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The Trans Effect In Water Exchange Reactions Of Chromium (iii) Complexes

Donald Edward Bracken

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THE *trans* EFFECT IN WATER EXCHANGE REACTIONS
OF CHROMIUM(III) COMPLEXES

by

Donald Edward Bracken

Department of Chemistry

Submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy

Faculty of Graduate Studies
The University of Western Ontario
London, Canada
September 1967

à ma femme

ABSTRACT

Study of the rates of water exchange of acidopenta-aquochromium(III) ions provides a unique opportunity to assess the *trans*-labilizing influence of various ligands in a model octahedral system.

Although recently reported studies on rhodium(III) substitution reactions and on water exchange of iodopenta-aquochromium(III) ions indicate that *trans* effects are of importance in these cases, they permit no comparison of the rate of reaction at a *trans* site with that at a *cis* site.

Rates of water exchange of chloro-, bromo-, and isothiocyanatopentaaquochromium(III) ions have been measured over the course of approximately eighty percent of complete exchange of the five waters. Fitting of the data to a derived curve allows calculation of the exchange rate constants for the single *trans* water and the four *cis* waters. Relative rates of *trans* water exchange permit serialization of ligands in order of decreasing *trans*-labilizing influence: $I^- > Br^- > Cl^- > NCS^- > H_2O$. Relative *cis* rates are uniform and independent of the ligand.

A water exchange study of the *trans*-dichlorotetra-aquochromium(III) ion indicates the effect of over-all charge on the complex on *cis* water exchange.

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INTRODUCTION

The *trans* effect 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 (1).

The concept of the *trans* effect, first introduced by Chernayev in 1926, continues to be extremely useful in correlating reactions of platinum(II) square-planar complexes. The literature contains many reviews of the *trans* effect; one of the most recent is by Basolo and Pearson (1). Because of the extensive empirical and theoretical discussions on the subject in the literature, this introduction serves not as a comprehensive review but rather focuses attention on recent efforts that clearly establish *trans* effects in octahedral complexes.

The functional definition of the *trans* effect implies that knowledge of ligand substitution rates is essential for demonstrating the phenomenon to be operative in any particular system. The paucity of appropriate kinetic data presently precludes meaningful correlations of *trans* effects in octahedral complexes. The most studied octahedral systems are cobalt(III), platinum(IV), and chromium(III).

Isomerization which appears to depend on the *trans* ligand and the leaving group often complicates the reactions of cobalt(III) complexes. Catalysis by platinum(II) frequently leads to ambiguities in reactions of the platinum(IV) system. As Basolo and Pearson argue (1), these kinetic complexities make assignment of a *trans* effect difficult, if not impossible. Evidence for the *trans* effect in substitution reactions of chromium(III) complexes is apparently sparse.

Poë *et al.* (2, 3, 4) present the only detailed study of an octahedral system in which manifestation of the *trans* effect is well documented. They examined the aqueous solution kinetics of substitution of X of selected rhodium (III) complexes of the type *trans*-RhA₄LX^{z+} (X = Cl, Br, I or H₂O; L = Cl, Br, I, or NH₃; A = en_{1/2} or NH₃; z = 1, 2, or 3). Since the reactions proceed without stereochemical rearrangement and undesirable catalytic effects, the complexes are suitable for a *trans* effect study. Blocking the *cis* sites with the "inert" ligand ethylenediamine (en) restricts the reaction to the *trans* sites.

An evaluation of both the relative rate constants and the activation enthalpies measured for the various reactions permitted the sequencing of L in order of its decreasing *trans* labilizing influence on X: I > Br > NH₃ ≥ Cl. Although the data do not allow an unambiguous mechanism to be specified for these substitution reactions, an "explanation" of the observed *trans* effect series in terms of Pearson's "soft and hard acid and base" concept (5) is rather successful. A postulation of *trans* bond weakening effects of the

ligands is also offered as a rationale.

Despite decades of study of the platinum(II) system, reconciliation of the various *trans* effect theories remains unrealized; the few reliable data available make predictions of *trans* effects in octahedral systems unwarranted. The thoroughness of these rhodium(III) studies indicates the direction that future experiments must take to clarify the *trans* effect in octahedral systems.

In chloride anation of hexaaquorhodium(III) ion, the sole product appears to be the *trans*(?)-dichlorotetraaquorhodium(III) ion (6). Swaminathan and Harris suggest that this result is due to the strong *trans* labilizing influence of chloride on ligand water in the probable intermediate monochloropentaaquorhodium(III) ion.

An interest in the effects of various ligands on the water exchange behavior of hydrated chromium(III) ions prompted the investigation described in this thesis. While the experimental part of this study was progressing, Moore, Basolo, and Pearson (7) published evidence for a *trans* effect of iodide on ligand water in iodopentaaquochromium(III) ion. They also observed that the chloropentaaquochromium(III) ion (abbreviated as chlorochromium(III) ion) only undergoes very slow water exchange; they calculated the rate constant for the exchange of one water molecule at 25°C to be *ca.* $7.6 \times 10^{-7} \text{ sec}^{-1}$. Not expecting a significant *trans* effect of chloride, the authors intimated that the reduced charge in $\text{CrX}(\text{H}_2\text{O})_5^{2+}$ (X = Cl, I) compared with $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ does not

have any large effect on the rate of water exchange. In view of the demonstrated *trans* effect of chloride in reactions of rhodium(III) complexes, the rate of water exchange of the chlorochromium(III) complex was reinvestigated. Particular attention was paid to early sampling in experiments with this and the other complexes.

The acidopentaaquochromium(III) complexes* used in this work represent model octahedral systems in which the effects of the acido ligand on the reactivities at both the *trans* and *cis* sites can be investigated simultaneously.

The results conclusively establish a *trans* effect in chromium(III) complexes, furnish this tentative series of ligands in order of their decreasing *trans* labilizing influence: $I^- > Br^- > Cl^- > NCS^- > H_2O$, and permit an estimate of a charge and/or *cis* effect on water exchange.

* The acidopentaaquochromium(III) complex (or ion) is abbreviated as either acidochromium(III) complex (or ion) or acido-complex (or -ion).

EXPERIMENTAL SECTION

A. Preparation of the Chromium(III) Complexes

Chloropentaaquochromium(III) Perchlorate.—A

solution containing the chloropentaaquochromium(III) ion was prepared by following the procedure described by Finholt, *et al.* (8). A 45-g sample of chromium(III) chloride hexahydrate (Fisher Reagent) was dissolved in 900 ml of water. The solution remained undisturbed for 2 hr at room temperature, then 15 ml of concentrated perchloric acid (Shawinigan - A.C.S. Reagent: 70-72%) was added. The resulting isomeric mixture was subsequently absorbed on a column of cation-exchange resin in the hydrogen form (Baker Analyzed Reagent: Dowex 50W-X8, 200-400 mesh). The resin column was 50 cm in length and had a cross sectional diameter of 4 cm. Individual hydrate isomers were consecutively removed from the column by displacement ion exchange. The eluent, 0.2 M $\text{Ba}(\text{ClO}_4)_2$ in 0.1 M HClO_4 , was prepared from barium hydroxide octahydrate (Mallinckrodt - A.C.S. Analytical Reagent) and excess perchloric acid. The formation of three sharply defined bands on the column during displacement permitted quantitative separation of the isomers. The middle band contained the monochlorochromium(III) species, as determined

by spectral and elemental analyses. The dilute effluent containing the desired complex was concentrated about 20-fold at room temperature by using a rotary flash evaporator (Buchler Model PTFE-1G) with vacuum and distillate removal provided by a vented exhaust vacuum pump (Welch Duo-Seal Model 1399). The viscous concentrate was evaporated to crystals on a high-vacuum line using liquid nitrogen traps. The very hygroscopic crystals were stored in tightly stoppered flasks in a freezer until use.

Bromopentaaquochromium(III) Perchlorate.—Using A. Recoura's method (9) with minor modifications, a mixture of chromium(III) bromide hydrate isomers was obtained. To 10 g of solid chromic oxide (Shawinigan - A.C.S. Reagent) was slowly added 140 ml of cold, fuming hydrobromic acid (Fisher - A.C.S. Reagent: 48%). The by-product, bromine, was removed from the resulting deep green solution by repeated extractions with carbon tetrachloride (Fisher - A.C.S. Reagent). Subsequent ion-exchange separations at 3°C, effluent concentration and evaporation to crystals were carried out in the same manner as described above for the chlorochromium(III) complex.

Isothiocyanatopentaaquochromium(III) Perchlorate.—The method of King and Dismukes (10) was used for the preparation of this complex, except the chromium salt was used in excess in order to obtain a more favorable amount of the isothiocyanatopentaaquochromium(III) ion in the equilibrium mixture. A 7-g sample of potassium thiocyanate (Fisher -

A.C.S. Reagent) and 50 g of chromium perchlorate hexahydrate (G. Frederick Smith Reagent) were dissolved in 400 ml of 0.1 M HClO_4 and heated at 100°C for 3 hr. Cooling the solution in a freezer induced precipitation of potassium perchlorate; the solid was subsequently removed by filtration. The isomeric mixture in the filtrate underwent the previously outlined ion-exchange treatment. Flash evaporation of the appropriate portion of effluent was sufficient to produce crystals of complex. Following filtration, which removed most of the mother liquor, the crystals were stored until use in a desiccator containing anhydrous magnesium perchlorate (Fisher Reagent).

trans-Dichlorotetraaquochromium(III) Chloride.—

The commercial form of chromic chloride hexahydrate was used directly, since it has been demonstrated by King, *et al.* (11) and crystallographically confirmed by Dance and Freeman (12) to be the *trans* isomer of dichlorotetraaquochromium(III) chloride (abbreviated as either dichlorochromium(III) chloride or dichloro-complex chloride).

B. Analytical Procedures

Spectra.—Spectra for all the complexes studied were measured with an ultraviolet-visible recording spectrophotometer (Cary Model 14) over the range 200-700 m μ . Samples of effluent taken directly from the ion-exchange column and diluted aliquots of the solutions used in kinetic runs were examined.

N. B. All the following analyses were made on 1-ml aliquots from solutions of the complexes studied.

Chromium.—A volume of 0.05 M KOH (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 10-fold excess of 30% hydrogen peroxide (Fisher Reagent) followed by heating, which was continued until evolution of oxygen gas was unnoticeable, resulted in a yellow chromate solution. Appropriate dilution with 0.05 M KOH gave samples suitable for absorbance measurements at 372 mμ (13). Readings were made on a manual ultraviolet-visible spectrophotometer (Unicam SP500) to a precision of ±0.002 absorbance units. The value of the molar absorptivity (ϵ) used to calculate the chromate ion concentration was $4.83 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.

Halogen.—To the aliquot was added excess 0.1 M AgNO₃ (prepared from Engelhard C.P.). The decomposition of the complex through precipitation of silver halide was aided by heating the solution. Standard gravimetric procedures were then followed (14).

Isothiocyanate.—To the sample was added sufficient 50% NaOH (prepared from Mallinckrodt - A.C.S. Analytical Reagent pellets) to destroy the complex. After acidification with 1 M HClO₄, the analysis was completed by a gravimetric procedure (15).

Perchloric Acid.—Upon complete absorption of the aliquot on a column of cation-exchange resin in the hydrogen

form (Baker Analyzed: Dowex 50W-X8, 20-50 mesh), the column was continuously rinsed with distilled water until the effluent was no longer acidic as indicated by pH paper (Anachemia "Accutint" pH 1-12 Wide Range B). The total effluent was titrated with 0.1 M NaOH, which was standardized with potassium hydrogen phthalate (Mallinckrodt - A.C.S. Analytical Reagent), using phenolphthalein as the indicator.

C. Measurement of Exchange Rates

To a sample of complex in a 50-ml round-bottomed flask, cooled in an ice water bath, was added 10 ml of cold 1.0 M HClO_4 which was prepared using enriched water (Yeda Research and Development Co., Ltd., Israel: 1.54 atom % ^{18}O). The solvent of the resulting solution was enriched about 5-fold in oxygen-18.

