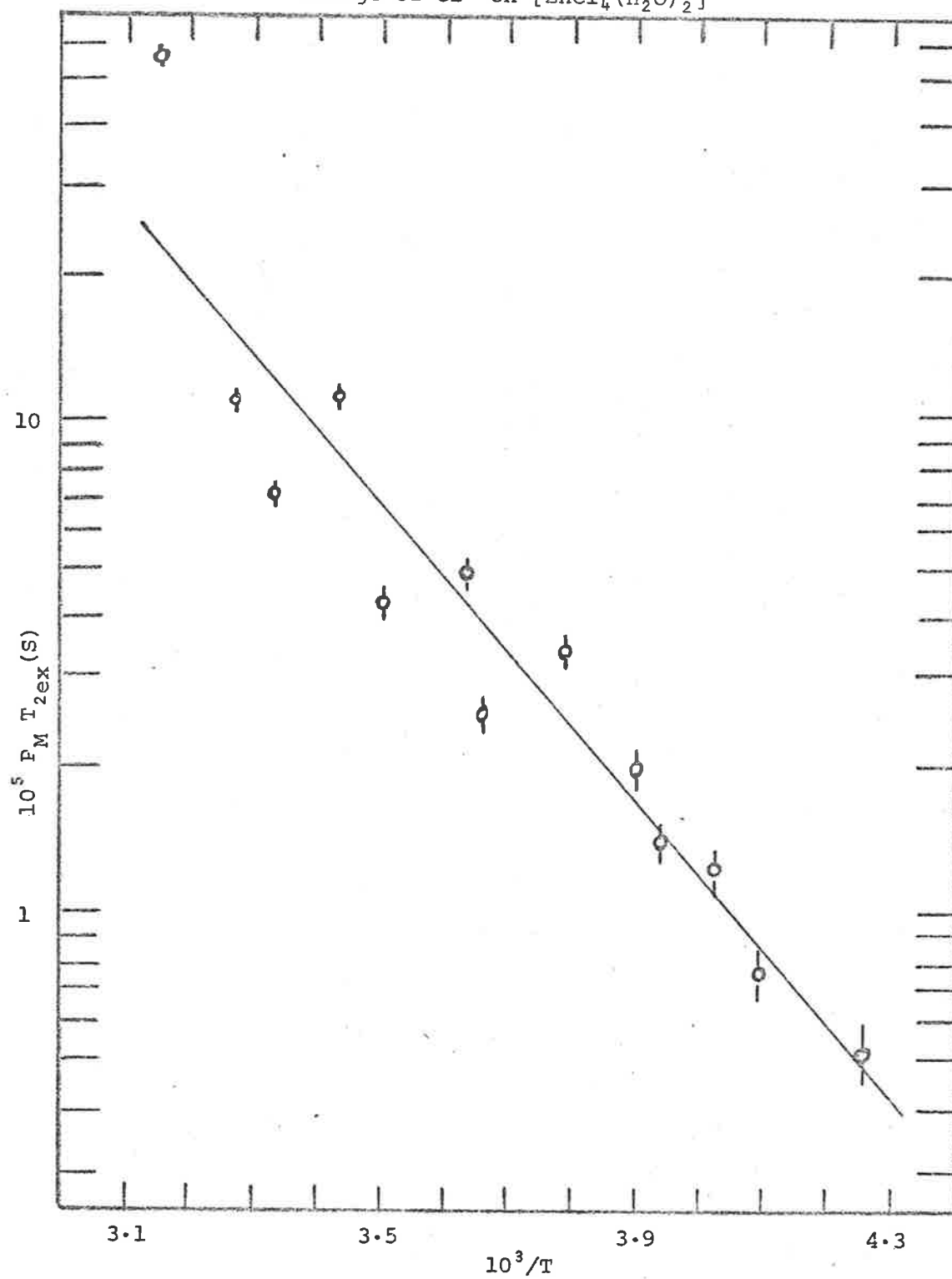
$$\text{Rate} = \tau_M^{-1} 4[ZnCl_4(H_2O)_2^{2-}] = k_{ex} 4[ZnCl_4(H_2O)_2^{2-}] \quad 2:23$$

This gives a rate constant (k_{ex}) $\geq 1.92 \times 10^5 \text{ s}^{-1}$ at 235K. (lowest temperature recorded). A value for the activation energy (E_q) for the quadrupolar process, of $28.9 \text{ k J mol}^{-1}$, is also calculated from the gradient of the theoretical line of best fit. The rotational correlation time (τ_c) for the aqua zinc chloride complex, is quoted by Ward³⁶ as 10^{-11} sec. This value probably refers to a zinc(II)-aqua-chloro complex of

Figure 2:5

^{35}Cl N.m.r. $P_M T_{2\text{ex}}$ data variation with $1/K$. The datum points were obtained in 11.8M hydrochloric acid for the zinc(II) system. The solid line represents the best fit of the Swift and Connick 2-site equation (2:10).

exchange of Cl^- on $[\text{ZnCl}_4(\text{H}_2\text{O})_2]^{2-}$



chloride coordination number less than 4, but in the absence of further data, this τ_c value is used to estimate an $e^2 Q q h^{-1}$ value of 15.2 MHz for the exchanging species.

DISCUSSION

A value for the chloride exchange time for aqueous zinc chloride of the order of 10^{-8} sec, quoted by Eigen and Wilkins³⁷, suggests that for the present study in high chloro content media, where zinc(II) exhibits a maximum chloride stoichiometry of 4 (as $[\text{ZnCl}_4(\text{H}_2\text{O})_2]^{2-}$)³⁵ the minimum rate estimation of $1.92 \times 10^5 \text{ sec}^{-1}$ would certainly be too low. In fact the rate could probably be $\geq 10^8 \text{ sec}^{-1}$ since the above reference most probably refers to zinc(II) species with chloride coordination less than 4, with an expected correspondingly lower rate of chloride exchange than a less sterically hindered tetra-chloro plus two aqua coordination which exists in the 11.8M chloride media.

This rapid rate of chloride exchange on zinc(II) is supported by electrostatic considerations when the aqua-chloro-zinc(II) species exchange rate is compared with the aqua-chloro-indium(III) chloride exchange rate. A surface charge density $+0.29 \text{ \AA}^{-2}$ for zinc(II) should lead to a greater chloride exchange rate for this cation than for indium(III) with a surface charge density of $+0.36 \text{ \AA}^{-2}$. Steric effects should be constant since in aqueous media the coordination of both species is the same, and so the chloride exchange rate on zinc(II) would exceed $8.84 \times 10^6 \text{ s}^{-1}$ on this basis.

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CHAPTER 3

AN ELECTROSTATIC MODEL FOR CHLORIDE EXCHANGE ON GROUP (III) CATIONS

AN ELECTROSTATIC MODEL FOR CHLORIDE EXCHANGE ON GROUP (III) CATIONS

The development of a theoretical model for electrostatic energy calculations in the $[\text{GaCl}_4]^-$ system, was inspired by the success of the Strehlow and Knoche calculations¹ based on sulphate substitution on $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$. This system is analogous to the chloride exchange on $[\text{GaCl}_4]^-$. The measure of success of the following calculations can be judged by the compatibility of sample results obtained for various proposed mechanisms, with the experimental results. As will be seen, the model does provide meaningful information on a proposed mechanism for chloride exchange, which supports other data obtained from wide-line studies.

(i) DEVELOPMENT OF THE MODEL

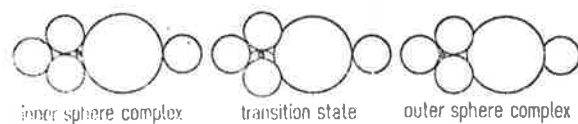
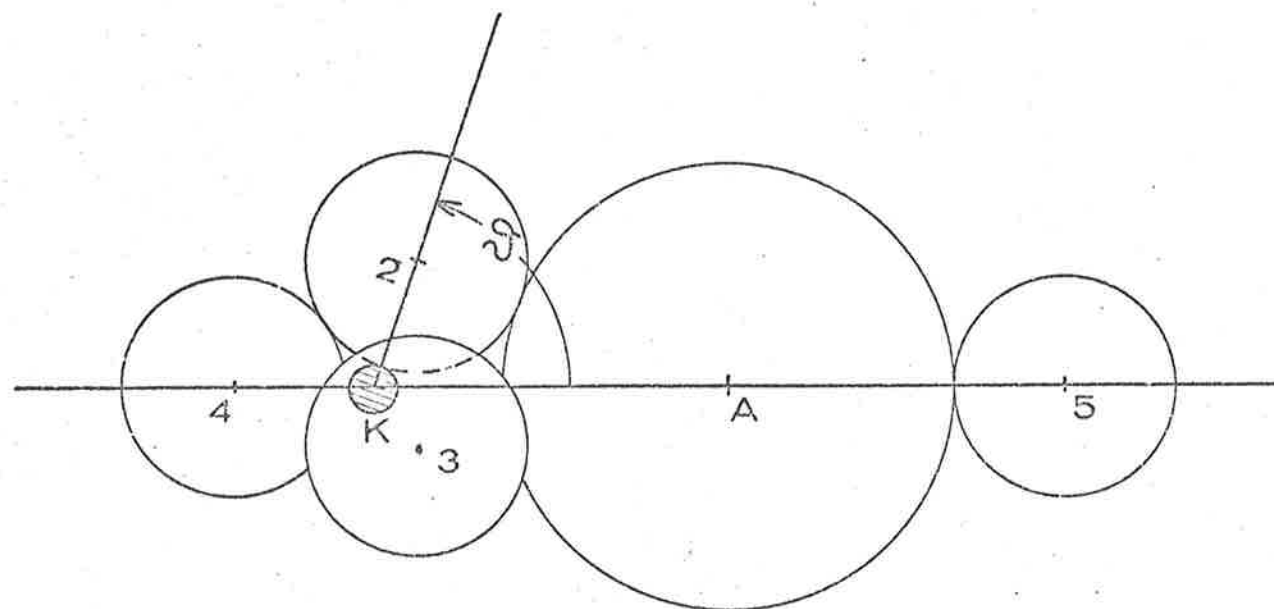
It was not necessary to approach the problem completely from first principles. The work of Strehlow and Knoche with a model for sulphate exchanging on a $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ species could obviously be adapted to chloride exchange on $[\text{GaCl}_4]^-$. To make the calculation involved sufficiently clear, the modification of the original BeSO_4 model will be followed through.

The original problem as presented in the above paper, is the calculation of a theoretical electrostatic energy profile for the reaction:



Figure 3:1

In this 2-dimensional representation of the sulphate exchange on tetra-aqua-beryllium(II), atom 3 is represented although it is out of plane. Atom 1 is out of plane *beneath* atom 3. The anion A is constrained to move along the straight line representing the three fold axis.



This amounts to the equilibrium between an inner and an outer sphere complex, where the beryllium(II) is surrounded tetrahedrally by four aqua species. The water molecule which is shown in the above reaction represents the outer sphere case. Advantage was taken, in designing the scheme of the original calculation, of the symmetrical nature of the system, to reduce the three dimensional situation to a two dimensional profile. The various orientations of the system are shown in figure 3:1. This illustrates the Strehlow and Knoche model, containing the following assumptions which are also valid after numerical change, when the calculations are modified for gallium(III) and chloride.

The cation, water molecules, and sulphate ion are hard spheres of radii: $r_+ = 0.34 \text{ \AA}$, $r_w = 1.38 \text{ \AA}$ and $r_- = 2.91 \text{ \AA}$ respectively. (Finite compressibilities of species and any deviation from a sphere are neglected). The polarizabilities are taken to be $\alpha_+ = 0$, $\alpha_w = 1.48 \text{ \AA}^3$, and $\alpha_- = 5.8 \text{ \AA}^3$. The permanent dipole moment of the water molecule is $\mu_o = 1.85$ Debye. In designing this electrostatic model - based on the Garrick² calculations - Strehlow and Knoche ignored the influence of an assumed Lennard Jones potential which led to only minor corrections. (Further modifications in the calculations presented later in this chapter do likewise). The system consists of a beryllium(II) cation surrounded *tetrahedrally* by four water molecules. The sulphate anion rests in contact with three of these water molecules, in an outer sphere configuration. In this system, a fifth water molecule is included on the side of the sulphate anion opposite to the beryllium(II).

The calculation follows the formation of the inner sphere complex,

by decreasing the inter-ionic distance (r_{+-}) with accompanying shift in the water molecules around the beryllium(II), to minimize the electrostatic energy of the system. This electrostatic energy ΔG_{el} is denoted by the expression:

$$-\frac{\Delta G_{el}}{N_L} = \frac{4e^2}{r_{+-}} + \sum_k \vec{E}_k \vec{\mu}_O + \frac{1}{2} \sum \alpha_w E_k^2 + \frac{1}{2} \alpha_- E_-^2 \quad 3:2$$

The use of the term ΔG_{el} for the electrostatic energy (or free enthalpy as denoted by Strehlow and Knoche) should not be confused with the Gibbs free energy. To avoid any such confusion, this term is always referred to as the *electrostatic energy*. The subscripts k, +, and - refer to the 5 water molecules, the beryllium(II), and the sulphate respectively. E is the electric field at the point indicated by the subscript. N_L is the Avogadro number and e, the electronic charge.

The electric field vector $\vec{E}$ on k water molecules is given by:

$$\vec{E}_k = \frac{2e\vec{r}_{k+}}{r_{k+}^3} - \frac{2e\vec{r}_{k-}}{r_{k-}^3} + \sum_{j \neq k} \left(\frac{\vec{\mu}_j}{r_{jk}^3} + \frac{3(\vec{\mu}_j \cdot \vec{r}_{jk})\vec{r}_{jk}}{r_{jk}^5} \right) - \frac{\vec{\mu}_-}{r_{k-}^3} + \frac{3(\vec{\mu}_- \cdot \vec{r}_{k-})\vec{r}_{k-}}{r_{k-}^5} \quad 3:3a$$

and on the sulphate ion by:

$$\vec{E}_- = \frac{2e\vec{r}_{+-}}{r_{+-}^3} + \sum_k \left(-\frac{\vec{\mu}_k}{r_{k-}^3} + \frac{3(\vec{\mu}_k \cdot \vec{r}_{k-})\vec{r}_{k-}}{r_{k-}^5} \right) \quad 3:3b$$

The sigma refers to the summation of the j waters other than the water molecule k for which the electric field is calculated. Induced

dipole moments are calculated from the electric fields using the equations:

$$\vec{\mu}_j = \vec{\mu}_o + \alpha_w \vec{E}_j \quad 3:4a$$

and $\vec{\mu}_- = \alpha_- \vec{E}_- \quad 3:4b$

The calculation proceeds by a convergence method which involves finding an initial approximation for the electric field by taking only charge contributions in equations 3:3a and 3:3b into account. The induced dipole moments resulting from this field are then calculated and resubstituted into equations 3:3a and 3:3b to obtain a better approximation for the electric field. Successive calculations refine the electric field value, and the electrostatic energy is obtained at each configuration between the inner and outer sphere complex by substituting the converged value of the electric field into equation 3:2.

The above general type of calculation is followed when the chloride exchange on $[\text{GaCl}_4]^-$ is examined. The system itself is analogous, since the tetrahedral configuration around the gallium(III) parallels the 4 waters in tetrahedral configuration around the beryllium(II) cation. A fifth chloride anion replaces the sulphate anion and the fifth water is eliminated from the calculation. The geometry of the system is therefore preserved, but the calculation of ΔG_{el} has to be modified considerably.

The first most obvious changes, are in the various physical constants

which define the types of species to be present. For the gallium(III) ion and the chloride ion, hard spheres are assumed, with radii $r_{\text{Ga}^{3+}} = 0.62 \text{ \AA}$ and $r_{\text{Cl}^-} = 1.81 \text{ \AA}$. Some calculations also involve water and hydrochloric acid which, for convenience of calculation, are considered to be spherical with radii $r_{\text{H}_2\text{O}} = 1.38 \text{ \AA}$ and $r_{\text{HCl}} = 1.81 \text{ \AA}$. The HCl radius and the chloride radius are assumed identical for the calculation. In the Strehlow and Knoche calculation the polarizability of the beryllium(II) is set at zero since this cation has a relatively high charge density. This considerably simplified the calculation, but the assumption is not made for gallium(III), because of the smaller charge density of the larger cation. Polarizabilities are as follows:

$$\alpha_{\text{Ga}^{3+}} = 0.198 \text{ \AA}^3, \quad \alpha_{\text{Cl}^-} = 3.45 \text{ \AA}^3, \quad \alpha_{\text{H}_2\text{O}} = 1.48 \text{ \AA}^3, \quad \text{and} \quad \alpha_{\text{HCl}} = 10.88 \text{ \AA}^3.$$

The permanent dipole moments (μ_o) for the water molecule and the hydrogen chloride molecule are respectively 1.85^1 and 1.08^6 Debye.

It is self evident that the equations 3:2, 3:3a and 3:3b, are specialized for the particular case of $[\text{Be}(\text{H}_2\text{O})_4\text{SO}_4]$. This system involves only one species with a 2+ charge, and one species with a 2- charge. For the $[\text{GaCl}_4]^-$ system, changes incorporated are in the charges, radii, polarizabilities and permanent dipole moments. Equation 3:2 therefore becomes:

$$\begin{aligned} \frac{-\Delta G_{\text{el}}}{N_L} = & \frac{3e^2}{r_{n+}} + \sum_k \frac{3e^2}{r_{k+}} - \sum_k \frac{e^2}{r_{kn}} - \sum_{j \neq k} \frac{e^2}{r_{jk}} + \frac{1}{2} \sum_k \alpha_{\text{Cl}^-k} E_k^2 + \frac{1}{2} \alpha_n E_n^2 + \frac{1}{2} \alpha_+ E_+^2 \\ & + (\vec{E}_n \cdot \vec{\mu}_o) \text{ if incoming nucleophile has permanent dipole moment} \end{aligned}$$

3:5

The subscripts k, n, and + refer to the four chlorides surrounding the gallium(III), the incoming nucleophile, and the gallium(III) respectively. The equation for the electric field vector E, on k chloride anions becomes:

$$\begin{aligned} \vec{E}_k = & \frac{3e\vec{r}_{k+}}{r_{k+}^3} - \sum_{j \neq k} \frac{e\vec{r}_{kj}}{r_{kj}^3} - \frac{e\vec{r}_{kn}}{r_{kn}^3} + \sum_{j \neq k} \left(-\frac{\vec{\mu}_j}{r_{jk}^3} + \frac{3(\vec{\mu}_j \cdot \vec{r}_{jk})\vec{r}_{jk}}{r_{jk}^5} \right) - \frac{\vec{\mu}_n}{r_{kn}^3} \\ & + \frac{3(\vec{\mu}_n \cdot \vec{r}_{kn})\vec{r}_{kn}}{r_{kn}^5} \end{aligned} \quad 3:6a$$

for the field vector on the incoming nucleophile:

$$\vec{E}_n = \frac{3e\vec{r}_{+n}}{r_{+n}^3} - \sum_k \frac{e\vec{r}_{kn}}{r_{kn}^3} + \sum_k \left(-\frac{\vec{\mu}_k}{r_{kn}^3} + \frac{3(\vec{\mu}_k \cdot \vec{r}_{kn})\vec{r}_{kn}}{r_{kn}^5} \right) \quad 3:6b$$

and for the field vector on the cation:

$$\vec{E}_+ = \frac{e\vec{r}_{n+}}{r_{n+}^3} - \sum_k \frac{e\vec{r}_{kn}}{r_{kn}^3} + \sum_k \left(-\frac{\vec{\mu}_k}{r_{k+}^3} + \frac{3(\vec{\mu}_k \cdot \vec{r}_{k+})\vec{r}_{k+}}{r_{k+}^5} \right) \quad 3:6c$$

Induced dipole moments are calculated from the electric fields using the equations:

$$\vec{\mu}_j = \alpha_{cl-j} \vec{E}_j \quad 3:7a$$

$$\vec{\mu}_n = \alpha_n \vec{E}_n + (\vec{\mu}_o \text{ if incoming nucleophile has permanent dipole moment}) \quad 3:7b$$

$$\vec{\mu}_+ = \alpha_+ \vec{E}_+ \quad 3:7c$$

It should be noted that where the incoming nucleophile is denoted by the subscript (-) in the initial system, this has been changed to the subscript n, to avoid confusion with the charged chloride anions coordinated to the gallium(III), and to be consistent with non-charged nucleophiles.

At this point, it is necessary to describe a modification to the parameters of the system which specify the positioning of the atoms. The modification is necessary to give the system the greater degrees of freedom needed to ensure minimization of the energy of the electrostatic interactions. The initial model is simple in that there are only two oppositely charged species, with a number of neutral species. In figure 3:1, depicting this system, the distance between the centres of K and A is specified and knowing the ionic radii, the angle θ is determined. A computer calculation of the energy of the system also simply shifts atom A towards atom K. Atom 2 shifts over and atom 4 moves away from atom K. All of these actions are concerted as the unmodified computer program for calculation is set up. There is no independent shifting of any interatomic distances, or of the angle θ . (Atoms 3 and 1 are above and below the plane of the diagram, and are accounted for by multiplying interactions with atom 2 by 3). Modification in the program, makes the energy calcula-

tion possible for any shifts in the angle θ independent of the position of atoms A and 4 along the three fold axis on which these atoms are constrained. (This constraint ensures calculation simplicity by providing symmetry, as well as presenting a minimum energy configuration in the outer sphere case).

It is now possible to simulate the ideal situation *in vacuo*, of the approach from infinity of a chloride nucleophile, to a $[\text{GaCl}_4]^-$ species, along the three fold axis - ensuring that for each distance of approach between A and K, the energy of the $[\text{GaCl}_4]^-$ species is minimized. It was not found necessary in the calculation to allow atom 2 (and hence 1 and 3) the freedom of changing its distance from K. A sample calculation supported the requirement that the minimum energy ensured when the distance between atom 2 and the central cation remained as the sum of their ionic radii. The minimum energy is dependent on the angle θ however; as the negatively charged chloride approaches the negatively charged symmetrical chlorides, they will repel each other and consequently, the option of allowing the angle θ to increase could increase stability. This will depend on the relative radii of the central cation and the tetrahedrally coordinated atoms; atom 4 may or may not be pushed outwards as angle θ increases, depending on this ratio, and the minimization of energy will not occur so readily if atom 4 does have to shift outwards initially. The importance of the relative ionic radii is thus noted; with a large cation, relative to the coordinating species, the tetrahedral disposition will be more pliable than when the cation is sitting within the tetrahedral hole. This factor assumes significance when the mechanism of

chloride exchange not only on gallium(III), but also on indium(III) and thallium(III) is considered.

For the purpose of the actual calculation, the incoming nucleophile was taken from 20 Å along the 3 fold axis up to the $[\text{GaCl}_4]^-$ species. An infinity value was determined by effectively removing the nucleophile from the calculation by specifying its charge, polarizability, and permanent dipole moment as zero. It should be noted that the system is made completely symmetrical by allowing atom 4 to be manipulated in an identical manner to the nucleophile. This operation is precluded in the original program. The calculation of an energy profile was therefore generally performed by altering the distance between the centre of the cation and the centre of the nucleophile by a 1 Å unit at a time. At each distance, the angle θ would be varied in 1 degree steps over a specific range; this range being determined in part, by the tetrahedral angle, since θ for the isolated tetrahedron is equal to $180^\circ - 109^\circ 28'$. (see figure 3:1). Thus a convenient lower limit to set on this angle was 70° . The upper limit will depend upon the ratio of ionic radii, as described above, but it was generally specified as 90° . When the calculation of the profile was performed for the outgoing species (atom 4), this range changed to 90° and 110° , but the energy calculation was still determined at 1 Å intervals. Because the electrostatic energy was calculated for approximately 20 different configurations for each inter-species distance, any minimization of energy can be readily determined. More accurate knowledge of the geometry of the species at minimum energy can be obtained by allowing steps of 0.1 Å or 0.1 of a degree and so on.

This precision was not usually necessary in the following cases.

