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The Kinetics Of Water Exchange In Some Aquoamminechromium(iii) Complexes

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THE KINETICS OF WATER EXCHANGE IN SOME

AQUOAMMINECHROMIUM(III) COMPLEXES

by

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to my family

ABSTRACT

The rates of water exchange of a series of octahedral chromium(III) aquotetraammine cations have been determined in aqueous solutions of 0.50 $\underline{M}$ ionic strength. This research has provided a unique opportunity to study the effect of different substituents *trans* to the exchanging water in a system where the four *cis* coordination positions are blocked with non-exchanging ligands.

The rate of water exchange has been found to decrease along the series *cis*-$Cr(NH_3)_4(OH_2)_2^{3+}$, *cis*-$Cr(NH_3)_4OH_2Cl^{2+}$, *trans*-$Cr(NH_3)_4OH_2Cl^{2+}$, and *trans*-$Cr(NH_3)_4(OH_2)_2^{3+}$. The relative rates of water exchange permit serialization of ligands in order of decreasing kinetic *trans* labilizing influence as; $NH_3 \geq Cl^- > OH_2$. This order agrees with the recently reported intrinsic kinetic *trans* labilizing series for rhodium(III) substitution reactions.

A comparison of the rates of water exchange of aquopentaamminechromium(III) cation and *cis*-chloroaquotetraamminechromium(III) cation indicates that the overall charge of the cation does not affect the water exchange rate.

The rate constants for water exchange of *cis*- and *trans*-diaquotetraamminechromium(III) and *cis*- and *trans*-chloroaquotetraamminechromium(III) cations have been measured at six temperatures and over a ten fold variation in acid concentration. From the temperature dependence of the rate constants, the activation parameters for the water exchange processes

have been calculated. From the magnitude of the activation entropy it has been proposed that for all the complexes of the series studied, the water exchange process can be rationalized on the basis of the same associative interchange (I_a) exchange mechanism.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

TABLE OF CONTENTS continued

LIST OF TABLES

LIST OF TABLES continued

LIST OF FIGURES

LIST OF FIGURES continued

INTRODUCTION

Water exchange studies are of great interest in elucidating the mechanism of substitution reactions of metal complexes. Solvent exchange is perhaps the most fundamental substitution reaction that an aquo-metal complex can undergo. Moreover, it has been pointed out[1,2] that it is possible to obtain indications of exchange mechanisms from activation data from solvent exchange reactions.

A great deal of work has recently been done on the water exchange reactions of the so-called "inert" octahedral complexes[2-6]. Water exchange studies of the "labile" systems were recently discussed by Hunt[7]. Earley and Cannon[8] have reviewed the aqueous chemistry of chromium(III) and more recently Garner and House[9] reviewed the amime complexes of chromium(III). Table 1 lists the water exchange rate constants for several complexes of the "inert" octahedral metal ions.

The terms labile and inert are empirical designations first used by Taube[10] to conveniently assign labels to reactions that are respectively fast and slow. The general rule is that reactions are considered labile if they are complete within the time of mixing at room temperature. Otherwise they are considered inert. It is obvious that special techniques must be used to measure labile reactions, whereas the inert systems may be followed by the more conventional method of isotopic dilution.

1

TABLE 1

Rate constants for water exchange in some
inert transition metal complexes at 25° C

Complex	$10^6 k_{ex}$ *cis*[a] sec^{-1}	$10^6 k_{ex}$ *trans*[b] sec^{-1}	Reference
$Cr(OH_2)_6^{3+}$	0.43		28, 36
$Cr(OH_2)_5Cl^{2+}$	2.9 (2.3)	24 (35.4)	3 (6)[c]
$Cr(OH_2)_5Br^{2+}$	1.8	55	6
$Cr(OH_2)_5I^{2+}$	3.1	84	3
$Cr(OH_2)_5NCS^{2+}$	3.0 (2.4)	17 (18)	3 (6)[c]
$Cr(OH_2)_4Cl_2^{+}$	80.3		6
$Cr(OH_2)_5SO_4^{+}$	540		6
cis-$Cr(C_2O_4)_2(OH_2)_2^{-}$	3.9		37
$Cr(NH_3)_5OH_2^{3+}$		52.4	5
$Co(NH_3)_5OH_2^{3+}$		5.9	1, 38
$Rh(NH_3)_5OH_2^{3+}$		10.7	2
$Ir(NH_3)_5OH_2^{3+}$		0.065	4

TABLE 1 (continued)

Complex	$10^6 k_{ex}$ *cis*[a] sec^{-1}	$10^6 k_{ex}$ *trans*[b] sec^{-1}	Reference
$Rh(OH_2)_6{}^{3+}$		0.029	39[d]
cis-$Co(en)_2NH_3OH_2{}^{3+}$		1.1	40
trans-$Co(en)_2NH_3OH_2{}^{3+}$		2.3	40[e]
cis-$Co(en)_2(OH_2)_2{}^{3+}$		7.5	41
trans-$Co(en)_2(OH_2)_2{}^{3+}$	11.3		41

a) *cis* refers to the exchanging water(s) *cis* to a ligand other than water, but may be *trans* to another water ligand

b) means *trans* to a ligand other than water

c) calculated in reference 6 from data in reference 3

d) calculated from data in reference 39

e) estimated from data in reference 40

It has been a popular notion that substitution reactions in octahedral transition metal complexes have a mechanism of dissociative activation[11,12]. Indeed, there is a great deal of evidence to support such a conviction.

Espenson[13], by comparing rates of formation in aqueous solution, found that complexation reactions of chromium(III) appear to have a common rate-determining feature, ligand assisted water loss (dissociative interchange). More recently, Thusius[14] compared rate constants and activation parameters for the formation of monosubstituted chromium(III) complexes and his conclusion was in agreement with that of Espenson. It was conceded however[13], that the small dependence on ligand of the formation rates suggests that bond making does play a role in the mechanism and that the mechanism is not purely dissociative in character.

Johnson *et al.*[15] studied the aquation and base hydrolysis of acidopentaamminerhodium(III) complexes and concluded that a bimolecular rate determining step is involved, with more participation of the entering group than for cobalt[16,17] and with a seven coordinate intermediate in the reaction profile. It was stressed however that the energy required to break the metal ligand bond is the major factor in determining activation parameters. Powell[18] felt the designation "dissociative bimolecular mechanism" was the more appropriate way to describe the solvolysis mechanism in rhodium(III). Poë *et al.*[19], who studied the anation and aquation reactions involved in the equilibria,

$$Rh(NH_3)_5X^{2+} \; \rightleftarrows \; Rh(NH_3)_5OH_2^{3+} + X^-$$
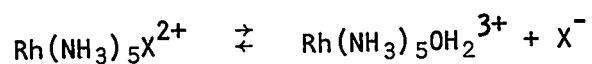
(where $X = Cl^-$, Br^-, I^-), concluded there was no reliable indication of substantial bond making taking place. Monacelli and Viel[2] interpreted the entropy and enthalpy of activation for the water exchange in $Rh(NH_3)_5OH_2^{3+}$ in terms of pronounced participation of a

solvent molecule in the transition state. Swaddle and Stranks[5] confirmed the above interpretation by studying the pressure dependence of water exchange for this cation.

Very recently, aquation studies on the haloaquotetraammine-chromium(III) complexes have shown that the leaving group rate sequence of $I^- > Br^- > Cl^-$ parallels that observed for $Cr(OH_2)_5X^{2+}$ [23] and $Cr(NH_3)_5X^{2+}$ [24] ($X = Cl^-, Br^-, I^-$). These data were interpreted to mean that a similar dissociative mechanism was operative in all species. Negative activation entropies for aquation were found for the chromium(III) tetraammine series which fit with Tobe's[25] ΔS^* correlation of low values of activation entropy as indicating little steric change. The low entropy of activation values for the tetraammines are thus considered consistent with dissociative aquation via a retentive square pyramidal intermediate or transition state[22].

It therefore appears that the Eigen[26] mechanism, with rate determining bond breaking, has generally been assumed to be operative in ligand substitution processes of di- and trivalent metal ions in solution[11]. It has long been recognized that the greater the charge of the central metal ion, the greater should be the tendency toward associative rather than dissociative activation. With respect to water exchange reactions for some chromium(III) complexes, Swaddle and Stranks[5,28] have shown evidence that a mechanism of associative activation may actually be the norm in substitution reactions of cationic complexes of trivalent metal ions. It is true, however, that the A (associative) mechanism, as a stoichiometric mechanism, has not yet been adequately demonstrated in octahedral systems, whereas the D (dissociative) has been.

From the work done on the acidopentaaquochromium(III) system Bracken[3] was able to arrange a series of ligands in the order of their decreasing *trans*-labilizing influence as,

$$I^- > Br^- > Cl^- > NCS^- > OH_2.$$
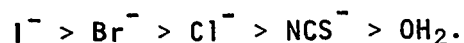
Keen[6] later confirmed the position of Br^- in this series. Poë *et al.*[19,29-33] have presented a very detailed study of an octahedral system in which manifestation of the *trans*-effect is well documented. They examined the aqueous solution kinetics of substitution (anation and aquation) of X of selected rhodium(III) complexes of the type *trans*-RhA_4LX^{z+} {X = Cl^-, Br^-, I^-, or OH_2; L = Cl^-, Br^-, I^-, OH, NH_3, or OH_2; A = $\frac{1}{2}$(en) or NH_3; z = 1, 2, or 3}. For these systems the kinetic *trans*-effect was found to depend, both qualitatively and quantitatively, on the particular reaction chosen to measure it. This resulted from the dependence of the kinetic behaviour on the thermodynamics of the reaction. When Poë allowed for this dependence a measure of the intrinsic kinetic *trans*-effect was obtained. This *trans*-effect was found to decrease in the order $I^- > Br^- > NH_3 \geq Cl^- \geq OH^- > OH_2$. On the other hand, from water exchange reactions direct measures of the kinetic *trans*-effect can be obtained free of complications from different thermodynamic contributions to the kinetics. Hence, the kinetic *trans*-effect series for water exchange studies can be compared directly to the intrinsic kinetic *trans*-effect series obtained from aquation and anation studies. It is interesting that the kinetic *trans*-effect series for Rh(III) parallels that previously established for Cr(III) from water exchange studies, as far as the data permit.

Although it has been shown for a number of labile systems[7,34] that the overall charge of the octahedral complex does not affect the rate of exchange in any specific way, there is a general lack of such evidence for the inert chromium(III) system. From Table 1 it can be seen that the rate of water exchange of *trans* water pairs increases, $Cr(OH_2)_6^{3+}$ < $Cr(OH_2)_5Cl^{2+}$ < *trans*-$Cr(OH_2)_4Cl_2^+$, as the overall positive charge of the cation decreases. On the other hand, the rate of water exchange for *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$ appears to be little affected by overall charge. That is, this anionic species of overall unit negative charge exchanges water at a rate similar to cationic species of dipositive charge.

The attempt to correlate the rate of water exchange of the unipositive sulphatopentaaquochromium(III) ion[6] with charge failed, even though the exchange was extremely rapid. The rapid water turnover was explained as the result of an internal "anation-aquation" process as the sulphato-ligand interchanges between mono- and bidentate modes of coordination. As the sulphato- ligand becomes bidentate a water molecule is expelled from the coordination sphere and as it returns to the monodentate form a solvent water is incorporated into the primary coordination sphere. Presumably, this mechanism is similar to the *cis*-activation by the nitrato-ligand in amminechromium(III) ions, via a transiently bidentate nitrato-complex, recently described by Swaddle[35].

It is the purpose of this thesis to examine in more detail the three general problems that have arisen. These are namely, the mechanism by which waters exchange, the "correct" position of ammonia in the *trans*-effect series, and the effect of overall charge on the rate of water interchange.

A series of aquotetraamminechromium(III) cations were chosen in this work to represent a model octahedral system. Chromium(III) has its three 3d electrons in separate t_{2g} orbitals of the same energy and the Jahn-Teller effect is inoperative. The aquotetraamminechromium(III) cations, unlike the much studied acidopentaaquochromium(III) cations, have the sites *cis* to the exchanging water blocked by non-exchanging ammonia ligands. In this way, each species studied has only one "type" of exchanging water and thus exchange can be restricted to specific positions in similar molecules. In contrast, acidopentaaquo-systems contain two "types" of exchanging water each of which, due to the *trans*-effect, has a different rate of exchange. One water is *trans* to the acido group while four (two *trans* water pairs) are *cis* to it. Therefore, in principle the tetraammines introduce less uncertainty for the water exchange study since only one "type" of water is exchanging rather than two "types" of water that exchange at different rates.

The results establish evidence for the concerted process of associative activation for water exchange, the position of ammonia relative to chloride in the *trans*-effect series, and the effect of overall charge on the rate of water interchange.

Figure 1 shows the spatial configurations of the four chromium-(III) complexes studied along with any abbreviations that might be encountered in the following text.

FIGURE 1

The four aquotetraamminechromium(III) cations used
in this study

cis-diaquotetraamminechromium(III) ion (or cation)
abbreviated as: *cis*-diaquo- ion (or cation)

cis-Cr(NH₃)₄(OH₂)₂³⁺

$$cis\text{-Cr(NH}_3)_4(\text{OH}_2)_2{}^{3+}$$
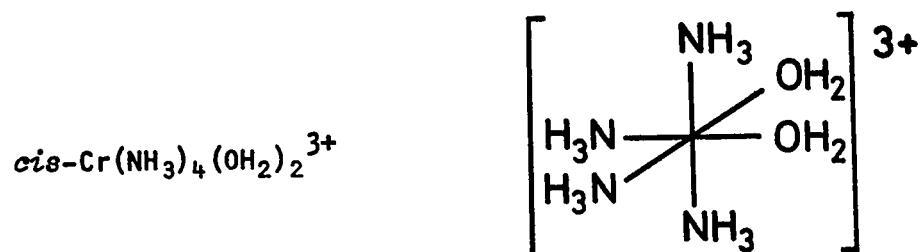
trans-diaquotetraamminechromium(III) ion (or cation)
abbreviated as: *trans*-diaquo- ion (or cation)

$$trans\text{-Cr(NH}_3)_4(\text{OH}_2)_2{}^{3+}$$
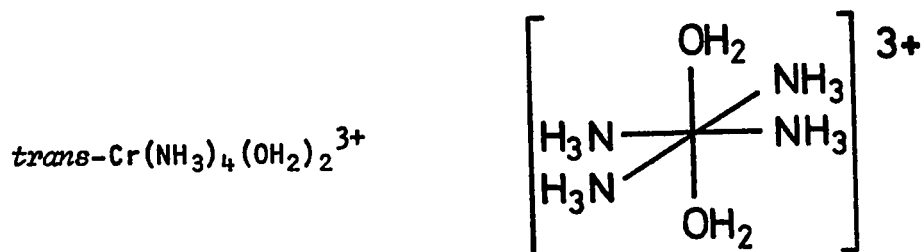
cis-chloroaquotetraamminechromium(III) ion (or cation)
abbreviated as: *cis*-chloroaquo- ion (or cation)

$$cis\text{-Cr(NH}_3)_4\text{OH}_2\text{Cl}^{2+}$$
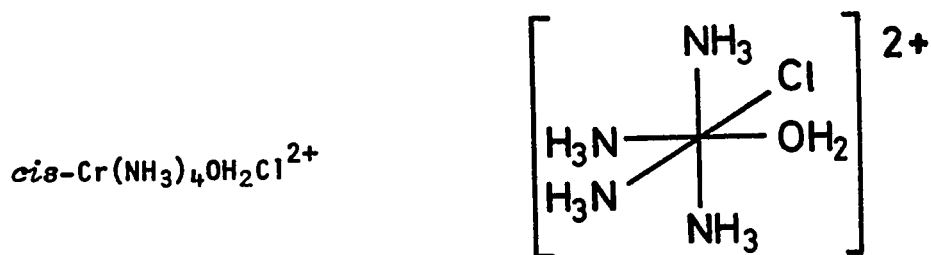
trans-chloroaquotetraamminechromium(III) ion (or cation)
abbreviated as: *trans*-chloroaquo- ion (or cation)

$$trans\text{-Cr(NH}_3)_4\text{OH}_2\text{Cl}^{2+}$$
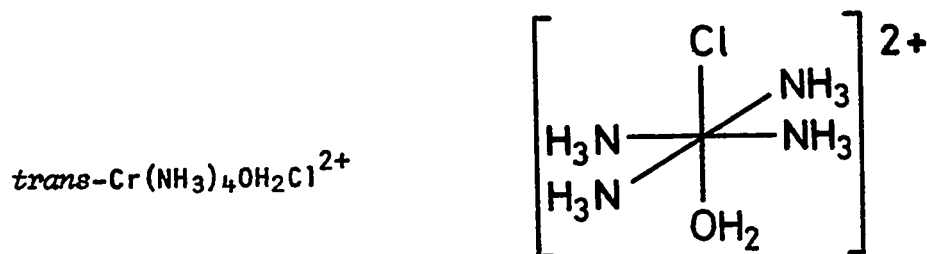
EXPERIMENTAL SECTION

A.   Preparation of the Chromium(III) Complexes

The *trans* chromium(III) tetraammine complexes were prepared by following procedures similar to those described by Hunt et al.[20,42,43]. These syntheses were based on the acid cleavage of chloroerythro chloride, $[(NH_3)_5CrOHCr(NH_3)_4Cl]Cl_4$, in which the chloro-ligand is located *trans* to the hydroxo bridge. The chloroerythro chloride was prepared from normal rhodo chloride by the method of Linhard and Weigel[44].

Normal Rhodo Chloride, $[(NH_3)_5CrOHCr(NH_3)_5]Cl_5$

A 60g portion of green chromic chloride hexahydrate (Allied Chemical - Reagent) was dissolved in a mixture of 50 ml of concentrated hydrochloric acid (Allied Chemical - A.C.S. Reagent) and 90 ml of distilled water. Fifty ml of a 2% zinc amalgam were placed in a long stemmed separatory funnel (250 ml capacity) equipped in such a way that an inert atmosphere of nitrogen could be maintained within the apparatus. The chromic chloride solution was poured in and the apparatus swept through with a brisk current of oxygen-free nitrogen. Oxygen was removed from commercial grade nitrogen by passing it through a copper furnace operating at 350-400°C. The mixture in the separatory funnel, after 20 to 30 minutes of occasional shaking had been reduced to the labile

chromous ion, indicated by the formation of a clear blue solution. The amalgam was carefully run out and the remaining solution drained into 500 ml of an ice cold solution of 28% aqueous ammonia (Shawinigan - Reagent) saturated with ammonium chloride (Baker - Reagent). In order to prevent premature oxidation to chromic ion, the tip of the funnel was kept well below the surface of the ammonia solution. In an ice bath, the resulting deep blue solution was stirred vigorously then air was bubbled through for two hours to ensure complete oxidation to chromium(III). Oxidation resulted in the formation of a pink precipitate which was collected on a glass filter and washed with a 10% hydrochloric acid solution, ethanol, and finally ether. Then it was allowed to dry in the air. The yield was about 25g of crude normal rhodo chloride.

Aquoerythro Chloride, $[(NH_3)_5CrOHCr(NH_3)_4OH_2]Cl_5$

Crude normal rhodo chloride (100g) was dissolved in a solution of 85 ml of 28% aqueous ammonia and 500 ml of distilled water. About 5 to 10 minutes were required for dissolution to form a deep blue solution. This solution was filtered to remove any insoluble material and then the filtrate was stirred at room temperature for at least 30 minutes. The resulting red solution was cooled in an ice bath while anhydrous hydrogen chloride (Matheson) was bubbled in until the formation of bright red crystals appeared complete. The temperature of the solution had been maintained below 20°C. The bright red crystals were filtered off and washed with cold concentrated hydrochloric acid, cold ethanol, and finally ether. The yield of aquoerythro chloride was about 75g.

Chloroerythro Chloride, $[(NH_3)_5CrOHCr(NH_3)_4Cl]Cl_4$

The water was removed from aquoerythro chloride to form chloroerythro chloride by heating the former in an air oven at 90° for at least 6 hours. The original deep red crystals changed to a deep purple colour with retention of luster.

trans-Chloroaquotetraamminechromium(III) Chloride

A sample of chloroerythro chloride (30g) was ground to a fine powder in a mortar and 90 ml of 72% perchloric acid (B.D.H. - Reagent) was added slowly with stirring, so as to permit the expulsion of most of the ionic chloride as HCl gas. When the evolution of HCl was essentially complete, the mixture was transferred to a flask and diluted with about 450 ml of water. The mixture was heated at 60° with constant stirring until dissolution of the solid was nearly complete (20 to 30 minutes). The solution was filtered while hot, then cooled in ice. One hundred ml of 72% perchloric acid was added to precipitate $[Cr(NH_3)_5OH_2](ClO_4)_3$ which was removed by filtration (about 20g). This product was washed with cold ethanol and ether and allowed to air dry. The filtrate was again cooled and anhydrous HCl bubbled in until the formation of crystals was complete. The cold mixture was filtered and the deep purple-brown coloured crystals washed with cold concentrated hydrochloric acid, ethanol, and ether. The yield was about 12g of small but well formed crystals.

trans-Chloroaquotetraamminechromium(III) Perchlorate

The dried *trans*-[Cr(NH$_3$)$_4$OH$_2$Cl]Cl$_2$ (50g) was triturated with 72% perchloric acid to expel the ionic chloride as HCl gas. The perchlorate salt was recrystallized from a nearly saturated water solution by the addition of 72% perchloric acid. Further purification was accomplished by recrystallization from methanol, in which the major impurities, [Cr(NH$_3$)$_5$Cl](ClO$_4$)$_2$ and [Cr(NH$_3$)$_5$OH$_2$](ClO$_4$)$_3$, are insoluble and *trans*-[Cr(NH$_3$)$_4$OH$_2$Cl](ClO$_4$)$_2$ is very soluble. A yield of about 60g was obtained.

Aquopentaamminechromium(III) Perchlorate

From the preparation of *trans*-[Cr(NH$_3$)$_4$OH$_2$Cl]Cl$_2$ the perchlorate salt of aquopentaamminechromium(III) was recovered as a by-product. Purification was accomplished by recrystallization from a nearly saturated water solution by the addition of 72% perchloric acid. The product was collected on a filter, washed with ethanol and ether, and air dried.

Oxalatotetraamminechromium(III) Perchlorate

The method of preparation of this salt is similar to that for the preparation of [Cr(NH$_3$)$_4$C$_2$O$_4$]NO$_3$ described by Schlessinger[45]. Aquopentaamminechromium(III) perchlorate (30g) was added to 15g of oxalic acid dihydrate (Allied Chemical - A.C.S. Reagent) dissolved in 150 ml of a 1:1 ethanol-water solution. The mixture was maintained at 60° and stirred vigorously until the aquopentaammine salt had dissolved (10 to 15 minutes). The solution was filtered while hot to remove the

crystals of $[Cr(NH_3)_4C_2O_4](ClO_4)$ which had formed. Another 5 to 10g

of oxalic acid was added to the filtrate and heated again for 10

minutes at 60°. Another crop of red crystals was collected from the hot

solution. The combined product was washed with 1 $\underline{M}$ perchloric acid on

the filter until the filtrate had changed from orange to almost colour-

less. Finally, the crystals were washed with ethanol and allowed to

dry in the air.

cis-Chloroaquotetraamminechromium(III) Chloride

A sample (12g) of crude oxalatotetraamminechromium(III)

perchlorate was mixed with 120 ml of concentrated hydrochloric acid,

and the mixture was allowed to stand for 24 hours at room temperature

with occasional agitation. A deep violet coloured solution soon

developed through the formation of readily soluble cis-$Cr(NH_3)_4Cl_2^+$

ion which underwent slow hydrolysis to form the rose product

cis-$[Cr(NH_3)_4OH_2Cl]Cl_2$ which was only sparingly soluble in the acid.

