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Kinetics of the acid hydrolysis (aquation) and isotopic exchange of choride with trichloroammineplatinate (II) complex in aqueous solution

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KINETICS OF THE ACID HYDROLYSIS (AQUATION)

AND ISOTOPIC EXCHANGE OF CHLORIDE WITH

TRICHLOROAMMINEPLATINATE(II) COMPLEX IN AQUEOUS SOLUTION

by

Thomas Smith Elleman

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I. INTRODUCTION

The purpose of this research has been to investigate the kinetics for the isotopic exchange of chloride ion with the ligand-chloride of trichloroammineplatinate(II) in aqueous solutions. It was hoped that this investigation would clarify the mechanism of substitution for reactions involving square planar platinum(II) complexes.

For this study, adequate procedures for following and quenching the exchange, separating the existing complexes, and measuring the amount of tracer isotope in these complexes have been developed. Chlorine-36 was used as the tracer for the isotopic exchange reaction. This nuclide decays through the emission of a 0.71 mev. (maximum) β ray with a half-life of 3.1×10^5 years. No corrections were made for the slight rate effects to be expected from the mass difference between Cl^{36} and the naturally occurring chlorine isotopes.

Platinum exists in solution either as the hexacoordinated platinate(IV) complex or as the tetracoordinated platinate(II) species. The element forms a large variety of complexes with both inorganic and organic ligands. Many of the complexes reported have been polynuclear, but these usually have been formed only under rigorous conditions. Platinum(II) complexes normally exist in a square, planar configuration rather than in the familiar tetrahedral arrangement. In general, platinum complexes represent an ideal class for ligand exchange studies

since the exchange rates are measurably slow. In addition, the square planar structure permits investigation of cis- and trans-effects of isomers.

Taube (1) has differentiated two classes of complexes, labile and inert, based on their kinetic behavior. By his definition, labile complexes are those complexes in which the ligands completely equilibrate in the short period of time required to dissolve the compound. Conversely, inert complexes require a longer and measurable exchange period. Taube has applied this distinction to octahedral complexes and has correlated the behavior with the electronic state of the central atom. He has shown that if the central metal atom has unutilized inner orbitals, the ligands will usually be labile; whereas if all sub-shells are filled (as in platinum), the complex will exhibit inert behavior. Taube interpreted this observation in terms of an exchange transition state which was stabilized by the donation of an electron pair from the entering ligand to an empty metal orbital.

One of the first exchange experiments involving a platinum complex was performed by Grinberg and Filinov (2) in 1939. Using bromine-80, they demonstrated that the reaction:

$$K_2[PtBr_4] + Br^{*-} \rightleftharpoons K_2[PtBr_3Br^*] + Br^-$$

resulted in complete isotopic equilibration of all four bromine atoms in the complex. Somewhat later, Grinberg (3) indicated that the exchange:

$$K_2[PtBr_6] + Br^{*-} \rightleftharpoons K_2[PtBr_5Br^*] + Br^-$$
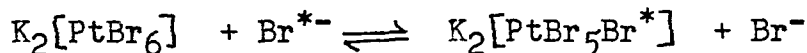
proceeded to a rapid isotopic equilibration of all six bromine atoms. Adamson and Grunland (4) showed that this exchange was slightly photo-accelerated.

Grinberg and Nikolskaya (5) investigated exchange reactions of the type: $[PtX_4]^= + X^{*-} \rightleftharpoons [PtX_3X^*]^= + X^-$ where X = CN$^-$, I$^-$, Br$^-$, Cl$^-$. They observed that the rate of exchange was in the order: CN$^-$ > I$^-$ > Br$^-$ > Cl$^-$. However, the stabilities of the tetra-substituted complexes of these ligands were in the same order. That is, the ΔF^o for the reactions:

$$4X^- \text{ (aq.)} + Pt^{++} \text{ (aq.)} \longrightarrow [PtX_4]^= \text{ (aq.)}$$
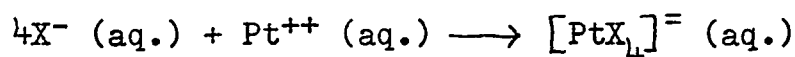
were Cl$^-$ > Br$^-$ > I$^-$ > CN$^-$. The cyanide complex is therefore the most stable. This contradiction indicated that the mechanism of exchange was not a simple heterolysis of the Pt-X bond.

Grantham, Elleman, and Martin (6) investigated the exchange of chloride with tetrachloroplatinate(II) complexes in aqueous solution. They observed that an acid hydrolysis reaction (aquation) occurred in which a chloride in the complex was reversibly replaced by water:

$$[PtCl_4]^= + H_2O \rightleftharpoons [PtCl_3(H_2O)]^- + Cl^-$$
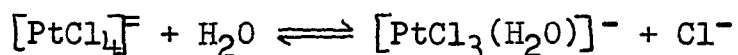
They stated that all the observed exchange was explained by the aquation reaction plus an additional first order reaction with the aquo-complex. The additional reaction could have been due to a second equation:

$$[PtCl_3(H_2O)]^- + H_2O \rightleftharpoons [PtCl_2(H_2O)_2] + Cl^-$$
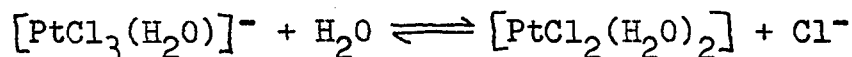
although this reaction was not detected.

Other workers had previously indicated the existence of

platinum-water complexes. In 1893, Werner and Miolate (7) measured the conductivity of solutions of cis-$[Pt(NH_3)_2Cl_2]$ as a function of time. The resulting increases in conductivity were interpreted as an indication of decomposition of the complex to form ammonium chloride. Present knowledge indicates that the increase was due to a reversible replacement of a chloride ligand by water.

In 1936, Jensen (8) reported that platinum(II) ammines in aqueous solutions underwent the following reaction:
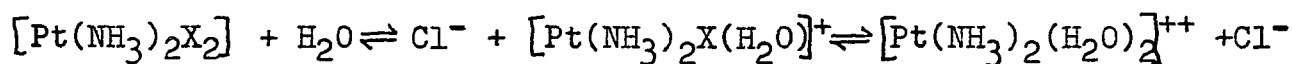
$$[Pt(NH_3)_2X_2] + H_2O \rightleftharpoons Cl^- + [Pt(NH_3)_2X(H_2O)]^+ \rightleftharpoons [Pt(NH_3)_2(H_2O)_2]^{++} + Cl^-$$

The formation of aquo-intermediates was more thoroughly explored by King (9, 10). While investigating compounds of the type $[Pt(NH_3)_2X_2]$ and $[Pt(NH_3)_3X]X$, he observed two distinct classes of behavior. No ligand dissociation was obtained for X = halides and nitrite, but for X = picrate, oxalate, carbonate, sulfate and nitrate, only the dipositive diaquodiammineplatinum (II) cation existed in solution.

Yakshin (11) measured the aquation rates of the cis- and trans-forms of potassium dithiosulfatoplatinate(II) by conductivity procedures. The cis-form of the salt was observed to aquate much more readily than the trans-isomer.

Gelman, Karandashova, and Essen (12) mentioned the formation of aquo-intermediates in halide pyridine platinum compounds and Babaeva and Mosyagina (13) studied the influence of ultraviolet radiation in promoting platinum complex hydrolysis reactions. Katzin and Gebert (14) investigated the ultraviolet

absorption spectra for aquo-complexes of cobalt and nickel and Schläfer (15) discussed the electron transitions involved in the various aquo-complex absorption bonds.

Leden and Chatt (16) measured the rate and equilibrium constant for the aquation of $[Pt(C_2H_4)Cl_3]^-$. They reported the equilibrium for the substitution was established within two minutes. Grinberg and Shagisultanova (17) stated that exchange of bromide with tetrabromoplatinate(II) ion occurred through an intermediate aquo-ion and Grinberg, Nikolskaya, and Kiseleva (18) supported the same mechanism for the exchange of palladium-halide complexes.

Many exchange experiments have been performed with the platinum(IV) complex series (19, 20) but in contrast to the platinum(II) compounds, ligand exchange does not appear to occur via an aquo-intermediate. Taube and Rich (21) have suggested that exchange proceeds through an oxidation-reduction equilibrium and Grinberg and Shagisultanova (17) have supported this viewpoint.

During the past fifty years, many different platinum compounds have been prepared. From a study of many of these preparations, it became possible to predict the approximate rate and position of substitution for a reacting group from a knowledge of the nature and position of the other ligands in the complex. These investigations were chiefly empirical and very little attention was given to the theoretical aspects of complex substitution. Recently, several theories have been

proposed to explain substitution reactions for square planar complexes. These attempts have been reasonably successful but several points of contradiction still exist.

Werner (22) was the first to suggest that the reactivity of a given group in a coordination compound was dependent in large measure upon the nature of the group coordinated in the trans-position. This idea of "trans-elimination" or "trans-effect" was an integral part of Werner's coordination theory and served as a model for later theories on the subject.

Chernyaev (23, 24) noted that in a number of cases, ligands coordinated in a position cis- to the reacting group appeared to exert little effect on the reaction rate, but that the group in the trans-position was very important in directing substitution. Chernyaev further estimated the degree of trans-directing effect for many common ligands. He showed that there was rough parallelism between increasing trans-effect and increasing polarizability.

On this basis, Grinberg (25) proposed an explanation of the trans-effect based on the ideas of electrostatic forces and polarization. He stated that if a central metal ion were surrounded by three identical groups and one which was relatively more negative or more easily polarized, then the symmetry of the field around the central ion was destroyed and a dipole was induced in the central metal ion. The bond which was adjacent to the negative end of the induced dipole, that is, the group which was trans- to the nonidentical ligand, was

weakened and trans-elimination occurred. These views are presently regarded as an oversimplification of the phenomena involved.

Syrkin (26) proposed a theory for the trans-effect based on the concept of resonating ionic and covalent forms. According to his views, the presence of a trans-directing group in the complex tended to add additional weight to certain resonance forms imparting ionic character to the bond of the trans-ligand. This tended to weaken the covalent bond and labilize the trans-position. This approach to the problem was criticized by Keller and Parry (27) who pointed out that certain logical resonance forms which would invalidate the argument were not included.

Tronev and Chulkov (28) have attempted to predict the degree of trans-effect of ligands from the standard free energies of formation of their complexes. They stated that the results of this approach agreed quite well with the experimentally obtained trans-order.

All of the theories so far presented have assumed that the trans-effect is due to a weakening of a platinum-ligand bond with resulting enhanced lability of the ligand. Theories proposed by Orgel (29) and Chatt, Duncanson, and Venanzi (30) have acknowledged bond weakening in some cases but have refuted this weakening as the principal mechanism for the trans-effect. Recent investigations (31, 32) have indicated that many ligands tend to form double bonds with the central metal atom and that

this tendency is in direct relation to their trans-directing properties. When a strong trans-directing group is coordinated to a complex, the resulting π-bond formation tends to reduce the electron density in the d orbitals trans- to the π-bond. This phenomenon may be illustrated by a schematic view along the plane of the complex showing the orbital size before and after hybridization.
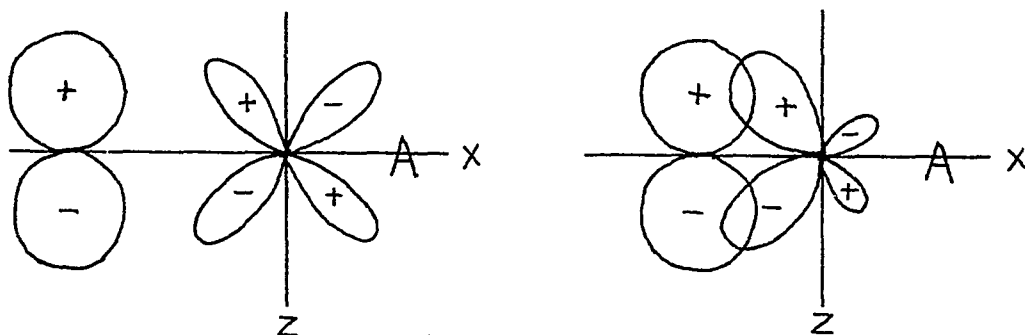
According to Chatt, this electron withdrawal may or may not affect the strength of the Pt-A bond, depending upon the tendency of A to also form π-bonds. The reduced electron density in the region of ligand A facilitates the approach of the substituting nucleophilic agent and thus reduces the energy of the transition state. In this manner, substitution is enhanced and directed into the trans-position.

This substitution theory has obtained strong support from recent infrared bond energy determinations by Chatt, Duncanson, and Venanzi (30). The results have indicated that the presence of strong trans-directing groups in a complex causes some weakening of the trans-bond but the order of weakening is not always in accord with the labilizing power of the ligand. With several slight changes these observations have been supported
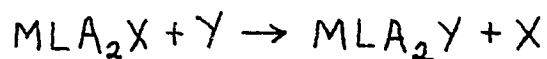
by Powell (33).

Bannerjea, Basolo, and Pearson (34) have investigated the effect of the entering ligand on the rate and position of substitution in platinum complexes. They have shown that for entering ligands which form strong π-bonds, the rate of substitution is 2nd order and is dependent upon the double bonding character of the entering nucleophile. Both observations are compatible with the double bond theory of trans-substitution. This theory requires 2nd order substitution and the strongly double bonding nucleophiles would tend to stabilize the transition state through the formation of an extra π-bond.

The authors also state that while the above is consistent with current theory, deviations begin to occur when the entering or leaving group cannot form strong π-bonds. In these cases the reaction rates approach a constant value and become independent of the concentration of reactant. This behavior is characteristic of either an S_N1 reaction or of a rate determining aquation reaction followed by rapid substitution of the entering ligand.

The authors indicate that crystal field calculations are consistent with an S_N1 mechanism when the entering reagent does not form strong π-bonds. The transition state used for this calculation involved the removal of one ligand while the remaining three groups maintained their original configuration. Opposed to this mechanism is the observation that the reaction rate of a complex is independent of its charge; a behavior
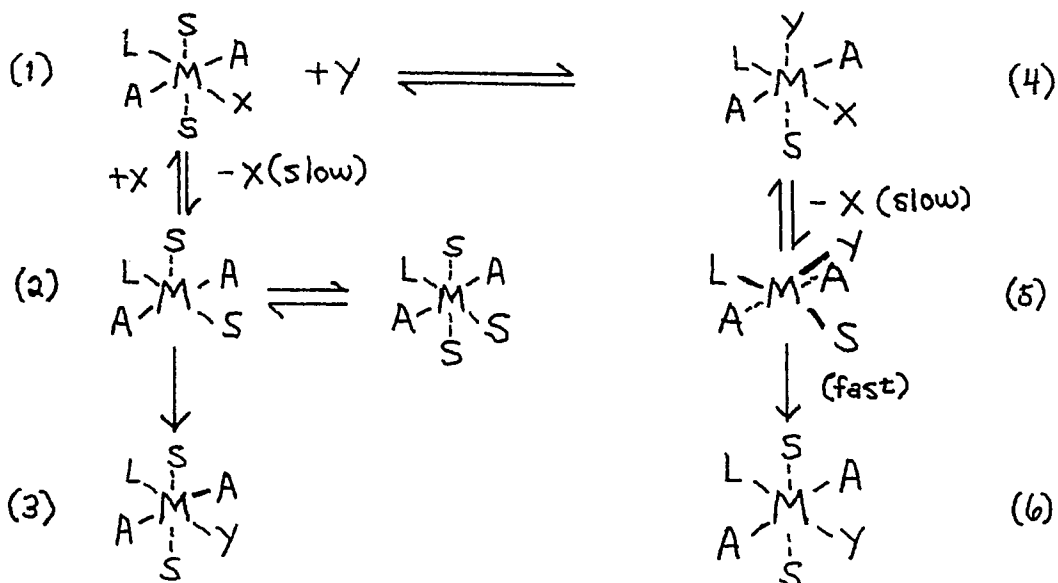
hardly compatible with an S_N1 mechanism.

To reconcile these differences, the authors have proposed the following substitution scheme:

$$MLA_2X + Y \rightarrow MLA_2Y + X$$

Path I   Path II

(1)   [complex] $+Y \rightleftharpoons$ (4)

$+X \updownarrow -X\text{(slow)}$ $\updownarrow -X\text{(slow)}$

(2)   [complex] $\rightleftharpoons$ [complex]   (5)

$\downarrow$ $\downarrow$ (fast)

(3)   [complex]   (6)

In this mechanism, the two groups above and below the plane of the complex move in and displace ligand X. If Y tends to form strong π-bonds, then the energy of the transition state (5) will be lowered and the reaction will proceed through path II. Since the concentration of structure (4) is depended upon the concentration of Y, this path will exhibit 2nd order kinetics. If Y does not tend toward double bond formation, then transition state (2) will be energetically more favorable than (5) and the reaction will proceed through path I and an aquo-

intermediate.

Since NH_3, H_2O, and Cl^- are weakly trans-directing, complexes containing these groups as ligands would be classed with the reaction type given in path I.

II. EXPERIMENTAL

A. Materials

1. Pt

Platinum was obtained as the foil from J. Bishop & Co., and as reagent grade hexachloroplatinic(IV) acid from Mallinckrodt Chemical Co. and Fisher Scientific Co.

Platinum recoveries were made on all waste solutions believed to contain platinum. The recovery was performed by heating alkaline waste solutions containing formate ion for several hours. Spectroscopic analysis of the resulting precipitate indicated platinum metal as the major component with moderate amounts of silicon, silver, and magnesium and trace amounts of palladium and rhodium. No osmium, ruthenium, or iridium were detected. After removal of the filtrate, the platinum was treated alternately with hot nitric acid and hot hydrochloric acid to remove the less noble metals. After washing with ammonia and water, the metal was ready for use in preparing compounds.
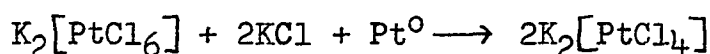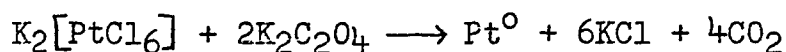
2. $K_2[PtCl_4]$

$K_2[PtCl_4]$ was prepared by the method outlined by Vezes (35). In this procedure, $H_2[PtCl_6]$ was prepared by treatment of platinum metal with hot aqua regia. This compound was treated with K_2CO_3 to form insoluble $K_2[PtCl_6]$ which was then reacted with stoichiometric amounts of $K_2C_2O_4$ to form $K_2[PtCl_4]$.

$$K_2[PtCl_6] + K_2C_2O_4 \longrightarrow K_2[PtCl_4] + 2CO_2 + 2KCl$$
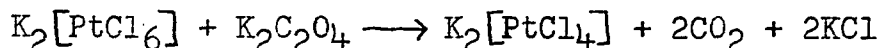
The $K_2[PtCl_4]$ was purified by recrystallizations from water and was finally obtained as long, reddish, needlelike crystals.

Mikhelis (36) has discussed the $K_2[PtCl_6]$ reduction and has observed that the reaction may be catalyzed by the addition of formalin and potassium hydroxide to the oxalate solution.

Grinberg (37) investigated the mechanism of the reduction and stated that the reaction involved an intermediate of platinum metal:

$$K_2[PtCl_6] + 2K_2C_2O_4 \longrightarrow Pt^o + 6KCl + 4CO_2$$

$$K_2[PtCl_6] + 2KCl + Pt^o \longrightarrow 2K_2[PtCl_4]$$

This mechanism was supported by the demonstration that freshly prepared platinum black reacted with $K_2[PtCl_6]$ to form $K_2[PtCl_4]$.

Many other methods for reducing platinum compounds from a valence of four to two are known. Sulfur dioxide (38), potassium hydrogen sulfide (39), cuprous chloride (40), and stannous chloride (41) have been used successfully. The chief difficulty with many of these procedures is that the purity of the product is not assured.

3. $[Pt(NH_3)_4]Cl_2$

$[Pt(NH_3)_4]Cl_2$ was prepared by the method outlined by Reiset (42) and by Gildengershel (43). The procedure involved treatment of $K_2[PtCl_4]$ solutions with large quantities of aqueous NH_3 until complete conversion to $[Pt(NH_3)_4]Cl_2$ was

obtained. The compound was then either crystallized from water solutions or precipitated by the addition of an ether, alcohol, and acetone solution. Since high purity was not required, the latter procedure was usually employed.

The dried salt exhibited a tendency to decompose when exposed to air, so samples were stored in an ammonia desiccator or in a tightly stoppered bottle.

4. $K[Pt(NH_3)Cl_3]$

The procedure employed in the preparation of $K[Pt(NH_3)Cl_3]$ was a modification of a method suggested by Lebedinskii and Golovnya (44). Since a large number of changes were made in the procedure and since the preparation was particularly difficult, the synthesis is discussed in detail.

Mixed platinum complexes are often prepared by direct substitution of the coordinated ligands by other chemical species. The difficulty in using this method lies in terminating the reaction at the proper stage of substitution. This difficulty has been particularly apparent in the preparation of $K[Pt(NH_3)Cl_3]$. Direct addition of aqueous ammonia to $K_2[PtCl_4]$ solutions resulted in formation of $K[Pt(NH_3)Cl_3]$ but this reaction was followed by rapid substitution of an additional chloride to yield cis-$[Pt(NH_3)_2Cl_2]$. For this reason, it was necessary to first prepare cis-$[Pt(NH_3)_2Cl_2]$ and then transform this to $[Pt(NH_3)Cl_3]^-$ by the addition of HCl.

Cis-$[Pt(NH_3)_2Cl_2]$ was prepared by refluxing a solution of

$K_2[PtCl_4]$ with $NH_4[C_2H_3O_2]$ and KCl. For every 2 grams of
$K_2[PtCl_4]$, 2 grams of KCl, 4 ml. of 20% $NH_4[C_2H_3O_2]$ and 15 ml.
of water were added to the reaction flask. The mixture was
refluxed for 1.5 - 2 hours or until the solution color changed
from ruby to light yellow. The hot solution was filtered and
the slightly soluble cis-$[Pt(NH_3)_2Cl_2]$ was precipitated by
cooling the solution in an ice bath. Prolonged refluxing of
the reaction mixture resulted in additional substitution of the
complex to form Magnus salt, $[Pt(NH_3)_4][PtCl_4]$. The presence
of this compound imparted a green color to the normally yellow
cis-$[Pt(NH_3)_2Cl_2]$.

After the cis-$[Pt(NH_3)_2Cl_2]$ was rinsed with alcohol and
ether and dried, it was refluxed with a small quantity of
platinum black and HCl for 1 - 1.5 hours. This treatment re-
sulted in the replacement of one NH_3 by Cl^- to form $H[Pt(NH_3)Cl_3]$.
Continued heating of the solution produced $H_2[PtCl_4]$ but the
second substitution was slow compared to the first. After re-
fluxing, the solution was cooled in an icebath, the unreacted
cis-$[Pt(NH_3)_2Cl_2]$ was precipitated, and the solution was fil-
tered. Although the filtrate contained the desired
$[Pt(NH_3)Cl_3]^-$ ion, the high HCl concentration prevented pre-
cipitation. An excess of $[Pt(NH_3)_4]Cl_2$ was added then to the
filtrate and slightly soluble $[Pt(NH_3)_4][Pt(NH_3)Cl_3]_2$ was pre-
cipitated. The compound was removed by filtration, washed with
alcohol and ether, and dried.

A stoichiometric quantity of $K_2[PtCl_4]$ based on the

reaction:

$$K_2[PtCl_4] + [Pt(NH_3)_4][Pt(NH_3)Cl_3]_2 \rightarrow [Pt(NH_3)_4][PtCl_4] + 2K[Pt(NH_3)Cl_3]$$
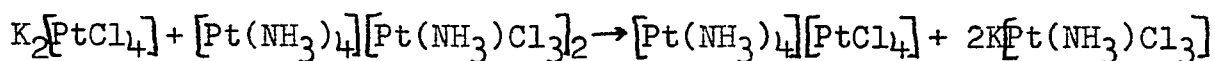
was transferred to a large beaker and dissolved in a small volume of water. The $[Pt(NH_3)_4]$ $[Pt(NH_3)Cl_3]_2$ was dissolved in a large volume of hot water (400 - 600 ml.) and added slowly to the $K_2[PtCl_4]$ solution. Extended heating of $[Pt(NH_3)_4]$ $[Pt(NH_3)Cl_3]_2$ resulted in isomerization to $[Pt(NH_3)_4]$ $[PtCl_4]$ so extreme care was exercised in dissolving the compound. After the mixing, the solution was cooled, the insoluble green Magnus salt was removed by filtration, and the filtrate was evaporated to dryness at 35°C. under reduced pressure. The residue was dissolved in a small quantity of hot water, the solution was filtered, and the $K[Pt(NH_3)Cl_3]$ was crystalized from a cold solution. The compound crystalized as long orange needles which have been characterized by Lyashenko (45) as belonging to the rhombic rhombopyramidal class.

Other workers have determined various physical properties of the compound, such as crystal structure (46), heats of solution (47) and oxidation potentials (48).

5. $[Pt(NH_3)Cl_2(H_2O)]$

This complex was prepared by aging an extremely dilute aqueous solution of $K[Pt(NH_3)Cl_3]$. One of the chlorides in $K[Pt(NH_3)Cl_3]$ was reversibly replaced by water to form the aquo-complex, $[Pt(NH_3)Cl_2(H_2O)]$. The percentage formation of this complex was increased by high temperatures and dilute

solutions, so these conditions were maintained during the preparation. Since the aquo-complex is uncharged, it was possible to separate it from the equilibrium solution by passing the solution an anion exchange resin, Dowex 1-x8, in the sulfate cycle. All attempts to precipitate the complex or to store it in concentrations higher than 0.01 M. resulted in decomposition of the complex to platinum black. It was possible, however, to store it indefinitely in 0.002 M. solutions at 0.0°C.

Attempts to extract the $[Pt(NH_3)Cl_2(H_2O)]$ complex into organic solvents were unsuccessful.

6. $[\emptyset_4As][C_2H_3O_2]$

This precipitating reagent was prepared by passing tetraphenylarsonium chloride, $[\emptyset_4As]Cl$, through a Dowex 1-x8 anion exchange resin in the acetate cycle. The product obtained was extremely soluble and no attempt was made to crystallize it from solution. Solutions of $[\emptyset_4As][C_2H_3O_2]$ were standardized gravimetrically by precipitating the insoluble $[\emptyset_4As][ClO_4]$. Complete replacement of chloride by acetate ion on the exchange resin was demonstrated by the failure of silver ion to give a precipitate when added to a portion of the effluent solution.

The $[\emptyset_4As]Cl$ was purchased from the Hach Chemical Co., Ames, Iowa. No purity analysis was included for the compound.

7. $Na[B\emptyset_4]$

This compound was purchased from the Hach Chemical Co.

under the trade name, "PotassiVer." No purity analysis was given for the compound but the presence of significant quantities of insoluble material indicated some impurity. The reagent functioned quite well, although it exhibited strong tendencies toward decomposition in both the solid form and in solution.

8. Additional reagents

In conjunction with various phases of this research, many common laboratory reagents were employed. Of these, a definite knowledge of purity was required for only KNO_2, KCl, Na_2SO_4, $LiClO_4$, and KNO_3.

KNO_2 was purchased as reagent grade from the Baker Chemical Co. Solutions of the salt were analyzed before use by titration with $KMnO_4$ (49) and by exchange resin conversion to HNO_2 followed by titration with standard base.

KCl, KNO_3, and Na_2SO_4 were reagent grade chemicals purchased from the Baker Chemical Co. Solutions were prepared on the basis of the formula weight given on the bottle.

$LiClO_4$ was obtained from the G. Frederick Smith Chemical Co., Columbus, Ohio. No purity analysis was enclosed with the compound but reagent grade was inferred.

Na_2SO_4, $LiClO_4$, and KNO_3 were used at various times to maintain the ionic strength in solutions. No difference in chemical behavior was observed as a result of interchanging the reagents.

9. Water

Tap distilled water was redistilled from alkaline perman-
ganate solutions and used in all experiments.

10. Chlorine-36

Chlorine-36 was obtained from the Isotopes Division, United
State Atomic Energy Commission, Oak Ridge Tennessee. The iso-
tope was shipped in ten microcurie lots in the form of approxi-
mately 2 N. HCl.

B. Equipment

1. Geiger-Muller counter

A TCG-1 end window, self quenching Geiger-Muller counter
tube, manufactured by Tracerlab Inc., was used to measure the
activity in the samples. The thickness of the mica window was
2.5 mg/cm.^{2} and the tube dead time was approximately 200 micro-
seconds. The tube was mounted in a lead housing to minimize
the background counting rate. The sample rack in the lead
housing was mounted directly below the vertical counter tube
and it was adjusted so the first shelf was approximately 7 mm.
from the tube window. Pulses from the counter tube were fed
into a Berkeley decimal scaler, model 100, which visually reg-
istered the total counts.

2. Filtering apparatus

The use of a tracer technique for following exchange rates

necessitated the preparation of smooth, reproducible counting samples. This was accomplished by using a filtering technique which deposited the radioactive precipitate directly on the mounting paper.

The filtering apparatus consisted of a sintered glass disk, 28 mm. in diameter, which was sealed into the top of a funnel tip. A glass chimney with inside diameter 28 mm. was ground on one end to fit flush with the outside rim of the sintered disk. For filtering, a weighed filterpaper was placed on the disk and the chimney was fastened on top of it by a system of rubber bands. The liquid to be filtered was introduced into the top of the chimney and forced through the filter paper by the application of a partial vacuum to the end of the funnel tip. This procedure resulted in the deposition of an even layer of precipitate on the weighed filterpaper.

Since the filtering operation left a deposit of precipitate on the walls of the chimney, the method was not suitable for analytical recovery of all the precipitate.

3. __Constant temperature bath__

The temperature of all reaction solutions was maintained at a constant value with a Sargent constant temperature bath. The bath consisted of a tank of circulated water in which the cooling effect of a water cooling coil was balanced by a series of intermitant heaters. For temperatures below 20°C., the water cooling coil was replaced by a portable refrigeration

coil manufactured for the purpose by the Blue M. Electric Co., Blue Island, Illinois. The design of the machine permitted only crude control of the refrigerant flow, so precise temperatures were maintained by balancing with the intermittant, thermo-regulated heaters.

Temperature regulation for experiments performed at 5.5°C. was obtained with a benzene bath consisting of solid and liquid benzene. This procedure proved highly unsatisfactory because temperature gradients were observed in the mixture.

Temperature control of 0.1°C. was obtained with the Sargent bath while solutions in the benzene bath fluctuated from 5.5°C. to 6.5°C.

4. pH meter

A Beckman model "G" pH meter was used in all pH determinations. Shielded electrodes, model 1190-80, permitted pH determinations outside the shielded cabinet. Since almost all solutions were in the pH range 4 - 10, the instrument was standardized against a pH 7 buffer. No indicator electrode corrections were made for the high pH region.

5. Spectrophotometers

A Beckman Model D. U. spectrophotometer was used for absorbance determinations of platinum solutions. One cm., glass stoppered, silica transmission cells were used to contain the experimental solutions. The temperature in the cell

compartment was maintained at a constant value by passing constant temperature water through the cell cooling coils. Controlled temperatures below 20.0°C. resulted in moisture condensation in the photocell compartment which affected the performance of the machine. Therefore, when rate processes below 20°C. were studied, the solutions were kept in an adjoining constant temperature bath and were transferred to the spectrophotometer only for the duration of the reading. This procedure proved quite satisfactory and the instrument operation was not impaired.

In those cases for which the absorbance over the entire spectrum was desired, a Cary recording spectrophotometer, model 12, manufactured by Applied Physics Corp., Pasadena, Cal., was used. Ten cm. silica transmission cells were used to contain the experimental solutions and the absorption spectrum was recorded from 220 $m\mu$ to 400 $m\mu$. No temperature control in the cell compartment was possible other than the constantly maintained room temperature of 27°C.