Immediately on complete dissolution a 0.5 ml aliquot was transferred to a male-jointed sampling flask. Upon connection to the high-vacuum line, the flask was partially evacuated and then immersed in liquid nitrogen. The time of immersion was recorded as "zero time." The actual time, read from an electric clock with a sweep second hand, with a maximum reading error of ± 10 sec, was recorded to the nearest 0.5 min. Evacuation to below 10^{-3} torr, as measured by a thermistor vacuum gauge (Jelrus Thermivac), was continued when the solution was completely frozen. Distillation of a water sample was then carried out as follows. The flask containing the frozen sample was immersed in a dewar of water at 25°C for a 3-min period; the distillate was trapped in a

nearby flask immersed in liquid nitrogen. The distillate (water sample) was then evaporated from the flask and condensed, with the aid of liquid nitrogen, in an evacuated sample tube. The preweighed sample tube was then reweighed to the nearest 0.1 mg to obtain the weight of the water sample.

A known weight of oxygen-18 enriched carbon dioxide was transferred from a storage bulb to the tube containing the water sample. After three days of contact at room temperature, the carbon dioxide was distilled from the equilibrated mixture into a U-shaped trap, using liquid nitrogen and Dry Ice baths consecutively. After a similar distillation from the trap into an evacuated sample tube, the carbon dioxide was ready for mass analysis.

The flask containing the sample for the kinetic run was immersed in a constant temperature bath immediately after removing the "zero time" aliquot. Kinetic runs of the four complexes were carried out in a bath at $24.78 \pm 0.02^{\circ}\text{C}$ maintained by a proportional temperature control (Fisher Model 22) using a 500-watt heater and a cold water cooling coil. Runs at $14.86 \pm 0.02^{\circ}\text{C}$ and $4.99 \pm 0.02^{\circ}\text{C}$ using chloro- and isothiocyanato- complexes were made in baths controlled by a thermostat (Haake Unitherm) and continuously cooled by one and two immersion coolers, respectively (Whirpool Thermoelectric). The temperature values reported here were corrected by comparing the readings on the bath thermometer with those on a thermometer calibrated by the United States National Bureau of Standards (Fisher: No. 9A5803).

Additional samples were taken at scheduled times over a period estimated to cover two to three half-lives on the approach to isotopic equilibrium, in the same manner as described above for the "zero time" samples. The "infinite time" sample was similarly taken after approximately ten half-lives of exchange.

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

Direct measurements of the ratio of peaks 46 ($^{12}\text{C}^{16}\text{O}^{18}\text{O}$) : $[44(^{12}\text{C}^{16}\text{O}^{16}\text{O}) + 45(^{13}\text{C}^{16}\text{O}^{16}\text{O}) + 45(^{12}\text{C}^{16}\text{O}^{17}\text{O})]$ were made alternately on the standard and unknown samples of carbon dioxide with an isotope ratio mass spectrometer. This double collector type of mass spectrometer has been described by Nier (16). The standard was a sample of the enriched carbon dioxide used in equilibration of the water samples.

RESULTS AND DISCUSSION

A. Identification of Prepared Species

Confirmation of the identity of the complexes prepared for this study was made through elemental and spectral analyses. From the elemental analysis was obtained the X:Cr ratio in $[\text{CrX}(\text{H}_2\text{O})_5](\text{ClO}_4)_2$, where X = Cl, Br, or NCS. Table I presents the observed spectral data with comparable values from the literature and the X:Cr ratios.

Since the X:Cr ratios were determined on 1-ml aliquots from solutions of the complexes, the values reported have a precision limit of *ca.* $\pm 5\%$. The values for the bromo- and isothiocyanato-complexes may reflect the presence of small amounts of hexaaquochromium(III) ion in the material used for the exchange experiments. Comparisons of the spectrophotometric data show very good agreement between the values obtained in this work and those reported in the literature for these acidopentaaquochromium(III) complexes.

These data and the observed ion-exchange elution characteristics of these dipositive ions confirm that the complexes prepared were indeed the desired species.

TABLE I

ANALYTICAL DATA ON PREPARED COMPLEXES

Spectral Data^a

Complex	X:Cr	This work	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>
[CrCl(H ₂ O) ₅] ²⁺	1.00	428 (21.7)	428 (20.8)		428 (21.9)	
		608 (17.4)	609 (16.4)		608 (17.4)	
		sh ^b 675 (7.9)	675 (6.7)		674 (7.5)	
[CrBr(H ₂ O) ₅] ²⁺	0.97	433 (22.4)			432 (23.7)	432 (22.4)
		sh 470 (15)			470 (15)	—
		622 (20.2)			622 (21.3)	622 (19.9)
		sh 675 (12)			675 (12)	675 (11.3)
[CrNCS(H ₂ O) ₅] ²⁺	0.98	411 (33.8)		410 (33.6)		
		570 (31.7)		570 (31.5)		

^a Reported as λ (ϵ), where λ = wave length of maximum absorption in m μ , and ϵ = molar absorptivity at the particular λ in $M^{-1} \text{ cm}^{-1}$. ^b sh = shoulder. ^c Reference 17.
^d Reference 10. ^e Reference 18. ^f Reference 19.

B. Concentration of Perchloric Acid

In the determination of perchloric acid by the ion-exchange procedure, the hydrogen ions in the effluent were derived from two sources: (1) perchloric acid, present in the original solution, (2) the resin. The dipositive complex, upon absorption on the column, displaced an equivalent number of hydrogen ions. Titration with base determined the number of mmoles of hydrogen ion in the effluent. It follows that

$$\begin{aligned} \text{no. mmole H}^+ (\text{effluent}) &= \text{no. mmole HClO}_4 (\text{aliquot}) + \\ &\quad 2 \times \text{no. mmole CrX}^{2+} (\text{aliquot}) \end{aligned}$$

For a 1-ml aliquot

$$[\text{HClO}_4] = \text{no. mmole H}^+ (\text{effluent}) - 2[\text{CrX}^{2+}] \quad [\text{B-1}]$$

Sample calculation: Run C1-3

Effluent titration: 35.60 ml of 0.0984 M NaOH = 3.503 mmoles H⁺

From eq [B-1]

$$[\text{HClO}_4] = 3.503 - 2(1.246) = 1.011$$

Thus for Run C1-3, $[\text{HClO}_4] = 1.01 \text{ M}$.

C. Initial Treatment of Exchange Data

Since mass analysis was effected on carbon dioxide, the oxygen isotopic composition of solvent water at "t time" (N_t) had to be calculated by the Dostrovsky and Klein equation (20). This equation takes into account the known equilibrium distribution of oxygen-18 between water and carbon dioxide (21), as well as dilution of the sample by the oxygen atoms

of carbon dioxide. Tables XI-XIV in Appendix A contain the data used in the calculations for each run. To reduce tedious and eliminate personal errors of manual calculation, a short program for calculation of N_t was written in Fortran IV for use on the University of Western Ontario computer (I.B.M. 7040). Appendix B contains the program source list. Values of $(1-F)$ and $-\log (1-F)$ were also calculated by the program. F is the fraction exchange at "t time"; the value $F = 1$ corresponds to complete exchange. In terms of N_t

$$(1-F) = \frac{N_t - N_\infty}{N_0 - N_\infty} \quad [C-1]$$

where N_0 and N_∞ = isotopic composition of solvent water at "zero time" and "infinite time", respectively.

Using time (in hours) and the calculated $-\log (1-F)$ values, plots based on the McKay equation (22) were made in order to determine the rate constant for isotopic exchange. Figures 1 and 2 show McKay plots for Run C1-3 and Run NCS-1 respectively, which are typical of those observed for water exchange reactions of these acidopentaaquochromium(III) complexes.

Two important features of the curves should be noted: (1) nonlinearity and (2) extrapolation of the linear limiting portion to "zero time" intersects the ordinate at a value of $(1-F) \approx 0.8$.

Implicit in the development of the McKay equation for "simple isotopic exchange" are the assumptions: (a) the composition of the reacting mixture remains chemically un-

Figure 1

Figure 2

ISOTHIOCYANATOCHROMIUM (III) ION - SOLVENT WATER EXCHANGE

changed throughout the approach to isotopic equilibrium and (b) if more than one atom of the same element in the compound undergoes exchange, these atoms are in equivalent structural positions.

Although slow decomposition by aquation occurs, assumption (a) may be held valid for these exchange reactions. That assumption (b) does not apply is readily apparent; in the octahedral structure of the complex one water is in a location structurally dissimilar to the other four, *i.e.*, in the position *trans* to the acido ligand.

Evidence presented by Moore, Basolo, and Pearson (7), as discussed in the introduction, may lead one to infer that the water exchange reaction of the chloropentaaquochromium(III) ion exhibits no abnormal features compared to water exchange of the aquo-ion. However, the persistent nonlinearity of the McKay plots coupled with the fact that the extrapolated intercepts correspond to exchange of about one water molecule, strengthened the viewpoint that indeed the *trans* water exchanges at a rate different from the remaining four waters, which are in positions *cis* to the acido ligand.

The premise was then made that the observed over-all exchange was due to a combination of two pseudo-first-order exchange processes: (a) *trans* water exchange plus (b) *cis* water exchange. Thus it became necessary to derive, on the basis of this assumption, an appropriate expression for the over-all exchange in terms of these two, different, independent processes.

D. Derivation of Rate Expression

In principle, for isotope exchange in a system of the nature assumed here, the derivation of a kinetic equation can be reduced to a simultaneous solution of the differential rate equations for the individual reactions (23).

The proposed reactions are

where

X = Cl, Br, or NCS

*O = oxygen-18

k_{trans} = reaction rate constant for *trans* water exchange

k_{cis} = reaction rate constant for *cis* water exchange

The final expression should relate the observed change in the oxygen isotopic composition of solvent water with time, as the solvent isotopically equilibrates with the *trans* and *cis* waters of the complex ion.

For the reactions [D-1] and [D-2] let:

t = time

a = $[0] + [^*0]$ in solvent water = $[\text{H}_2\text{O}] + [\text{H}_2^*\text{O}]$

b = $[0] + [^*0]$ in *cis* positions of complex ion

$$= 4\{[\text{CrX}(\text{cis-H}_2\text{O})_4(\text{trans-H}_2\text{O})^{2+}] +$$

$$[\text{CrX}(\text{cis-H}_2\text{O})_4(\text{trans-H}_2^*\text{O})^{2+}] +$$

$$[\text{CrX}(\text{cis-H}_2\text{O})_3(\text{cis-H}_2^*\text{O})(\text{trans-H}_2\text{O})^{2+}]\}$$

$$c = [0] + [*0] \text{ in trans position of complex ion}$$

$$= \{[\text{CrX}(\text{cis-H}_2\text{O})_4(\text{trans-H}_2\text{O})^{2+}] +$$

$$[\text{CrX}(\text{cis-H}_2\text{O})_4(\text{trans-H}_2^*\text{O})^{2+}] +$$

$$[\text{CrX}(\text{cis-H}_2\text{O})_3(\text{cis-H}_2^*\text{O})(\text{trans-H}_2\text{O})^{2+}]\}$$

$$x = [*0] \text{ in solvent water at "t time"}$$

$$y = [*0] \text{ in cis positions of complex ion at "t time"}$$

$$= [\text{CrX}(\text{cis-H}_2\text{O})_3(\text{cis-H}_2^*\text{O})(\text{trans-H}_2\text{O})^{2+}]$$

$$z = [*0] \text{ in trans position of complex ion at "t time"}$$

$$[\text{CrX}(\text{cis-H}_2\text{O})_4(\text{trans-H}_2^*\text{O})^{2+}]$$

Inherent in the concentration expressions above are two assumptions: (1) since oxygen-18 enrichment of the water is low (5-fold), the amount of double-labeling is negligibly small, (2) there is no isotopic discrimination.

From above

$$a - x = [0] \text{ in solvent water}$$

$$b - y = [0] \text{ in cis positions of complex ion}$$

$$c - z = [0] \text{ in trans position of complex ion}$$

Since fractionation is assumed absent, at equilibrium ("infinite time") the distribution of isotopes is completely random, *i.e.*, the fractional oxygen-18 content is equal in all species, or

$$x_{\infty}/a = y_{\infty}/b = z_{\infty}/c \quad [D-3]$$

Since the total oxygen-18 content of the system remains constant

$$x_0 + y_0 + z_0 = x + y + z = x_{\infty} + y_{\infty} + z_{\infty} \quad [D-4]$$

The equations for the rates of water exchange at *cis* and *trans* positions can now be developed.