After cooling in an ice bath the material was collected on a filter,

washed with ethanol, and air dried. Yield: 8g.

cis-Chloroaquotetraamminechromium(III) Perchlorate

This was prepared from the cis-chloroaquotetraamminechromium(III)

chloride by a method analogous to that described for the preparation of

the $trans$ isomer.

cis-Diaquotetraamminechromium(III) Perchlorate

Coordinated chloride was removed from *cis*-[Cr(NH$_3$)$_4$OH$_2$Cl]Cl$_2$ by base hydrolysis. *Cis*-chloroaquotetraamminechromium(III) chloride (10g) was stirred into 50 ml of 1.0 $\underline{M}$ NaOH at room temperature and stirring was continued for five minutes. This mixture was filtered rapidly and the filtrate poured into 75 ml of ice cold 72% perchloric acid. The product *cis*-[Cr(NH$_3$)$_4$(OH$_2$)$_2$](ClO$_4$)$_3$ was collected on a filter and washed generously with absolute ethanol and finally ether. The salt was purified by dissolving it in the minimum amount of distilled water, filtering, precipitating with 72% perchloric acid, and treating as above. The final air dried product gave a yield of about 16g.

trans-Diaquotetraamminechromium(III) Perchlorate

This compound was prepared from *trans*-[Cr(NH$_3$)$_4$OH$_2$Cl]Cl$_2$ by a procedure exactly analogous to that described for the preparation of *cis*-[Cr(NH$_3$)$_4$(OH$_2$)$_2$](ClO$_4$)$_3$ from *cis*-[Cr(NH$_3$)$_4$OH$_2$Cl]Cl$_2$.

After thorough drying, all complexes were stored in tightly capped brown bottles in a refrigerator.

Figure 2 summarizes schematically the preparation of the various complexes.

B. Analytical Procedures

Spectra

Spectra for all the complexes studied were measured with an

FIGURE 2

Systematic synthesis of ammine series
of chromium(III) complexes

$$Cr^{2+} + NH_{3(aq)} + NH_4^+ + O_2$$

$$\downarrow HCl$$

$$\left[(NH_3)_5CrOHCr(NH_3)_5\right]Cl_5$$

$$\downarrow \begin{array}{l} 1)\ OH^- \\ 2)\ HCl \end{array}$$

$$\left[(NH_3)_5CrOHCr(NH_3)_4OH_2\right]Cl_5$$

$$\downarrow \triangle$$

$$\left[(NH_3)_5CrOHCr(NH_3)_4Cl\right]Cl_4$$

$$\downarrow \begin{array}{l} 1)\ HClO_4 \\ 2)\ HCl \end{array}$$

$$Cr(NH_3)_5OH_2^{3+} + \textit{trans}-Cr(NH_3)_4OH_2Cl^{2+}$$

$$\downarrow C_2O_4^{2-} \qquad\qquad \downarrow \begin{array}{l} 1)\ OH^- \\ 2)\ HClO_4 \end{array}$$

$$Cr(NH_3)_4C_2O_4^+ \qquad \textit{trans}-Cr(NH_3)_4(OH_2)_2^{3+}$$

$$\downarrow HCl$$

$$\textit{cis}-Cr(NH_3)_4OH_2Cl^{2+}$$

$$\downarrow \begin{array}{l} 1)\ OH^- \\ 2)\ HClO_4 \end{array}$$

$$\textit{cis}-Cr(NH_3)_4(OH_2)_2^{3+}$$
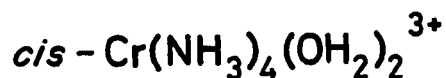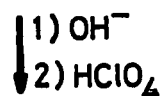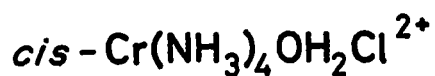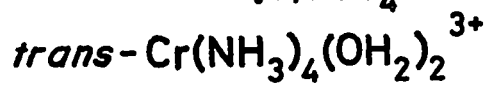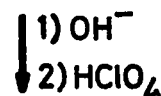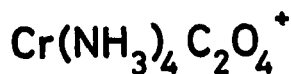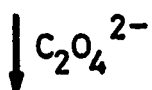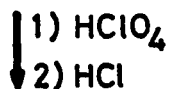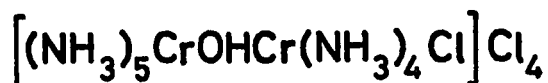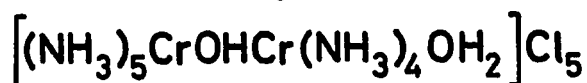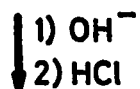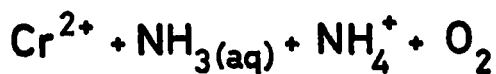
ultraviolet-visible recording spectrophotometer (Cary Model 14 or Beckman DK-1). Molar extinction coefficients were calculated from the recorded absorption spectra of the complexes and from the chromium concentration of the solutions, as determined by chemical analysis.

Chromium

A volume of 0.05 $\underline{M}$ potassium hydroxide (prepared from Mallinckrodt - A.C.S. Analytical reagent pellets) sufficient to neutralize the acid and destroy the complex was added to the solution sample. Addition of a ten-fold excess of 30% hydrogen peroxide (Fisher - Reagent), followed by heating until the evolution of gas was complete, resulted in a yellow chromate solution. Appropriate dilution with 0.05 $\underline{M}$ potassium hydroxide gave samples suitable for absorbance measurements. Readings of absorbance were made on a recording ultraviolet-visible spectrophotometer (Beckman DK-1) in the region of 373 nm[46], and the concentration of chromium determined from a calibration graph. The calibration graph was obtained from measurements of known chromate solutions prepared from chromium metal (B.D.H. - 99.9%).

Nitrogen

The boric acid modification[47] of the Kjeldahl method was used for nitrogen analysis. A sample of the complex to be analysed was digested with sodium hydroxide (B.D.H. - Reagent), and the ammonia released was distilled into a saturated solution of boric acid. The ammonium borate which formed was titrated with standard hydrochloric

acid solution (prepared from B.D.H. concentrated volumetric solution, N/10) to a bromo-cresol green endpoint.

Chloride

Chloride was determined by first digesting the complex with excess base to release bound halogen and then titrating the acidified solution to a potentiometric endpoint with standard silver nitrate solution (prepared from B.D.H. concentrated volumetric solution, N/10).

C. Complex Enrichment

The perchlorate salts of the aquotetraamminechromium(III) complexes to be studied, were labelled with water enriched in oxygen-18 (Yeda Research and Development Co. Ltd. Israel: 1.54 atom percent ^{18}O). Conditions were so chosen that the complexes were only about 4-fold enriched ($ca.$ 0.75 atom percent). This ensured that no double labelling of the complexes with two coordinated waters took place.

All complexes were enriched in essentially the same manner. The purified complexes were dissolved in the minimum amounts of 5-fold enriched water made 0.1 $\underline{M}$ in perchloric acid, and kept at room temperature in the dark for 24-48 hours. The solutions were then cooled and the enriched complexes precipitated from solution by the addition of cold 72% perchloric acid. The crystals were collected on a filter, washed with ethanol and ether, and dried in a vacuum desiccator over silica gel in the dark. After drying, the spectra of the complexes were taken and

the remaining solids stored in brown bottles covered with aluminum foil in a refrigerator.

D.   Measurement of Exchange Rates

Because the solvent water is so much more abundant than is water in the coordination sphere of the solute, the method of isotopic analysis based on sampling the solute is more sensitive, and therefore, was used for this work.

For all kinetic runs the concentration of the complexes was 0.050 $\underline{M}$ in a perchloric acid solution of ionic strength 0.50 $\underline{M}$, adjusted with sodium perchlorate (G.F. Smith - Reagent). Large volumes of the reaction mixtures were prepared such that when the solution was made 0.050 $\underline{M}$ in complex, the resulting ionic strength would be 0.50 $\underline{M}$. This also assured that for each complex, the kinetic experiment always took place in the same reaction medium. All solutions were prepared from doubly distilled, freshly boiled water, and stored to exclude atmospheric carbon dioxide.

A kinetic experiment was initiated by dissolving a known quantity of enriched complex in a known volume of the reaction mixture, thermostated in a bath. An aliquot of this solution was immediately pipetted into a test tube and rapidly cooled in a dry ice methanol bath. The reaction vessel was then flushed with nitrogen to remove any carbon dioxide. The precaution of excluding carbon dioxide was taken because Earley and Alexander[48] reported catalysis of chromium(III) exchange reactions by carbon dioxide.

For a run at any given temperature a total of six to nine samples was taken at scheduled times over a period to cover several half-lives of water exchange on the approach to isotopic equilibrium.

In the case of *cis-* and *trans*-diaquotetraamminechromium(III) ion a 3 ml aliquot of reaction solution was found satisfactory as a sample. For *cis-* and *trans*-chloroaquotetraamminechromium(III) ion, a 6 ml aliquot of solution was required.

Since it has been found that chromium(III) complexes undergo photochemical reactions[5,36,49,52], all experiments were carried out in darkened reaction vessels.

The first sample removed from the reaction flask (1 to 2 minutes after mixing) was considered to be the "zero time" sample. The actual time, read from an electric clock with a sweep second hand and maximum reading error of ± 10 seconds, was recorded to the nearest 30 seconds.

To the very cold or frozen aliquot of sample, 1 to 2 ml of acetone was added and anhydrous hydrogen bromide gas (Matheson) was bubbled in to precipitate the complex as the bromide salt. A low temperature was maintained by immersing the sample in a dry ice methanol bath to prevent anation or other loss of coordinated water which could otherwise take place in a warm solution. The precipitated solid was collected on a small sintered glass filter, washed with acetone and ether, and allowed to dry. Further drying was accomplished by heating the solid sample to 50°C *in vacuo* for 2-3 hours. It was important to remove the water of hydration from the labelled samples because exchange of ligand and hydrate water might otherwise have taken place. The solid samples were protected from bright light to reduce photo-chemically induced anation[5].

For all experiments above 19°C the kinetic runs were carried

out in a water bath maintained by a proportional temperature controller

(Fisher Model 22) using a 250 or 500 watt heater and a cold water

cooling coil. Runs below 19°C were carried out in a room with an ambient

temperature of 2 to 3°C and the bath was controlled by a thermostat

(Haake Unitherm). In all cases the temperature could be controlled to

within ± 0.05°C as measured by a certified precision thermometer

(Baird and Tatlock, London, Ltd. No. 85860).

Isotopic mass analysis was effected on carbon dioxide because

it is a more convenient substance to handle in a mass spectrometer than

is water. The method used for the direct conversion of the coordinated

water to carbon dioxide for mass analysis is similar to that described

by Monacelli[2]. The dry bromide salt from the original kinetic sample

was transferred to a pyrex tube (10 x 120 mm) fitted with a 14/35 cone

and placed on a vacuum line. Using an "Ultra-Torr" fitting (Cajon 4UT-6),

a pyrex tube (6 x 200 mm) sealed at one end and containing 15-20mg of

dry mercuric cyanide ($Hg(CN)_2$ - Alfa) was also placed on the vacuum line

(see Figure 3). Both tubes were evacuated to below 10^{-3} torr as measured

by a thermocouple vacuum gauge. After evacuation the tubes were isolated

from the vacuum line and the tube containing the mercuric cyanide was

immersed in liquid nitrogen while the tube containing the complex salt

was heated to about 200°C for 3-5 minutes using a heat gun (Master

Appliance Corp. Model HG301C). This step removed the coordinated water

from the complex and condensed it into the tube containing the mercuric

cyanide which was then sealed off at a point 145 mm from the bottom.

After all the sealed tubes from samples of a complete run were collected,

the water was converted to carbon dioxide by heating the tubes and

FIGURE 3
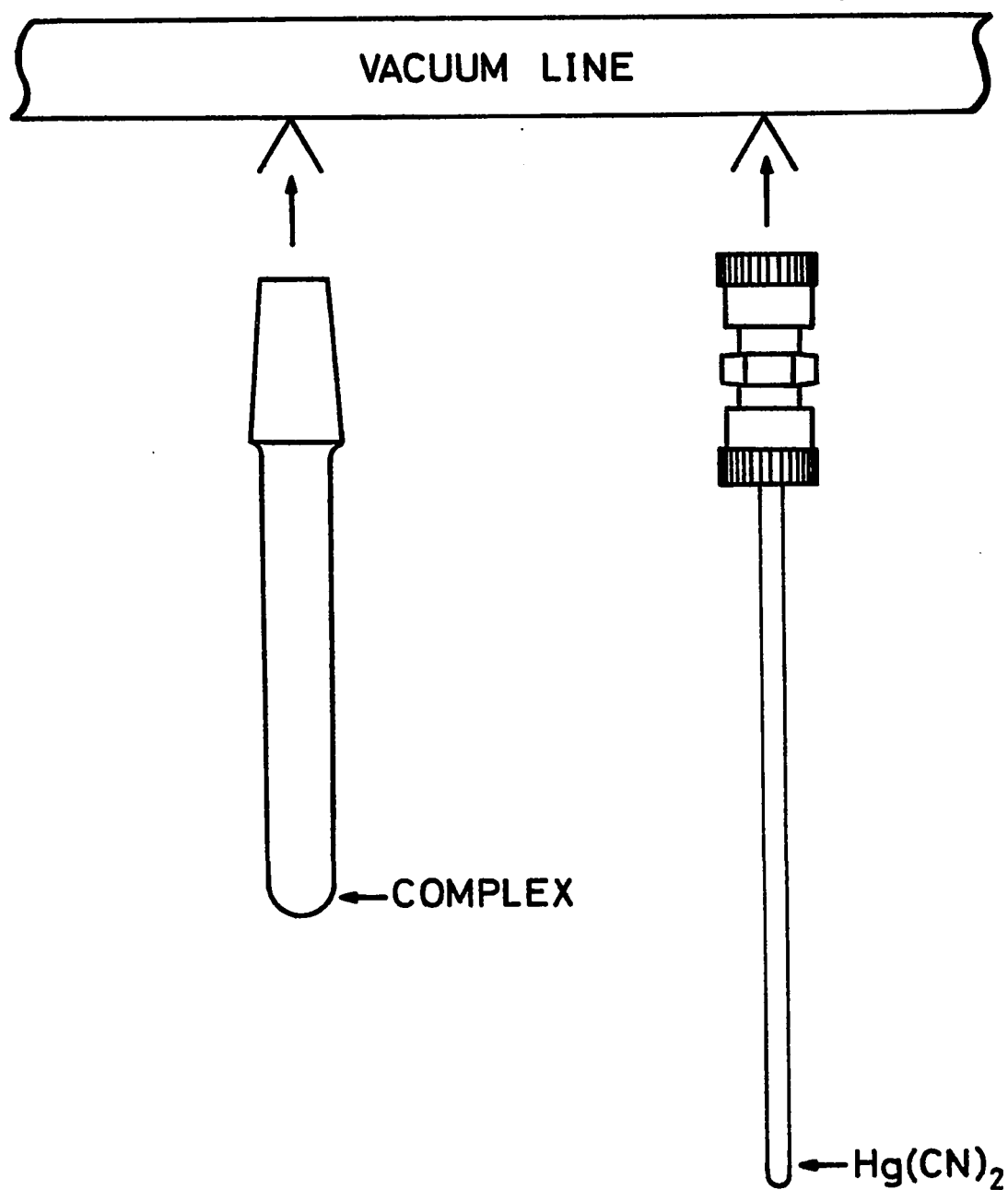
The apparatus for isolating the water samples

contents at 400-500°C for about 3 hours in a muffle furnace.

The sealed tubes were opened on the vacuum line and the carbon dioxide treated with concentrated sulphuric acid to remove any ammonia[50] and to destroy any ammonium carbamate. The apparatus used to open the sealed tubes and treat the carbon dioxide is given in Figure 4. The well in the glass tube (A in Figure 4) was filled with concentrated sulphuric acid and placed on the vacuum line. Next, the apparatus (B in Figure 4) consisting of a piece of rubber vacuum tubing ($\frac{1}{4}$ inch I.D. x 130 mm) with a ground glass cone on one end and a "Ultra-Torr" adaptor (Cajon 4UT-A-6BT) on the other, was attached to the well assembly (A). A sealed tube containing the labelled carbon dioxide was scratched about 5 mm from the sealed tip and inserted through the "Ultra-Torr" fitting into the rubber tubing which was fractionally larger in diameter than the glass tube. After the "O-ring" of the "Ultra-Torr" fitting was tightened around the sealed tube the whole assembly was evacuated. By holding the glass sample tube (C) and bending the rubber tubing at the scratch mark, the tube was broken open. The protruding end of the glass tube (C) was heated to vapourize any solid pyrolysis products (possibly, $NH_2CO_2NH_4$) and the gas was allowed to remain in contact with the concentrated sulphuric acid for one minute and then released. The carbon dioxide was purified by passage through two traps cooled by dry ice methanol baths. Finally, the purified carbon dioxide was condensed into a sample tube suitable for use on the mass spectrometer.

The conventional high vacuum line used in the above, consisting of a mechanical fore-pump (Welch-Duo Seal - Model 1400), a mercury diffusion pump, and a liquid nitrogen trap, provided a vacuum better than 10^{-4} torr.

FIGURE 4

$H_2SO_4 \longrightarrow$

WELL ASSEMBLY   A

ASSEMBLY   B

TUBE   C
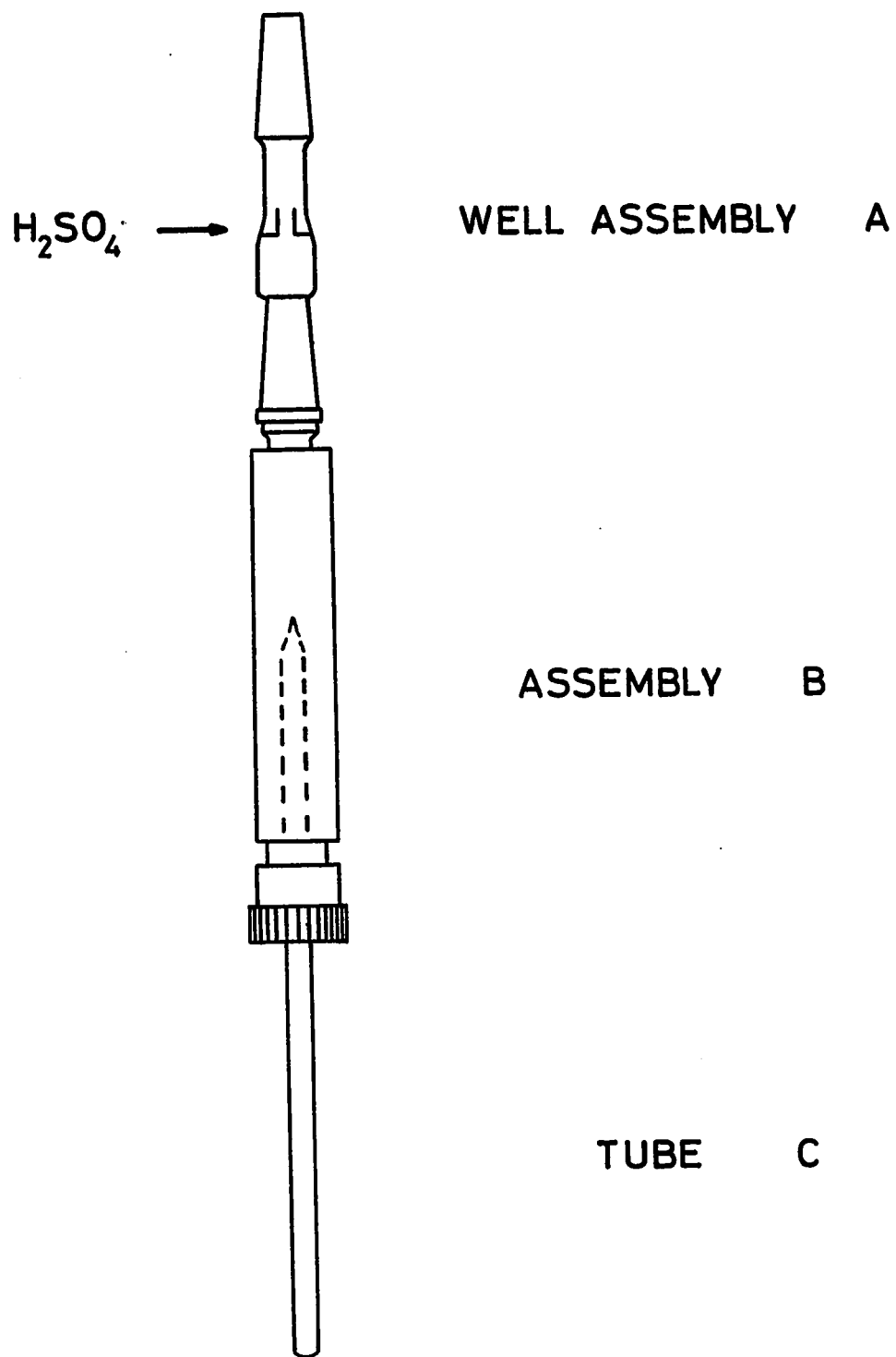
The apparatus for opening the sealed tubes

Direct measurements of the ratio of peaks 46 ($^{12}C^{16}O^{18}O$) : 44 ($^{12}C^{16}O^{16}O$) + 45 ($^{13}C^{16}O^{16}O$) + 45 ($^{12}C^{16}O^{17}O$) were made on the samples of carbon dioxide with an isotope ratio mass spectrometer. It was found by measurement of a large number of samples prepared from water of identical isotopic composition that the isotopic ratio could be measured with a standard deviation of less than 0.5%. The double collector type of mass spectrometer used in this study has been described by Nier[51].

RESULTS SECTION

A. Identification of the Prepared Species

Confirmation of the identity of the complexes prepared for this study was made through elemental and spectral analyses. Table 2 contains the observed spectral data along with the values from the literature for comparison. Table 3 presents the results of the elemental analysis. These values were averaged from at least three determinations.

Comparisons of the spectrophotometric data show very good agreement between the values obtained in this work and those reported in the literature. Good spectral data are important because elemental analysis will not aid in distinguishing *cis* and *trans* isomers. The results of the elemental analysis for *trans*-chloroaquotetraammine-chromium(III) perchlorate is given as a ratio because the salt was always obtained as a hydrate with a variable hydration number.

B. Removal of Coordinated Water

Although each of the complexes was precipitated from solution during a kinetic run as the bromide salt, preliminary experiments were performed on the chloride salts.

TABLE 2

Visible absorption maxima and minima of the prepared species[a]

Complex	This Work	Literature Value
$Cr(NH_3)_5OH_2^{3+}$	360 (29.0)[b]	360 (28.5)[b,53]
	405 (8.7) min	405 (6) min
	480 (35.0)	480 (35)
		360 (29)[54]
		405 (10) min
		480 (34)
		360 (29.0)[c,55]
		484 (35.0)
cis-$Cr(NH_3)_4(OH_2)_2^{3+}$	366 (26.6)[d]	366 (26.6)[d,43]
	419 (8.0) min	419 (7.8) min
	496 (36.0)	495 (36.1)
$trans$-$Cr(NH_3)_4(OH_2)_2^{3+}$	369 (29.6)[d]	368 (29.7)[d,43]
	415 (10.8) min	415 (10.8)
	476 (20.6)	476 (20.6)
	529 (shoulder)	-
cis-$Cr(NH_3)_4OH_2Cl^{2+}$	384 (33.0)[d]	384 (33.3)[d,43]
	439 (9.0) min	439 (9.0) min
	520 (40.0)	518 (40.4)
$trans$-$Cr(NH_3)_4OH_2Cl^{2+}$	383 (40.0)[d]	383 (39.2)[d,43]
	435 (13.7) min	434 (13.1) min
	469 (18.4)	468 (18.2)
	508 (14.0) min	506 (14.1) min
	555 (19.9)	555 (20.0)

TABLE 2 continued

a) Reported as λ (ε), where λ = wavelength of absorption in nm, and ε = molar absorptivity at the particular in mol^{-1} cm^{-1}

b) 0.1 $\underline{M}$ $HClO_4$

c) 0.05 $\underline{M}$ $HClO_4$

d) 1.0 $\underline{M}$ $HClO_4$

TABLE 3

Elemental analysis of the prepared species

Complex[a]	Percentage	Cr	N	Cl
$Cr(NH_3)_5OH_2^{3+}$	calculated	11.50	15.45	
	found	11.51	15.53	
$cis\text{-}Cr(NH_3)_4(OH_2)_2^{3+}$	calculated	11.44	12.33	
	found	11.48	12.39	
$trans\text{-}Cr(NH_3)_4(OH_2)_2^{3+}$	calculated	11.44	12.33	
	found	11.44	12.39	
$cis\text{-}Cr(NH_3)_4OH_2Cl^{2+}$	calculated	13.96	15.04	9.51
	found	13.83	14.80	9.30
$trans\text{-}Cr(NH_3)_4OH_2Cl^{2+}$	calculated[b]	1	4	1
	found[b]	1	3.98	1.01

a) as the perchlorate salt
b) ratio Cr:N:Cl

When $trans$-[Cr(NH$_3$)$_4$(OH$_2$)$_2$]Cl$_3$ was dehydrated in $vacuo$, it was noticed that the product did not have the green colour of $trans$-[Cr(NH$_3$)$_4$Cl$_2$]Cl as was expected but rather a purple coloured compound which was reminiscent of cis-[Cr(NH$_3$)$_4$Cl$_2$]Cl resulted. This purple product was very soluble in 1 $\underline{M}$ perchloric acid as was the cis-dichlorotetraamminechromium(III) complex whereas the $trans$-dichlorotetraamminechromium(III) complex was only sparingly soluble in strong acid.