6. Additional equipment

In addition to the apparatus listed, the following non-routine pieces of equipment was utilized.

All analytical electroplating determinations were made on a Sargent-Slomin Electrolytic Analyzer. Laboratory titrations requiring high accuracy were performed with a Machlett Auto-Burette, a self-filling burette calibrated in hundredth's of a

milliliter. Solution exchange of anions was accomplished with Dowex I-x8 anion exchange resin of 20 - 50 mesh. The resin was usually employed in either the sulfate or acetate exchange cycle.

C. Analyses

1. Pt

On several occasions during the experimental work, it was necessary to make accurate platinum analyses on samples containing a maximum of one milligram of platinum. A colorimetric technique based on the bright yellow color exhibited by chloroplatinic acid in the presence of stannous chloride was employed (50, 51). Transmission measurements were taken at $403 m\mu$ and good analytical results were obtained over the concentration range 5 - 30 p.p.m. platinum.

2. K[Pt(NH$_3$)Cl$_3$] and K$_2$[PtCl$_4$]

Analyses were performed on these compounds for potassium, platinum, ammonia, and chloride. Some difficulty was encountered in adequately drying the K[Pt(NH$_3$)Cl$_3$] complex, so several analyses were performed with the salt as the monohydrate. With the technique employed, it was possible to analyze for potassium, platinum, and ammonia on a single sample with an additional sample being used for the chloride determination.

Platinum was determined by electroplating the metal from

a weighed sample onto a weighed platinum gauze cathode. The electroplating solution was acidified with several drops of H_2SO_4 and HNO_3 and plating was carried out for one hour at a current under 0.2 ampere. The platinum in the solution was then determined gravimetrically from the increase in weight of the weighed cathode.

Ammonia and potassium were determined from the same solution by the gravimetric procedure outlined by Gloss (52). This method involved precipitation of potassium and ammonia as the insoluble $K[B\emptyset_4]$ and $NH_4[B\emptyset_4]$ salts which were then weighed. Treatment of the precipitate with acetone and sodium hydroxide resulted in the removal of NH_3. The addition of water then reprecipitated only $K[B\emptyset_4]$. In this way, $K[B\emptyset_4]$ was determined directly and $NH_4[B\emptyset_4]$ was obtained from the difference in precipitate weights.

Chloride was determined gravimetrically as AgCl. The chloride was first displaced from the platinum complex by either electroplating basic solutions of $[Pt(NH_3)Cl_3]^-$ or reacting $[Pt(NH_3)Cl_3]^-$ with aqueous NH_3 to form $[Pt(NH_3)_4]^{++}$ and $3Cl^-$. Typical analyses for $K[Pt(NH_3)Cl_3]$ were:

Group analyzed	Calc. %	Observed %		
Pt	54.5	54.6	54.6	54.3
K	10.9	10.9	11.1	11.1
NH_3	4.8	4.7	5.1	4.6
Cl	29.8	28.4	30.5	29.8

3. $[\phi_4As][Pt(NH_3)Cl_3]$

Precipitates of this compound were analyzed for $[\phi_4As]^+$ ion by dissolving $[\phi_4As][Pt(NH_3)Cl_3]$ in acetone and water and then precipitating insoluble $[\phi_4As][ClO_4]$ by the addition of $Na[ClO_4]$. The weight of this compound gave the $[\phi_4As]^+$ content. The remaining elements in the compound were determined by the procedures outlined.

D. Procedures

Two slightly different procedures were used to carry out the exchange of Cl$^-$ with $[Pt(NH_3)Cl_3]^-$. Under one set of conditions, exchange was carried out in solutions in which the platinum complex was equilibrated with all its hydrolysis products before the addition of Cl^{36}. Such solutions which were at chemical equilibrium before exchange was initiated have been designated as "aged" solutions. In the other condition, all platinum existed as the $[Pt(NH_3)Cl_3]^-$ ion at the time of exchange initiation. From the nature of their preparation, such solutions are called "fresh" solutions.

In an "aged" solution exchange run, the proper quantities of dried $K[Pt(NH_3)Cl_3]$, KCl, and Na_2SO_4 were weighed and transferred to the reaction flask. The only purpose of the Na_2SO_4 was to maintain the ionic strength of the solution at a constant value of 0.318 moles/liter. Since many platinum reactions are known to be accelerated by light, the reaction flask was

completely wrapped with opaque electrician's tape unless otherwise designated. After the reagent transfer, the proper quantity of water was added and the reagents were dissolved. The flask was then placed in a constant temperature bath until a hydrolysis steady state was reached. This process required approximately 24 hours at 20°C. At the end of the equilibration period, the exchange reaction was initiated by the introduction of 5 to 25 λ of Cl^{36} solution. Since both the concentration and volume of the tracer solution were small compared to the platinum solution, no appreciable concentration change was caused by its introduction. The time of introduction of the tracer solution was called the "zero time" of the exchange reaction.

In a "fresh" solution exchange, the KCl and Na$_2$SO$_4$ were dissolved in water of the proper volume and temperature. The solid K[Pt(NH$_3$)Cl$_3$] was then added to this solution in the reaction flask and immediately after it dissolved, the exchange was initiated by the addition of the tracer solution. From this point, "fresh" and "aged" solutions were treated in an identical manner.

Aliquots of the reaction solution were removed a number of later times. To each aliquot was added [Ø$_4$As][C$_2$H$_3$O$_2$] to precipitate the slightly soluble [Ø$_4$As][Pt(NH$_3$)Cl$_3$] compound. In general, a fivefold excess of [Ø$_4$As]$^+$ ion was added, and the sample was stirred during the 1 - 3 minutes required for precipitation of [Ø$_4$As][Pt(NH$_3$)Cl$_3$]. Complete precipitation

of the $[Pt(NH_3)Cl_3]^-$ ion was never obtained and in solutions containing particularly low concentrations of platinum, it was often difficult to obtain an adequate amount of precipitate. This incomplete precipitation was believed to reflect a finite solubility of the $[\phi_4As][Pt(NH_3)Cl_3]$ salt, however experiments indicated that the exchange of solid $[\phi_4As][Pt(NH_3)Cl_3]$ with solution chloride was negligible over two hours.

$[\phi_4As][Pt(NH_3)Cl_2(OH)]$ apparently was not precipitated by the $[\phi_4As]$ ion. The absence of this compound was indicated by the constant solution pH before and after precipitation.

After precipitation was complete, each sample was transferred to the filtering apparatus described in the apparatus section and the precipitate was collected on a weighed filter paper. Since the $[\phi_4As][Pt(NH_3)Cl_3]$ salt was soluble in organic solvents, it was washed three times with water only. After washing, the paper and sample were dried overnight at $30^\circ C$.

The exchange of chloride with $[Pt(NH_3)Cl_2(H_2O)]$ was followed in a slightly different manner. The exchange was initiated by adding Cl^{36} tracer to an equilibrated solution of $[Pt(NH_3)Cl_3]^-$ and $[Pt(NH_3)Cl_2(H_2O)]$. At intervals, aliquots were removed and H_2SO_4 was added to lower the solution pH to approximately 2. The exchange in the aliquot samples was then quenched by the addition of sufficient Ag_2SO_4 to remove the $[Pt(NH_3)Cl_3]^-$ and free Cl^- as insoluble silver salts. The precipitation of slightly soluble $Ag[Pt(NH_3)Cl_2(OH)]$ was

partially suppressed by the low solution pH but it was still necessary to add a 20 - 30% calculated excess of Ag^+ to remove all the chloride.

After precipitation was complete, the mixture was filtered through a sintered glass filtering crucible and the filtrate was collected in a test tube. Approximately 10 ml. of concentrated aqueous NH_3 was added to the test tube and the resulting solution was heated for three to six hours at 80°C. The purpose of this step was to replace the two chlorides in $[Pt(NH_3)Cl_2(H_2O)]$ with ammonia and leave all the chloride free for precipitation. After heating, the solution was acidified with HNO_3. A slight clouding at this point indicated that an excess of silver ion had been added to the original solution. An excess of Ag^+ was added and the AgCl precipitates were filtered and washed.

The filter papers used in collecting the precipitate were found to absorb moisture from the air so their weights varied from day to day. For this reason, several tare papers containing no precipitate were carried along with each set of samples and the change in their weight was used to calculate the moisture content of the precipitate papers. All weighings were made to the nearest tenth of a milligram on an Ainsworth & Sons Chain-Weight balance. Since humidity corrections were occasionally large, the papers were thoroughly equilibrated with room air before weighing.

After weighing, the individual sample papers were placed

on cardboard squares and covered with a disk of cellophane (density 2.5 mg. per cm.). The disk was fastened at the edges with tape and the cardboard square was then mounted on a metal planchet which held the sample directly beneath the window of the detecting Geiger-Muller tube. The sample was then ready for counting.

During the sampling period, most precipitations were made before the exchange reaction was complete. Two samples, however, were always taken long after the original addition of tracer, at a time when the tracer was known to be completely equilibrated between the ionic chloride and the chloride in the platinum complex. These samples were known as "infinity" samples since they essentially corresponded to the distribution of tracer isotope at equilibrium or infinite time. In counting the precipitates, it was not necessary to know the absolute disintegration rate of the isotope in the sample but rather the ratio of this rate to the rate observed in the infinity samples. Therefore it was not necessary to know the counting geometry or backscattering factor of the counting equipment but merely to know that these values remain constant for all the samples.

All samples were counted for a sufficient length of time to assure that the standard deviation of the total counts was less than one per cent. A 300 microsecond tube deadtime correction was applied to correct for loss of counts at high counting rates. From the corrected rates were subtracted the normal background counting rate to give the counting rates of

the samples. For any given experiment the sample weights were essentially constant, so no self scattering correction was applied.

From the formula and molecular weight of the precipitated compound, the weight of chloride in the sample was calculated. The specific activity S, was obtained by dividing the corrected counting rate of a sample by the weight of chloride in the sample (cts./min. mg. Cl^-). This quantity was then used in the experimental treatment of the exchange results.

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III. RESULTS

A. First Aquation Equilibrium

When a sample of $K[Pt(NH_3)Cl_3]$ was dissolved in water, a slow, reversible aquation reaction took place:

(1) $\quad [Pt(NH_3)Cl_3]^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Pt(NH_3)Cl_2(H_2O)] + Cl^-$
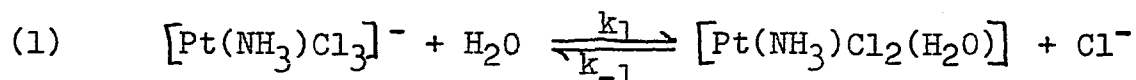
The occurrence of this reaction was demonstrated by several distinct changes in the system.

1. The solution pH decreased as aquation proceeded due to the acid dissociation of the aquo-complex:

$$[Pt(NH_3)Cl_2(H_2O)] \rightleftharpoons [Pt(NH_3)Cl_2(OH)]^- + H^+$$
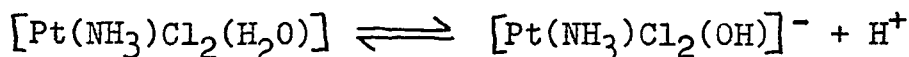
2. Ultraviolet absorption spectra taken from $220\,m\mu$ to $400\,m\mu$ showed pronounced changes as the fresh $K[Pt(NH_3)Cl_3]$ solution was allowed to age.

3. Potentiometric titrations of the system with standardized NaOH indicated slow formation of a weak acid which approached an equilibrium value.

All of these observations were consistent only with the replacement of a compound ligand by one or more solvent water molecules.

Further experiments indicated that ammonia was not replaced by water. This substitution would not be accompanied by a solution pH decrease due to the reactions:

$$[Pt(NH_3)Cl_3]^- + H_2O \rightleftharpoons [PtCl_3(OH)]^= + NH_3 + H^+$$
$$H^+ + NH_3 \rightleftharpoons NH_4^+$$
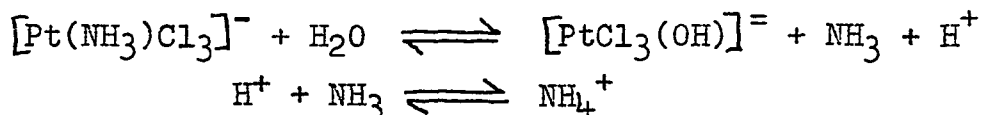
However, a significant pH decrease was observed. Also, the replacement of NH_3 by H_2O yields $[PtCl_3(H_2O)]^-$ which Grantham, Elleman, and Martin (6) have observed to be in equilibrium with $[PtCl_4]^=$. Spectrophotometric examination revealed that $[PtCl_4]^=$ ion had several absorption peaks in a region where where $[Pt(NH_3)Cl_3]^-$ absorbed only slightly. Experiments indicated that 1% $[PtCl_4]^=$ in $[Pt(NH_3)Cl_3]^-$ solutions caused observable deviations in the $[Pt(NH_3)Cl_3]^-$ spectrum. No corresponding deviations were observed in solutions of $[Pt(NH_3)Cl_3]^-$ aged for long periods. It was thus concluded that only the chlorides were replaced by water.

The concentration equilibrium constant was determined for the aquation reaction by direct potentiometric titration of the steady state aquo-complex. This titration was performed on solutions equilibrated at constant temperature and 0.318 moles/l. ionic strength. The titration disturbed the equilibrium through the neutralization of $[Pt(NH_3)Cl_2(H_2O)]$, so it was necessary to correct for the equilibrium shift during the titration. A solution aliquot was withdrawn from an equilibrated solution and a preliminary titration was made to locate the approximate endpoint. An additional sample was then withdrawn and the amount of base indicated for complete neutralization by the preliminary titration was rapidly added to the sample. A comparison of this solution pH with the first sample pH at equivalent base titer gave an indication of the amount of $[Pt(NH_3)Cl_2(H_2O)]$ formed during the first

titration. This amount was subtracted from the concentration
of acid given by the end-point in the first titration.

A typical titration curve with the single titration cor-
rection point is shown in Fig. 1. For equilibrium determina-
tions below $25^{\circ}C.$, the base titer correction was less than 3%
of the total amount of added base. This correction became
quite large at higher temperatures and contributed signifi-
cantly to the uncertainty in the equilibrium constant. Sol-
vent titration corrections were made for all samples even
though this correction was quite small. Also shown in Fig. 1
is a titration curve obtained immediately after solution of
the $K[Pt(NH_3)Cl_3]$ salt. The low equivalent base titer indi-
cated that the aquo-complex was not initially present in the
salt.

To verify the existence of a true equilibrium constant,
titrations were performed on solutions containing different
initial concentrations of $K[Pt(NH_3)Cl_3]$. The values obtained
for the aquation equilibrium constant were compatable. In
Fig. 2, the temperature dependence of the equilibrium constant
has been illustrated by $\ln K_1$ versus $1/T$ plot.

Since the activity coefficients for the platinum species
in solution were not unity, the titrations actually yielded a
concentration equilibrium constant rather than a true equilib-
rium constant. However, on the basis of the assumption that co-
efficients did not vary at fixed ionic strength, the concen-
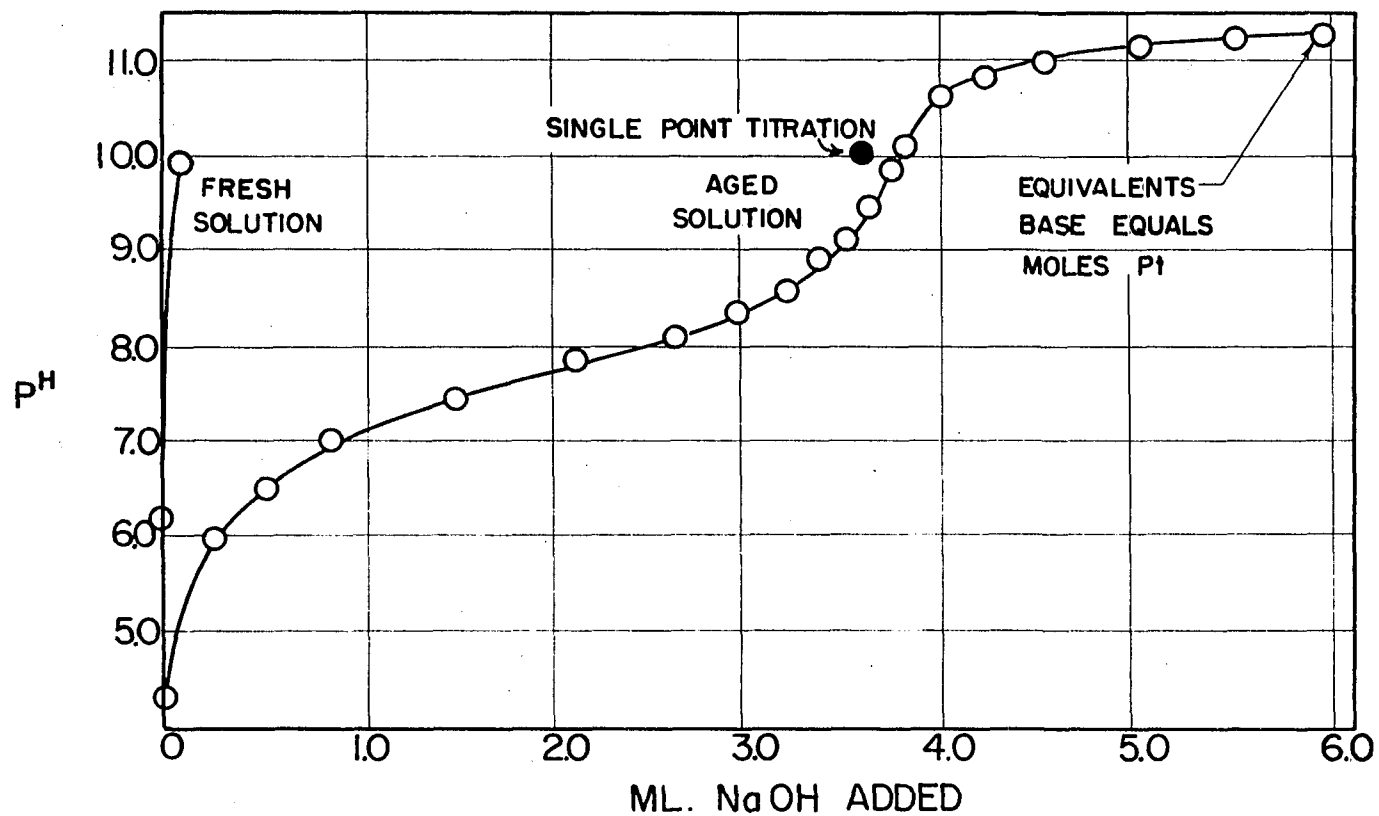tration equilibrium constant differed from the true constant

Fig. 1. Titration curves for fresh and aged solutions of $K[Pt(NH_3)Cl_3]$. Temp. = 20.0°C., initial conc. of $K[Pt(NH_3)Cl_3]$ = 0.0166 M., μ = 0.318 M.
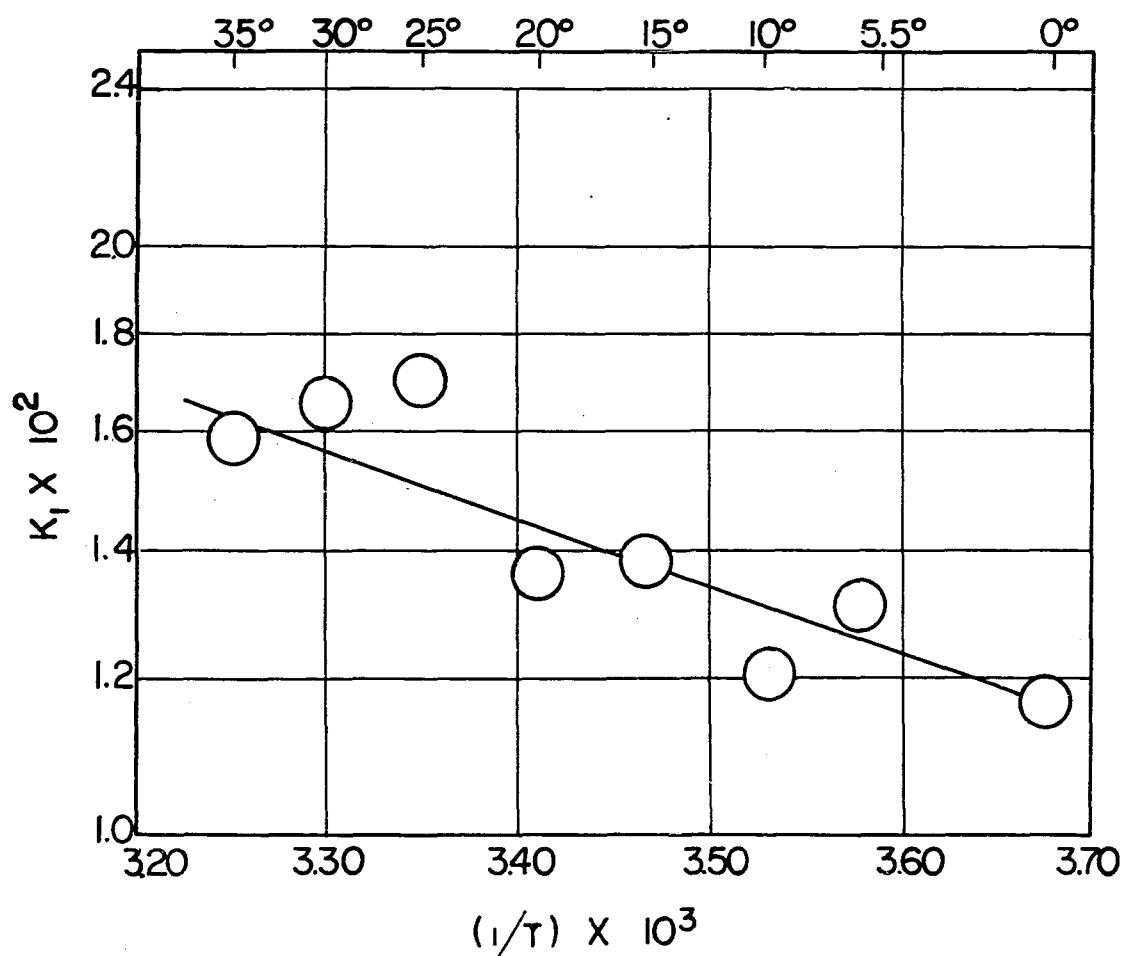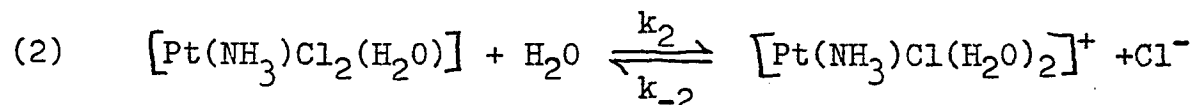
Fig. 2. Equilibrium constant for the first acid hydrolysis

(aquation) reaction, log K_1 versus 1/T.   = 0.318 M.

only by the constant ratio of the activity coefficients.

In a later portion of this thesis, the existence and equilibrium of a second aquation reaction is discussed:

(2) $\quad [Pt(NH_3)Cl_2(H_2O)] + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Pt(NH_3)Cl(H_2O)_2]^+ + Cl^-$

The acid titre contribution of $[Pt(NH_3)Cl(H_2O)_2]^+$ was negligible under the conditions for the determination of the first aquation equilibrium.

B. Determination of First Aquation Rate

The pronounced spectrum changes observed in the preceding section for the aquation of $[Pt(NH_3)Cl_3]^-$ afforded a method for measuring the rate of aquation. The absorption spectra for the nearly pure $[Pt(NH_3)Cl_3]^-$ and $[Pt(NH_3)Cl_2(H_2O)]$ complexes have been illustrated in Fig. 3. Since both platinum species were present at equilibrium, the spectrum of the equilibrium solution was intermediate between the two spectra indicated.

The aquation reaction was initiated by transferring the proper quantities of reagents to a flask containing a known amount of water at the thermostated temperature. The salts were dissolved, and an aliquot of the solution was transferred to the absorption cell in which the initial $[Pt(NH_3)Cl_3]^-$ absorbance was measured. The time lapse between the addition of solvent and the first reading was approximately three

minutes. The solution absorbancy was observed at intervals during the reaction and also at approximate chemical equilibrium.

From the initial absorbance of the $[Pt(NH_3)Cl_3]^-$ solution, the molar absorptivity of $[Pt(NH_3)Cl_3]^-$ at $343 m\mu$ was obtained. From the absorption spectrum of the equilibrium solution and the equilibrium constant, the molar absorptivity of $[Pt(NH_3)Cl_2(H_2O)]$ was calculated. From a knowledge of both these values, and the solution absorbance at time, t, the concentrations of both platinum species were obtained. In this manner, the concentration of $[Pt(NH_3)Cl_2(H_2O)]$ was determined as a function of time.

It was assumed that the aquation reaction was first order in platinum complex and the reverse step was first order in chloride and aquo-complex. A linear function of the time involving initial concentrations, the equilibrium constant and the aquo-complex concentration was then obtained. The differential equation was expressed:

$$\frac{d[Pt(NH_3)Cl_2(H_2O)]}{dt} = k_1[Pt(NH_3)Cl_3^-] - k_{-1}[Pt(NH_3)Cl_2(H_2O)][Cl^-]$$

$$= k_1(a-x) - k_{-1}(x)(b+x)$$

with a solution:

$$f(x) = -\sqrt{4k_1 a + (b+k_1)^2} \, k_{-1}t$$

The equations for determining $[Pt(NH_3)Cl_2(H_2O)]$ concentrations, the derivation of the rate equation and the expression for f(x) have been presented in the section dealing with kinetics

Fig. 3. Absorption spectra for solutions of $[Pt(NH_3)Cl_3]^-$, $[Pt(NH_3)Cl_2(OH)]^-$, and $[Pt(NH_3)Cl_2(H_2O)]$. Temp. = $24 \neq 1^{O}C$. All concentrations 0.001 M., 10 cm cells. (The $[Pt(NH_3)Cl_3]^-$ spectrum was obtained immediately after the dissolution of the complex; no KCl was added to suppress the aquation.)