It is also obviously feasible to determine the electrostatic energies for a range of static configurations. For example, the energies of the trigonal planar, trigonal pyramidal, tetrahedral, and trigonal bipyramidal structures can be compared.

The second aspect of the complex determination of the electrostatic energy profile involved reintroducing the calculation for the shifting of the atoms from an outer sphere to an inner sphere complex in a concerted process. This then records the electrostatic energy values as the incoming nucleophile still effectively approaches the central cation, with the difference now being that it is in contact with the symmetrical chlorides: the angle θ being widened at intervals of 1 degree in this shift towards an inner sphere complex. Atom 4 is also in contact with the *distorted* (from the tetrahedral angle) symmetrical chlorides if the incoming nucleophile is a negatively charged Cl^- , and as they shift around (opening up the angle θ) it is pushed *away* from the cation. If the incoming nucleophile is uncharged then atom 4 may or may not rest in contact with the *undistorted* (from the tetrahedral angle) symmetrical chlorides, depending on the ratio of ionic radii of chloride to cation. It will still be pushed *away* from the cation when the symmetrical chlorides come in contact with it.

Born Hydration Energy

The above calculations are determined for the species existing *in*

vacuo. This obviously does not represent the true situation; i.e. the reaction as it occurs in an aqueous solvent medium. The effect of the solvent on the electrostatic energy calculation will be quite pronounced for the charged species. Solvation will occur, resulting in a stabilization of the system and this stabilization can be accounted for by introducing the concept of the Born hydration energy.⁷ This states that for a species with charge q and a radius r in a solvent of dielectric constant D , the free energy and entropy of hydration are calculated using the following equations:

$$\Delta G = \frac{-q^2}{2r} \times (1 - 1/D) \quad 3:8$$

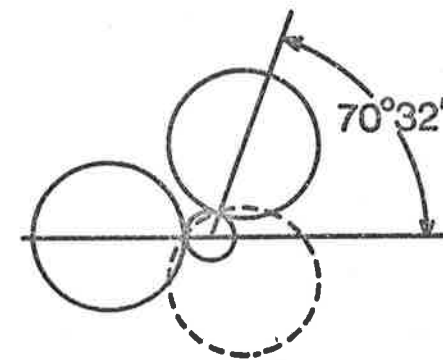
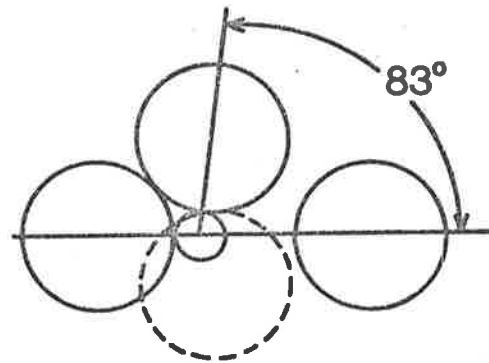
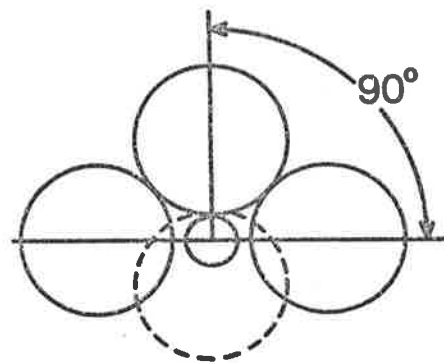
$$\Delta S = \frac{q^2}{2Dr} \left(\frac{\partial D}{\partial T} \right) \quad \text{where } \frac{\partial D}{\partial T} = 0.0046 \text{ for } H_2O \quad 3:9$$

$$\Delta H = \Delta G + T\Delta S \quad 3:10$$

Since these equations determine the hydration energy correction for a charged sphere, the outer and inner sphere exchanging tetrachloro species is assumed to be spherical for the purpose of the calculation; i.e. no distinction for example, is made in determining the Born hydration energy terms, between the symmetrical bipyramidal $[GaCl_5]^{2-}$ with a double negative charge, and the *distorted* bipyramidal species. (See fig. 3:2).

Figure 3:2

This represents from right to left, the isolated and undistorted tetrachlorogallate(III) (dotted circle for out of plane chloride), the same species in distorted configuration due to the presence of a 5th chloride and the transition state pentachloro species.



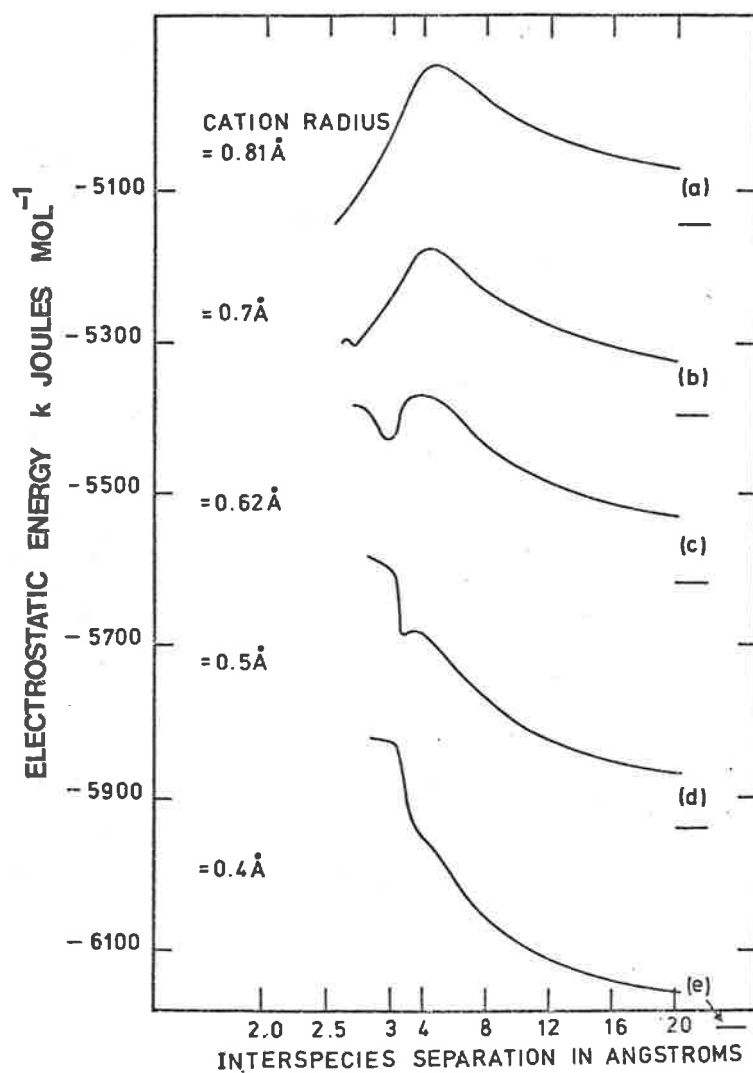
(ii) RESULTS

The calculation incorporating the modified program, was initially performed for a cation radius of $0.62 \text{ \AA}$ and a polarizability α of $0.198 \text{ \AA}^3$ as described above. Chloride anions were characterized using the figures for radius, polarizability and charge as given previously. The resulting electrostatic energy profile is shown as (c) in figure 3:3. Geometrically, the system during exchange can be described as follows. At a $\text{Cl}^-/[\text{GaCl}_4]^-$ separation of infinity, the tetrahedral chlorides assume the tetrahedral angle around the gallium(III). The electrostatic energy for the $[\text{GaCl}_4]^-$ is as shown on figure 3:3. At the $20 \text{ \AA}$ separation between incoming chloride and central gallium(III), the angle θ shows a distortion away from the tetrahedral situation, to 74° , as a consequence of the negative charge of the incoming chloride repelling the negatively charged symmetrical chlorides. As the inter-species distance decreases, this particular high energy repulsive contribution to the total free energy, increases at first. This effect, which tends to distort the angle θ still further, is counterbalanced to a certain extent, by the polarizability of the ions, but ultimately the electrostatic charge attractive and repulsive terms determine the angle θ . At a $4.1 \text{ \AA}$ distance, the angle θ is 83° , and this represents the middle situation in figure 3:2 where further distortion will involve atom 4 shifting away from the gallium(III). As the incoming chloride approaches still closer to the $[\text{GaCl}_4]^-$ species along the 3 fold axis, the attractive energy contribution between it and the triple positively charged gallium(III), exceeds the repulsive terms. The electrostatic energy profile has actually passed

Figure 3:3

A comparison is made of the electrostatic energy profiles calculated on decreasing the interspecies separation between a chloro nucleophile and the tetrachloro cation(III) complexes of changing cation radii.

The energy level shown on the right hand side below each letter depicts the electrostatic energy of the tetrachloro species *in vacuo* (at infinite separation from the nucleophile) for that particular ionic radius.



through a maximum when the interspecies distance is $4.1 \overset{\circ}{\text{\AA}}$ - the situation represented by the middle configuration of figure 3:2. The electrostatic energy decreases until the incoming 5th chloride rests against the face of the symmetrical chlorides, in an outer sphere configuration. This configuration is a stable distorted bipyramid and it requires addition of energy to move the 5th chloride in either direction. Formation of the inner sphere complex from this situation, now proceeds in the same manner as that described in the Strehlow and Knoche paper.¹ Energy is required since the fourth chloride is now moving away from the gallium(III). The second half of the profile represents the removal of the 4th chloride from the 5 coordinate species and is the exact reverse of the approach of the 5th chloride nucleophile.

With the behaviour of the $0.62 \overset{\circ}{\text{\AA}}$ cation characterized, it is instructive to construct profiles for a series of cation radii and make a comparison between them. Consequently electrostatic energy profiles of chloride exchange have been determined for cation radii of 0.4, 0.5, 0.62, 0.7 and $0.81 \overset{\circ}{\text{\AA}}$. The polarizabilities are adjusted accordingly (see table 3:1), knowing that the variation is as the cube of the radius. The cation charge remains at +3, and so the comparison becomes, effectively a study of the relative associative mechanisms for chloride exchanging on group(III) elements in descending order down the group as the radii increase. The above ionic radii represent the increase in ionic radii from aluminium(III) through to indium(III). A further profile at a thallium(III) radius of $0.95 \overset{\circ}{\text{\AA}}$ was not calculated since the essential character of such a profile remains as the $0.81 \overset{\circ}{\text{\AA}}$ case. (see

Table 3:1

Physical Parameters Characterizing Species in Electrostatic Calculations.

Species	Radius ($\text{\AA}$)	Charge (e.u.)	α ($\text{\AA}^3$)	μ_o (debye)
Cl^-	1.81	-1	3.45	-
HCl	1.81	-	10.88	1.08
H_2O	1.38	-	1.48	1.85
Ga^{3+}	0.62	+3	0.198	-
-	0.4	+3	0.059	-
-	0.5	+3	0.115	-
-	0.7	+3	0.314	-
-	0.81	+3	0.469	-

below). Figure 3:3 shows very clearly that as the cation radius increases, the minimum (outer sphere) point on the profiles become more pronounced. This simply reflects the increased freedom of the trigonal chlorides which can be distorted to a greater extent as the cation radius increases, thereby enabling the incoming nucleophile to reside closer to the cation in the outer sphere situation. The minimum becomes more pronounced since the attractive term between the incoming chloride and the central cation is increasingly more dominant than the repulsive chloride-chloride interaction involving the trigonal chlorides.

The trigonal bipyramidal structure also becomes relatively more stable as the cation radius increases, until at the $0.81 \overset{\circ}{\text{\AA}}$ radius the outer sphere situation no longer exists because 5 chlorides can coordinate around the cation without coming into contact with each other. The outer to inner sphere curve can no longer exist, since all 5 chlorides are in contact with the central cation. As the 5th chloride enters, for this *extreme* profile, the trigonal chlorides distort away towards 90° and a maximum point occurs, representing the energy needed to overcome this repulsive term. The incoming chloride, when closer than $4 \overset{\circ}{\text{\AA}}$, is in the attractive region and coordinates directly to the cation with the angle θ reaching 90° and of course with no trigonal chloride contact with the 4th chloride occurring.

At the other extreme ($0.4 \overset{\circ}{\text{\AA}}$), the incoming chloride approaches the tetrachloro species without any distortion in the angle θ occurring, since the coordinating chlorides are in contact with each other. The

outer sphere complex is then formed at a cation-nucleophile distance that is not going to ensure a minimum in the profile. More energy is then required in pushing the system through the trigonal bipyramid stage, to produce the inner sphere species.

Results are presented in table 3:2 for the electrostatic energies of trigonal planar, tetrahedrally distorted trigonal, tetrahedral, bipyramidal and diaquatrichloro gallium(III)-chloro structures, assuming a gallium(III) radius of $0.62 \overset{\text{O}}{\text{\AA}}$. A theoretical value, for the electrostatic energy required for the distortion from the trigonal planar to the tetrahedrally distorted trichloro-gallium(III) species, of 86 kJ mol^{-1} compares reasonably well with the experimental calculation³ of 126 kJ mol^{-1} . Although there is a difference of 40 kJ mol^{-1} , this is for absolute theoretical values of $\approx 5000 \text{ kJ mol}^{-1}$, giving an acceptable percentage error of 0.8%.

The contribution of Born hydration energy terms to the electrostatic energy of the various species is considered in table 3:3. It should be noted that the systems are only considered in the two general extreme situations - the single isolated tetrachloro species, and the pentachloro species for which no differentiation between configuration is or can be made upon determination of the Born hydration value. The calculation is not considered for the intermediate steps along the electrostatic energy profile, because the so called spheres which are used as part of the model, become less and less distinct as discrete entities, as the species move together.

Table 3:2

Electrostatic Energies of various chloro-gallium(III) complex configurations.

(In all of these structures the gallium(III) radius is $0.62\text{\AA}$.)

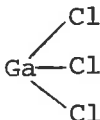
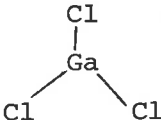
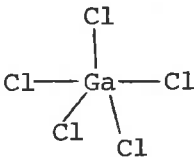
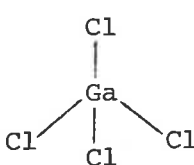
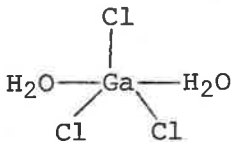
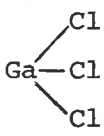
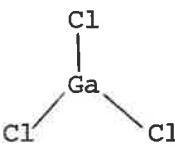
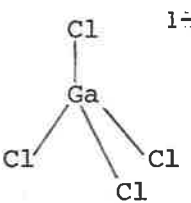
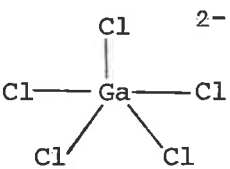
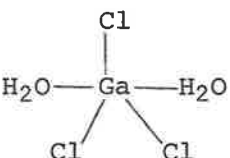
<u>Structure</u>		<u>Electrostatic energy (kJ mol⁻¹)</u>
trigonal with chlorides at tetrahedral angle		-5062
trigonal planar		-5148
3 equatorial chlorides sitting against Ga ³⁺ with two axial chlorides sitting on the faces - pentachloro bipyramid.		2- -5384
tetrahedron		1- -5589
3 equatorial chlorides sitting against Ga ³⁺ with two aqua molecules sitting against each Ga ³⁺ in axial position.		-6891

Table 3:3

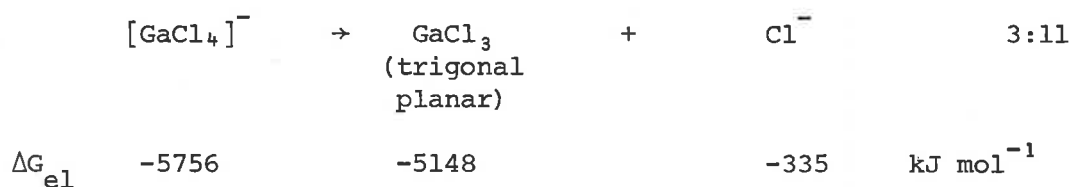
Electrostatic energies of gallium(III) complex configuration after

Born hydration correction has been made. Ga^{3+} radius = $0.62\text{\AA}$.

<u>Structure</u> (as in table 3:2)		<u>Electrostatic Energy (kJ mol⁻¹)</u>
distorted trigonal		-5062
trigonal planar		-5148
tetrahedron		-5756
bipyramid		-6008
3 equatorial chlorides and 2 axial aqua molecules		-6891

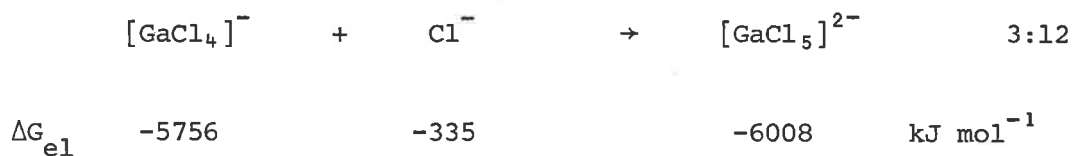
Considering the $0.62 \overset{\circ}{\text{\AA}}$ cation radius representing gallium(III), the theoretical associative and dissociative mechanisms can now be established, using the corrected values of the electrostatic energies as depicted in table 3:3, and a value of -335 kJ mol^{-1} ⁸ for the enthalpy of hydration of free chloride.

For the dissociative pathway:



Energy difference is 273 kJ mol^{-1} .

For the associative pathway:



Energy difference is 83 kJ mol^{-1}

It appears from these calculations, that an associative pathway is more favourable for chloride exchanging on $[\text{GaCl}_4]^-$. In the DISCUSSION section, the nature and reliability of the figures will be fully considered.

The approach of a charged chloride to the $[\text{GaCl}_4]^-$ can be compared with the situation that results when a neutral species approaches the

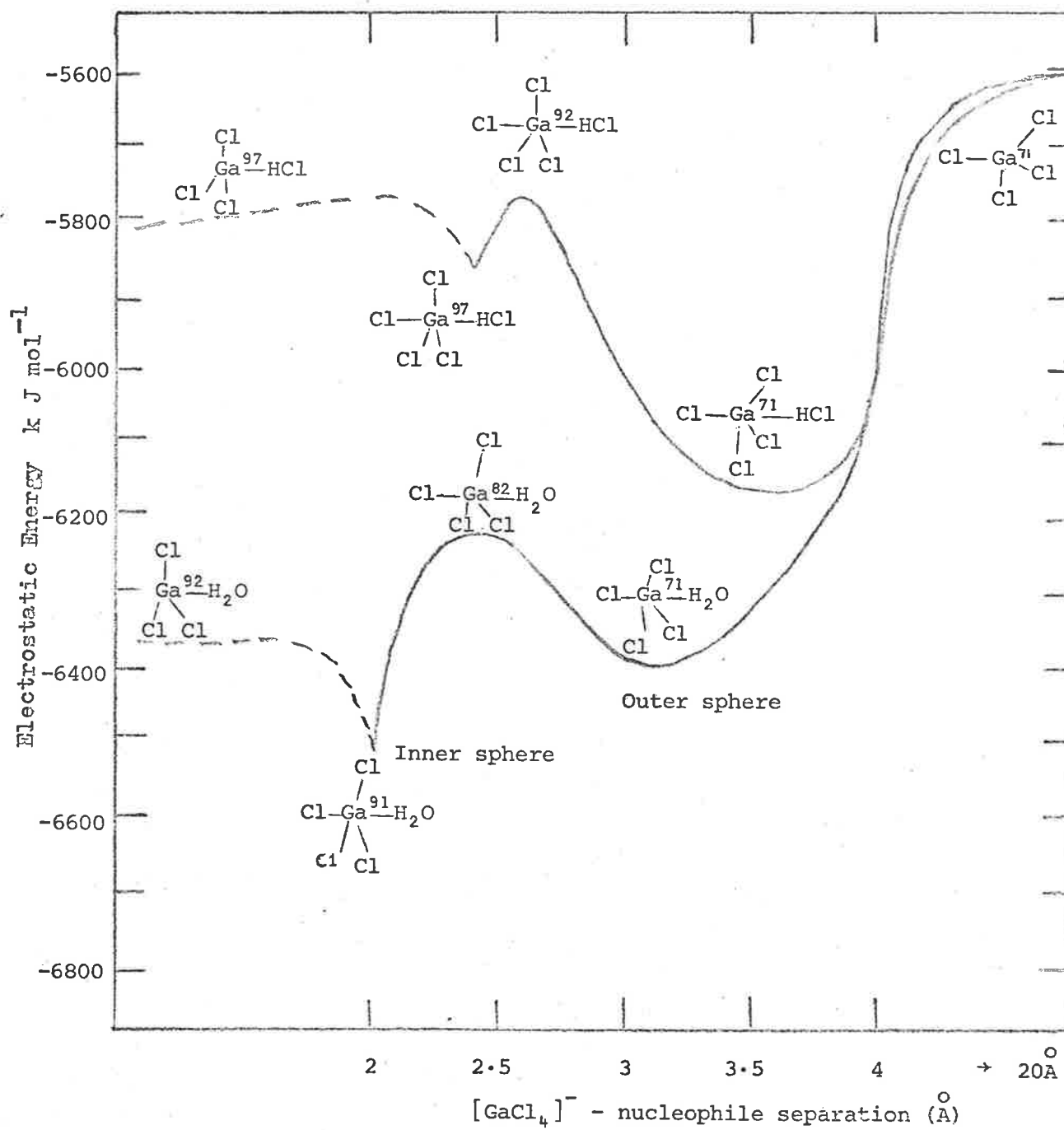
complex. The calculation of electrostatic energy profiles was performed for both water and hydrogen chloride acting as nucleophiles. It seems likely from experimental results, that there will be aqua species involved in the chloride exchange reaction and possibly some sort of protonated pre-equilibrium (see chapter 2) and so calculations involving H_2O and HCl could be relevant. The electrostatic energy profiles for the exchange of a chloride for a water or an HCl molecule are shown on figure 3:4. It is immediately obvious from both profiles that the neutral, polarizable species tend to stabilize the $[\text{GaCl}_4]^-$ complex. The profiles are not of course, symmetrical and the configurations of the coordinating species are given at each critical point along the reaction coordinate. The angle θ is notably undistorted from 71° by the presence of the uncharged nucleophile. The profile for H_2O exchanging with Cl^- is first considered.

When the H_2O enters along the 3 fold axis from $20^\circ \text{ \AA}$, it forms an outer sphere stabilized complex initially. Stabilization occurs as a result of the permanent dipole effect with some stabilization also occurring due to induced dipole formation in the polarizable neutral species. In forming the inner sphere complex the water displaces the symmetrical chlorides to an angle of 91° and these chlorides in turn displace the fourth chloride outwards. The inner sphere situation is quite stable with the gallium(III) resting against the polarizable aqua species. Removal of the 4th chloride destabilizes the species to a certain extent. (The polarizabilities of Cl^- , H_2O and HCl respectively are 3.45, 1.48 and $10.98 \text{ \AA}^3$). The lesser degree of stabilization with HCl reflects the larger radius of this molecule coupled with smaller permanent dipole

Figure 3:4

These two diagrams show the electrostatic energy profiles produced on letting H_2O and HCl approach tetrachlorogallate(III) from $20\text{\AA}$. Configurations of the species along the profiles are given where the angle refers to θ , the deviation of the symmetrical chlorides away from the 3-fold axis (see figure 3:1).

--- 4th chloride departs to $20\text{\AA}$.



moment; in other respects the profile for HCl is very similar to the H₂O profile. The configurations during both exchanges undergo the same type of alterations.

(iii) DISCUSSION

The results obtained using this electrostatic model should be interpreted with caution. The sequence of profiles reflect the trend towards increased ligand exchange rate, on descent of the group. The activation energies are lowered as the cation radius increases, as a direct result of the increased availability of coordination sites. This trend finally results in the five coordinate species of cation radius 0.81 Å (analogous to the indium(III) situation) being more stable than the tetrachloro species. Figure 3:3 therefore shows a trend towards a dissociative pathway becoming the predominant mechanism, especially when profile (a), with its relatively stable 5 coordinate species is considered. Such stability, calculated in this theoretical profile for the 0.81 Å cation ($r_{\text{In}^{3+}} = 0.81$ Å; $r_{\text{Tl}^{3+}} = 0.95$ Å), parallels the increased coordination number in aqueous high [Cl⁻] media observed on descending group (III) to indium(III) ($[\text{InCl}_4(\text{H}_2\text{O})_2]^-$)^{9,10} and more particularly thallium(III) with its five chlorides and an aqua ligand coordinated around it.⁹ (or $[\text{TlCl}_6]^{3-}$)^{11,12} Indeed, a dissociative mechanism is consistent with the possible trend towards positive entropy of activation values for chloride exchange, on descending group (III). (see chapter 2 table 2:5).