Let R_{cis} be the constant rate of exchange of oxygen in *cis* positions with oxygen in solvent water in a pseudo-first-order process. When enriched solvent is added to the system, the rate of enrichment in *cis* positions, dy/dt , is equal to the rate of appearance of oxygen-18 in those positions minus the rate of disappearance of oxygen-18 from those positions. The rate of appearance is given by the expression

$$R_{cis} \cdot x/a \cdot (b-y)/b$$

where x/a is the fraction of the forward reaction occurring with oxygen-18 in H_2^*O and $(b-y)/b$ is the fraction of the forward reaction occurring with oxygen-16 (and oxygen-17) in the unlabeled *cis* positions. The rate of disappearance is

$$R_{cis} \cdot y/b \cdot (a-x)/a$$

where y/b is the fraction of the reverse reaction occurring with labeled *cis* positions and $(a-x)/a$ is the fraction of reverse reaction occurring with oxygen-16 (and oxygen-17) in H_2O .

Thus

$$dy/dt = [R_{cis} \cdot x/a \cdot (b-y)/b] - [R_{cis} \cdot y/b \cdot (a-x)/a]$$

or

$$dy/dt = R_{cis}/ab \cdot (bx-ay) \quad [D-5]$$

Similarly, the rate of enrichment in the *trans* position

$$dz/dt = [R_{trans} \cdot x/a \cdot (c-z)/c] - [R_{trans} \cdot z/c \cdot (a-x)/a]$$

or

$$dz/dt = R_{trans}/ac \cdot (cx-az) \quad [D-6]$$

where R_{trans} is the constant rate of exchange of the *trans* oxygen in the complex with solvent water oxygen.

Since x is a function of both y and z , the complete solution of the simultaneous differential equations [D-5] and [D-6] is complex. However, a limiting condition, which was employed in the experiments, simplifies the solution by allowing separate integrations of eq [D-5] and [D-6]. The condition is the essential constancy of x ; on complete exchange the value of x had altered by only ca. 10%, whereas y and z had undergone changes of ca. 400%. This permits the following approximations: (a) for *cis* exchange, the depletion of x by *trans* exchange is ignored, (b) for *trans* exchange, the depletion of x by *cis* exchange is disregarded. This is simply a restatement of the initial premise; the two exchange processes are independent of each other. This "independence" has been experimentally attained by using a large reservoir of oxygen-18 so that x underwent virtually no change in the over-all process.

Solving for x from eq [D-3] and eq [D-4]

$$x_{\infty} = (a/b)y_{\infty} = (a/c)z_{\infty}$$

and

$$x = x_{\infty} + y_{\infty} + z_{\infty} - y - z$$

Applying the above approximations, for *cis* exchange

$$x = (a/b)y_{\infty} + y_{\infty} - y = [(a+b)/b]y_{\infty} - y \quad [D-7]$$

and for *trans* exchange

$$x = (c/a)z_{\infty} + z_{\infty} - z = [(a+c)/c]z_{\infty} - z \quad [D-8]$$

By substituting eq [D-7] in eq [D-5] and separating the variables, the rate equation for *cis* water exchange becomes

$$dy/(y_{\infty}-y) = R_{cis} \cdot (a+b)/ab \cdot dt \quad [D-9]$$

Integrating eq [D-9] between the limits $y = y_0$ at $t = 0$ and $y = y_t$ at $t = t$ gives

$$\ln [(y_{\infty}-y_t)/(y_{\infty}-y_0)] = R_{cis} \cdot (a+b)/ab \cdot t$$

or

$$1 - F_{cis} = \exp [-R_{cis} \cdot (a+b)/ab \cdot t] \quad [D-10]$$

where

$$F_{cis} = (y_t - y_0)/(y_{\infty} - y_0)$$

For the pseudo-first-order exchange

$$R_{cis} = k_{cis} \cdot b$$

Therefore eq [D-10] becomes

$$F_{cis} = 1 - \exp [-k_{cis} \cdot (a+b)/a \cdot t] \quad [D-11]$$

Similarly, after substituting eq [D-8] in eq [D-6] and realizing

$$R_{trans} = k_{trans} \cdot c$$

for *trans* water exchange

$$F_{trans} = 1 - \exp [-k_{trans} \cdot (a+c)/a \cdot t] \quad [D-12]$$

The relative contributions of *cis* and *trans* exchange to the total fraction exchange, *F*, is 4:1, *i.e.*, the ratio of sites available for exchange. Thus

$$F = 1/5 (4 F_{cis} + F_{trans}) \quad [D-13]$$

where 1/5 is the normalizing factor.

Substituting 4*c* for *b* and eq [D-11] and [D-12] in eq [D-13], gives upon rearrangement

$$1 - F = 0.8 \exp [-k_{cis} \cdot (a+4c)/a \cdot t] + 0.2 \exp [-k_{trans} \cdot (a+c)/a \cdot t] \quad [D-14]$$

The rate of exchange was followed by sampling the solvent water as its fractional oxygen-18 content decreased, *i.e.*, measuring the fraction unexchanged (1-*F*) where

$$1 - F = (x_t - x_\infty)/(x_0 - x_\infty) = (N_t - N_\infty)/(N_0 - N_\infty)$$

since *x*₀, *x*_t, and *x*_∞ are proportional to the *N*₀, *N*_t, and *N*_∞ values calculated from the mass spectrometric data.

E. Computation of Rate Constants, Activation Parameters, and Associated Random Errors

Rate Constants.—The two first-order rate constants, k_{trans} and k_{cis} , were calculated by substituting experimental data in the rate expression derived in the previous section, eq [D-14]. A non-linear, weighted least squares computer program facilitated calculations. The program found values for the two parameters which gave the best fit of experimental data to the derived equation. The program source list of the subroutines encoded for this particular problem is located in Appendix B.

Since the program required trial values for the parameters, an approximate value for k_{cis} was determined graphically from the limiting linear portion of the McKay plot, and k_{trans} was estimated to be ten times k_{cis} .

Tables II-IV contain the experimental data used in the program. The approximate value 55.0 *M* was substituted for a , the concentration of solvent water. The rate constants were little affected by approximating a , since the ratios $(a+c)/a$ and $(a+4c)/a$, where c is the concentration of the complex ion, were close to unity. In a trial run, a ten per cent change in c produced a negligible change in the rate constants. Division of the computed parameter values by 3600 sec/hr converted them to the approved time notation for rate constants, sec^{-1} .

The program also generated a curve based on the "best fit" values of the parameters. The solid lines in

TABLE II

MONOCHLOROPENTAAQUOCHROMIUM(III) IONSOLVENT WATER EXCHANGE

A. Temperature: 25°C

Run C1-1, 0.73 M CrCl^{2+}

Time, hr	(1-F)
0.000	1.000
0.983	0.997
1.875	0.977
4.100	0.925
6.033	0.899
8.975	0.854
11.925	0.828
24.075	0.717
36.017	0.647
62.900	0.543
84.283	0.395
120.283	0.330
155.942	0.247
541.833	0.000

Run C1-2, 0.99 M CrCl^{2+}

Time, hr	(1-F)
0.000	1.000
0.817	0.965
1.858	0.924
3.800	0.887
5.900	0.853
9.067	0.797
11.858	0.748
23.850	0.642
36.283	0.576
59.967	0.438
83.592	0.363
119.608	0.248
156.917	0.201
518.483	0.000

Run C1-3, 1.25 M CrCl^{2+}

0.000	1.000
0.900	0.987
1.850	0.964
3.725	0.910
5.992	0.875
8.767	0.815
11.950	0.760
23.733	0.638
36.200	0.540
59.792	0.403
83.800	0.307
120.117	0.208
156.900	0.134
559.767	0.000

Run C1-4, 1.42 M CrCl^{2+}

0.000	1.000
1.092	0.973
1.975	0.933
4.042	0.951
7.075	0.810
9.058	0.781
12.133	0.718
23.567	0.582
35.575	0.497
60.350	0.336
85.675	0.253
121.817	0.177
154.933	0.117
514.100	0.000

TABLE II - *Continued*Run C1-5, 1.53 M CrCl^{2+}

Time, hr	(1-F)
0.000	1.000
0.875	0.957
1.817	0.923
5.042	0.825
7.492	0.771
11.675	0.695
14.658	0.654
26.250	0.544
35.500	0.475
60.533	0.326
83.825	0.242
120.158	0.152
155.717	0.104
553.183	0.000

TABLE II - *Continued*

B. Temperature: 15°C

Run Cl-6, 1.25 M CrCl^{2+}

Time, hr	(1-F)
0.000	1.000
4.967	0.974
10.033	0.951
15.058	0.919
19.983	0.886
24.967	0.860
29.983	0.837
45.125	0.778
60.058	0.728
74.958	0.686
91.175	0.650
109.517	0.609
121.267	0.581
530.608	0.000

C. Temperature: 5°C

Run Cl-7, 1.29 M CrCl^{2+}

0.000	1.000
30.617	0.985
59.183	0.953
103.108	0.906
126.008	0.875
148.275	0.856
173.317	0.826
380.050	0.713
714.750	0.458
1,505.442	0.376
1,637.233	0.334
2,590.075	0.000

TABLE III

ISOTHIOCYANATOPENTAAQUOCHROMIUM(III) IONSOLVENT WATER EXCHANGE

A. Temperature: 25°C

Run NCS-1, 1.04 M CrNCS ²⁺		Run NCS-2, 1.12 M CrNCS ²⁺	
Time, hr	(1-F)	Time, hr	(1-F)
0.000	1.000	0.000	1.000
1.283	0.963	1.108	0.974
2.592	0.938	2.400	0.954
3.658	0.923	4.317	0.925
7.508	0.863	9.075	0.826
10.725	0.779	12.583	0.795
21.308	0.696	21.733	0.666
28.158	0.619	27.883	0.630
34.342	0.572	35.033	0.556
48.283	0.481	47.542	0.479
67.725	0.363	69.092	0.368
99.850	0.250	98.925	0.256
129.492	0.178	133.958	0.165
507.867	0.000	507.942	0.000

Run NCS-3, 1.32 M CrNCS²⁺

Time, hr	(1-F)
0.000	1.000
1.100	0.974
2.233	0.951
4.633	0.897
8.700	0.841
12.283	0.783
21.267	0.677
28.017	0.593
36.133	0.524
51.067	0.408
70.067	0.326
102.983	0.224
132.050	0.166
521.642	0.000

TABLE III - *Continued*

B. Temperature: 15°C

Run NCS-4, 1.02 M CrNCS²⁺

Time, hr	(1-F)
0.000	1.000
8.992	0.948
19.175	0.911
29.083	0.863
39.267	0.833
49.125	0.809
59.092	0.775
69.408	0.758
79.200	0.710
91.150	0.705
101.133	0.670
109.733	0.605
124.375	0.616
531.183	0.000

C. Temperature: 5°C

Run NCS-5, 1.13 M CrNCS²⁺

0.000	1.000
27.083	1.009
97.417	0.956
121.442	0.929
143.858	0.916
169.425	0.859
374.258	0.758
713.658	0.591
1,649.625	0.338
2,579.975	0.000

TABLE IV

BROMOPENTAAQUOCHROMIUM(III) IONSOLVENT WATER EXCHANGE

A. Temperature: 25°C

Run Br-1, 0.75 M CrBr^{2+}

Time, hr	(1-F)
0.000	1.000
0.642	0.931
1.233	0.979
1.750	0.912
2.217	0.911
3.325	0.890
5.083	0.892
8.600	0.848
12.300	0.809
24.342	0.744
37.333	0.630
61.708	0.433
73.558	0.369
84.067	0.335
554.200	0.000

Run Br-2, 0.97 M CrBr^{2+}

0.000	1.000
0.617	0.966
1.142	0.943
1.642	0.965
2.183	0.923
3.708	0.941
5.242	0.855
9.925	1.925
21.942	0.656
25.675	0.705
31.325	0.578
36.308	0.564
46.033	0.471
59.417	0.384
504.017	0.000

Figures 1 and 2 represent such a generation, whereas the circles denote the experimental points. The closeness of fit of experimental data to the derived equation, as illustrated in these plots, supported the assumptions about the exchange process.

Random Errors in Rate Constants.—Since no duplicate runs were made, random errors in the calculated rate constants had to be estimated. Common error treatment (24), using the precision limits of the experimental measurements, permitted approximation of errors in the calculated values.