To confirm the suspicion that there was a $trans$ to cis isomerization during dehydration, the diffuse reflectance spectrum of $trans$-[Cr(NH$_3$)$_4$(OH$_2$)$_2$]Cl$_3$ after dehydration was taken and compared to the diffuse reflectance spectra of $trans$-[Cr(NH$_3$)$_4$Cl$_2$]Cl[20] and cis-[Cr(NH$_3$)$_4$Cl$_2$]Cl[56] prepared independently. By comparing the absorption maxima of the diffuse reflectance spectra of the above compounds, as given in Table 4, it indeed seems that there was a $trans$ to cis isomerization during dehydration.

$Trans$-[Cr(NH$_3$)$_4$OH$_2$Cl]Cl$_2$ was also dehydrated but it appeared that ammonia was lost before the water and therefore, $trans$ to cis isomerization was not determined. The two analogous cis isomers, cis-diaquotetraamminechromium(III) chloride and cis-chloroaquotetraamminechromium(III) chloride, when dehydrated, formed cis-[Cr(NH$_3$)$_4$Cl$_2$]Cl as confirmed by their visible absorption spectra.

When cis- and $trans$-[Cr(NH$_3$)$_4$(OH$_2$)$_2$]Br$_3$ were dehydrated under similar conditions, and the resulting solids dissolved in acid solutions, the resulting visible spectra were very similar. The existence of only two peaks in the absorption spectra tended to indicate the presence of the cis isomer only, because such $trans$ complexes usually exhibit three absorption maxima.

TABLE 4

Diffuse reflectance absorptions from 350nm to 1700nm[a]

cis-$[Cr(NH_3)_4Cl_2]Cl$	trans-$[Cr(NH_3)_4Cl_2]Cl$	trans-$[Cr(NH_3)_4(OH_2)_2]Cl_3$ after dehydration[b]
393	400	393
446 min	445 min	443 min
533	470	533
1556	523 min	1555
	600	
	1423	
	1548	

a) Cary Model 14 with visible-infrared diffuse reflectance attachment

b) 120°C for 1 hour *in vacuo*

This study was not taken any further but it is interesting to note that similar solid state *trans→cis* isomerizations have been reported elsewhere. Martin and Tobe[40] noticed that both *cis-* and *trans-* $[Co(en)_2OH_2NH_3](NO_3)_3$ lose their coordinated water smoothly when heated above 80°C at 5 mm pressure, to yield the corresponding *cis*-nitroammine complex. The *trans→cis* isomerization of *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ has been investigated by several workers[57-59]. LeMay and Bailer[58] proposed that the isomerization occurs by an aquation-anation pathway as the two waters are lost. The thermal deaquation of both *cis-* and *trans-* $[Co(en)_2(OH_2)_2]Cl_3 \cdot 2H_2O$ has been investigated by Chang and Wendlandt[60] who found that only *cis*-$[Co(en)_2Cl_2]Cl$ was produced as the product. More recently Nagase and Tanaka[61] found that *trans*-$[Cr(NH_3)_4Cl_2]Cl \cdot H_2O$ underwent *trans* to *cis* isomerization in the solid state at 200°C.

It seems likely that there are two distinct mechanisms by which *trans*-$[Cr(NH_3)_4(OH_2)_2]Cl_3$ can undergo isomerization on dehydration. Both coordinated waters could first be lost to form the *trans*-dichloro- complex which would then spontaneously undergo *trans→cis* isomerization. Or, the isomerization could take place as the coordinated waters were being replaced by chloride ligands since the possibility that transition states with different coordinations would exist.

It would be desirable to do more experimental work on this and similar systems.

C. Treatment of Exchange Data

The general equation for an isotopic exchange reaction may be

written as,

$$A\ X\ +\ B\ ^*X\ \rightleftarrows\ A\ ^*X\ +\ B\ X$$
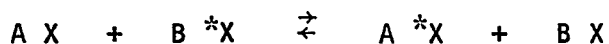
where * designates the distinguishable isotope. A more specific case

of exchange is the water exchange reaction which may be written,

$$M(^*OH_2)\ +\ OH_2\ \rightleftarrows\ M(OH_2)\ +\ ^*OH_2$$
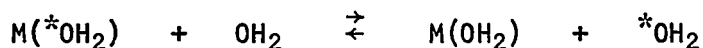
where M is a metal ion.

The rate of disappearance of the isotopic species from an

initially labelled reactant, B $^*X$, or rate of appearance in an initially

unlabelled reactant, A X, is described by a first order rate law.

It has been shown[62] that this first order exchange law will be

applicable irrespective of the actual exchange mechanism; the number of

chemically equivalent exchangeable groups; the reactant concentrations;

any differences in isotopic reaction rates; or the concentration of the

labelling isotope, provided small amounts of isotope are used[63].

Several workers[62-66] have shown that the rate (R) at which X

atoms interchange between A X and B X is

$$R\ =\ -\ 1/\tau\ \cdot\ \alpha\beta/(\alpha+\beta)\ \cdot\ \ln\ (1-F) \qquad [1]$$

where α and β signify the total concentrations (A X + A $^*X$) and (B X +

B $^*X$) respectively and τ is time. The law in this form was first devised

by McKay[64] and consequently it is called the McKay equation.

The rate constant for the water exchange process may be cal-

culated from the McKay equation where,

R = constant rate of exchange

α = concentration of solvent water (labelled and unlabelled)

β = concentration of ligand water (labelled and unlabelled)

F = fraction of exchange

τ = time,

and from the rate equation for the pseudo-first-order reaction,

$$R = k_{ex} \cdot \beta \qquad [2]$$

where,

k_{ex} = rate constant for exchange of an individual water.
Combining equations [1] and [2] and rearranging gives

$$k_{ex} = - \alpha/(\alpha+\beta) \cdot \ln (1-F)/\tau. \qquad [3]$$

Since for this study only one or two ligand waters were present with a concentration of 0.05 $\underline{M}$ or 0.1 $\underline{M}$ respectively, and since α = 55.6 $\underline{M}$ then, $\alpha \simeq \alpha+\beta$. Using this approximation, equation [3] now reduces to

$$k_{ex} = - \ln (1-F)/\tau. \qquad [4]$$

It is evident from equation [4] that a plot of $- \ln (1-F)$ versus time or a function of $- \ln (1-F)$ versus time will yield a straight line with slope equal to k_{ex}, the rate constant for exchange of one water for a first order reaction. Such a plot is called a McKay plot.

For the loss of label from an initially labelled species F, the fraction of exchange at time τ is given by

$$F = (y_0 - y_\tau)/(y_0 - y_\infty) \qquad [5]$$

and hence,

$$- \ln (1-F) = - \ln (y_\tau - y_\infty)/(y_0 - y_\infty) \qquad [6]$$

where,

y_0 = concentration of labelled species at $\tau = 0$

y_τ = concentration of labelled species at $\tau = \tau$

y_∞ = concentration of labelled species at $\tau = \tau_\infty$.

At τ_∞ the exchange reaction is assumed to have reached isotopic equilibrium.

Norris[66] has given a number of useful alternative expressions for the fraction of exchange. Earley[67] used a function (E-1) in place of (1-F) for the McKay plot for the water exchange reaction in the aquopentaamminechromium(III) cation. The enrichment, E, is obtained by dividing the 46/(44 + 45) isotope abundance ratio of carbon dioxide prepared from the coordinated water of the complex sample by the 46/(44 + 45) ratio of carbon dioxide prepared from water of normal isotopic composition. The function (E-1) corresponds to the expression $(y_\tau - y_\infty)/y_\infty$. Equation [4] may now be rewritten as

$$k_{ex} = \ln (E-1)/\tau. \qquad [7]$$

Thus, a plot of ln (E-1) versus time in seconds will yield a straight line with slope of k_{ex} in the unit of sec^{-1}.

Often in exchange reactions where the concentration of the labelled species is very small the infinite time concentration of label, y_∞, is assumed to be the same as that corresponding to the isotopic composition of natural water[4,67]. In this approximation the contribution of the enriched complex to the equilibrium composition as well as any isotope effect are neglected.

All raw experimental data and calculated values of (E-1) are given in the Appendix. The rate constants for the water exchange processes of all the complexes studied, at the various temperatures, are tabulated in Tables 5-9. These values were determined from a least squares analysis[68] of the raw data and the errors quoted are standard deviations. Figures 5-8 show specimen McKay plots for each of the four aquotetraamminechromium(III) complexes studied.

TABLE 5

First order rate constants for the exchange reaction

$$Cr(NH_3)_5{}^{18}OH_2{}^{3+} \quad + \quad OH_2 \quad \rightleftarrows \quad Cr(NH_3)_5OH_2{}^{3+} \quad + \quad {}^{18}OH_2$$
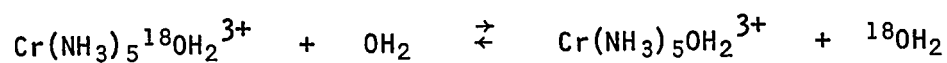
$$[Cr(III)] \quad = \quad 0.050 \ \underline{M}$$

$$[HClO_4] \quad = \quad 0.025 \ \underline{M}$$

$$\mu \quad\quad = \quad 0.50 \ \underline{M} \ (NaClO_4)$$

Run	T°C	$10^5 k_{ex}$, sec^{-1}
1	10.00	0.733 ± 0.010
2	20.10	3.10 ± 0.04
3	30.10	12.1 ± 0.1

TABLE 6

First order rate constants for the exchange reaction

$$cis\text{-}Cr(NH_3)_4OH_2{}^{18}OH_2{}^{3+} + OH_2 \rightleftarrows cis\text{-}Cr(NH_3)_4(OH_2)_2{}^{3+} + {}^{18}OH_2$$

$$[Cr(III)] = 0.050 \ \underline{M}$$

$$[HClO_4] = 0.025 \ \underline{M}$$

$$\mu = 0.50 \ \underline{M} \ (NaClO_4)$$

Run	T°C	$10^5 k_{ex}$, sec^{-1}
1	10.00	0.694 ± 0.026
2	15.00	1.60 ± 0.03
3	19.90	3.06 ± 0.12
4	25.00	6.28 ± 0.05
5	25.00	6.20 ± 0.06
6	30.00	12.9 ± 0.1
7	30.00	12.9 ± 0.1
8	35.00	22.5 ± 0.3
9*	20.10	2.99 ± 0.09
10*	35.00	23.0 ± 0.05

*$[HClO_4] = 0.200 \ \underline{M}$

TABLE 7

First order rate constants for the exchange reaction

$$trans\text{-}Cr(NH_3)_4OH_2{}^{18}OH_2{}^{3+} + OH_2 \rightleftarrows trans\text{-}Cr(NH_3)_4(OH_2)_2{}^{3+} + {}^{18}OH_2$$
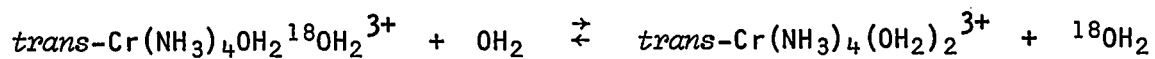
$$[Cr(III)] = 0.050 \ \underline{M}$$

$$[HClO_4] = 0.025 \ \underline{M}$$

$$\mu = 0.50 \ \underline{M} \ (NaClO_4)$$

Run	T°C	$10^5 k_{ex}$, sec^{-1}
1	19.90	0.707 ± 0.001
2	19.90	0.731 ± 0.009
3	25.00	1.47 ± 0.01
4	25.00	1.47 ± 0.02
5	30.00	3.17 ± 0.03
6	30.00	3.19 ± 0.02
7	35.00	5.93 ± 0.06
8	35.00	5.99 ± 0.13
9	40.00	11.4 ± 0.3
10	40.00	11.5 ± 0.1
11	44.90	21.5 ± 0.2
12	44.90	21.8 ± 0.1
13*	35.00	4.76 ± 0.07
14*	40.00	8.43 ± 0.18

*$[HClO_4] = 0.200 \ \underline{M}$

TABLE 8

First order rate constants for the exchange reaction

$$cis\text{-}Cr(NH_3)_4{}^{18}OH_2Cl^{2+} + OH_2 \underset{\leftarrow}{\rightarrow} cis\text{-}Cr(NH_3)_4OH_2Cl^{2+} + {}^{18}OH_2$$
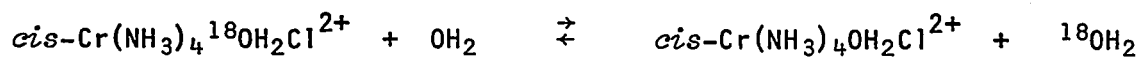
$$[Cr(III)] = 0.050 \underline{M}$$

$$[HClO_4] = 0.025 \underline{M}$$

$$\mu = 0.50 \underline{M} \ (NaClO_4)$$

Run	T°C	10^5k_{ex}, sec^{-1}
1	10.00	0.594 ± 0.010
2	15.00	1.26 ± 0.03
3	19.90	2.32 ± 0.03
4	19.90	2.28 ± 0.03
5	25.10	5.10 ± 0.26
6	30.00	10.2 ± 0.1
7	30.00	10.0 ± 0.2
8	35.00	19.9 ± 0.3
9*	25.10	5.26 ± 0.09

$$*[HClO_4] = 0.350 \underline{M}$$

TABLE 9

First order rate constants for the exchange reaction

$$trans\text{-}Cr(NH_3)_4{}^{18}OH_2Cl^{2+} + OH_2 \rightleftharpoons trans\text{-}Cr(NH_3)_4OH_2Cl^{2+} + {}^{18}OH_2$$
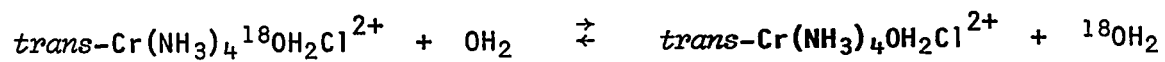
$$[Cr(III)] = 0.050 \underline{M}$$

$$[HClO_4] = 0.025 \underline{M}$$

$$\mu = 0.50 \underline{M} \ (NaClO_4)$$

Run	T°C	$10^5 k_{ex}$, sec^{-1}
1	10.00	0.499 ± 0.005
2	15.00	0.991 ± 0.013
3	19.90	2.31 ± 0.03
4	19.90	2.28 ± 0.03
5	25.10	4.42 ± 0.05
6	30.00	8.94 ± 0.10
7	30.00	8.61 ± 0.11
8	35.00	17.0 ± 0.2
9*	25.10	4.54 ± 0.06

$$*[HClO_4] = 0.350 \underline{M}$$

FIGURE 5

cis– DIAQUOTETRAAMMINECHROMIUM(III) ION

SOLVENT WATER EXCHANGE

RUN = CATA – 8 (35°)

FIGURE 6

trans–DIAQUOTETRAAMMINECHROMIUM(III) ION

SOLVENT WATER EXCHANGE

RUN = TATA–IO (40°)
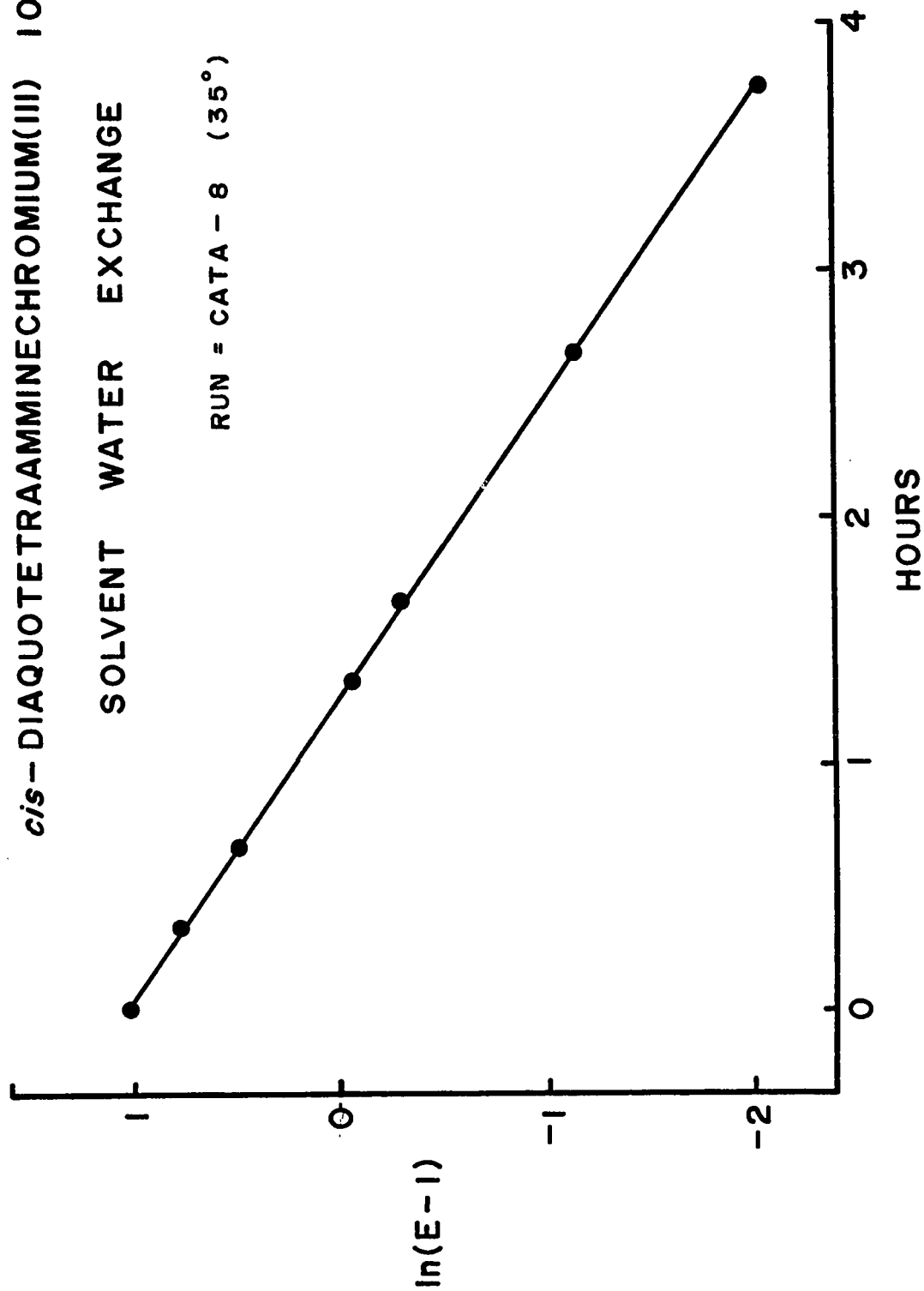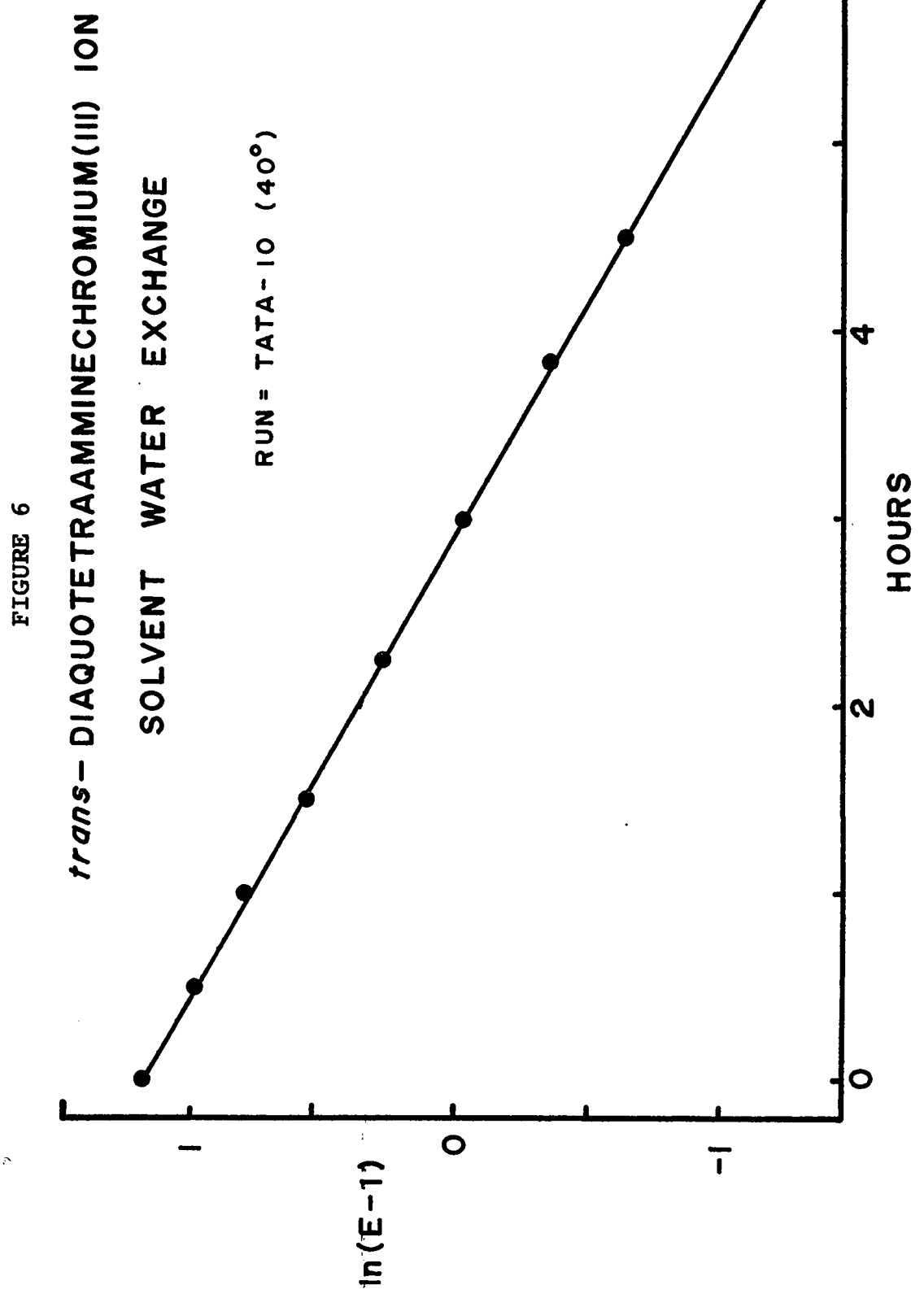
FIGURE 7