One of the difficulties that arises with this model, is the recon-

ciliation of the calculated activation energy with the experimental value, for although the activation energy of the associative mechanism is more compatible than that of the dissociative mechanism, there is still a considerable difference in values. It is not sufficient therefore, to consider only the Born hydration energy correction.

If a realistic model is to be postulated, then the inter-species separation of $20 \text{ \AA}$ can no longer be valid. The actual average distance between chloride ions in solution can be evaluated as follows: For the $11\text{M}[\text{Cl}^-]$ solution, the total number of chlorides in 1000 cm^3 is $11 \times 6.02 \times 10^{23}$. The volume occupied by one chloride is therefore $151 \text{ \AA}^3$.

The volume can be considered as a cube with the chloride sited in the centre. This results in a 3 dimensional lattice of chlorides, each separated by the length of one side of the cube. Therefore the average distance between chlorides is $\sqrt[3]{151} = 5.3 \text{ \AA}$. A similar calculation for $7\text{M}[\text{Cl}^-]$ results in an average separation between chlorides of $6.2 \text{ \AA}$.

To consider the $11\text{M}[\text{Cl}^-]$ situation: Since each chloride is no further on average, than about $5 \text{ \AA}$ from every other chloride, then it is obvious that no gallium(III) will be further away from a chloride than $5 \text{ \AA}$. In fact of course, the gallium(III) cations must be closer to the chlorides than $5 \text{ \AA}$ in an 11M solution. In treating the solution as a 3 dimensional lattice of chlorides, it can be seen that if the corners of each cube (intersection points of lattice lines) represent a chloride, then the maximum separation from a chloride of a gallium(III) will place it at the centre of one of the cubes. The maximum separation will there-

fore be $\sqrt{3}/2 \times 5.3 \text{ \AA} = \underline{4.6 \text{ \AA}}$. In the 7M solution the separation of gallium(III) from chloride is $\sqrt{3}/2 \times 6.2 = \underline{5.4 \text{ \AA}}$.

Clearly any chloride exchange occurring from a separation of $20 \text{ \AA}$ represents an unreal situation. The question to be considered now is whether the chloride exchange on tetrachloro species discussed above can be validly represented by the electrostatic energy profiles. The profiles at small (4 or 5 $\text{\AA}$) interspecies separation should still be valid; in fact the situation is considerably simplified since the complex species now exists in a higher energy state surrounded by chlorides which can form ion pairs with less energy requirement as a result of the proximity of all species. The electrostatic energy of the free species can be considered to be that energy of the profile corresponding to a 4.6 or 5.4 $\text{\AA}$ separation of chloride from the complex centre. If the electric field surrounding the central cation is considered uniform and an extra chloride is added, then the profile should approximate to the situation *in vacuo* at least as far as the relative energy changes observed on the profiles are concerned. The important energy requirement will now involve formation of the inner sphere transition state from the outer sphere state, and this energy should not be affected by the presence of a uniform distribution of negatively charged anions around the complex.

It also follows that the Born hydration correction will not be needed, or at least calculations using the crude model involving charged spheres, will not yield different hydration terms for the configuration changes involved. This can be compared to the situation described by

Strehlow and Knoche¹ in which they calculate Born hydration energies for the sulphate proceeding from the outer to the inner sphere state of the beryllium(II) hexaaqua complex. The calculation was made on the basis of the change in permanent dipole moment orientation - a calculation which of course cannot be performed in the case of chloride interactions.

When the profiles of figure 3:3 are examined from the viewpoint of commencing chloride exchange at either 4 or 5 Å interspecies separation, then it is apparent that the greatest activation energy requirement for the associative mechanism, is for the 0.4 Å cation radius. This trend parallels the activation energies required assuming a dissociative mechanism for an electrostatic model, as the surface charge densities of cations decrease down the group. The energy required at the 0.6 Å cation radius corresponding to the gallium(III), approximates very well to experimental results. This energy value of $\approx 40 \text{ kJ mol}^{-1}$ is of the same order of magnitude as the experimental result of 29 kJ mol^{-1} .

It can be seen that if this trend is continued, then for 0.7 and 0.8 Å cation radii, there would be no activation energy required, which is nonsense. The situation *does* indicate however, that these cations are more highly coordinated. The simple example involving only 4 chlorides surrounding the central cation is no longer valid. Consequently, profiles (a) and (b), although applying to theoretical calculations for *non existent species*, are still included to complete the trend which develops as the cation radius increases. There must in fact, be a balancing of associative-dissociative type mechanism possibilities.

As the cation radius increases, the dissociative case becomes more energetically favourable due to the increased freedom of the coordinating anions, until the coordination number itself is permanently increased. A dissociative mechanism must then be considered viable. The model therefore clearly demonstrates this complication (mentioned in chapter 2) to the straight forward expectation of a simple increase in reaction rate with similar mechanisms, down a group as surface charge density on the cation decreases.

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CHAPTER 4

HIGH RESOLUTION N.M.R. STUDIES OF FLUORIDE
EXCHANGE ON BERYLLIUM

HIGH RESOLUTION N.M.R. STUDIES OF FLUORIDE EXCHANGE ON BERYLLIUM

(i) INTRODUCTION-THEORY

The system under study is the fluoride exchange on beryllium(II) species in aqueous solution. Provided that the fluoride concentration is kept equal to or greater than 4 times the beryllium(II) plus twice the acid concentrations¹ the cation species in solution will be $[\text{BeF}_4]^{2-}$ only. The fluorine nucleus, with a spin of $1/2$, does not have a quadrupolar moment associated with it and therefore ^{19}F does not undergo the quadrupolar broadening exhibited by ^{35}Cl . High resolution n.m.r. can now be used in detecting the fine structure that occurs from fluorine nuclear spin interaction with the beryllium nucleus of $3/2$. The symmetrical tetrahedral disposition of fluoride around the beryllium(II) is particularly important, as this ensures that there will be no quadrupolar relaxation of the beryllium nucleus between the four possible spin states: $-3/2, -1/2, 1/2, 3/2$. The completely symmetrical electric field gradients result in a vector addition of zero for the gradients, and a consequent non-interaction with the electric quadrupolar moment of beryllium.² This now ensures long lived spin states, so that at low temperature (no exchange conditions) the fluorine nucleus will "see" four different magnetic environments - all equally probable, according to the random distribution of fluorides on these four equally probable spin states. The high resolution spectrum for ^{19}F in beryllium fluoride solution will therefore consist of a free fluoride signal (fast exchange average of F^- ,

HF and $[\text{HF}_2]^-$) 48.3 ± 1.5 ppm downfield from the $[\text{BeF}_4]^{2-}$ quartet ($J = 33.75$ Hz). In a situation involving no chemical exchange between spin sites, the width for the quartet peaks at half height ($\Delta\nu_{1/2}$) is $1/(\pi T_2)$ Hz. where T_2 for the Lorentzian curve, is the ^{19}F transverse relaxation time.³

Fluoride ions can now, on exchange, occupy any of the 4 spin sites, and with increasing temperature the 4 peaks will coalesce into 1, since more rapid exchange cause the ^{19}F nucleus to experience an averaging of the magnetic field associated with the beryllium spin states. The degree of coalescence will depend on the mean lifetime (τ) of the ^{19}F nucleus on each particular spin site. Since the fluorine will have equal probabilities of being on any spin site, there is only one τ value characterizing the four different sites.

The n.m.r. spectra for this exchange process can be fully described mathematically by considering the Bloch equations. The basic equation used in the calculation of n.m.r. spectra for multi-site exchange problems is the following:³

$$I(\nu) \propto \text{Re}(P \cdot A^{-1} \cdot 1) \quad 4:1$$

where P is a row vector with elements corresponding to the N fractional populations of the nuclear "sites", A is an $N \times N$ complex matrix and 1 is a column vector with all elements equal to unity. Re means "the real part of".

The Bloch equations⁴ are now used to derive the above general equation.³ The initial derivation only involves a simple 2 site case which can then be generalized to the N site case. This will lead to a formulation of the theoretical spectrum needed for the $[\text{BeF}_4]^{2-}$ situation which is, of course, a 4-site exchange problem. A nucleus is considered to exist in two sites which are characterized by the resonance frequencies ν_A and ν_B . The complex magnetizations G_A and G_B , satisfy the Hahn-Maxwell-McConnell equations:^{5,6}

$$\frac{dG_A}{dt} = -\alpha_A G_A - \frac{G_A}{\tau_A} + \frac{G_B}{\tau_B} + i\omega_r P_A M_O \quad 4:2$$

$$\frac{dG_B}{dt} = -\alpha_B G_B - \frac{G_B}{\tau_B} + \frac{G_A}{\tau_A} + i\omega_r P_B M_O \quad 4:3$$

where $G_n = (G_x + iG_y)_n$; $n = A, B$; $i = \sqrt{-1}$; $\alpha_n = i2\pi(\nu - \nu_n)$

$-1/T_2$; $1/T_2 = \pi\Delta\nu_{1/2}$ (linewidth in the absence of exchange);

τ_n = mean lifetime of a nucleus in the nth site; M_O = total nuclear magnetization; $\omega_r = \gamma H_1$; and P_n = fractional population of nth site ($P_A + P_B = 1$).

The absorption mode component is given by:

$$I(\nu) = I_m(G_A + G_B) \quad 4:4$$

where I_m means "imaginary part of".

Assuming steady state conditions: $(dG_A/dt = dG_B/dt = 0)$ and writing equations 4:2 and 4:3 in matrix form:

$$-i\omega_{rO} \begin{pmatrix} P_A \\ P_B \end{pmatrix} = \begin{pmatrix} -(\alpha_A + 1/\tau_A) & 1/\tau_B \\ 1/\tau_A & -(\alpha_B + 1/\tau_B) \end{pmatrix} \begin{pmatrix} G_A \\ G_B \end{pmatrix} \quad 4:5$$

Taking the transpose of both sides (i.e. transposing columns and rows) gives:

$$-i\omega_{rO} (P_A, P_B) = (G_A, G_B) \begin{pmatrix} -(\alpha_A + 1/\tau_A) & 1/\tau_A \\ 1/\tau_B & -(\alpha_B + 1/\tau_B) \end{pmatrix} \quad 4:6a$$

This can be abbreviated to matrix notation:

$$\text{Thus } -i\omega_{rO} P = GA \quad 4:6b$$

Since from above: $I(v) = I_m(G \cdot 1)$, equation 4:6b is multiplied by A^{-1} followed by 1 to obtain:

$$I(v) = -i\omega_{rO} I_m (PA^{-1} \cdot 1) \quad 4:7a$$

A is referred to as the Kubo-Sack matrix, after the two authors who independently developed the method.^{7,8} Writing out equation 4:7a in full, it becomes:

$$I(v) = -\omega_{rO} R_e (P_A, P_B) \begin{pmatrix} -(\alpha_A + 1/\tau_A) & 1/\tau_A \\ 1/\tau_B & -(\alpha_B + 1/\tau_B) \end{pmatrix}^{-1} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad 4:7b$$

This method can now be generalized to N sites. A becomes N x N matrix

of the form:

$$A = \Omega + D \quad 4:8$$

$$\text{where } \Omega_{ij} = -\delta_{ij} \alpha_i$$

$$D_{ij} = p_{ij}/\tau_i \quad (i \neq j)$$

$$D_{ii} = -1/\tau_i$$

where τ_i is the mean lifetime of site i and p_{ij} is the fraction of transfers from site i which terminate in site j .*

* Because the exchange of fluorides between different spin sites is a completely random process, the derivation of the theoretical ^{19}F n.m.r. spectra for the spin spin interaction can be accomplished using the following equation, shown by Piette and Anderson⁹ to represent the system:

$$I(\nu) = \frac{\omega_M \text{Re} \sum_i P_i / (1 + \alpha_i \tau)}{\sum_i P_i \alpha_i / (1 + \alpha_i \tau)}$$

where τ is the mean time between exchanges. This equation was not used in the present calculation however.

Construction of the Kubo - Sack Matrix A

Equation 4:8 gives an expression requiring N different values of τ , but since only one value of the rate is measured experimentally, it would be most convenient to express A in terms of the single lifetime τ . Thus:

$$A = \begin{bmatrix} -\alpha_1 & 0 & . & . & . & 0 \\ 0 & -\alpha_2 & & & & . \\ . & & & & & . \\ . & & & & & . \\ . & & & & & . \\ 0 & . & . & . & . & -\alpha_N \end{bmatrix} + \begin{bmatrix} p_{11}, p_{12}, . & . & . & p_{1N}, \\ p_{21}, p_{22}, . & & & . \\ . & & & . \\ . & & & . \\ . & & & . \\ p_{N1}, . & . & . & . & p_{NN}, \end{bmatrix} \quad \begin{array}{l} \text{X Rate} \\ (=1/\tau) \end{array}$$

. . . . 4:9

The problem now becomes one of correct selection of the transfer probabilities p'_{ij} , and this can be quite tricky - depending on a clear enunciation of spin states and various configurations. Some rules set out below help clarify the determination of elements p_{ij} . They suffice for sites determined either by chemical shift or by spin spin coupling.³

- 1) Write out all configurations accessible from the initial configuration, by a single step exchange.
- 2) List the set of fractional populations of the sites: $P_1, P_2 \dots P_N$ where $P_i = (\text{number of spins of type } i)/(\text{total number of spins})$.
- 3) Choose a reasonable mean lifetime τ to describe the rate process. The rate constant is then defined as $1/\tau$.

- 4) Determine the off - diagonal transition probabilities p'_{ij} ($i \neq j$) for:

a) *chemical shift site determination* as follows:

$$p_{ij}' = \sum_{\alpha} R_{\alpha} F_{ij}^{\alpha} \quad 4:10$$

where R_{α} = probability of reaching configuration α when exchange occurs. F_{ij}^{α} = fraction of spins of type i which become type j , in new configuration α .

b) *spin spin site determination*

$$p_{ij}' = P_j F \quad 4:11$$

where P_j is the fractional population of the j th site and F is the fraction of resonant nuclei which exchange.

- 5) For chemical shift site determination, diagonal elements are as follows:

$$-p_{ii}' = \sum_{\alpha} R_{\alpha} F_{ii}^{\alpha} \quad 4:12$$

where F_{ii}^{α} = fraction of spins of type i which change type in new configuration α .

- 6) Test transition probabilities for consistency under steady state conditions by ensuring that the rate of transfers into and out of the i th site, are equal.

The following equations must be satisfied:

$$P_{ii'} + \sum_{j \neq i} P_{ij'} = 0 \quad 4:12a$$

$$P_i P_{ii'} + \sum_{j \neq i} P_j P_{ji'} = 0 \quad 4:12b$$

For all spin coupling problems, this rule will suffice for the determination of the diagonal elements of p' .

In the preceding rules it will be noticed that a distinction is made in rule (4) between two types of site determination. This serves not only the case where *intramolecular* configuration changes are involved - where there are chemical shift changes - but also the *intermolecular* exchange between identical species, in which the sites are determined only by differing spin states. The beryllium fluoride exchange system study, involves the relatively simple spin spin coupling site determination. The Kubo - Sack matrix is now determined for ^{19}F exchanging on $[\text{BeF}_4]^{2-}$.

- 1) Accessible spin states are $3/2, 1/2, -1/2, -3/2$.
- 2) Fractional populations are $1/4, 1/4, 1/4, 1/4$.
- 3) τ = mean lifetime of one F^- on $[\text{BeF}_4]^{2-}$.
- 4) The F factor is $1/4$ since only one of the 4 fluorides surrounding beryllium(II) exchange at any one time. Since $p_{ij'} = P_j \text{F}$:

$$p_{12'} = p_{13'} = p_{14'} = p_{21'} = p_{23'} = p_{24'}$$

$$= p_{31}' = p_{32}' = p_{34}' = p_{41}' = p_{42}' = p_{43}' = (1/4) \times (1/4) = 1/16$$

$$5) -p_{11}' = -p_{22}' = -p_{33}' = -p_{44}' = p_{12}' + p_{13}' + p_{14}' = p_{21}' + p_{23}' +$$

$$p_{24}' = p_{31}' + p_{32}' + p_{34}' = p_{41}' + p_{42}' + p_{43}' = 3/16$$

Thus

$$p' = \begin{bmatrix} -3/16 & 1/16 & 1/16 & 1/16 \\ 1/16 & -3/16 & 1/16 & 1/16 \\ 1/16 & 1/16 & -3/16 & 1/16 \\ 1/16 & 1/16 & 1/16 & -3/16 \end{bmatrix}$$

Therefore the Kubo - Sack matrix A is:

$$\begin{bmatrix} -\alpha_1 - 3/(16\tau) & 1/(16\tau) & 1/(16\tau) & 1/(16\tau) \\ 1/(16\tau) & -\alpha_2 - 3/(16\tau) & 1/(16\tau) & 1/(16\tau) \\ 1/(16\tau) & 1/(16\tau) & -\alpha_3 - 3/(16\tau) & 1/(16\tau) \\ 1/(16\tau) & 1/(16\tau) & 1/(16\tau) & -\alpha_4 - 3/(16\tau) \end{bmatrix}$$

The theoretical n.m.r. curve describing the rate controlled relaxation of a spin of 1/2 (^{19}F) interacting with a spin of 3/2 (^7Be) is thus described by the summation of the real elements of the inverse of this matrix A, since equation 4:7a describes two matrix multiplications: firstly of a row vector (P) with A^{-1} (summing column elements of A^{-1}) to give a row vector, and secondly with a column unit vector, resulting in total summation of all A^{-1} elements. Any constant factors appearing as

part of equation 4:7a - including the constant and equal components of P - can be ignored, since they will only contribute to the intensity of the Lorentzian line shapes, and do not affect the rate. In view of the relative simplicity of obtaining theoretical spectra from the inverse Kubo - Sack matrix, it was decided to actually calculate the inverse of A in its algebraic form. This 4 x 4 matrix is shown below.

$$A^{-1} = \begin{bmatrix} \frac{\gamma}{\delta} & -\frac{\tau}{(\alpha_2 - \tau)\delta} & -\frac{\tau}{(\alpha_3 - \tau)\delta} & -\frac{\tau}{(\alpha_4 - \tau)\delta} \\ -\frac{\tau}{(\alpha_2 - \tau)\delta} & \frac{1}{\alpha_2 - \tau} + \frac{\tau(\tau - \alpha_1)}{(\alpha_2 - \tau)^2\delta} & \frac{\tau(\tau - \alpha_1)}{(\alpha_2 - \tau)(\alpha_3 - \tau)\delta} & \frac{\tau(\tau - \alpha_1)}{(\alpha_2 - \tau)(\alpha_4 - \tau)\delta} \\ -\frac{\tau}{(\alpha_3 - \tau)\delta} & \frac{\tau(\tau - \alpha_1)}{(\alpha_2 - \tau)(\alpha_3 - \tau)\delta} & \frac{1}{\alpha_3 - \tau} + \frac{\tau(\tau - \alpha_1)}{(\alpha_3 - \tau)^2\delta} & \frac{\tau(\tau - \alpha_1)}{(\alpha_3 - \tau)(\alpha_4 - \tau)\delta} \\ -\frac{\tau}{(\alpha_4 - \tau)\delta} & \frac{\tau(\tau - \alpha_1)}{(\alpha_2 - \tau)(\alpha_4 - \tau)\delta} & \frac{\tau(\tau - \alpha_1)}{(\alpha_4 - \tau)(\alpha_3 - \tau)\delta} & \frac{1}{\alpha_4 - \tau} + \frac{\tau(\tau - \alpha_1)}{(\alpha_4 - \tau)^2\delta} \end{bmatrix}$$

where $\gamma = 1 + \tau[1/(\alpha_2 - \tau) + 1/(\alpha_3 - \tau) + 1/(\alpha_4 - \tau)]$;

$$\delta = \alpha_1 - \tau(\tau - \alpha_1)[1/(\alpha_2 - \tau) + 1/(\alpha_3 - \tau) + 1/(\alpha_4 - \tau)]$$

The algebraic terms of this matrix are summed using a computer program, the real component of the sum extracted, and values of the intensity calculated over a range of frequency (ν) values, since $\alpha_n = i2\pi(\nu - \nu_n) - 1/T_2$. Program Summat which sums the matrix, is listed

in the appendix, along with the larger Program Match - of which Summat is a subroutine - which is used to compare theoretical and experimental n.m.r. curves and consequently extract experimental values of τ (hence the rate constants). This is achieved by obtaining a series of theoretical τ values at a constant T_2 value, until the curve of best fit with the experimental spectrum at a given temperature is obtained. The transverse relaxation time (T_2) is derived from measurement of the width at half height of a spectrum of a cooled down sample of $[\text{BeF}_4]^{2-}$ and free fluoride, where no exchange is occurring, and applying the equation: $T_2 = 1/(\Delta\nu_{1/2}\pi)$. Values of ν_n are also determined from the n.m.r. spectrum at these low temperatures.

Quadrupolar Relaxation

The above calculations describe the situation for the rate controlled ^{19}F relaxation process, which is the correct mechanism for the system under study. It is informative however, to briefly compare this mechanism with a quadrupolar relaxation process of ^{19}F on beryllium(II). This would occur if the beryllium(II) was in a non-spherical environment of coordinating species and was therefore capable of relaxing from one spin state to another as a result of interaction between the non-zero resultant electric field vector of say, 3 coordinating fluorides plus an aqua ligand (for $[\text{BeF}_3\bar{3}]$ and the beryllium(II) nuclear quadrupolar moment.² The ^{19}F nucleus in this case would be relaxed, but only at certain temperatures. When relaxation is not occurring the ^{19}F nucleus experiences the 4 spin states $3/2, 1/2, -1/2, -3/2$, in equal proportion, while an increasingly efficient

quadrupolar relaxation ensures with *decreasing* temperature - the reverse of the rate controlled relaxation. (see fig. 4:1). This result is brought about by the increase in the efficiency of the above mentioned quadrupolar coupling with the resultant ligand electric field vector, as the complex tumbling time decreases.¹⁰ The second important difference with this type of relaxation, is that the transitions by electric quadrupolar moments only occur for:¹¹

$$\Delta M = \pm 1 \text{ or } \pm 2. \quad \text{For } I = 3/2$$

Therefore transition probabilities are:

$$P_{3/2, \pm 1/2} = P_{\pm 1/2, 3/2} = P_{-3/2, \pm 1/2} = P_{\pm 1/2, -3/2} = \frac{1}{20} \left(\frac{e^2 q Q}{\hbar} \right)^2 \tau_q$$

..... 4:13a

$$\text{and } P_{3/2, -3/2} = P_{-3/2, 3/2} = P_{1/2, -1/2} = P_{-1/2, 1/2} = 0$$

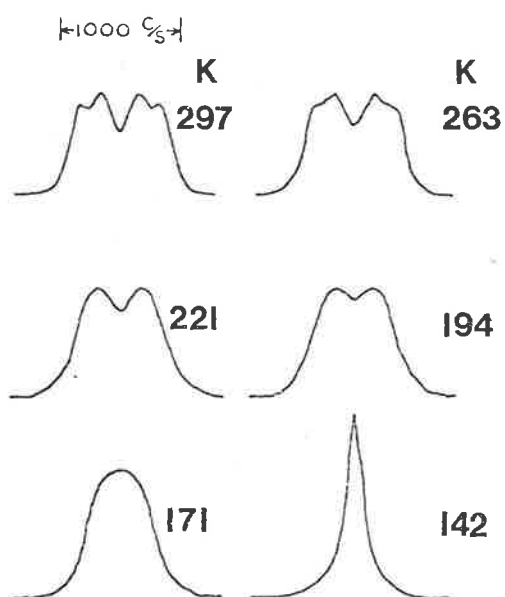
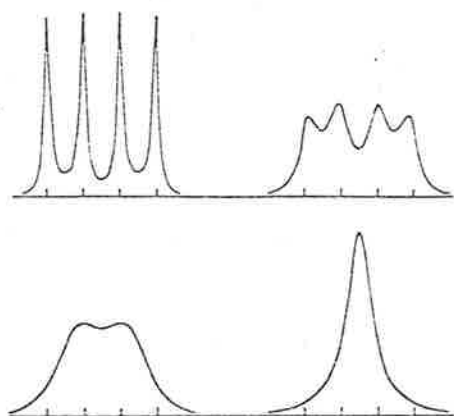
..... 4:13b

This condition affects the collapse of the 4 peaks resulting from the ¹⁹F spin spin coupling to the relaxing ⁷Be, so that instead of observing a symmetrical coalescence into a single peak as shown in fig. 4:2, the collapse of the quartet will reveal outer lines moving inwards, but the inner lines going outwards resulting in a broad doublet-like structure which finally collapses to a single line as shown in fig. 4:1. The absence of the above transitions (4:13b) is reflected in the Kubo - Sack matrix which is no longer symmetrical - containing a zero for the forbidden transitions.⁹ The matrix is presented in a slightly different

Figure 4:1

The top diagram demonstrates the quadrupolar relaxation of spin $1/2$ coupled to spin $3/2$. The molecule tumbling time decreases from upper left to lower right. The initial collapse to the doublet is quite evident. The bottom diagram follows the ^{19}F resonance spectra of liquid ClO_3F as the temperature decreases, clearly showing accompanying narrowing of the signal due to the quadrupolar relaxation.