The error in N_t , $\sigma(N_t)$, is the square root of the variance of N_t , $\sigma^2(N_t)$, where

$$\sigma^2(N_t) = (\delta N_t / \delta K)^2 \cdot \sigma^2(K) + (\delta N_t / \delta R_e)^2 \cdot \sigma^2(R_e) + (\delta N_t / \delta R_o)^2 \cdot \sigma^2(R_o) + [\delta N_t / \delta (b/a)]^2 \cdot \sigma^2(b/a) \quad [E-1]$$

In eq [E-1], the partial derivatives are obtained by operating on the Dostrovsky and Klein equation (20)

$$N_t = [R_e / (K + R_e)] + (b/a) \cdot \{[2R_e / (2 + R_e)] - [2R_o / (2 + R_o)]\}$$

The variances, $\sigma^2(K)$, $\sigma^2(R_e)$, $\sigma^2(R_o)$, and $\sigma^2(b/a)$, were obtained by squaring estimated errors in the parameters.

The error in K , the equilibrium constant for isotopic equilibration of water and carbon dioxide, was calculated from the Hunt equation (25)

$$K_\theta = K_{25} \cdot [1 + 0.0002(25 - \theta)]$$

where

θ = temperature in $^{\circ}\text{C}$

$K_{25} = K$ at $25^{\circ}\text{C} = 2.078$

by assuming an extreme variation in room temperature of $\pm 5^{\circ}\text{C}$.

The error in the mass spectrometric ratio reading was estimated at $\pm 0.05\%$. Thus $\sigma^2(R_e)$ and $\sigma^2(R_o)$ were calculated as $(.0005 R_e)^2$ and $(.0005 R_o)^2$, respectively.

The variance of b/a is a function of the variances of the factors involved in the quotient. Since

$$b/a = (\text{g CO}_2/\text{M.W. CO}_2) \div (\text{g H}_2\text{O}/\text{M.W. H}_2\text{O}) = (w/w') \cdot Q$$

where

M.W. = molecular weight

w = weight of carbon dioxide used in equilibration

w' = weight of water sample

Q = molecular weight ratio $\text{CO}_2:\text{H}_2\text{O}$

then

$$\sigma^2(b/a) = [\delta(b/a)/\delta w]^2 \cdot \sigma^2(w) + [\delta(b/a)/\delta w']^2 \cdot \sigma^2(w') + [\delta(b/a)/\delta Q]^2 \cdot \sigma^2(Q)$$

where

$\sigma^2(w)$ = square of error in weight of carbon dioxide

$\sigma^2(w')$ = square of error in weight of water sample

$\sigma^2(Q)$ = square of error in molecular weight ratio

Two sources provide the main error in the weight of carbon dioxide. An error of ± 0.2 mg, equal to the precision in weighing, was incurred in the calibration of the manometer

used to meter out carbon dioxide samples. Because of fluctuations about the calibration temperature, the mmoles of gas measured at constant volume and constant pressure varied. Assuming a temperature variation of $\pm 5^\circ\text{C}$ and ideal gas behavior of carbon dioxide, a error of *ca.* 0.1 mg is introduced.

Error in water sample weights was considered to be that incurred in weighing, *i.e.*, ± 0.2 mg.

The error in the molecular weight ratio is obtained from the variance

$$\sigma^2(Q) = (\delta Q/\delta P)^2 \cdot \sigma^2(P) + (\delta Q/\delta P')^2 \cdot \sigma^2(P')$$

where

$\sigma^2(P)$ = variance of molecular weight of carbon dioxide

$\sigma^2(P')$ = variance of molecular weight of water

For both water and carbon dioxide, errors in molecular weight originate from atomic weight error and enrichment. Enrichment to about 1 atom % in ^{18}O and 0.08 atom % in ^{17}O gave differences of *ca.* 0.1% between molecular weights for normal and enriched species.

The above error analysis, incorporated in the program used to calculate N_t (Appendix B), gave a computed error in N_t of about 0.1%.

Similarly, for $(1-F)$

$$\begin{aligned} \sigma^2(1-F) = & [\delta(1-F)/\delta N_t]^2 \cdot \sigma^2(N_t) + \\ & [\delta(1-F)/\delta N_o]^2 \cdot \sigma^2(N_o) \quad [\delta(1-F)/\delta N_\infty]^2 \cdot \sigma^2(N_\infty) \end{aligned}$$

where the partial derivatives are obtained from eq [C-1] and

the variances of N_o , N_t , and N_∞ are those previously calculated. Following evaluation of $\sigma(1-F)$, the computer program provided two sets of values: $[(1-F) + \sigma(1-F)]$ and $[(1-F) - \sigma(1-F)]$. These sets were used in the best fit program to calculate "new" values for the rate constants. The errors in k_{cis} and k_{trans} were considered to be the average differences between these "new" rate constants and those previously calculated. This approach was chosen because the small difference in magnitude of the rate constants precluded assignment of appropriate contributions to their interdependent errors.

Table V presents the rate constants at 25°C with their estimated errors. Also included are original and recalculated data for iodopentaaquochromium(III) ion.

Activation Parameters.—In Table VI are found exchange rate constants for chloro- and isothiocyanato-complexes for runs at 25, 15, and 5°C obtained under similar experimental conditions. This temperature dependence data enabled calculation of enthalpies and entropies of activation for interchange of *cis* and *trans* waters with solvent.

According to transition-state theory, a rate constant may be expressed as a function of activation parameters, *i.e.*,

$$k' = \kappa \cdot kT/h \cdot \exp(\Delta S^*/R) \cdot \exp(-\Delta H^*/RT) \quad [E-2]$$

where

k' = reaction rate constant

κ = transmission coefficient

TABLE V
ACIDOPENTAQUOCHROMIUM(III) ION — SOLVENT WATER EXCHANGE

RATE CONSTANTS at 25°C						
Run	$[\text{CrX}^{2+}]^a$ <i>M</i>	$[\text{HClO}_4]$, <i>M</i>	I^b , <i>M</i>	$[\text{ClO}_4^-]$, <i>M</i>	$k_{\text{trans}} \times 10^6$, sec^{-1}	$k_{\text{cis}} \times 10^6$, sec^{-1}
NCS-1	1.04	1.17	4.29	3.25	16. ± 2.	3.0 ± 0.2
NCS-2	1.12	1.04	4.39	3.27	15. ± 2.	3.0 ± 0.1
NCS-3	1.32	0.98	4.94	3.62	19. ± 2.	3.1 ± 0.1
Cl-1	0.73	1.02	3.19	2.47	15. ± 6.	2.0 ± 0.2
Cl-2	0.99	1.31	4.28	3.29	39. ± 11.	2.4 ± 0.1
Cl-3	1.25	1.01	4.75	3.50	24. ± 4.	2.9 ± 0.2
Cl-4	1.42	1.45	5.70	4.28	33. ± 4.	3.2 ± 0.2
Cl-5	1.53	1.18	5.77	4.24	55. ± 8.	3.4 ± 0.2
Br-1	0.75	1.22	3.47	2.72	—	2.9 ± 0.1
Br-2	0.97	1.62	4.52	3.56	—	3.0 ± 0.6
I ^c	0.40	1.00	2.6	1.00 ^d	270. (260.) ^e	3.1 — 84.) ^e

^a $\text{CrX}^{2+} = \text{CrX}(\text{H}_2\text{O})_5^{2+}$; X = Cl, Br, NCS, or I. ^b I = ionic strength.

^c Reference 7. ^d $[\text{SO}_4^{2-}] = 0.4 \text{ M}$. ^e Calculated using data from Reference 7.

TABLE VI
CHLORO- and ISOTHIOCYANATOCHROMIUM(III) IONS — SOLVENT WATER EXCHANGE

RATE CONSTANTS at 25, 15, and 5°C						
Run	Temp, °C	$[\text{CrX}^{2+}]^a$, <i>M</i>	$[\text{HClO}_4]$, <i>M</i>	I^b , <i>M</i>	$[\text{ClO}_4^-]$, <i>M</i>	$k_{trans} \times 10^6$, $k_{cis} \times 10^6$, <i>sec</i> ⁻¹
Cl-3	24.78	1.25	1.01	4.75	3.50	24. ± 4.
Cl-6	14.86	1.25	1.19	4.93	3.69	5.8 ± 1.2
Cl-7	4.99	1.29	1.20	5.07	3.98	0.93 ± 0.20
NCS-2	24.78	1.12	1.04	4.39	3.27	15. ± 2.
NCS-4	14.86	1.02	0.74	3.80	2.78	3.3 ± 1.3
NCS-5	4.99	1.13	1.01	4.39	3.26	0.46 ± 0.09
						3.0 ± 0.1
						0.73 ± 0.06
						0.140 ± 0.002

a, b See corresponding footnotes in Table V.

k = Boltzmann constant = 1.3805×10^{-16} erg/°K

T = absolute temperature in °K

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

R = gas constant = 1.9872 cal °K⁻¹ mole⁻¹

ΔS^* = entropy of activation in eu

ΔH^* = enthalpy of activation in cal/mole

Transformations of eq [E-2] give

$$\log (k'/T \cdot h/k) = (\Delta S^*/2.303R) - (\Delta H^*/2.303R) \cdot 1/T \quad [E-3]$$

and

$$T \cdot \log (k'/T \cdot h/k) = (\Delta S^*/2.303R) \cdot T - (\Delta H^*/2.303R) \quad [E-4]$$

Inspection of eq [E-3] shows that a plot of $\log (k'/T \cdot h/k)$ versus $1/T$, if linear, has a slope equal to $-\Delta H^*/2.303R$. It is readily apparent from Figure 3, which contains plots of data from Table VI, that ΔH^* for *cis* water exchange is virtually the same for both complexes, whereas ΔH^* for *trans* water exchange is greater for the isothiocyanato-complex than for the chloro-complex.

Figure 4 depicts plots of $T \cdot \log (k'/T \cdot h/k)$ versus T for the data from Table VI. cursory examination of Figure 4 indicates the slopes, which equal $\Delta S^*/2.303R$, are in effect identical for *cis* water exchange, whereas ΔS^* of *trans* water exchange is evidently larger for the isothiocyanato-ion than for the chloro-ion.

In Figures 3 and 4, the best straight lines and slopes were obtained from least squares analysis of each set of three points.

Figure 4

ENTROPY of ACTIVATION for WATER EXCHANGE

Benson (26) presents an equation which allows an estimate of error in energy of activation. Since activation energy and enthalpy of activation are essentially equivalent the equation becomes

$$[\sigma^2(\Delta H^*)]^{1/2} = \pm \frac{\text{highest temp}}{\text{temp interval}} \cdot \frac{r}{18} \text{ per cent} \quad [\text{E-5}]$$

where r is equal to per cent error in the rate constants used in calculating ΔH^* . This equation is valid providing $E/RT \approx 35$. For these experiments

$$\sigma(\Delta H^*) = (297.94/20) \cdot (r/18) \text{ per cent}$$

where r is taken as average per cent error in the rate constants. For example, the average per cent error in the rate constants is 20% for *trans* exchange in the chlorochromium (III) ion. Thus

$$\sigma(\Delta H^*) = \pm 16.6\% = \pm 4 \text{ kcal/mole}$$

The error in entropy of activation was that obtained from least squares analysis.

Table VII lists a summary of the activation parameters with estimated errors. It also includes comparable values for water exchange reactions of other complex ions of interest.

F. Effect of Systematic Errors on Rate Constants

"Zero Time" Exchange.—Although it was usually obtained in much less time, the "zero time" sample may have

TABLE VII

ACTIVATION PARAMETERS for *trans* and *cis* WATER EXCHANGE

Complex	ΔH^* , kcal/mole		ΔS^* , eu	
	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>
CrNCS^{2+a}	29. $\pm$ 4.	24.9 $\pm$ 1.0	15. $\pm$ 6.	-0.3 $\pm$ 2.4
CrCl^{2+a}	26. $\pm$ 4.	25.1 $\pm$ 0.7	9. $\pm$ 5.	0.2 $\pm$ 3.5
$\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+b}$	22. $\pm$ 4.	—	-4. $\pm$ 14.	—
Cr^{3+c}	—	26. $\pm$ 1.0	—	-0.4
$\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+d}$	25.9 $\pm$ 0.5	—	4.4 $\pm$ 1.6	—

^a This work. ^b Calculated from data in Reference 27. ^c Reference 28.
^d Calculated from data in Reference 29.

been taken up to ten minutes after mixing enriched water and solute. This delay, which corresponds to exchange of about one-tenth of a water molecule for chloro- and isothiocyanato-complexes, may be partly responsible for inconsistencies and low precision in the k_{trans} values. A similar delay for the bromo-complex means roughly 30% of the *trans* water will have exchanged before an initial sample is taken, if k_{trans} is assumed to be 10^{-4} sec^{-1} . The discrepant experimental data preclude reporting a reasonable value of k_{trans} for the bromo-ion.