cis—CHLOROAQUOTETRAAMMINECHROMIUM(III) ION

SOLVENT WATER EXCHANGE

RUN = CACTA — 9   (25.1°)
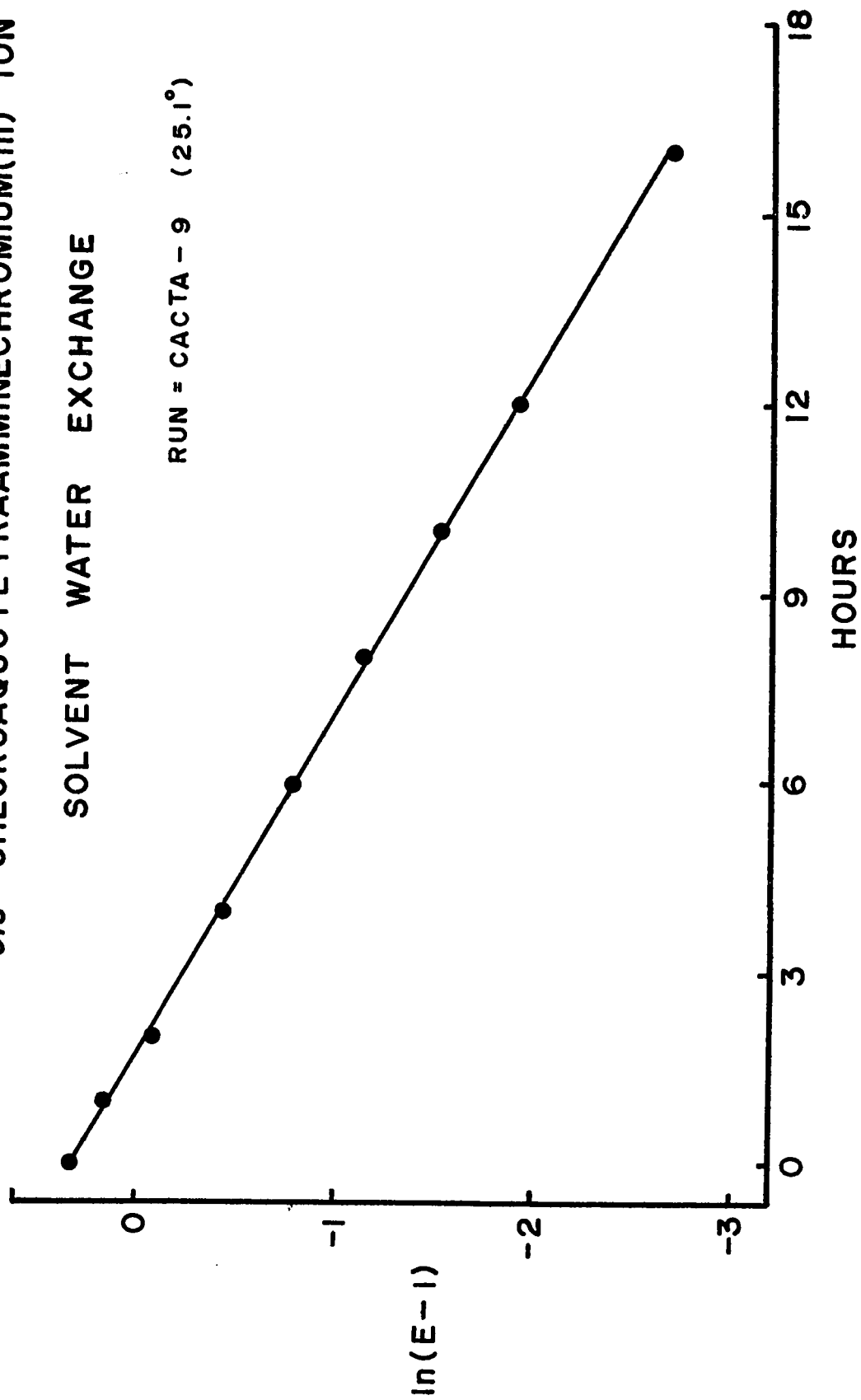
FIGURE 8

trans–CHLOROAQUOTETRAAMMINECHROMIUM(III) ION

SOLVENT WATER EXCHANGE

RUN = TACTA – 5   (25.1°)
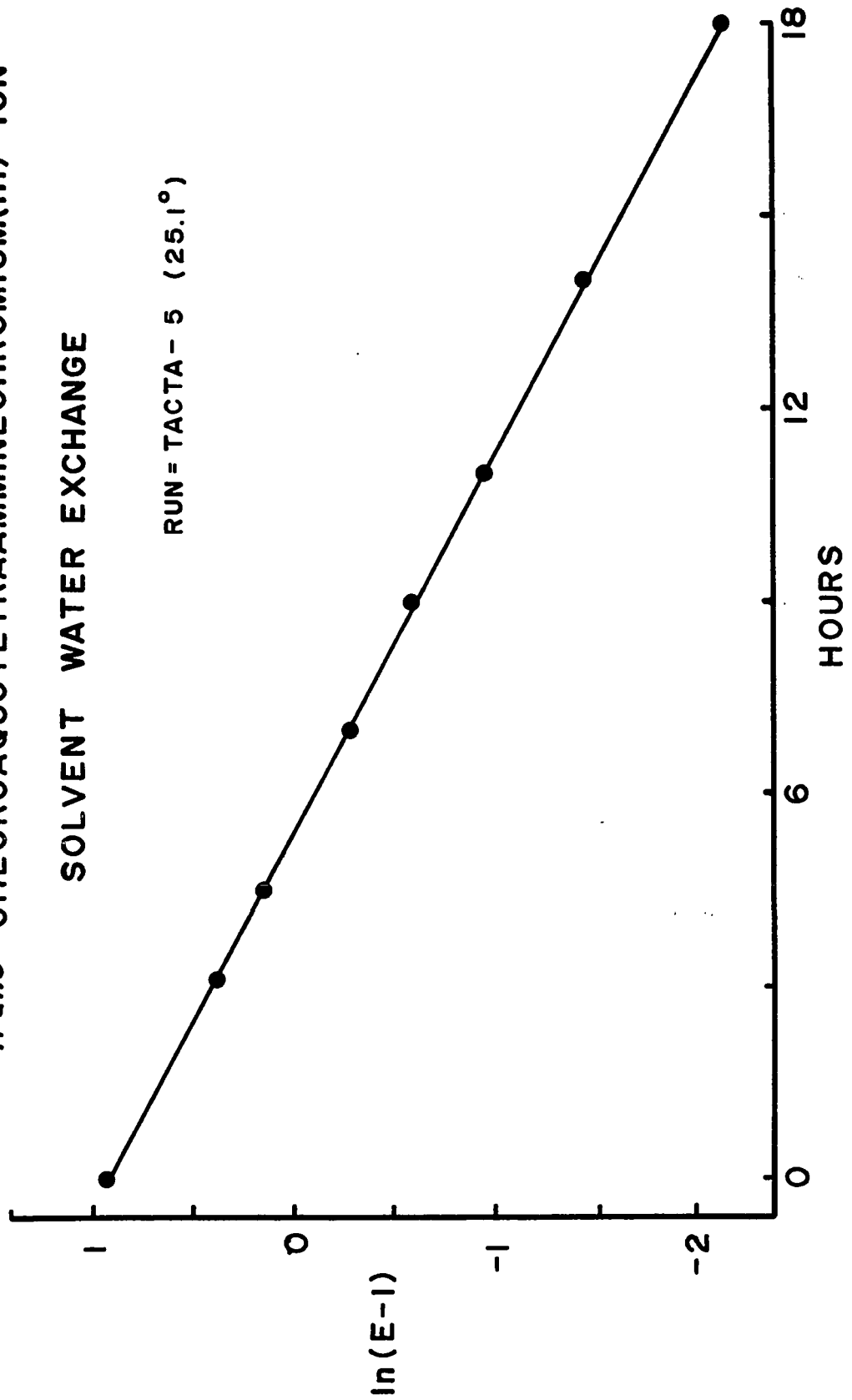
D.   Calculation of Activation Parameters

The temperature dependent data of Tables 5 to 9 enabled the calculation of the enthalpies and entropies of activation, ΔH^* and ΔS^* respectively, for the interchange of ligand water with solvent.

According to transition state theory[70] a rate constant may be expressed as a function of activation parameters, that is,

$$K = \kappa \cdot kT/h \cdot \exp(\Delta S^*/R) \cdot \exp(-\Delta H^*/RT) \qquad [8]$$

where,

K   =   reaction rate constant (sec^{-1})

κ =   transmission coefficient

k   =   Boltzman constant (1.3805×10^{-16} erg $^{\circ}K^{-1}$)

T   =   absolute temperature ($^{\circ}K$)

h   =   Planck constant (6.6256×10^{-27} erg sec)

R   =   gas constant (1.9872 cal $^{\circ}K^{-1}$ mol^{-1})

ΔS^* =   entropy of activation (cal deg^{-1} mol^{-1})

ΔH^* =   enthalpy of activation (cal mol^{-1})

The activation parameters ΔH^* and ΔS^* represent the difference in the enthalpy and entropy between the activated complex in the transition state and the ground state of the reactants. The free energy of activation is defined as

$$\Delta G^* = \Delta H^* - T\Delta S^*. \qquad [9]$$

The Arrhenius activation energy, E_a, is given by equation [10].

$$E_a = \Delta H^* + RT \qquad [10]$$

The activated complex consists of the aggregate of several reactant molecules in the configuration of highest potential energy and is shown as the maximum in a reaction coordinate diagram. As a rule, the less the energy (E_a) required to form the activated complex,

the faster a reaction will proceed. The entropy of activation is, however, a non-energy factor that can retard a reaction as seen by equation [9]. The entropy of activation is largely determined by the change of translational and rotational freedom as several particles come together or disperse in the activated complex.

The transmission coefficient, κ, as given in equation [8] is considered to be very close to unity. It may be defined as the fraction of times that the activated complex crosses the potential energy barrier of the transition state and successfully forms the products of reaction. Thus by setting $\kappa = 1$, equation [8] may be rewritten as,

$$\ln (k_{ex}/T \cdot h/k) = (\Delta S^*/R) - (\Delta H^*/RT) \qquad [11]$$

or,

$$T \cdot \ln (k_{ex}/T \cdot h/k) = (T\Delta S^*/R) - (\Delta H^*/R). \qquad [12]$$

From inspection of equation [11] it is evident that a plot of $\ln (k_{ex}/T \cdot h/k)$ versus $1/T$ or $\ln (k_{ex}/T)$ versus $1/T$, if linear, has a slope equal to $-\Delta H^*/R$. Figure 9 shows such plots for the complexes studied. Table 10 lists the values for the enthalpy of activation for the various complexes studied. These values were obtained from a weighted least squares analysis[68] of the linear dependence of $\ln (k_{ex}/T)$ on $1/T$ using the uncertainties in k_{ex} as listed in Tables 5-9.

Figure 10 depicts plots of $T \cdot \ln (k_{ex}/T \cdot h/k)$ versus T for the data in Tables 5-9. Examination of equation [12] shows that the slope for such a plot is equal to $\Delta S^*/R$. The experimental values of the entropy of activation along with the associated uncertainties are presented in Table 10.

FIGURE 9

ENTHALPY of ACTIVATION for WATER EXCHANGE

$cis-Cr(NH_3)_4(OH_2)_2{}^{3+}$

$cis-Cr(NH_3)_4 OH_2 Cl{}^{2+}$

$trans-Cr(NH_3)_4 OH_2 Cl{}^{2+}$

$trans-Cr(NH_3)_4 (OH_2)_2{}^{3+}$
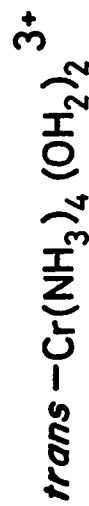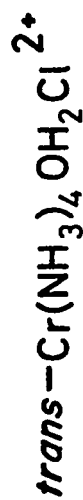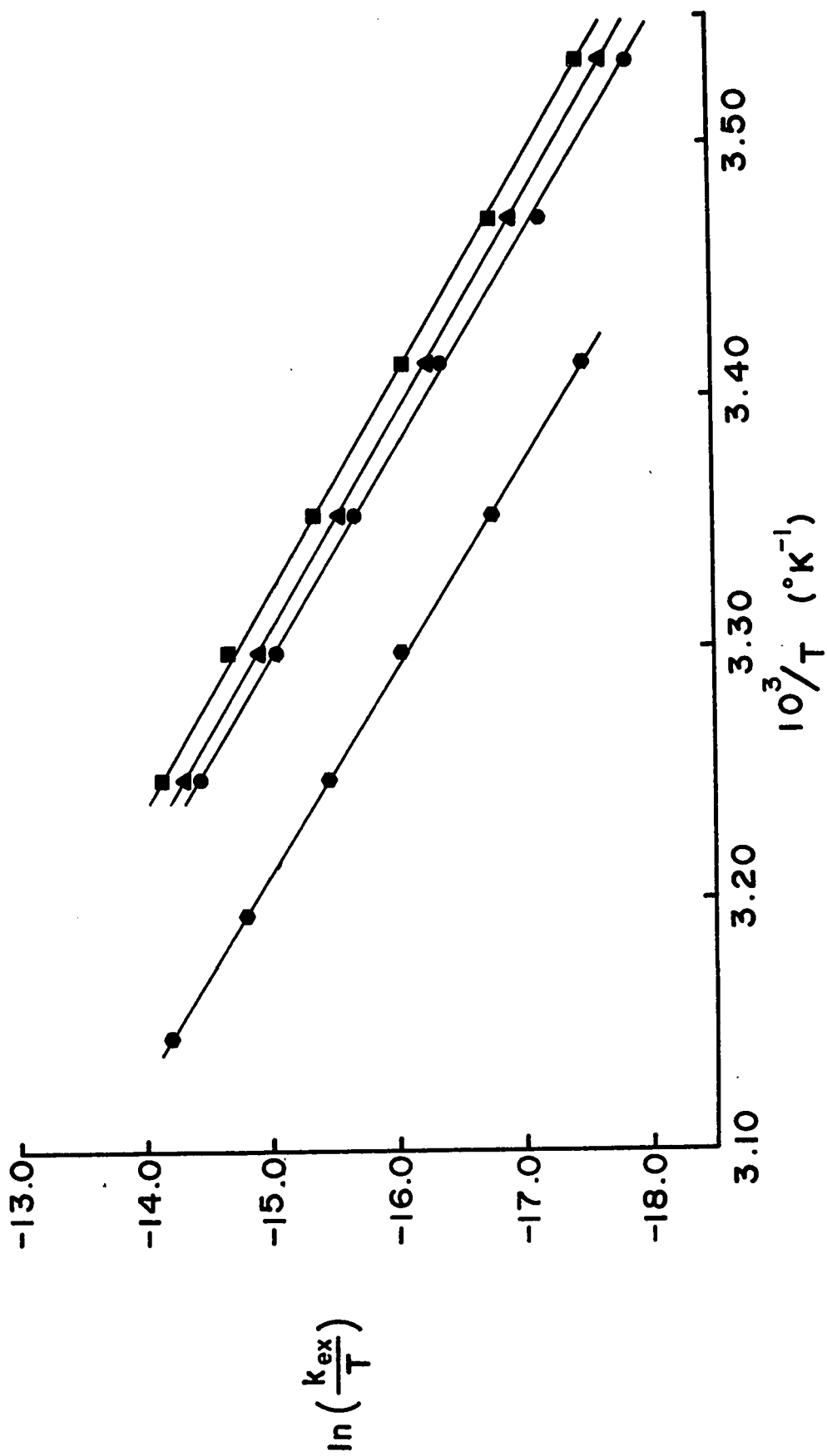
FIGURE 10

ENTROPY of ACTIVATION for WATER EXCHANGE

$cis-Cr(NH_3)_4(OH_2)_2{}^{3+}$

$cis-Cr(NH_3)_4 OH_2Cl{}^{2+}$

$trans-Cr(NH_3)_4 OH_2Cl{}^{2+}$
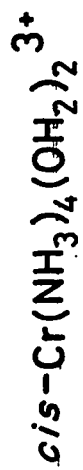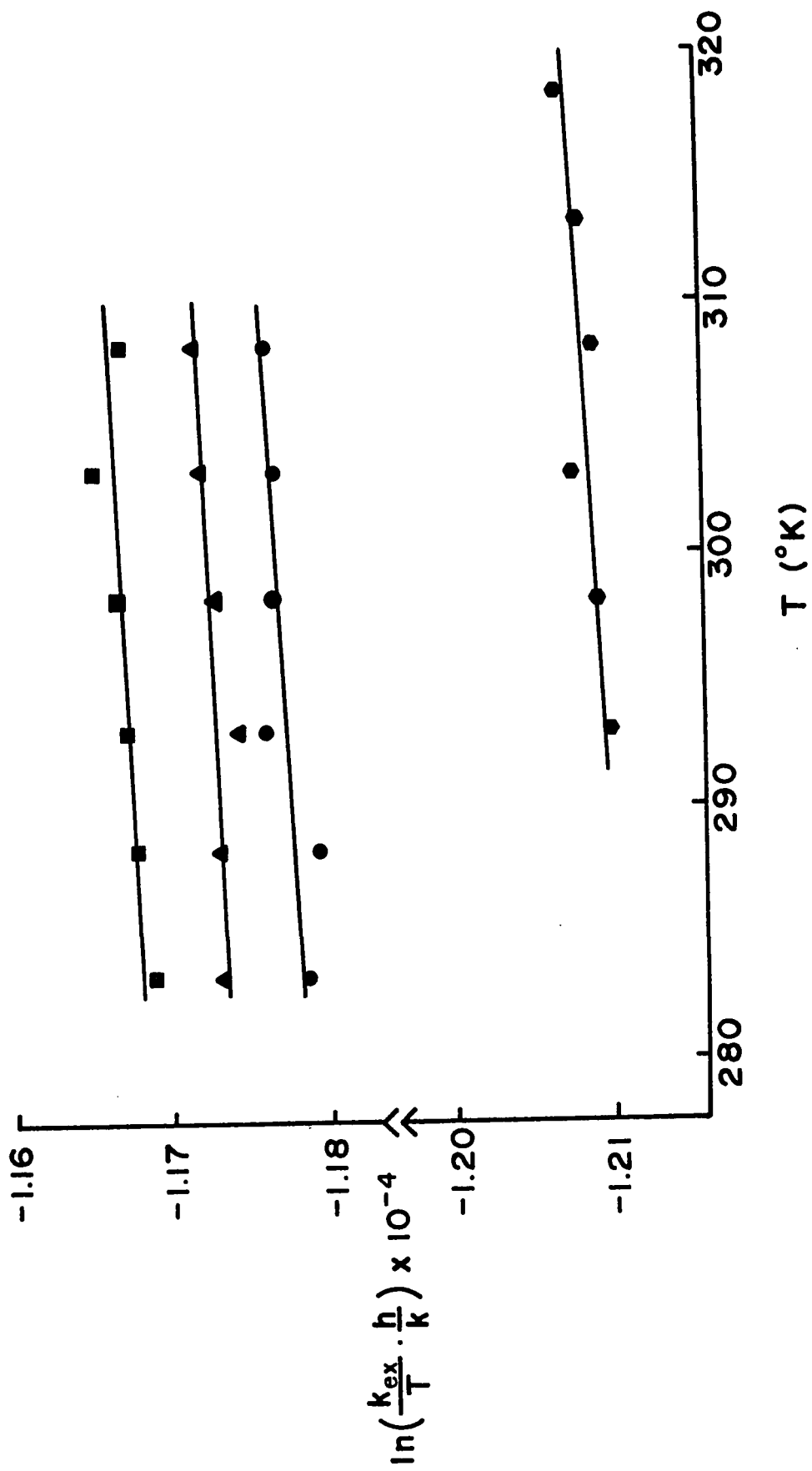
$trans-Cr(NH_3)_4(OH_2)_2{}^{3+}$

TABLE 10

The activation parameters for the water exchange process complexes in this study

Complex	ΔH^* kcal mol^{-1}	ΔS^* cal deg^{-1} mol^{-1}
$Cr(NH_3)_5OH_2^{3+}$	23.2 ± 0.3	$+0.1 \pm 0.5$
$cis\text{-}Cr(NH_3)_4(OH_2)_2^{3+}$	23.6 ± 0.4	$+1.2 \pm 1.2$
$trans\text{-}Cr(NH_3)_4(OH_2)_2^{3+}$	24.8 ± 0.2	$+1.8 \pm 1.0$
$cis\text{-}Cr(NH_3)_4OH_2Cl^{2+}$	23.9 ± 0.3	$+1.6 \pm 1.1$
$trans\text{-}Cr(NH_3)_4OH_2Cl^{2+}$	24.0 ± 0.3	$+1.8 \pm 1.2$

E. Effect of Systematic Errors on the Rate Parameters

Control of Concentration Factors

Large volumes of reaction solutions were carefully prepared so that for any one complex, the same solution and concentration factors would prevail for all kinetic runs. Accurately weighed amounts of complex were added to known volumes of solution to initiate a reaction. The presence of any water of hydration was accounted for when the complex was weighed out. An aliquot of the actual reaction solution was used to analyse for the chromium concentration in each run to ensure constant (± 2%) complex concentration throughout a series of experiments. This precaution was taken in order to minimize any effect that changes in ionic strength or complex concentration might have on the rate constants.

It has been pointed out[70] that a change in the activity of water as the ionic strength of the medium increases must be taken into account for kinetic experiments. Contributions from these activity-coefficient terms to the activation entropy make it difficult to compare entropies determined in media of different ionic strength. Hunt and Plane[36] reported that the first order rate coefficient for water exchange of the hexaaquochromium(III) ion increased with increased ionic strength. Albeit the increase was small, the rate approximately doubled for a twenty fold increase in ionic strength. Although experimental uncertainties were large, Bracken[3] found that the exchange rate constants for *cis* and *trans* waters increased as ionic strength increased in the acidopentaaquochromium(III) cations. A rather large increase for *cis* water exchange was found; doubling the ionic strength caused an apparent doubling of the rate constant.

Aquation and Isomerization

If cis- or $trans$-$Cr(NH_3)_4(OH_2)_2^{3+}$, or cis- or $trans$-$Cr(NH_3)_4$ OH_2Cl^{2+} were to isomerize in solution at rates faster than, or approaching the rates of water exchange, the McKay plots would no longer be linear and the resulting rate constants would be of dubious value. Fortunately, isomerization is not important and error from this source can be considered negligible[20].

Aquation for cis- and $trans$-$Cr(NH_3)_4OH_2Cl^{2+}$ is a more serious problem, as can be seen from Table 11 which compares aquation rate constants and water exchange rate constants. In exchange experiments at 25°C with the cis- and $trans$-chloroaquo- complexes, the penultimate samples were removed at about 16 and 18 hours after "zero time" respectively. The hydrolytic decomposition of these complexes, to the more rapidly exchanging cis-diaquo- ion in the case of the cis isomer and to the less rapidly exchanging $trans$-diaquo- ion in the case of the $trans$ isomer, amounts to $ca.$ 26% and $ca.$ 4% respectively for this time interval. The measured rate constants are little affected by aquation as the McKay plots show (figures 7 and 8), since the latter portions exhibit excellent linearity. It is evident from Table 11 that if an exchange reaction were to slow down as it progressed, the resulting McKay plot would exhibit a concave curvature, or if the exchange were to speed up, a convex curvature.

Since the rate constants for water exchange of the cis-diaquo- ion and the cis-chloroaquo- ion are very similar, the effect of aquation on the exchange rate constant may not be readily apparent even after substantial aquation. The rate constants for the $trans$-diaquo- ion and the $trans$-chloroaquo- ion differ by a factor of three; hence it is assumed

TABLE 11

Water exchange and aquation rates at 25°C

Complex	$10^5 k_{ex}$[a], sec^{-1}	$10^5 k_{aq}$[b], sec^{-1}
cis-Cr(NH$_3$)$_4$(OH$_2$)$_2$$^{3+}$	6.2	-
$trans$-Cr(NH$_3$)$_4$(OH$_2$)$_2$$^{3+}$	1.5	-
cis-Cr(NH$_3$)$_4$OH$_2$Cl^{2+}	5.2	0.54
$trans$-Cr(NH$_3$)$_4$OH$_2$Cl^{2+}	4.4	0.065

a) this research

b) aquation rate constant in 1 $\underline{M}$ HClO$_4$ extropolated from data in reference 20 by reference 22

that the limited aquation is not reflected in the exchange rate constant because of the small amount of aquation product present (*ca.* 4%). In practice however, the lack of an observed effect of the aquation products on the exchange rates may be a result of the method used to measure the exchange. Since analysis of label is effected directly on the solid complex, the greater apparent solubility of the aquation product (the diaquo- species) in acid solution means less of the diaquo- salt would be recovered as a solid, and hence contamination by the aquation product would be minimized.

Since decomposition of the species under investigation by aquation could certainly introduce error in the exchange rate constants, sampling was done over fewer than five half-lives for water exchange, to minimize this effect.

It has been shown that isomerization for both *cis-* and *trans-* $Cr(NH_3)_4OH_2Cl^{2+}$ during aquation is not important for the conditions used in this study[20,22].

Photochemical and Carbon Dioxide Catalysis

As mentioned earlier, chromium(III) complexes are known to undergo photochemically induced reactions, especially aquation. This possible source of error was eliminated by using darkened reaction vessels for all kinetic experiments. How the complexes reacted with light would have determined the actual affect on the rate constants, but this was not pursued.

It has been shown[48] that the rate of water exchange for the aquopentaamminechromium(III) ion is increased in the presence of carbon

dioxide, possibly through the formation of an intermediate carbonato-chromium(III) species. The presence of carbon dioxide would probably also increase the rate of water turnover in the aquotetraamminechromium-(III) cations and give spuriously large rate constants. This source of error was controlled by the use of carbon dioxide free reaction media and by flushing the reaction vessel with nitrogen after withdrawing samples to avoid contamination by atmospheric carbon dioxide.

Precipitation of Labelled Sample

When an aliquot of reaction solution was taken, it was immediately quenched by rapid cooling in a dry ice methanol bath. Extreme care was taken not to allow the mixture to warm up to room temperature while anhydrous HBr was dissolved in the sample to pre-cipitate the complex. If the solution were to become warm there would be two alternatives. Anation by bromide ion would cause a loss of coordinated water, but more important, water exchange might still occur, giving isotopic dilution. Isotopic dilution would lead to uncertainties in the rate constants, while anation could reduce the subsequent water sample to the size where it would be unsatisfactory for mass analysis.