^{19}F Quadrupolar Relaxation



form as well.

Thus

$$A = \begin{bmatrix} i[(\omega_0 - \omega) + 3\pi J] - 1/\tau & 1/(2\tau) & 1/(2\tau) & 0 \\ 1/(2\tau) & i[(\omega_0 - \omega) + \pi J] - 1/\tau & 0 & 1/(2\tau) \\ 1/(2\tau) & 0 & i[(\omega_0 - \omega) - \pi J] - 1/\tau & 1/(2\tau) \\ 0 & 1/(2\tau) & 1/(2\tau) & i[(\omega_0 - \omega) - 3\pi J] - 1/\tau \end{bmatrix}$$

where ω_0 is the centre of the multiplet, and J is the spin spin coupling constant in Hz. The n.m.r. curve is given by equation 4:7a.

(ii) RESULTS

Fluorine-19 measurements were obtained for a series of beryllium(II)/fluoride solutions of varying $[\text{Be}^{2+}]:[\text{F}^-]_{\text{total}}$ ratios. It was decided to follow in part, the solution concentrations used in the work of Baldwin¹, so that a direct comparison of results could be obtained. Table 4:1 presents the solutions used, together with the variation in concentration of the different species in solution. It should be noted that in all cases the concentration of total fluoride is such that all beryllium(II) is present as the $[\text{BeF}_4]^{2-}$ species. As stated above, this is so as long as $[\text{F}^-]_{\text{t}} \geq (4[\text{Be}^{2+}] + 2[\text{H}^-])$ (the species $[\text{HF}_2]^-$ isn't observed in solution) ; lower fluoride concentrations result in the complication of observable $[\text{BeF}_3.\text{H}_2\text{O}]^-$ being present^{12,13} and a consequent duplicating of the observed quartet at slightly higher field strength, so that the two quartet patterns merge. The present concentrations resulted in a simple $[\text{BeF}_4]^{2-}$ quartet being observed - the magnitude of which depending upon the actual concentration of $[\text{BeF}_4]^{2-}$. Figure 4:2 records the experimental spectral variation with temperature for solution Be6. The continuous line overlapping the experimental spectra represents the best fit theoretical line shape, computer generated from the inverse Kubo-Sack matrix - the procedure described in the introduction. Rate constants are obtained from the correlation times and are visually presented in figure 4:3 in the form of a series of Arrhenius plots. This presentation of $\log(k_{\text{obs}})$ versus reciprocal temperature on the same

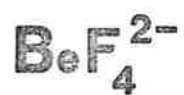
Table 4:1

Solution Concentrations for $[\text{BeF}_4]^{2-}$ samples. Total Fluoride Concentration is 4.5M for all samples.

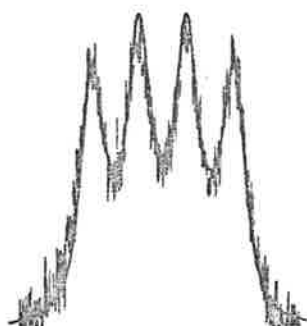
Sample	$[\text{BeF}_4^{2-}]$	$[\text{F}^-]_{\text{free}}$	$[\text{H}^+]$
Be 1	0.5	2.5	0.18
Be 2	0.7	1.7	0.18
Be 3	0.25	3.5	0.18
Be 4	0.9	0.9	0.18
Be 5	0.35	3.1	0.18
Be 6	0.5	2.5	0.54
Be 7	0.5	2.5	0.18 + $1\text{MK}_2\text{SO}_4$

Figure 4:2

This shows the temperature dependence of the ^{19}F n.m.r. spectrum for 4.5M total $[\text{F}^-]$, 0.5M $[\text{Be}^{2+}]$ and 0.18M $[\text{H}^+]$ when the quartet obtained from spin spin coupling between fluorine and beryllium nuclear spins, is observed. The solid line passing through each spectrum represents the theoretical line of best fit. This set of spectra is typical of the results obtained.



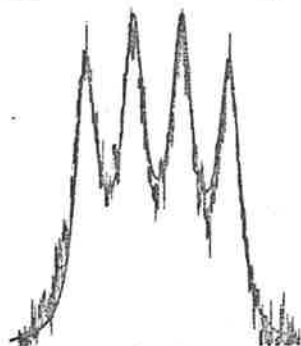
325 K
4.5 ms



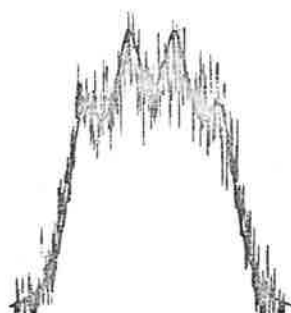
345
2.1



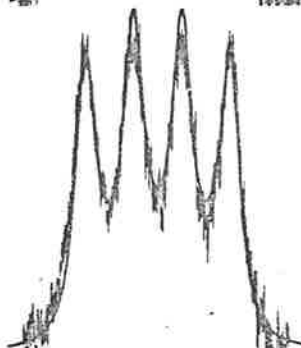
320
5.0



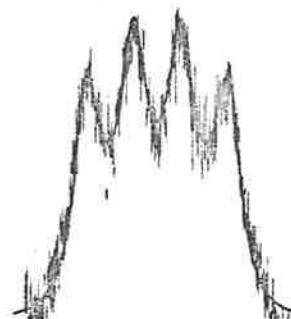
335
2.7



315
5.3



330
3.6

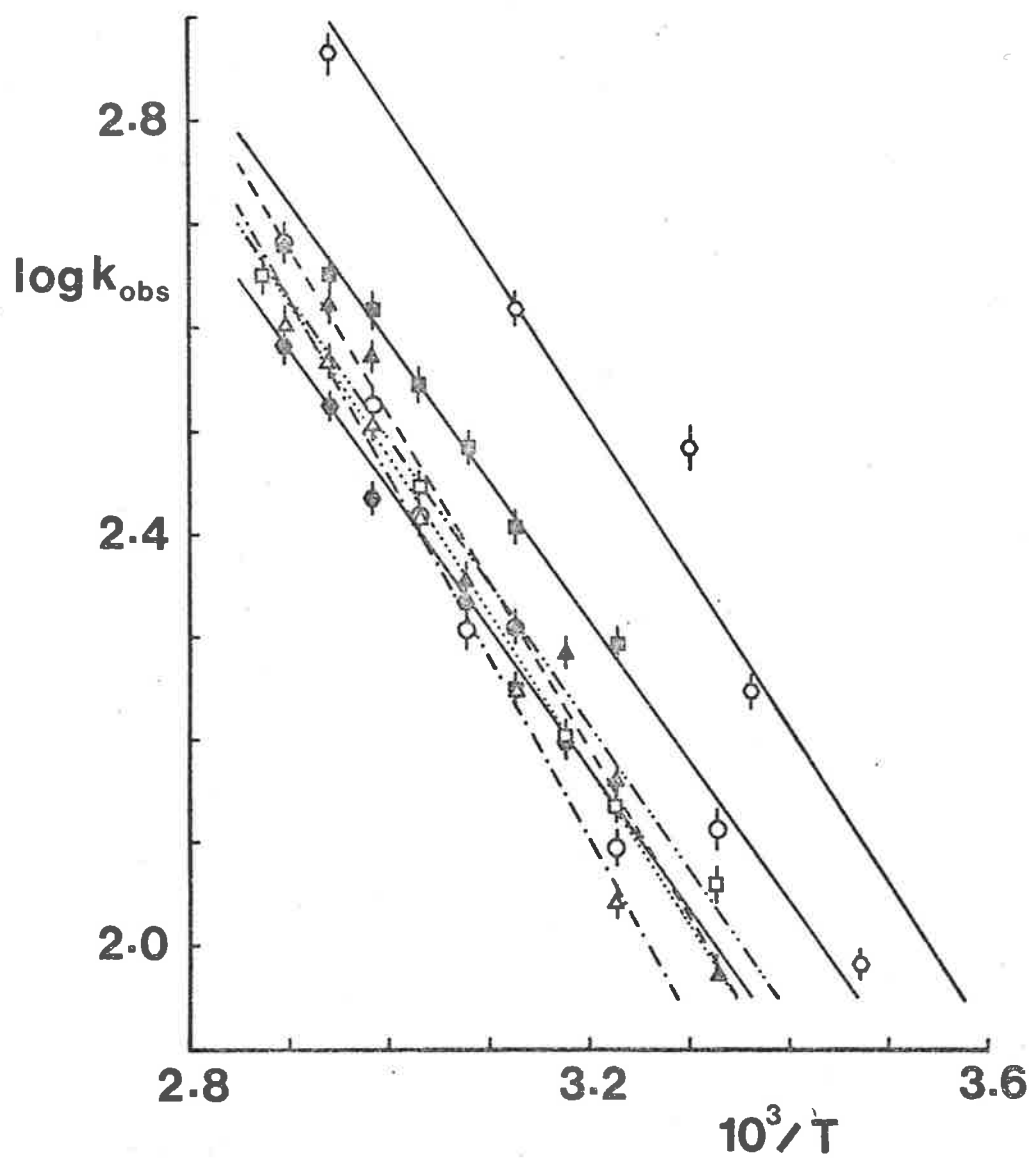


60 Hz
|-----|

Figure 4:3

Representation of the ^{19}F results as a family of Arrhenius plots of $\log(k_{\text{obs}})$ against reciprocal temperature, where k_{obs} is the reciprocal of the lifetime (τ) of a fluoride upon a beryllium(II) cation.

—○— = Be4
—■— = Be2
---○--- = Be1
—●— = Be7
---▲--- = Be6
...□... = Be5
---△--- = Be3



graph, enables a direct comparison between solutions to be made. In each case the line of best fit is shown, after least squares analysis of each set of data.

The data was next shown to be related to the change in free fluoride concentration. Rate constants were calculated for 6 different temperatures, from the straight lines of figure 4:3, and plotted against reciprocal fluoride concentration. Figure 4:4 shows these results for temperatures 298.5, 305.8, 312.5, 322.6, 330.6 and 339K. The straight line represents the line of best fit calculated once again by least squares analysis. The results demonstrate that the datum points fit a linear equation within a minimum error of $\pm 3\%$ at 322.6K to a maximum error of $\pm 7\%$ at 298.5K.

Since the plots *do* satisfactorily demonstrate linear relationships, a mechanism that accounts for the reciprocal free fluoride dependence must be invoked. If it is assumed that the tri-fluoro-beryllium(II) species takes place in the reaction then:

$$\text{Rate} = k_{\text{obs}} [\text{BeF}_4^{2-}]_t = k_1 [\text{BeF}_4^{2-}]_t + k_2 [\text{BeF}_3 \cdot \text{H}_2\text{O}^-] [\text{BeF}_4^{2-}]_t \quad 4.14$$

$$\therefore k_{\text{obs}} = k_1 + Kk_2 \times \frac{[\text{BeF}_4^{2-}]}{[\text{F}^-]} \quad 4.15a$$

$$\begin{aligned} \text{where } K &= \frac{[\text{BeF}_3 \cdot \text{H}_2\text{O}^-] [\text{F}^-]^*}{[\text{BeF}_4^{2-}]} \\ &= k_1 - \frac{k_2 K}{4} + \frac{Kk_2 [\text{F}^-]_t}{4[\text{F}^-]} \end{aligned} \quad 4.15b$$

$$\text{where } [\text{F}^-]_t - 4[\text{BeF}_4^{2-}] = [\text{F}^-]$$

It can be seen that equation 4.15b corresponds to the plots of figure 4:4, where the gradient gives $Kk_2[\text{F}_2]_t/4$ and the y intercept

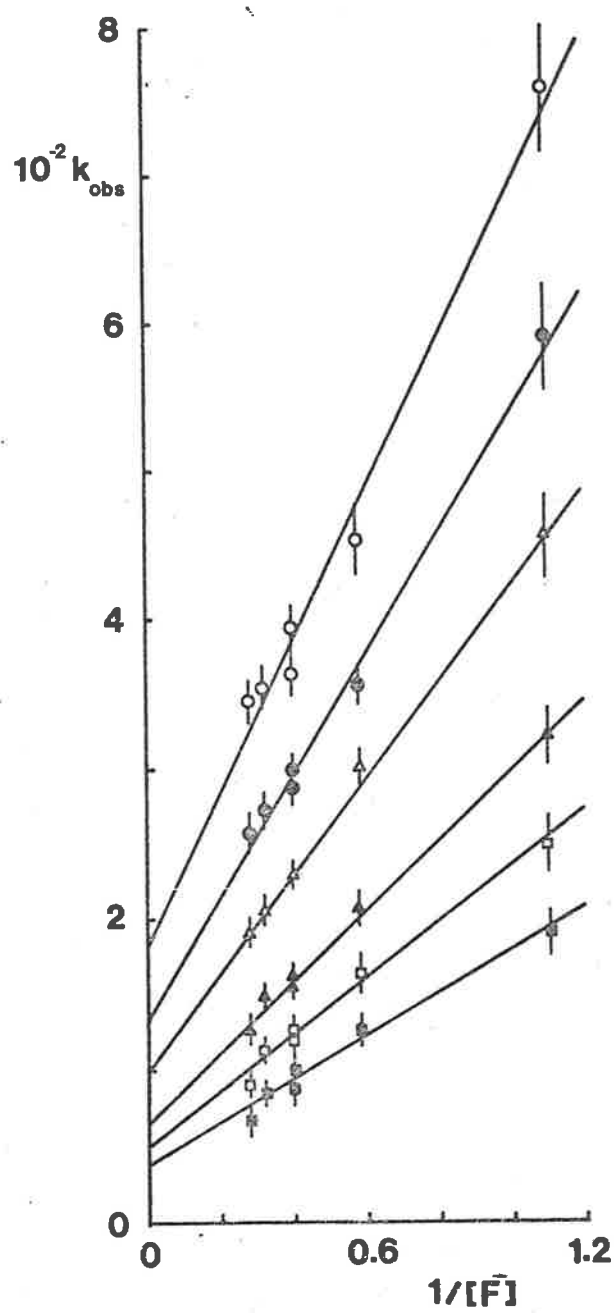
* It should be noted that $[\text{BeF}_4^{2-}] \gg [\text{BeF}_3 \cdot \text{H}_2\text{O}^-]$. Thus $[\text{BeF}_4^{2-}]_t \approx [\text{BeF}_4^{2-}]$

Figure 4:4

The 6 straight lines represent the lines of best fit to plots of k_{obs} versus reciprocal free fluoride concentration, according to equation:

$$k_{\text{obs}} = k_1 - k_2 K / 4 + K k_2 [F^-]_t / 4 [F^-].$$

From top to bottom the 6 linear plots correspond to temperatures 339, 330.6, 322.6, 312.5, 305.8 and 298.5K.



gives $k_1 - k_2K/4$.

An attempt was also made to fit the data by linear regression, to an equation with *two* independent variables, representing $1/[F^-]$ and $[F^-]$. The fit was unsuccessful and gave negative values for k_3 in the equation:

$$k_{\text{obs}} = k_1 + k_2K[\text{BeF}_4^{2-}]/[F^-] + k_3[F^-] \quad 4:16$$

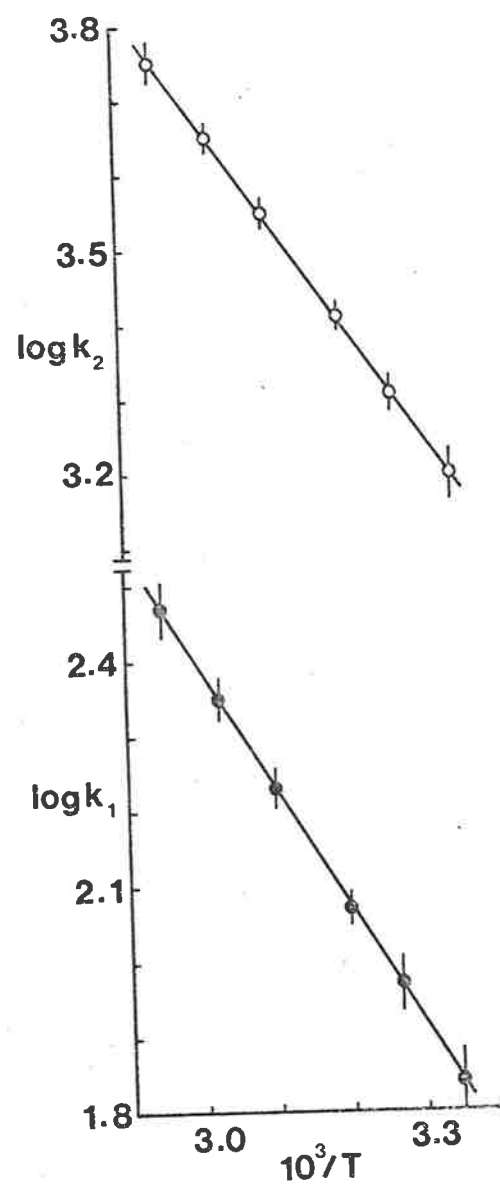
It is therefore concluded that there is no direct rate dependence on free fluoride. A contrary claim has been made by Feeney, et.al.¹², but their data was obtained from linewidth studies which are inaccurate.

The possibility that the observed rate changes were caused by the changing $[\text{SO}_4^{2-}]$ rather than $[F^-]$ was discounted by addition of K_2SO_4 to sample Be7 (of identical free fluoride concentration to Bel) and noting that the Arrhenius plot of the data for this solution with 1M of separate $[\text{SO}_4^{2-}]$, essentially repeats the Bel results (see figures 4:3). Sample Be6 increases the acid content by a factor of 3 (see table 4:1) but once again the results equate to those of Bel, with identical free fluoride concentration, thus demonstrating that $[\text{H}^+]$ also does not enter into the rate equation.

Using the six plots of figure 4:4 at the six temperatures, values of k_1 and k_2 were established, given the above relationships for the gradient and y intercept. In the calculation, the value for K of $(8.0 \pm 2) \times 10^{-2} \text{ mol. l}^{-1}$ was used at all six temperatures, in the absence of any temperature dependence (as reported by Feeney et.al.¹²), for constant concentrations of ammonium fluoride. At 298K the respective values of k_1 and k_2 were calculated as $69 \pm 3 \text{ s}^{-1}$ and $(1.6 \pm 0.5) \times 10^3 \text{ l. M}^{-1}\text{s}^{-1}$.

Figure 4:5

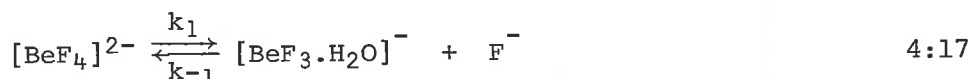
The top line is the Arrhenius plot for the 2nd order process involving $[\text{BeF}_4]^{2-}$ and $[\text{BeF}_3\cdot\text{H}_2\text{O}]^-$ characterized by the rate constant k_2 . The bottom line is the Arrhenius plot for the 1st order process with the k_1 rate constant. Both straight lines represent the line of best fit to the data according to a least squares calculation.



Plots of both $\log(k_2)$ and $\log(k_1)$ versus reciprocal temperature are shown in figure 4:5, and result when using the transition state model, in values at 298K for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the k_1 step, of 29.9 ± 3.0 kJ mol⁻¹ and -110 ± 10 J K⁻¹mol⁻¹ respectively, and for the k_2 step, values of 26.2 ± 3.0 kJ mol⁻¹ and -96 ± 9 J K⁻¹mol⁻¹ respectively.

(iii) DISCUSSION

It is seen from the results that the kinetics of fluoride exchange on $[\text{BeF}_4]^{2-}$ can be explained in terms of two reaction pathways. One step characterized by $k_1 = 69 \pm 3$ s⁻¹ would appear to be a dissociative D process, involving the reversible dissociation of fluoride from $[\text{BeF}_4]^{2-}$ as in the following reaction:



(It is assumed that beryllium(II) maintains a co-ordination number of four in the ground state as shown, but no experimental evidence for the inclusion of an aqua ligand in the first co-ordination sphere of the tri-fluoro species is available.) The reaction must be as shown since even a pre-dissociation ion pair mechanism (I_d) will be reflected in a direct dependence on free fluoride concentration ($[\text{F}^-]$). Because of the low equilibrium constant (K) for this reaction (8.0×10^{-2} M) the concentration of $[\text{BeF}_3.\text{H}_2\text{O}]^-$ in solution will be small compared with $[\text{BeF}_4^{2-}]$. A value of $k_{-1} = 8.6 \times 10^2$ M s⁻¹ for the dissociative release of H₂O from $[\text{BeF}_3.\text{H}_2\text{O}]^-$ is calculated from the determined values of $k_1 = 69$ s⁻¹ and K as above.

The actual concentration of $[\text{BeF}_3.\text{H}_2\text{O}]^-$ is determined by this $K = [\text{BeF}_4^{2-}][\text{BeF}_3.\text{H}_2\text{O}]^{-1}[\text{F}^-]^1$ and thus if the total fluoride concentration ($= 4[\text{BeF}_4^{2-}] + 3[\text{BeF}_3.\text{H}_2\text{O}] + [\text{F}^-]$) is maintained constant at 4.5M, variation of the total beryllium(II) concentration ($= [\text{BeF}_4^{2-}] + [\text{BeF}_3.\text{H}_2\text{O}]$) also produces a variation in $[\text{BeF}_3.\text{H}_2\text{O}]^-$. It is seen (fig. 4:4) over a range of 6 temperatures, that an increase in $[\text{BeF}_3.\text{H}_2\text{O}]^-$ (decrease in $[\text{F}^-]$) results in a considerable increase in the observed rate constant k_{obs} .

This increase in k_{obs} indicates a dependence on $[\text{BeF}_3.\text{H}_2\text{O}]^-$. The fluoride exchange pathway, characterized by k_2 thus involves (see fig. 4:8) $[\text{BeF}_3.\text{H}_2\text{O}]^-$ reacting with $[\text{BeF}_4]^{2-}$ in a reversible associative (A) reaction for which a fluoride bridged $[\text{Be}_2\text{F}_7]^{3-}$ is proposed. (It is envisaged that the associative intermediate $[\text{F}_3\text{Be}-\text{F}-\text{BeF}_3]^{3-}$ arises as a consequence of the actual reaction between $[\text{BeF}_4]^{2-}$ and a reactive $[\text{BeF}_3]^-$ intermediate formed by dissociation of H_2O from $[\text{BeF}_3.\text{H}_2\text{O}]^-$.)