Fractionation upon Distillation.—Hunt and Taube (30) have shown that there may be as much as 1% fractionation of oxygen isotopes upon vacuum distillation of water from concentrated salt solutions. To minimize this effect on N_t , a standard sampling procedure was developed in this study. For each sample, controlled distillation removed about 30% of the water in the aliquot.

Control of Concentration Factors.—Obtaining the complex perchlorate in a suitable form posed a main experimental difficulty. In each preparation, not all of the perchloric acid could be removed by vacuum evaporation. A saturated solution of complex in perchloric acid is a more apt description of the wet crystals of prepared complex. As a result, solutions of exactly known concentrations of complex and perchloric acid could not be prepared. This hindered control of ionic strength and acid concentration. Although a known amount of acid was added to each solution, undetermined residues of perchloric acid help account for the di-

verse acid concentrations. Under these circumstances, the ionic strength was not adjusted.

What effects did the above concentration factors have on the rate constants? Scrutiny of Table III reveals certain trends. Increases in concentrations of complex ion and perchlorate ion, as well as ionic strength, parallel increases in both k_{trans} and k_{cis} . In all cases, except k_{trans} for the chloro-complex, the rates are directly proportional to each of these factors. Compared to the chloro-complex, effects on the isothiocyanato-complex appear to be somewhat less. The k_{trans} value for the chloro-ion approximately quadruples for a doubling of all three factors. Since the ionic strength and perchlorate ion concentration are functions of the complex concentration, the dependence of the rate on any particular factor cannot be resolved on the basis of the data presented here.

At high concentrations of complex, an apparent rate dependence on anion concentration and ionic strength is found for solvent water exchange with hexaaquochromium(III) ion (31). These same factors may account for the rate variation found here, although k_{trans} for the chloro-complex appears markedly dependent. In any case, it does seem reasonable to conclude that total salt concentration directly affects the exchange rate constants.

Aquation.—Quite another type of systematic error encountered in these systems is aquation. The *cis* water exchange and aquation rates for the three complexes appear in

Table VIII. Using expressions in the literature, the aquation rate constants were calculated for solutions one molar in hydrogen ion.

TABLE VIII

cis WATER EXCHANGE and AQUATION RATES for CrX^{2+} at 25°C

Complex	$k_{cis} \times 10^6,$ sec ⁻¹	$k_{aq}^a \times 10^6,$ sec ⁻¹
CrNCS ²⁺	3.0	0.0090 ^b
CrCl ²⁺	2.9	0.31 ^c
CrBr ²⁺	3.0	5.0 ^d

^a k_{aq} = aquation rate constant. ^b Reference 32.

^c Reference 17. ^d Extrapolated from data in Reference 33.

In exchange experiments at 25°C with the chloro- and isothiocyanato-complexes, the penultimate sample was removed about 120 hr after "zero time." The hydrolytic decomposition of these complexes, to the less rapidly exchanging aquo-ion, amounts to ca. 0.4% and ca. 13%, respectively for this time interval. Since the percentages represent the upper limit of aquation, the fraction exchange measured for the samples will be little affected. The McKay plots bear this out, since the later portions exhibit excellent linearity. The formation of a large amount of aquo-ion would tend to

curve the plot downward as exchange progresses.

The penultimate sample in bromo-ion exchange was taken approximately 60 hr after "zero time." Decomposition by aquation over this period amounts to *ca.* 66%. A significant amount of aquo-ion in the solution during much of the exchange will certainly affect the rate constants. Since the McKay plots are somewhat irregular, a trend downward is not detectable. The early points, for which aquation is less important, are favored by weighting in the best fit computer program. Therefore, the computed k_{cis} value may not be low. Although the closeness of fit of data to the derived equation was less (*ca.* 10% deviation) than for the other complexes (*ca.* 2-3% deviation), the very similar values for the two runs indicate that k_{cis} is probably valid to $\pm 20\%$.

Certainly aquation should not prevent determination of k_{trans} for the bromo-complex, since only a few percent decomposition would occur during the sampling time required to cover *trans* exchange. The "zero time" sampling is believed to be the more critical aspect of the experimental problem in this case.

G. Discussion

The ensuing discussion focuses on data in Tables V and VII. After establishing the *trans* effect in the complexes studied, their relative values are compared, the relative *cis* exchange rates are considered, and suitable models for these observations are proposed.

trans Effect in Complex Ion.—The criterion chosen for demonstrating a *trans* effect in a complex ion is the ratio of exchange rate constants, $k_{trans}:k_{cis}$. The intrinsic advantage of this measure is that both rates were determined simultaneously in exactly the same environment on the identical group of molecules. Therefore, within limits of the systematic errors previously discussed, the ratio for a particular kinetic run is completely independent of variations in: (a) concentration of complex ion, (b) ionic strength, (c) perchlorate ion concentration.

For Run C1-1, the ratio of $k_{trans}:k_{cis}$ is *ca.* 8, *i.e.*, *trans* water exchanges with solvent water eight times as fast as *cis* waters of chloropentaaquochromium(III) ion, under the particular conditions of the kinetic experiment. This means that chloride ion, as a ligand replacing water in the first coordination sphere of chromium(III) ion, exerts a significant labilizing influence on the neutral water ligand *trans* to itself in the octahedral structure.

Despite variations, an estimate of the *trans* effect for these experiments can be obtained by averaging the ratios. The average $k_{trans}:k_{cis}$ value for chlorochromium(III) ion is 12. For purposes of discussion, this value is considered the *trans*-labilizing factor of chloride ligand on water exchange (at 25°C).

Application of the same approach to isothiocyanatopentaaquochromium(III) ion yields a *trans*-labilizing factor of 5.5 for isothiocyanate ligand (at 25°C).

Lack of sufficiently precise data for k_{trans} precludes calculation of a *trans* effect factor for bromopentaaquochromium(III) ion. Experimental observations and an accurate case of predilection, however, prompt guessing a value. It probably is twice that for chloride, *i.e.*, *ca.* 25.

To derive the *trans*-labilizing influence of iodide in iodopentaaquochromium(III) ion, the data of Moore, Basolo, and Pearson (7) were reevaluated. The recalculation, based on the presumption that *cis* water exchange occurs at the same rate observed for the other complexes, gave values cited in Table V. From these the *trans* effect factor is found to be 84.

These factors, derived from experimental observations, confirm existence of a *trans* effect in chromium (III) complexes.

Why is k_{trans} greater than k_{cis} ? Table VII may throw light on some reasons for differences in the rate constants. Relative values of the activation parameters also may lead to a reasonable model for these exchange reactions.

The difference in enthalpies of activation does not cause k_{trans} to be greater than k_{cis} ; The relative ΔH^* values indicate the opposite order of exchange rates is expected, for both chloro- and isothiocyanato-complexes. A large, positive entropy of activation for the *trans* exchange process, in contrast to a zero entropy of activation for the *cis* process, counteracts the enthalpic reversal of rate constants. Interestingly, in a comparison of *trans* rates for chloro- and

isothiocyanato-complexes, a larger entropy of activation partially compensates the larger enthalpy of activation for the isothiocyanato-complex.

Since the rate differences appear to arise from entropy differences, an argument based on the significance of entropy of activation, similar to that advanced by Hunt and Taube (29), may be useful.

If a solvent water molecule becomes bound to the complex ion to form a seven-coordinated species in the transition state, a negative entropy of activation is implied. This assumes the reasonably correct values for the entropies of bound water and solvent water (9.4 and 16.7 eu, respectively) (34), from which the formation entropy of such an activated complex is calculated as -7.3 eu. Although approximate, the value does indicate the direction and magnitude of the entropy associated with such a mechanism.

For complete bond fissure in the activated complex, ΔS^* would be +7.3 eu. The positive experimental ΔS^* values for the *trans* process certainly are of this order of magnitude. This indicates that bond breaking, or at least considerable bond stretching, is critical in exchange of the *trans* water. However, as Stranks (35) points out, it may be unreasonable to press one mechanism in preference to the other when the water molecules in the second coordination sphere are at distances approaching those of chemical bonding. This solitary piece of evidence does not prove the second proposal.

Another observation that must be accounted for is

the large increase in k_{trans} as the total salt concentration increases. Although the data do not distinguish the influences of the various factors on the rate, it does not seem unreasonable to assume a rather strong rate dependence on the concentration of the perchlorate ion. The reason for this obvious analogy to the water exchange studies on hexaaquo-chromium(III) ion (31) may become clear below.

In all experiments, concentration of perchlorate ion was about three times that of complex ion. Although no evidence is offered here for the presence of ion pairs in these concentrated salt solutions, the phenomenon of ion pairing is not uncommon. With a preponderance of perchlorate ions, it seems justified to suggest that ion pairing is an important aspect of the solution structure and therefore may play an essential part in the water exchange process. The role of the ion pair may not be unambiguous; a reasonable description will be attempted, however.

The presence of negative ions (restricted to ClO_4^- in these experiments) in the vicinity of the second coordination sphere of the dipositive acidopentaaquochromium(III) species is very probable. There are restrictions as to which "end" of the complex ion will provide the best sites for ion pairing. Bulkiness of the X^- ligand, where X^- is NCS^- , Cl^- , Br^- , or I^- , and its electronegative character will repel the close approach of the large, negative ClO_4^- ion toward its position. The X^- group also produces a small dipole in the complex, resulting in a more positive end in the position

trans to X^- . The more probable orientation for the perchlorate ion will be near the *trans* water site.

The mechanism of anion assistance becomes quite speculative. Hydration waters of perchlorate ion, which are presumably hydrogen-bonded to the anionic oxygens, exchange rapidly. In the ion pair, ligand water may become part of the hydration sphere of perchlorate ion; the interaction energy causes the bond to the central chromium atom to weaken and stretch. After the chromium-to-oxygen bond breaks, nearby water may rapidly replace it. This nearby water may have been part of the hydration sphere of the anion. The closeness of the hydration waters of the perchlorate ion suggests the possibility of partial bond formation of such a water to the chromium nucleus, accompanied by rapid expulsion of a ligand water.

Up to this point in the discussion, attention has been directed to *trans* water exchange. The question now arises: how do *cis* waters exchange? Since *cis* exchange rates are slower than *trans* exchange rates, apparently the zero entropies of activation counteract the lower enthalpies of activation. Although k_{cis} is affected to about half the extent by perchlorate ion as k_{trans} , the large perchlorate ion certainly provides some assistance in *cis* water exchange. Arguments similar to those used above make stressing one or the other mechanism unjustified. Nevertheless, some contrasts to the *trans* process are evident. The approximately zero values for ΔS^* reduce the significance of bond breaking in

the transition state. If partial bond formation is important, the interaction energy must be very weak since a zero entropy indicates no difference between solvent water and bound water in the activated complex. The proximity of the perchlorate ion may provide paths for an intermediate type mechanism for *cis* exchange. In any case, the negative ligand likely prevents ion-pair formation and solvent water attack at *cis* positions from the direction of X^- . In terms of collision theory, *cis* exchange has a lower steric factor than *trans* exchange.

Relative *trans* Effects.—Comparison of the *trans*-labilizing factors calculated above indicates the following series of ligands in order of decreasing *trans* effect on water exchange in chromium(III) complexes:

Bromide ion is included on speculation. The position of water in the series is based on a *trans*-labilizing factor of 1, since all waters in hexaquo chromium(III) ion exchange at the same rate.

The above series could also have been developed by comparison of k_{trans} at 25°C. The advantage of this alternate approach is the possibility of adding to the series independently of *cis* rates. A case in point is the position of the ligand ammonia. The recent data of Duffy and Earley (27) on water exchange of aquopentaamminechromium(III) ion contain the supposed *trans*-labilizing influence of ammonia on water.