Control of Water of Hydration

Since isotopic analysis was effected on solid samples of the complexes, the presence of hydration water had to be rigorously eliminated. The water of hydration, of approximately normal isotopic

composition, could either exchange with the labelled coordinated water or dilute the enriched sample during total dehydration. In either case the effect would be to lower the actual concentration of the label and lead to inconsistent data and hence dubious rate constants. Thus, strict measures were taken to eliminate water of hydration from the complexes as explained in the experimental section.

Oxygen Exchange Between Sample and Container

Since glass is composed of silicon dioxide, it is possible that the oxygen atoms of the sample (now carbon dioxide) could interchange with the oxygen atoms of the glass container. This is especially true since the samples are heated to 500°C for several hours. Since the glass walls are composed of oxygen atoms of normal isotopic composition and the sample was enriched in oxygen-18, isotopic dilution of the sample was possible. The error from this source was minimized by making all sample tubes of identical size and pyrolysing all samples from any one experiment simultaneously. That is, all samples were treated in the same way, and therefore any isotopic dilution would be similar for all samples in a given experiment. The good experimental results show that the error from isotopic dilution was minimized.

THEORY OF SUBSTITUTION REACTIONS

Since water exchange is a substitution process whereby a coordinated water molecule interchanges with a water molecule in the bulk solvent and since later use will be made of this, it is most useful to review the established substitution mechanisms and their nomenclature.

Over the past two decades, ligand substitution reactions of coordination compounds have been studied extensively. From these studies a formalized nomenclature for the mechanisms of these substitution reactions has developed.

A general ligand substitution reaction is given by reaction {1} in which M is a metal atom or ion and X and Y are any two ligands

$$MX_n + Y \rightleftharpoons MX_{n-1}Y + X \qquad \{1\}$$

while n represents the number of ligands coordinated. One or more of the ligands involved is often also the solvent species. In fact, in the specific case of water exchange the ligands in question are two water molecules. The ligands bound directly to the metal are considered to be in the inner or first coordination sphere. In solution there will be a contact solvation shell surrounding this metal complex. This solvation shell is usually referred to as the outer or second coordination sphere or solvation sheath.

Mechanistically, this outer coordination sphere can play an important role in the substitution reactions of many transition metal complexes in solution. In aqueous solution the water molecules in the second coordination sphere may be hydrogen bonded to the ligands of the first coordination sphere which may allow outer sphere ligands access to the metal centre at distances approaching chemical bonding. Figure 11 depicts a metal centre surrounded by a first coordination sphere consisting of five ammonia molecules and one water molecule, and a partial second coordination sphere consisting of water molecules hydrogen bonded (dashed lines) to the molecules of the first coordination sphere.

The most convenient general terminology for substitution reactions is perhaps that developed by Hughes and Ingold[71] in describing organic reactions. Substitution reactions can be called S_N or S_E, which refers to nucleophilic substitution and electrophilic substitution respectively. A nucleophilic reagent may be regarded as one which donates electrons to an atomic nucleus in a reaction and an electrophilic reagent as one which acquires electrons from a nucleophilic reagent. In coordination chemistry which is the concern here, the central atom (M) is a electrophilic reagent and the ligands are nucleophilic reagents, hence our discussion will centre on nucleophilic substitution.

Fundamentally, there are at least two different pathways that can be conceived for a substitution reaction, namely, displacement and dissociation, called S_N2 and S_N1 respectively by Hughes and Ingold. An S_N2 reaction is one involving a bimolecular rate determining step in which one nucleophilic reagent replaces another as given by reaction {2}.

FIGURE 11

Primary and secondary coordination spheres
of a metal ion in aqueous solution
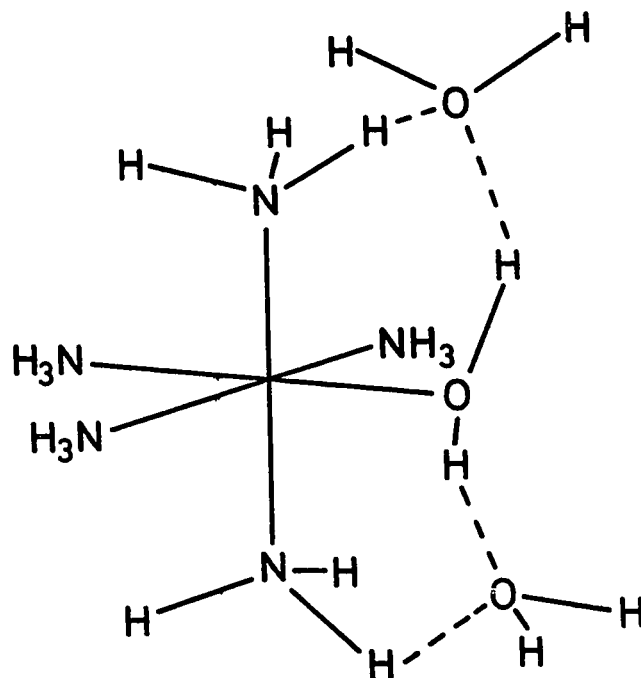
FIGURE 12
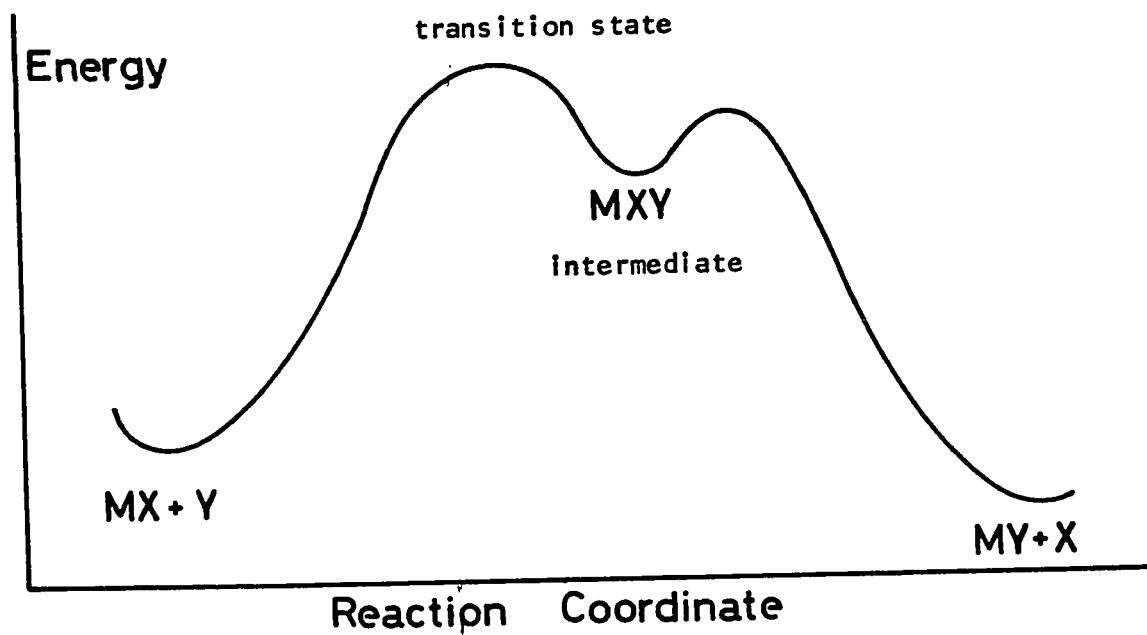
Reaction coordinate diagram for an S_N2 process

This means that the coordination number of the metal increases by one

in the transition state. Figure 12 shows a reaction coordinate diagram

for an S_N2 process, where both leaving and entering groups are

participants in the transition state.

$$Y + MX \rightleftharpoons Y \text{ --- } M \text{ --- } X \rightleftharpoons YM + X \qquad \{2\}$$
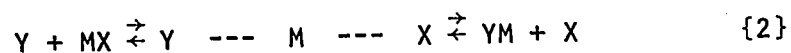
On the other hand, an S_N1 reaction proceeds by a two step

process in which the first step is a slow unimolecular heterolytic

dissociation

$$MX \rightleftharpoons M + X \qquad \{3\}$$

followed by a rapid coordination of M with a second reagent

$$M + Y \rightleftharpoons MY \qquad \{4\}.$$

In this scheme the coordination number of the metal decreases by one

and there exists as an intermediate, the metal of reduced coordination.

This process is shown on a reaction coordinate diagram in Figure 13.

As Basolo and Pearson[11] have pointed out, one of the great

complicating factors in assigning fmechanisms to substitution reactions

is the existence of borderline or intermediate mechanisms between S_N1

and S_N2. This does not necessarily mean that a reaction may be a mix-

ture of S_N1 and S_N2 steps, but one in which the participation of the

external reagent may be small. For example Y might be in the transition

state of MX but without having any significant contribution to the

activation. Experimentally, it becomes impossible to tell the difference

between a strictly defined S_N2 reaction and an S_N1 reaction where Y is

present. This is an example of what Langford and Gray call "accidental

bimolecularity".

FIGURE 13
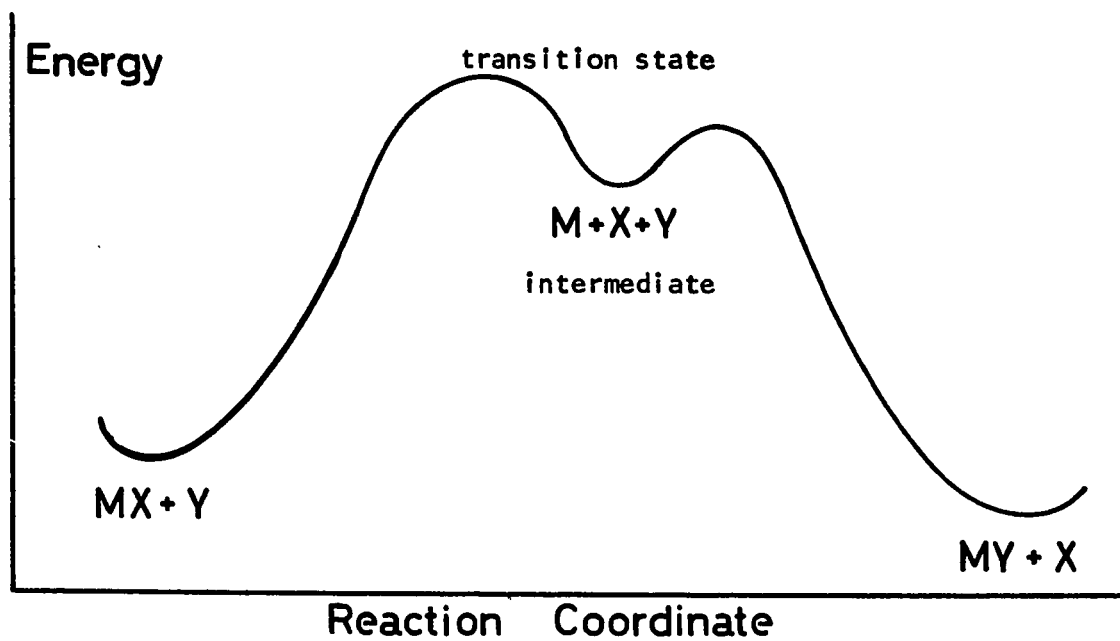
Reaction coordinate diagram for an $S_{N}1$ process

FIGURE 14
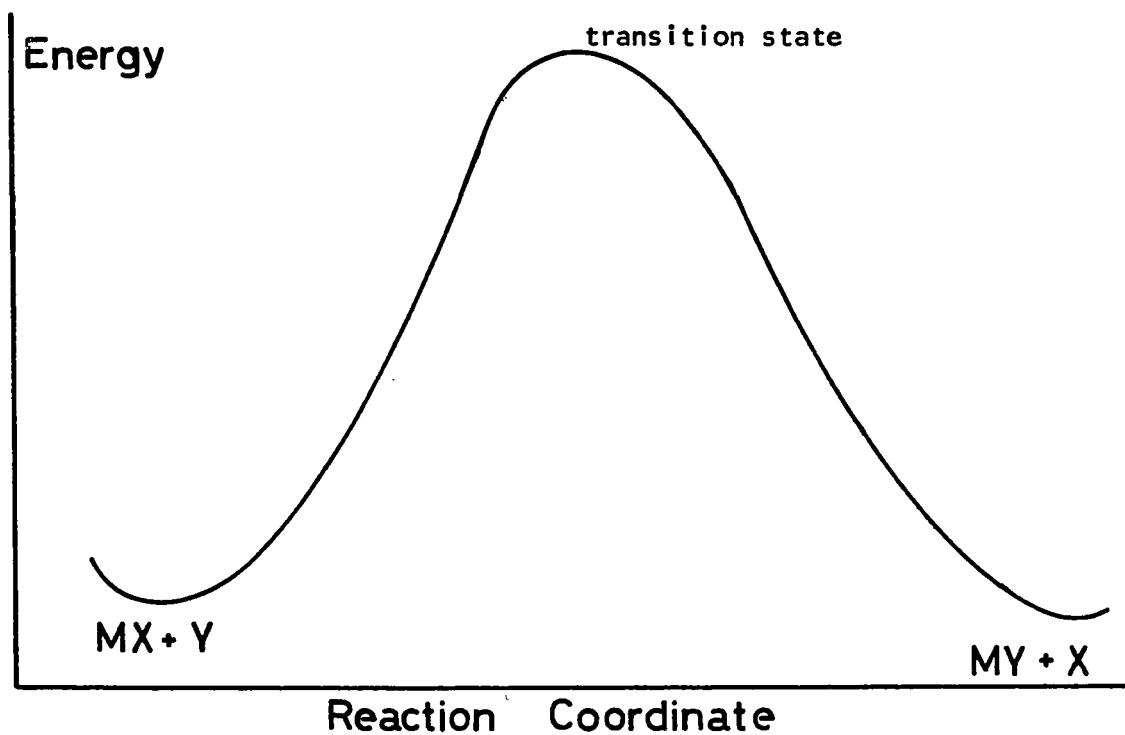
Reaction coordinate diagram for an interchange
(concerted) process

Basolo and Pearson[11] have presented a revised scheme for classification of nucleophilic substitution reactions into four classes. An $S_{N}1$ (limiting) mechanism is one in which definite evidence for the existence of an intermediate of reduced coordination number can be found. An $S_{N}1$ mechanism will designate one in which evidence for a lower coordination number intermediate cannot be presented but which otherwise satisfies the requirements of a dissociation mechanism, while failing the requirements of a displacement (association) mechanism. That is, the rate determining step involves only bond breaking of the M-X bond whether Y is present or not. An $S_{N}2$ mechanism requires that the rate determining step involves about equal bond breaking in M-X and bond making Y-M. On the other hand, $S_{N}2$ (limiting) is best described as the rate determining step involving only bond making as in Y-M. This classification scheme is summarized schematically in Table 12.

Langford and Gray[72] have also developed a useful nomenclature for a comprehensive discussion of ligand substitutions. They divided the study of reaction rate processes into two distinct phases. The sequence of elementary steps by which a complicated overall reaction is accomplished, is labelled the stoichiometric mechanism, but the rearrangements of atoms and bonds in terms of the magnitude of the rate constants for the individual steps is considered the intimate mechanism.

In this scheme three possible simple pathways for a substitution reaction are "stoichiometrically" distinct. A dissociative path (D) is defined in which the leaving ligand is lost in the first step, producing an intermediate of reduced coordination number as given by reaction {5} (*cf.* {3}).

$$MX_{n} \underset{+X}{\overset{-X}{\rightleftharpoons}} MX_{n-1} \underset{-Y}{\overset{+Y}{\rightleftharpoons}} MX_{n-1}Y \qquad (D) \ \{5\}$$
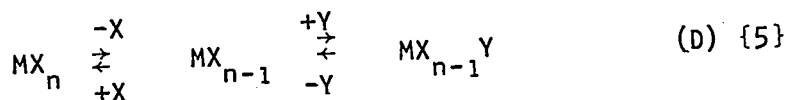
TABLE 12

CLASSIFICATION OF NUCLEOPHILIC SUBSTITUTION REACTIONS[a]

$S_{N}1$ (lim)	$S_{N}1$	$S_{N}2$	$S_{N}2$ (lim)
degree of bond breaking in rate step			
large	large	appreciable	none
degree of bond making in rate step			
none	none to small	appreciable	large
evidence for intermediate of reduced coordination			
definite	none	none	none
evidence for intermediate of expanded coordination			
none	none	indefinite	definite

a) Reference 11, page 128

An associative path (A) is defined as one in which the entering ligand
is added in the first step, producing an intermediate of increased
coordination number. This is shown in reaction {6} (*cf.* {2}).

$$MX_n \quad \underset{-Y}{\overset{+Y}{\rightleftarrows}} \quad MX_nY \quad \underset{+X}{\overset{-X}{\rightleftarrows}} \quad MX_{n-1}Y \qquad (A) \quad \{6\}$$
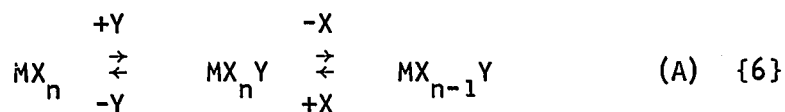
The third path defined is a concerted or interchange path (I) in which
exchange of positions between ligands in the first and second coordination
spheres takes place. The limiting characteristic of the interchange
process is the absence of an intermediate in which the primary
coordination number of the metal is modified. That is, there is no
kinetically detectable intermediate. The interchange path is shown in
reaction {7}

$$MX_n \; \text{---} \; Y \quad \overset{\rightarrow}{\rightleftarrows} \quad MX_{n-1}Y \; \text{---} \; X \qquad (I) \; \{7\}$$
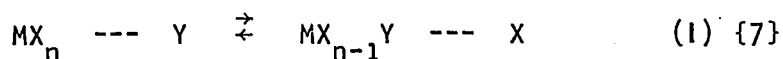
and the reaction coordinate diagram is shown in Figure 14. The lack
of a shallow minimum in the reaction coordinate diagram is significant
because it implies that the interchange substitution takes place
smoothly in a single step. However, this implies nothing about the
coordination number of the activated complex which is at the maximum
on any reaction coordinate diagram.

In the classification of the intimate mechanism of substitution,
a distinction is made between those reactions whose activation energy is
affected by the entering group and those reactions whose activation energy
is determined by the requirements of dissociation. If the activation
energy is determined by the entering group then the intimate mechanism
is associative activation (a) and conversely if the activation energy is
determined by the leaving group, the intimate mechanism is dissociative
activation (d). As a consequence of the intimate mechanism the interchange

process may take place by either associative activation or dissociative activation, in which case the interchange is designated I_a or I_d respectively.

There are now a total of four mechanisms which may be used for the characterization of ligand substitutions, namely, A, I_a, I_d, and D. These present mechanistic designations may be correlated with those on the Hughes-Ingold scheme or the revised version of Basolo and Pearson. The A mechanism of ligand substitution would be labelled S_{N2} (lim). It is a process in which the rate determining step is bimolecular. The D mechanism has a unimolecular rate determining step with an intermediate of reduced coordination and corresponds to the S_{N1} (lim) process. The I_a case corresponds to the S_{N2} (not lim) mechanism. The I_d mechanism depends on the leaving group as an important aspect of activation but has no available evidence for an intermediate of reduced coordination. The process termed I_d is essentially S_{N1} even in cases of "accidental bimolecularity" which some regard as S_{N2}. In this thesis the four mechanisms (A, I_a, I_d, and D) will be considered sufficient for the characterization of ligand substitutions. Table 13 summarizes the correlation between the different nomenclatures.

Even though the distinction among mechanisms is straightforward conceptually, Basolo and Pearson have pointed out that no matter how much evidence can be provided in defense of a particular reaction mechanism, this evidence can never be said to prove it. This is because reaction mechanisms are essentially theories and as such are not entirely capable of proof. With this in mind then, it is the intent in the next section to discuss certain preferred mechanisms with respect to the data at hand.

TABLE 13

Correlation and Classification of Ligand Substitution Mechanisms

STOICHIOMETRIC MECHANISM

INTIMATE MECHANISM	INTERMEDIATE OF INCREASED COORDINATION NUMBER	INTERCHANGE PROCESS	INTERMEDIATE OF REDUCED COORDINATION NUMBER
ASSOCIATIVE ACTIVATION (a)	A S_N2 (lim)	I_a S_N2	
DISSOCIATIVE ACTIVATION (d)		I_d S_N1	D S_N1 (lim)

DISCUSSION

The discussion which follows is essentially divided into two parts. The first part emphasizes individually each of the complexes studied and their exchange rates. The second section recognizes the individual complexes as members of a series; the effect of overall charge is evaluated; the kinetic *trans*-effect series is established; the relative exchange rates and activation parameters are compared; and suitable models for these observations are proposed.

A. The Individual Complexes

Aquopentaamminechromium(III) Ion

The values of the rate constants and activation parameters obtained experimentally for this cation (see Table 5) agree very well with those recently reported by Swaddle and Stranks[5] which are considered to be more precise than those published by Duffy and Earley[67] previously.

In one study[67] it was found that an increase in pH (1-3) increased the water exchange rate considerably but did not affect the rate of anation. This fact might be consistent with conjugate base formation which causes a *trans* labilization of the water ligand, although it has been shown[48] to be due to carbon dioxide catalysis. Changes in

69

ionic strength (0.1 $\underline{M}$ - 1.7 $\underline{M}$) did not affect the rate of water exchange, nor did the presence of chloride or isothiocyanate ion.

The excellent agreement between the results of this study and those of Swaddle and Stranks[5] under slightly different conditions strengthens the validity of the methods used throughout this study.

cis-Diaquotetraamminechromium(III) Ion

By comparing the rate constants of exchange for the *cis*-diaquotetraamminechromium(III) ion and the aquopentaamminechromium(III) ion that were determined in this study (Table 6 and interpolation of data in Table 5), *ca.* 6.2 x 10^{-5} sec^{-1} and 6.0 x 10^{-5} sec^{-1} respectively at 25°C, it is obvious that the complexes are closely related. It would be anticipated that the observed rate of water exchange for the two systems, both with water ligands *trans* to ammonia, would not be very different unless the presence of the second water in the *cis*-diaquo- ion somehow influenced the behaviour of the first water. This is especially reasonable since $Co(NH_3)_5OH_2^{3+}$, *cis*-$Co(en)_2(OH_2)_2^{3+}$, and *trans*-$Co(en)_2NH_3OH_2^{3+}$ all exchange water at a similar rate (see Table 1).

The small difference in the rates of water exchange in the two chromium(III) complexes cited above might be considered to be due to *cis*-effects, although Bracken[3] argued convincingly against such effects in acidopentaaquochromium(III) cations.

An eight-fold increase in acid concentration at constant ionic strength did not affect the rate of water turnover in the *cis*-diaquo- cation, thus ruling out any conjugate base catalysis of the water exchange under the conditions used.

trans-Diaquotetraamminechromium(III) Ion

In this study it was found that the rate of water exchange of the *trans*-diaquotetraamminechromium(III) ion is about four times slower than that of its *cis* analogue (*cf*. Tables 6 and 7). It might therefore be argued that the *trans* labilization of water on water is less than that of ammonia on water.

The water exchange rate of the hexaaquochromium(III) ion is very slow (*ca*. 4.3×10^{-7} sec^{-1} at 25°C) relative to other chromium(III) complexes as shown in Table 1. Hexaaquochromium(III) ion may be regarded as consisting of three *trans* water pairs. A brief examination of Table 1 (page 2) shows that in general, *trans* water pairs exchange slowly.

The water exchange rate of the *trans*-diaquotetraamminechromium(III) ion decreased on increasing the acid concentration as shown in Table 7. It is generally known that waters *trans* to one another in many chromium(III) complexes exhibit a rather low pk$_a$ as compared to water ligands *cis* to one another or water ligands *trans* to other ligands in similar complexes[69]. For example, the pk$_a$ of the *cis*-diaquotetraamminechromium(III) ion, whose rate is not affected by an increase in acid concentration, is 5.1 and that of the *trans* isomer, 4.2.

A consequence of the greater acidity of the *trans* complex could be the formation of some *trans*-hydroxyaquotetraamminechromium(III) species, especially in media of low acid concentration. The *trans* labilization of hydroxyl ligand on water has been reported by Krause and Taube[41] in cobalt(III) complexes. By comparing the water exchange of *trans*-diaquobis(ethylenediamine)cobalt(III) ion with the water exchange of a mixture of 80% *trans*-diaquobis(ethylenediamine)cobalt(III) ion and 20% *trans*-hydroxyaquobis(ethylenediamine)cobalt(III) ion, whose rates of exchange are 1.1×10^{-6} sec^{-1} and 25×10^{-6} sec^{-1} at 25°C, respectively, the *trans* labilizing influence of hydroxyl ligand is easily appreciated.