The type of fluoride bridging proposed, has been postulated by Gillespie, Hartman and Parekh,¹⁴ as part of a mechanism for fluoride exchange on $[\text{BF}_4]^-$, which is analogous to the mechanism considered here, in that it consists of the same dissociative and associative pathways. They have also postulated a bridged intermediate for the fluoride exchange on $[\text{PF}_6]^-$, where the relevant associative reaction involves $[\text{PF}_5]$ and $[\text{PF}_6]^-$ and the intermediate is $[\text{P}_2\text{F}_{11}]^-$. Actual evidence of a $[\text{B}_2\text{F}_7]^-$ fluoride bridged species is provided by Browstein and co-workers.¹⁵

The k_2 pathway therefore involves the beryllium(II) tri-fluoro species (which will be particularly reactive relative to $[\text{BeF}_4]^{2-}$ because of its reduced coordination number) attacking the $[\text{BeF}_4]^{2-}$ in a purely associative process involving the transfer of a fluoride from the $[\text{BeF}_4]^{2-}$. Such a dependence has been observed over 6 temperatures and it is from the well resolved family of straight lines in fig. 4:4 - visually representing the data as fitting equation 4:15 (k_{obs} versus $1/[\text{F}^-]$) - that Arrhenius plots of $\log(k_1)$ and $\log(k_2)$ versus $1/\text{Temperature}$ give values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$. The magnitudes of these quantities are considered below, but first the magnitudes of k_1 and k_2 at 298K are examined.

These k_1 and k_2 values, representing 1st and 2nd order rate constants respectively, may be compared with values previously determined by Feeney, Haque, Reeves and Yue.¹² These workers quote values for the equivalent k_1 and k_2 constants, of 32.8 s^{-1} and $4.5 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ respectively. Rate constants for further reactions are also calculated, but the above values are the relevant ones to consider in comparison with this present study. These earlier values are consistent with the present ones to within the quoted error of a factor of 3. The actual $k_1:k_2$ ratio values are identical in both cases. The work of Baldwin¹ yields estimates for the rate constants of $< 29 \text{ s}^{-1}$ and $\leq 4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for k_1 and k_2 respectively and it is obvious that once again inherent difficulties in determining such rates from line width measurement only, rather than by complete line shape analysis, has adversely affected accuracy.

The value of $\Delta H^\ddagger = 29.9 \pm 3.0 \text{ kJ mol}^{-1}$ may be compared with values for water dissociating from $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ ^{16,17} (which is assumed to be identical for $\Delta H^\ddagger$ for the formation of $[\text{BeF}(\text{H}_2\text{O})_3]^+$) in an I_d mechanism, of 30.1 kJ mol^{-1} , and with the exchange of trimethylphosphate on $[\text{Be}(\text{TMP})_4]^{2+}$ ¹⁸, which is characterized by $\Delta H^\ddagger = 56.9 \pm 4.2 \text{ kJ mol}^{-1}$ for the first order TMP exchange process. It is difficult in the absence of a greater range of beryllium(II) complex $\Delta H^\ddagger$ values, to comment on trends in $\Delta H^\ddagger$ magnitudes, but it should be noted that the $\Delta H^\ddagger$'s for water and fluoride dissociation from the beryllium(II) are similar and in view of their similar ionic radii but different charges, tends to suggest a greater dependence of $\Delta H^\ddagger$ on ligand steric effects, as opposed to electrostatic effects, for beryllium(II).

The slightly lower value of $\Delta H^\ddagger = 26.2 \pm 3$ for the k_2 path is consistent with some degree of Be-F bond weakening in the associative process.

The value of $\Delta S^\ddagger = -110 \pm 10 \text{ J K}^{-1}\text{mol}^{-1}$ for the dissociative path shares a negative value for this quantity with that for the analogous dissociation of water from $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ which has a magnitude of $-93 \text{ J K}^{-1}\text{mol}^{-1}$, as calculated from the work of Stranks and Baldwin.¹⁶ A similar negative $\Delta S^\ddagger$ is also obtained for the exchange of TMP on $[\text{Be}(\text{TMP})_4]^{2+}$ - a dissociative process.¹⁸

The above negative $\Delta S^\ddagger$ for the fluoride exchange on $[\text{BeF}_4]^{2-}$ may be explained in terms of the model of Bennetto and Caldin¹⁹

which assumes that the transition state extends beyond the first coordination sphere to a major extent. In this model it is considered that beyond the first coordination sphere lies a region in which the solvent is highly disordered and that this region gradually phases into the relatively ordered bulk solvent. A negative $\Delta S^\ddagger$ value for a dissociative process is accommodated by postulating that synchronously with the dissociation of the ligand from the first coordination sphere there is a net transfer of solvent from the highly disordered region, adjacent to the first coordination sphere, to the ordered bulk solvent region, producing an overall negative $\Delta S^\ddagger$ value. Of course this model assumes the validity of the Frank and Wen concept of the solvated metal ion,²⁰ which may not be strictly applicable at the electrolyte concentrations prevalent in this study.

Attempts to explain the sign of $\Delta S^\ddagger$ in a manner analogous to that used in the $[\text{GaCl}_4]^-$ system, are confounded by the fact that the cratic term²¹ for the dissociative $[\text{BeF}_4]^{2-}$ system should be substantially positive ($+30 \text{ J K}^{-1}\text{mol}^{-1}$) and would be accompanied by a hydration entropy contribution calculated on the basis of the Born model²¹, of $+12 \text{ J K}^{-1}\text{mol}^{-1}$ to give the total value of $\Delta S^\ddagger \approx +40 \text{ J K}^{-1}\text{mol}^{-1}$.

Clearly the interpretation of the observed $\Delta S^\ddagger$ values is a subtle problem. Probably the only conclusion which can be drawn from the negative $\Delta S^\ddagger$ values for the above three beryllium(II) exchange systems, which appear to be dissociative in nature, is that the formation of the transition state leads to a net ordering which can apparently only be accommodated by postulating extension of the transition state beyond the first coordination sphere.

There is of course, no problem in explaining a value of -96 ± 9 J. K⁻¹mol⁻¹ for the associative path $\Delta S^\ddagger$, since on cratic entropy theory alone, a negative value will be predicted as two species react to form a single species transition state, but such a conclusion should be viewed in the light of the earlier discussion.

Electrostatic Model

It was decided to examine the various mechanisms for the fluoride exchange, as postulated above, using the electrostatic model developed in chapter 3 for the gallium(III)/chloride exchange. This system was accommodated to the beryllium(II)/fluoride exchange by simply adjusting the values of the charge, ionic radii, and polarizability terms. For fluoride $r_{F^-} = 1.33\overset{O}{\text{\AA}}$, $\alpha = 1.37\overset{O}{\text{\AA}}^*$. The beryllium(II) polarizability was assumed to be zero because of its high charge density, and values for H₂O were as described in Chapter 3. Such calculations were used to test the *energetic* likelihood of the possible mechanisms for a fluoride exchange on $[\text{BeF}_4]^{2-}$. It is not possible with the present model, to calculate the electrostatic energies for the $[\text{BeF}_4]^{2-}$ reaction with $[\text{BeF}_3.\text{H}_2\text{O}]^-$ which characterizes the k_2 path, but it will be seen that information concerning the nature of the $[\text{BeF}_3.\text{H}_2\text{O}]^-$ structure can be gained from these calculations.

As in the gallium(III)/chloride system, a series of electrostatic energy calculations for the structures: $[\text{BeF}_5]^{3-}$ (trigonal bipyramid), $[\text{BeF}_4]^{2-}$, $[\text{BeF}_3.\text{H}_2\text{O}]^-$, $[\text{BeF}_4.\text{H}_2\text{O}]^{2-}$ (outer sphere *and* transition state) and $[\text{BeF}_3(\text{H}_2\text{O})_2]^-$ were determined (see table 4.2) so that associative

* Obtained from $(3.45\overset{O}{\text{\AA}}^3 = \text{known Cl}^- \text{ value}) \times (r_{\text{Cl}^-}/r_{F^-})^3$.

Table 4:2

Electrostatic Energies for Beryllium(II)-Fluoride Species.

Complex	Electrostatic Energy (kJ mol ⁻¹)	Born Hydration Energy (kJ mol ⁻¹)
[BeF ₅] ³⁻	-3127	-1894
[BeF ₄] ²⁻	-3980	-898
[BeF ₃] ⁻	-4067	-224
[H ₂ OBeF ₃ $\xrightarrow[TS]{4\text{\AA}}$ F ⁻]	-4887	-
[BeF ₃ .H ₂ O] ⁻	-5042	-
[BeF ₄ .H ₂ O] ²⁻ (outer sphere)	-5184	-
[BeF ₃ . (H ₂ O) ₂] ⁻	-5456	-
F ⁻	-	-456

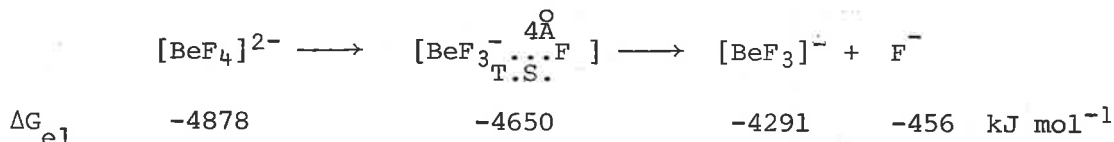
and dissociative possibilities can be considered. As shown above, the associative (A) path for fluoride exchange on $[\text{BeF}_4]^{2-}$ can be rejected, since the experimental data could not be fitted to a rate equation which included a direct fluoride dependence. The energetic possibility is still considered below.

The gas phase electrostatic energy for the 5 coordinate species ($[\text{BeF}_5]^{3-}$) is $-3127.6 \text{ kJ mol}^{-1}$ for the more stable structure with the equatorial fluorides resting directly upon the beryllium(II), thus pushing away the axial fluorides so that they rest upon the trigonal faces at $2.07 \text{ \AA}$ Be-axial-F distance. The other structural possibility, where the axial fluorides bond directly to the beryllium(II) and cause the equatorial fluorides to rest at $2.07 \text{ \AA}$ Be-equat-F separation, (closer approach being hindered by the axial fluorides' presence), is less stable by 234 kJ mol^{-1} . This possibility thus has an electrostatic energy of $-2893.6 \text{ kJ mol}^{-1}$ and since it represents a less stable transition state, it is not considered further as a pathway for an associative mechanism.

The two mechanistic possibilities are now considered, using the Born hydration corrected values (see equations 3:8 & 3:9) of the electrostatic energies, and a value of $-456^* \text{ kJ mol}^{-1}$ for the hydration energy of free fluoride. As described in the calculations for the gallium(III)/chloride system, the model reduces the 3 dimensional situation to a 2 dimensional process, with incoming and outgoing species being constrained to the 3 fold axis, and advantage

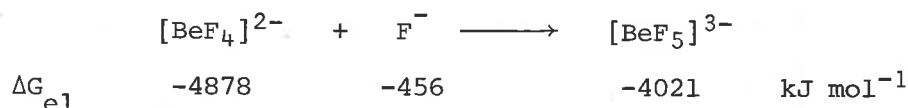
* This value is derived from $(335 \text{ kJ mol}^{-1} = \text{known Cl value}) \times r_{\text{Cl}}/r_{\text{F}^-}$, since the value varies as the reciprocal of the ionic radius.

being taken of symmetry, to represent the 3 dimensional species. In the following pathways, this incoming or outgoing species represents a fluoride or a water molecule. The structures of the species mentioned below (obtained in the manner described in chp. 3 - allowing both the trigonal fluoride/3 fold axis angle to vary independently of interspecies distance) are shown in fig. 4.6 and 4.7.



Energy difference is $-4650 - (-4878) = 228 \text{ kJ mol}^{-1}$.

For the associative pathway:



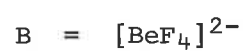
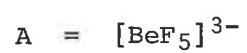
Energy difference is 313 kJ mol^{-1} .

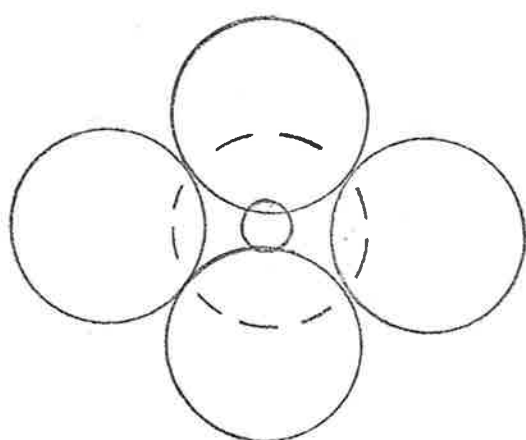
The electrostatic energy calculations are therefore *also* consistent with the dissociative pathway, although the calculated activation energy is considerably higher than the experimental results. This result is now considered and a possible activation energy lowering modification suggested.

The above calculations have ignored the fact that there could be a co-ordinated water molecule in the first co-ordination sphere of the beryllium(II) trigonal fluoride species, to give $[\text{BeF}_3 \cdot \text{H}_2\text{O}]^-$.¹² Consequently identical electrostatic energy calculations were performed for $[\text{BeF}_4 \cdot \text{H}_2\text{O}]^{2-}$ (outer sphere H_2O) undergoing a dissociative

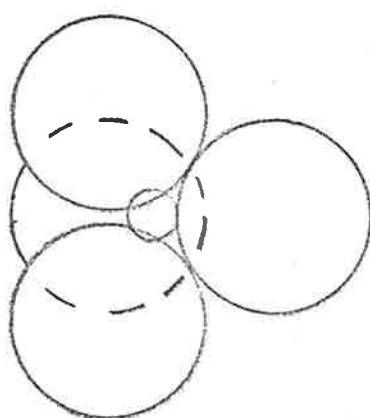
Figure 4:6

Minimum energy configurations for beryllium(II)
complexes in the gas phase.

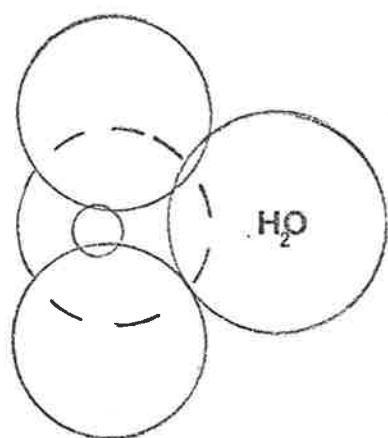




A



B



C

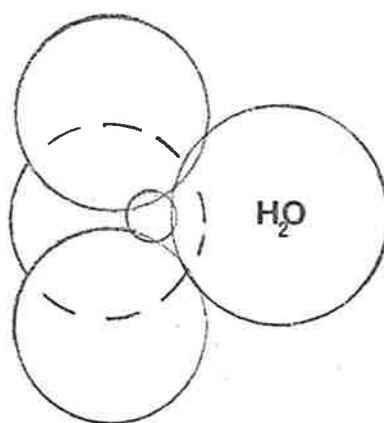
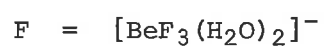
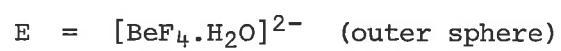
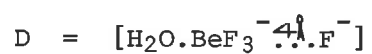


Figure 4:7

Minimum energy configurations for beryllium(II)
complexes in the gas phase.



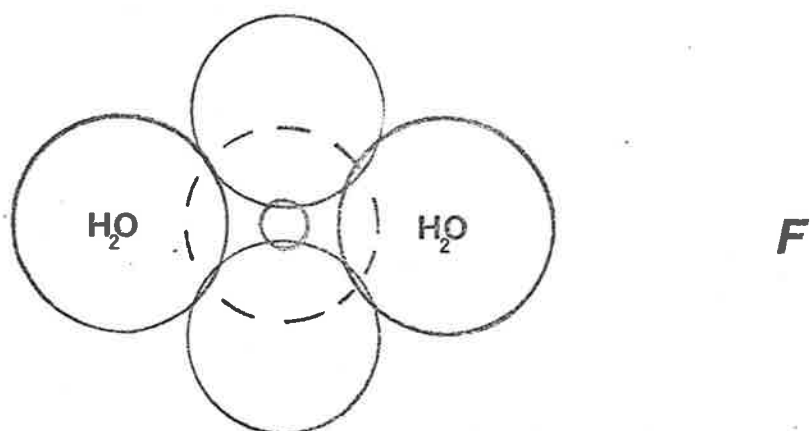
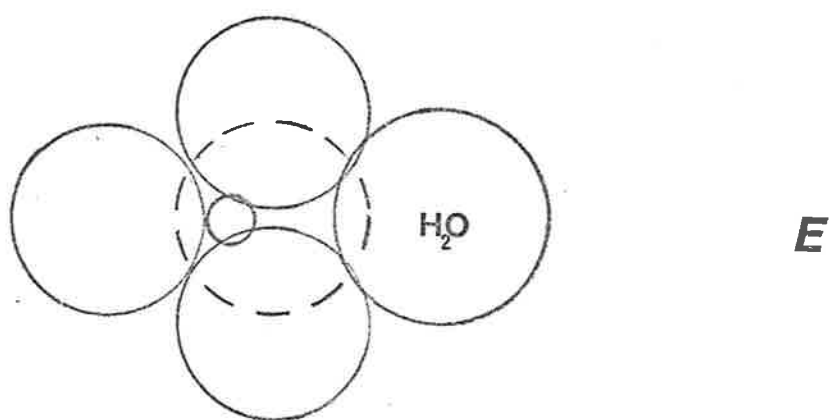
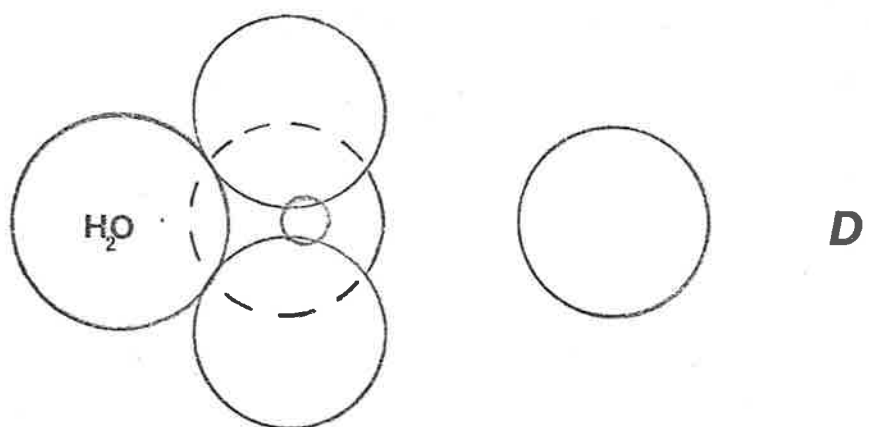
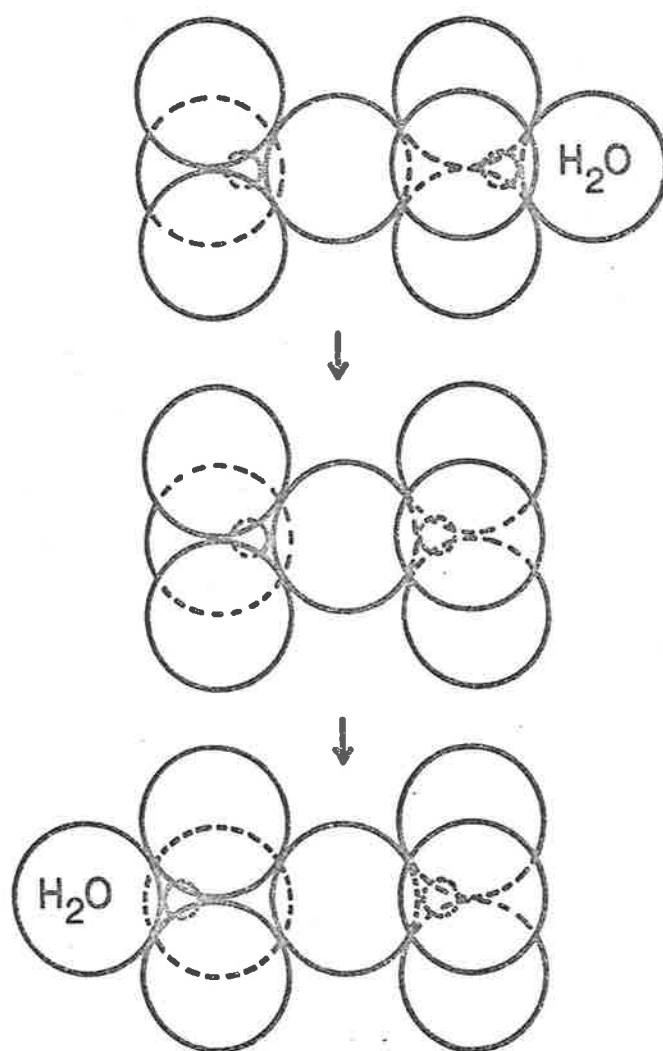


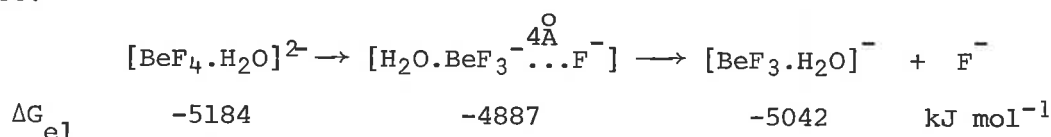
Figure 4:8

Represents the configurations of the various species involved in the k_2 reaction pathway for fluoride exchange on $[\text{BeF}_4]^{2-}$. From the top it shows the $[\text{BeF}_4]^{2-}$ and a $[\text{BeF}_3\cdot\text{H}_2\text{O}]^-$ which react to form the bridged species $[\text{Be}_2\text{F}_7]^{3-}$ in a reversible process.



process to form $[\text{BeF}_3.\text{H}_2\text{O}]^-$ (inner sphere H_2O). The structure of the reactant is tetrahedral, with a water molecule sitting on one of the trigonal fluoride faces in an outer sphere configuration, while the structure of the $[\text{BeF}_3.\text{H}_2\text{O}]^-$ intermediate species is somewhat uncertain from electrostatic energy calculations, in that the fluorides appear to move away from the plane, having stable configurations at 83° (water sitting on trigonal fluoride face) and 106° (water bonded directly to the beryllium(II)) to the 3 fold axis. These two minimum energy configurations are shown in fig. 4.6. The distinction between configurations is not critical as far as mechanistic possibilities including $[\text{BeF}_3.\text{H}_2\text{O}]^-$ are concerned.

The dissociative path with the inclusion of a water molecule now becomes:



These calculations do not include Born hydration terms. Such inclusion will not affect the activation energy required to form the transition state if the same degree of hydration for the transition state as $[\text{BeF}_4.\text{H}_2\text{O}]^{2-}$ is assumed in the absence of further information. Thus $E_a = -4887 - (-5184) = 297 \text{ kJ mol}^{-1}$. The important thing to note is that the water *does* stabilize the trigonal species, but it does not lower the actual activation energy for the dissociative step. However the presence of a *second* water molecule in the transition state, where the outgoing fluoride-beryllium(II) interspecies distance is $4\text{\AA}$, will

stabilize this transition state still further, since such a water can now bond to the beryllium(II) on the 3 fold axis, in the space left by the departing fluoride. Such inner sphere coordination *does* seem likely in view of the fact that the trigonal fluorides are repelled (leaving room for such coordination) at an angle of 81° to the three fold axis, by the presence of the outgoing fluoride (see fig. 4:7). Stabilization of the transition state by coordination of this type, is shown to be plausible by calculating the electrostatic energy for the species $[\text{H}_2\text{O}.\text{BeF}_3.\text{H}_2\text{O}]^-$ (the outgoing fluoride cannot be included because of the nature of the model) in which the two water molecules are in the axial positions sitting on the fluoride faces. For this structure the electrostatic energy is $-5458 \text{ kJ mol}^{-1}$ which is once again, *not* including a Born hydration term. It does seem therefore, that the activation energy for the dissociative step can be reduced considerably by the presence of a water bonding in the first coordination sphere between the beryllium(II) and the fluoride at $4\text{\AA}$, together with the second water which is in an outer sphere configuration. At a $4\text{\AA}$ interspecies separation there would be sufficient room for such bonding to occur. The figure of $-5458 \text{ kJ mol}^{-1}$ does not, of course strictly refer to the transition state postulated in the above model, but the calculation of electrostatic energies with two added waters to a trigonal fluoride species shows *in general* the stabilizing effect of water molecules in the vicinity of the complex.