For the tripositive ion, the water exchange rate constant, k_{ex} , was found by extrapolation to 25°C to be *ca.* $70 \times 10^{-6} \text{ sec}^{-1}$. For comparing this exchange to that in dipositive complexes, the rate should be increased by about a factor of four. This factor is based on results of the effect of charge on exchange rate (section H). Thus, for ammonia k_{trans} is $280 \times 10^{-6} \text{ sec}^{-1}$. This places ammonia *before* iodide in the *trans* effect series! This puzzling result suggests the rate constants reported for this chromium complex are doubtful, particularly in light of the exchange rate ($k_{\text{ex}} = 6 \times 10^{-6} \text{ sec}^{-1}$) that Hunt and Taube report for the identical cobalt(III) salt (29). The charge factor puts k_{trans} for the cobalt(III) complex equal to $24 \times 10^{-6} \text{ sec}^{-1}$, placing ammonia between chloride and isothiocyanate ions. Errors in the activation parameters, which are 8-fold larger for the chromium(III) complex than the cobalt(III) complex, reduce the reliability of the reported water exchange rate in the ammine-chromium(III) complex.

This *trans* effect series parallels the nephelauxetic series. It therefore is tempting to relate the *trans*-labilizing influence of the ligands to their polarizability. The success of Poë (3) in relating the two factors for Rh(III) octahedral complexes is noteworthy. The "correct" position of the isothiocyanate ligand in the Cr(III) *trans* effect series strengthens the argument for polarizability. It would be of interest to locate thiocyanate in the Rh(III) series (where it is presumed to be S-bonded), especially since the *trans* effect series for Rh(III) parallels that for Cr(III) as

far as the data permit.

Constancy of *cis* Rates.—Since the value of k_{cis} at 25°C is the same for all complexes studied, it is inferred that *cis* water exchange is independent of the nature of the acido ligand. This implies a similar mechanism for *cis* exchange in each complex; constancy of the activation parameters lends support to this idea.

H. Solvent Water Exchange with
trans-Dichlorotetraaquo-chromium(III) Chloride

To ascertain the effect of charge of the complex ion on water exchange rates, an experiment was performed in which ligand water in the *trans* isomer of dichlorotetraaquo-chromium(III) chloride exchanged with enriched solvent water. The measured experimental data are found in Table XIV of Appendix A. Table IX presents the calculated data for the kinetic run.

TABLE IX

trans-DICHLOROTETRAAQUOCHROMIUM(III) ION
SOLVENT WATER EXCHANGE at 25°C

Run <i>t</i> -Cl, 1.56 M CrCl ₂ ⁺	
Time, hr	(1- <i>F</i>)
0.000	1.000
0.358	1.022
0.700	0.975
1.050	0.923
1.392	0.871
1.717	0.829
2.067	0.798
2.383	0.752
29.267	0.000

Since the McKay plot of this data, Figure 5, exhibits excellent linearity, this system undergoes "simple isotopic exchange," *i.e.*, the four waters of the complex ion exchange at the same rate. Incidentally, linearity of exchange also confirms assignment of the *trans* configuration to this isomer.

The assumed exchange reaction is

where H_2^*O represents water enriched in oxygen-18. Virtually no double-labeling was expected, since the oxygen-18 enrichment of solvent water was only 1%. Isotope fractionation was also assumed to be negligible.

Calculating the exchange rate constant from the McKay equation

$$R = 2.303 \cdot ab/(a+b) \cdot [-\log (1-F)]/t \quad [\text{H-2}]$$

where

R = constant rate of exchange

a = concentration of solvent water

b = concentration of ligand water

$$= 4\{[\text{trans-CrCl}_2(\text{H}_2\text{O})_4^+] + [\text{trans-CrCl}_2(\text{H}_2\text{O})_3(\text{H}_2^*\text{O})^+]\}$$

F = fraction exchange

t = time

and from the rate equation for the pseudo-first-order reaction
[H-1]

$$R = k'' \cdot b \quad [\text{H-3}]$$

Figure 5

where

k'' = rate constant for exchange of individual
"cis" waters in *trans* isomer

after substituting eq [H-3] in eq [H-2] and rearranging, gives

$$k'' = 2.303 \cdot a/(a+b) \cdot [-\log (1-F)]/t \quad [\text{H-4}]$$

where

$$[-\log (1-F)]/t = \text{slope of McKay plot}$$

Using least squares analysis for the slope, 55.0 *M* for a , and 4(1.56 *M*) for b , eq [H-4] gives $(3.76 \pm 0.08) \times 10^{-5} \text{ sec}^{-1}$ for k'' at $[\text{HClO}_4]$ equal to 1.01 *M*.

Besides aquation to monochlorochromium(III) ion, another complication in water exchange of *trans*-dichlorochromium(III) ion is isomerization. Even though aquation is the more important of the two, since at 34.8°C k_{aquation} (k_{aq}) is $1.8 \times 10^{-4} \text{ sec}^{-1}$ and $k_{\text{isomerization}}$ [*trans*→*cis*] (k_{is}) is $7.8 \times 10^{-5} \text{ sec}^{-1}$ (36), neither can be ignored. Before estimating the effect of these systematic errors on the rate constant, k_{aq} and k_{is} are extrapolated to 25°C. Assuming the activation energy for aquation is ca. 26 kcal/mole, as reported by Johnson and Reynolds for the *trans* isomer (37), and that this is also a reasonable approximation of the activation energy for isomerization, then at 25°C k_{aq} equals $4.3 \times 10^{-5} \text{ sec}^{-1}$ and k_{is} equals $1.9 \times 10^{-5} \text{ sec}^{-1}$. Calculation of maximum per cent decomposition of *trans* isomer to monochlorochromium(III) ion and to *cis* isomer, by the time of

penultimate sampling, 8580 sec, gives *ca.* 30% and *ca.* 15%, respectively.

These side reactions lead to interesting effects. On the basis of the apparent effect of ionic strength on water exchange the over-all exchange rate for the monochloro-complex in this experiment is roughly estimated to be one-half that of the *trans* isomer. Therefore, the aquation product of the *trans* complex will tend to curve the McKay plot downward as exchange proceeds. Conversely, isomerization produces a species which will exchange more rapidly than the *trans* isomer. The presence of two *trans*-labilizing chlorides would lead to an upward curvature with time in the McKay plot, although aquation of the *cis* isomer (36) would partially compensate this effect. That the exchange curve remains linear over the time period studied suggests that these opposite effects exactly cancel.

Use of only the first three experimental points for the plot would minimize the above effects, since the time interval covered would allow but a few percent decomposition. Evidently, this would not affect the value of the exchange rate constant already calculated. No explanation can be offered for the negative "zero time" fraction exchange, but the intercept has no effect on the slope from which the rate is calculated.

A quantitative correction for effect of isomerization on *trans* isomer exchange probably could be obtained from a study of water exchange of *cis*-dichlorotetraaquo-

chromium(III) ion. Both aquation and isomerization rates of the *cis* isomer are smaller than those of the *trans* isomer (36). These facts, together with the assumption that the isomerization product of the *cis* isomer exchanges more slowly than the *cis* complex, should enhance the reliability of data from such an experiment.

Interestingly, the *trans*-labilizing influence of chloride on chloride in the *trans* isomer probably accounts for the higher rate of aquation in comparison with the *cis* isomer.

Table X lists rate constants for exchange of similarly disposed "*cis*" waters in complex ions of differing over-all charge. Although the ionic strengths are not strictly

TABLE X

INFLUENCE of CHARGE on *cis* WATER EXCHANGE RATES at 25°C

Ion	<i>I</i> , <i>M</i>	<i>k</i> _{<i>cis</i>} × 10 ⁶ , sec ⁻¹
[<i>trans</i> -CrCl ₂ (H ₂ O) ₄] ⁺	2.56	38. ^a
[CrCl(H ₂ O) ₅] ²⁺	3.19	2.0 ^b
[Cr(H ₂ O) ₆] ³⁺	2.97	0.47 ^c

^a This study: Run *t*-Cl. ^b This study: Run Cl-1. ^c Extrapolated from data in Reference 28 {[HClO₄] = 0.42 *M*}.

comparable in Runs *t*-Cl and Cl-1, the apparent effect of ionic

strength on rate constants would only heighten the difference between rates for the dipositive and unipositive ions.

Table X indicates a definite inverse trend: higher exchange rates occur upon lowering charge on the complex ion. There is evidence for analogous effects in aquation of some cobalt(III) complexes. Pearson and Basolo report for the unipositive ion, *cis*-Coen₂Cl₂⁺, and for the dipositive ion, *cis*-Coen₂(NH₃)Cl₂²⁺, aquation rate constants of $2.5 \times 10^{-4} \text{ sec}^{-1}$ and $4.6 \times 10^{-7} \text{ sec}^{-1}$, respectively (38); the ratio of the rate constants is *ca.* 540. Similarly, the aquation rate ratio for *trans*-Co(NH₃)₄Cl₂⁺ and Co(NH₃)₅Cl₂²⁺ is 800. Stranks (35) reports that application of the Kirkwood and Westheimer electrostatic treatment (39) indicates the ratio of aquation rates for a singly and doubly charged complex would be 450 at 25°C for a dissociative mechanism. Results of this study show a value of *ca.* 20 for the ratio of water exchange rates of uni- and dipositive ions. In aquation the reaction involves removal of a negative ligand from a positively charged complex, whereas in exchange a neutral, although polar, ligand is being removed from a positive species. The effect of charge on exchange should therefore be less; whether 20 times less is reasonable is a moot question. Nevertheless, it does appear that charge may exert a significant effect on reaction rates.

In the considerably more labile nickel(II) system, Margerum and Rosen(40) have found that varying charge on the complex from 2- to 2+ had no particular effect on rate of replacement of bound water. All complexes studied, of the

type $\text{NiL}(\text{H}_2\text{O})_n^z$ (where L = multidentate ligand with p coordination sites, z = charge, and $n + p = 6$), have rate constants equal to or less than the corresponding $2+$ complex. Accordingly, they claim electron-donating ability of coordinated groups is more important than over-all charge on the complex. But it is not clear whether analogies can be stretched from the d^8 system to the d^3 system of chromium(III).

An alternative explanation invokes *cis* effects of ligands on water exchange. From Table X it is seen that replacement of one ligand water by chloride increases the *cis* rate exchange by a factor of *ca.* 4.3. Assuming introduction of a second chloride produces a similar effect, the rate for the unipositive ion should be *ca.* 19 times that for the dipositive (*i.e.*, 4.3×4.3). The excellent agreement with observation is strong, but solitary, evidence for *cis* effects. If *cis* effects are important in these water exchange reactions, they cannot be specific; *cis* exchange rates for monoacidochromium(III) ions are observed to be independent of ligand character.

A water exchange study of the unipositive unidentate sulfatopentaaquochromium(III) ion may aid in settling the question of charge effects versus *cis* effects. Very recent studies by Finholt, *et al.*, on preparation and aquation of this ion (41, 42), indicate feasibility of such an exchange experiment. The aquation rate constant, extrapolated from their data and equal to $8 \times 10^{-7} \text{ sec}^{-1}$ at 25°C , indicates negligible error from decomposition can be expected in

the exchange. On the basis that the observed *trans* rates parallel aquation rates, the *trans* exchange of the sulfato-ion would be close to that of the chloro-ion. The *cis* water exchange may be influenced by either a charge effect or a *cis* effect. If a charge effect is operating, the rate of *cis* water exchange should be that found for *trans*-dichlorochromium(III) ion, *i.e.*, *ca.* $4 \times 10^{-5} \text{ sec}^{-1}$. If a *cis* effect is operative, the rate would be similar to that for other monoacido-ions, *i.e.*, *ca.* $3 \times 10^{-6} \text{ sec}^{-1}$.

APPENDIX A

Tables XI-XIV below contain the experimental water exchange data obtained in these studies on acidoaquo-chromium(III) ions. Included are the N_t values calculated by the computer program listed in Appendix B.