Thus, the observed increase in rate of water exchange of the *trans*-diaquotetraamminechromium(III) ion in the media of decreased acid strength can probably be attributed to hydroxyl labilization of the *trans* water. This formation of the conjugate base is the same process as proposed earlier for the effect of increased pH on the rate of exchange in the aquopentaamminechromium(III) ion.

The rate of water exchange for *cis*-$Cr(NH_3)_4OH_2Cl^{2+}$ was found to be *ca.* 5.1×10^{-5} sec^{-1} at 25°C and independent of acid concentration (see Table 8), and that for $Cr(NH_3)_5OH_2^{3+}$, *ca.* 5.2×10^{-5} sec^{-1} at 25°C.

It is tempting to regard the effect of lowering the overall charge of the cation as enhancing the rate of water exchange, since the neutral but dipolar water is held to a less positive cation offering less electrostatic attraction. The ratio of aquation rate constants for the unipositive ion, *cis*-$Co(en)_2Cl_2^+$, and the dipositive ion, *cis*-$Co(en)_2NH_3Cl^{2+}$ was found[74] to be approximately 540, which indicates that the lower the overall charge on the complex, the faster the rate

of aquation. In aquation the reaction involves removal of a negative ligand from a positively charged complex, whereas in this study of water exchange, a neutral ligand is being removed from a positive species. The effect of charge on the exchange rate should therefore be less.

The results of this research show that the structurally similar cations, *cis*-chloroaquotetraamminechromium(III) and aquopentaamminechromium(III), of different overall charge exchange their aquo ligand with solvent at essentially the same rate. This cannot be reconciled with the above argument. It appears, as was noted in cobalt(II) and nickel(II) systems[7,34], that the magnitude of the overall charge of a complex gives no simple general correlation to its water exchange rate. It is clear, that one should be cautious when comparing the exchange rates of systems with different substituents and different overall charges because it is not empirically certain how much these effects alter the exchange rates.

trans-Chloroaquotetraamminechromium(III) Ion

As can be seen from Table 9, the rate of water exchange for the *trans*-chloroaquo- ion is essentially independent of acid concentration over the range of 0.025 $\underline{M}$ to 0.350 $\underline{M}$ in perchloric acid. The exchange rate of this complex is only slightly lower than that of its *cis* analogue. This rate difference is probably due to the small difference in the enthalpy of activation for the two complexes, as shown in Table 10, rather than to an entropy effect.

The comparison of the *cis* and *trans* isomers of chloroaquo-tetraamminechromium(III) ion also indicates that the *trans* labilizing influence of ammonia is slightly greater than that of chloride ligand. The rate of water exchange of the *trans*-chloroaquotetraamminechromium(III) ion is similar to that of the water *trans* to the chloride ligand in chloro-pentaaquochromium(III) ion[3,6], *ca.* 4.5×10^{-5} sec^{-1} and 3.5×10^{-5} sec^{-1} respectively, at 25°C. This interesting similarity will be dealt with in more detail later.

B. The Complexes as a Series

The Effect of Overall Charge

Bracken[3] originally proposed that the observed increase of the rate of water exchange of *trans* water pairs as the charge decreases in the series,

$$Cr(OH_2)_6^{3+} \quad < \quad Cr(OH_2)_5X^{2+} \quad < \quad \text{trans-}Cr(OH_2)_4Cl_2^{+}$$
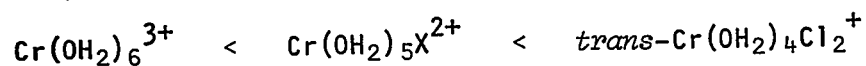
(X = Cl$^-$, Br$^-$, and NCS$^-$), was due to a charge effect. Keen[6] on the other hand, attempted to relate the observed increase of the rate of water exchange, not to a charge effect, but rather to a decrease in the crystal field stabilization energy, C.F.S.E., of the complexes in this series. That is, the trend appears to follow the spectrochemical series. Although when using limited data the trend can be seen to fit such a scheme, when additional data is considered (see Table 16, page 96) one realizes that the original supposition is, at best, fortuitous.

It is clear, that the C.F.S.E. is but a small part of the total bonding energy in a transition metal complex. The crystal field stabilization energy has been useful quantitatively when used as a correction term. The observed hydration energies of the di- and tri-valent cations of the first row transition metal series have been shown to lie on an irregular curve. However, when these experimental values are corrected using crystal field terms they all lie on a smooth curve. Also using crystal field arguments, the preferential bonding of some transition metal cations to nitrogen rather than to oxygen can be explained, since nitrogen bonding ligands such as ammonia have a greater C.F.S.E. than oxygen bonding ligands such as water. Unfortunately, when this concept is applied to chromium the argument fails due to the oft noted greater tendency of Cr(III) to form metal oxygen bonds in place of metal nitrogen bonds.

The obvious explanation for this observed trend in the exchange rates would be that a charge effect is operating. As the charge on the central metal decreases, the rate of reaction, and hence the water exchange rate, increases. Unfortunately, this electrostatic approach fails, as was noted in the previous section, in the case of the dipositive *cis*-chloroaquotetraamminechromium(III) ion which exchanges ligand water at the same rate as does the tripositive aquopentaamminechromium(III) ion. The rate constant for the water exchange of the tripositive *trans*-diaquotetraamminechromium(III) ion which also contains a *trans* water pair, does not correlate with this series on the basis of either charge or C.F.S.E. considerations. On the basis of its rate of water exchange the *trans*-diaquo- ion would be positioned in this series

as, $Cr(OH_2)_6^{3+}$ < $Cr(OH_2)_5X^{2+}$ < $trans\text{-}Cr(NH_3)_4(OH_2)_2^{3+}$ <

$trans\text{-}Cr(OH_2)_4Cl_2^+$, where X is the same as before. If a charge effect

were operating it would be expected that the $trans$-diaquo- ion would

exchange at a rate similar to that for the hexaaquochromium(III) ion,

but the present research shows that this is not the case. If a decrease

in the C.F.S.E. were causing the rate of water exchange to increase,

then it would be anticipated that the water exchange of both the $trans$-

diaquotetraamminechromium(III) ion and the $trans$-chloroaquotetraammine-

chromium(III) ion would be much slower than that for the hexaaquochromium(III)

ion rather than much faster as was discovered in this research.

Thus, the reason why the rate of water exchange increases as

one advances along the series $Cr(OH_2)_6^{3+}$, $Cr(OH_2)_5X^{2+}$ (X = Cl⁻, Br⁻, and

NCS⁻), and $trans\text{-}Cr(OH_2)_4Cl_2^+$, remains a moot question.

The $trans$-Effect Series

From Tables 5-9 it can be seen that this research shows that

the rate of water exchange decreases along the series $Cr(NH_3)_5OH_2^{3+}$ >

$trans\text{-}Cr(NH_3)_4OH_2Cl^{2+}$ > $trans\text{-}Cr(NH_3)_4(OH_2)_2^{3+}$. The magnitude of

the kinetic $trans$-effect of the various ligands on the rate of water

exchange can be given as the ratio of the water exchange rate constants

(at 25°C), where the $trans$-effect of water on water in $trans$-diaquotetraa-

mminechromium(III) ion is taken arbitrarily as unity, as

$$4 : 3 : 1 \quad \text{for} \quad NH_3 : Cl^- : OH_2.$$
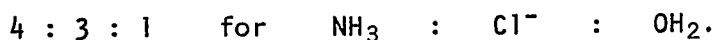
The order of decreasing labilization of ligand water by *trans* ligand

influence from this study is therefore given as

$$NH_3 \gtreqless Cl^- > OH_2.$$
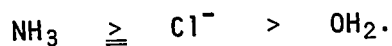
Bracken[3] gave the kinetic *trans*-effect series for acidopentaaquochromium(III)

species as

$$I^- > Br^- > Cl^- > NCS^- > OH_2.$$
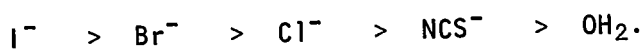
By combining the water exchange data from this research with that of

other workers, it is found that for chromium(III) the kinetic *trans*-effect

series in decreasing order is

$$I^- > Br^- > NH_3 \gtreqless Cl^- > NCS^- > OH_2.$$
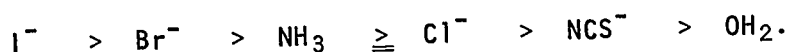
It is interesting that the kinetic *trans*-effect series of both Cr(III)

and Rh(III) (see Introduction), especially with respect to the position

of ammonia, appear to be identical as far as data permit.

The *trans*-effect[76] is the term applied to the empirical

phenomenon wherein a coordinated group in a square planar or octahedral

metal complex affects the rate of substitution reactions of ligands

opposite to it. The concept of the *trans*-effect was first introduced

by Chernayev in 1926[77]. Many accounts of this phenomenon have recently

been described[30-33].

Since *trans* interactions are manifested in ways other than

substitution rates, *viz.* bond strength and bond length[78], the more

comprehensive term *trans*-influence was defined[79]. The *trans*-influence

may be considered as the extent to which a ligand weakens the bond *trans*

to itself in the equilibrium state of a complex.

The order of decreasing *trans*-influence of the halogens in

chromium(III) and rhodium(III) complexes has been shown to be

$$I^- > Br^- > Cl^- > OH_2,$$
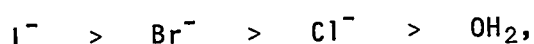
which parallels the nephelauxetic series. It is therefore tempting to relate the *trans* labilizing influence of the ligands to their polariza- bility. The ligands in this series are also in the order of their capacity to cause d-orbital splittings, or in the order of the spectro- chemical series. The correct position of NCS⁻ in this series and the nephelauxetic series but not in the spectrochemical series, does lend support to the polarizability concept.

To date, the electrostatic polarization theory[80] most simply explains qualitatively the *trans*-influence in octahedral metal complexes. The primary charge on the central metal ion induces a dipole on the ligands, which in turn induces a dipole in the central metal ion. If there is a *trans* pair of ligands, X and Y, and Y is more polarizable than X, then the orientation of this second and now negative dipole is such that it repels negative charge in group X. Hence, the attraction of X for the metal is reduced and the M-X bond is lengthened and weakened. There is considerable experimental support for this bond weakening hypothesis. It is clear that metal water bond weakening will lead to an increase in the rate of water exchange reactions.

Chatt *et al.*[81] and Orgel[82] independently proposed a π-bonding stabilization of the activated complex to account for a *trans*-effect. This approach was successful in explaining the *trans*-influence of covalent π-bonding ligands.

The most recent approach to the *trans*-influence in transition metal complexes comes from molecular orbital theory[83] (ligand field theory) which emphasizes the importance of σ-metal-ligand orbital overlap. According to this theory the *trans* ligand, Y, and the leaving ligand, X, must share the same σ-orbital in the overall molecular orbital arrangement.

It follows that a strong σ-bonding ligand, Y, will overlap with the larger share of the bonding σ-molecular orbital, leaving a much smaller share for X. Thus, as was the case in the electrostatic polarization model, the M-X bond will be weakened. Langford[84] has shown that empirical measures of σ-bonding in $Cr(NH_3)_5X^{n+}$ ($X = I^-$, Br^-, Cl^-, F^-, NCS^-, and NH_3 and $n = 2$ or 3), $Cr(OH_2)_5X^{n+}$ ($X = I^-$, Br^-, Cl^-, F^-, N_3^-, and NH_3 and $n = 2$ or 3), and $Co(NH_3)_5X^{n+}$ ($X = I^-$, Br^-, Cl^-, F^-, NCS^-, N_3^-, and NH_3 and $n = 2$ or 3) correlate with lability in X, in a sense indicating that the relative reactivity is controlled by the variation of ligand-metal σ-orbital interaction.

Interestingly, none of the theories mentioned above accounts for the position of ammonia in the kinetic *trans*-effect series for either Rh(III) or Cr(III).

The Mechanism of Water Exchange

From the sign of the entropy of activation one is tempted to assign either a dissociative or an associative mechanism for the water exchange process. A positive activation entropy is considered indicative of a dissociative mechanism, while a negative one indicates an associative mechanism of water exchange.

From the relative values of the enthalpy and the entropy of activation found in this study (see Table 10) it is apparent that the water exchange process probably proceeds via the same mechanism for all four of the aquotetraamminechromium(III) complexes. Evidently the differences in the rates of water exchange are due to the differences

in the activation enthalpies of the complexes. The increase in the rates of water exchange of this series of aquotetraamminechromium(III) complexes parallels the decrease in their activation enthalpies while the activation entropies remain essentially constant and approximately zero.

The work of Bracken[3] and Keen[6] leads one to believe that the labilizing influence of the ligand *trans* to the exchanging water may dictate whether the mechanism is relatively more associative or dissociative in character. Stranks[75] has pointed out that it may be unreasonable to stress one mechanism in preference to the other when the water molecules in the second coordination sphere are at distances approaching those of chemical bonding.

The study of the water exchange process for $Co(NH_3)_5OH_2{}^{3+}$ by Hunt and Taube[1] was the first complete detailed study of water exchange in an inert octahedral complex. Not only were the enthalpy and entropy of activation obtained, but a study of water exchange as a function of pressure provided a measure of the volume of activation, ΔV^*. This ΔV^* represents the difference between the molal volumes of the initial and activated complexes. Their observation that ΔV^* was independent of pressure for this cation has great mechanistic significance.

Stranks and Swaddle[28] have also commented on the magnitude and sign of ΔV^*. The volume decrease due to the partial formation of an aquo-metal bond in the transition state of an I_a process, may be offset by a volume increase due to concomitant stretching of the bond to the ligand being replaced so that the contribution of bond making and breaking to ΔV^* could be zero or even positive. Thus in a water exchange experiment, a small positive ΔV^* is not necessarily indicative of a dissociative mechanism, but a negative ΔV^* is strong evidence for an associative process.

The fact that ΔV^* for the process

$$Co(NH_3)_5{}^{18}OH_2{}^{3+} + OH_2 \overset{\rightarrow}{\leftarrow} Co(NH_3)_5OH_2{}^{3+} + {}^{18}OH_2 \qquad \{8\}$$

is $+1.2$ cm^3 mol^{-1} and pressure independent, supports a dissociatively activated exchange process. Since other workers[17,72,85] have found that replacement of coordinated water in aquopentaamminecobalt(III) ion seems to proceed by a dissociative interchange (I_d) mechanism, and for water exchange no direct evidence for the existence of a five coordinate intermediate has been found, then the water exchange mechanism for this cation as given in process $\{8\}$ is best described as I_d.

In principle, ΔV^* data can serve to distinguish between various alternative mechanistic models, since volume requirements of these can usually be readily visualized. In water exchange reactions there are no changes in formal charges involved, the entering and leaving groups are identical and there is no net chemical reaction. Therefore many complicated contributions to ΔV^* are eliminated.

Since the activated complex must either transiently gain a water molecule from the solvent (seven coordination) or transiently lose a water molecule to the bulk solvent (five coordination) before an interchange can be initiated, the activation volume may essentially be regarded as the difference in volume between a water molecule bound in the first coordination sphere and a water molecule in the bulk solvent. That is,

$$\Delta V^* = V_{bound} - V_{solvent}.$$

Hunt and Taube[1] point out that the volume of coordinated water (V_{bound}) is almost pressure independent compared to the great compressibility of solvent water $(V_{solvent})$. Thus, if ΔV^* is pressure dependent, it would imply a water exchange process which involves an

equilibrium between solvent water and coordinated water such as that required for an associatively activated exchange. On the other hand, the pressure independence of ΔV^* would imply that only bound water is involved, indicative of a dissociatively activated process.

In principle, the magnitude of values of the pressure dependence of the volume of activation, $(\partial \Delta V^*/\partial \Delta P)_T$, for solvent exchange processes can be used to distinguish I_a from A mechanisms[28], depending upon whether the observed values are, respectively, much less than or comparable with the mean molar compressibility of water ($ca.$ 7 X 10^{-4} cm^3 $bar^{-1}mol^{-1}$).

In a fashion similar to that used for the volume of activation, the significance of the measure of the activation entropy to the exchange mechanism can be demonstrated.

If a solvent water molecule becomes bound to the complex ion to form a seven coordinate species in the transition state, as in associative activation, a negative entropy of activation is implied because the water molecule loses freedom of movement in the activation process. This proposal is verified if one accepts the reasonably correct values for the entropies of bound water and solvent water (9.4 cal deg^{-1} mol^{-1} and 16.7 cal deg^{-1} mol^{-1}, respectively)[86] from which the formation entropy of such an activated complex is calculated to be -7.3 cal deg^{-1} mol^{-1}. Conversely, for the complete fissure of the bond between a water ligand and the metal in the activated complex, as with a process of dissociative activation, ΔS^* would be +7.3 cal deg^{-1} mol^{-1}. Although the calculation at best is approximate, it does indicate the direction and magnitude of the entropy associated with such activations.

This argument can be shown to be qualitatively correct when applied to the aquopentaamminecobalt(III) complex. Previously it has been shown that this cation exchanges water by an I_d mechanism. The experimental value of the entropy of activation for the aquopentaamminecobalt(III) cation was found to be +6.7 cal deg^{-1} mol^{-1} which is consistent with an I_d exchange mechanism. Consequently, a positive entropy of activation is supported by a mechanism of dissociative activation.

The values of ΔS^* of the aquotetraamminechromium(III) cations studied in this thesis are all approximately equal to zero. The mechanistic significance of a zero activation entropy will be discussed later.

Table 14 lists the values of the activation parameters for the water exchange process of several complexes.

Monacelli[2,87] has shown that water replacement in the aquopentaamminerhodium(III) cation behaves differently than that in the cobalt analogue. The rate of anation for the rhodium(III) species is generally faster than the water exchange reaction (see Table 15). This behaviour[2,87,88] has been considered indicative of nucleophilic participation of the incoming ligand in the transition state. This proposal was supported by the fact that the activation entropy for water exchange was calculated as -0.65 cal deg^{-1} mol^{-1} [89].

It has also been argued that the lowering of the activation enthalpy on going from Co(III) to Rh(III) favours a more associative process for Rh(III) water exchange. From the pressure dependent water exchange studies of Swaddle and Stranks[5] it appears that the aquopentaamminerhodium(III) ion solvent exchange reaction is still somewhat unresolved. Evidence was found that indicated I_a and I_d mechanisms were operating

TABLE 14

Activation parameters for water exchange of some transition metal complexes

Complex	ΔH^* kcal mol^{-1}	ΔS^* cal deg^{-1} mol^{-1}	ΔV^* cm^3 mol^{-1}	Reference
$Cr(OH_2)_6^{3+}$	26.2 ± 0.3	$+0.3 \pm 1.0$	-9.3 ± 0.3	28
$Cr(NH_3)_5OH_2^{3+}$	23.2 ± 0.5	0.0 ± 1.6	-5.8 ± 0.2	5
$Co(NH_3)_5OH_2^{3+}$	26.6 ± 0.3	$+6.7 \pm 1.0$	$+1.2 \pm 0.2$	1
$Rh(NH_3)_5OH_2^{3+}$	24.6 ± 0.3	$+0.8 \pm 1.1$	-4.1 ± 0.4	5
$Ir(NH_3)_5OH_2^{3+}$	28.2 ± 0.2	$+3.0$		4
$t\text{-}Cr(OH_2)_5Cl^{2+}$	26 ± 4	$+9 \pm 5$		3
	27.7 ± 0.2	$+14 \pm 2$		6[a]
$c\text{-}Cr(OH_2)_5Cl^{2+}$	25.1 ± 0.7	$+0.2 \pm 3.5$		3
	25.8 ± 0.3	$+2 \pm 3$		6[a]
$t\text{-}Cr(OH_2)_5Br^{2+}$	29.6 ± 4.5	$+16 \pm 6$		6
$c\text{-}Cr(OH_2)_5Br^{2+}$	24.8 ± 0.7	-1 ± 3		6

TABLE 14 continued

Complex	ΔH^* kcal mol^{-1}	ΔS^* cal deg^{-1} mol^{-1}	ΔV^* cm^3 mol^{-1}	Reference
t-Cr(OH$_2$)$_5$NCS^{2+}	30.2 ± 2.3	+22 ± 5		3
	29 ± 4	+15 ± 6		6[a]
c-Cr(OH$_2$)$_5$NCS^{2+}	24.2 ± 2	- 1 ± 4		3
	24.9 ± 1.0	- 0.3 ± 2.4		6[a]
$trans$-Cr(OH$_2$)$_4$Cl$_2^+$	23.2 ± 0.5	+ 1.8 ± 1.6		6

a) data of reference 3 recalculated in reference 6

Note: t refers to the water ligand *trans* to the acido ligand

c refers to the water ligand *cis* to the acido ligand

TABLE 15

Ratio of anation[a] rate constants and water exchange
rate constants (k_{an}/k_{ex}) for some complexes

Complex	k_{an}/k_{ex}	Reference
$Cr(OH_2)_6^{3+}$	0.01	14, 102[b]
$Cr(NH_3)_5OH_2^{3+}$	0.04	67
$Co(NH_3)_5OH_2^{3+}$	0.2	92, 94
$Rh(NH_3)_5OH_2^{3+}$	2.2	2, 103
$Ir(NH_3)_5OH_2^{3+}$	3	4

a)   anation by chloride ion
b)   anation by bromide ion

competitively, the former predominating at high and the latter at low pressures.

Harris and co-workers[90,91] studied the chloride anation of hexaaquorhodium(III) ion and chloropentaaquorhodium(III) ion in aqueous solution and found the data were compatible with a five coordinate intermediate type mechanism (D) rather than an ion pair interchange (I_d) mechanism. A five coordinate intermediate of square pyramidal geometry was proposed.

Monacelli and Borghi[87] extended both the water exchange and anation studies to the aquopentaammineiridium(III) cation in order to investigate the existence of a trend in the changing behaviour along the series of aquopentaammine complexes of Co(III), Rh(III), and Ir(III). The activation parameters found for iridium(III) did not follow the trend expected by the extension of the results obtained with the cobalt and rhodium complexes (*cf.* Tables 14 and 15). The fact that the activation entropy for the water exchange of aquopentaammineiridium(III) ion is +3 cal deg^{-1} mol^{-1} indicates a decrease of associative character with respect to the exchange reaction of the rhodium(III) analogue. Monacelli had supposed the converse would be true, considering the results obtained with the cobalt and rhodium complexes. His supposition was not unreasonable, since the increased importance of the associative mechanism as one descends a periodic group should be enhanced because of the tendency of the larger central metal ion to engage in covalent bonding with the incoming nucleophile, and to the reduced steric hindrance to the entry of the seventh ligand.

It has been suggested that the comparison between water exchange rate constants and first order anation rate constants (Table 15) may give

indications of bond formation between the metal and the entering anion[87,88,92]. Complex formation is believed to proceed via the rapid pre-formation of an outer sphere complex, followed by a slower interchange reaction in which the new ligand replaces the solvent ligand in the first coordination sphere. Generally, this interchange reaction has been found to be independent of the nature of the incoming ligand[92,93] and a dissociative mechanism is therefore thought to be operating[11], $i.e.$, bond breaking preceeds bond making. Aquopentaamminecobalt(III) cation, for instance, exchanges its coordinated water with anionic ligands at a rate which is never higher than that of water exchange and is generally a constant fraction (0.2) of the latter. Langford and Muir[92] interpreted this fact as a criterion of the I_d mechanism by which cobalt(III) substitutions have been considered to take place[17,85,94]. The fact that the rate of anation was less than the rate of water exchange was related to a statistical factor connected with the probability that the anion is not always in a suitable position to enter immediately into the inner sphere when the water ligand leaves, and another water molecule enters instead. The rate of anation of $Co(NH_3)_5OH_2^{3+}$ by azide ion is equal to its rate of water exchange[94]. This fact was accounted for by the superior ion pairing ability of the azide ion.

In cases where the substitution of the coordinated water by anions becomes faster than the concomitant water exchange, the mechanism might be considered indicative of associative interchange $(I_a)^2$. Poë et $al.$[89] studied the anation reaction of $Rh(NH_3)_5OH_2^{3+}$ and postulated that the process proceeds by a rapid pre-formation of an ion-pair[95] followed by a slow interchange reaction. The ten-fold enhancement of

the ratio of the rate of anation to the rate of water exchange, (k_{an}/k_{ex}), of the aquopentaamminerhodium(III) ion over the analogous cobalt complex was ascribed to the greater ability of the rhodium complex to form ion pairs. The fact that the rate of anation exceeds the rate of water exchange implies that the interaction of the nucleophile assists in the loss of coordinated water. The mechanism of the loss of coordinated water in this case must be considered one of associative activation hence, I_a.