Overall, it should be realised that the model *is* a crude one but nevertheless it demonstrates that the dissociative case is energetically more favourable than the associative case, as well as providing useful information on the likely geometries of the various species, and the effect of hydration upon the transition state energy. All of this information is consistent with the kinetic data.

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CHAPTER 5

EXPERIMENTAL DETAILS

EXPERIMENTAL DETAILS.

Samples - for ^{35}Cl Broad-line N.m.r. Studies.

Preparation of $[\text{GaCl}_4]^-$ Solutions

The stock solution of the gallium(III) complex was prepared by dissolving a weighed amount of gallium metal (Alpha 99.999%) in a fixed volume of analytical grade hydrochloric acid. The A.R. hydrochloric acid was standardized against 1M. sodium hydroxide solution. This gave the concentration of chloride in the solvent. The stock solution was similarly standardized after passing it through a cation exchange column (Zeocarb 225 H^+ form) to replace the gallium(III) (which would otherwise precipitate in the basic solution) with titratable H^+ ions. All other gallium(III)-chloride solutions (viii - xiv in chpt.2) were then prepared by adjusting the relative volumes of stock solution of known [gallium(III)] and A.R. hydrochloric acid, and the weight of lithium chloride, in a 10ml volumetric flask. Thus, solutions of both 11 and 7M chloride concentrations were prepared of varying $[\text{Li}^+]:[\text{H}^+]$ ratios.

Three samples of solution viii were prepared - 0.10, 0.20 and 0.30M in gallium(III) - and so on in the 0.1 - 0.3M range, for solutions ix, x and xi. In the case of solutions xii - xiv, single samples, each 0.18M in gallium(III) were prepared in 7.00M total [chloride] media over a range of hydrochloric acid concentrations. The reference chloride solutions were of the same total chloride and hydrochloric acid concentration as the gallium(III)-chloride solutions, with the total chloride concentration once again being adjusted with lithium chloride.

Preparation of Indium(III)-Chloride Solutions

The technique of preparation was similar to gallium(III) solutions. Indium metal (Halewood Chemicals 6N.) in weighed amount, was dissolved in analytical grade hydrochloric acid to produce the stock solution. Standardization of the stock and acid reference solution was identical to the gallium(III) solutions, and indium(III) concentrations were 0.05, 0.15 and 0.30M in the 10.95M [chloride]_{total} solutions, and 0.10 and 0.15M in the 7.00M [chloride]_{total} solutions which were prepared, in 10ml volumetric flasks, from the stock.

Preparation of Thallium(III)-Chloride Solutions

In this case thallic oxide(BDH) was dissolved in analytical grade hydrochloric acid to give a stock solution of thallium(III). It is necessary to use the oxide in this case to ensure that the higher oxidation state thallium(III) complex is prepared. The thallium(III) concentrations were 0.01 and 0.04M in the 11.00M [chloride]_{total} solutions, and 0.005, 0.087 and 0.019M in the 7.00M [chloride]_{total} solutions.

Preparation of Aluminium(III)-Chloride Solutions

For the stock solution, a weighed amount of aluminium wire (A.R.) was dissolved in analytical grade hydrochloric acid. This 1M stock solution was used in the n.m.r. of ^{35}Cl measurements.

Preparation of Beryllium(II)-Chloride Solutions

A test solution was prepared by dissolving a weighed amount of BeCl_2 in a calculated volume of A.R. hydrochloric acid in a 10ml volumetric flask, to give $[\text{Be}^{2+}] = 0.15\text{M}$ and $[\text{chloride}]_{\text{total}} = 11\text{M}$.

Preparation of Zinc(II)-Chloride Solutions

A weighed amount of ZnCl_2 (A.R.) was dissolved in 10ml of A.R. hydrochloric acid in a 10ml volumetric flask. Two solutions were prepared: the initial 11M $[\text{chloride}]_{\text{total}}$ at $[\text{Zn}^{2+}]$ of 0.15M and a second at half the initial zinc(II) concentration.

Samples - for ^{71}Ga Broad-line N.m.r. Measurements.

These solutions were prepared using the stock solution of gallium (III) in hydrochloric acid, and lithium chloride. Acid concentrations were the same as the initial concentrations employed for ^{35}Cl measurements. In all cases except viii, solutions were stoichiometrically 0.5M in GaCl_3 . The concentration for viii was 0.25M. The increase in gallium(III) concentration resulted in a more intense signal. Hexa-aqua gallium(III) perchlorate was dissolved in 1M perchloric acid for use as a ^{71}Ga shift reference sample.

Preparation of Beryllium(II)-Fluoride Solutions for High Resolution N.m.r.

A stock solution of 1.5M beryllium sulphate was prepared by weighing out the appropriate amount of analytical reagent beryllium sulphate into

a 50ml volumetric flask, which was then topped up with distilled water. A typical sample for measurement would then be prepared by weighing out the required amount of ammonium fluoride into a 10ml volumetric flask, adding the required volume of stock beryllium sulphate solution, adding A.R. conc. sulphuric acid in the desired amount, and finally topping the sample to the 10ml mark with distilled water plus 5% D₂O for the n.m.r. lock signal. It was decided not to prepare a stock ammonium fluoride solution in view of the known HF reactivity with glass. A stock solution could have been prepared in a polyethylene container, but it was just as convenient to weigh out the solid for each sample.

Using this method, a series of solutions at $[\text{fluoride}]_{\text{total}} = 4.5\text{M}$ was prepared. Beryllium(II) concentrations ranged from 0.9M down to 0.25M with acid concentration remaining constant at 0.18M. Certain other combinations of concentrations were prepared: changing the acid concentration, and also changing the sulphate concentration independent of beryllium(II) concentration. These were prepared by simply varying the proportion of con. H₂SO₄ added in the former case, and by adding K₂SO₄ in the latter.

Preparation of Gallium(III)-Bromide Solutions for Broad-line N.m.r. Measurements.

The A.R. hydrobromic acid supplied was first purified to remove dissolved Br₃⁻ that forms in solutions after oxidation of the bromide,

according to the reaction: $\text{Br}_2 + \text{Br}^- \rightleftharpoons \text{Br}_3^-$. This polybromide species will of course, interfere with the bromide exchange on $[\text{GaBr}_4]^-$, and was removed by the use of an anion exchange resin. Zeolite FFP anion exchange resin in the chloride form was first loaded onto a column, and then converted into the bromide form - first by passing through 5M NaOH, and followed with a ($\approx 2\text{M}$) solution of potassium bromide. The hydrobromic acid was now passed down this column which was in the bromide form. The Br_3^- in solution is replaced by the bromide on the column.¹ Standard stock solution (1.1M in Ga^{3+}) was prepared by dissolving gallium metal as described above for HCl, in this purified hydrobromic acid. Unfortunately as it turned out, this purified solution could still not be used because the presence of actual hydrogen bromide molecules (from the equilibrium $\text{HBr} \rightleftharpoons \text{H}^+ + \text{Br}^-$) broadened the ^{81}Br signal.²

Preparation of Gallium(III)-Bromide in Lithium Bromide Solutions.

The lithium bromide could only be obtained in laboratory reagent grade and so it was first recrystallized. A sample for n.m.r. measurement was prepared using a calculated volume of initial stock $\text{Ga}^{3+}/\text{HBr}$ solution and a weighed amount of LiBr in a 10ml volumetric flask. The total acid content was therefore reduced to what should be acceptable levels for this $8\text{M} [\text{bromide}]_{\text{total}}$ solution. Initially, two gallium(III) solutions were prepared in $8\text{M} [\text{bromide}]_{\text{total}}$, and $0.87\text{M} [\text{H}^+]$ media; they were $[\text{Ga}^{3+}] = 0.08$ and 0.04M . A solvent reference was also prepared. ^{81}Br n.m.r. measurements were abandoned however, when it was realized that the high solution viscosity caused excessive signal broadening at

temperatures below zero, while quadrupolar broadening induced by gallium(III) at room temperature and above was *also* great enough to make the signal at 0.08 *and* 0.04M $[\text{Ga}^{3+}]$ indistinguishable from the noise.

EXPERIMENTAL DETAILS OF N.M.R. MEASUREMENTS

(i) Preparation of Broad-line ^{35}Cl N.m.r. Sample Tubes.

A 2.5 to 3.5ml aliquot of one of the sample solutions was transferred to a specially designed Pyrex broad-line n.m.r. tube by Pasteur pipette. Fig. 5:1 shows the form of the apparatus. It consists of an *inverted* Pyrex sample tube (9mm diam.) into which is sealed a concentric thermocouple well (2mm diam.). The tube is attached *through its base* to a high vacuum tap and joint. The tube containing the sample was attached to a vacuum line and, by means of the tap, placed under partial vacuum. Since the solution contained within the tube was aqueous, it was not considered necessary to freeze it before sealing. A completed sealed tube is shown on the right hand side of fig. 5:1.

The measurement of broadenings produced by two or three *different* gallium(III) concentrations differing over a factor of three or four, and subsequent normalization, ensures that sufficient overlap of points is obtained in their region of *effective broadening*. The measurements of samples and solvent references must be made in accordance with the following 3 limiting factors for ^{35}Cl work.

- (a) less than *ca.* 7% of all halide species must be coordinated^{3,4}

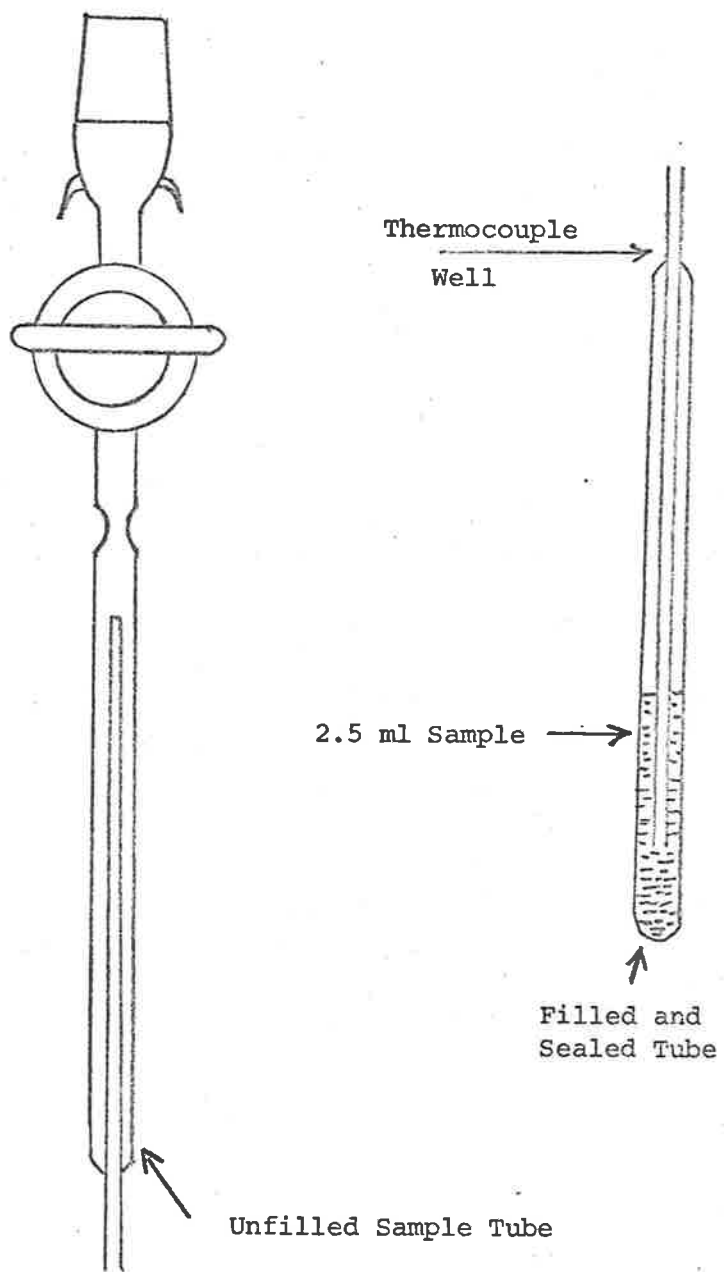


Figure 5.1 Broad-line Sample Tubes.

- (b) broadening of the ^{35}Cl resonance induced by the metal ion should be *at least equal* to the reference chloride linewidth. This will ensure that errors in measurement of linewidth ($\pm 5\%$) which are additive when a difference has to be found, will be minimized. The error is mainly due to the relatively poor signal to noise ratio for ^{35}Cl measurements. (The relative sensitivity of ^{35}Cl to ^1H at constant field is 4.70×10^{-3})⁵
- (c) broadening in excess of about 8 solvent linewidths (approx $3.4 \times 10^{-4}\text{T}$) results in the amplitude of the signal dropping too close to the noise level for accurate linewidth determination.

(ii) Preparation of Broad-line ^{71}Ga N.m.r. Sample Tubes.

Samples were placed in a 15mm diameter n.m.r. tube, and since the measurements were taken at 298K, the tubes did not have to be sealed. The shift measurements were achieved by placing a reference sample of $[\text{Ga}(\text{H}_2\text{O})_6](\text{ClO}_4)_3$ in 1M HClO_4 , sealed into a 5 mm diameter n.m.r. tube, into the larger n.m.r. tube and recording the signals produced from both solutions, simultaneously.

(iii) Preparation of High-Resolution ^{19}F N.m.r. Sample Tubes.

A sample solution was added by Pasteur pipette to a 5ml n.m.r. tube to which is attached a glass joint in the same manner as for the broad-line tubes, for the purpose of sealing under vacuum. Because of the

greater ease of loss of the smaller sample in this smaller tube, the solution was first frozen before the tube was placed under vacuum, and degassing was also carried out before sealing. The tube was then placed in the freezer to ensure that HF reaction with the glass walls of the tube was minimized, before the n.m.r. measurements were made.

(iv) Instrumental Details.

(a) Broad-line Spectrometer.

Measurements of the ^{35}Cl , ^{71}Ga and ^{81}Br resonances were obtained using a Varian V - 4502 dual purpose spectrometer, that had been converted into a broad-line instrument. The specific operation modes of vital components used, were as follows:

1) V - 4210A - *variable frequency R.F. unit.*

This is both a transmitter and a receiver tuned to the required frequency; 4.172 MHz for ^{35}Cl , 12.984 MHz for ^{71}Ga and 11.498 MHz for ^{81}Br . The frequency was constantly monitored by a "Solartron" EM1616 frequency counter. The R.F. power level was maintained during each measurement, at a value well below saturation level for that sample.

2) V - 4230B 4 to 8 MHz n.m.r. probe operated in the absorption (V) mode with finely tuned built in "paddles". Any dispersion (u) mode leakage, was quite detectable from the readily observable asymmetry of the signal.

3) V - 4230B 8 to 16 MHz n.m.r. probe operated in the same way as the above unit.

- 4) 9" pole face electromagnet - operated at approximately 0.99T and regulated by a "Mark II" Fieldial in association with a centrally positioned "Hall effect" crystal sensor.
- 5) V - 4250B - Sweepunit - this produces the low frequency (40Hz) sweep field fed into the n.m.r. probe. To obtain meaningful and reproducible results in line broadening experiments, the sweep field control must be adjusted to give a balance between least modulation broadening and adequate signal amplitude. Final modulation broadening effects can be corrected for by the method of "Wahlquist"⁶ for such broadening being less than about 10% of the total linewidth. The sweep field is thus kept at sufficiently low amplitude for accurate line-width determination.
- 6) V - 4270B - output control unit - the original mechanical "chopper" from this unit has been replaced by an electronic equivalent. Also fitted, was a large bandwidth 2 KHz band-pass filter in the "external" position (for use in side band operation). The amplified phase detected output was fed into a 10" Riken-Denshi graphic recorder.

The instrument was set, using the above controls, to record measurements of the broadenings, by the first derivative method. The sweep frequency was 40 Hz. An initial calibration of the chart paper was obtained using the sideband method. A modulating frequency of 1900 Hz was used and since the distance between peaks equals twice the modulating frequency:

$$\text{Distance} = 21.3\text{cm.} \equiv 3800 \text{ Hz} \equiv (3800 \times 2\pi)/\gamma T.$$

$$\text{where } \gamma = 2620 \times 10^4 \text{ rad. T}^{-1} \text{ sec.}^{-1}$$

therefore $1\text{cm} \equiv 4.3 \times 10^{-5} \text{ T}$.

First derivative spectra were produced in triplicate and the line-widths used were the average of the three determinations. The readings were taken by sweeping both upfield and downfield, since any small variation in the field caused by drift will be averaged out. The measurement error was considered to be $\pm 5\%$. These signals were corrected for modulation broadening (which never exceeded 7% of the full absorption line width at half maximum signal amplitude), by the Wahlquist method.⁶ Chemical shifts were determined using the calibrated sweep unit control. From this control, the sweep offset could be read conveniently from the centre of the resonance of the sample to the centre of the pure solvent reference. It was found however, when measuring ^{71}Ga spectra, that field drift was occurring, which was why a sealed tube of solvent reference was actually introduced into the large n.m.r. tube; this facilitated the chemical shift measurement. The samples were thermostatted in the probe using a standard Varian nitrogen flow thermostat ($\pm 1\text{K}$). Dry nitrogen was used as it was found that ordinary industrial nitrogen contained enough water vapour to freeze the tube in the probe and block the nitrogen flow during low temperature measurements. The sample temperature was constantly monitored between n.m.r. determinations, with a calibrated copper constantan thermocouple placed within the inbuilt well in the n.m.r. tube (see fig. 5:1). One junction of the thermocouple was thermostatted in a melting ice bath contained in a Dewar, to act as a temperature reference. The E.M.F. produced by the thermocouple was monitored on a 10" Riken-Denshi graphic recorder.

(b) The High Resolution ^{19}F N.m.r. Spectrometer.

Measurements of the fluorine resonance quartet produced by spin spin coupling to beryllium were performed on the Bruker HX90E instrument. The 5mm sample tubes were spun and variable temperature work incorporated the B - ST 100/700 temperature unit, that conveniently allows a temperature to be dialled up with an error of $\pm 0.3\text{K}$, and equilibrium of the sample attained in only 10 minutes or so. Ambient temperature is 300K and lower temperature measurements were obtained by use of liquid nitrogen cooling of the nitrogen gas flow, with an attached liquid N_2 pump. The actual ^{19}F measurements were taken in the Pulse Free Precession mode which allowed the use of D_2O as a hetero locking device, because of a time sharing electronic arrangement incorporated into the transmitter coils of the probe. A plot of the spectrum at each temperature was taken on the calibrated paper but with the machine, and controls under the instruction of a B - NC 12 computer with teletype attached. Each spectrum was also digitized by computer and transferred to paper tape via the teletype. The tedious process of visually transferring data points from the n.m.r. spectrum onto data cards was therefore bypassed and the data was read directly into the CDC 6400 computer through a NOVA teletype.

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APPENDIX

COMPUTING TECHNIQUES

APPENDIX

COMPUTING TECHNIQUES

Three main computing programs were used for the work contained in this thesis, corresponding to the different calculations involved in chapters 2, 3 and 4.

(i) The work contained in chapter 2 necessitated the solving of two different problems associated with interpretation of the ^{35}Cl relaxation data:

- (1) A correction of the Lorentzian absorption (ν), for modulation broadening due to the finite magnitude of the low-frequency (40Hz) modulation applied to the magnetic field in the n.m.r. probe.
- (2) The determination of the theoretical best fit curve to the experimental $T_{2\text{ex}}$ data points and the corresponding activation parameter values ($\Delta H^\ddagger$, $\Delta S^\ddagger$ and $k_{298\text{K}}$)

The main program MODFIT reads in the temperature (XA) (in centigrade), sample concentration (XB), first derivative "peak to peak" distances of the n.m.r. absorption signal for the solution in centimeter units of chart paper (XC), solvent "peak to peak" distance (XD), the sweep field magnitude of the sample in gauss (XE), where 10^4 gauss = 1 Tesla, and the sweep field magnitude of the solvent in gauss (XS). These last values were obtained from the manual of broad-line operation, supplied with the n.m.r. equipment. The accuracy of the sweep fields,

although their values weren't of high precision, was suitable for modulation corrections to the linewidths in which the total modulation broadening is <0.1 of the total linewidth.

Such corrections are determined in SUBROUTINE SOLVE, FUNCTION ANR and FUNCTION FUNCT, to give a solution to the Wahlquist expressions,^{*} which are incorporated to deal with the problem. These routines calculate a solution for $H_{1/2}$ in the polynomial:

$$H_{\delta} = \{ (H_{\omega})^2 + 5/12(H_{1/2})^2 - 2/3(H_{1/2})[(H_{1/2})/4 + 3(H_{\omega})^2/4]^{1/2} \}^{1/2}$$

where $2H_{\delta}$ is the magnetic field difference across the "peak to peak" distance of the first derivative curve.

$H_{1/2}$ is the true halfwidth of the Lorentzian line.

H_{ω} is the amplitude of the sinusoidal modulation.

SUBROUTINE REG calculates the T_{2ex} value at the temperature of each datum point, and sums the squares of the residuals of the experimental values from the calculated values over all points. This fit corresponds to the minimum *relative* error over the T_{2ex} data set. Since each linewidth has approximately the same percentage error, this is considered reasonable.

SUBROUTINE FIT detects any minimum in the sum of the sequence of the residuals, as the parameters are varied by small constant increments in a direction determined by this subroutine.

* H.J. Wahlquist, *J. Chem. Phys.*, 1961, 35, 1708.

A listing of the program is shown below. As it is set up it will fit the T_{2ex} variation for 11M chloride exchange on $[GaCl_4]^-$.

Parameters used are:

- UPSLA - Controls quadrupolar activation energy.
- UPSL - Controls activation energy of halide exchange.
- XINT, YINT - Coordinates of the intersection points of the
 components τ_M and T_{2M} .