TABLE XI

$[\text{CrCl}(\text{H}_2\text{O})_5]^{2+} \text{ --- } \text{H}_2^{18}\text{O} \text{ EXCHANGE}$

A. Temperature: 25°C Weight of CO_2 : 13.2 mg

Mass Ratio of Standard CO_2 : 5000×10^{-6}

Run C1-1

Time, min	H ₂ O Sample, mg	Mass Ratio $\times 10^6$, 46/(44+45)	$N_t \times 10^6$
0.0	208.9	4539	2168
59.0	219.5	4537	2167
112.5	220.3	4532	2165
246.0	228.4	4518	2158
362.0	223.0	4512	2155
538.5	212.3	4502	2149
715.5	233.2	4493	2146
1,444.5	243.8	4464	2132
2,161.0	211.0	4450	2123
3,774.0	251.8	4419	2110
5,057.0	122.9	4408	2091
7,217.0	219.3	4369	2083
9,356.5	196.1	4352	2072
32,510.0(∞)	191.3	4291	2041

TABLE XI - *Continued*

Run C1-2

Time, min	H ₂ O Sample, mg	Mass Ratio $\times 10^6$, 46/(44+45)	N _t $\times 10^6$
0.0	181.8	4497	2145
49.0	161.2	4488	2138
111.5	131.4	4481	2131
228.0	137.4	4466	2124
354.0	127.5	4457	2117
544.0	122.8	4439	2107
711.5	129.9	4419	2098
1,431.0	141.5	4377	2078
2,177.0	186.1	4342	2066
3,598.0	185.3	4292	2041
5,015.5	188.0	4264	2027
7,176.5	171.9	4226	2005
9,415.0	155.8	4214	1997
31,109.0(∞)	157.8	4141	1960

Run C1-3

0.0	150.7	4500	2143
54.0	166.3	4491	2140
111.0	165.3	4481	2135
223.5	161.2	4458	2123
359.5	208.4	4434	2115
526.0	153.3	4418	2101
717.0	152.7	4394	2089
1,424.0	159.5	4338	2061
2,172.0	162.1	4294	2039
3,587.5	137.9	4242	2008
5,028.0	148.6	4196	1986
7,207.0	157.2	4149	1964
9,414.0	152.6	4118	1947
33,586.0(∞)	157.8	4057	1916

TABLE XI - *Continued*

Run C1-4

Time, min	H ₂ O Sample, mg	Mass Ratio $\times 10^6$, 46/(44+45)	$N_t \times 10^6$
0.0	128.9	4452	2115
65.5	127.4	4439	2108
118.5	123.2	4421	2098
242.5	131.6	4427	2102
424.5	124.3	4360	2066
543.5	129.0	4344	2059
728.0	133.4	4311	2043
1,414.0	130.7	4245	2008
2,134.5	127.9	4204	1986
3,621.0	123.9	4127	1944
5,140.5	126.0	4085	1923
7,309.0	119.4	4052	1903
9,296.0	128.9	4016	1888
30,846.0 (∞)	118.1	3966	1858

Run C1-5

0.0	119.9	4236	2000
52.5	126.1	4211	1989
109.0	123.9	4195	1980
302.5	92.4	4169	1954
449.5	125.8	4117	1940
700.5	125.1	4079	1920
879.5	118.9	4062	1909
1,575.0	114.5	4010	1880
2,130.0	121.3	3970	1861
3,632.0	119.6	3896	1822
5,029.5	125.3	3849	1799
7,209.5	126.4	3803	1776
9,343.0	124.6	3780	1763
33,191.0 (∞)	106.4	3745	1736

TABLE XI - Continued

B. Temperature: 15°C

Weight of CO₂: 6.6 mgMass Ratio of Standard CO₂: 4560×10^{-6}

Run C1-6

Time, min	H ₂ O Sample, mg	Mass Ratio $\times 10^6$, 46/(44+45)	$N_t \times 10^6$
0.0	75.2	5930	2895
298.0	114.0	5945	2885
602.0	129.9	5936	2877
903.5	130.9	5914	2866
1,199.0	130.6	5890	2854
1,498.0	121.7	5868	2845
1,799.0	129.3	5855	2837
2,707.5	128.1	5812	2815
3,603.5	109.7	5768	2798
4,497.5	128.6	5747	2783
5,470.5	125.6	5720	2770
6,571.0	111.1	5684	2755
7,276.0	124.9	5670	2745
31,836.5(∞)	119.2	5255	2538

C. Temperature: 5°C

Weight of CO₂: 6.6 mgMass Ratio of Standard CO₂: 4560×10^{-6}

Run C1-7

0.0	76.9	6031	2945
1,837.0	103.6	6047	2940
3,551.0	92.8	6016	2929
6,186.5	95.2	5986	2913
7,560.5	101.5	5970	2902
8,896.5	104.8	5959	2895
10,399.0	83.7	5921	2885
22,803.0	105.0	5861	2846
42,885.0	104.4	5685	2757
90,326.5	132.4	5640	2729
98,234.0	111.6	5603	2714
155,404.5(∞)	112.8	5373	2598

TABLE XII
 $[\text{CrNCS}(\text{H}_2\text{O})_5]^{2+} \text{ — } \text{H}_2^{18}\text{O} \text{ EXCHANGE}$

Weight of CO_2 : 13.2 mg

Mass Ratio of Standard CO_2 : 5000×10^{-6}

A. Temperature: 25°C

Run NCS-1

Time, min	H_2O Sample, mg	Mass Ratio $\times 10^6$, $46/(44+45)$	$N_t \times 10^6$
0.0	180.8	4577	2185
77.0	173.3	4563	2177
155.5	167.4	4554	2172
219.5	194.5	4544	2169
450.5	177.3	4522	2157
643.5	172.3	4489	2140
1,278.5	170.3	4456	2123
1,689.5	171.5	4425	2107
2,060.5	167.1	4407	2097
2,897.0	159.5	4372	2078
4,063.5	178.9	4320	2054
5,991.0	188.3	4272	2031
7,769.5	180.6	4245	2016
30,472.0(∞)	210.2	4166	1979

Run NCS-2

0.0	184.5	4571	2182
66.5	184.4	4560	2177
144.0	179.7	4552	2172
259.0	178.0	4540	2166
544.5	152.2	4503	2145
755.0	175.6	4485	2138
1,304.0	173.2	4431	2110
1,673.0	176.6	4415	2102
2,102.0	165.2	4386	2086
2,852.5	170.9	4352	2070
4,145.5	175.4	4304	2046
5,935.5	169.6	4258	2021
8,037.5	167.3	4220	2002
30,476.5(∞)	161.5	4152	1966

TABLE XII - *Continued*

Run NCS-3			
Time, min	H ₂ O Sample, mg	Mass Ratio $\times 10^6$, 46/(44+45)	N _t $\times 10^6$
0.0	173.2	4609	2201
66.0	175.0	4595	2194
134.0	176.8	4583	2188
278.0	157.7	4558	2174
522.0	147.6	4531	2159
737.0	152.7	4500	2143
1,276.0	154.3	4445	2115
1,681.0	164.9	4399	2093
2,168.0	150.8	4367	2075
3,064.0	143.9	4309	2044
4,204.0	141.4	4268	2022
6,179.0	158.9	4209	1995
7,923.0	147.7	4183	1979
31,298.5(∞)	128.7	4107	1935

B. Temperature: 15°C

Run NCS-4			
0.0	148.1	6271	3040
539.5	107.0	6216	3024
1,150.5	129.0	6208	3013
1,745.0	100.6	6160	2998
2,356.0	117.9	6154	2989
2,947.5	130.8	6147	2982
3,545.5	114.2	6117	2972
4,164.5	116.7	6108	2966
4,752.0	103.0	6070	2952
5,469.0	109.0	6071	2950
6,068.0	120.6	6057	2940
6,584.0	84.1	5990	2920
7,462.5	102.3	6013	2923
31,871.0(∞)	122.0	5652	2737

TABLE XII - *Continued*

C. Temperature: 5°C

Run NCS-5			
Time, min	H ₂ O Sample, mg	Mass Ratio $\times 10^6$, 46/(44+45)	$N_t \times 10^6$
0.0	145.6	6231	3020
1,625.0	92.1	6202	3024
5,845.0	127.9	6190	3004
8,631.5	117.4	6154	2989
10,165.5	114.3	6110	2968
22,455.5	102.4	6027	2931
42,819.5	111.9	5910	2868
98,977.5	106.6	5720	2774
154,798.5(∞)	101.5	5468	2649

TABLE XIII

Temperature: 25°C

Weight of CO_2 : 13.2 mgMass Ratio of Standard CO_2 : 4550×10^{-6}

Run Br-1

Time, min	H ₂ O Sample, mg	Mass Ratio $\times 10^6$, 46/(44+45)	$N_t \times 10^6$
0.0	210.9	3987	1901
38.5	189.4	3976	1893
74.0	189.2	3986	1898
105.0	217.1	3968	1891
133.0	167.5	3976	1891
199.5	198.8	3966	1889
305.0	208.2	3965	1889
516.0	247.1	3951	1885
738.0	194.6	3950	1881
1,460.5	249.8	3929	1874
2,240.0	141.0	3926	1862
3,702.5	141.5	3886	1841
4,413.5	121.6	3881	1835
5,044.0	147.6	3864	1831
33,252.0(∞)	194.3	3783	1796

Run Br-2

0.0	132.7	3854	1823
37.0	128.1	3848	1819
68.5	151.1	3834	1816
98.5	121.1	3851	1819
131.0	135.3	3835	1814
222.5	196.0	3822	1816
314.5	131.0	3821	1805
595.5	161.0	4062	1935
1,316.5	113.8	3784	1781
1,540.5	127.4	3788	1787
1,879.5	142.1	3752	1772
2,178.5	104.7	3769	1770
2,762.0	110.2	3744	1759
3,565.0	139.1	3708	1749
30,241.0(∞)	142.2	3617	1702

TABLE XIV

trans-[CrCl₂(H₂O)₄]⁺ — H₂¹⁸O EXCHANGE

Temperature: 25°C

Weight of CO₂: 6.6 mg

Mass Ratio of Standard CO₂: 4560 × 10⁻⁶

Run t-Cl

<u>Time, min</u>	<u>H₂O Sample, mg</u>	<u>Mass Ratio × 10⁶, 46/(44+45)</u>	<u>N_t × 10⁶</u>
0.0	96.6	5939	2888
21.5	392.4	6007	2892
42.0	122.6	5946	2884
63.0	81.8	5898	2874
83.5	114.3	5904	2865
103.0	81.4	5864	2857
124.0	162.1	5896	2851
143.0	114.4	5861	2843
1,756.0(∞)	186.9	5607	2706

APPENDIX B

The Fortran IV source lists, for the program used to calculate N_t and for the particular subroutines of the best fit program encoded for the derived equation [D-14], are presented here.

N.B. The program statements on these pages are based on a 60-character line for marginal purposes only.