$[P_t (NH_3) Cl_3]^-$

$[P_t (NH_3) Cl_2 (H_2O)]$

$[P_t (NH_3) Cl_2 (OH)]^-$

ABSORBANCE

WAVELENGTH IN MILLIMICRONS

38b
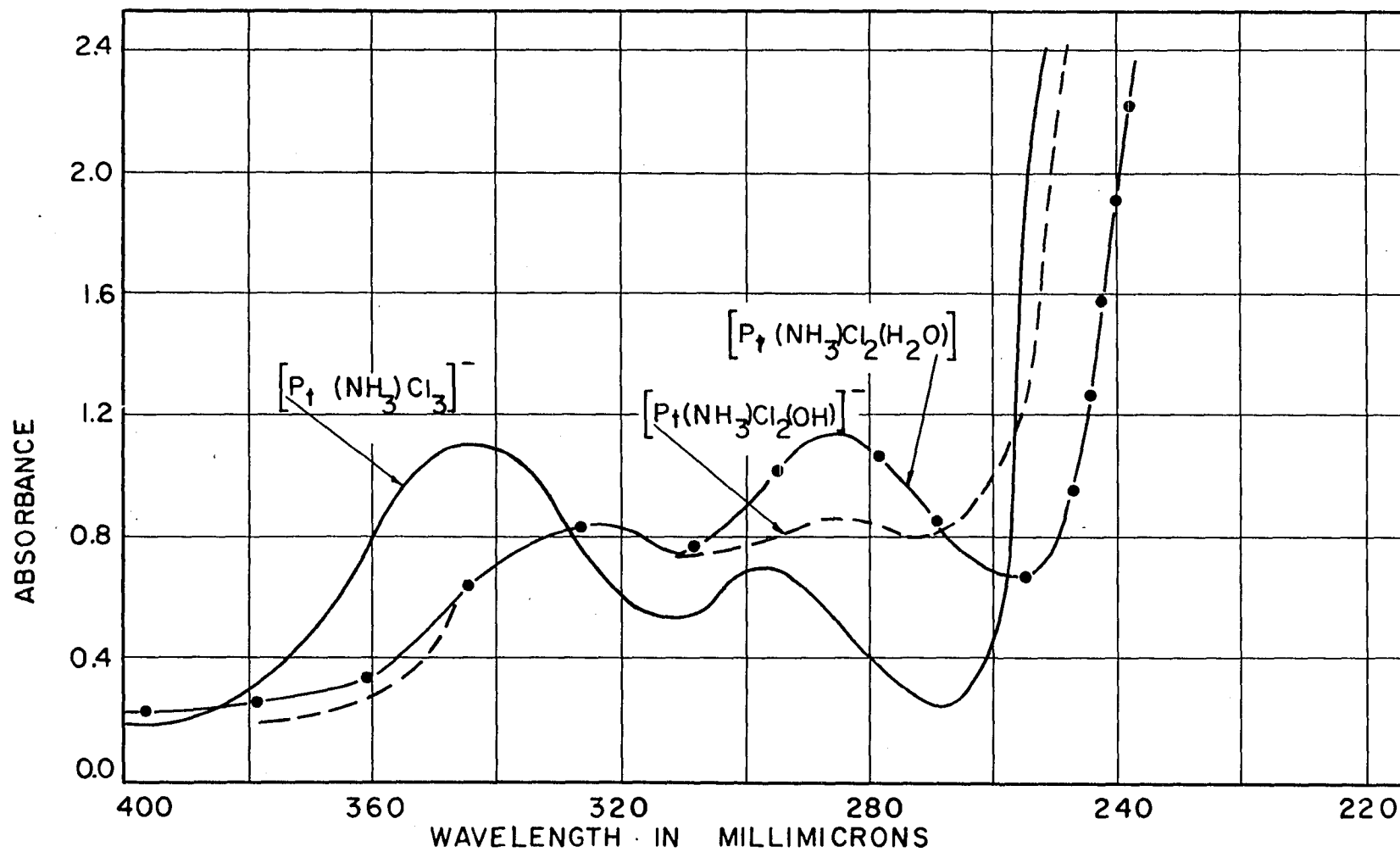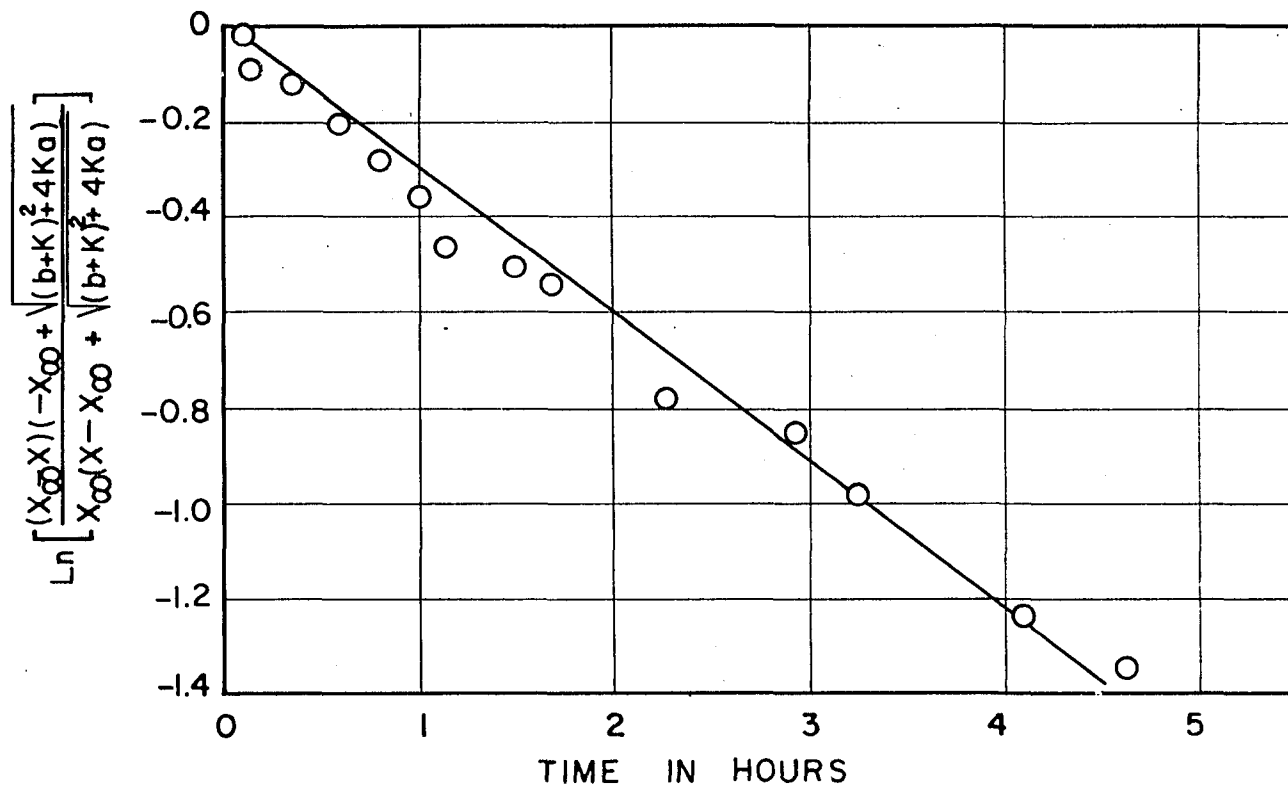
Fig. 4. Kinetics of the aquation of $[Pt(NH_3)Cl_3]^-$. Temp. $= 25.0^\circ C$. Absorbance at $343\ m\mu$. $a = 0.0166$ M. $b = 0.010$ M. $x_\infty = 0.00745$ M. $\mu = 0.318$ M.
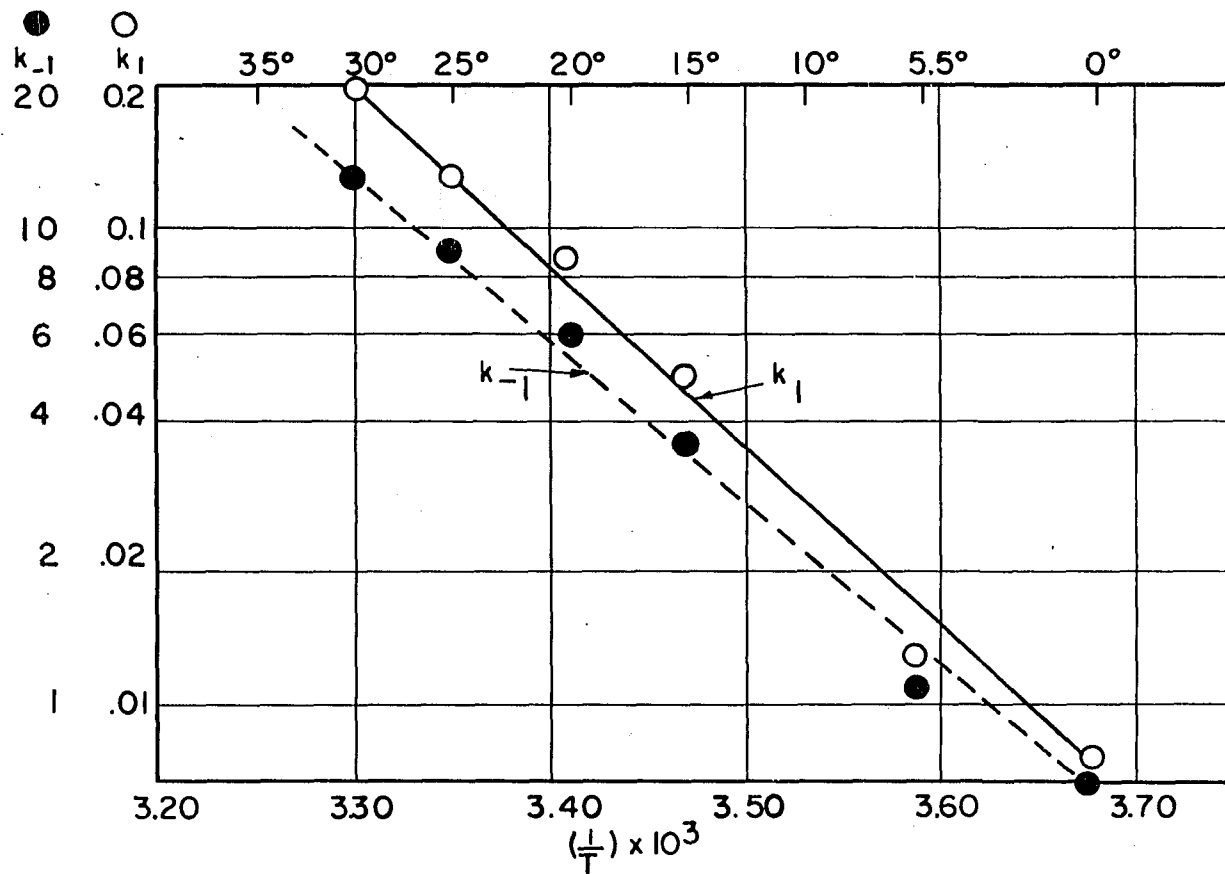
Fig. 5. Rate constants for the first acid hydrolysis (aquation) reaction, log k versus 1/T. Units: k_{-1} (1. moles^{-1}hr.$^{-1}$), k_1 (hr.$^{-1}$). $\mu = 0.318$ M.

Fig. 6.   Absorption spectra for five platinum compounds.   Temp. = 24 ≠ 1°C., all con-

centrations 0.001 M., 10 cm. cells, no ionic strength reagents added.

Legend (top-left of figure):
- ● TRANS–Pt(NH$_3$)$_2$Cl$_2$
- – – – CIS–Pt(NH$_3$)$_2$Cl$_2$
- –●– Pt(NH$_3$)Cl$_2$(H$_2$O)
- ○ K Pt(NH$_3$)Cl$_3$
- —— K$_2$PtCl$_4$

Y-axis: ABSORBANCE (2.00, 1.60, 1.20, 0.80, 0.40)

X-axis: WAVELENGTH IN MILLIMICRONS (370, 350, 330, 310, 290, 270, 250, 230)

41b
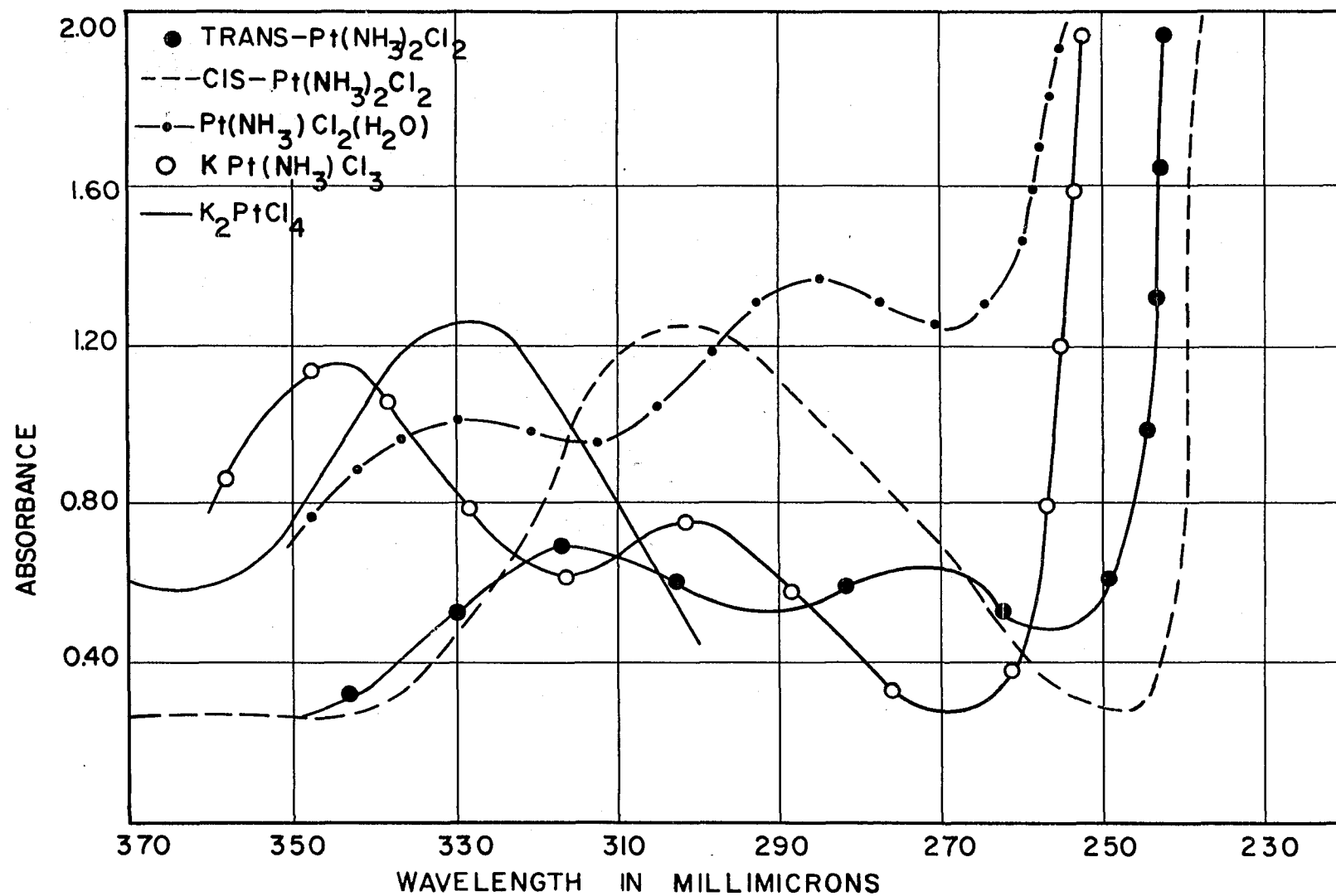
Table 1. Rate and equilibrium constants for the first aquation reaction[a]

Temp. ($^\circ$C.)	$K_{eq.}$ (moles/l.)	k_1 (hr.$^{-1}$)	k_{-1} (l. moles^{-1}hr.$^{-1}$)
0.0	0.0115	0.0077	0.669
5.5	0.0122	0.013	1.10
10.0	0.0128	---	--
15.0	0.0134	0.047	3.53
20.0	0.0142	0.085	5.97
25.0	0.0148	0.131	8.88
30.0	0.0154	0.210	13.62
35.0	0.0162	---	--

[a] $[Pt(NH_3)Cl_3]^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Pt(NH_3)Cl_2(H_2O)] + Cl^-$
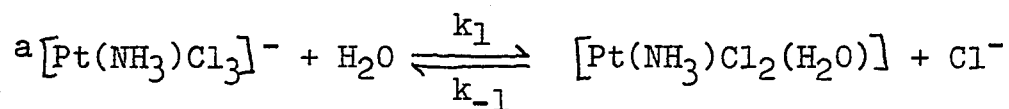
$$K_{eq.} = \frac{[Pt(NH_3)Cl_2(H_2O)][Cl^-]}{[Pt(NH_3)Cl_3^-]}$$

$\Delta H^o = 1.6$ kcal./mole
$\Delta S^o = -1$ e.u.
for k_1: $\Delta H^{\ddagger} = 18.4$ kcal./mole
$\Delta S^{\ddagger} = -15$ e.u.
for k_{-1}: $\Delta H^{\ddagger} = 16.8$ kcal./mole
$\Delta S^{\ddagger} = -14$ e.u.

calculations.

A straight line was obtained when experimental determinations of the aquo-complex concentration were plotted as f(x) versus t. From the slope of the line, the value for k_{-1} was calculated.

A typical plot of f(x) versus t is expressed in Fig. 4. Despite the experimental scatter in the points, all the kinetics experiments were consistent with linear plots. In Fig. 5, the temperature dependence of the rate constants has been given as a log k versus t plot. Fig. 6 illustrates the absorption spectra of various platinum complexes. In Table 1, the equilibrium and rate constants obtained for the first aquation reaction have been tabulated.

C. Chloride Exchange with $[Pt(NH_3)Cl_3]^-$

When tracer chloride was added to solutions of $[Pt(NH_3)Cl_3]^-$, it was observed that all three chlorides in the complex were equilibrated with the tracer solution. Since this point is quite important to the future development of the problem, the details of the defining experiment have been discussed.

If only two of the three chlorides in $[Pt(NH_3)Cl_3]^-$ undergo exchange, the final specific activity of the chloride in the platinum complex may be expressed:

$$S_\infty (2) = \frac{2b(S_b)}{3(b+2a)}$$

where a = concentration of $[Pt(NH_3)Cl_3]^-$, b = concentration
of tracer chloride solution, and S_b = specific activity of the
tracer chloride solution. However, if all three of the ligand
chlorides exchange:

$$S_\infty (3) = \frac{b(S_b)}{b+3a}$$

If b << a, then $S_\infty (2) \cong S_\infty (3)$, but if b >> a,
$S_\infty (2) \cong 2/3\, S_\infty (3) \cong 2/3\, S_b$. It is under the latter condi-
tions that the greatest difference between $S_\infty (2)$ and $S_\infty (3)$
is obtained.

The chloride tracer solution was prepared by dissolving
a known quantity of KCl salt in 100 ml. of water and adding
100λ of Cl^{36} tracer solution. The specific activity of the
solution was obtained by precipitating aliquots as AgCl and
mounting and counting the precipitates in the manner described
in the "Experiments" section. A definite aliquot of this
tracer solution was then added to a known concentration of
$[Pt(NH_3)Cl_3]^-$. The exchange was allowed to proceed for a
period of time believed to be sufficient for near equilibra-
tion of the ligands. The platinum complex was precipitated
as $[\emptyset_4As][Pt(NH_3)Cl_3]$ and the activity in the sample was deter-
mined. The conditions and results of this experiment have
been summarized in Table 2.

The results indicated that all three chlorides were equi-
librated. With this feature established, it was then possible
to study the kinetics for the exchange of the three chloride

Table 2. Lability of all three chlorides in $[Pt(NH_3)Cl_3]^{-}$ [a]

Temp.	(a) $[Pt(NH_3)Cl_3^{-}]$ (moles/l.)	(b) Added $[Cl^{-}]$ (moles/l.)	Time of contact (hr.)	$S_\infty(3)$	$S_\infty(2)$	S_∞ (obs.)
20.0°	0.0083	0.134	144	92	65	97.8 ± 1.6
20.0°	0.0083	0.134	144	92	65	96.9 ± 1.6
20.0°	0.0083	0.134	144	92	65	94.2 ± 1.5
20.0°	0.0083	0.134	145	92	65	96.7 ± 1.6
20.0°	0.0166	0.075	100	66	51	65.2 ± 1.0
20.0°	0.0166	0.075	100	66	51	65.4 ± 1.0

[a] Specific activity of stock chloride solution: 109 ± 4 cts./min. mg. Cl^{-}.

If two chlorides exchanged: $S_\infty = S_\infty(2) = \dfrac{2b(S_b)}{3(b+2a)}$

If three chlorides exchanged: $S_\infty = S_\infty(3) = \dfrac{b(S_b)}{(b+3a)}$

45

ligands.

A large number of "aged" exchange experiments were performed by the method outlined in the "Procedures" section. The conditions of the experiments have been tabulated in Table 3.

The specific activities of the precipitated samples were determined for each exchange experiment. These values were then individually divided by the equilibrium specific activity (S_∞) for the experiment to yield a quantity defined as the fraction of exchange, F. For each set of exchange conditions, six to eight values of F were obtained. When log (1-F) was plotted versus time for any experiment, an apparent straight line was observed. This function appeared linear for values of F as high as 0.8. In Fig. 7, log (1-F) values for two sets of initial concentration conditions have been plotted versus time to illustrate the apparent linearity. The exchange time at which F = 0.5 has been called the time of half reaction. This time has been designated by the symbol $T_{\frac{1}{2}}$ (obs.) and has been tabulated in Table 3 for all the exchange experiments.

In addition to the $T_{\frac{1}{2}}$ (obs.) values, other information was obtained from the exchange experiments. The addition of hydrogen ion and exposure to room light did not affect the exchange rate. The latter observation was somewhat unexpected, since Grantham, Elleman, and Martin (6) observed a small photo-acceleration of chloride exchange in $[PtCl_4]^=$ solutions. Solution aging far beyond the time required for satisfactory

equilibration of the aquo-complex caused no change in the rate of exchange. This observation indicated that no slow chemical process occurred which affected the exchange rate. The addition of small quantities of oxidizing agent greatly accelerated the exchange rate.

Since log (1-F) versus time plots were linear over the observed range, it was inferred that all three chlorides exchanged at approximately the same rate. For the mathematical derivations, all the chlorides were taken to be equal. With this assumption, the rate of appearance of activity in the $[Pt(NH_3)Cl_3]^-$ complex due only to the first aquation reaction was determined. This derivation has been given in detail in the section dealing with kinetics calculations. The solution of the exchange equation was of the form:

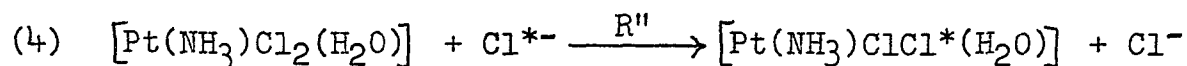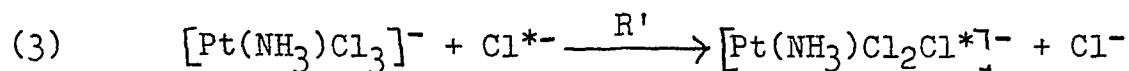$$1 - \frac{S}{S_\infty} = 1 - F = A_1 e^{-\alpha_1 t} + A_2 e^{-\alpha_2 t}$$

where F is the fraction of exchange in $[Pt(NH_3)Cl_3]^-$ at time t and A_1, A_2, α_1, and α_2 are known functions of the initial solution concentrations and the aquation rate. Under conditions where the chloride concentration was large, $A_1 \rightarrow 1$, $A_2 \rightarrow 0$, and the rate equation was expressed in the form:

$$1 - F = e^{-\alpha_1 t}$$

The times of half reaction predicted from the aquation process have been tabulated in Table 3 under the column heading; $T_{\frac{1}{2}}$ (aquation). In Fig. 7, calculated log (1-F) versus time plots for two typical sets of initial concentration

conditions have been given to indicate the general slope of the functions. A comparison of the exchange times of half reaction predicted from aquation data with those experimentally obtained showed that in all cases, the experimental half-times were shorter.

It was believed that the observed deviations were too large to be explained by errors in the aquation rate determination. The short observed exchange halftimes must therefore be due to the presence of an additional means of exchange. This additional exchange reaction could be either a direct exchange with the $[Pt(NH_3)Cl_3]^-$ complex or an exchange with the $[Pt(NH_3)Cl_2(H_2O)]$ aquo-complex.

(3) $[Pt(NH_3)Cl_3]^- + Cl^{*-} \xrightarrow{\quad R' \quad} [Pt(NH_3)Cl_2Cl^*]^- + Cl^-$

(4) $[Pt(NH_3)Cl_2(H_2O)] + Cl^{*-} \xrightarrow{\quad R'' \quad} [Pt(NH_3)ClCl^*(H_2O)] + Cl^-$

The occurrence of either reaction would increase the rate of appearance of activity in the $[Pt(NH_3)Cl_3]^-$ species.

An expression was derived to give the rate of appearance of activity in the $[Pt(NH_3)Cl_3]^-$ complex by a combination of the first aquation reaction with reaction (3). The details of the calculations have been given in the section dealing with kinetics calculations. Since the rate constant for the proposed additional reaction was unknown, the rate equations were solved in terms of the unknown rate, R'. For mathematical convenience, R' was expressed as the ratio R'/R where:

$$\gamma = \frac{R'}{R} = \frac{k'[Pt(NH_3)Cl_3^-]^m[Cl^-]^n}{k_1[Pt(NH_3)Cl_3^-]}$$

Table 3. Conditions and results of exchange experiments involving $[Pt(NH_3)Cl_3]^-$ and Cl^-

a^a (moles/l.)	b^b (moles/l.)	x_∞^c (moles/l.)	Aging time (hr.)	Sol. pH	Obs. $T_{\frac{1}{2}}$ (hr.)	Aquation $T_{\frac{1}{2}}$ (hr.)	γ	β	Temp. °C.
0.0166	0.010	0.00745	--	--	4.3	8.0	0.7		20.0
0.0166[d]	0.010	0.00745	42	--	4.0				
0.0166[e]	0.010	0.00745	50	5.58	5.1				
0.0166[f]	0.010	0.00745	49	5.41	4.9				
0.0166[g]	0.010	0.00745	30	3.92	1 min				
0.0166[h]	0.010	0.00745	42	0.90	4.5				
0.0166	0.025	0.00530	34	--	6.2	12.2	0.8	3.0	
0.0166	0.050	0.00348	34	--	9.5	15.8	0.7	0.8	
0.0166	0.075	0.00257	34	--	9.5	17.3	0.8	1.1	
0.0166	0.268	0.00745	40	6.58	13.0	21.5	0.6		

[a] a = Initial conc. of $[Pt(NH_3)Cl_3]^-$.

[b] b = Initial conc. of KCl.

[c] x_∞ = Equilibrium conc. of $[Pt(NH_3)Cl_2(H_2O)]$.

[d] Exchange solution exposed to room light.

[e] Ionic strength = 0.0266 moles/l.

[f] Ionic strength = 0.080 moles/l.

[g] 5×10^{-4} M. $(NH_4)_2Ce(NO_3)_6$ added.

[h] Solution swamped with H_2SO_4.

Table 3. (Continued)

| a^a (moles/l.)	b^b (moles/l.)	x_∞^c (moles/l.)	Aging time (hr.)	Sol. pH	Obs. $T_{\frac{1}{2}}$ (hr$^{\frac{1}{2}}$)	Aquation $T_{\frac{1}{2}}$ (hr$^{\frac{1}{2}}$)	γ	β	Temp. °C.
0.0083	0.010	0.00416	42	4.98	6.0	11.5	0.7	15.0	
0.0083^d	0.134	0.00079	0	--	14.0	22.3	0.6	0.7	
0.0083	0.134	0.00079	0	--	14.0				
0.0083	0.201	0.00055	40	5.96	14.0	22.9			
0.0083	0.268	0.00041	42	6.02	14.5	23.3	0.6	0.7	
0.00415	0.010	0.00223	42	4.89	9(?)	18.5	0.8	8.0	
0.0166	0.010	0.00772	24	5.51	1.8		0.6		30.0
0.0083	0.134	0.00085	24	6.19	4.5		1.0		
0.0166	0.010	0.00759	12	5.01	3.2		0.5		25.0
0.0083	0.134	0.00082	12	6.10	7.2		1.0		
0.0166	0.010	0.00726	42	--	8.0		0.6		15.0
0.0166	0.010	0.00695	216	5.51	25.5		0.8		5.5
0.0166	0.050	0.00236	216	5.78	58.0		0.6		
0.0083	0.134	0.00069	144	6.32	96.0		0.5		
0.0166	0.010	0.00676	117	--	48.0		0.7		0.0
0.0083	0.134	0.00065	117	--	159.0		0.5		
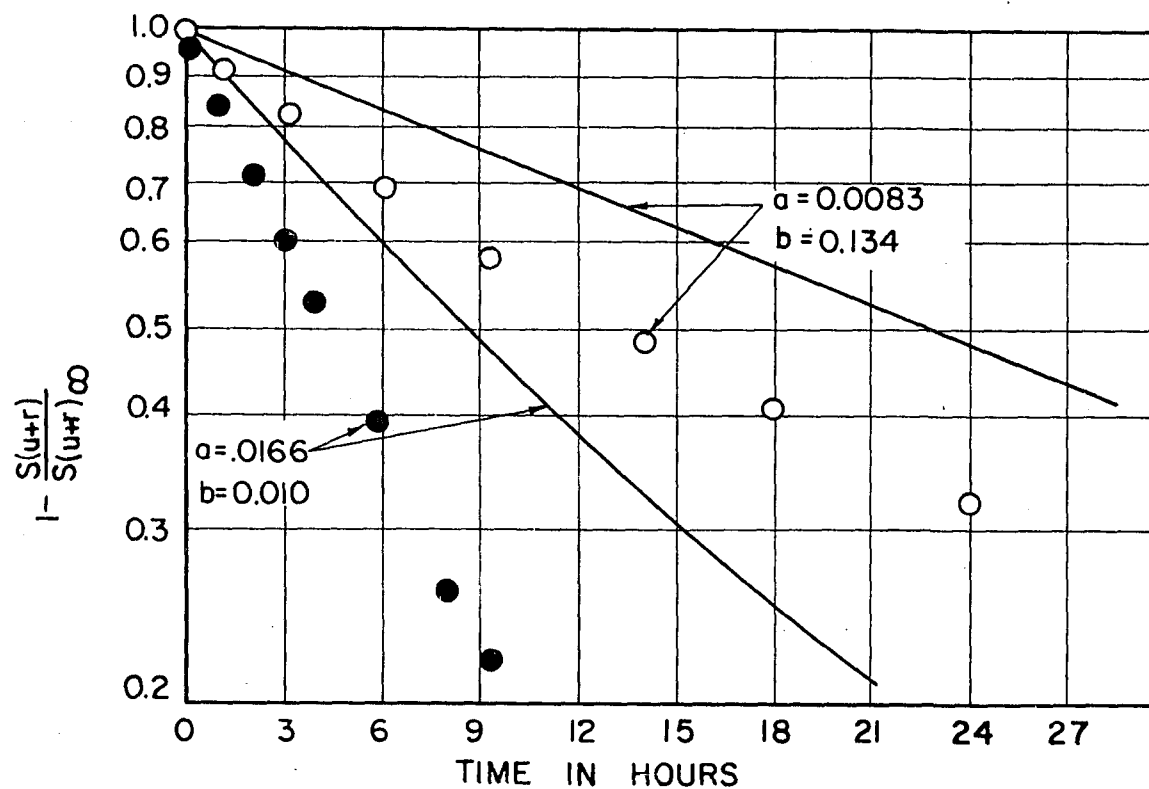
Fig. 7. Fraction of exchange in equilibrium $[Pt(NH_3)Cl_3]^-$ solutions versus time.

O , ● = observed exchange, —— = exchange calculated on basis of aquation reaction only, a = initial conc. $[Pt(NH_3)Cl_3]^-$, b = initial conc. $[Cl^-]$, μ = 0.318 M.

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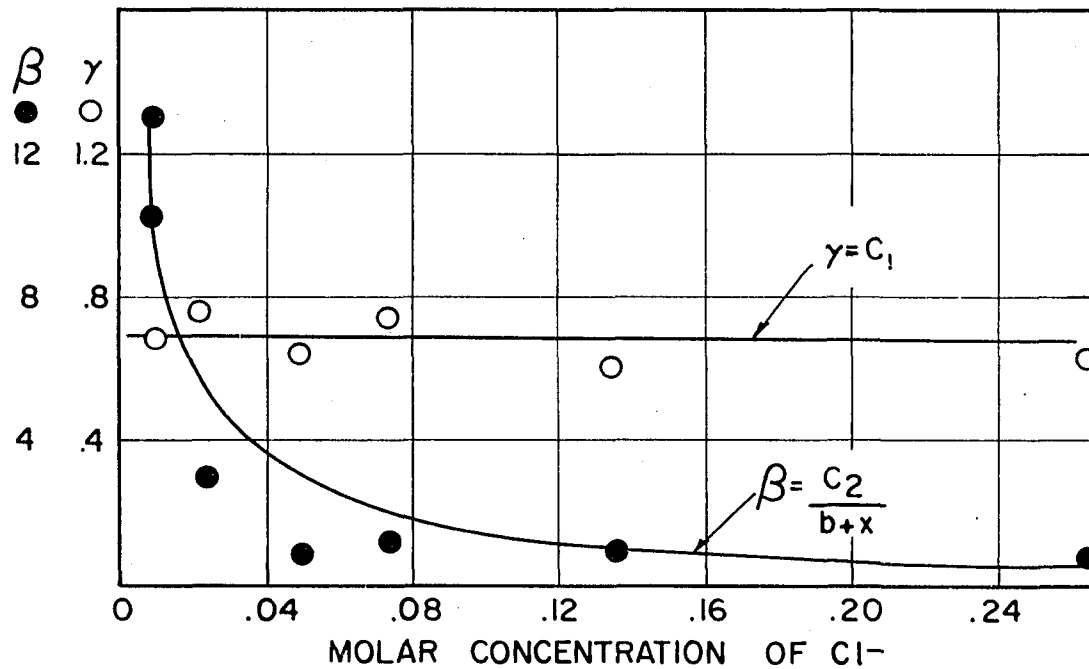
Fig. 8. Calculated values of γ and β obtained from exchange experiments versus chloride concentration. Temp. = 20.0°C.

Trial values of γ were inserted into the rate equations which were solved to give calculated times of half reaction. For a given solution concentration, the value of γ was independently varied until the calculated time of half reaction corresponded to the observed time of half reaction. This operation was performed for all experimental conditions and a single value of γ was obtained for each experiment. Within reasonable error, all the γ values were constant. Thus it was possible to explain all the observed exchange in $[Pt(NH_3)Cl_3]^-$ by the aquation reaction plus an additional reaction with the kinetic equation:

$$R' = k'[Pt(NH_3)Cl_3^-]$$

The values of γ obtained from the calculations have been tabulated in Table 3. In Fig. 8, the values of γ obtained at $20.0^\circ C$. have been plotted versus the chloride concentration.

A similar procedure was carried out for the exchange of chloride with $[Pt(NH_3)Cl_2(H_2O)]$. The symbol β was used to represent the rate R'' where:

$$\beta = \frac{R''}{R} = \frac{k''[Pt(NH_3)Cl_2(H_2O)]^m[Cl^-]^n}{k_{-1}[Pt(NH_3)Cl_2(H_2O)][Cl^-]}$$

The values of β required to give identical experimental and observed times of half reaction for $[Pt(NH_3)Cl_3]^-$ have been tabulated in Table 3 for each set of experimental conditions. These values have also been plotted in Fig. 8 against chloride concentration. The curve passing through the β values is of the form $\beta = \frac{C_2}{b+x}$, which corresponds to a rate R'' where $m = 1$, $n = 0$.

The γ and β values fit calculated curves of the form $\gamma = c_1$, and $\beta = \dfrac{c_2}{b + x}$ quite well. Thus the additional observed exchange could be explained for all experimental conditions by either an additional exchange with the $[Pt(NH_3)Cl_3]^-$ complex or an additional exchange with the $[Pt(NH_3)Cl_2(H_2O)]$ complex. The first reaction would be of the form:

$$R' = k'[Pt(NH_3)Cl_3^-]$$
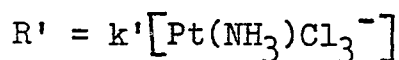
while the second reaction would be:

$$R'' = k''[Pt(NH_3)Cl_2(H_2O)]$$
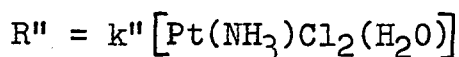
Rather than differentiate between possible processes, our treatment thus far has merely indicated that either one will explain the additional exchange.