Values of the rate at 298K, $\Delta H^\ddagger$, $\Delta S^\ddagger$ and E_a for the exchange reaction are calculated using the derived values of UPSL, XINT and YINT as shown below in the main program.

```
PROGRAM MODIFIT(INPUT,OUTPUT,TAPE1=INPUT)
COMMON YEXP(90),X(90),YNEW(90),UPSLA,UPSL,YINT,XINT,SDIFF,J,FF1
DIMENSION YREX(90),YRN(90)
UPSLA=2119.62
UPSL=3920.32
YINT=-12.2582
XINT=0.00390289
J = 0
7 J=J+1
  READ 14,XA,XB,XC,XD,XE,XS
14 FORMAT(F5.1,F9.3,F8.1,F10.1,F12.3,F11.3)
  IF(E OF,1)10,8
8 CALL SOLVE(XC,XE)
  P1=XC
  IF(XS.EQ.0)6,10
6 XS=0.125
10 CALL SOLVE(XD,XS)
  P2=XD
  P3=(P1-P2)/(XB*10)
  T2PM=(0.2*4./110)/(P3*417.2)
  YEXP(J)=ALOG(T2PM)
  XA=XA+273.2
  X(J)=1/XA
  GO TO 7
19 J=J-1
  CALL REG
  DO 107 JN=1,J
  YREX(JN)=EXP(YEXP(JN))
107 YRN(JN)=EXP(YNEW(JN))
  PRINT 106,(X(JN),YREX(JN),YRN(JN),JN=1,J)
  FF1=SDIFF
  M=1 $N=0
101 D=1000
108 UPSLA=UPSLA+UPSLA/D
  M=M+1
  CALL FIT(M,D)
  IF(M.NE.1) GO TO 108
  UPSLA=UPSLA-UPSLA/D
109 PRINT105,M,D,UPSLA
98 UPSL=UPSL+UPSL/D
  M=M+1
  CALL FIT(M,D)
  IF(M.NE.1)GO TO 98
  UPSL=UPSL-UPSL/D
110 PRINT105,M,D,UPSL
  D=2500
104 YINT=YINT+YINT/D
  M=M+1
  CALL FIT(M,D)
```

```
      IF (M.NE.1) GO TO 104
      YINT=YINT-YINT/D
111  PRINT 105,M,D,YINT
103  XINT=XINT+XINT/D
      M=M+1
      CALL FIT(M,D)
      IF (M.NE.1) GO TO 103
      XINT=XINT-XINT/D
112  PITNT105,M,D,XINT
105  FORMAT(10X,I2,*INCREMENTS OF MAGNITUDE PARAMETER/* ,F5,* GIVES
      *   PARAMETER =*,E12.5,/)
      EA=(UPSL*1.9871)/(1000)
      YNEW2=YINT-UPSL*(XINT-0.003354)
      XRATE=1/(EXP(YNEW2))
      PRINT203,EA,XRATE
      DELTAH=EA-(1.9871*298.15)/1000
      DELTAS=1.9871*ALOG((XRATE*6.6256*(10.**-11))/(1.3805*298.15))+
1DELTAH*1000/298.15
203  FORMAT(1H1,20X,F7.4,*KCALs*,20X,*RATE AT 25DEGS = *,E8.2)
      PRINT204,DELTAH,DELTAS
204  FORMAT(1H0,20X,*DELTA H = *,F7.4,*KCALs*,20X,*ENTROPY = *
1,F10.6,*E.U.*)
      IF (N.EQ.4) 123,113
113  N=N+1
      GO TO 101
123  DO 114 JN=1,J
      YREX(JN)=EXP(YEXP(JN))
114  YRN(JN)=EXP(YNEW(JN))
      PRINT 106,(X(JN),YREX(JN),YRN(JN),JN=1,J)
106  FORMAT(24X,*1/T*,20X,*T2P(EXPTL)*,22X,*T2P(CALC)*,/,/, (
      * 20X,F9.7,18X,E10.3,21X,E10.3)
      GO TO 128
128  CONTINUE
      STOP
      END
```

```
      SUBROUTINE FIT(M,D)
      COMMON Y(90),X(90),YNEW(90),UPSLA,UPSL,YINT,XINT,SDIFF,J,FF1
      DIMENSION FF(91)
      IF (M.GE.91) GOTO3
      CALL REG
      FF(M)=SDIFF
      IF (M.GE.3) GOTO4
      IF (FF(2).GT.FF1) 1,2
1  D=-D
2  RETURN
4  IF (FF(M).GT.FF(M-1)) 5,2
3  E=ABS(2000/D)
```

```
PRINT 7,E
7 FORMAT(10X,*MINIMUM IN SQUARES OF RESIDUALS OUTSIDE*,F2,* P.C.*) FIT
STOP
5 FF1=FF(M-1)
M=1
RETURN
END
```

```
SUBROUTINE REG
COMMON Y(90),X(90),YNEW(90),UPSLA,UPSL,YINT,XINT,SDIFF,J,FF1
DIMENSION DIFF(90)
SDIFF=0
DO 1 I=1, J
T2M=EXP(-UPSLA*(X(I)-XINT)+YINT)
TAUM=EXP(UPSL*(X(I)-XINT)+YINT+ALOG(X(I)/XINT))
YNEW(I)=ALOG(T2M+TAUM)
DIFF(I)=(Y(I)-YNEW(I))**2
1 SDIFF=SDIFF+DIFF(I)
PRINT3,SDIFF
3 FORMAT(10X,*SDIFF=*,E13.5)
RETURN
END
```

```
SUBROUTINE SOLVE (Y,A)
EXTERNAL DERIV,FUNCT.
A=A/2.
Y=Y*0.214
X=3.464*Y
EPS=1.0E-6
X=ANR(A,X,Y,FUNCT,DERIV,EPS)
Y=X
RETURN
END SOLVE
```

```
FUNCTION ANR (A,X,Y,F,D,EPS)
B=5./12.
1 ANR=X-F(A,B,X,Y)/D(A,B,X,Y)
IF (ABS(ANR-X).LT.EPS) RETURN
X=ANR
GOTO 1
END
```

```
FUNCTION FUNCT(A,B,X,Y)
FUNCT=B*X*X-X*SQRT(X*X+3*A*A)/3+A*A-Y*Y
RETURN
ENTRY DERIV
DERIV=2*B*X-(2*X*X+3*A*A)/(3*SQRT(X*X+3*A*A))
RETURN
END FUNCT
```

(ii) In chapter 3 the series of calculations involved in determining the electrostatic energy for a series of tetrachloro complexes, is described. The actual main computer program used in this calculation is MXFOR. After introducing the various parameters needed for the electrostatic calculation, this program sets up the geometry of the complex species plus incoming species, and calculates the final energy of the system after the converged electric field has been obtained.

REAL FUNCTION LAENGE calculates the actual length of a 2 dimensional vector. Since the program works in 2 dimensional vectors, this function is needed for electrostatic energy calculations that require direct inter-species distances.

SUBROUTINE EKA, SUBROUTINE BLOG and SUBROUTINE TRID calculate the electric field resulting from the various charged species, at specified distances from those species, corresponding to other atom locations.

SUBROUTINE MYI calculates the induced dipole moment at any atom location given a particular electric field value, and values for the polarizability at that point. It then calculates the total dipole moment by including the permanent dipole contribution.

SUBROUTINE DIPOL calculates the electric field resulting from dipoles at specified distances from these dipoles corresponding to other atom locations.

SUBROUTINE ELEC calculates a potential energy value at a given distance from an electrostatic charge.

```

PROGRAM MXFOR (OUTPUT,TAPE6=OUTPUT)
C*****
C PROGRAM MX4
C THIS PROGRAM CALCULATES THE POTENTIAL ENERGIES FOR VARIOUS DISTANCES OF
C APPROACH OF AN INCOMING ANION TO A TETRAHEDRAL SPECIES. THE 3-DIMEN-
C SIONAL PROBLEM IS SIMPLIFIED TO A 2-DIMENSIONAL ONE.
C*****
      DIMENSION RK2(2),RK4(2),EO2( ),EO4(2),EOA(2),
1  SEO2(2),SEO4(2),SEOA(2),P2(2),P4(2),PA(2),
2  ED42(2),ED4A(2),ED24(2),
3  ED2A(2),EDA2(2),EDA4(2),ED132(2),
4  EVO(26),EV(26),EOZ(2),EOY2(2),EOX2(2),EOY4(2),EOX4(2),
5  EOWA(2),EOYA(2),EOXA(2),GA(2),EOK(2),EOXK(2),EOWK(2),
6  SEOK(2),EDK2(2),EDT4(2),EDKA(2),EDAK(2),ED2K(2),ED4K(2),PK(2)
      COMMON RKA(2),ZA,ZK,RW,RK,COST,SINT,R23,ZAN
      REAL MYOW,LAENGE,MYDA,MYOK
      EQUIVALENCE (EV(1),P2(1)),(EV(3),P4(1)),
1  (EV(5),PA(1)),(EV(7),ED24(1)),(EV(9),ED2A(1)),
2  (EV(11),ED42(1)),(EV(13),ED4A(1)),
3  (EV(15),EDA2(1)),(EV(17),EDA4(1)),
4  (EV(19),ED132(1)),(EV(21),SEO2(1)),(EV(23),SEO4(1)),
5  (EV(25),SEOA(1)),(EV(27),PK(1)),(EV(29),EDK2(1)),
6  (EV(31),EDK4(1)),EV(33),EDKA(1)),(EV(35),EDAK(1)),(EV(37),
7  ED2K(1)),(EV(39),ED4K(1)),(EV(41),SEOK(1))
      DATA EVO/42*0./,PI/3.14159/,GAMA/331.931/
C*****
C INPUT
C RW IS THE RADIUS OF TETRAHEDRAL ANIONS.
C RK IS THE RADIUS OF CATION
C RA IS THE RADIUS OF THE INCOMING ANION
C MYOW IS THE PERMANENT DIPOLE MOMENT OF TETRAHEDRAL ANIONS
C MYOA IS THE PERMANENT DIPOLE MOMENT OF THE INCOMING ANION
C MYOK IS THE PERMANENT DIPOLE MOMENT OF THE INCOMING CATION
C AW IS THE POLARIZABILITY OF TETRAHEDRAL ANIONS
C AA IS THE POLARIZABILITY OF THE INCOMING ANION
C AK IS THE POLARIZABILITY OF THE CATION
C ZK IS THE CHARGE NUMBER OF CATION
C ZA IS THE CHARGE NUMBER OF TETRAHEDRAL ANIONS
C ZAS IS THE CHARGE NUMBER OF INCOMING ANION
C GA IS THE NULL VECTOR FOR CATION
C*****
      DATA RA,MYOW,MYOA,AW,AA/1.8 ,0.,0.,3.45,3.45/
      ZK=3,$ZA=1.$RW=1.81$RK=0.70$MYOK=0.$AK=0.198$ZAN=1.
      GA(1)=0.
      GA(2)=0.
      WRITE (6,11)
11 FORMAT (1H1,/,13X,5HTHETA,6X,3HRK4,11X,3HRKA,12X,1HU,13X,
* 3HUKA,12X,3HUWO,12X,3HUWI,13X,3HUAI,/)
      MYOW=MYOW/4.8029

```

```

C*****
C  DATA FOR THE GEOMETRY OF THE COMPLEX FOR THE GIVEN THETA      *
C  RKA IS THE VECTOR FROM CATION TO INCOMING ANION                 *
C  RK4 IS THE VECTOR FROM CATION TO ANION 4                        *
C  RK2 IS THE VECTOR FROM CATION TO ANION 2                        *
C*****
      RK2(2)=-2.*SQRT((RW+RK+RA)*RW*RK*RA)/(RK+RA)
      NO=IFIX(180.*(1.-ATAN(RK2(2)/SQRT((RW+RK)**2-RK2(2)**2))/PI))
      N=IFIX(180.*(1.-ATAN(SQRT(4./3.)*RW/(SQRT((RT+RA)**2-4.*RW**2/3.)
* -(RA+RK)))/PI))
      N=MINO(NO,N)
      NO=1+IFIX(180.*ATAN(SQRT(4./3.)*RW/SQRT((RW+RK)**2-4./3.*RW**2))
* /PI)
      DO 10 M10=NO,N
      THETA=M10*PI/180.
      COST=COS(THETA)
      SINT=SIN(THETA)
      IF (M10-180+NO) 31,31,32
32 RK2(2)=RW*SQRT(4./3.)
      RK2(1)=RK2(2)*COST/SINT
      GO TO 30
31 RK2(1)=(RW+RK)*COST
      RK2(2)=(RW+RK)*SINT
30 RKA(1)=RK2(1)+SQRT((RW+RA)**2-RK2(2)**2)
      RKA(2)=RK+RA
      RKA(1)=AMAX1(RKA(1),RKA(2))
      RKA(2)=0.
      RK4(1)=RK2(1)-SQRT(4.*RW**2-RK2(2)**2)
      RK4(2)=-RK-RW
      RK4(1)=AMINI(RK4(1),RK4(2))
      RK4(2)=0.
      R23=SQRT(3.)*RK2(2)
C*****
CC  CALCULATION OF THE ELECTRICAL FIELD OF THE CATION AND ANION    *
C*****
      CALL EKA(RK2,EO2)
      CALL EKA(RK4,EO4)
      CALL EKA(RKA,EOA)
      CALL EKA(GA,EOK)
      CALL BLOG(RK2,RK4,EOY2)
      CALL BLOG(RK4,RK2,EOX4)
      CALL BLOG(RKA,RK2,EOXA)
      CALL BLOG(RKA,RK4,EOWA)
      CALL BLOG(GA,RK2,EOXK)
      CALL BLOG(GA,RK4,EOWK)
      CALL TRID(RK2,EOZ)
      DO 1 M1=1,2
      EO2(M1)=EO2(M1)+EOY2(M1)+EOZ(M1)

```

```

EO4 (M1)=EO4 (M1)+EOX4 (M1) *3
EOA (M1)=EO4 (M1)+EOXA (M1) *3+EOWA (M1)
EOK (M1)=EOK (M1)+EOXK (M1) *3+EOWK (M1)
1 CONTINUE
DO 5 M1=1,2
SEO2 (M1)=EO2 (M1)
SEO4 (M1)=EO4 (M1)
SEOA (M1)=EOA (M1)
SEOK (M1)=EOK (M1)
5 CONTINUE
25 N4=0
C*****
C BEGINNING OF THE ITERATION *
C*****
4 CONTINUE
C*****
C DETERMINATION OF THE DIPOLE MOMENTS FROM THE LAST CALCULATED FIELD *
C STRENGTH *
C*****
CALL MYI (SEO2,MYOW,AW,P2)
CALL MYI (SEO4,MYOW,AW,P4)
CALL MYI (SEOA,MYOA,AA,PA)
CALL MYI (SEOK,MYOK,AK,PK)
C*****
C CALCULATION OF THE ELECTRICAL FIELD OF THE ABOVE DETERMINED DIPOLE *
C MOMENTS *
C*****
CALL DIPOL (ED42,RK2,RK4,P4)
CALL DIPOL (ED4A,RKA,RK4,P4)
CALL DIPOL (ED24,RK4,RK2,P2)
CALL DIPOL (ED2A,RKA,RK2,P2)
CALL DIPOL (EDA2,RK2,RKA,PA)
CALL DIPOL (EDA4,RK4,RKA,PA)
CALL DIPOL (EDK2,RK2,GA,PK)
CALL DIPOL (EDK4,RK4,GA,PK)
CALL DIPOL (EDKA,RKA,GA,PK)
CALL DIPOL (EDAK,GA,RKA,PA)
CALL DIPOL (ED2K,GA,RK2,P2)
CALL DIPOL (ED4K,GA,RK4,P4)
C*****
C SETTING UP THE TOTAL ELECTRICAL FIELD *
C*****
ED132 (1)=-2./R23**3*P2 (1)
ED123 (2)=-3.5/R23**3*P2 (2)
ED24 (2)=0.
ED2A (2)=0.
ED2K (2)=0
DO 2 M2=1,2

```

```

      SEOA(M2)=EOA(M2)+ED4A(M2)+ED2A(M2)*3+EDKA(M2)
      SEO4(M2)=EO4(M2)+EDA4(M2)+ED24(M2)*3+EDK4(M2)
      SEO2(M2)=EO2(M2)+ED42(M2)+EDA2(M2)+ED123(M2)+EDK2(M2)
2    SEOK(M2)=EOK(M2)+ED4K(M2)+ED2K(M2)*3+EDAK(M2)
      DO 253 JJJ=1.42
      IF (ABS(EVO(JJJ)-EV(JJJ)).GT.1E-6) GO TO 228
253  CONTINUE
C*****
C  CALCULATION OF THE ENERGY IN CASE OF THE FIELDSTRENGTH CONVERGES *
C  UKA IS THE ELECTROSTATIC ENERGY BETWEEN IONS. *
C  UWO IS THE FIELD ENERGY OF THE PERMANENT DIPOLE MOMENTS OF ANIONS *
C  UWI IS THE FIELD ENERGY OF THE INDUCED DIPOLE MOMENTS OF ANIONS *
C  UAI IS THE FIELD STRENGTH OF THE INDUCED DIPOLE MOMENT OF *
C    INCOMING ANION *
C    U IS THE TOTAL ENERGY *
C*****
      CALL ELEC(RK2,RK4,U24)
      CALL ELEC(RK2,RKA,U2A)
      CALL ELEC(RK4,RKA,UA4)
      UKA=-ZAN*ZK/RKA(1)-ZA*ZK/LAENGE(RK2)*3-ZA*ZK/LAENGE(RK4)
      *+U24*3+UZA*3+(ZA*ZA/R23)*3+UA4
      UWO=(MYOW*LAENGE(SEO2)*3.+MYO4*LAENGE(SEO4)+MYOA*LAENGE(SEOA))*
      * (-1.)
      UWI=0.5*AW*(LAENGE(SEO2)**2*3.+LAENGE(SEO4)**2)
      * * (-1.)+0.5*AK*LAENGE(SEOK)**2*(-1.)
      UAI=0.5*AA*LAENGE(SEOA)**2*(-1.)
      U=UKA+UWO+UWI+UAI
      UKA=UKA*GAMA
      UWO=UWO*GAMA
      UWI=UWI*GAMA
      UAI=UAI*GAMA
      U=U*GAMA
C*****
C  OUTPUT *
C*****
      WRITE(6,12)M10,RK4(1),RKA(1),U,UKA,UWO,UWI,UAI
12  FORMAT(1H0,BX,IB,3X,F7.3,5X,F10.3,5(3X,F12,2)
      GO TO 10
C*****
C  CONTINUATION OF THE ITERATION *
C*****
228 DO 256 JJJ=1,42
256 EVO(JJJ)=EV(JJJ)
      N4=N4+1
      IF (N4.LE.500) GO TO 4
      WRITE(6,77) M10
17  FORMAT(10X,17HNO CONVERGENCE BY,2X,13,2X,SHGRADE)
10  CONTINUE
      STOP
      END

```

```

      REAL FUNCTION LAENGE (X)
C*****
C  THIS FUNCTION CALCULATES THE LENGTH LAENGE OF THE VECTOR X      *
C*****
      DIMENSION X(2)
      IF ((ABS(X(1)).LT.1E-10).AND.(ABS(X(2)).LT.1E-10)) GO TO 1
      LAENGE = SQRT(X(1)**2+X(2)**2)
      RETURN
1  X(1)=X(1)*10.**24
   X(2)=X(2)*10.**24
   LAENGE=SQRT(X(1)**2+X(2)**2)
   LAENGE=LAENGE/10.**24
   RETURN
   END

```

```

      SUBROUTINE EKA(R,EQ)
C*****
C  THIS SUBROUTINE CALCULATES THE ELECTRICAL FIELD EO OF THE CATION *
C  AND ANION.                                                         *
C  R IS THE VECTOR FROM THE CATION TO THE POINT UNDER CONSIDERATION *
C*****
      REAL LAENGE
      DIMENSION R(2),EO(2),Z(2)
      COMMON RKA(2),ZA,ZK,RW,RK,COST,SINT,R23,ZAN
      ZAS=ZAN
      ZKS=ZK
      X=LAENGE(R)
      Z(1)=R(1)-RKA(1)
      Z(2)=R(2)-RKA(2)
      Y=LAENGE(Z)
      IF(Y.LE.0.00001) ZAS=0.
      IF(Y.LE.0.00001) Y=1.
      IF(X.LE.0.00001) ZKS=0.
      IF(X.LE.0.00001) X=1.
      DO 1 M1=1,2
1  EO(M1)=(ZKS*R(M1))/X**3-(ZAS*Z(M1))/Y**3
      RETURN
      END

```

```

      SUBROUTINE NYI(E,MYO,A,P)
C*****
C  THIS SUBROUTINE CALCULATES THE DIPOLE MOMENT P FROM THE GIVEN      *
C  ELECTRICAL FIELD E, THE PERMANENT DIPOLE MOMENT MYO AND THE        *
C  POLARIZABILITY A.                                                  *
C*****
      DIMENSION E(2),P(2)
      REAL MYO,LAENGE
      IF ((ABS(E(1)).LT.1E-30).AND.(ABS(E(2)).LT.1E-30)) GO TO 1

```

```

X=LAENGE(E)
PABS=MYO+A*X
P(1)=PABS*E(1)/X
P(2)=PABS*E(2)/X
RETURN
1 X=LAENGE(P)
P(1)=MYO*P(1)/X
P(2)=MYO*P(2)/X
RETURN
END

```

```

SUBROUTINE DIPOL (E1,R1,R2,ED21)
C*****
C THIS SUBROUTINE CALCULATES THE ELECTRICAL FIELD E1 AT THE POINT R1 *
C FROM THE GIVEN DIPOLE MOMENT ED21 AT R2 *
C*****
REAL LAENGE
DIMENSION E1(2),R1(2),R2(2),R(2),ED21(2)
DO 2 M2=1,2
2 R(M2)=R1(M2)-R2(M2)
X=LAENGE(R)
DO 1 M=1,2
E1(M1)=-ED21(M1)/X**3+(3.*(ED21(1)*R(1)*ED21(2)*R(12))
* /X**5)*R(M1)
1 CONTINUE
RETURN
END

```

```

SUBROUTINE BLOG(R,RX,EO)
C*****
C THIS SUBROUTINE CALCULATES THE ELECTRICAL FIELD EO AT THE POINT R, *
C FROM THE GIVEN ELECTROSTATIC CHARGE AT RX *
C*****
REAL LAENGE
DIMENSION R(2),EO(2),ZZ(2),RX(2)
COMMON RKA(2),ZA,ZK,RW,RK,COST,SINT,R23,ZAN
ZAS=ZA
ZZ(1)=R(1)-RX(1)
ZZ(2)=R(2)-RX(2)
Y=LAENGE(ZZ)
IF(Y.LE.0.00001)ZAS=0.
IF(Y.LE.0.00001)Y=1.
DO 1 M1=1,2
1 EO(M1)=-ZAS**ZZ(M1)/Y**3
RETURN
END

```

SUBROUTINE ELEC (R,RX,U)

```

C*****
C  THIS SUBROUTINE CALCULATES THE POTENTIAL ENERGY U AT THE POINT R,      *
C  FROM THE GIVEN ELECTROSTATIC CHARGE AT RX.                             *
C*****
      REAL LAENGE
      DIMENSIONS (2),Z(2),RX(2)
      COMMON RKA(2),ZA,ZK,RW,RK,COST,SINT,R23,ZAN
      ZAS=ZA
      Z(1)=R(1)-RX(1)
      Z(2)=R(2)-RX(2)
      Y=LAENGE(Z)
      IF (RX(1).EQ.RKA(1)) 1,2
2  U=ZAS*ZAS/LAENGE(Z)
      GO TO 3
1  U=ZAS*ZAN/LAENGE(Z)
3  RETURN
      END

```

SUBROUTINE TRID (R,EO)

```

C*****
C  THIS SUBROUTINE CALCULATES THE ELECTRICAL FIELD EO AT ATOM 2,          *
C  DUE TO THE ELECTROSTATIC CHARGE ON ATOMS 2 AND 3.                      *
C*****
      DIMENSION RKN2(2),RZ(2),R(2),EO(2)
      COMMON RKA(2),ZA,ZK,RW,RK,COST,SINT,R23,ZAN
      RKN2(1)=(RW+RK)*COST
      RKN2(2)=-2*(RW+RK)*SINT
      RZ(1)=R(1)-RKN2(1)
      RZ(2)=R(2)-RKN2(2)
      DO 1M1=1.2
1  EO(M1)=-ZA*RZ(M1)/R23**3
      RETURN
      END

```

(iii) The third program used was a development of an early program which could calculate theoretical n.m.r. lineshapes for collapsing doublets. The work contained in chapter 4 required a series of theoretical n.m.r. lineshapes depicting the collapse of a quartet produced by the spin spin splitting of a spin of $1/2$ with a spin of $3/2$.

PROGRAM MATCH, a program devised to calculate the pseudo first order rate constants is based on a program developed by Nakagawa^{*}, with modifications by Siddall *et. al.*[†]. The flexibility of the program may appeal to future users of the high resolution spectrometer.

1 : General Description of Program MATCH

For each solution of accurately known mole ratio dissolved complex: bulk solvent: diluent, the pseudo-first-order rate constants (i.e. τ_c^{-1}) at fixed, known temperatures are calculated as follows:

- (a) A set of theoretical lineshapes are plotted out over a wide range of rate constants, from slow to fast exchange ($KNTL2 = 1$).
- (b) A set of appropriate experimental spectra covering the coalescence region are then *visually matched* against these theoretical lineshapes to determine the approximate rate constant at each chosen temperature.

* T. Nakagawa, *Bull. Chem. Soc. Jap.* 1966, 39, 1006.

† T.H. Siddall, W.E. Stewart and F.D. Knight, *J. Phys. Chem.*, 1970, 74, 3580.