I. Calculation of N_t

```
CALCULATION OF NZERC, (1-F), -LOG(1-F), AND ERRORS
C
C NZERC = ATOM FRACTION OF OXYGEN-18
C       IN WATER SAMPLE BEFORE EQUILIBRATION
C A = MILLIGRAMS OF WATER SAMPLE
C B = MILLIGRAMS OF CARBON DIOXIDE FOR EQUILIBRATION
C K = EQUILIBRIUM CONSTANT FOR EQUILIBRATION REACTION
C RE = MASS SPECTROMETER READING OF RATIO OF MASS PEAKS
C     46 TO (44+45) FOR CARBON DIOXIDE AFTER EQUILIBRATION
C RC = RATIO READING FOR CARBON DIOXIDE BEFORE EQUILIBRATION
C
C CMFEX IS (1-F) AND LCMFEX IS -LOG(1-F)
C WHERE F = FRACTION EXCHANGE
C
C     REAL K, LCMFEX(50), MINUTE(50), NZERO(50), NOMFEX(50)
C     DIMENSION A(50), HOUR(50), CMFEX(50), RE(50), SECOND(5
C 10), TITLE(12), PCMFEX(50), DCMFEX(50), VOMFEX(50), DZ(
C 250), DT(50), DI(50), VNT(50), DK(50), DRE(50), DRC(50)
C 3, CRA(50), VRE(50), VBA(50), DNT(50)
C 85 READ(5,1) TITLE
C 1 FORMAT(12A6)
C
C N = NUMBER OF NZERC VALUES
C
```

```

      READ(5,3) N
3  FORMAT(I2)
      IF (N.EQ.0) GO TO 96
      DC111I=1,N
      A(I)=0.
      LCMFEX(I)=0.
      NZERC(I)=0.
      CMFEX(I)=0.
      RE(I)=0.
      SECOND(I)=0.
      MINUTE(I)=0.
      HOUR(I)=0.
      NCMFEX(I) = 0.
      PCMFEX(I) = 0.
      DCMFEX(I) = 0.
      VCMFEX(I) = 0.
      EZ(I) = 0.
      CT(I) = 0.
      CI(I) = 0.
      VNT(I) = 0.
      CK(I) = 0.
      DRE(I) = 0.
      DRC(I) = 0.
      DBA(I) = 0.
      VRE(I) = 0.
      VBA(I) = 0.
      DAT(I) = 0.
111 CONTINUE
      READ(5,5) B, K, RC
5  FORMAT(F6.2,F7.4,F11.8)
      DC222I=1,N
      READ(5,7) A(I), RE(I), MINUTE(I)
7  FORMAT(F7.2,F11.8,F10.1)
      NZERC(I)=1./((K/RE(I)+1.)+(1.49347*B/A(I))*((1./((1./RE(I)
      1+.5))-1./((1./RC+.5))))
      SECOND(I)=MINUTE(I)*60.0
      HOUR(I)=MINUTE(I)/60.0
222 CONTINUE
      DC333I=1,N
      CMFEX(I)=(NZERC(I)-NZERO(N))/(NZERO(1)-NZERO(N))
333 CONTINUE
      J=N-1
      DC444I=1,J
      LCMFEX(I)=-ALOG10(CMFEX(I))
444 CONTINUE
      LCMFEX(N)=99999999999.9
      WRITE(6,2) TITLE
2  FORMAT(1H1,30X,12A6)
      WRITE(6,4) N, B, K, RC
4  FORMAT(1H-,15X,26HNUMBER OF WATER SAMPLES = ,I2,13X,4H
      1B = ,F6.2,10X,4HK = ,F7.4,10X,5HRC = ,F11.8)
      WRITE(6,6)
6  FORMAT(1H-,37X,3HNC.,9X,1HA,18X,2HPE,18X,7HMINUTES)
      DC555I=1,N

```

```

      WRITE(6,8) I, A(I), RE(I), MINUTE(I)
      8 FORMAT(1H0,37X,12,7X,F7.2,10X,F11.8,10X,F10.1)
555 CONTINUE
      WRITE(6,2) TITLE
      WRITE(6,10)
      10 FORMAT(1H-,13X,5HNZERO,16X,5H(1-F),14X,9H-LOG(1-F),4X,
        16HSAMPLE,25X,4HTIME)
      WRITE(6,12)
      12 FORMAT(1H ,66X,6HNUMBER,5X,7HSECONDS,13X,7HMINUTES,13X
        1,5HHOURS)
      DO666I=1,N
      WRITE(6,14) NZERO(I), CMFEX(I), LOMFEX(I), I,
        1 SECCND(I), MINUTE(I), HOUR(I)
      14 FORMAT(1H0,3(10X,F11.8),5X,12,5X,F10.0,9X,F10.1,9X,F10
        1.3)
666 CONTINUE

C
C VK = VARIANCE OF K
C VRC = VARIANCE OF RO
C VRE = VARIANCE OF RE
C VBA = VARIANCE OF B/A
C VNT = VARIANCE OF NZERO
C DK = PARTIAL DERIVATIVE OF NZERO WITH RESPECT TO K
C DRC = PARTIAL DERIVATIVE OF NZERO WITH RESPECT TO RO
C DRE = PARTIAL DERIVATIVE OF NZERO WITH RESPECT TO RE
C DBA = PARTIAL DERIVATIVE OF NZERO WITH RESPECT TO B/A
C CNT = ERROR IN NZERO
C
      VK = 0.000004318084
      VRC = 0.00000025 * (RC**2)
      DO777I=1,N
      VRE(I) = 0.00000025 * (RE(I)**2)
      VBA(I) = (0.01846968/(A(I)**2)) + (0.00670259*(B**2)/(
        1A(I)**4)) + (0.00000023 * (B**2)/(A(I)**2))
      1(0.00000023 * (B**2)/(A(I)**2))
      DK(I) = ( RE(I)/((K+RE(I))**2))**2
      DRC(I) = ((4.*B/A(I))*(1./((2.+RO)**2)))**2
      DRE(I) = ((K/((K+RE(I))**2))+(4.*B/A(I)*(1./((2.+RE(I)
        1)**2))))**2
      DBA(I) = ((2.*RE(I)/(2.+RE(I)))-(2.*RO/(2.+RO)))**2
777 CONTINUE
      DO888I=1,N
      VNT(I) = (DK(I)*VK)+(DRE(I)*VRE(I))+(DRO(I)*VRC)+(DBA(I)
        1)*VBA(I))
888 CONTINUE
      Q = (NZERO(1) - NZERO(N))**2
      DO999I=1,N
      CZ(I) = ((NZERO(N)-NZERO(I))/Q)**2*VNT(I)
      DT(I) = 1./Q*VNT(I)
      DI(I) = ((NZERO(I)-NZERO(1))/Q)**2*VNT(N)
      DNT(I) = SQRT(VNT(I))
999 CONTINUE

C
C VOMFEX = VARIANCE OF (1-F)

```

C DCMFEX = ERROR IN (1-F)

C

```

      DC1111I=1,N
      VCMFEX(I) = CZ(I) + DT(I) + DI(I)
1111 CONTINUE
      DC2222I=1,N
      CMFEX(I) = SORT(VCMFEX(I))
2222 CONTINUE
      DC3333I=1,N
      PCMFEX(I) = CMFEX(I) + DCMFEX(I)
      NCMFEX(I) = CMFEX(I) - DCMFEX(I)
3333 CONTINUE
      WRITE(6,2) TITLE
      WRITE(6,16)
16  FORMAT(1H-,14X,9HDEV-NZERO,17X,7H(1-F)+D,17X,5H(1-F),1
      19X,7H(1-F)-D,19X,5HHCURS/)
      1,19X,5HHCURS/)
      DC4444I=1,N
      WRITE(6,18) DNT(I),PCMFEX(I),CMFEX(I),NCMFEX(I),HOUR(I)
18  FORMAT(1H0,4(13X,F11.8),13X,F10.3)
4444 CONTINUE
      GO TO 85
96  STOP
      END

```

II. Best Fit

```

C PROGRAM TO FIND THE VALUES OF N PARAMETERS WHICH GIVE THE
C BEST FIT OF EXPERIMENTAL DATA TO ANY SPECIFIED EQUATION
C
COMMON CCX, CSW, M, N, CMFEX(100), T(100), TITLE(12)
DIMENSION X(6)
340 READ(5,150) TITLE
150 FORMAT(12A6)
C
C M = NUMBER OF EXPERIMENTAL POINTS
C CCX = CONCENTRATION OF COMPLEX ION
C CSW = CONCENTRATION OF SOLVENT WATER
C
READ(5,151) M, CCX, CSW
151 FORMAT(I3,2F8.4)
IF (M.EQ.0) GO TO 350
C
C CMFEX = (1-F) EXPERIMENTAL VALUE, F = FRACTION EXCHANGE
C T = TIME IN HOURS - EXPERIMENTAL VALUE
C
READ(5,152) (CMFEX(I),T(I),I=1,M)
152 FORMAT(F11.8,F11.3)
WRITE(6,250) TITLE
250 FORMAT(1H1,30X,12A6)
WRITE(6,251) M, CCX, CSW
251 FORMAT(1H0,14X,31HNUMBER OF EXPERIMENTAL POINTS =,I3.1
10X,17H( COMPLEX ION ) =,F6.3,2F M,5X,19H( SOLVENT WATE
2R ) =,F7.3,2F M)
WRITE(6,252)
252 FORMAT(1H0,41X,3HNC.,14X,4HTIME,15X,5H(1-F))
WRITE(6,253)
253 FORMAT(1H ,58X,5HFCURS)
WRITE(6,254) (I, T(I), CMFEX(I), I = 1,M)
254 FORMAT(1H0,40X,I3,10X,F10.3,10X,F11.8)
C
C L = A CONTROL INTEGER
C N = NUMBER OF PARAMETERS
C E = FRACTIONAL RELATIVE ERROR
C IPRINT = A PRINTING CONTROL INTEGER
C X = TRIAL VALUE OF PARAMETER
C
345 READ(5,153) L
153 FORMAT(I3)
IF (L) 340,240,240
240 READ(5,154) N, E, IPRINT, (X(I),I=1,N)
154 FORMAT(I2/F10.5/I2/(E11.4))
L=1
WRITE(6,255) E, (X(I),I=1,N)
255 FORMAT(1H1,10X,13HERROR LIMIT =,F9.6,5X,41HINITIAL VAL
1UES OF PARAMETERS - KTRANS =,E11.4,5H HR-1,5X,6HKCIS
2 =,E11.4,5H HR-1)
RES=0

```

```

      L=L-1
      CALL FUNMIN (N,L,X,RES,E,IPRINT)
      WRITE(6,256) RES, (X(I),I=1,N)
256  FORMAT(1H-, 3X,28HPERCENT RELATIVE DEVIATION =,E11.4,5
      1X,39HFINAL VALUES OF PARAMETERS - KTRANS =,E11.4,5H
      2HR-1,5X,6HKCIS =,E11.4,5H HR-1)
      GO TO 345
350  STOP
      END

```

SUBROUTINE FUNMIN (N,L,X,RES,E,IPRINT)

FUNMIN, the longest subroutine in the program, is not presented since it exhibits no features peculiar to the problem. Essentially, it operates by altering the initial estimates for the parameters systematically until the calculated kinetic curve gives the best possible fit to the experimental data. The common least squares criterion for the fit is employed.

END

```

      SUBROUTINE FUNVAL (L,X,F1)
      COMMON CCX, CSW, M, N, CMFEX(100), T(100), TITLE(12)
      DIMENSION X(6)
31  FUNCT=0
      DO 35 J=1,M
      TRANS = C.2*EXP(-X(1)*((CSW+CCX)/CSW)*T(J))
      CIS = C.8*EXP(-X(2)*((CSW+4.*CCX)/CSW)*T(J))
      CMFEX = TRANS + CIS
      CMFEX = ((CMFEX - CMFEX(J))/CMFEX(J))**2
35  FUNCT = FUNCT + CMFEX
      F1=100.*SQRT(FUNCT/FLOAT(M-1))
      L=L+1
      WRITE(6,77) L,F1
77  FORMAT (25H0 NUMBER OF ITERATIONS = ,I5,3X,11HFUNCTION
      1 = ,F11.4)
      RETURN
      END

```

```

      SUBROUTINE FIAFUN(X)
      COMMON CCX, CSW, M, N, CMFEX(100), T(100), TITLE(12)
      REAL LCMFEX(100)
      DIMENSION X(6), U(100), TIME(100)
      DO 50J=1,63

```



```

TIME(J) = 0.+2.*FLCAT(J-1)
TRANS = 0.2*EXP(-X(1)*((CSW+CCX)/CSW)*TIME(J))
CIS = 0.8*EXP(-X(2)*((CSW+4.*CCX)/CSW)*TIME(J))
COMFEX = TRANS + CIS
U(J) = COMFEX
50 LOMFEX(J) = -ALOG10(U(J))
WRITE(6,250) TITLE
250 FORMAT(1H1,30X,12A6)
WRITE(6,260)
260 FORMAT(1H0,43X,46H'' BEST FIT '' VALUES FOR GIVEN TIME
1 INTERVALS)
WRITE(6,261)
261 FORMAT(1H0,4X,2(3HPT.,2X,4HTIME,7X,5H(1-F),5X,9H-LOG(1
1-F),9X),3HPT.,2X,4HTIME,7X,5H(1-F),5X,9H-LOG(1-F))
WRITE(6,262)
262 FORMAT(1H ,9X,5HHOURS,2(39X,5HHOURS))
DO 60J =1,21
JJ = J+21
JJJ = J+42
WRITE(6,263) J, TIME(J), U(J), LOMFEX(J), JJ, TIME(JJ)
1,U(JJ), LOMFEX(JJ), JJJ, TIME(JJJ), U(JJJ), LOMFEX(JJJ)
263 FORMAT(1H0,4X,2(I2,3X,F5.0,5X,F7.4,5X,F7.4,10X),I2,3X,
1F5.0,5X,F7.4,5X,F7.4)
60 CONTINUE
RETURN
END

```

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