Monacelli[2] found that anation by chloride was about three times faster than the water exchange of the aquopentaammineiridium(III) ion under certain conditions. This fact was interpreted as confirming the tendency of this cation to react by an associative pattern, although it was cautioned that this did not entirely preclude a dissociative mechanism especially when ΔS^* for the water exchange process was found to be +3 cal deg^{-1} mol^{-1}.

The results of Duffy and Earley[67] showed that for water exchange of aquopentaamminechromium(III) ion, the activation entropy was -4 cal deg^{-1} mol^{-1}. It was also found that the ratio of rates of anation to water exchange for this cation was of the order of 0.04. These facts were used to interpret the mechanism as a rate limiting loss of coordinated water followed by the collapse of the solvation shell to fill the vacancy created. The reliability of this work was suspect, however. Owing to the uncertainty of the ΔH^* value of this reaction, Monacelli calculated that ΔS^* may actually range from -17 to +9 cal deg^{-1} mol^{-1}. It was this uncertainty in the chromium(III) pentaammine system which prompted further study by the author.

Results from the present research show that ΔS^* is approximately zero and recent results by other workers[5] confirm this. Present findings of the magnitudes of ΔS^* and ΔV^* indicate that the water exchange process of the aquopentaamminechromium(III) ion proceeds by an associatively activated mechanism which can be considered I_a on the basis of the magnitude of the pressure dependence of ΔV^* (see Table 14).

The small value of k_{an}/k_{ex} does not necessarily contradict the prediction of an I_a mechanism for the water exchange process of the aquopentaamminechromium(III) ion because Thusius[14] pointed out, that the "abnormally" small ratio of anation to water exchange rates may be thought of as reflecting the feeble thermodynamic stability of the chromium(III) cation.

Stranks and Swaddle[28] found the volume of activation of reaction {9} to be -9.3 cm^3 mol^{-1}. Using this fact and the pressure

$$Cr(OH_2)_6^{3+} + {}^{18}OH_2 \rightleftharpoons Cr(OH_2)_5{}^{18}OH_2^{3+} + OH_2 \qquad \{9\}$$

dependence of ΔV^* as well as the value of ΔS^* (see Table 14), the process was described as being I_a and represented by reaction {10}.

$$[\{Cr(OH_2)_6\}(OH_2)_x]^{3+} \rightleftharpoons [\{Cr(OH_2)_7\}(OH_2)_{x-1}]^{3+*} \qquad \{10\}$$
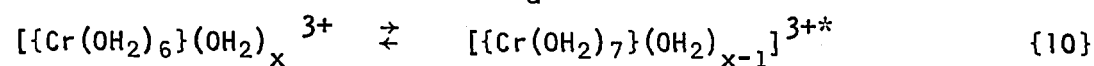
In this model, the major contributor to ΔV^* is presumably the collapse of part of the solvation sheath when one of its x water molecules is transferred to the first coordination sphere to form an activated complex of increased coordination. That is, associative bond formation precedes bond breaking for the exchange process. The near zero value of ΔS^* is consistent with an I_a process since involving only modest relocations of water molecules within an independent $[\{Cr(OH_2)_6\}(OH_2)_x]^{3+}$ entity; the transition state, $[\{Cr(OH_2)_7\}(OH_2)_{x-1}]^{3+*}$, need not be significantly more or less ordered than the initial states.

Now, the mechanistic significance of a zero entropy of activation is apparent. A zero activation entropy for water exchange indicates that the process most probably takes place by an I_a mechanism.

By this criterion, an I_a water exchange mechanism is proposed for the four complexes of the aquotetraamminechromium(III) series studied here. The entropies of activation for the exchange of water of cis- and trans-$Cr(NH_3)_4(OH_2)_2^{3+}$ and cis- and trans-$Cr(NH_3)_4OH_2Cl^{2+}$ are all approximately zero (within experimental error) which indicates the same mechanism is probably operating in each of these cations. This mechanism is proposed to be analogous to that described above for the hexaaquochromium(III) cation as given in reaction {10}.

Because of their structural similarity, it would not be anticipated that there would be any difference in the water exchange mechanisms between aquopentaamminechromium(III) and cis-diaquotetra-amminechromium(III) ions. Indeed, experimentally the systems appear to be very similar (cf. k_{ex} and ΔH^*). Since the cis-chloroaquotetra-amminechromium(III) ion is structurally similar to the aquopentaammine-chromium(III) ion, then the extension of the I_a mechanism to the cis-chloroaquo- species should not be unreasonable. In the case of the trans-diaquotetraamminechromium(III) ion, its close structural re-semblance to the hexaaquochromium(III) cation and the trans water pairs of both the acidopentaaquochromium(III) ions and the trans-dichlorotetra-aquochromium(III) ion would indicate the same I_a water exchange mechanism would be probable. This is borne out experimentally since the near zero ΔS^* value for all such complexes with trans water pairs suggests the same I_a exchange mechanism is operative. Bracken[3] has shown that changing the substituents cis to the trans water pair does not alter

the rate at which the *trans* water pairs exchange with solvent and hence should nct change the mechanism of exchange.

As pointed out previously, the experimental rate of water exchange for the *trans*-chloroaquotetraamminechromium(III) cation and the rate of exchange for the water *trans* to the chloride in the chloropentaaquochromium(III) cation are comparable considering the different media used to study the kinetics. As before, the near zero value of ΔS^* for the *trans*-diaquotetraammine species suggests that the mechanism of water exchange is one of associative activation, whereas the very positive ΔS^* value of the pentaaquo- species suggests the mechanism is one of dissociative activation (see Table 14).

It should be noted that because there is an established *trans*-effect, and because the metal oxygen bond opposite such a *trans* activating ligand does in fact weaken this bond, it does not necessarily follow that the exchange process is destined to be only one of dissociative activation. This is especially true since no evidence has been presented to show the degree of chromium oxygen bond breaking for various *trans* ligands. However, it does seem reasonable that the increased importance of the dissociative mechanism might be attributed to the tendency of the *trans* ligand to become more polarizable or in the language of Pearson, "softer"[96].

It is interesting to note that the ΔG^* values as calculated from equation [9] for *trans*-chloroaquotetraamminechromium(III) ion and chloropentaaquochromium(III) ion are identical within experimental error (*ca.* 23.5 $\pm$ 0.5 kcal mol^{-1}).

It can be shown that the different modes of activation of
these two species is probably not a result of their different solvation
structures. The chloropentaaquochromium(III) ion should have a well
structured solvation sheath because of the ability of its relatively
acidic and numerous aquo-protons to hydrogen bond solvent molecules.
On the other hand, the tetraammine with its weakly acidic ammine protons,
should form a relatively poorly structured solvation sheath. However,
by the same argument both the hexaaquochromium(III) ion, which would be
expected to have a very well structured solvation shell, and the aquo-
pentaamminechromium(III) ion, which would be expected to have a poorly
structured solvation shell, have been shown to exchange water by the
same I_a mechanism. Since the two species in question are analogous in
structure to the latter two species respectively, it is reasonable to
assume that it is not the different solvation structures that causes the
modes of activation to be different. Similarly, the different modes
of activation for *trans*-chloroaquotetraamminechromium(III) ion and
chloropentaaquochromium(III) ion are probably not due to any *cis*-effects
by the four ammonia ligands in one complex and the four water ligands
in the other on the basis of the different electro-negativities of
nitrogen and oxygen respectively. Unfortunately no explanation can be
offered for the fact that the water *trans* to chloride ligand in similar
complexes does not always exchange by the same mode of activation. The
precision of the rate constants and consequently the activation parameters
as reported by Bracken[3] for the chloropentaaquochromium(III) ion is
suspect, however. The fact that the activation parameters were based
on only three temperature dependent experiments, two of which were not
repeated, plus the lack of control of ionic strength from experiment to

experiment, make the results doubtful indeed.

In any case, the data in this thesis consistently suggest that the four aquotetraamminechromium(III) cations studied exchange ligand water by an I_a mechanism.

The concept of the electrostatic theory, which considers the central metal ion to be a sphere with its electrons symmetrically disposed over the surface, may be improved by the crystal field theory[97]. In the latter, the five d-orbitals of a transition metal are considered degenerate in the free ion, but the electrostatic field due to the presence of ligands (charged or dipolar) removes this degeneracy. In octahedral complexes for instance, the d-orbitals that coincide with ligand orbitals will be at a higher energy (because of electrostatic repulsions) than those that do not coincide. Since physical systems strive for the lowest energy configuration it is obvious that the three d-electrons of the chromium(III) ion will occupy the orbitals which are lowest in energy. Thus, the presence of six ligands in an octahedral environment will remove the five fold d-orbital degeneracy by raising the energy of the two orbitals that coincide with the ligands and lowering the energy of the remaining three orbitals which do not coincide with the ligands. These doubly and triply degenerate orbitals are designated e_g and t_{2g} respectively. The three electrons of the chromium(III) system will occupy the t_{2g} orbitals. The energy of separation between the e_g and t_{2g} orbitals is called 10Dq and is a function of the ligands coordinated. The spectrochemical series is an arrangement of a series of ligands according to their capacity to cause d-orbital splittings (or 10Dq). The magnitude of 10Dq is calculated from the lowest energy spin allowed d-d electronic band in the visible

spectrum of the complex (see Table 16). The energy gained by the system by preferentially filling the low lying t_{2g} orbitals is called the crystal field stabilization energy, C.F.S.E. This crystal field splitting scheme is summarized in Figure 15.

The concept of the crystal field activation energy, C.F.A.E., as introduced by Hush[98], may be useful in predicting the configurations of transition states or intermediates of a reaction. The C.F.A.E. is the difference between the C.F.S.E. of the initial and the C.F.S.E. of the transition state configuration. According to the results listed in Table 17 the transition states predicting various coordinations are given in terms of C.F.A.E. as,

pentagonal bipyramid > square pyramid > octahedral wedge.

From this theoretical approach it can be seen that the seven coordinate octahedral wedge structure for the activated complex is favoured on the basis of energy requirements alone. This suggests associative activation as an intimate mechanism of reaction which is consistent with the I_a mechanism of water exchange as formerly proposed from reaction kinetics. Swaddle[99] has reported experimental evidence that indicates the substitution reactions of acidopentaaquochromium(III) complexes are best understood in terms of an associative interchange (I_a) mechanism. The structure of the octahedral wedge, which will now be regarded as the transition state or activated complex structure for the I_a process, is given in Figure 16.

A more detailed calculation utilizing concepts from both crystal field theory and molecular orbital theory also indicates that substitution reactions for chromium(III) species are associatively activated while those for cobalt(III) are dissociatively activated.

TABLE 16

$10Dq^a$ values and rate constants[b] for water exchange in
various aquochromium complexes at 25°C

Complex	$10Dq$, cm^{-1}	10^6k_{ex}, sec^{-1}
$Cr(OH_2)_6^{3+}$	17,400	0.43
$c\text{-}Cr(OH_2)_5Br^{2+}$	16,077	1.8
$c\text{-}Cr(OH_2)_5Cl^{2+}$	16,447	2.3
$c\text{-}Cr(OH_2)_5NCS^{2+}$	17,544	2.4
$c\text{-}Cr(OH_2)_5I^{2+}$	15,408	3.1
$trans\text{-}Cr(NH_3)_4(OH_2)_2^{3+}$	21,008	15^d
$t\text{-}Cr(OH_2)_5NCS^{2+}$	17,544	18
$t\text{-}Cr(OH_2)_5Cl^{2+}$	16,447	35
$trans\text{-}Cr(NH_3)_4OH_2Cl^{2+}$	18,018	44^d
$cis\text{-}Cr(NH_3)_4OH_2Cl^{2+}$	19,305	51^d
$Cr(NH_3)_5OH_2^{3+}$	20,661	52^d
$t\text{-}Cr(OH_2)_5Br^{2+}$	16,077	55
$cis\text{-}Cr(NH_3)_4(OH_2)_2^{3+}$	20,202	62^d
$trans\text{-}Cr(OH_2)_4Cl_2^{+}$	15,750	80
$t\text{-}Cr(OH_2)_5I^{2+}$	15,408	84

a) $10Dq$ = energy of the lowest spin allowed d-d transition absorption
band

TABLE 16 continued

b)   references given in Table 1

c)   data taken in part from reference 101

d)   this work

Note: t refers to the water ligand *trans* to the acido ligand
       c refers to the water ligand *cis* to the acido ligand

FIGURE 15
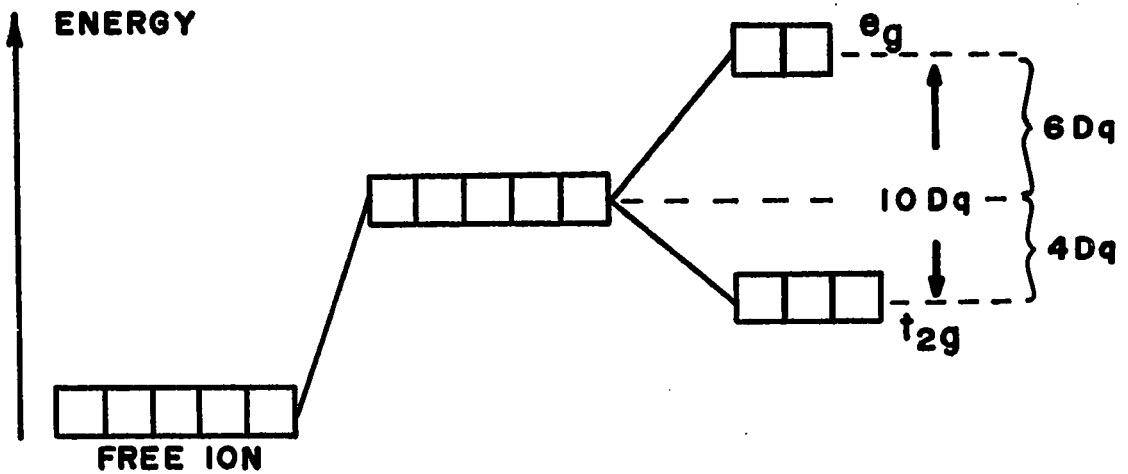
The splitting of a set of d-orbitals by an octahedral electrostatic crystal field

FIGURE 16
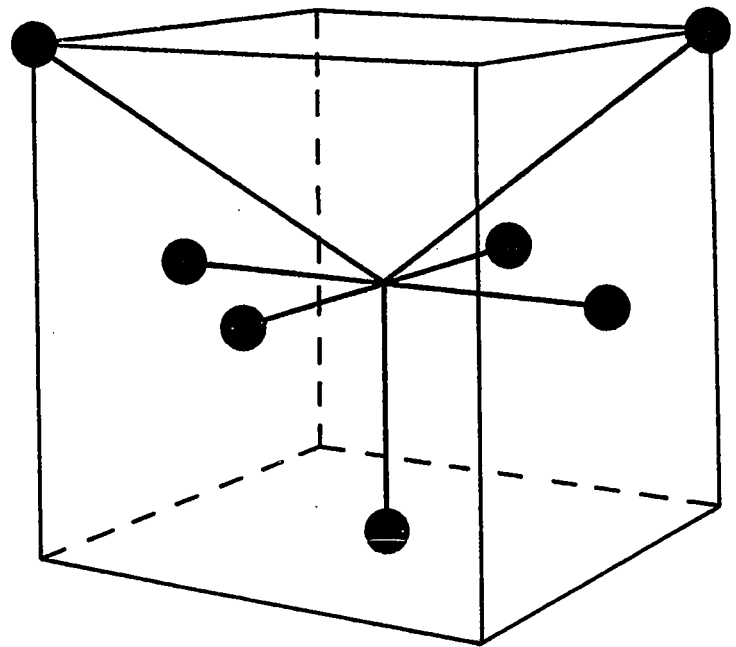
The seven coordinate octahedral wedge structure

TABLE 17

Crystal Field Activation Energies, C.F.A.E., for formation
of activated complexes of Cr(III) in Dq[a]

Mechanism	Transition State Structure	C.F.S.E.	C.F.A.E.
	octahedron	12.00	-
D	square pyramid	10.00	2.00
A	pentagonal bipyramid	7.74	4.26
I$_a$	octahedral wedge	10.20	1.80

a)   taken from reference 11 pages 146 and 147

Spees, Perumareddi, and Adamson[100], assuming a low spin transition state, calculated the activation energies required to form activated complexes with various structures and coordinations for several substitution reactions and compared these to the experimentally determined values. Table 18 gives the calculated activation energies for the aquation of some chromium(III) and cobalt(III) complexes for various transition state structures. Such calculations for chromium(III) suggest that a seven coordinate transition state of D_{5h} symmetry (pentagonal bipyramid) is favoured over an alternative dissociative pathway of reduced coordination. On the other hand, a five coordinate transition state of C_{4v} symmetry (square pyramid) appears to be favoured for analogous cobalt(III) systems. Stranks and Swaddle[5] point out that the general observation of the rarity of stereochemical change in chromium(III) substitutions is difficult to reconcile with a transition state of D_{5h} symmetry. The most probable stereoretentive seven coordinate transition state would have C_{2v} symmetry (octahedral wedge). The calculated activation energy of the seven coordinate octahedral wedge structure is slightly higher than that for the seven coordinate pentagonal bipyramid but is much lower than any structure with reduced coordination. Hence, these theoretical calculations support the general trend that substitutions of chromium(III) complexes tend to be associatively activated and those of cobalt(III) dissociatively activated.

It appears that the I_a mechanism as proposed for the water exchange process of the aquotetraamminechromium(III) series studied in this thesis is supported by an abundance of experimental and theoretical evidence.

TABLE 18

Calculated and Observed activation energies for aquation
of some complexes[a]

Complex	Calculated kcal mol^{-1}				Observed kcal mol^{-1}
	C_{4v}	D_{3h}	C_{2v}	D_{5h}	
$Cr(NH_3)_6^{3+}$	49.1	59.6	34.3	27.9	26.0
$Cr(NH_3)_5Cl^{2+}$	47.3	56.8	33.9	28.2	22.4
$Cr(NH_3)_5Br^{2+}$	47.1	56.5	34.1	28.4	21.5
$Cr(NH_3)_5I^{2+}$	47.0	56.0	34.3	29.0	21.4
$Cr(OH_2)_6^{3+}$	47.3	55.7	35.2	30.1	28.0
$Cr(OH_2)_5Cl^{2+}$	46.3	54.2	35.0	30.2	24.3
$Cr(OH_2)_5I^{2+}$	44.6	52.3	34.2	29.7	23.0
$Co(NH_3)_5OH_2^{3+}$	27.0	52.0	59.7	31.6	27.0
$Co(NH_3)_5Cl^{2+}$	26.8	51.5	59.3	31.1	23.0
$Co(NH_3)_5Br^{2+}$	26.7	50.9	58.8	30.8	24.0

a)   data taken from reference 95 and reference therein

SUMMARY and CONCLUSIONS

The rate of water exchange decreases along the series cis-$Cr(NH_3)_4(OH_2)_2^{3+}$, cis-$Cr(NH_3)_4OH_2Cl^{2+}$, $trans$-$Cr(NH_3)_4OH_2Cl^{2+}$, and $trans$-$Cr(NH_3)_4(OH_2)_2^{3+}$. The mechanism of the water exchange process for all of the aquoamminechromium(III) complexes studied is one of associatively activated interchange (I_a). This proposed mechanism is summarized by the following equation using the $trans$-diaquotetraamminechromium(III) cation as an example,

$$[\{trans\text{-}Cr(NH_3)_4(OH_2)_2\}(OH_2)_x]^{3+} \rightleftarrows [\{trans\text{-}Cr(NH_3)_4(OH_2)_3\}(OH_2)_{x-1}]^{3+*}$$
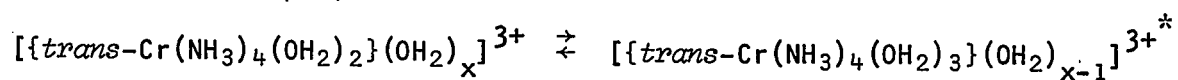
The seven coordinate transition state is considered to have the octahedral wedge structure:
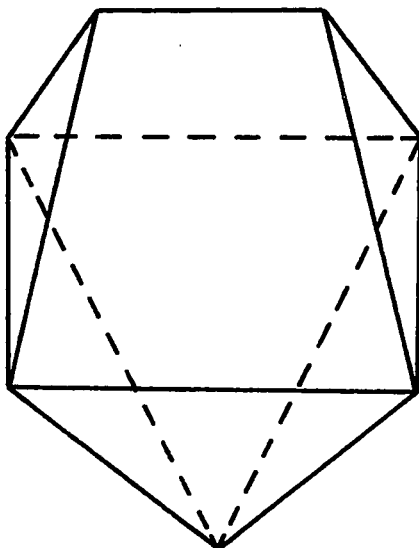
The factors favouring an associative mechanism for chromium(III) substitutions as opposed to a dissociative one remain unresolved but it is becoming increasingly evident that associative activation is important.

Ammonia has been placed relative to chloride in the *trans*-effect series and combining this with the work of others the kinetic *trans*-effect series for chromium(III) becomes,

$$I^- > Br^- > NH_3 \geq Cl^- > NCS^- > OH_2.$$
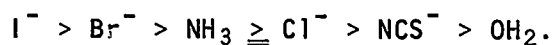
This is remarkably similar to the intrinsic kinetic *trans*-effect series for rhodium(III).

It has been shown for one case that the overall charge of the complex does not affect the rate at which the water exchanges. This might indicate that the electron donating ability of the coordinated groups is a more important factor governing the kinetics than the overall charge of the complex.

FUTURE CONSIDERATIONS

The extension of the present work to investigate the water exchange rates and modes of activation of other ligands for the water exchange process in *trans*-aquotetraamminechromium(III) systems would be of considerable interest. Studies using *trans* ligands such as Br^- and I^- which are known to have a greater *trans*-influence than NH_3 and Cl^- might indicate whether there is a change in mode of activation of water exchange to a more dissociative one. The analogous *cis* complexes would allow any effects due to *cis*-activation to be evaluated.

The recent report of *cis*-activation by the nitro-ligand in the pentaamminechromium(III) ion could perhaps be meaningfully extended to some aquotetraamminechromium(III) systems. *Cis*-oxyanionoaquotetraammin-chromium(III) cations with the postulated *cis*-activating oxyaniono-ligands such as NO_2^-, NO_3^-, SO_3^{2-}, and SO_4^{2-} would demonstrate any *cis*-activation on the exchange rate of the one ligand water. *Trans*-oxyanionotetraammine-chromium(III) ions in which the *cis* sites are blocked by non-exchanging ammonias would also permit the evaluation of the *trans*-effect of such ligands.

It has often been noted in both the aquo and ammine series of chromium(III) complexes that the rate of aquation is increased by the presence of oxygen containing ligands or anions. The study of the kinetics of the water exchange of *cis*- and *trans*-oxyanionoaquotetraammine-chromium(III) cations would therefore be valuable in assessing the

mechanistic role played by these oxygen containing species in ligand

substitution processes.

APPENDIX

Tables A-1 to A-5 below contain the experimental water exchange data found for the complexes in this study. Included are the values of E-1 used in the least squares calculations for the rate constants. Since all samples of a particular experiment were analysed continuously on the mass spectrometer, the relative mass ratio reading for "normal" carbon dioxide is also included.