For each experimental spectrum, the following procedure is undertaken:

- (c) The spectrum is "digitised", i.e. the spectral amplitude (arbitrary units: usually mm) is calculated, relative to an arbitrary baseline, for each millimetre spacing on the ordinate or x-axis (frequency of absorption axis). This x-axis spacing is denoted SINC, where

$$\text{SINC} = \frac{\text{sweep width (Hz)}}{\text{max. no. of points on chart page}}$$

$$\text{e.g. SINC} = 100 \text{ Hz}/1200 = 0.08 \text{ Hz}$$

for each system studied.

For each spectrum, 1200 to 1600 points are needed, depending on the breadth of the spectrum. These points are punched on to paper-tape and fed straight into the Computer.

These data points, together with the approximate range of rate constants (estimated visually) and a number of other parameters which will be defined below, are read into the program.

- (d) From a predetermined starting point (LPX: in units of SINC), the theoretical lineshape, corresponding to the first rate constant in the estimated range, is plotted out. This lineshape is fitted against the experimental spectrum and the root-mean-square (RMS) error is calculated.
- (e) The starting point for the theoretical lineshape is shifted upfield by one SINC unit and another lineshape is plotted out. Once again, the RMS error is calculated.

- (f) Step (e) is repeated over a preset shift range, which is usually 20-50 SINC units.
- (g) A graph of RMS error *vs.* shift is recorded.
- (h) Steps (d) to (g) are repeated for the next rate constant in the visually estimated range, until the entire preset range of rate constants is covered.
- (i) A graph of minimum RMS error *vs.* rate constant is also recorded, and printed out.
- (j) Steps (d) to (g) are finally repeated for the "best-fit" rate constant, i.e. the rate constant which gave the smallest minimum RMS error. A graph of RMS error *vs.* shift at this particular rate constant is printed out, together with the experimental spectrum and theoretical lineshape corresponding to the "best-fit" rate constant. This facilitates further visual matching.

This is denoted the "Coarse Run".

- (k) From the graphs printed out in steps (i) and (j), the shift range and the range of rate constants are narrowed down. The data deck is re-run and the "best-fit" rate constant is calculated more accurately. This is denoted the "Fine Run".

2 : Data Cards

Card Type	Columns	Parameter(s)	Format	Comments
1	1-8	ident (1)	A8	tape file ident (if required).
	9-80	ident (2)-(10)	9A8	label.
2	<i>Control card</i>			
	1-3	TERM	I3	= blank for last data deck read. = 1 for all other decks.
	4-6	LPX	I3	point no. to start fit.
	7-9	KNTL 1	I3	= 1; the QIKPLTS of RMS error vs. shift are suppressed except for the "best-fit" rate constant.
	10-12	KNTL 2	I3	= 1; theoretical lineshapes only will be produced.
	13-15	KNTL 3	I3	= 1; a CALCOMP plot will be produced, exptl. and theoretical on same plot.
	16-18	KNTL 4	I3	= 1; suppresses printout of exptl. and theoretical spectral ampli- tude values for the best-fit rate constant.
	19-21	KNTL 5	I3	= 1; GENERATES THE <i>QUARTET</i> COALESCENCE.

3	1-10		F10.3	Lower limit of visually estimated range of rate constants.
	11-20		F10.5	Step size.
	21-23		I3	Number of steps.
4	1-2		I2)	Dummies
			)	
	3-4		I2)	
	5-6		I2	Number of coalescing doublets (= 2 for coalescing quartet studied).
5	<i>Set of cards: one card per coalescing doublet</i>			
	1-10	RA	F10.5	= T2 at no exchange for quartet
	11-20	RB	F10.5	= T2 as above
	21-30	PA	F10.5	Fractional population of component A (coordinated solvent).
	31-40	PB	F10.5	= 1 - PA = mole fraction of component B (bulk solvent). (For quartet, PA = PB = 0.25).
	41-50	FRA	F10.5	Position (in Hz) of downfield peak of coalescing doublet.
	51-60	FRB	F10.5	Position (in Hz) of upfield peak of coalescing doublet. - taking L.H. side of chart page as zero Hz.

	61-70	FSCAL	F10.5	= 1 (scaling factor).
6	1-3	LPT	I3	Number of exptl. data points.
	4-6	NSH	I3	Total shift range, in units of SINC.
	7-16	FRF	F10.5)	Only if (exptl. start freq. LPT > 0, (
	17-26	FRE	F10.5)	KNTL2≠1. (" stop "
	27-36	START	F10.5	start freq., theoretical.
	37-46	END	F10.5	= end " "
7			10F.8.3	2nd - LPT theoretical rate consts. (if KNTL2 = 1)
8	1-80		10F.8.3	Experimental data points. (only if KNTL2≠1, LPT > 0.

```

PROGRAM MATCH(TAPE2,INPUT,OUTPUT)
C  PROGRAM TO MATCH EXPERIMENTAL AND THEORETICAL SPECTRA FOR SEVERAL
C  COALESCING DOUBLET (UP TO 10).
C  WILL DO SAME FOR COALESCING QUARTET WHERE RA(1),RB(1),RA(2),
C  RB(2) ARE CONSIDERED AS 4 PEAKS OF QUARTET RATHER THAN 2 DOUBLETS
C  FOR THIS CASE RA IS SIMPLY EQUAL TO T2
C  THE TOTAL NUMBER OF POINTS IN THE THEORETICAL SPECTRUM MUST BE
C  LESS THAN OR EQUAL TO 2000
C  T.M. SPOTSWOOD   AUGUST 1973

DIMENSION HEAD(10,RA(10),RB(10),PA(10),PB(10),FRA(10),FRB(10)
DIMENSION FSCAL(10),YT(2000),NN(2000,2),F(2000),B(4000)
DIMENSION XDIF(200),AXMIN(200),AR(200),SHIFF(200)
COMMON/A/YT,NN,F,B,XDIF,SHIFF
COMMON/B.NPT,LPT,IL,LL,JTDT,NSH,LPX
COMMON/C.STV(200),SDV(200)
COMMON/D.RA,FRA,FRB,R,PA
REAL K,L,NN
PI=3.14159
ISW=1
IRCNT=1
1 READ 1010,(HEAD(J),J=1,10)
  READ 1015,TERM,LPX,KNTL1,KNTL2,KNTL3,KNTL4,KNTL5
  READ 1020,R,STEP,NO
  READ 1030,NPOP,NR1,NPEK
  DO 10 I=1,NPEK
10 READ 1040, RA(I),RB(I),PA(I),PB(I),FRA(I),FRB(I),FSCAL(I)
  READ 1050,LPT,NSH,FRF,FRE,START,END
C  FRA AND FRB GIVE PEAK FREQUENCIES FOR EACH PAIR OF COALESCING
C  LINES. LPT IS THE NO. OF EXPERIMENTAL POINTS, FRF THE STARTING
C  FREQUENCY, FRE THE FINISHING FREQUENCY, BOTH IN HZ
C  SHN IS THE TOTAL SHIFT FOR THE THEORETICAL SPECTRUM TO MATCH IN
C  UNITS OF SINC = POINT SPACING ON INPUT
C
C  KNTL1 ETC ARE CONTROL PARAMETERS. IF KNTL1 = 1 THE QUICKPLOT
C  OF ERROR VS SHIFT IS SUPPRESSED EXCEPT FOR THE BEST VALUE OF R
C  IF KNTL2 = 1 THEORETICAL SPECTRAL PLOTS ONLY WILL BE PRODUCED
C  THE CORRESPONDING VALUE OF R IS RECORDED BELOW EACH PLOT
C  IF KNTL3 = 1, A CALCOMP PLOT WILL BE PRODUCED, EXPTL AND THEOR
C  KNTL5 ALLOWS THE OPTION OF QUARTET COALESCENCE OR DOUBLET
C  CALCULATE NO OF POINTS IN PLOT
  IBKT=0
  IF(LPT.LT.0)101,1021
101 CONTINUE
      CALL BININ(HEAD,IBKT,FRF,FRE)
      FRF=0.5*FRF
      FRE=0.5*FRE
1021 CONTINUE
  IF(KNTL2.NE.1)GO TO 1022
  LPTT=LPT
  LPT=500

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1022 CONTINUE
      IF (END.EQ.0.)END=100.
      ALPT=LPT
      FR=FRE-FRF
      SINC=FR/ALPT
      ANPT=(END-START)/SINC
      NPT=ANPT+0.5
C      CLEAR Y AND PLACE EXPTL POINTS IN CORRECT POSITION
      DO 15 I=1,2000
15      YT(I)=0.
          AIL=(FRF-START)/SINC
          IL=AIL+0.5
          IF (IL.LE.0) IL=1
          LL=IL+LPT-1
          PRINT 1501,IL,LL
1501 FORMAT (2110)
          25 IF (IBKT.EQ.0) 251,252
          252 READ (2) (YT(I),I=IL,LL)
          GO TO 253
          251 READ 1060,(YT(I),I=IL,LL)
          253 CONTINUE
          PRINT 2533,(YT(I),I=IL,LL)
2533 FORMAT(B(XE14.7))
          254 CONTINUE
          AMN=R
          ADR=R
          PRINT2010,(HEAD(J),J=1,10)
          PRINT2020,(I,RA(I),RB(I),PA(I),PB(I),FRA(I),FRB(I),FSCAL(I),I=1.
1          NPEK)
          PRINT 2030,LPT,NPT,NSH
          PRINT 2040,START,END,FRF,FRE
          PRINT 2080,R,STEP,NO
          PRINT 2090,KNTL1,KNTL2,KNTL3,KNTL4,KNTL5
          IM=1
          IF (FRF.LT.FRE) IM=-1
21 CONTINUE
          IF (ISW.EW.0)NO=1
          DO 100 IJK=1,NO
          R=AMN+(IJK-1)*STEP
          DO 35 IM=1,2000
          NN(IM,1)=0.
35      NN(IM,2)=0.
          IF (KNTL5.EQ.1)52.53
          52 DO51J=1,NPT
          F(J)=START+J*SINC
          51 CONTINUE
          CALL SUMMAT(F,NN)
          GO TO 31
          53 CONTINUE
          DO 30 I=1,NPEK
          DAB=FRB(I)-FRA(I) RRA=RA(I)
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RRA=RA(I)
RRB=RB(I)
PPA=PA(I)
PPB=PB(I)
A=2.*PI*FAB/R
1*IM
DO 40 J=1,NPT
FL= (START+ J*SINC-FRA(I))/DAB
1*IM
K=(RRA*PPA+RRB*PPB)+A*(RRA*RRB-FL*(FL-1.))
L=FL*(1.+A*RRA+A*RRB)-(A*RRA+PPB)
TEMP=FSCAL(I)*((1.+A*RRA*PPB+A*RRB*PPA)K+A*(FL+PPB-1.)*L)/(K*K+
1 L*L)
TEMP=ABS(TEMP)
NN(J,1)=NN(J,1)+TEMP
F(J)=START+J*SINC
40 CONTINUE
30 CONTINUE
31 CONTINUE
IF(KNTL2.Ge.1)43.44
43 CALL QIKPLT(F,NN(1,1),NPT,1,3H*F*,3H*I*)
PRINT 2270,R
IF(KNTL2.EQ.1) GO TO 100
44 CONTINUE
CALL NORM
C COMP IS FOR A NON SHIFTED COMPARISON
CALL COMP(1)
CALL SHIFT
IF(KNTL1.EQ.1.AND.NO.GT.1)GO TO 41
CALL QIKPLT(SHIFT.XDIF,JTOT,1.7H*SHIFT*,11H*RMS ERROR*)
41 CONTINUE
AMIN=XDIF(1)
IM=1
DO 50 I=2,JTOT
IF(XDIF(I).LT.AMIN)42.50
42 AMIN=XDIF(I)
IM=1
II=2*(I-1)+LPX
C DETERMINE ACTUAL INCREMENT FROM INDEX I
50 CONTINUE
C STORE THE MINIMUM VALUE FOR COMPARISON
AXMIN(IJK)=AMIN
AR(IJK)=R
SDV(IJK)=STV(IM)
C SHIFT THEORETICAL SPECTRUM AND ADJUST POSITION B LOCATION
DO 60 I=1,2000
60 B(I)=0.
MX=II-IL
DO 70 KK=1,NPT
IF(KK+MX.GT.NPT.OR.KK+MX.LE.0)62,64

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62 B(KK)=0.
   GO TO 70
64 B(KK)=NN(KK+MX,1)
70 CONTINUE
100 CONTINUE
   IF(KNTL2.EQ.1)GO TO 129
   IF(NO.EQ.1)PRINT 2060
   PRINT 2050,(I,AR(I),AXMIN(I),SDV(I),I=1,NO)
   XMN=AXMIN(1)
   IFL=1
   IF(NO.EQ.1)GO TO 115
   DO 110 I=1,NO
   IF(AXMIN(I).LT.XMN)102,110
102 XMN=AXMIN(I)
   IFL=I
110 CONTINUE
   CALL QIKPLT(AR,AXMIN,NO,1.9H*R VALUE*,11H*RMS ERROR*)
C   NOW RECALCULATE THE THEORETICAL SPECTRUM AND ADJUST WITH THIS R
   ISW=0
   AMN=AR(IFL)
   GO TO 21
115 CONTINUE
   CALL QIKPLT(F,NN(1,2),NPT,1,3H*F*,3H*1*)
   PRINT 2100
   CALL QIKPLT(F,8,NPT,1,3H*F*,3H*I*)
   PRINT 2110
   IF(KNTL4.EQ.1)GO TO 112
   PRINT 2250
   PRINT 2260,(F(I),YT(I),NN(I,2),B(I),I=1,NPT)
112 CONTINUE
   IF(KNTL3.EQ.1)116,118
116 CONTINUE
C   PACK NN( ,2) INTO B FOR PLOTTING
   NPT1=NPI+1
   NPT2=2*NPT
   DO 117 LF=NPT1,NPT2
   B(LF)=NN(LF-NPT,2)
117 CONTINUE
   IF (PLT1.EQ.0)GO TO 1171
   CALL PLOTS(5HMATCH,5)
   CALL XLIMIT(1200.)
   PLT1=0
1171 CONTINUE
   CALL AUTPLT(F,NN(1,2),NPT,1.8H*EXPT F*.3H*I*)
   CALL AUTPLT(F,B,NPT,1,3H*F*,3H*I*)
118 CONTINUE
   IF (TERM.NE.0.)120,130
120 ISW=1
   GO TO 1

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129 IF(IRCNT,GE,LPTT)GO TO 130
    R=YT(IRCNT)
    IRCNT=IRCHT+1
    GO TO 254
130 CONTINUE
1010 FORMAT(10A8)
1015 FORMAT(10I3)
1020 FORMAT(2F10.5,13)
1030 FORMAT(3I2)
1040 FORMAT(7F10.5)
1050 FORMAT(2I3,4F10.5)
1060 FORMAT(10F8.1)
2010 FORMAT(1H1,10X,10A8)
2020 FORMAT(1H ,5X,*DOUBLET*15,5X,*RA = *,F10.5,2X,*RB= *,F10.5,2X,
1 *PA=*,F10.5,2X,*PB= *,F10.5,2X,*FRA=*,F10.5,2X,*FRB=*,F10.5,
1 2X,*FSCAL=*,F10.5/)
2030 FORMAT(1H ,*EXPTL POINTS*,15,*THEOR POINTS*,15,*SHIFT RANGE*,15/)
2040 FORMAT(1H ,*START*,F10.5,10X,*END*,F10.5,10X,*START(EXPT)*F10.5,
1 10X,*END(EXPT)*,F10.5/)
2050 FORMAT(1H ,*RUN NO*,15,5X,*VALUE OF R*,F8.2,5X,*RMS ERROR*,F10.5,
15X,*STANDARD DEVIATION*,F10.5)
2060 FORMAT(1H,*THE BEST VALUES OF R AND ERRORS ARE*)
2080 FORMAT(1H ,40X,*VALUE OF R = *,F10.3,10X,*STEP =*,F10.5,10X*NO =*
1,15/)
2090 FORMAT(1H,40X,*VALUES OF CONTROL PARAMETERS ARE*,5X,4(5X,15))
2100 FORMAT(1H,40X,*EXPERIMENTAL SPECTRUM*)
2110 FORMAT(1H,40X,*SHIFTED THEORETICAL SPECTRUM*)
2250 FORMAT(1H1,2(5X,*FREQUENCY*,7X,*Y(EXPT)*,7X,*Y(EXPT)NORM*,4X,*
1 Y(CALC)*))
2260 FORMAT(1H,8(5X,F10.2))
2070 FORMAT(1H,10X,*THEORETICAL PLOT FOR R =*F10.5/)
    STOP
    END

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SUBROUTINE NORM
DIMENSION HEAD(10,RA(10,RB(10,PA(10),PB(10),FRA(10),FRB(10)
DIMENSION FSCAL(10),YT(2000),NN(200.2),F(2000),B(4000)
DIMENSION XDIF(200),AXMIN(200),AR(200),SHIFF(200)
COMMON/A,YT,NN,F,B,XDIF,SHIFF
COMMON/3/NPT,LPT,IL,LL,JTOT,NSH,LPX
COMMON/C/SIV(200),SDV(200)
REAL K,L,NN
C SCALES EXPTL SPECTRUM TO THEORETICAL ON AREAS AND STORES IN NN( ,2
SUM1=0.
SUM2=0.
SUM=0.
DO I I-1,10
IA=IL+I-1
IB=LL-I+1

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1 SUM=SUM+YT(IA)+YT(IB)
  SUM=SUM/20.
  YMAX=YT(1)
  DO 5 IJ=1,NPT
    IF(YT(IJ).GT.YMAX)YMAX=YT(IJ)
5 CONTINUE
  YS=(YMAX-SUM)/30.
  DO 10 I=1,NPT
C  AN ARBITRARY CUT OFF YOUR NORMALIZING DISCARDING LOW INTENSITY
    IF((YT(I)-SUM).LE.YS)GO TO 10
    SUM1=SUM1+NN(I,1)
    SUM2=SUM2+YT(I)
  1-SUM
10 CONTINUE
  RE=SUM1/SUM2
  DO 20 J=1,NPT
    NN(J,2)=(YT(J)-SUM)*RE
    IF(NN(J,2).LT.0)NN(J,2)=0
    IF(J.LT.IL.OR.J.GT.LL)NN(J,2)=0.
20 CONTINUE
  RETURN
  END
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SUBROUTINE COMP(LQ)
  DIMENSION HEAD(10),RA(10),RB(10),PA(10),PB(10),FRA(10),FRB(10)
  DIMENSION FSCAL(10),YT(2000),NN(200,2),F(2000),B(4000)
  DIMENSION XDIF(200),ASMIN(200),AR(200),SHIFF(200)
  COMMON/A/YT,NN,F,B,XDIF,SHIFF
  COMMON/B.NPT,LPT,IL,LL,JTDT,NSH,LPX
  COMMON/C.STV(200),SDV(200)
  REAL K,L,NN
  S2=0.
  DO 10 I=1,NPT
    S=NN(I,1)-NN(I,2)
10 S2=S*S+S2
  XDIF(LQ)=SQRT(S2/FLOAT(NPT))
  RETURN
  END
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SUBROUTINE SHIFT
  DIMENSION HEAD(10),RA(10),RB(10),PA(10),PB(10),FRA(10),FRB(10)
  DIMENSION FSCAL(10),YT(2000),NN(200,2),F(2000),B(4000)
  DIMENSION XDIF(200),AXMIN(200),AR(200),SHIFF(200)
  COMMON/A.YT,NN,F,B,XDIF,SHIFF
  COMMON/B.NPT,LPT,IL,LL,JTOT,NSH,LPX
  COMMON/C.STV(200),SDV(200)
  REAL K,L,NN
  KI=0
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IF (LPX.EQ.0) LP=2
JSH=LPX+NSH
DO 20 J=LPX,JSH,2
IF (LPT+J.GT.NPT) GO TO 20
KI=KI+1
DIF1=0.
DIF2=0.
DO 10 IP=IL,LL
JP=IP-IL+J
DIF=NN(JP,1)-NN(IP,2)
DIF1=DIF1+DIF
DIF2=DIF*DIF+DIF2
10 CONTINUE
XDIF (KI)=SQRT (DIF2/FLOAT (LPT))
SHIFF (KI)=J
STV (KI) SQRT ( (DIF2-DIF1*DIF1/FLOAT (LPT)) / (FLOAT (LPT)-1.))
20 CONTINUE
JTOT=KI
RETURN
END

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SUBROUTINE BININ(IHEAD,IBKT,FRF,FRE)
COMMON/B.NPT,LPT,IL,LL,JTOT,NSH,LPX
DIMENSION IHEAD(10),IDENT(8)
1 READ(2),IDENT,FRF,FRE,LPT
IF (EOF,2) 99.2
2 ID=IDENT(1).AND.77777777777777770000B
ID=ID.OR.5555B
IF (ID,EQ.IHEAD(1)) GO TO 3
READ (2)
GO TO 1
3 IBKT=1
PRINT 31,IDENT,FRF,FRE,LPT
RETURN
31 FORMAT(*1*5X*FULL TAPE LABEL IS [*8A10*]*/*LHS FREQUENCY IS *F10.
14/* RHS FREQUENCY IS *F10.4/X,14* POINTS ARE USED.*)
99 PRINT 991,IHEAD(1)
991 FORMAT(*1 NO LABEL HAVING THE 1ST 8 CHARACTERS (*AB*) CAN BE FOUN
LD.*/* RUN ABORTED.*)
STOP 10
END

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SUBROUTINE SUMMAT(FR,FN)
C COMPONENT WHICH GIVES SPECTRUM
C T2 IS RELAXATION TIME IN ABSENCE OF EXCHANGE
C R IS EQUAL TO 1/16*T WHERE T IS TAU, THE MEAN LIFETIME OF A
C NUCLEUS IN THE NTH SITE
C THE 1/16 TERM ENTERS AS A PROBABILITY FACTOR

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C   THE A TERMS ARE THE ELEMENTS OF THE KUBO-SACK MATRIX
C   THE B TERMS ARE THE ELEMENTS OF THE INVERSE KUBO-SACK MATRIX
    DIMENSION HEAD(10),RA(10),RB(10),PA(10),PB(10),FRA(10),FRB(10)
    DIMENSION FR(2000),FN(2000)
    COMMON/B/NPT,LPT,IL,LL,JTOT,NSH,LPX
    COMMON/D,RA,FRA,FRB,R,PA
    COMPLEX A(4,4),B(4,4),C(4,4),G,D,Z,SUM ,X2,X3,X4
    PI = 3.14159
    T2=RA(1)
    DO 100 JN=1,NPT
    AA=1/T2-3*R
    BA=2*PI*(FR(JN)-FRA(1))
    BB=2*PI*(FR(JN)-FRB(1))
    BC=2*PI*(FR(JN)-FRA(2))
    BD=2*PI*(FR(JN)-FRB(2))
    A(1,1)=CMPLX(AA,BA)
    A(2,2)=CMPLX(AA,BB)
    A(3,3)=CMPLX(AA,BC)
    A(4,4)=CMPLX(AA,BD)
    X2=1./(A(2,2)-R)
    X3=1./(A(3,3)-R)
    X4=1./(A(4,4)-R)
    Z=R-A(1,1)
    G=1.+R*(X2+X3+X4)
    D=A(1,1)-R*Z*(X2+X3+X4)
    B(1,1)=G/D
    B(1,2)=-R*X2/D
    B(1,3)=-R*X3/D
    B(1,4)=-R*X4/D
    B(2,2)=X2+R*Z*X2*X2/D
    B(2,3)=R*Z*X2*X3/D
    B(2,4)=R*Z*X2*X4/D
    B(3,2)=R*Z*X2*X3/D
    B(3,3)=X3+R*Z*X3*X3/D
    B(3,4)=R*Z*X3*X4/D
    B(4,4)=X4+R*Z*X4*X4/D
    B(2,1)=B(1,2)
    B(3,1)=B(1,3)
    B(4,1)=B(1,4)
    B(4,2)=B(2,4)
    B(4,3)=B(3,4)
    SUM=(0.,0.)
    DO12 J=1,4
    DO 12 K=1,4
    BR=B(K,J)
    SUM=SUM+BR
12  CONTINUE
    FN(JN)=-SUM
100 CONTINUE
    RETURN
    END
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