To resolve this difficulty, experiments were designed to exploit basic differences in the two methods of exchange. An exchange experiment was performed using a "fresh" $[Pt(NH_3)Cl_3]^-$ solution and a very low concentration of added chloride ion. Aliquots were removed immediately after the initiation of the reaction and at intervals up to two hours. The results of this exchange experiment indicated a rapid introduction of chloride tracer into the $[Pt(NH_3)Cl_3]^-$ complex. Since the fresh solution contained initially only the $[Pt(NH_3)Cl_3]^-$ ion, any exchange involving the aquo-complex could not take place until appreciable concentration of $[Pt(NH_3)Cl_2(H_2O)]$ were formed. Therefore, the rapid appearance of activity in the $[\emptyset_4As][Pt(NH_3)Cl_3]$ precipitates could be due only to an

additional exchange with $[Pt(NH_3)Cl_3]^-$, as represented by Reaction No. (3).

Fig. 9 compares the observed initial exchange slope with the slope predicted for a reaction with a γ of 0.7 and a γ of 0.5. It is evident that the correspondence is quite good. For comparison, the lower curve along the abscissa indicates the fastest possible rate at which activity can be introduced into the $[Pt(NH_3)Cl_3]^-$ complex by a reaction with the $[Pt(NH_3)Cl_2(H_2O)]$ aquo-complex.

Other similar experiments were performed with fresh solutions and different concentrations of added chloride ion. It was observed that if chloride concentration were kept below 0.020 M., the experimental initial slope points agreed quite well with the curves predicted for a γ of about 0.7. At higher chloride concentrations, it became impossible to determine the initial slope for the exchange. Under these conditions, the equilibrium concentration of $[Pt(NH_3)Cl_2(H_2O)]$ was much lower. The introduction of significant activity to $[Pt(NH_3)Cl_3]^-$ by the reversal of aquation therefore occurred at much shorter reaction times. This reaction resulted in a rapidly increasing exchange curve which prevented the evaluation of the initial slope.

It was believed that the initial slope experiments were conclusive in demonstrating the existence of an additional exchange with the $[Pt(NH_3)Cl_3]^-$ complex. However, the variation in experimental points prevented the assignment of an

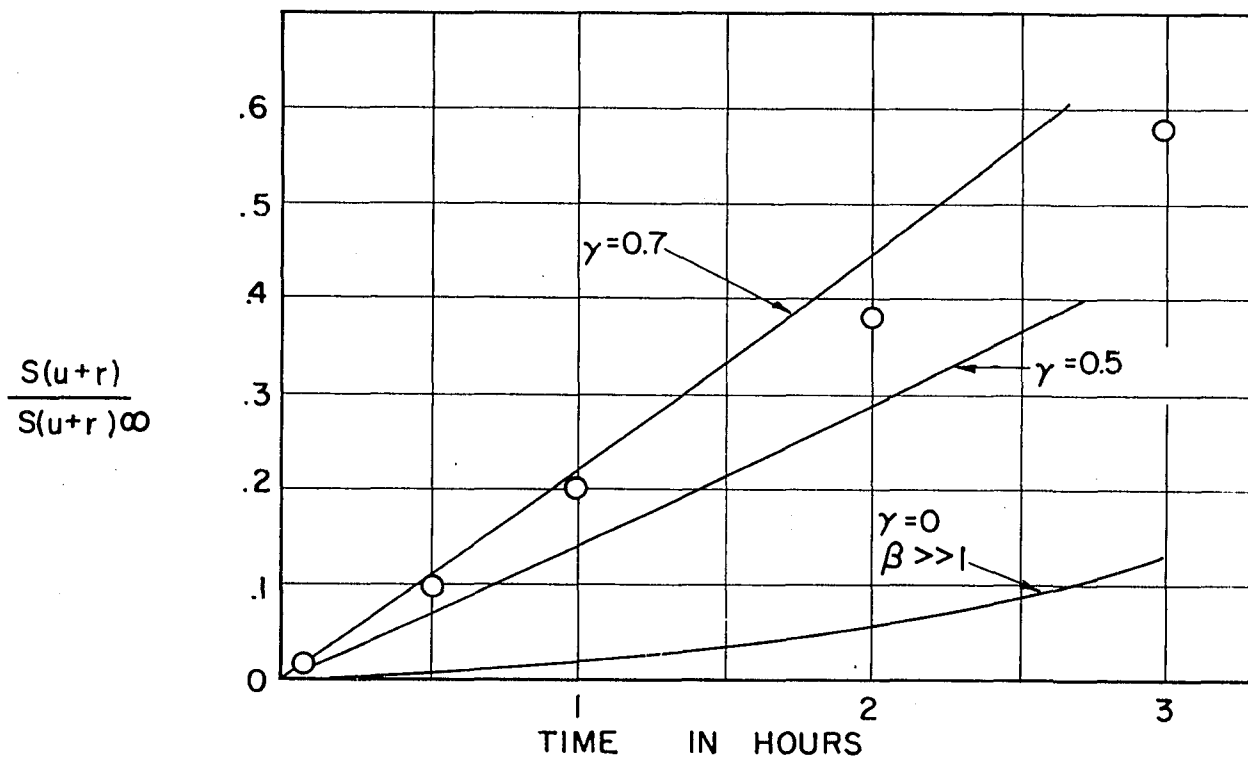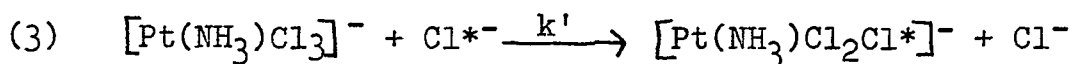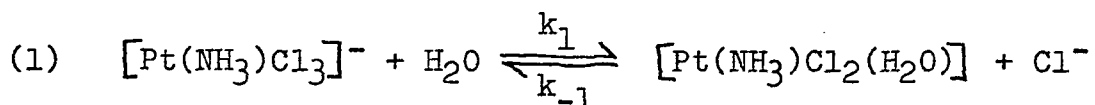Fig. 9. Observed fraction of exchange versus time for fresh $[Pt(NH_3)Cl_3]^-$ solution. Temp. = 20.0°C., initial conc. $[Pt(NH_3)Cl_3]^- = 0.0166$ M., initial conc. $[Cl]^- = 0.0050$ M., $\mu = 0.318$ M. O = experimental points, — = calculated exchange fractions.

accurate value of γ more specific than the general range $\gamma = 0.5$ to 0.8. The value $\gamma = 0.7$ was employed as a general average. The data in Table 3 indicated that this value most closely explained the additional observed exchange for the largest number of cases.

Two reactions have now been determined by which chloride activity was introduced into the $[Pt(NH_3)Cl_3]^-$ complex:

$$(1) \quad [Pt(NH_3)Cl_3]^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Pt(NH_3)Cl_2(H_2O)] + Cl^-$$

$$(3) \quad [Pt(NH_3)Cl_3]^- + Cl*^- \overset{k'}{\longrightarrow} [Pt(NH_3)Cl_2Cl*]^- + Cl^-$$

The rate constants for the first reaction have been accurately determined and a good approximation ($\gamma = 0.7 \pm 0.2$) has been obtained for the rate in the second reaction. Within the accuracy of the data, these two reactions adequately explained all the observed exchange times of half reaction for $[Pt(NH_3)Cl_3]^-$.

An additional experiment was devised to support the above two reactions as the only means of exchange. The predicted rate of appearance of activity in the $[Pt(NH_3)Cl_2(H_2O)]$ complex is much slower than the rate of appearance in $[Pt(NH_3)Cl_3]^-$. Therefore, an experiment demonstrating low specific activities in $[Pt(NH_3)Cl_2(H_2O)]$ would be convincing proof of the validity of the above reaction scheme. This exchange experiment was performed by the method outlined in the "Procedures" section.

Contrary to the predicted slow activity increase in the $[Pt(NH_3)Cl_2(H_2O)]$ complex, a rapid specific activity increase
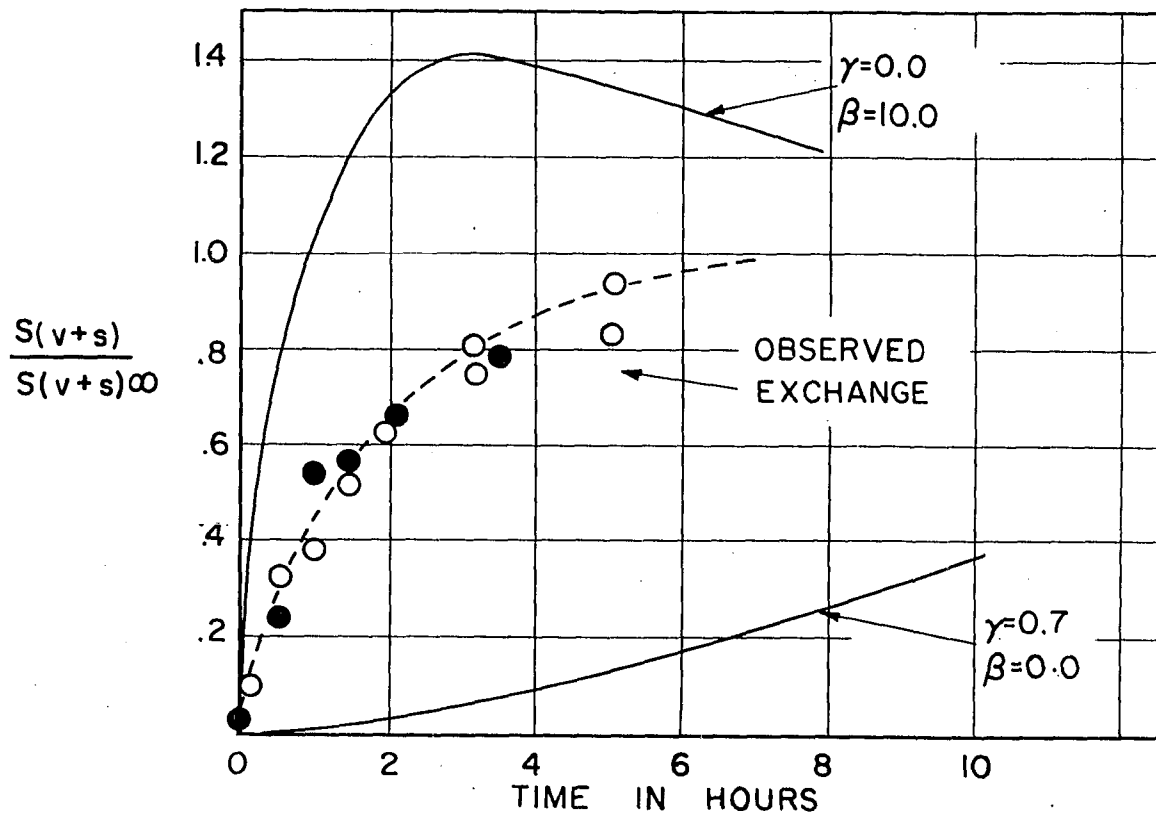
Fig. 10. Observed fraction of exchange in $[Pt(NH_3)Cl_2(H_2O)]$ versus time. Temp. = 20.0°C., conc. $[Pt(NH_3)Cl_3]^-$ = 0.00915 M., conc. $[Pt(NH_3)Cl_2(H_2O)]$ = 0.00745 M., conc. $[Cl]^-$ = 0.0175 M., μ = 0.318 M. (The solid curves correspond to calculated exchange curves for the indicated conditions.)

Fig. 11. Observed fraction of exchange in $[Pt(NH_3)Cl_2(H_2O)]$ versus time. Temp. = 20.0°C., conc. $[Pt(NH_3)Cl_3]^- = 0.00915$ M., conc. $[Pt(NH_3)Cl_2(H_2O)] = 0.00745$ M., conc. $[Cl]^- = 0.0175$ M., $\mu = 0.318$ M. Upper curve: equivalent chlorides in $[Pt(NH_3)Cl_2(H_2O)]$. Lower curve: only one labile chloride in $[Pt(NH_3)Cl_2(H_2O)]$.
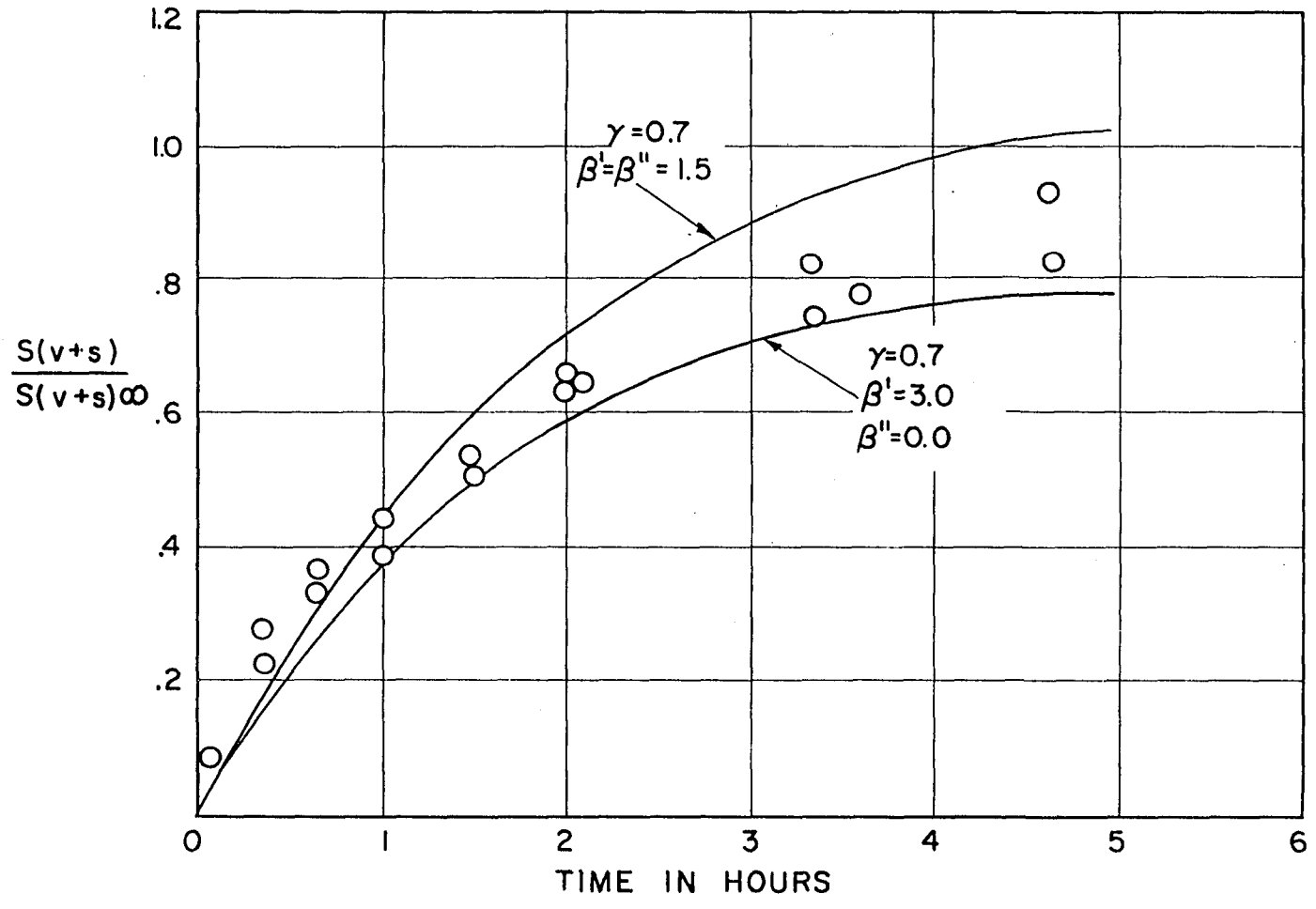
was observed. Fig. 10 shows the S/S_∞ experimental points plotted against time for the $[Pt(NH_3)Cl_2(H_2O)]$ exchange. Also included in the graph is the curve predicted on the basis that exchange occurs only through aquation and an additional γ reaction with $[Pt(NH_3)Cl_3]^-$ complex (reaction 3). The rapidly increasing curve ($\beta = 10$) given on the graph shows the rate of activity increase necessary to explain all the activity in the $[Pt(NH_3)Cl_3]^-$ complex by an aquation reaction and an additional β-reaction.

The only possible conclusion to be drawn from the rapid activity increase in the $[Pt(NH_3)Cl_2(H_2O)]$ complex was that an additional exchange reaction was occurring directly with the aquo-complex.

(4) $\quad [Pt(NH_3)Cl_2(H_2O)] + Cl^{*-} \xrightarrow{\;\;k''\;\;} [Pt(NH_3)ClCl^*(H_2O)] + Cl^-$
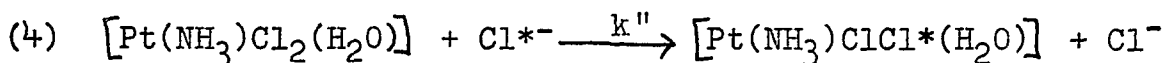
This reaction was not detected by exchange studies with the $[Pt(NH_3)Cl_3]^-$ complex because the rate constant k'' was not high enough to cause appreciable decrease in the $[Pt(NH_3)Cl_3]^-$ times of half reaction. What reduction did result was probably reflected in the uncertainty of the determination of γ.

Henceforth, for convenience, the additional exchange process with the $[Pt(NH_3)Cl_3]^-$ complex shall be referred to as the γ-reaction while the additional reaction with $[Pt(NH_3)Cl_2(H_2O)]$ will be designated as the β-reaction. This designation will be used since these parameters represent their respective reactions in the rate equations.

D. Behavior of $[Pt(NH_3)Cl_2(H_2O)]$ Solutions

1. Chloride exchange with $[Pt(NH_3)Cl_2(H_2O)]$

In the preceding section, it was observed that one or both of the chlorides in $[Pt(NH_3)Cl_2(H_2O)]$ exchanged rapidly. Additional exchange experiments were performed at $0.0^{\circ}C.$, $20.0^{\circ}C.$, and $30.0^{\circ}C.$ on "aged" $[Pt(NH_3)Cl_3]^-$ solutions. The rate of appearance of activity in $[Pt(NH_3)Cl_2(H_2O)]$ was determined by the method outlined in the "Procedures" section.

The rate constants for the β-exchange reaction were determined by fitting experimental (S/S_∞) versus time plots with calculated exchange curves. The method of calculation has been given in detail in the "Kinetics Calculations" section. The initial portion of the exchange curve was believed to be the most accurate so the greatest emphasis was placed on fitting this portion. In Fig. 11, the points obtained from an exchange experiment at $20.0^{\circ}C.$ have been plotted along with two calculated curves. The upper calculated curve was obtained by assuming that both chlorides in $[Pt(NH_3)Cl_2(H_2O)]$ exchanged at the same rate. This curve satisfactorily fit the observed points over the early portion of the exchange but did not fit well beyond two exchange halftimes. The lower curve was obtained by assuming that only one of the chlorides in $[Pt(NH_3)Cl_2(H_2O)]$ exchanged with solution chloride. This curve also did not fit the experimental points beyond two exchange halftimes. In a later portion of this thesis,

additional experiments of this nature are discussed with regard to unequal exchange rates for the two chlorides in $[Pt(NH_3)Cl_2(H_2O)]$.
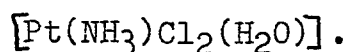
In Table 4, the rate constants for the chloride exchange with $[Pt(NH_3)Cl_2(H_2O)]$ have been tabulated for $0.0^\circ C.$, $20.0^\circ C.$, and $30.0^\circ C.$ These values were obtained from the calculated curves which fit the observed initial slope for (S/S_∞) versus time plots. It was assumed that both chlorides in the $[Pt(NH_3)Cl_2(H_2O)]$ complex exchanged at the same rate. Since $[Pt(NH_3)Cl_2(H_2O)]$ formed $[Pt(NH_3)Cl_3]^-$ at moderate chloride concentrations, all the exchange experiments were performed at very low chloride concentrations. Therefore, a direct determination of chloride dependence for the exchange process was precluded. However, the chloride dependence must have been nearly zero order; otherwise the observed introduction of activity into $[Pt(NH_3)Cl_3]^-$ would have been much faster in the high chloride experiments.

Table 4. Rate constants for exchange of Cl^- with $[Pt(NH_3)Cl_2(H_2O)]^a$

Temp. ($^\circ C.$)	k'' (hr.$^{-1}$)
0.0	0.02
20.0	0.31
30.0	0.72

$^a [Pt(NH_3)Cl_2(H_2O)] + Cl^{*-} \xrightarrow{k''} [Pt(NH_3)ClCl^*(H_2O)] + Cl^-$
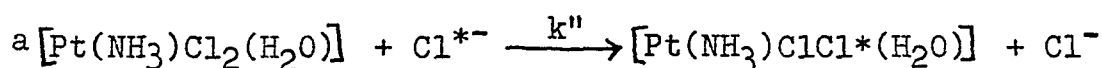
Calculated exchange times of half reaction for
$[Pt(NH_3)Cl_3]^-$ have been tabulated in Table 5. In this calcu-
lation, the combined effect of exchange by aquation, γ -
reaction and β-reaction have been considered. The calcula-
tions involved in this determination have been presented in
the "Kinetics Calculation" section. In view of the uncertainty
in the γ values, the calculated times of half reaction have
been expressed for γ values of both 0.7 and 0.5. The infor-
mation listed under the headings, (a), (b), and $T_{\frac{1}{2}}$ (obs.) was
originally tabulated in Table 3.

A few of the exchange experiments yielded noticeably
different observed and calculated times of half reaction. How-
ever, since three independently determined reactions were in-
volved in the calculations, some discrepancy was expected. In
general, the agreement between observed and calculated results
was believed to be satisfactory.

2. Aquation of $[Pt(NH_3)Cl_2(H_2O)]$

Relatively pure $[Pt(NH_3)Cl_2(H_2O)]$ solutions were prepared
by passing equilibrium solutions of $[Pt(NH_3)Cl_3]^-$ through an
anion exchange resin. When elemental analyses were performed
on these aquo-solutions, an apparent inconsistency was ob-
served. Although the formula indicated only one acid hydrogen
per platinum, analyses consistently indicated a higher acid
titre than predicted from the platinum analyses. Chloride
analyses were quite consistent with platinum and all values

Table 5. Calculated exchange halftimes of Cl^- with $[Pt(NH_3)Cl_3]^-$ by aquation, γ reaction, and β reaction[a]

Temp. (°C.)	(a)[b] (moles/l.)	(b)[c] (moles/l.)	Observed $T_{\frac{1}{2}}$ (hr.?)	Calculated $T_{\frac{1}{2}}$ ($\gamma = 0.7$) (hr.)	($\gamma = 0.5$) (hr.)
20.0	0.0166	0.010	4.3	4.2	4.4
	0.0166	0.025	6.2	5.8	6.1
	0.0166	0.050	9.5	7.0	7.7
	0.0166	0.075	9.5	8.3	9.2
	0.0166	0.268	13.0	11.7	13.2
	0.0083	0.010	6.0	5.7	6.3
	0.0083	0.134	14.0	11.4	13.2
	0.0083	0.201	14.0	12.3	13.7
	0.0083	0.268	14.5	12.7	14.5
	0.0042	0.010	9(?)	7.2	7.9
30.0	0.0166	0.010	1.8	1.8	2.0
	0.0083	0.134	4.5	4.6	5.1
25.0	0.0166	0.010	3.1	2.8	3.3
	0.0083	0.134	7.2	7.4	8.2
15.0	0.0166	0.010	8.0	7.2	8.1
5.5	0.0166	0.010	25.5	23.9	27.0
	0.0166	0.050	58.0	41	47
	0.0083	0.134	96.0	72	80
0.0	0.0166	0.010	48.0	46	50
	0.0083	0.134	159	125	139

[a] $[Pt(NH_3)Cl_3]^- + H_2O \xrightleftharpoons{k_1} [Pt(NH_3)Cl_2(H_2O)] + Cl^-$

$[Pt(NH_3)Cl_3]^- + Cl^{*-} \xrightarrow{\gamma k_1} [Pt(NH_3)Cl^*Cl_2]^- + Cl^-$

$[Pt(NH_3)Cl_2(H_2O)] + Cl^{*-} \xrightarrow{\beta k_{-1}(b+x)} [Pt(NH_3)ClCl^*(H_2O)] + Cl^-$
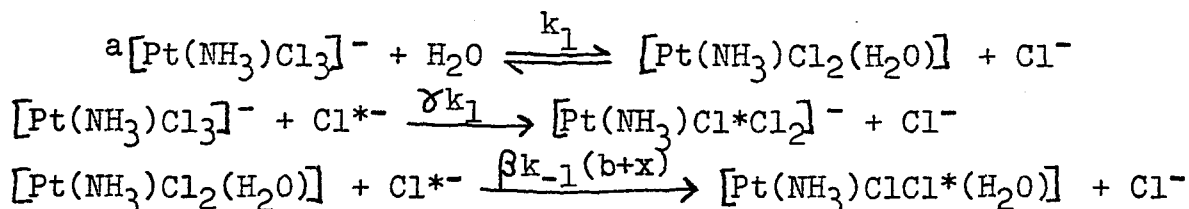
[b] a = Initial concentration of $[Pt(NH_3)Cl_3]^-$.

[c] b = Initial concentration of KCl.

were reproducible. In addition to this inconsistency, distinct changes were observed in the potentiometric titration curves. While the solution pH for equilibrium $[Pt(NH_3)Cl_3]^-$ -- $[Pt(NH_3)Cl_2(H_2O)]$ solutions was approximately 4.6, the pH for pure $[Pt(NH_3)Cl_2(H_2O)]$ solutions of the same approximate concentration was 3.9. Potentiometric titration curves still yielded only a single break, but the presence of a slightly stronger acid in the solution was indicated.

It was concluded that an additional aquation reaction was occurring with the first aquo-complex:

$$(2) \quad [Pt(NH_3)Cl_2(H_2O)] + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Pt(NH_3)Cl(H_2O)_2]^+ + Cl^-$$
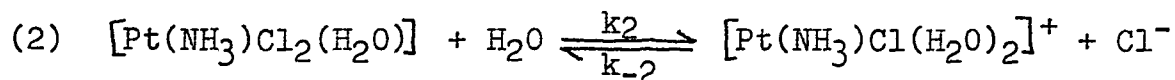
The observed higher acid titre was due to the presence of two replaceable hydrogens in the diaquo-complex. The second aquation reaction existed with the equilibrium far to the left under the relatively high chloride concentrations found in $[Pt(NH_3)Cl_3]^-$ -- $[Pt(NH_3)Cl_2(H_2O)]$ equilibrium solutions. When the equilibrium solution was passed through an anion exchange resin, all of the free chloride, which suppressed the second aquation, was exchanged for sulfate. This treatment resulted in increased formation of the second aquo-complex which then existed in sufficient concentration to be detected by chemical analyses.
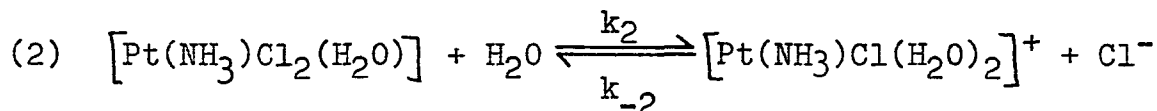
To determine the equilibrium constant for the second aquation reaction, a known quantity of $K[Pt(NH_3)Cl_3]$ was dissolved in a large volume of water and allowed to equilibrate at room

temperature. After the aquation equilibrium had been established, the solution was passed through an anion exchange resin in the sulfate cycle and the column was rinsed to assure removal of all the aquo-complex. The effluent solution was concentrated to the original solution volume by evaporation at 35°C. under reduced pressure. The solution was then allowed to establish a new equilibrium, after which analyses were performed for coordinated water (taken equal to the acid titre), platinum, and chloride. The equilibrium constant calculation procedure and final result have been given in Table 6.

Although the equilibrium constant was calculated from solutions at room temperature (27°C.), the temperature dependence of aquation equilibrium constants is quite small, so the value within the accuracy attained is satisfactory for 25.0°C.

3. Determination of second aquation reaction kinetics

The investigation of the second aquation reaction established one mechanism for the introduction of activity into the $[Pt(NH_3)Cl_2(H_2O)]$ complex. If it were possible to determine independently either k_2 or k_{-2} for the reaction:

(2) $[Pt(NH_3)Cl_2(H_2O)] + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Pt(NH_3)Cl(H_2O)_2]^+ + Cl^-$

then it would be possible to determine if the second aquation reaction completely explained the observed exchange rate for the $[Pt(NH_3)Cl_2(H_2O)]$ complex. The following discussions are

Table 6. Calculation of equilibrium constant for the second aquation[a]

Quantity analyzed	Results		
	#1 (moles/l.)	#2 (moles/l.)	#3 (moles/l.)
Total Pt $(x_\infty + y_\infty)$	2.27×10^{-3}	2.40×10^{-3}	2.92×10^{-3}
Total Cl $(2x_\infty + y_\infty)$	---	4.73×10^{-3}	5.42×10^{-3}
Acid equiv. $(x_\infty + 2y_\infty + \Delta y)$	2.63×10^{-3}	2.74×10^{-3}	3.35×10^{-3}
Calc. x_∞	2.22×10^{-3}	2.35×10^{-3}	2.86×10^{-3}
Calc. y_∞	0.05×10^{-3}	0.05×10^{-3}	0.06×10^{-3}
Calc. Δy	0.31×10^{-3}	0.30×10^{-3}	0.37×10^{-3}
K_2 [b]	5.8×10^{-5}	4.4×10^{-5}	6.4×10^{-5}

[a] $[Pt(NH_3)Cl_2(H_2O)] + H_2O \rightleftharpoons [Pt(NH_3)Cl(H_2O)_2]^+ + Cl^-$
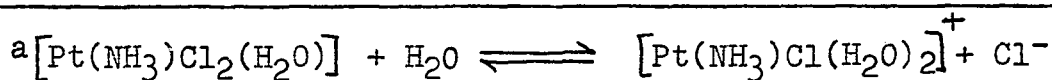
x_∞ = Equilibrium conc. of $[Pt(NH_3)Cl_2(H_2O)]$ before passage through exchange resin.

y_∞ = Equilibrium conc. of $[Pt(NH_3)Cl(H_2O)_2]^+$ before passage through exchange resin.

Δy = Additional conc. of $[Pt(NH_3)Cl(H_2O)_2]^+$ formed after passage through exchange resin.

$x_\infty - \Delta y$ = Equilibrium conc. of $[Pt(NH_3)Cl_2(H_2O)]$ after passage through exchange resin.

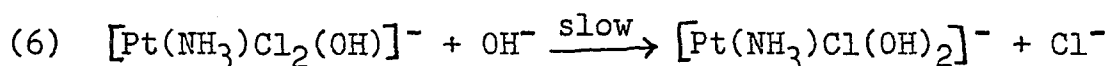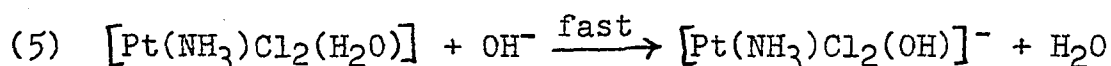$y_\infty + \Delta y$ = Equilibrium conc. of $[Pt(NH_3)Cl(H_2O)_2]^+$ after passage through exchange resin.

$x_\infty + 2y_\infty$ = Equilibrium conc. of Cl^- before passage through exchange resin.

[b] $K_2 = (5 \pm 5) \times 10^{-5}$ moles/l.

$$K_2 = \frac{y_\infty (x_\infty + 2y_\infty)}{x_\infty} = \frac{(y_\infty + \Delta y)(\Delta y)}{x_\infty - \Delta y}.$$

concerned with the methods employed for the determination of
the rate constant, k_{-2}.

a. Absorption spectra of $[Pt(NH_3)Cl(H_2O)_2]^+$ solutions
at high chloride concentrations. When ammonium acetate was
added to solutions of $[Pt(NH_3)Cl_2(H_2O)]$, it was expected that
NH_3 would replace H_2O to form $[Pt(NH_3)_2Cl_2]$. However, the re-
sulting solution absorption spectrum bore no resemblance to
the spectra for either cis- or trans-$[Pt(NH_3)_2Cl_2]$. Similar
experiments were performed with potassium acetate, ammonium
hydroxide, and sodium hydroxide as the added reagent. All the
solutions exhibited nearly the same change in absorption spec-
trum, and a decrease in solution pH occurred during the course
of the reaction. It was therefore concluded that the observed
reaction was a replacement of ligand chloride by hydroxide ion.