TABLE A-1

$$Cr(NH_3)_5OH_2^{3+} \quad - \quad {}^{18}OH_2 \text{ EXCHANGE}$$

A. Run CAPA-1   Temperature: 10.00°C

TIME (sec)	MASS RATIO X 10^6 46/(44+45)	(E-1)
0	2850	1.957
28800	2530	1.624
57600	2280	1.365
87300	2029	1.105
130500	1720	0.7842
172800	1507	0.5623
216000	1361	0.4119
261000	1250	0.2972
normal	964	-

B. Run CAPA-2   Temperature: 20.10°C

0	3150	2.243
7200	2802	1.886
14400	2383	1.454
21600	2120	1.183
32400	1753	0.8057
43200	1555	0.6012
54000	1378	0.4190
612000	1310	0.3500
normal	971	-

C. Run CAPA-3   Temperature: 30.10°C

0	3560	2.666
1800	2993	2.083
3600	2654	1.734
5400	2340	1.410
8100	1918	0.9755
10800	1649	0.7045
13500	1470	0.5125
16200	1335	0.3756
normal	971	-

TABLE A-2
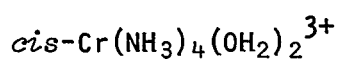
cis-$Cr(NH_3)_4(OH_2)_2^{3+}$ — $^{18}OH_2$ EXCHANGE

A. Run CATA-1   Temperature: 10.00°C

TIME (sec)	MASS RATIO X 10^6 46/(44+45)	(E-1)
0	2748	1.846
57600	2372	1.451
87300	2116	1.185
130500	1810	0.8699
216130	1369	0.4144
261130	1282	0.3243
345600	1150	0.1894
normal	968	–

B. Run CATA-2   Temperature: 15.00°C

0	2877	1.983
14400	2586	1.682
28800	2273	1.358
43200	2023	1.100
86400	1454	0.5091
129600	1199	0.2455
174600	1090	0.1321
normal	964	–

C. Run CATA-3   Temperature: 19.90°C

0	3500	2.669
14400	2530	1.652
21600	2110	1.213
28800	1963	1.058
36000	1729	0.8117
43200	1620	0.6981
50400	1495	0.5661
normal	954	

TABLE A-2 (continued)

D.   Run CATA-4   Temperature: 25.00°C

TIME (sec)	MASS RATIO X 10^6 46/(44+45)	(E-1)
0	3540	2.488
10800	2265	1.232
16200	1940	0.9082
21600	1650	0.6203
32400	1350	0.3269
43200	1180	0.1632
normal	1015	-

E.   Run CATA-5   Temperature: 25.00°C

0	3585	2.533
5400	2787	1.747
10800	2348	1.314
21600	1670	0.6375
32400	1360	0.3385
43200	1185	0.1722
normal	1015	-

F.   Run CATA-6   Temperature: 30.00°C

0	3975	2.936
1800	3380	2.346
3600	2830	1.802
7200	2156	1.134
10800	1762	0.7456
14400	1468	0.4546
21700	1189	0.1774
normal	1010	-

G.   Run CATA-7   Temperature: 30.00°C

0	3400	2.963
1800	3305	2.273
3600	2810	1.781
7200	2157	1.136
10800	1727	0.7099
14400	1472	0.4578
21730	1189	0.1774
normal	1010	-

TABLE A-2 (continued)

H.   Run CATA-8   Temperature: 35.00°C

TIME (sec)	MASS RATIO X 10^6 46/(44+45)	(E-1)
0	2476	2.599
1200	3056	2.184
2400	2526	1.631
3600	2063	1.143
4800	1870	0.9473
6000	1648	0.7163
9600	1263	0.3170
13500	·1084	0.1291
normal	960	-

I.   Run CATA-9   Temperature: 20.10°C

0	2601	1.687
7200	2238	1.312
14400	2002	1.068
46800	1330	0.3735
54000	1315	0.3627
82800	1103	0.1373
normal	968	-

J.   Run CATA-10   Temperature: 35.00°C

0	3602	2.752
1200	2986	2.111
2400	2508	1.613
4800	1842	0.9188
7800	1375	0.4321
9600	1265	0.3175
normal	960	-

TABLE A-3

trans-$Cr(NH_3)_4(OH_2)_2^{3+}$ — $^{18}OH_2$ EXCHANGE

A. Run TATA-1   Temperature: 19.9°C

TIME (sec)	MASS RATIO X 10^6 46/(44+45)	(E-1)
0	3810	2.969
3600	3736	2.892
7200	3676	2.829
21600	3415	2.557
36000	3170	2.302
172800	1800	0.8759
normal	960	—

B. Run TATA-2   Temperature: 19.9°C

0	3880	2.968
14400	3490	2.562
21600	3377	2.446
36000	3140	2.203
86400	2460	1.511
122400	2101	1.143
172800	1780	0.8163
normal	980	—

C. Run TATA-3   Temperature: 25.00°C

0	3940	2.867
14400	3365	2.303
28800	2880	1.827
43200	2540	1.492
86400	1853	0.8187
129600	1455	0.4169
172800	1250	0.2263
normal	1019	—

TABLE A-3 (continued)

D.   Run TATA-4   Temperature: 25.00°C

TIME (sec)	MASS RATIO X 10^6 46/(44+45)	(E-1)
0	4006	2.932
14400	3350	2.288
28800	2846	1.793
43200	2525	1.477
86400	1825	0.7903
129600	1440	0.4106
172800	1250	0.2263
normal	1019	-

E.   Run TATA-5   Temperature: 30.00°C

0	3670	3.047
3600	3290	2.627
7200	2948	2.251
14400	2565	1.828
21600	2283	1.152
32400	1885	1.079
43200	1584	0.7470
86400	1080	0.1907
normal	907	-

F.   Run TATA-6   Temperature: 30.00°C

0	3660	3.035
14400	2660	1.933
21600	2286	1.519
32400	1860	1.052
43200	1600	0.7617
86400	1082	0.1927
normal	907	-

TABLE A-3 (continued)

G.   Run TATA-7   Temperature: 35.00°C

TIME (sec)	MASS RATIO X 10^6 46/(44+45)	(E-1)
0	4056	3.056
3600	3640	2.640
7200	3089	2.089
16200	2190	1.191
21600	1890	0.8900
270000	1620	0.6200
32400	1470	0.4700
43200	1245	0.2450
normal	1000	-

H.   Run TATA-8   Temperature: 35.00°C

TIME (sec)	MASS RATIO X 10^6 46/(44+45)	(E-1)
0	3492	2.492
3600	3139	2.134
7200	2579	1.579
12600	2218	1.218
18000	1903	0.9026
23400	1657	0.6569
39600	1232	0.2320
normal	1000	-

I.   Run TATA-9   Temperature: 40.00°C

TIME (sec)	MASS RATIO X 10^6 46/(44+45)	(E-1)
0	4376	3.376
1800	3851	2.851
3600	3197	2.197
5400	2740	1.740
8100	2355	1.355
10800	2062	1.062
13500	1665	0.6650
16200	1505	0.5050
21600	1298	0.2980
normal	1000	-

TABLE A-3 (continued)

J. Run TATA-10   Temperature: 40.00°C

TIME (sec)	MASS RATIO X 10^6 46/(44+45)	(E-1)
0	4197	3.197
1800	3687	2.687
3600	3226	2.226
5400	2702	1.702
8100	2239	1.239
10800	1956	0.9560
13500	1674	0.6740
16200	1520	0.5200
21600	1269	0.2690
normal	1000	-

K. Run TATA-11   Temperature: 44.90°C

0	4030	3.172
1200	3224	2.336
2400	2720	1.816
4800	2040	1.112
6000	1804	0.8672
7800	1522	0.5757
9600	1352	0.3998
12000	1190	0.2306
normal	966	-

L. Run TATA-12   Temperature: 44.90°C

0	4184	3.332
1200	3452	2.574
2400	2864	1.964
3600	2429	1.515
4800	2094	1.167
6000	1845	0.9106
7800	1565	0.6199
9600	1360	0.4079
12000	1200	0.2421
normal	966	-

TABLE A-3 (continued)

M.   Run TATA-13   Temperature: 35.00°C

TIME (sec)	MASS RATIO X 10^6 46/(44+45)	(E-1)
0	4075	3.075
3600	3589	2.589
7200	3061	2.061
10800	2846	1.846
16200	2422	1.422
21600	2096	1.096
270000	1852	0.8520
32400	1643	0.6430
normal	1000	–

N.   Run TATA-14   Temperature: 40.00°C

0	4033	3.033
3600	3121	2.121
5400	2796	1.796
8100	2416	1.416
10800	2118	1.118
13500	1907	0.9070
16200	1734	0.7340
21600	1461	0.4610
normal	1000	–

TABLE A-4

cis-Cr(NH$_3$)$_4$OH$_2$Cl^{2+} – ^{18}OH$_2$ EXCHANGE

A.   Run CACTA-1   Temperature: 10.00°C

TIME (sec)	MASS RATIO X 10^6 46/(44+45)	(E-1)
0	2277	1.361
36000	1985	1.058
87300	1710	0.7739
115200	1594	0.6542
172800	1442	0.4974
227830	1303	0.3521
288000	1200	0.2459
345600	1122	0.1646
normal	964	–

TABLE A-4 (continued)

B. Run CACTA-2   Temperature: 15.00°C

TIME (sec)	MASS RATIO X 10^6 46/(44+45)	(E-1)
0	2355	1.445
18000	2176	1.257
36000	1813	0.8801
56700	1670	0.7323
86530	1450	0.5042
140160	1226	0.2719
174600	1115	0.1564
228600	1044	0.08335
normal	964	-

C. Run CACTA-3   Temperature: 19.90°C

0	2760	1.825
1800	2783	1.802
3600	2680	1.742
7200	2497	1.556
10800	2424	1.479
21600	2037	1.085
86400	1224	0.2501
normal	977	-

D. Run CACTA-4   Temperature: 19.90°C

0	2707	1.731
1800	2668	1.771
3600	2566	1.627
7200	2500	1.560
10800	2350	1.406
14400	2260	1.313
21600	2025	1.072
36000	1770	0.8119
86400	1223	0.2492
normal	977	-

TABLE A-4 (continued)

E.   Run CACTA-5   Temperature: 25.10°C

TIME (sec)	MASS RATIO X 10^6 46/(44+45)	(E-1)
0	2328	1.397
3600	2151	1.216
7200	1852	0.9079
14400	1544	0.5895
36000	1158	0.1920
43200	1134	0.1678
normal	971	-

F.   Run CACTA-6   Temperature: 30.00°C

0	2461	1.548
1800	2250	1.330
7200	1678	0.7367
10800	1471	0.5224
18000	1215	0.2560
21600	1132	0.1698
28800	1045	0.08202
normal	966	-

G.   Run CACTA-7   Temperature: 30.00°C

0	2376	1.460
1800	2169.	1.245
3600	2007	1.078
7200	1650	0.7075
21600	1132	0.1594
28800	1063	0.08698
normal	966	-

H.   Run CACTA-8   Temperature: 35.00°C

0	2428	1.529
1200	2150	1.240
2400	1911	0.9909
3600	1685	0.7553
5400	1450	0.5093
7200	1329	0.3839
9000	1213	0.2627
10800	1133	0.1789
normal	960	-

TABLE A-4 (continued)

I. Run CACTA-9   Temperature: 25.05°C

TIME (sec)	MASS RATIO X 10^6 46/(44+45)	(E-1)
0	2315	1.384
3600	2150	1.214
7200	1810	0.8647
14400	1587	0.6343
21600	1412	0.4632
28800	1293	0.3319
36000	1180	0.2152
43200	1107	0.1396
56700	1036	0.06704
normal	971	-

TABLE A-5

$trans$-Cr(NH$_3$)$_4$OH$_2$Cl^{2+} - ^{18}OH$_2$ EXCHANGE

A. Run TACTA-1   Temperature: 10.00°C

0	3160	2.278
43200	2732	1.834
90900	2413	1.503
130500	2126	1.205
194400	1797	0.8636
261000	1556	0.6133
388800	1285	0.3327
normal	964	

B. Run TACTA-2   Temperature: 15.00°C

0	3186	2.306
21600	2720	1.821
43200	2405	1.494
56700	2239	1.322
90000	1854	0.9227
129600	1579	0.6381
normal	964	-

TABLE A-5 (continued)

C. Run TACTA-3   Temperature: 19.90°C

TIME (sec)	MASS RATIO X 10^6 46/(44+45)	(E-1)
0	3042	2.123
7200	2679	1.750
14000	2485	1.552
25200	2099	1.154
36000	1872	0.9215
79200	1300	0.3400
normal	974	-

D. Run TACTA-4   Temperature: 19.90°C

0	3315	2.403
3600	3147	2.231
7200	2882	1.959
14400	2650	1.722
21600	2385	1.448
32400	2085	1.140
43200	1866	0.9164
86400	1298	0.3311
normal	974	-

E. Run TACTA-5   Temperature: 25.10°C

0	3412	2.554
11030	2415	1.516
16200	2088	1.175
25200	1718	0.7889
32400	1526	0.5890
39600	1365	0.4203
50400	1227	0.2763
64800	1096	0.1404
normal	960	-

TABLE A-5 (continued)

F.   Run TACTA-6   Temperature: 30.00°C

TIME (sec)	MASS RATIO X 10^6 46/(44+45)	(E-1)
0	3330	2.449
1800	2920	2.023
3600	2738	1.833
7200	2224	1.302
10800	1894	0.9603
14400	1626	0.6828
18000	1445	0.4948
21600	1305	0.3500
normal	966	-

G.   Run TACTA-7   Temperature: 30.00°C

0	3290	2.407
3600	2693	1.788
14400	1618	0.6752
18000	1440	0.4907
21600	1364	0.3794
28800	1164	0.2042
normal	966	-

H.   Run TACTA-8   Temperature: 35.00°C

0	3137	2.268
1200	2713	1.826
2400	2438	1.540
5400	1865	0.9432
7200	1590	0.6574
9000	1433	0.4923
10800	1307	0.3610
normal	960	-

REFERENCES

1. Hunt, H.R. and Taube, H., J. Amer. Chem. Soc., $\underline{80}$, 2642 (1958).

2. Monacelli, F. and Viel, E., Inorg. Chim. Acta, $\underline{1}$, 467 (1967).

3. Bracken, D.E., Ph.D. Thesis, Department of Chemistry, University of Western Ontario, London (Ont.), 1967.

4. Borghi, E. and Monacelli, F., Inorg. Chim. Acta, $\underline{5}$, 211 (1971).

5. Swaddle, T.W. and Stranks, D.R., J. Amer. Chem. Soc., $\underline{94}$, 8357 (1972).

6. Keen, R.A., Ph.D. Thesis, Department of Chemistry, University of Western Ontario, London (Ont.), 1973.

7. Hunt, J.P., Coord. Chem. Revs., $\underline{7}$, 1 (1971).

8. Earley, J.E. and Cannon, R.D., Trans. Metal Chem., $\underline{1}$, 34 (1965).

9. Garner, C.S. and House, D.A., Trans. Metal Chem., $\underline{6}$, 59 (1970).

10. Taube, H., Chem. Rev., $\underline{50}$, 69 (1952).

11. Basolo, F. and Pearson, R.G., "Mechanisms of Inorganic Reactions" second edition, J. Wiley and Sons, Inc., New York, N.Y., 1967.

12. Tobe, M.L., "Inorganic Reaction Mechanisms", Thomas Nelson and Sons Ltd., London, England, 1972.

13. Espenson, J.H., Inorg. Chem., $\underline{8}$, 1554 (1969).

14. Thusius, D., Inorg. Chem., $\underline{10}$, 1106 (1971).

15. Johnson, S.A., Basolo, F., and Pearson, R.G., J. Amer. Chem. Soc., $\underline{85}$, 1741 (1967).

16. Hughes, R.G. and Garner, C.S., Inorg. Chem., $\underline{7}$, 1988 (1968); $\underline{7}$, 2678 (1968).

17. Jones, W.E., Carey, L.R., and Swaddle, T.W., Can. J. Chem., $\underline{50}$, 2739 (1972).

18. Powell, H.K.J., Inorg. Nucl. Chem. Letters, $\underline{8}$, 891 (1972).

19. Poë, A.J., Shaw, K., and Wendt, M.J., Inorg. Chim. Acta, 1, 371 (1967).

20. Hoppenjans, D.W., Hunt, J.B., and Gregoire, C.R., Inorg. Chem., 7, 2506 (1968).

21. Hoppenjans, D.W., Gordon, G., and Hunt, J.B., Inorg. Chem., 10, 754 (1971).

22. Fee, W.W., Jackson, W.G., and Vowels, P.D., Aust. J. Chem., 25, 459 (1972).

23. Swaddle, T.W. and Guastalla, G., Inorg. Chem., 7, 1915 (1968).

24. Ogard, A.E. and Taube, H., J. Amer. Chem. Soc., 80, 1084 (1958).

25. Tobe, M.L., Inorg. Chem., 7, 1260 (1968).

26. Eigen, M. and Wilkins, R.G., "Mechanisms of Inorganic Reactions", Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D.C., 1965, p. 55.

27. Basolo, F. and Pearson, R.G., "Mechanisms of Inorganic Reactions", first edition, J. Wiley and Sons, Inc., New York, N.Y., 1958, p. 102.

28. Stranks, D.R. and Swaddle, T.W., J. Amer. Chem. Soc., 93, 2783 (1971).

29. Basolo, F., Bounsall, E.J., and Poë, A.J., Proc. Chem. Soc., 366 (1963).

30. Bott, H.L., Bounsall, E.J., and Poë, A.J., J. Chem. Soc., (A), 1275 (1966).

31. Bott, H.L. and Poë, A.J., J. Chem. Soc., (A), 205 (1967).

32. Poë, A.J. and Shaw, K., J. Chem. Soc., (A), 393 (1970).

33. Poë, A.J. and Vuik, C.P.J., J. Chem. Soc., Dalton, 2250 (1972).

34. Margerum, D.W. and Rosen, H.M., J. Amer. Chem. Soc., 89, 1088 (1967).

35. Guastalla, G. and Swaddle, T.W., Chem. Comm., 61 (1973).

36. Hunt, J.P. and Plane, R.A., J. Amer. Chem. Soc., 76, 5960 (1954).

37. Stieger, H., Harris, G.M., and Kelm, H., Ber. Bunsenges. Phys. Chem., 74, 262 (1970).

38. Rutenberg, A.C. and Taube, H., J. Chem. Phys., 20, 825 (1952).

39. Plumb, W. and Harris, G.M., Inorg. Chem., 3, 542 (1964).

40. Martin, D.F. and Tobe, M.L., J. Chem. Soc., 1388 (1962).

41. Krause, W. and Taube, H., J. Amer. Chem. Soc., 83, 1280 (1961).

42. Hoppenjans, D.W., Hunt, J.B., and DeChant, Sr. M.J., Chem. Comm., 510 (1968).

43. Hoppenjans, D.W. and Hunt, J.B., Inorg. Chem., 8, 505 (1969).

44. Linhard, M. and Weigel, M., Z. anorg. allgem. Chem., 15, 299 (1959).

45. Schlessinger, G.G., "Inorganic Laboratory Preparations", The Chemical Publishing Co. Inc., New York, N.Y., 1962, p. 225.

46. Haupt, G.W., J. Res. Natl. Bur. Std., 48, 414 (1952).

47. Vogel, A.I., "A Text-Book of Quantitative Inorganic Analysis", Longman Group Limited, third edition, London, England., 1961, p. 257.

48. Earley, J.E. and Alexander, W., J. Amer. Chem. Soc., 92, 2294 (1970).

49. Edelson, M.R. and Plane, R.A., J. Phys. Chem., 63, 327 (1959).

50. Boyer, P.D., Graves, D.J., Suelter, C.H., and Dempsey, M.E., Anal. Chem., 33, 1906 (1963).

51. Nier, A.O., Rev. Sci. Inst., 18, 398 (1947).

52. Adamson, A.W., J. Inorg. Nucl. Chem., 13, 275 (1960).

53. Bjerrum, J. and Lamm, C.G., Acta Chem. Scand., 9, 216 (1955).

54. Jorgensen, E. and Bjerrum, J., Acta Chem. Scand., 12, 1047 (1958).

55. Edelson, M.R. and Plane, R.A., Inorg. Chem., 3, 231 (1964).

56. Kyuno, E., Kamada, M., and Tanaka, N., Bull. Chem. Soc. Japan, 40, 1848 (1967).

57. Lobonov, N.I., Russ. J. Inorg. Chem., 4, 151 (1959).

58. LeMay, H.E., Jr. and Bailer, J.C., Jr., J. Amer. Chem. Soc., 89, 5577 (1967).

59. LeMay, H.E., Jr., Sheen, J.R., and Babich, M.W., J. Inorg. Nucl. Chem., 34, 149 (1972).

60. Chang, F.C. and Wendlant, W.W., J. Inorg. Nucl. Chem., 32, 3535 (1970).

61. Nagase, K. and Tanaka, N., Bull. Chem. Soc. Japan, 45, 1097 (1972).

62. Harris, G.M., Trans. Taraday Soc., 47, 716 (1951).

63. Talaishi, T., Bull. Chem. Soc. Japan, 42, 1266 (1969).

64. McKay, H.A.C., Nature, 142, 997 (1938); J. Amer. Chem. Soc.,
    65, 702 (1943).

65. Duffield, R.B. and Calvin, M., J. Amer. Chem. Soc., 68, 557 (1946).

66. Norris, T.H., J. Phys. and Colloid. Chem., 54, 777 (1950).

67. Duffy, N.V. and Earley, J.E., J. Amer. Chem. Soc., 89, 272 (1967).

68. Bevington, P.R., "Data Reduction and Error Analysis for the
    Physical Sciences", McGraw-Hill Book Company, New York, N.Y.,
    1969.

69. Frost, A.A. and Pearson, R.G., "Kinetics and Mechanism", John
    Wiley and Sons Inc., second edition, New York, N.Y., 1965,
    Chapter 5.

70. Plane, R.A. and Hunt, J.P., J. Amer. Chem. Soc., 79, 3343 (1957).

71. Ingold, C.K., "Structure and Mechanism in Organic Chemistry",
    Cornell University Press, Ithaca, N.Y., 1953.

72. Langford, C.H. and Gray, H.B., "Ligand Substitution Processes",
    W.A. Benjamin Inc., New York, N.Y., 1965.

73. Garner, C.S. and House, D.A., Trans. Metal Chem., 6, 177 (1970).

74. Pearson, R.G. and Basolo, F., J. Amer. Chem. Soc., 78, 4878 (1956).

75. Stranks, D.R., "Modern Coordination Chemistry", J. Lewis and
    R.G. Wilkins, Ed., Interscience Publishers, Inc., New York,
    N.Y., 1960, pp. 119-120.

76. Basolo, F. and Pearson, R.G., Prog. Inorg. Chem., 4, 381 (1962).

77. Chernyaev, I.I., Ann. inst. platine, U.S.S.R., 4, 261 (1926).

78. Ballhausen, C.J. and Gray, H.B., Inorg. Chem., 1, 111 (1962).

79. Pidcock, A., Richards, R.E., and Veranzi, L.M., J. Chem. Soc.,
    (A), 1707 (1966).

80. Grinberg, A.A., "An Introduction to the Chemistry of Complex
    Compounds", Pergamon Press, Oxford, 1962, p. 219.

81. Chatt, J., Duncanson, L.A., and Veranzi, L.M., J. Chem. Soc.,
    4456 (1955).

82. Orgel, L.E., J. Inorg. Nucl. Chem., 2, 137 (1956).

83. Van Vleck, J.H., J. Chem. Phys., 3, 803 & 807 (1935).

84. Langford, C.H., Can. J. Chem., 49, 1497 (1971).

85. Jones, W.E. and Swaddle, T.W., Chem. Comm., 998 (1969).

86. Latimer, W.M. and Jolly, W.J., J. Amer. Chem. Soc., 75, 1548 (1953).

87. Monacelli, F., Inorg. Chim. Acta, 2, 263 (1968).

88. Langford, C.H. and Gray, H.B., "Ligand Substitution Processes", W.A. Benjamin Inc., New York, N.Y., 1965, pp. 86 & 92.

89. Bott, H.L. and Poë, A.J., J. Chem. Soc., (A), 1745 (1969).

90. Swaminathan, K. and Harris, G.M., J. Amer. Chem. Soc., 88, 4411 (1966).

91. Pavelich, M.J. and Harris, G.M., Inorg. Chem., 12, 423 (1973).

92. Langford, C.H. and Muir, W.R., J. Amer. Chem. Soc., 89, 3141 (1967).

93. Hamm, R.E., Johnson, R.L., Perkins, R.H., and Davis, R.E., J. Amer. Chem. Soc., 80, 4469 (1958).

94. Swaddle, T.W. and Gaustalla, G., Inorg. Chem., 8, 1604 (1969).

95. Szwarc, M., Acc. Chem. Res., 2, 87 (1969).

96. Pearson, R.G., J. Amer. Chem. Soc., 85, 3533 (1963).

97. Orgel, L.E., J. Chem. Soc., 4756 (1952).

98. Hush, N.S., Aust. J. Chem., 15, 378 (1962).

99. Carey, L.R., Jones, W.E., and Swaddle, T.W., Inorg. Chem., 10, 1566 (1971).

100. Spees, S.T., Perumareddi, J.R., and Adamson, A.W., J. Amer. Chem. Soc., 90, 6626 (1968).

101. Perumareddi, J.R., Coord. Chem. Rev., 4, 73 (1969).

102. Spreer, L.O. and King, E.L., Inorg. Chem., 10, 916 (1971).

103. Borghi. E., Monacelli, F., and Prosperi, T., Inorg. Nucl. Chem. Letters, 6, 667 (1970).