(5) $[Pt(NH_3)Cl_2(H_2O)] + OH^- \xrightarrow{fast} [Pt(NH_3)Cl_2(OH)]^- + H_2O$

(6) $[Pt(NH_3)Cl_2(OH)]^- + OH^- \xrightarrow{slow} [Pt(NH_3)Cl(OH)_2]^- + Cl^-$

These reactions were further supported by the observation that
no decrease in $[NH_4]^+$ concentration occurred during the reac-
tion of ammonium acetate with $[Pt(NH_3)Cl_2(H_2O)]$.

The rate constant, k_{-2}, was determined from experiments
involving aquo-hydroxide solutions. A solution, 0.001 M. in
$[Pt(NH_3)Cl_2(H_2O)]$ and 0.001 M. in NaOH was prepared, and the
change in the absorption spectrum was followed with time.
The absorption changes for the reaction have been illustrated

in Fig. 12. After the hydroxide substitution had proceeded to an appreciable extent, the solution pH was lowered to 2-3 with H_2SO_4. This addition transformed $[Pt(NH_3)Cl(OH)_2]^-$ to $[Pt(NH_3)Cl_2(H_2O)_2]^+$. A large, known quantity of KCl was then added to the solution and the rapid replacement of water by chloride occurred. The spectrum changes involved in the chloride substitution have been illustrated in Fig. 13.

Although there was little doubt that the addition of Cl^- definitely reformed the $[Pt(NH_3)Cl_2(H_2O)]$ complex as the major component, the absorption spectrum did not quite return to the original curve. It was felt that this indicated the minor formation of additional platinum compounds. Bannerjea, Basolo, and Pearson (34) observed that trans-$[Pt(NH_3)_2Cl_2]$ formed a polymer when reacted with NaOH followed by the addition of HCl. A similar reaction could be occurring to some extent with $[Pt(NH_3)Cl_2(H_2O)]$.

The rate equation for the reaction of $[Pt(NH_3)Cl(H_2O)_2]^+$ with Cl^- was given by the expression:

$$\frac{d[Pt(NH_3)Cl(H_2O)_2^+]}{dt} = -k_{-2}[Pt(NH_3)Cl(H_2O)_2^+][Cl^-] = -k_{-2}(y)(b+x)$$

where $(y) = [Pt(NH_3)Cl(H_2O)_2^+]$ and $(b+x) = [Cl^-]$.

From the absorption spectra of the reacting solutions:

$$A_0 = \epsilon_0 \ell (x)$$

where A_0 was the absorbance of the pure $[Pt(NH_3)Cl_2(H_2O)]$ solution, (x) was the concentration of $[Pt(NH_3)Cl_2(H_2O)]$, ℓ was
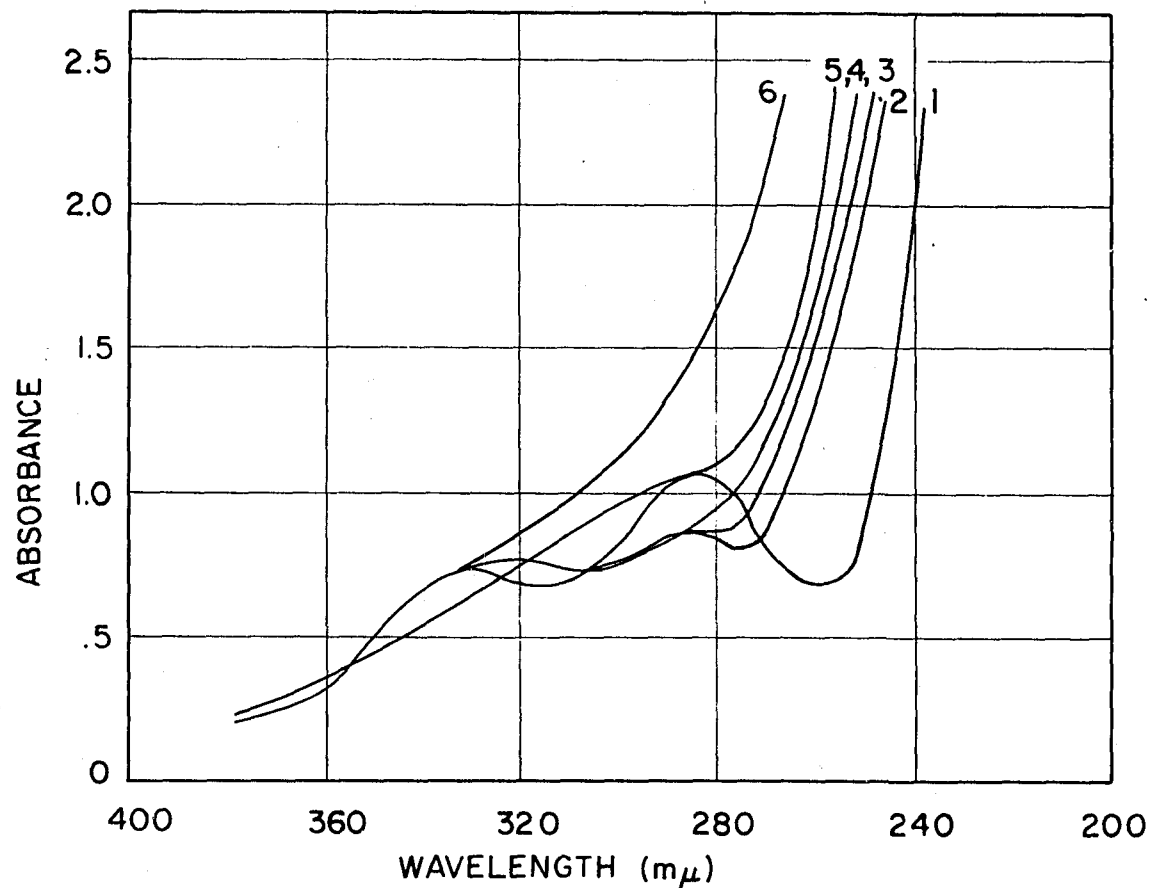
Fig. 12. Observed spectral change during reaction of $[OH]^-$ with $[Pt(NH_3)Cl_2(H_2O)]$. Total Pt conc. = 0.001 M., aqueous NH_3 conc. = 0.0015 M., 10 cm. cells. Temp. = 24∓1°C. (1) initial $[Pt(NH_3)Cl_2(H_2O)]$ spectrum (2) 2 min. (aqueous NH_3 added t = 0) (3) 17 min. (4) 53 min. (5) 85 min. (6) 154 min.
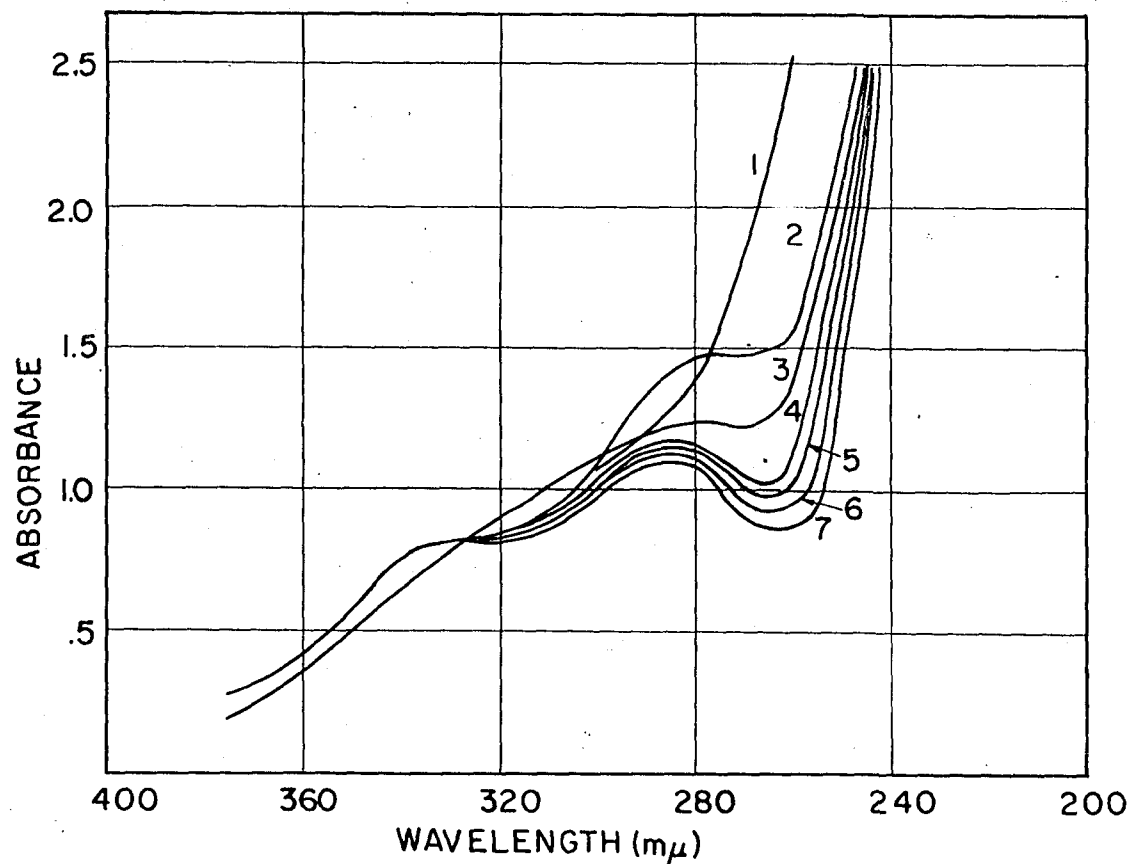
Fig. 13. Observed spectral change during reaction of $[Cl]^-$ with $[Pt(NH_3)Cl(H_2O)_2]^+$. Total Pt conc. = 0.001 M., $[Cl]^-$ conc. = 0.010 M., pH $\cong$ 2. (1) same as curve 6 in Fig. 12 (2) 3 min. (H_2SO_4 added at t = 0) (3) 10 min. (4) 13 min. (5) 18 min. (6) 31 min. (7) 56 min.

the length of the transmission cell and ϵ_o was the molar

absorptivity for the [Pt(NH$_3$)Cl$_2$(H$_2$O)] complex. Absorbance

readings were taken in the valley of the solution absorption

spectrum and corresponded to a wavelength of 260 - 265$m\mu$.

The equilibrium absorbance actually approached by the reaction,

rather than the absorbance of the initial aquo-solution, was

used for A_o. The absorbance, A, of the solution as a function

of the relative amounts of the two platinum species present

was given by the expression:

$$A = \epsilon_o \ell (x - y) + \epsilon \ell y$$

where ϵ was the molar absorptivity for [Pt(NH$_3$)Cl(H$_2$O)$_2$]$^+$

By subtraction:

$$A - A_o = \epsilon \ell y - \epsilon_o \ell y = \epsilon' y$$

The substitution, $y = \dfrac{A - A_o}{\epsilon'}$, transformed the differential rate

equation to the following expression:

$$\frac{d[\ln(A - A_o)]}{dt} = -k_{-2}(b + x)$$

In Fig. 14, $\ln(A - A_o)$ has been plotted versus time. The

initial slope of the curve was used in computing the value of

k_{-2}. The value obtained by this method was

$$k_{-2} = 710 \text{ liter moles}^{-1}\text{hr.}^{-1}.$$
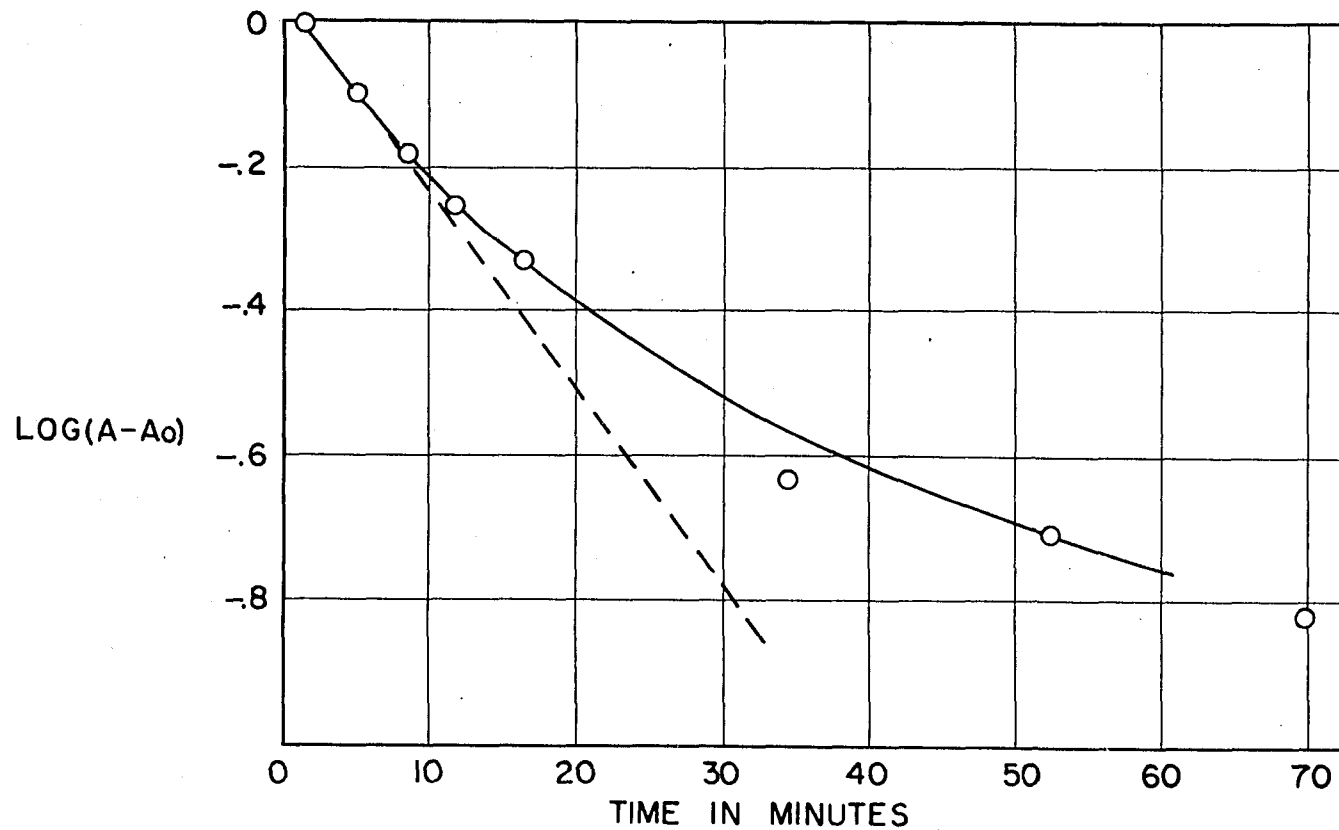
Fig. 14. Determination of k_{-2} rate constant from slope of log $(A - A_o)$ versus time plot. Temp. $= 24 \pm 1^\circ C.$, 10 cm. cells. Total Pt conc. $= 0.001$ M., $[Cl]^-$ conc. $= 0.005$ M., pH $\cong$ 2.

b. Absorption spectra of $[Pt(NH_3)Cl(H_2O)_2]^+$ solutions at

low chloride concentrations. An additional independent

method was employed for the determination of the k_{-2} rate con-

stant. In this procedure, NaOH was added to solutions of

$[Pt(NH_3)Cl_2(H_2O)]$ and the reaction was allowed to proceed. At

regular intervals, a solution aliquot was acidified with H_2SO_4

and an excess of Ag_2SO_4 solution was added to precipitate the

chloride liberated by reactions (5) and (6). The AgCl precipi-

tate was then collected, dried, and weighed. The extent of

hydroxide substitution was calculated as a function of time

from the precipitate weights. Fig. 15 illustrates the values

obtained for $[Pt(NH_3)Cl(OH)_2]^-$ concentration at different re-

action intervals. The approximate value of the first order

rate constant for the formation of $[Pt(NH_3)Cl(OH)_2]^-$ was

0.2 hr.$^{-1}$ at room temperature.

A solution of 0.001 M. $[Pt(NH_3)Cl_2(H_2O)]$ and 0.001 M.

NaOH was prepared and the hydroxide substitution was allowed

to proceed for several hours. The solution was then acidified

with H_2SO_4 and an aliquot was rapidly transferred to a cell

where the absorption spectrum was recorded. No additional KCl

was added to the reaction solution. Recordings of the absorp-

tion spectrum were made at intervals until the equilibrium was

attained.

The rate of replacement of water by chloride has been

given by the equation:
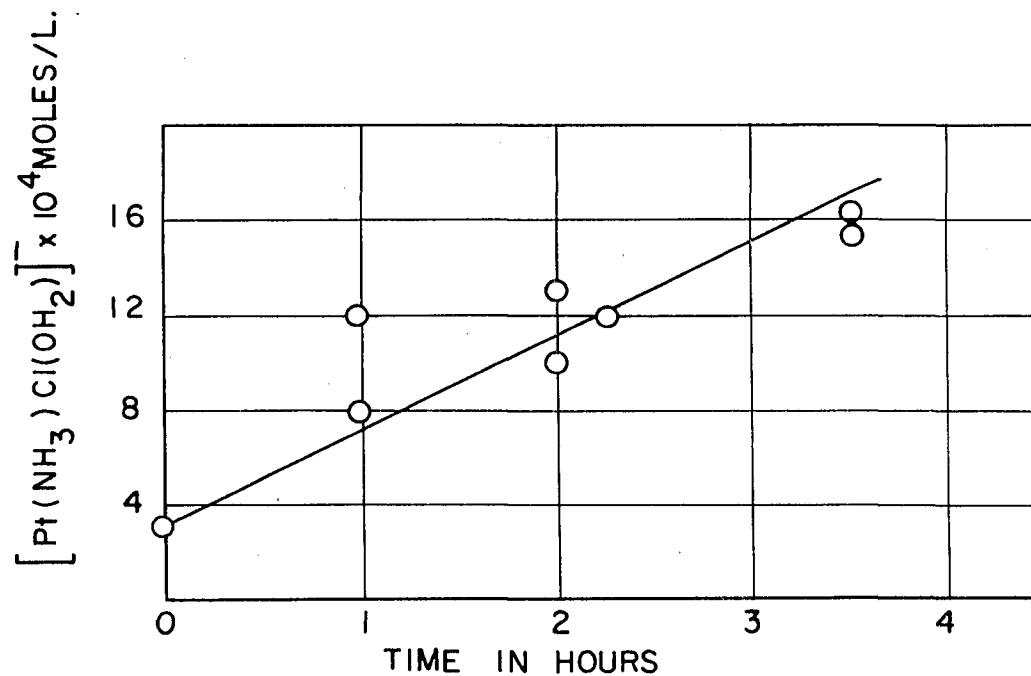
Fig. 15. Rate of formation of $[Pt(NH_3)Cl(OH)_2]^-$ through the reaction:

$$[Pt(NH_3)Cl_2(H_2O)] + OH^- \longrightarrow [Pt(NH_3)Cl(OH)_2]^-.$$
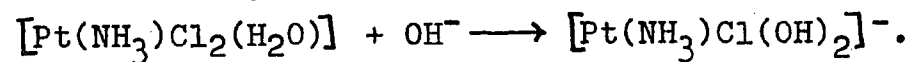
Temp. = 20.0°C. Initial conc. of $[Pt(NH_3)Cl_2(OH)]^- = 0.0024$ M. Initial conc. of $[OH]^- = 0.003$ M. $\mu = 0.318$ M.

$$\frac{d[Pt(NH_3)Cl(H_2O)_2{}^+]}{dt} = -k_{-2}[Pt(NH_3)Cl(H_2O)_2{}^+][Cl^-] = -k_{-2}(y)(b+x)$$

Under the conditions of this experiment, $(b+x) = (y)$ and the rate equation yielded the solution:

$$\frac{1}{y} - \frac{1}{y_o} = k_{-2}t$$

The term, y_o, is the concentration of $[Pt(NH_3)Cl(H_2O)_2]^+$ at the time the H_2SO_4 was added and y is the concentration of $[Pt(NH_3)Cl(H_2O)_2]^+$ at time, t. The value of y_o was obtained from Fig. 15 and from a knowledge of the reaction time of OH^- with $[Pt(NH_3)Cl_2(OH)]^-$.

In the preceding determination of k_{-2}, an expression was given relating the concentration of $[Pt(NH_3)Cl(H_2O)_2]^+$ to the solution absorbance at a given wavelength.

$$y = \frac{A - A_o}{\epsilon'}$$

The value of the constant, ϵ', was obtained at $260 m\mu$ by substituting the value of y_o for y, the initial absorbance of the solution at $260 m\mu$ for A, and the observed equilibrium absorbance at $260 m\mu$ for A_o. The value of y at any time, t, was then obtained from the solution absorbance by means of the above equation.

In Fig. 16, the quantity $\frac{1}{y} - \frac{1}{y_o}$ has been plotted versus time. The value of the rate constant, k_{-2}, obtained from the slope of the experimental plot was 1500 liter moles^{-1}hr.$^{-1}$.
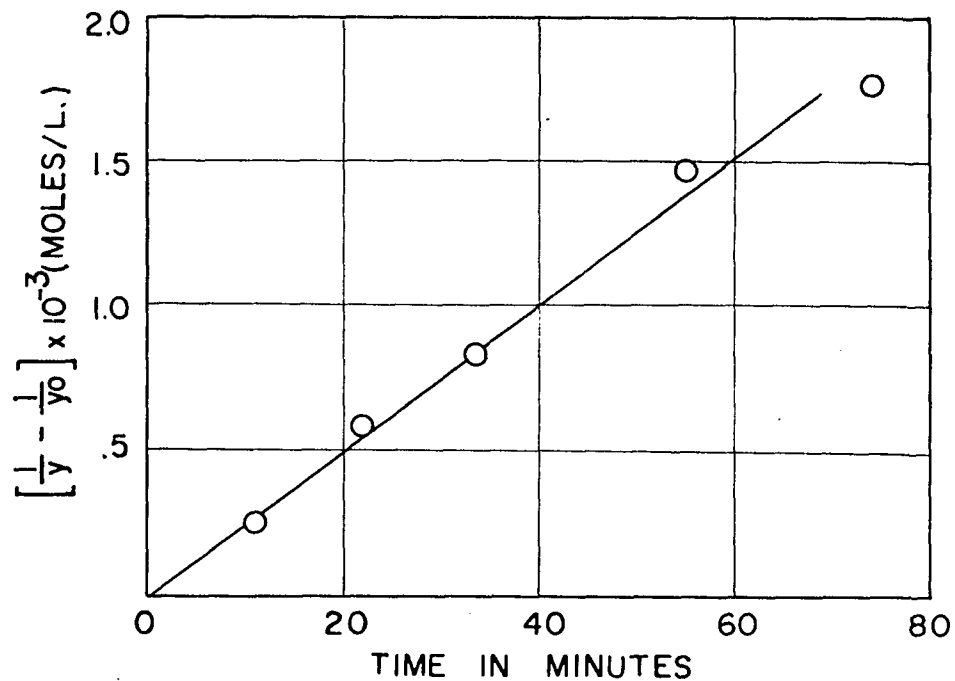
Fig. 16. Determination of k_{-2} rate constant from slope of $(1/y - 1/y_0)$ versus time plot. Temp. $= 24 \mp 1^\circ C.$ $y_0 =$ initial conc. of $[Pt(NH_3)Cl(H_2O)_2]^+ =$ 0.0006 M. $y =$ conc. of $[Pt(NH_3)Cl(H_2O)_2]^+$ at time, t.

c. Chloride tracer experiment with $[Pt(NH_3)Cl(H_2O)_2]^+$

solutions. In view of the discrepancy between the values

of k_{-2} obtained by the two procedures, an additional method of

determination was employed. An aquo-complex solution of

0.0023 M. $[Pt(NH_3)Cl_2(H_2O)]$ and 0.00036 M. $[Pt(NH_3)Cl(H_2O)_2]^+$

was used for the experiment. The concentration values given

represent the equilibrium concentrations of the two complexes

after all the Cl^- and $[Pt(NH_3)Cl_3]^-$ were removed by an anion

exchange resin.

An isotopic tracer experiment was performed in which the

tracer and carrier chloride were added together to the equi-

librium solution. Under these conditions, an initially fast

introduction of activity into the $[Pt(NH_3)Cl_2(H_2O)]$ complex

occurred by the reaction:

$$[Pt(NH_3)Cl(H_2O)_2]^+ + Cl*^- \xrightarrow{k_{-2}} [Pt(NH_3)ClCl*(H_2O)] + H_2O$$
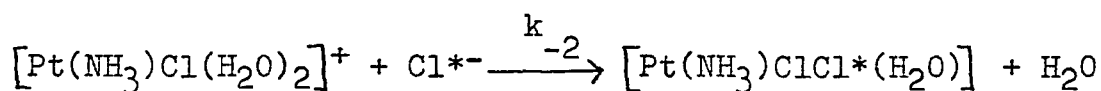
By comparing this rate of initial introduction of activity

with the rate observed for the exchange experiment in which

no $[Pt(NH_3)Cl(H_2O)_2]^+$ was present, an approximate value for

the rate constant, k_{-2} was obtained. The two experimental

curves obtained for the initial exchange have been illustrated

in Fig. 17.

The calculations involved in the rate constant determina-

tion have been presented in the section dealing with kinetics

calculations. The value of k_{-2} obtained by this method was

600 1. moles^{-1}hr.$^{-1}$.
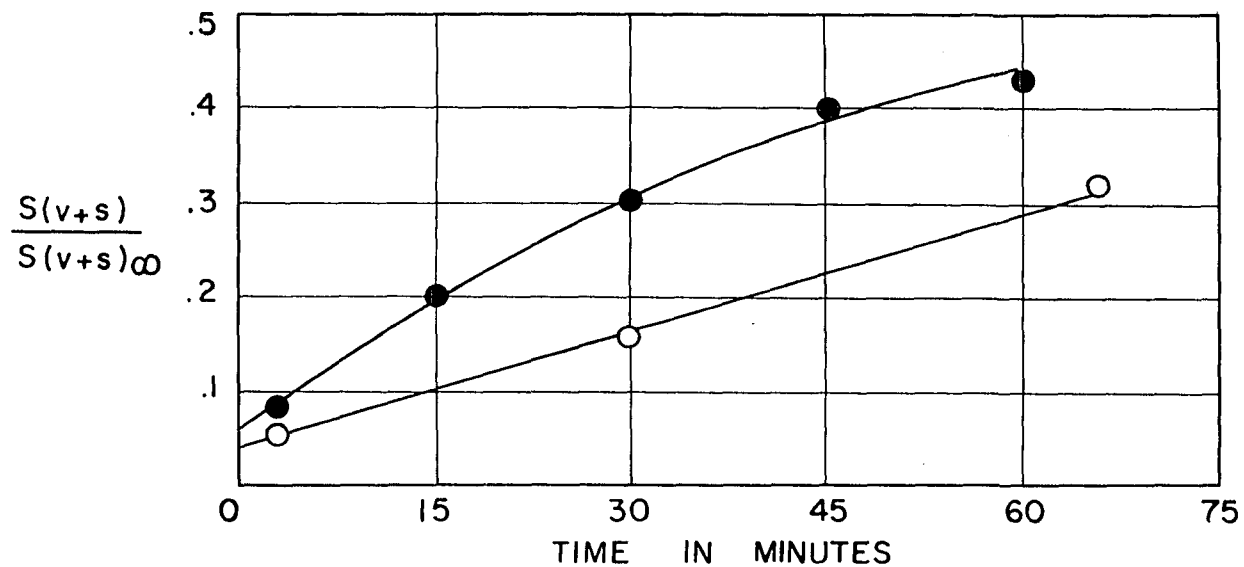
Fig. 17. Determination of k_{-2} rate constant from exchange experiments with
$[Pt(NH_3)Cl_2(H_2O)]$ - $[Pt(NH_3)Cl(H_2O)_2]^+$ solutions. Temp. = 20.0°C., μ =
0.318 M. For upper curve: conc. of $[Pt(NH_3)Cl_2(H_2O)]$ = 0.0020 M., conc.
of $[Pt(NH_3)Cl(H_2O)_2]^+$ = 0.00036 M. For lower curve: conc. of
$[Pt(NH_3)Cl_2(H_2O)]$ ≅ 0.0024 M., conc. of $[Pt(NH_3)Cl(H_2O)_2]^+$ ≅ 0.

Three independent determinations of k_{-2} have yielded the values 1500, 600, and 710 l. moles^{-1}hr.$^{-1}$. In retrospect, the experiment yielding the highest value might be expected to be the least accurate. This experiment was performed under extremely low chloride concentrations and any decomposition of the platinum complex to form chloride would greatly change the reaction rate. This condition would tend to indicate a high value of k_{-2}. An average value of 700 l. moles^{-1}hr.$^{-1}$ for k_{-2} was therefore adopted.

Although the agreement among the values was not good, the difficulties encountered in devising experiments to measure the rate constant were great. It was felt that the precision of the results was commensurate with the accuracy of the experiments employed.

4. Discussion of second aquation results

It has been observed that the rate constant for the direct exchange of chloride with $[Pt(NH_3)Cl_2(H_2O)]$ was approximately 0.31 hr.$^{-1}$ at 20.0°C. This value is listed in Table 4 and was obtained from the value of β best fitting the experimental exchange curve for the case of both chlorides assumed equivalent. It was further observed that the equilibrium constant for the second aquation reaction

$$[Pt(NH_3)Cl_2(H_2O)] + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Pt(NH_3)Cl(H_2O)_2]^+ + Cl^-$$

$$K_2 = \frac{k_2}{k_{-2}} = \frac{[Pt(NH_3)Cl(H_2O)_2^+][Cl^-]}{[Pt(NH_3)Cl_2(H_2O)]}$$
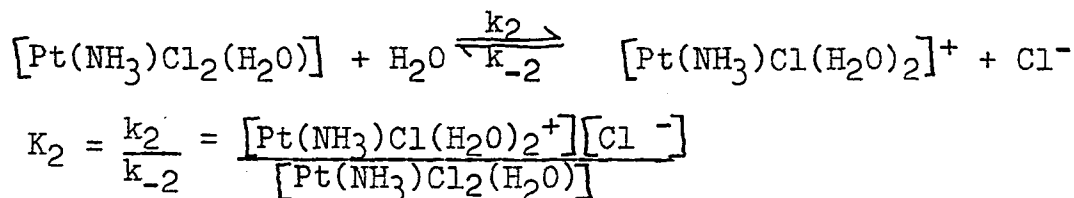
was $K_2 = 5 \times 10^{-5}$ moles/liter. If all the activity in the $[Pt(NH_3)Cl_2(H_2O)]$ complex were introduced through the second aquation reaction, then the predicted value for k_{-2} would be:

$$k_{-2} = \frac{k_2}{K_2} = \frac{0.31 \text{ hr.}^{-1}}{5 \times 10^{-5} \text{ moles/l.}} = 6200 \text{ liter moles}^{-1}\text{hr.}^{-1}$$

This value is more than eight times the approximate observed value of $k_{-2} = 700$ liter moles^{-1}hr.$^{-1}$. It would thus appear that a parallel exists between the exchange of chloride with $[Pt(NH_3)Cl_3]^-$ and with $[Pt(NH_3)Cl_2(H_2O)]$. In the first case, exchange proceeded through an observed aquation reaction plus an additional first order exchange. The same appears to be true for the exchange of chloride with $[Pt(NH_3)Cl_2(H_2O)]$.

E. Nonequivalence of $[Pt(NH_3)Cl_2(H_2O)]$ Chlorides

1. Exchange experiments with $[Pt(NH_3)Cl_2(H_2O)]$ solutions

Relatively pure $[Pt(NH_3)Cl_2(H_2O)]$ solutions were prepared by passing equilibrium solutions of $[Pt(NH_3)Cl_3]^-$ through an anion exchange resin. Exchange experiments were performed with these solutions in the manner described in the "Procedures" section. In all of the experiments, the total platinum concentration was 0.0024 M. and the added chloride concentration was 0.0029 M. The unlabeled chloride was added to the solution long before the exchange was initiated. The $[Pt(NH_3)Cl(H_2O)_2]^+$ complex was thus completely equilibrated before the addition of tracer. Since the amount of chloride

added in these experiments was quite small, the amount of $[Pt(NH_3)Cl_3]^-$ formed was negligible.

The experimental points obtained from three exchange runs at C.0°C., 20.0°C., and 30.0°C. have been plotted as (S/S_∞) versus time in Figs. 18, 19, and 20. The steeply rising curve in each of the three Figures was obtained by assuming that both of the chlorides in $[Pt(NH_3)Cl_2(H_2O)]$ exchanged at the same rate. The exchange rate constants in Table 4 were employed for the calculation. It should be noted that the initial slopes of the calculated curves corresponded to the experimental points for each experiment. However, the two curves deviate noticeably beyond one exchange halftime. Also plotted for each experiment is the curve predicted if only one of the chlorides in $[Pt(NH_3)Cl_2(H_2O)]$ exchanged. Again the calculated curve did not fit all of the experimental points.

In the "Kinetics Calculations" section, the equations have been derived for the separate treatment of the chlorides in $[Pt(NH_3)Cl_2(H_2O)]$. The exchange of the chloride trans- to the water was governed by the parameter β'' whereas exchange of the chloride trans- to ammonia was governed by β'. These assumptions are implied in the following expressions for the reaction rates:

$$(7) \quad \begin{array}{c} \beta' \\ \text{reaction} \end{array} \quad NH_3 - \overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle H_2O}{|}}{Pt}} - Cl + Cl^{*-} \xrightarrow{k_t''} NH_3 - \overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle H_2O}{|}}{Pt}} - Cl^* + Cl^-$$

$$(8) \quad \beta'' \atop \text{reaction} \qquad \underset{\underset{H_2O}{|}}{\overset{\overset{Cl}{|}}{NH_3 - Pt - Cl}} + Cl^{*-} \xrightarrow{k_c''} \underset{\underset{H_2O}{|}}{\overset{\overset{Cl^*}{|}}{NH_3 - Pt - Cl}} + Cl^-$$
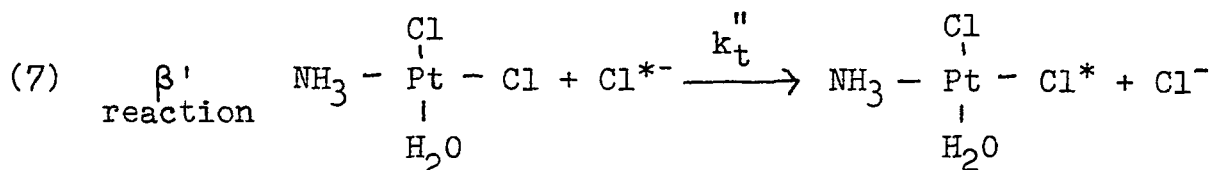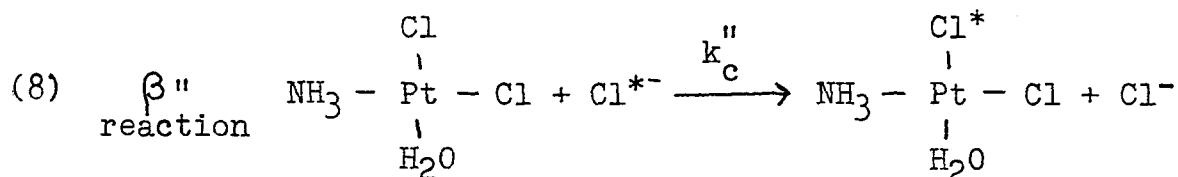
where

$$\beta' = \frac{k_t'' \, [Pt(NH_3)Cl_2(H_2O)]^{m'} [Cl^-]^{n'}}{k_{-1} \, [Pt(NH_3)Cl_2(H_2O)] \, [Cl^-]}$$

$$\beta'' = \frac{k_c'' \, [Pt(NH_3)Cl_2(H_2O)]^{m} [Cl^-]^{n}}{k_{-1} \, [Pt(NH_3)Cl_2(H_2O)] \, [Cl^-]}$$

Values of β' and β'' were independently varied to find what combination of these numbers gave a calculated exchange curve most closely approximating the observed curve. The most satisfactory curves obtained from this calculation have been plotted in Figs. 18, 19 and 20. The agreement with the experimental points was quite good. For all three experiments, the best calculated curve was obtained for a value of β'' approximately four times the value of β'.

The values obtained for k_t'' and k_c'' have been tabulated in Table 7. In Fig. 21, the temperature dependence of the rate constants has been illustrated by a ln k vs. 1/T plot.
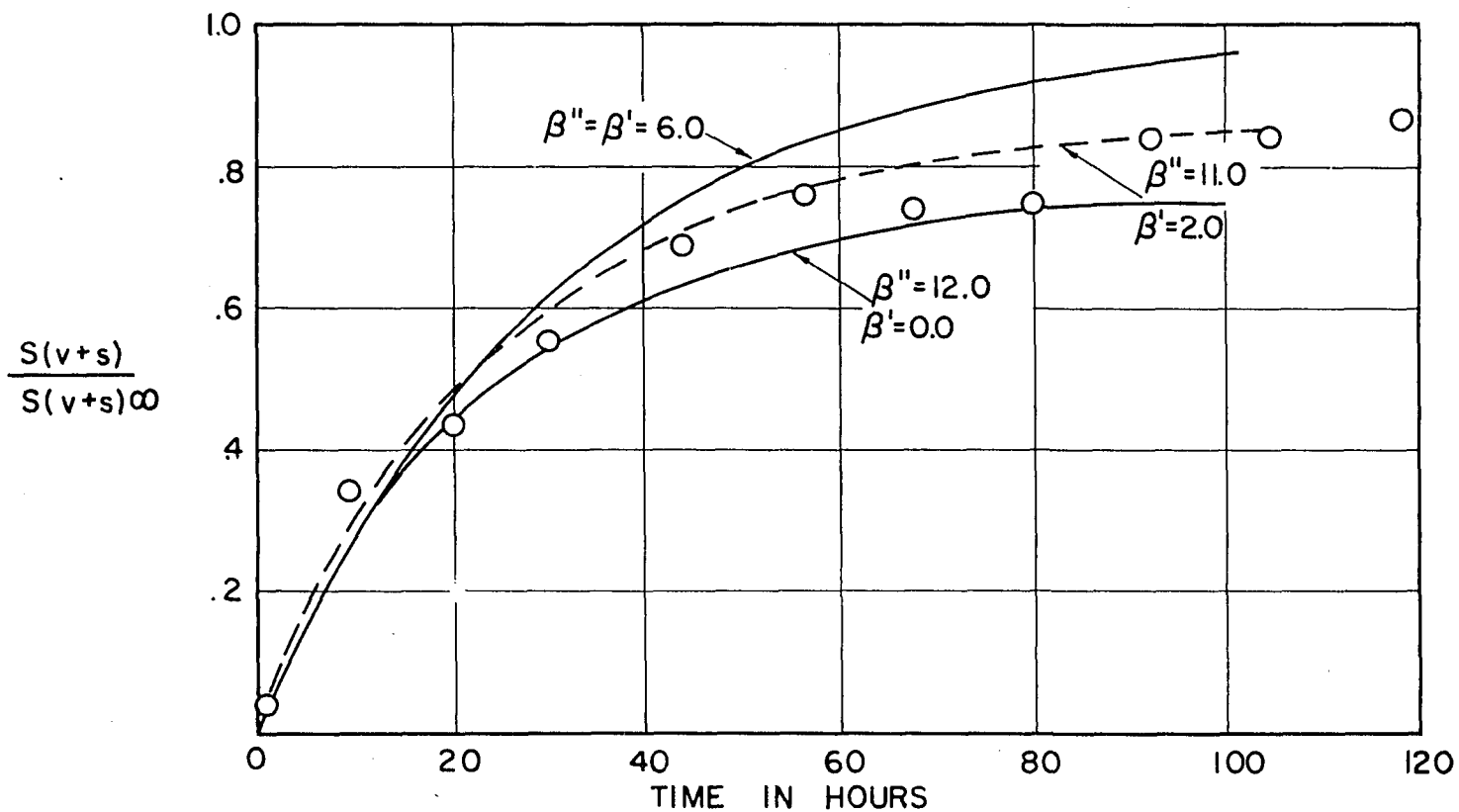
Fig. 18. Observed fraction of exchange in $[Pt(NH_3)Cl_2(H_2O)]$ versus time. Temp. = 0.0°C., conc. of $[Pt(NH_3)Cl_2(H_2O)]$ = 0.0024 M., conc. of $[Cl]^-$ = 0.0029 M., μ = 0.318 M. Upper curve: chlorides assumed equivalent. Lower curve: only one labile chloride. Dotted curve: chlorides assumed nonequivalent.
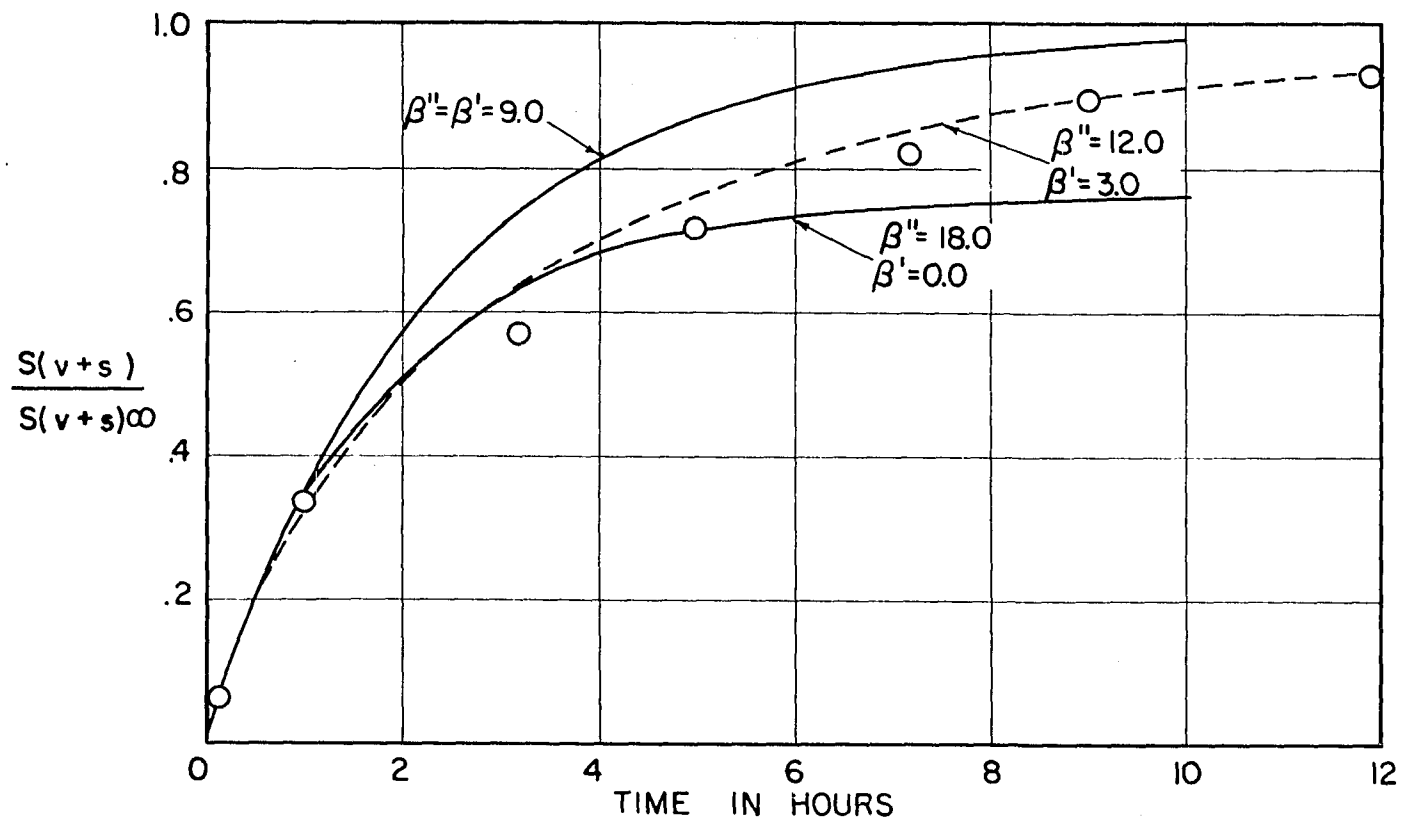
Fig. 19. Observed fraction of exchange in $[Pt(NH_3)Cl_2(H_2O)]$ versus time. Temp. = 20.0°C., conc. of $[Pt(NH_3)Cl_2(H_2O)]$ = 0.0024 M., conc. of $[Cl]^-$ = 0.0029 M., μ = 0.318 M. Upper curve: chlorides assumed equivalent. Lower curve: only one labile chloride. Dotted curve: chlorides assumed nonequivalent.
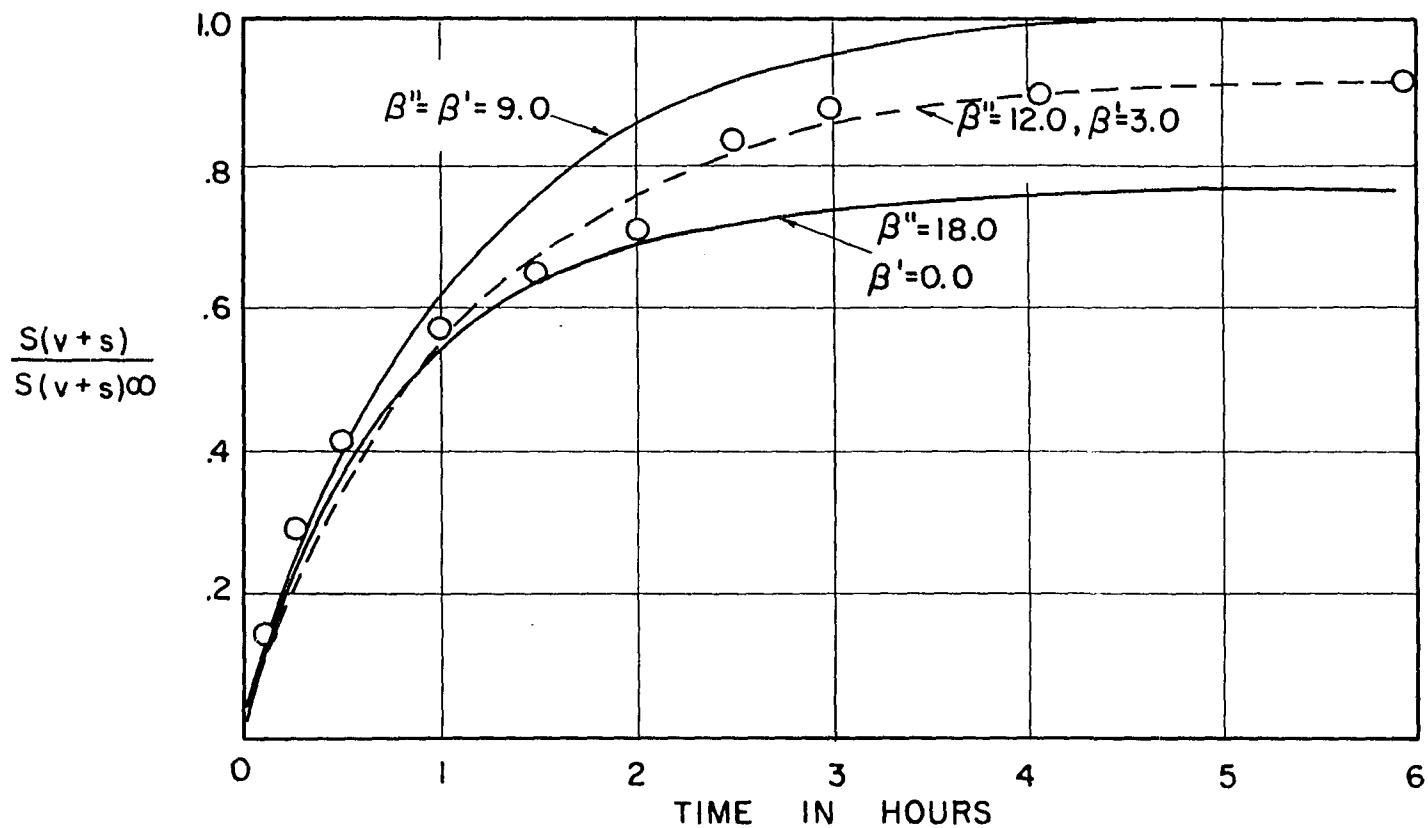
Fig. 20. Observed fraction of exchange in $[Pt(NH_3)Cl_2(H_2O)]$ versus time. Temp. = 30.0°C., conc. of $[Pt(NH_3)Cl_2(H_2O)]$ = 0.0024 M., conc. of $[Cl]^-$ = 0.0029 M., μ = 0.318 M. Upper curve: chlorides assumed equivalent. Lower curve: only one labile chloride. Dotted curve: chlorides assumed nonequivalent.
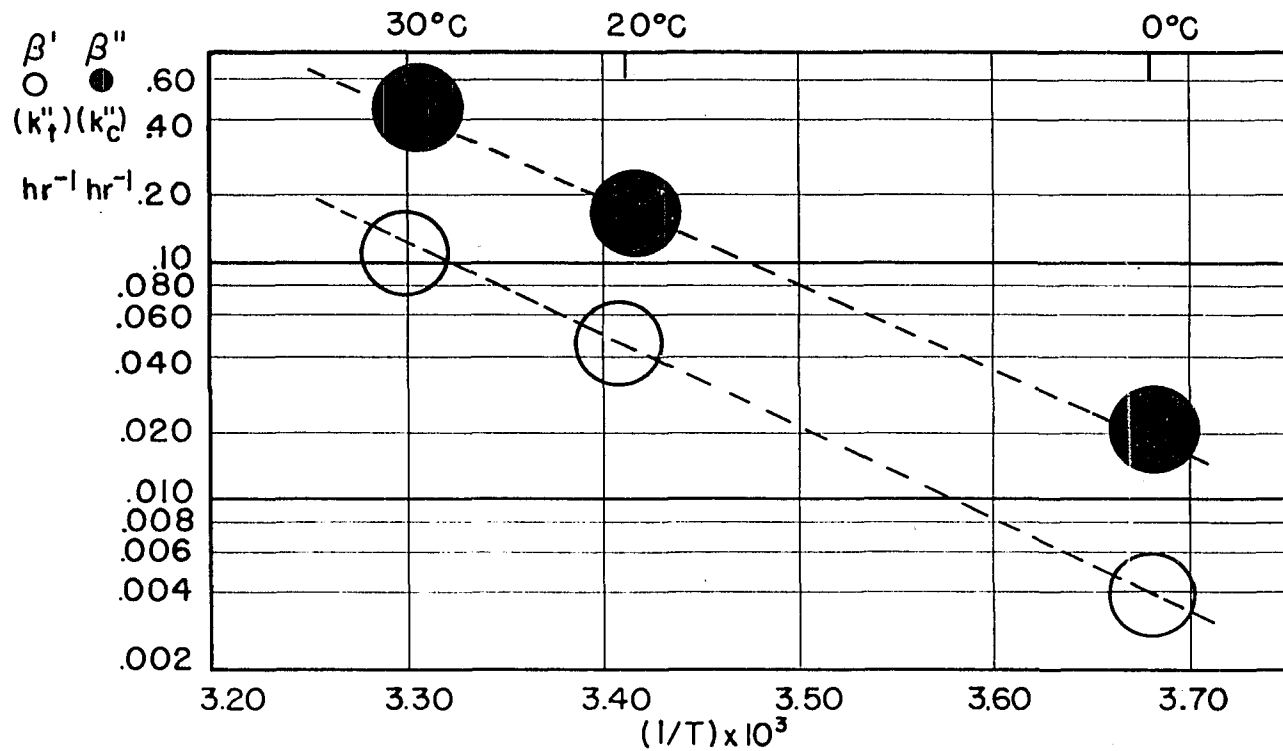
Fig. 21. Rate constants k_c'' and k_t'' for the β' and β'' exchange reactions, log k versus 1/T. $\mu = 0.318$ M.

Table 7. Rate constants for exchange of Cl^- with
$[Pt(NH_3)Cl_2(H_2O)]$

Temp. (°C.)	k_c'' (hr.$^{-1}$)	k_t'' (hr.$^{-1}$)
0.0	0.021	0.004
20.0	0.17	0.05
30.0	0.47	0.12

2. Reaction of $[Pt(NH_3)Cl_2(H_2O)]$ with NO_2^-

If the two chlorides in $[Pt(NH_3)Cl_2(H_2O)]$ exchange with
ionic chloride at different rates, then during the early por-
tion of an exchange experiment, the amount of tracer in the
two positions should be different. If the exchange were
quenched during this early portion and the two chlorides were
somehow separated, then it should be possible to detect the
chloride nonequivalence by counting the activity in the two
chloride fractions. The difficulties and results of such an
experiment have been given in the following discussion.

Sodium iodide, potassium nitrite, pyridine, hydroxylamine,
ethylamine, and thiourea were investigated as substituting re-
agents. The reaction of these compounds with $[Pt(NH_3)Cl_2(H_2O)]$
was followed by changes in the solution absorption spectrum
and through variations in the solution pH with time. The re-
sults of these substitution reactions have been summarized in
Table 8.

Table 8. Reaction of various reagents with $[Pt(NH_3)Cl_2(H_2O)]$[a]

Added reagent	Absorption spectrum	pH	Solution color	Remarks
1. Sodium iodide	Pronounced increase in absorption from 220 mμ to 370 mμ	Slight increase 4.3 to 4.8	Reddish brown	Brown precip. containing no Cl⁻ formed after 30 min.
2. Potassium nitrite	Pronounced increase in absorption from 220 mμ to 370 mμ	Slight decrease 4.7 to 4.4	Colorless	Reaction apparently complete in 50 min.
3. Pyridine	------	Decrease 5.6 to 4.3	Yellow	
4. Hydroxylamine	No observed reaction			
5. Ethylamine	Spectrum changes correspond to OH⁻ substitution	Decrease 6.2 to 5.4	Yellow	Decomposition to Pt black after 120 min.
6. Thiourea	Pronounced increase in absorption from 220 mμ to 370 mμ	Decrease 4.2 to 2.6	Red	Yellow precip. containing no Cl⁻ formed after 20 min.

[a] $[Pt(NH_3)Cl_2(H_2O)]$ and all reagent concentrations 0.0029 M.

Potassium nitrite was selected as the most promising reagent for further investigation. The compound reacted rapidly, the pH decreased during reaction (apparently indicating that water was not replaced by nitrite), the reagent was easily standardized in solutions, and it did not form an insoluble precipitate with silver ion.

As a result of additional experiments, the following reaction sequence was proposed for nitrite substitution.

$$\underset{\underset{H_2O}{|}}{\overset{\overset{Cl}{|}}{NH_3-Pt-Cl}} + NO_2^- \xrightarrow[]{\overset{mod.}{fast}} \underset{\underset{NO_2}{|}}{\overset{\overset{Cl}{|}}{NH_3-Pt-Cl}} \xrightleftharpoons[k_{-x}]{k_x} \underset{\underset{NO_2}{|}}{\overset{\overset{H_2O}{|}}{NH_3-Pt-Cl}} + Cl^-$$
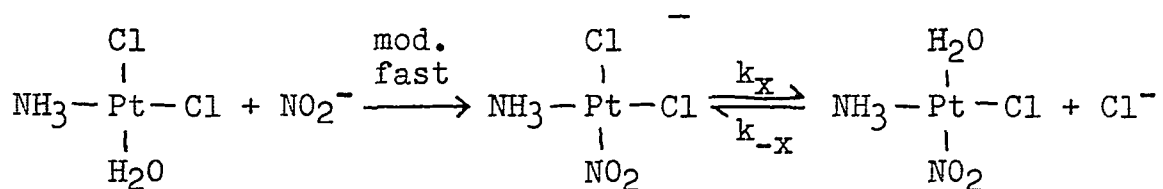
with $k_x \gg k_{-x}[Cl^-]$

This reaction sequence was deduced from several observations. (1) The reaction involving a 1:1 mole ratio of NO_2^- to Pt did not result in appreciable reduction of the acid titre yet a large amount of chloride was displaced from the complex. (2) The most likely ligand for attack by NO_2^- was the H_2O group since this group was easily replaced by chloride. (3) The existence of a different aquo-complex in the final solution was demonstrated by a lower observed acid pK in the potentiometric titration curves.

An exchange experiment was performed with a solution 0.0024 M. in $[Pt(NH_3)Cl_2(H_2O)]$ and 0.0029 M. in KCl. The solution was thermostated at 20.0°C. and the reaction flask was wrapped with tape to exclude light. One to two hours

after the initiation of exchange, two aliquots were removed for infinity samples, the remaining solution was acidified, and an excess of Ag_2SO_4 solution was added. This addition effectively quenched the exchange process by precipitating all the free chloride in the solution. After precipitation, the solution was filtered, the filtrate pH was raised to 4 - 4.5 with sodium hydroxide, and the filtrate was divided into three or four equal fractions. Varying quantities of potassium nitrite solution were then added to the aliquots. At the end of the nitrite reaction period, the solutions were acidified with H_2SO_4 and Ag_2SO_4 was added to precipitate the chloride liberated by the substitution of nitrite. This AgCl precipitate was then collected on weighed filter papers.

The chloride remaining in solution was displaced from the complex by aqueous NH_3 and precipitated in the manner described in the "Procedures" section. The two sets of precipitated samples were dried, weighed, and counted.

In most of the experiments, one sample was not reacted with nitrite ion but instead was treated directly with ammonium hydroxide. The displaced chlorides were then precipitated as AgCl and the precipitate was mounted for counting. In this manner, the average specific activity of the two chlorides in the sample was obtained.

In the early experiments, the results obtained indicated that the chloride displaced by nitrite (sample precipitates)

had a higher specific activity than the chloride remaining coordinated to the platinum (filtrate precipitates). The specific activity obtained when both chlorides were simultaneously precipitated was intermediate between the two values.

As the experimental procedure was refined, the discrepancy between the filtrate and sample precipitate activities disappeared and a constant value was obtained for both sets of samples. The high specific activity originally observed in the sample precipitates was found to be due to incomplete removal of the tracer chloride solution. Therefore, on the basis of the proposed nitrite substitution reaction, it must be concluded that the two chlorides exchanged at the same rate.

Further study of the nitrite substitution reaction revealed several factors which did not fit the originally proposed mechanism. In all cases, the weight of chloride liberated by nitrite was much greater than the amount calculated on the basis that one nitrite liberated one chloride. The addition of two moles of nitrite per mole of platinum removed only 70% of the acid hydrogen but the addition of silver ion precipitated almost all of the chloride. It was believed that this behavior was best explained by a reaction in which both chlorides rapidly equilibrated with their corresponding aquo-complexes when nitrite was substituted into the complex:

$$\begin{array}{c} H_2O \\ | \\ NH_3 - Pt - Cl + Cl^- \\ | \\ NO_2 \end{array}$$

$$\begin{array}{c} Cl \\ | \\ NH_3 - Pt - Cl \\ | \\ H_2O \end{array} + NO_2^- \xrightarrow{\begin{array}{c} mod. \\ fast \end{array}} \begin{array}{c} Cl \\ | \\ NH_3 - Pt - Cl \\ | \\ NO_2 \end{array}^- + H_2O$$

$$\begin{array}{c} Cl \\ | \\ NH_3 - Pt - H_2O + Cl^- \\ | \\ NO_2 \end{array}$$

When 2 NO_2^- added:

$$\begin{array}{c} Cl \\ | \\ NH_3 - Pt - Cl \\ | \\ H_2O \end{array} + 2NO_2^- \longrightarrow \begin{array}{c} NO_2 \\ | \\ NH_3 - Pt - Cl \\ | \\ NO_2 \end{array}^- \underset{\text{}}{\overset{fast}{\rightleftharpoons}} \begin{array}{c} NO_2 \\ | \\ NH_3 - Pt - H_2O + Cl^- \\ | \\ NO_2 \end{array}$$
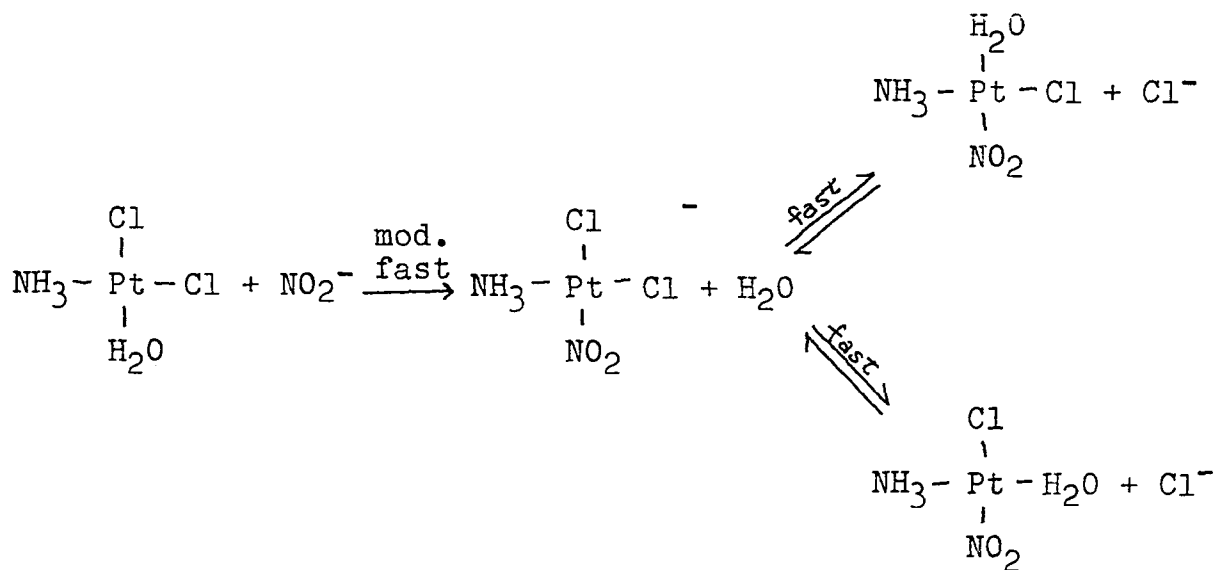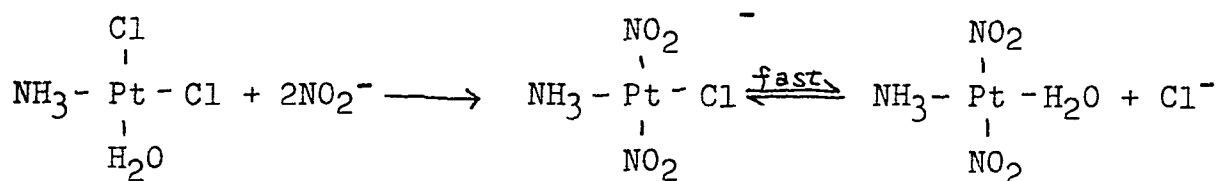
This reaction was further supported by the observation that the addition of a small amount of silver ion to an equilibrium solution resulted in an immediate increase in the acid titre.

If both chlorides were immediately equilibrated with their aquo-complexes, then the tracer chloride in the two positions would also rapidly equilibrate. Thus the results obtained from the nitrite experiments do not conclusively prove that both chlorides exchanged at the same rate before the addition of nitrite ion.

The results of the various substitution experiments performed with nitrite ion have been tabulated in Table 9.

Table 9. Reaction of NO_2^- with $[Pt(NH_3)Cl_2(H_2O)]^a$

Reaction time (hr.)	$\dfrac{NO_2^-}{[Pt(NH_3)Cl_2(H_2O)]}$	Predicted wt. of Cl^- (mg.)	Observed wt. of Cl^- (mg.)	% reduction of acid titre
0	0	0	2.9	0
0.5	1:1	-	9.5	15
1.0	1:1	-	9.7	25
2.0	1:1	8.3	9.7	30
5.0	1:1	8.3	9.5	30
Equil.	1:2	4.2	9.2	13
"	1:1	8.3	9.5	30
"	2:1	16.6	15.9	70
"	2:3	5.5	7.8	
"	3:2	12.5	11.3	
"	1:1	8.3	10.2	
"	1:1	8.3	9.6	
"	1:1	8.3	9.3	
"	1:1	8.3	9.4	
"	1:1	8.3	9.1	
"	1:1	8.3	9.2	

a..0029 M. KNO_2
.0029 M. $[Pt(NH_3)Cl_2(H_2O)]$

The predicted chloride weight was obtained by assuming one NO_2^- liberates one Cl^-.

3. Reaction of $[Pt(NH_3)Cl_2(H_2O)]$ with OH^-

A series of exchange experiments were performed with hydroxide replacing nitrite as the substituting agent. The chloride exchange was quenched by first acidifying the solution with H_2SO_4 and then adding a calculated excess of Ag_2SO_4. After the AgCl was removed by filtration, the pH was raised with NaOH. When the solution became basic, the excess silver

ion precipitated as silver oxide and was removed by filtration through a ground glass filtering crucible. The solution pH was maintained at a value 11 - 11.5 during the substitution. Hydroxide substitution proceeded much more slowly than the corresponding reaction with nitrite, so hydroxide reaction times of 1 - 2½ hours were required. Even with these undesirably long contact times, the sample precipitates obtained were quite small.

In Table 10, the results of three hydroxide experiments have been tabulated. The results indicated a significantly lower specific activity in the replaced chloride precipitates than in the complexed chloride precipitates. These results supported different exchange rates for the two chlorides and showed that the chloride replaced by hydroxide had the lower exchange rate.

In spite of the consistency of the date, there were several undesirable features connected with the experiment. The sample weights obtained for the replaced chloride samples were quite low. Slight errors in the humidity correction while weighing or the presence of small quantities of impurity would be sufficient to lower significantly the specific activity in these samples. Some of the precipitated samples did in fact have a slightly yellow or brown tinge which could have indicated the presence of an impurity. This possibility was checked through coloimetric analyses of several precipitates for platinum content. Calculations indicated that the most

Table 10. Demonstration of nonequivalence of chlorides in $[Pt(NH_3)Cl_2(H_2O)]$[a]

Reaction time (hr.)	Wt. of (A) as AgCl (mg.)	S_A[b]	Wt. of (B) as AgCl (mg.)	S_B[c]	Wt. of (C) as AgCl (mg.)	S_C[d]
1.8	4.1	242	11.4	276		
2.0	4.8	236	11.3	289		
3.5	5.7	245	10.2	281	7.9	280
3.5	5.9	263	10.2	287		
2.0	3.1	280	11.3	358	5.1	343
1.0	3.1	569	20.8	640		
2.0	5.1	482	17.8	615		
1.0	2.1	311	11.9	352	7.6	361

[a] $[Pt(NH_3)Cl_2(OH)]^- + OH^- \longrightarrow [Pt(NH_3)Cl(OH)_2]^- + Cl^-$

      (C)   (B)   (A)
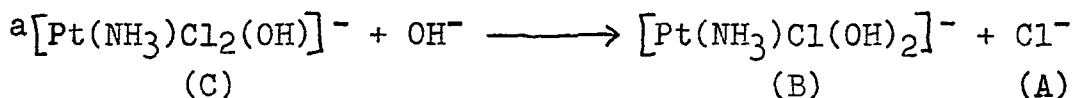
[b] S_A = Specific activity of Cl^- liberated by OH^- substitution. (cts./min. mg.)

[c] S_B = Specific activity of Cl^- in $[Pt(NH_3)Cl(OH)_2]$. (cts./min. mg. Cl)

[d] S_C = Specific activity of both Cl^-'s in $[Pt(NH_3)Cl_2(OH)]$. (cts./min. mg. Cl)

likely impurity, $Ag[Pt(NH_3)Cl_2(OH)]$, would yield a solution concentration of 15 p.p.m. if present in sufficient quantity to explain the lowering of the sample specific activities. The colorimetric method, which was quite accurate for known solutions, indicated less than 1 p.p.m. platinum for all the sample solutions.

Another unsatisfactory feature of the experiment was the

very slight difference in exchange rates obtained for the two chlorides. The replaced chloride had a specific activity only 10 - 20% lower than the complexed chloride although previous estimates had indicated a difference of a factor of four in the exchange rates. It might be felt that the two chlorides partially equilibrated during the hydroxide substitution but a converging of the activities was not observed in the experiments with longer hydroxide reaction times.

In view of these unexplained factors, it was felt that the hydroxide experiments should be considered as one indication of chloride nonequivalence but not as a convincing demonstration of this condition.

IV. DISCUSSION

A. Interpretation of Results

The following reaction scheme consistent with the experimental observations, is believed to represent the mechanism for the chloride exchange with $[Pt(NH_3)Cl_3]^-$ and $[Pt(NH_3)Cl_2(H_2O)]$.

$$
(9) \quad
\begin{matrix} & Cl & \\ & | & \\ NH_3- & Pt-Cl \\ & | & \\ & Cl & \end{matrix}^{-}
+ H_2O
\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}
\begin{matrix} & Cl & \\ & | & \\ NH_3- & Pt-Cl \\ & | & \\ & H_2O & \end{matrix}
+ Cl^-
$$

$$
(10) \quad
\begin{matrix} & Cl & \\ & \backslash & \\ NH_3- & Pt-Cl \\ & | & \\ & Cl & \end{matrix}^{-}
+ H_2O
\underset{k'_{-t}}{\overset{k'_t}{\rightleftharpoons}}
\begin{matrix} & Cl & \\ & | & \\ NH_3- & Pt-H_2O \\ & | & \\ & Cl & \end{matrix}
+ Cl^-
$$

$$
(11) \quad
\begin{matrix} & Cl & \\ & | & \\ NH_3- & Pt-Cl \\ & | & \\ & H_2O & \end{matrix}
+ H_2O
\underset{k''_{-t}}{\overset{k''_t}{\rightleftharpoons}}
\begin{matrix} & Cl & \\ & | & \\ NH_3- & Pt-H_2O \\ & | & \\ & H_2O & \end{matrix}^{+}
+ Cl^-
$$

$$
(12) \quad
\begin{matrix} & Cl & \\ & \backslash & \\ NH_3- & Pt-Cl \\ & | & \\ & H_2O & \end{matrix}
+ H_2O
\underset{k''_{-c}}{\overset{k''_c}{\rightleftharpoons}}
\begin{matrix} & H_2O & \\ & \backslash & \\ NH_3- & Pt-Cl \\ & \backslash & \\ & H_2O & \end{matrix}^{+}
+ Cl^-
$$

$$k'_t \cong 0.5\, k_1$$

$$k'_{-t} >> k_{-1}$$

$$k_t^i \cong k_t^{ii}$$

$$k_t^{ii} \cong 0.1 \; k_c^{ii}$$

$$k_{-c}^{ii} > > k_{-t}^{ii}$$
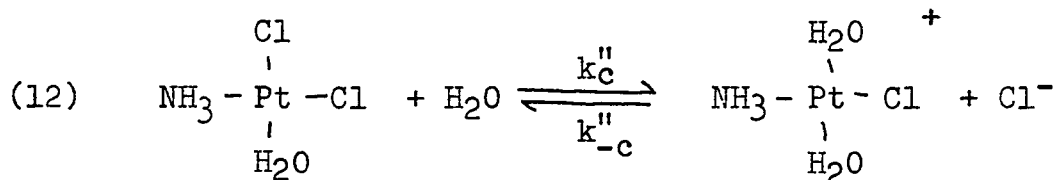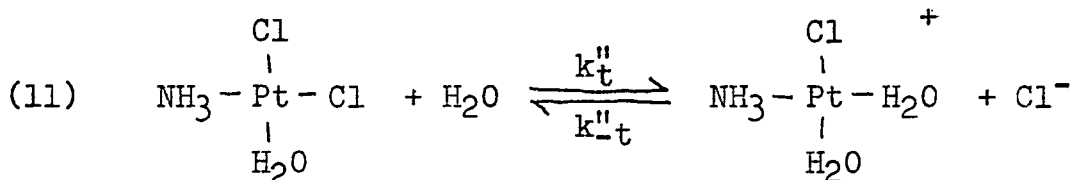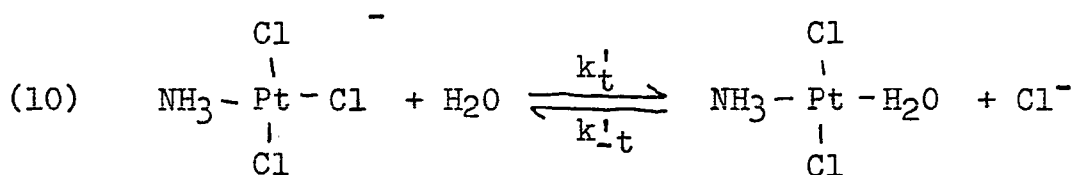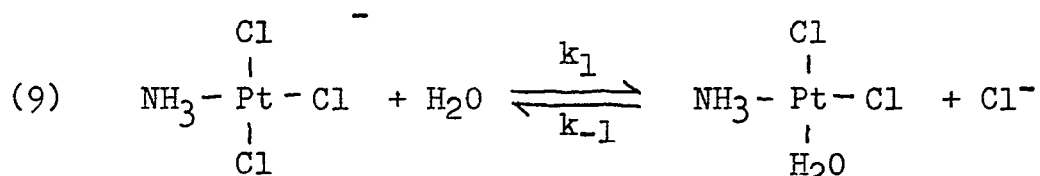
The reasons for this choice of mechanism and rate constants are given in the following discussion.

The replacement of chloride by water in $[Pt(NH_3)Cl_3]^-$ apparently yielded the cis- rather than the trans-aquo-complex. Several experiments have been discussed which indicated that the chlorides in $[Pt(NH_3)Cl_2(H_2O)]$ were not equivalent. The S/S_∞ versus time curves for chloride exchange with $[Pt(NH_3)Cl_2(H_2O)]$ solutions were satisfactorily explained for all experiments if the two chlorides exchanged at different rates. Also, when OH^- was substituted in tagged $[Pt(NH_3)Cl_2(H_2O)]$, the replaced chloride had a lower specific activity than the average of the two chlorides. In trans-$[Pt(NH_3)Cl_2(H_2O)]$, the two chlorides are completely indistinguishable whereas, in cis-$[Pt(NH_3)Cl_2(H_2O)]$, the two chlorides may exhibit different exchange behavior. Thus, the existence of the latter isomer was supported.

The additional exchange reaction with $[Pt(NH_3)Cl_3]^-$ (γ-reaction) was quite similar to the first aquation reaction in many respects. The rate constants for the two processes were of the same order of magnitude, neither reaction rate was noticeably influenced by changes in solution ionic strength, and both reactions had the same activation energy.

From these similarities, it was concluded that the γ-reaction was an aquation reaction which occurred with the chloride trans-to ammonia. The equilibrium constant for the reaction was apparently quite low since exchange experiments with "fresh" $[Pt(NH_3)Cl_3]^-$ solutions showed an immediate introduction of activity into the complex. Thus the equilibrium concentration of trans-$[Pt(NH_3)Cl_2(H_2O)]$ was formed quite soon after the dissolution of the complex.

The rate constant determination for the observable second aquation reaction accounted for only one-fifth of the observed exchange in $[Pt(NH_3)Cl_2(H_2O)]$. By analogy to the chloride exchange with $[Pt(NH_3)Cl_3]^-$, it was concluded that the additional reaction was an aquation reaction with a very low equilibrium constant.

The first order rate constant, k_2, for the observed second aquation reaction was quite similar to the k_t' rate constant for the aquation of the trans-chloride in $[Pt(NH_3)Cl_3]^-$. From the trans-effect, it might be expected that the chloride trans- to ammonia would exchange at approximately the same rate in both the $[Pt(NH_3)Cl_3]^-$ and $[Pt(NH_3)Cl_2(H_2O)]$ complexes. On this basis, the cis-$[Pt(NH_3)Cl(H_2O)_2]^+$ complex was taken to be more stable than the trans-isomer. In any event, the aquation of the chloride ligand in $[Pt(NH_3)Cl_2(H_2O)]$ which gives the more stable diaquo-isomer provides the slower exchange.

The predicted greater stability of the cis-diaquo complex

over the trans-complex was partially supported by experimental potentiometric titrations of equilibrium platinum complex solutions. Ryabchikov (53) titrated solutions of cis- and trans-$[Pt(NH_3)_2(OH)_2]$. Although both isomers required two acid equivalents for neutralization, the cis- form exhibited only a single titration break while the trans- form yielded the double break characteristic of a dibasic acid with separable dissociation constants. In the titrations of $[Pt(NH_3)Cl(H_2O)_2]^+$ solutions, only a single titration break was obtained.

From the above observations, the initially indicated reactions and relative order of rate constants were proposed. A rigorous solution of the exchange kinetics was next attempted using the rate constants determined for the individual chlorides. The values for k_1, k_{-1}, k_c'', and k_t'' have been tabulated in Tables 1 and 7. The value for k_t' was obtained at 20.0°C. from the Υ values in Table 3.

The differential equations for the exchange process have been presented in the "Kinetics Calculations" section. Although it was possible to solve these equations manually, the procedure was difficult and quite time consuming. For this reason, most solutions were obtained from a Heathkit Analogue Computer operated in conjuection with a Brush recorder. For a particular set of equation coefficients, the computer presented the solution in the form of a graphical plot of the specific activity versus time for either the $[Pt(NH_3)Cl_3]^-$ or

$[Pt(NH_3)Cl_2(H_2O)]$ complex. It was also possible to obtain the rate of appearance of activity in each of the distinguishable chlorides as a function of time. Under conditions of high chloride concentration, the rate equations reduced to two equations in two unknowns which were solved manually by conventional methods.

Calculated times of half reaction for $[Pt(NH_3)Cl_3]^-$ have been tabulated in Table 11. In this calculation, the cis- and trans- chlorides in $[Pt(NH_3)Cl_3]^-$ have been assumed to exchange by means of the aquation reactions given at the beginning of the "Discussion" section. Thus, the k_1, k_{-1} aquation rate constants apply only to the cis-chlorides and the γ rate constant applies only to the trans-chloride. Contrary to proposed behavior, the two chlorides in $[Pt(NH_3)Cl_2(H_2O)]$ are assumed to exchange at the same rate. At the time of calculation, the estimated rate constants for the individual chlorides were unknown so it was necessary to employ this simplification. Recently, the calculations have been repeated for the high chloride experiments using the rate constants for the individual chlorides in $[Pt(NH_3)Cl_2(H_2O)]$ exchange. The calculated times of half reaction obtained from these calculations were identical to the values obtained by the earlier procedure.

The calculated times of half reaction, assuming equivalent chlorides (taken from Table 5), and the corresponding experimental values have also been presented in Table 11. Although

Table 11. Complete calculated exchange halftimes for exchange of chloride with $[Pt(NH_3)Cl_3]^-$

Temp. (°C.)	$[Pt(NH_3)Cl_3]^-$ (moles/l.)	KCl (moles/l.)	γ	β	Calculated halftimes Nonequiv. Cl's $T\frac{1}{2}$ (hr.)	Equiv. Cl's $T\frac{1}{2}$ (hr.)	Observed $T\frac{1}{2}$ (hr.)
0.0	0.0166	0.010	0.5	3.0	63 (?)	46	48
	0.0166	0.010	0.7	3.0	44	42	48
	0.0083	0.134	0.5	0.25	132	125	159
5.5	0.0083	0.134	0.7	0.26	68	72	96
	0.0083	0.134	0.5	0.26	79	80	96
20.0	0.0166	0.010	0.7	4.0	4.0	4.0	4.3
	0.0166	0.010	0.6	3.0	4.2	4.2	4.3
	0.0166	0.010	0.7	3.0	4.1	4.0	4.3
	0.0083	0.134	0.7	0.26	11.0	11.4	14.0
	0.0083	0.134	0.5	0.26	12.2	12.7	14.0
	0.0083	0.201	0.7	0.17	11.7	12.3	14.0
	0.0083	0.201	0.5	0.17	13.2	13.7	14.0
	0.0083	0.268	0.7	0.13	12.1	12.7	14.5
	0.0083	0.268	0.5	0.13	13.8	14.3	14.5
	0.0166	0.268	0.7	0.13	11.4	11.7	13.0
	0.0166	0.268	0.5	0.13	13.4	13.2	13.0
25.0	0.0083	0.134	0.7	0.26	6.9	7.4	7.2
	0.0083	0.134	0.5	0.26	8.2	8.2	7.2
30.0	0.0166	0.010	0.6	3.0	1.8	1.8	1.8
	0.0166	0.010	0.7	3.0	1.7	1.7	1.8
	0.0083	0.134	0.7	0.28	4.3	4.6	4.5
	0.0083	0.134	0.5	0.28	5.0	5.1	4.5

some discrepancy exists between the nonequivalent and equiva-
lent chloride exchange times, the difference is not large.
In general the observed results can be considered equivalent
with either set of the calculated values.

Although the proposed exchange reactions are completely
consistent with all of the experimental results, an additional
exchange mechanism may be proposed which is also consistent
with experiment.

If all three chlorides in $[Pt(NH_3)Cl_3]^-$ behaved in an
equivalent manner, the resulting aquo-solution would be com-
posed of two-thirds cis-$[Pt(NH_3)Cl_2(H_2O)]$ and one-third trans-
$[Pt(NH_3)Cl_2(H_2O)]$.

$$
\begin{array}{c}
Cl \\
| \\
NH_3 - Pt - Cl \\
| \\
Cl
\end{array}
+ H_2O
\xrightleftharpoons{k_{1/3}}
\begin{array}{c}
Cl \\
| \\
NH_3 - Pt - Cl \\
| \\
H_2O
\end{array}
+ Cl^-
$$

$$
\begin{array}{c}
Cl \\
| \\
NH_3 - Pt - Cl \\
| \\
Cl
\end{array}
+ H_2O
\xrightleftharpoons{k_{1/3}}
\begin{array}{c}
H_2O \\
| \\
NH_3 - Pt - Cl \\
| \\
Cl
\end{array}
+ Cl^-
$$

$$
\begin{array}{c}
Cl \\
| \\
NH_3 - Pt - Cl \\
| \\
Cl
\end{array}
+ H_2O
\xrightleftharpoons{k_{1/3}}
\begin{array}{c}
Cl \\
| \\
NH_3 - Pt - H_2O \\
| \\
Cl
\end{array}
+ Cl^-
$$
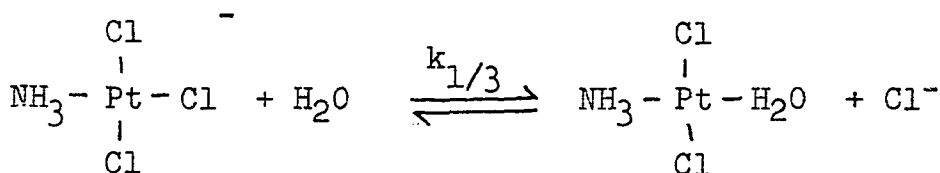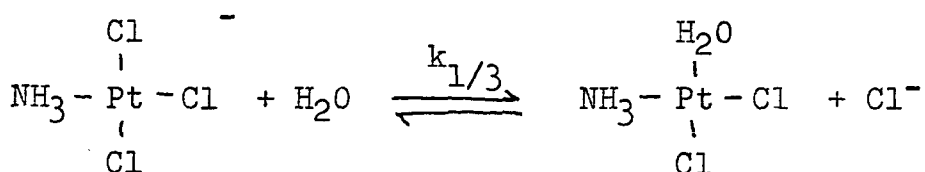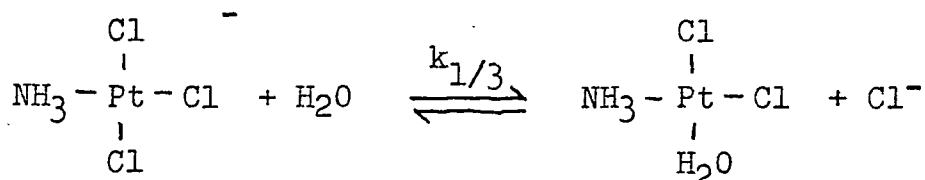
The different chloride specific activities observed in
$[Pt(NH_3)Cl_2(H_2O)]$ solutions could be explained by different

exchange rates for the cis- and trans- forms of

$[Pt(NH_3)Cl_2(H_2O)]$. The additional observed exchange with

$[Pt(NH_3)Cl_3]^-$ and $[Pt(NH_3)Cl_2(H_2O)]$ would then be due to S_N1

reactions in which chloride ligands were replaced directly by

the tracer chloride.

This exchange mechanism requires two distinct exchange

processes where before, one sufficed. It also requires that

the nearly identical behavior of the aquation and additional

exchange reactions be regarded solely as coincidental. For

these reasons, the exchange reactions involving aquo-complex

formation have been regarded as the more tenable of the two

mechanisms.

B. Comparison of Results and Theory

In the Introduction, the views of Chatt et. al. (30) and

Bannerjea et. al. (34) on substitution mechanisms in square

planar complexes have been summarized. The following discus-

sion compares these views with the results obtained for the

chloride exchange with $[Pt(NH_3)Cl_3]^-$.

In the aquation of $[Pt(NH_3)Cl_3]^-$, the theory proposed by

Chatt predicts greater stability for transition state (I) in-

volving two chlorides and one water in the trigonal plane than

for transition state (II) involving water, chloride, and am-

monia in the trigonal plane.

$$
\begin{array}{cc}
\text{(structure I)} & \text{(structure II)} \\
\end{array}
$$

Structure I: NH₃, Cl, Cl—M, Cl, H₂O

Structure II: Cl, Cl, NH₃—M, Cl, H₂O

(I)   (Ⅱ)
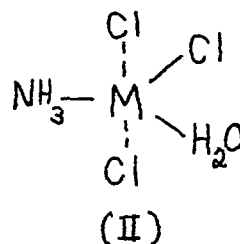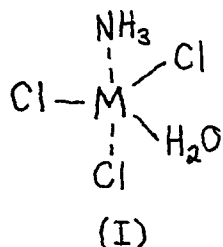
This increased stabilization is due to the slightly greater
π-bonding tendency of chloride over ammonia. It would there-
fore be expected that for this transition state, the chlorides
cis-to ammonia would be noticeably more labile than the chlo-
ride trans-to ammonia. The experimental results have shown
that all three chlorides in $[Pt(NH_3)Cl_3]^-$ are replaced at ap-
proximately the same rate. For the purpose of the above com-
parison, this may be restated by saying that the cis-chlorides
are replaced twice as fast as the trans-chlorides. However,
contrary to the theory, the activation energies for the two
processes do not differ.

The reaction mechanism proposed by Bannerjea, Basolo and
Pearson (34) is somewhat more compatable with the observed re-
sults. In this theory, the rate determining step in first
order substitution reactions involves the removal of a complex
ligand by the two solvent molecules above and below the plane
of the complex. The reaction sequence is illustrated on page
10. For weakly π-bonding ligands, the authors state that the
transition state would not necessarily rearrange to a trigonal
bipyramid. Under these conditions, the transition energies

for the replacement of either cis- or trans-chlorides might be the same and the chlorides would then exhibit equal lability.

Bannerjea, Basolo and Pearson (34) extensively studied the reactions of cis- and trans-$[Pt(NH_3)_2Cl_2]$ with a variety of reagents. From conductivity measurements, they showed that cis-$[Pt(NH_3)_2Cl_2]$ formed an equilibrium aquo-compound in solution but that trans-$[Pt(NH_3)_2Cl_2]$ apparently did not undergo the same reaction. However, many reactions with trans-$[Pt(NH_3)_2Cl_2]$ were independent of the entering reagent and yielded a constant value for the rate constant. It was therefore concluded that the trans-compound did form an aquo-complex but that the equilibrium constant for the process was quite low.

$$\text{cis-}[Pt(NH_3)_2Cl_2] + H_2O \underset{k'_-}{\overset{k}{\rightleftharpoons}} \text{cis-}[Pt(NH_3)_2Cl(H_2O)]^+ + Cl^-$$

$$\text{trans-}[Pt(NH_3)_2Cl_2] + H_2O \underset{k_-}{\overset{k}{\rightleftharpoons}} \text{trans-}[Pt(NH_3)_2Cl(H_2O)]^+ + Cl^-$$
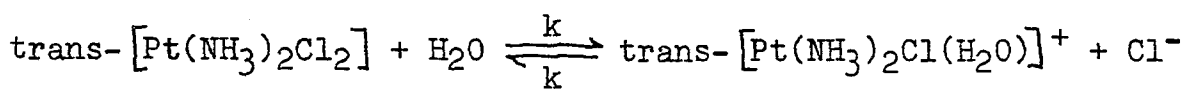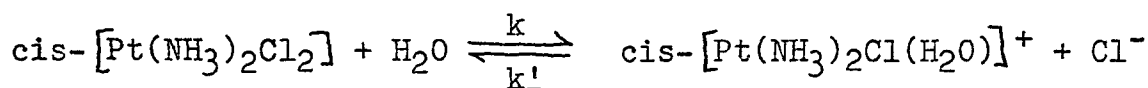
$$k_- > > k'_-$$

Thus for cis- and trans-$[Pt(NH_3)_2Cl_2]$, the more stable aquo-complex was formed with water trans- to ammonia rather than trans- to chloride.

When these observations were applied to the aquation of $[Pt(NH_3)Cl_3]^-$, it was concluded that trans-$[Pt(NH_3)Cl_2(H_2O)]$ should be more stable than the cis-isomer. Further support

for this order of stability was obtained from considerations of the relative thermodynamic stabilities of cis- and trans-$[Pt(NH_3)_2Cl_2]$. The trans-isomer has been demonstrated to be the more stable. If H_2O were considered to behave in the same manner as NH_3, a similar greater stability of trans-$[Pt(NH_3)Cl_2(H_2O)]$ over the cis-isomer would be predicted. These conclusions are contrary to the observed results.

No explanation for the inconsistent behavior of $[Pt(NH_3)Cl_3]^-$ with cis- and trans-$[Pt(NH_3)_2Cl_2]$ has been found. However, the assumed similarity of NH_3 and H_2O in platinum complexes is not strictly valid. The two groups are quite similar in trans-directing effects but they are not similar in substitution behavior. Ammonia is not easily replaced in platinum complexes while water is quite labile. Therefore, a comparison of the two types of compounds may not be possible.

V. KINETICS CALCULATIONS

In various sections of this thesis, experiments and re-
sults were discussed which required relatively extensive
mathematical treatment. Whenever practical, these results
were presented without details of the calculation procedure
but with a reference to this section. In most cases, these
calculations have been presented here in the order of their
discussion in the text.

A. Equilibrium Constant for the First Aquation

The equilibrium constant was determined by titration of
the equilibrium concentration of $[Pt(NH_3)Cl_2(H_2O)]$ in a
$[Pt(NH_3)Cl_3]^-$ - $[Pt(NH_3)Cl_2(H_2O)]$ equilibrium solution.

$$[Pt(NH_3)Cl_3]^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Pt(NH_3)Cl_2(H_2O)] + Cl^-$$
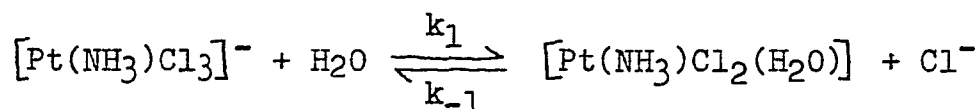
In all calculations, the following symbols have been used
to denote concentrations.

a = original concentration of $[Pt(NH_3)Cl_3]^-$ (moles/l.)

b = original concentration of Cl^- (moles/l.)

x = concentration of $[Pt(NH_3)Cl_2(H_2O)]$ (moles/l.)

x_∞ = equilibrium concentration of $[Pt(NH_3)Cl_2(H_2O)]$
(moles/l.)

$a - x$ = concentration of $[Pt(NH_3)Cl_3]^-$ (moles/l.)

$b + x$ = concentration of Cl^- (moles/l.)

K_1 = equilibrium constant for the first aquation reaction (moles/l.)

The concentration equilibrium constant was given by the expression:

$$K_1 = \frac{x_\infty (b + x_\infty)}{(a - x_\infty)}$$

Under the conditions of the equilibrium determination, b = 0, so:

$$K_1 = \frac{x_\infty^2}{a - x_\infty}$$

Values of x_∞ were obtained from the titration curves and substituted into the above expression.

B. Aquation Rate Constant for First Aquation Reaction

The aquation rate was obtained by following the time rate of change of the absorption spectra for a reacting solution. The absorption wavelength was $343 m\mu$ which corresponded to the absorption maximum for the $[Pt(NH_3)Cl_3]^-$ complex. From the absorption spectrum of a fresh solution, the molar absorptivity, ϵ_a, was obtained for the $[Pt(NH_3)Cl_3]^-$ complex from the equation:

$$A = absorbance = \ln \frac{I_o}{I} = \epsilon_a \ell (a)$$

where ℓ was the length of the transmission cell, and (a) was the molar concentration of $[Pt(NH_3)Cl_3]^-$ in solution. At aquation equilibrium, the molar absorptivity for the $[Pt(NH_3)Cl_2(H_2O)]$ complex was obtained from the equation:

$$A_\infty = \epsilon_a \ell (a - x_\infty) + \epsilon_x \ell (x_\infty)$$

where A_∞ was the equilibrium absorbance, x_∞ was the equilibrium concentration of $[Pt(NH_3)Cl_2(H_2O)]$ obtained from the equilibrium constant, and ϵ_x was the molar absorptivity for $[Pt(NH_3)Cl_2(H_2O)]$. After the determination of ϵ_a and ϵ_x, the value of $\underline{x}$ was determined for any time, t, by the relationship:

$$A(t) = \epsilon_a \ell (a - x) + \epsilon_x \ell (x)$$

where $A(t)$ equalled the absorbance at time t. This equation was rearranged to give:

$$x(t) = \frac{A_0 - A(t)}{\ell [\epsilon a - \epsilon_x]}$$

The aquation reaction was taken as first order in $[Pt(NH_3)Cl_3]^-$ while the reverse reaction was first order in $[Pt(NH_3)Cl_2(H_2O)]$ and first order in Cl^-.

$$[Pt(NH_3)Cl_3]^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Pt(NH_3)Cl_2(H_2O)] + Cl^-$$
$$(a - x) \qquad\qquad\qquad (x) \qquad (b + x)$$
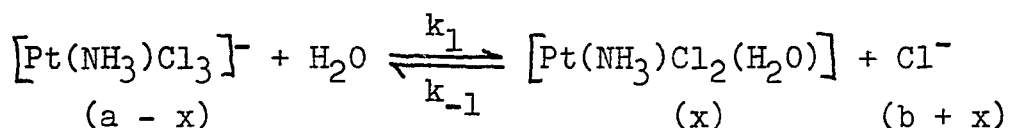
$$\frac{dx}{dt} = k_1(a - x) - k_{-1}(x)(b + x)$$

Since $K_1 = \dfrac{k_1}{k_{-1}}$, the differential equation rearranged to:

$$\frac{dx}{x^2 + (b + K_1)x - K_1 a} = -k_{-1}dt$$

which was integrated to give the solution:

$$\int \frac{dx}{x^2+(b+K_1)x-K_1 a} = \frac{1}{\sqrt{4K_1 a+(b+K_1)^2}} \ln \frac{\left[2x+b+K_1-\sqrt{4K_1 a+(b+K_1)^2}\right]}{\left[2x+b+K_1+\sqrt{4K_1 a+(b+K_1)^2}\right]} = -k_{-1}t$$

Substitution of the limits x = 0 when t = 0, x = x when t = t

and the expression for x_∞ obtained from the equilibrium con-

stant: $x_\infty = \dfrac{-(b+K_1) + \sqrt{4K_1a+(b+K_1)^2}}{2}$

yielded the expression:

$$-k_{-1}t = \frac{1}{\sqrt{4K_1a+(b+K_1)^2}} \ln\frac{[(x_\infty-x)(-x_\infty+\sqrt{4K_1a+(b+K_1)^2}]}{[x_\infty(x-x_\infty+\sqrt{4K_1a+(b+K_1)^2}]} = \frac{1}{\sqrt{4K_1a+(b+K_1)^2}} f(x)$$

A typical plot of f(x) versus t was given in Fig. 4. The

value k_{-1} was obtained from the slope of the plot and k_1 was

obtained from the relationship; k_1/k_{-1}. The values obtained

for k_1 and k_{-1} at different temperatures have been tabulated

in Table 1.

C. Exchange Equations

In the final discussion of the exchange results, it was

concluded that the observed exchange of chloride was explained

by the following reactions:

$$
\begin{array}{ccc}
\underset{\substack{|\\ \text{Cl}\\ (u)}}{\overset{\substack{(u)\\ \text{Cl}\\ |}}{\text{NH}_3 - \text{Pt} - \text{Cl}(r)}} + \text{H}_2\text{O} & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & \underset{\substack{|\\ \text{H}_2\text{O}}}{\overset{\substack{(v)\\ \text{Cl}\\ |}}{\text{NH}_3 - \text{Pt} - \text{Cl}(s)}} + \text{Cl}^-
\end{array}
$$

$$
\begin{array}{ccc}
\underset{\substack{|\\ \text{Cl}\\ (u)}}{\overset{\substack{(u)\\ \text{Cl}\\ |}}{\text{NH}_3 - \text{Pt} - \text{Cl}(r)}} + \text{H}_2\text{O} & \underset{k'_{-t}}{\overset{k_t}{\rightleftharpoons}} & \underset{\substack{|\\ \text{Cl}}}{\overset{\substack{\text{Cl}\\ |}}{\text{NH}_3 - \text{Pt} - \text{H}_2\text{O}}} + \text{Cl}^-
\end{array}
$$

$$(v)$$

$$\text{NH}_3 - \overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle H_2O}{|}}{Pt}} - Cl(s) \quad + H_2O \underset{k''_{-t}}{\overset{k''_t}{\rightleftharpoons}} \quad \text{NH}_3 - \overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle H_2O}{|}}{Pt}} - H_2O \quad + Cl^-$$

$$(v)$$

$$\text{NH}_3 - \overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle H_2O}{|}}{Pt}} - Cl(s) \quad + H_2O \underset{k''_{-c}}{\overset{k''_c}{\rightleftharpoons}} \quad \text{NH}_3 - \overset{\overset{\displaystyle H_2O}{|}}{\underset{\underset{\displaystyle H_2O}{|}}{Pt}} - Cl \quad + Cl^-$$
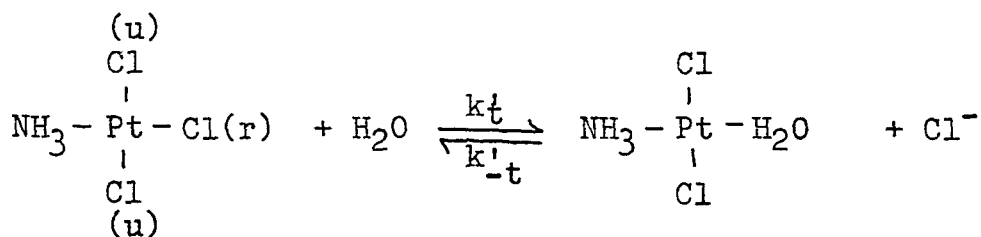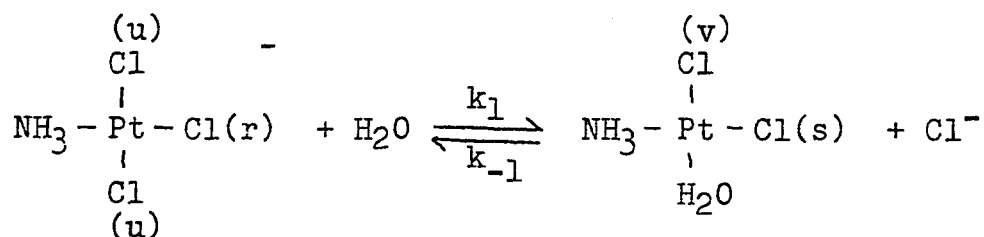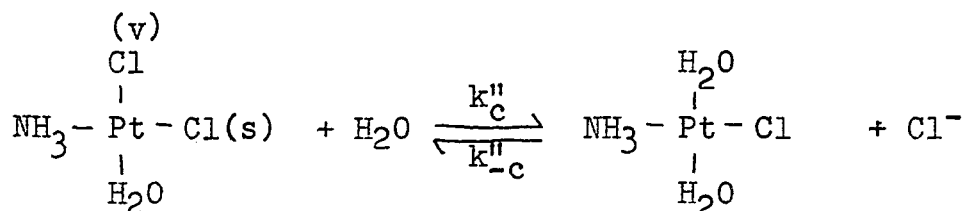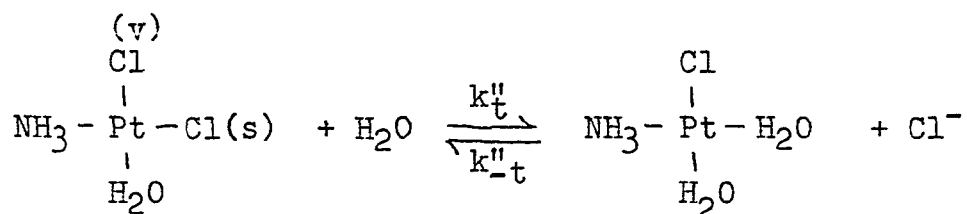
The letters adjacent to the complexed chlorides refer to the quantity of activity in the position at any time, t. The chlorides having no symbols are substituted in aquo-complexes of negligible concentration.

The following quantities shall be used in the following sections:

u = atoms of Cl^{36} in the two chlorides cis- to ammonia in $[Pt(NH_3)Cl_3]^-$ (atoms/ml.)

r = atoms of Cl^{36} in the chloride trans- to ammonia in $[Pt(NH_3)Cl_3]^-$ (atoms/ml.)

v = atoms of Cl^{36} in the chloride cis- to ammonia in $[Pt(NH_3)Cl_2(H_2O)]$ (atoms/ml.)

s = atoms of Cl^{36} in the chloride trans- to ammonia in $[Pt(NH_3)Cl_2(H_2O)]$ (atoms/ml.)

w = atoms of Cl^{36} in the carrier chloride (atoms/ml.)

I = total atoms of Cl^{36} = $u + r + v + s + w$

$$S_u = \frac{u}{2(a - x)} = \text{specific activity of two chlorides}$$
$$\text{cis- to ammonia in } [Pt(NH_3)Cl_3]^-$$

$$S_r = \frac{r}{a - x} = \text{specific activity of chloride trans-}$$
$$\text{to ammonia in } [Pt(NH_3)Cl_3]^-$$

$$S_v = \frac{v}{x} = \text{specific activity of chloride cis-}$$
$$\text{to ammonia in } [Pt(NH_3)Cl_2(H_2O)]$$

$$S_s = \frac{s}{x} = \text{specific activity of chloride trans-}$$
$$\text{to ammonia in } [Pt(NH_3)Cl_2(H_2O)]$$

1. Exchange by aquation only

For this derivation, it has been assumed that all exchange takes place through the reaction:

$$[Pt(NH_3)Cl_3]^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Pt(NH_3)Cl_2(H_2O)] + Cl^-$$
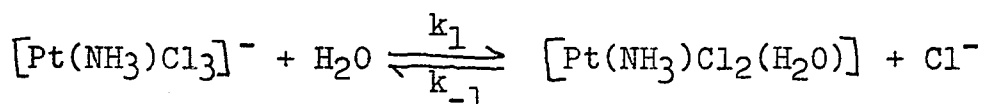
where all the chlorides in $[Pt(NH_3)Cl_3]^-$ are equivalent. At chemical equilibrium, the following equations apply for the rate of appearance of tracer chlorine in the two platinum compounds.

$$\frac{d(u+r)}{dt} = -3RS_{(u+r)} + 2RS_{(v+s)} + RS_\omega$$

$$\frac{d(v+s)}{dt} = 2RS_{(u+r)} - 2RS_{(v+s)}$$

where $R = k_1(a - x) = k_{-1}(x)(b + x)$

From the equivalence of chlorides:

$$u = 2r$$

$$v = s$$

$$S_u = S_r = S_{(u + r)} = \frac{u + r}{3(a - x)} = \text{specific activity of}$$

the three chlorides

in $[Pt(NH_3)Cl_3]^-$

$$S_v = S_s = S_{(v + s)} = \frac{v + s}{2x} = \text{specific activity of}$$

the two chlorides in

$[Pt(NH_3)Cl_2(H_2O)]$

$$S_w = \frac{I - (u + r) - (v + s)}{(b + x}$$

By substituting and rearranging:

$$\frac{1}{R}\frac{d(u+r)}{dt} + \left(\frac{1}{a-x} + \frac{1}{b+x}\right)(u+r) + \left(\frac{1}{b+x} - \frac{1}{x}\right)(v+s) = \frac{I}{b+x}$$

$$\frac{1}{R}\frac{d(v+s)}{dt} + \left(\frac{-2}{3(a-x)}\right)(u+r) + \left(\frac{1}{x}\right)(v+s) = 0$$

These equations have the general form:

$$\frac{1}{R}\frac{d(u+r)}{dt} + \ell(u+r) + m(v+s) = \frac{I}{b+x}$$

$$\frac{1}{R}\frac{d(v+s)}{dt} + \sigma(u+r) + n(v+s) = 0$$

where ℓ, m, n, and σ are known functions of the equilibrium solution concentration. The differential equations have the general solutions:

$$(u+r) - (u+r)_\infty = A_1 e^{-\alpha_1 t} + A_2 e^{-\alpha_2 t}$$

$$(v+s) - (v+s)_\infty = B_1 e^{-\alpha_1 t} + B_2 e^{-\alpha_2 t}$$

where A_1, A_2, B_1, B_2, α_1, and α_2 are known functions of the equilibrium solution concentrations and the rate constants.

If the first and second equations are divided respectively by $(u + r)_\infty$ and $(v + s)_\infty$:

$$\frac{(u+r)}{(u+r)_\infty} - 1 = A_1' e^{-\alpha_1 t} + A_2' e^{-\alpha_2 t}$$

$$\frac{(v+s)}{(v+s)_\infty} - 1 = B_1' e^{-\alpha_1 t} + B_2' e^{-\alpha_2 t}$$

but $\dfrac{(u+r)}{(u+r)_\infty} = \dfrac{S_{(u+r)}}{S_{(u+r)_\infty}} = F_{(u+r)}$

the fraction of exchange in $[Pt(NH_3)Cl_3]^-$ and

$$\frac{(v+s)}{(v+s)_\infty} = \frac{S_{(v+s)}}{S_{(v+s)_\infty}} = F_{(v+s)}$$

the fraction of exchange in $[Pt(NH_3)Cl_2(H_2O)]$. By application of the above equations, the fraction of exchange versus time for either the $[Pt(NH_3)Cl_3]^-$ or the $[Pt(NH_3)Cl_2(H_2O)]$ complex can be calculated and compared with the experimentally obtained curve. The results of the calculated exchange curves have been tabulated as times of half reaction in Table 3.

2. Exchange by aquation and γ reaction

If it is assumed all the exchange proceeds through an aquation reaction plus an additional reaction with $[Pt(NH_3)Cl_3]^-$.

$$[Pt(NH_3)Cl_3]^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Pt(NH_3)Cl_2(H_2O)] + Cl^-$$

$$[Pt(NH_3)Cl_3]^- + Cl^{*-} \xrightarrow{k'} [Pt(NH_3)Cl_2Cl^*]^- + Cl^-$$
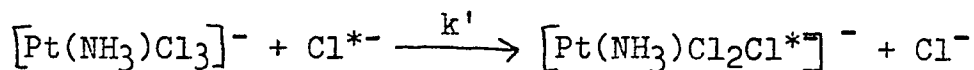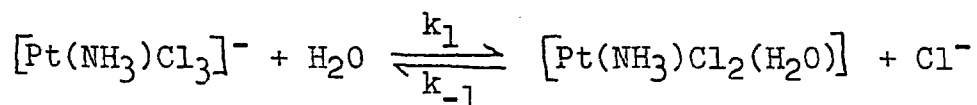
the following equations will apply:

$$\frac{d(u+r)}{dt} = -3R\,S_{(u+r)} + 2R\,S_{(v+s)} + R\,S_\omega - R'S_{(u+r)} + R'S_\omega$$

$$\frac{d(v+s)}{dt} = 2RS_{(u+r)} - 2RS_{(v+s)}$$

R is the rate of the aquation reaction and R' is the rate of the additional reaction. If both rate expressions are divided by R, then two of the terms involve the ratio R'/R which has been defined as γ. Since R' is unknown in the final solution, it was necessary to employ a trial and error substitution of γ to match the observed and calculated exchange curves.

By substitution of the specific activity expressions given in the preceeding section, the differential equations rearrange to:

$$\frac{1}{R}\frac{d(u+r)}{dt} + \left(\frac{1+\gamma}{b+x} + \frac{1+\gamma/3}{a-x}\right)(u+r) + \left(\frac{1+\gamma}{b+x} - \frac{1}{x}\right)(v+s) = \frac{I(1+\gamma)}{b+x}$$

$$\frac{1}{R}\frac{d(v+s)}{dt} + \left(\frac{-2}{3(a-x)}\right)(u+r) + \left(\frac{1}{x}\right)(v+s) = 0$$

which may be expressed in the general form:

$$\frac{1}{R}\frac{d(u+r)}{dt} + \ell'(u+r) + m'(v+s) = \frac{I(1+\gamma)}{b+x}$$

$$\frac{1}{R}\frac{d(v+s)}{dt} + \Theta(u+r) + \eta(v+s) = 0$$

These equations are analagous to the equations obtained for the case of aquation only, so the solution is of the same general form.

$$\frac{S_{(u+r)}}{S_{(u+r)\infty}} - 1 = F_{(u+r)}1 = A_1'' e^{-\alpha_1't} + A_2'' e^{-\alpha_3't}$$

$$\frac{S_{(\upsilon+s)}}{S_{(\upsilon+s)\infty}} - 1 = F_{(\upsilon+s)} - 1 = B_1'' e^{-\alpha_1' \tau} + B_2'' e^{-\alpha_2' \tau}$$

A_1'', A_2'', B_1'', B_2'', α_1', and α_2' are known functions of the solution concentrations, the aquation rate, R, and γ.

This derivation has been based on an aquation reaction plus an additional reaction of the form:

$$[Pt(NH_3)Cl_3]^- + Cl^{*-} \xrightarrow{k'} [Pt(NH_3)Cl_2Cl^*]^- + Cl^-$$
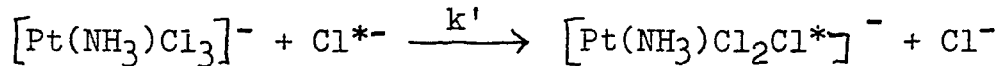
However, present interpretation of the results indicates that the γ reaction is actually an aquation reaction with a very low equilibrium constant:

$$[Pt(NH_3)Cl_3]^- + H_2O \underset{k'_{-t}}{\overset{k_t}{\rightleftarrows}} [Pt(NH_3)Cl_2(H_2O)] + Cl^-$$
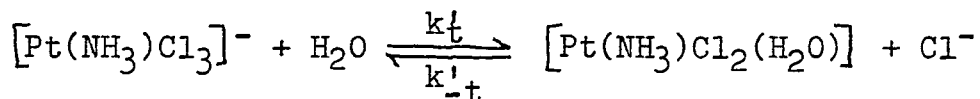
$$[Cl^-]k'_{-t} >> k_t$$

To be completely rigorous in the exchange derivation, the effect of this aquo-complex in the rate equations should be considered. If z is the activity in the γ aquo-complex and S_z is the specific activity of this complex, the resulting exchange differential equations are:

$$\frac{d(u+r)}{dt} = -3RS_{(u+r)} + 2RS_{(\upsilon+s)} + RS_\omega - R'3S_{(u+r)} + 2R'S_z + R'S_\omega$$

$$\frac{d(\upsilon+s)}{d\tau} = 2RS_{(u+r)} - 2RS_{(\upsilon+s)}$$

$$\frac{dz}{dt} = 2R'S_{(u+r)} - 2R'S_z$$

However, if the concentration of aquo-complex produced by the reaction is quite small, then:
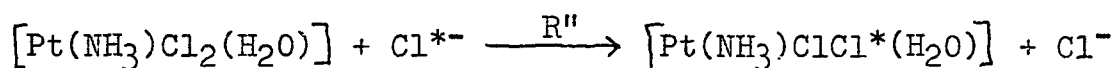
$$\frac{dz}{dt} \cong 0$$

and $S_{(u + r)} \cong S_z$

When the latter expression is substituted into the equation for $\frac{d(u+r)}{dt}$, the rate equation reduces to the original form given in this section. Thus, even though exchange may take place through an aquation step, the reaction will appear to be a simple substitution of one chloride for another when the aquation equilibrium constant is low. Since the constant is quite low for the γ and β exchange reactions, these reactions have been mathematically reduced to simple, first order exchange processes in this and in the following derivations.

3. Exchange by aquation and β reaction

The results of the calculations in the preceding section showed that all the observed exchange in $[Pt(NH_3)Cl_3]^-$ could be explained by the observed aquation reaction plus an additional first order exchange with $[Pt(NH_3)Cl_3]^-$. In this section the equations required if all exchange proceeded through aquation plus an additional reaction with $[Pt(NH_3)Cl_2(H_2O)]$ have been presented.

$$[Pt(NH_3)Cl_3]^- + H_2O \xrightleftharpoons{R} [Pt(NH_3)Cl_2(H_2O)] + Cl^-$$

$$[Pt(NH_3)Cl_2(H_2O)] + Cl^{*-} \xrightarrow{R''} [Pt(NH_3)ClCl^*(H_2O)] + Cl^-$$
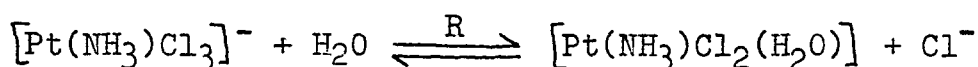
The differential equations for the appearance of activity in the platinum species are:

$$\frac{d(u+r)}{dt} = -3R\,S_{(u+r)} + 2RS_{(v+s)} + RS_\omega$$

$$\frac{d(v+s)}{dt} = 2RS_{(u+r)} - 2R\,S_{(v+s)} + R''S_\omega - R''S_{(v+s)}$$

When both expressions are divided by R, the last two terms in the second equation contain the ratio R"/R. This ratio has been defined as β. As in the case involving the γ reaction, arbitrary values of β were used in the final solutions to find which value gave the best fit with the experimental curves.

The above equations can be rearranged to fit the general form:

$$\frac{1}{R}\frac{d(u+r)}{dt} + \ell(u+r) + m(v+s) = \frac{I}{b+x}$$

$$\frac{1}{R}\frac{d(v+s)}{dt} + \ell'(u+r) + n'(v+s) = \frac{\beta I}{b+x}$$

These equations have the general solution:

$$F_{(u+r)} - 1 = A_1''' e^{-\alpha_1'' t} + A_2 e^{-\alpha_2'' t}$$

$$F_{(v+s)} - 1 = B_1''' e^{-\alpha_1'' t} + B_2''' e^{-\alpha_2'' t}$$

where the constants are again a function of β, the solution concentrations, and the aquation rate.

4. Initial slope exchange with fresh solutions

The differential equation for the appearance of activity in $[Pt(NH_3)Cl_3]^-$ due to the γ reaction is:

$$\frac{d(u+r)}{dt} = -3R_f S_{(u+r)} + 2R_b S_{(v+s)} + R_b S_w - R_f \gamma S_{(u+r)} + R_f \gamma S_w$$

Since the exchange does not take place at chemical equilibrium, R_f refers to the forward rate of the aquation reaction while R_b refers to the reverse step.

$$R_f = k_1(a - x) \cong k_1 a$$

$$R_b = k_{-1}(x)(b + x)$$

Since only $[Pt(NH_3)Cl_3]^-$ was present initially in the solution and since sampling was stopped before appreciable exchange took place, it was assumed that:

$$S_{(v+s)} \cong S_{(u+r)} \cong 0$$

$$S_w \cong \frac{I}{b}$$

Therefore:

$$\frac{d(u+r)}{dt} = R_b S_w + R_f \gamma S_w$$

If it is assumed that:

$$\frac{dx}{dt} \cong k_1 a$$

then:

$$x \cong k_1 a t$$

and

$$S_{(u+r)} = \frac{(u+r)}{3(a-x)} \cong \frac{(u+r)}{3a}$$

The proper quantities were substituted into the differential equation to give:

$$\frac{d(S_{(u+r)})}{dt} = \frac{I k_1 k_{-1}}{3} t + \frac{k_1 \gamma I}{3b}$$

When this equation was integrated and the expression,

$S_{(u + r)_\infty} = I/(b + 3a)$, substituted, then:

$$\frac{S_{(u+r)}}{S_{(u+r)_\infty}} = F_{(u+r)} = \frac{k_1 k_{-1}(b+3a)}{6} t^2 + \frac{k_1 \gamma(b+3a)}{3b} t$$

From this expression, the predicted initial slopes were obtained for different values of γ and different chloride concentrations.

The following calculations were employed to show that the β reaction was not the principle reaction introducing tracer chloride in $[Pt(NH_3)Cl_3]^-$. The rate of introduction of activity into $[Pt(NH_3)Cl_3]^-$ by the β reaction was expressed:

$$\frac{d(u+r)}{dt} = -3 R_f S_{(u+r)} + 2 R_b S_{(v+s)} + R_b S_w$$

where once again, $R_f = k_1(a)$, $R_b = k_{-1}(x)(b + x)$, and:

$$X = k_1 a t$$

$$S_{(u+r)} = \frac{u+\gamma}{3a}$$

$$S_\infty = \frac{I}{b+3a}$$

The fastest possible rate will occur when $[Pt(NH_3)Cl_2(H_2O)]$ exchanges immediately. This may be expressed in the differential equation by equating $S_{(u + s)}$ with S_w. Since $S_{(u + r)}$ is insignificant compared to S_w, it may be dropped from the expression to yield:

$$\frac{d(u+r)}{dt} = 3R_b S\omega$$

This equation may be integrated to give the following expression for the fraction of exchange.

$$\frac{S(u+r)}{S(u+r)_\infty} = \frac{(b+3a)\,k_1\,k_{-1}}{2}\,t^2$$

This equation represents the fastest possible rate that activity can be introduced into the $[Pt(NH_3)Cl_3]^-$ complex by a reaction with $[Pt(NH_3)Cl_2(H_2O)]$. The function has been plotted in Fig. 9 along with the initial slope plots predicted for a γ exchange. The rate of introduction of activity into $[Pt(NH_3)Cl_3]^-$ is quite different for the two processes.

As further experiments were performed, it was observed that exchange occurred by both a γ and a β reaction. Since the β reaction introduced a small amount of activity into $[Pt(NH_3)Cl_3]^-$, it was necessary to correct the calculated initial slope equation for this additional reaction. In this revised calculation, the simplifying assumptions were kept to a minimum. $S_{(u + r)}$ was no longer assumed insignificant and a time dependent rather than a constant function was derived for $S_{(v + s)}$. The resulting equation was:

$$\frac{S(u+r)}{S(u+r)_\infty} = \frac{(b+3a)\,k_1\,k_{-1}}{6}\,t^2 + \frac{\gamma k_1 (b+3a)}{3b}\,t - \frac{(3+\delta)\,k_1 C}{6}\,t^2 + \frac{k_1\,k_{-1}\,k''(b+3a)}{18}\,t^3$$

The complete derivation has not been included for several reasons. The operations involved were somewhat long and tedious and the curve obtained did not differ appreciably from the simplified curve derived for the γ exchange. The first two terms in the rigorous derivation make by far the

greatest contribution over the observed time of exchange and these terms are identical to the simplified treatment solution. The calculated initial slope curves for the Υ reaction in Fig. 9 were obtained from the above expression rather than the simplified treatment.

5. Exchange by aquation, Υ reaction, and β reaction

From the initial slope experiments, it was observed that a Υ reaction occurred. From exchange experiments involving $[Pt(NH_3)Cl_2(H_2O)]$ solutions, it was observed that a β reaction also occurred. The three exchange reactions may be expressed:

$$[Pt(NH_3)Cl_3]^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Pt(NH_3)Cl_2(H_2O)] + Cl^-$$

$$[Pt(NH_3)Cl_3]^- + Cl^{*-} \overset{k'}{\longrightarrow} [Pt(NH_3)Cl_2Cl^*]^- + Cl^-$$

$$[Pt(NH_3)Cl_2(H_2O)] + Cl^{*-} \overset{k''}{\longrightarrow} [Pt(NH_3)ClCl^*(H_2O)] + Cl^-$$
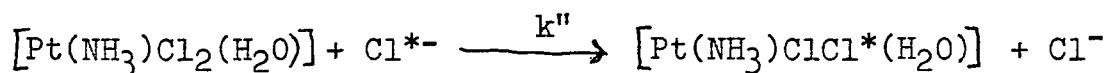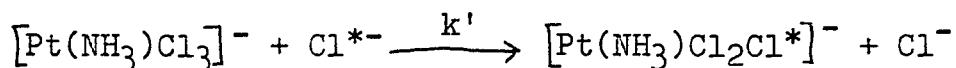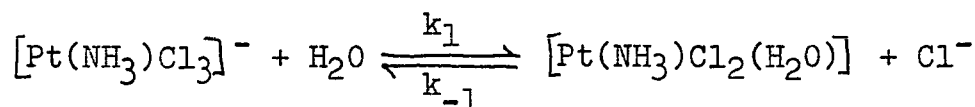
The differential equations expressing the rate of appearance of activity in the two platinum complexes are:

$$\frac{1}{R}\frac{d(u+r)}{dt} = -3S_{(u+r)} + 2S_{(v+s)} + S\omega - \Upsilon S_{(u+r)} + \Upsilon S\omega$$

$$\frac{1}{R}\frac{d(v+s)}{dt} = 2S_{(u+r)} - 2S_{(v+s)} - \beta S_{(v+s)} + \beta S\omega$$

As with the previous derivations, these equations are easily transformed to the general expressions:

$$\frac{1}{R}\frac{d(u+r)}{dt} + l'(u+r) + m'(v+s) = \frac{I(1+\gamma)}{b+x}$$

$$\frac{1}{R}\frac{d(v+s)}{dt} + \theta'(u+r) + n'(v+s) = \frac{\beta I}{b+x}$$

with solutions:

$$F_{(u+r)} - 1 = A_1''''e^{-\alpha_1'''t} + A_2'''e^{-\alpha_2'''t}$$

$$F_{(v+s)} - 1 = B_1''''e^{-\alpha_1'''t} + B_2''''e^{-\alpha_2'''t}$$

The coefficients in this solution are functions of both γ and β as well as the solution concentrations and the aquation rate.

6. Four-component exchange

From the results of the exchange studies, it was concluded that different chlorides exchanged at different rates. On the basis of certain experiments, approximate values for these different rate constants were obtained. The complete reaction scheme finally adopted has been given in the opening paragraph of this mathematics section.

The differential equations expressing the change in activity in the different chloride positions are:

$$\frac{du}{dt} = -2RS_u + RS_v + RS_w$$

$$\frac{dr}{dt} = -RS_r + RS_s + \gamma RS_w - \gamma RS_r$$

$$\frac{dv}{dt} = RS_u - RS_v + \beta''RS_w - \beta''RS_v$$

$$\frac{ds}{dt} = RS_r - RS_s + \beta' RS_\omega - \beta' RS_s$$

where R is associated with the reaction involving k_1, k_{-1}, γR with k_t', k_{-t}', $\beta'' R$ with K_c'', k_{-c}'', and $\beta' R$ with k_t'', k_{-t}''.

For high solution chloride concentrations:

$$\frac{d\upsilon}{dt} \cong \frac{ds}{dt} \cong 0$$

For exchange experiments in which the equilibrium concentration of $[Pt(NH_3)Cl_3]^-$ was quite small:

$$\frac{d\alpha}{dt} \cong \frac{d\gamma}{dt} \cong 0$$

For these two cases, the rate expressions reduced to two equations in two unknowns and these were solved conventionally to give a solution:

$$1 - F = C_1 e^{-k_1 \tau} + C_2 e^{-k_2 t}$$

For the remainder of the exchange studies, the predicted exchange curves were obtained with the electronic analogue computer.

7. Determination of k_{-2} rate constant from exchange experiments

One of the methods for determining the k_{-2} rate constant involved following the initial exchange rate of chloride with equilibrium $[Pt(NH_3)Cl_2(H_2O)]$ - $[Pt(NH_3)Cl(H_2O)_2]^+$ solutions. The fraction of exchange obtained was then compared with a similar exchange experiment performed with a solution containing only $[Pt(NH_3)Cl_2(H_2O)]$. The difference in the observed exchange rates was due to the introduction of activity in the

first solution by the reaction:

$$[Pt(NH_3)Cl(H_2O)_2]^+ + Cl^{*-} \xrightarrow{k_{-2}} [Pt(NH_3)ClCl^*(H_2O)] + H_2O$$
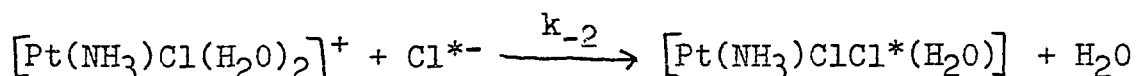
The rate of appearance of activity in $[Pt(NH_3)Cl_2(H_2O)]$ due to the replacement of a second water by chloride was given by the expression:

$$\frac{d(v + s)}{dt} = k_{-2}(y)(b + x)S_w$$

If (x) is assumed to be constant during the course of the reaction:

$$\frac{1}{2x}\frac{d(v+s)}{dt} = \frac{d[S_{(v+s)}]}{dt} = [S_{(v+s)\infty}]\frac{d[S_{(v+s)}/S_{(v+s)\infty}]}{dt}$$

By substitution:

$$\frac{d[S_{(v+s)}/S_{(v+s)\infty}]}{dt} = \frac{k_{-2}[y][b+x]S_w}{2x\,S_{(v+s)\infty}} = \frac{k_{-2}[y][b+3a]}{2x}$$

The quantity $\frac{d[S_{(v+s)}/S_{(v+s)\infty}]}{dt}$ was obtained experimentally from the difference in the initial slopes for the two experimental exchange curves. The value for k_{-2} was then obtained by substituting the known values for (x), (b), and (y) and solving the above equation.

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VII. ACKNOWLEDGMENTS