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Exchange of H2O ligand of trichloroaquoplatinate (II) with solvent

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EXCHANGE OF H_2O LIGAND OF

TRICHLOROAQUOPLATINATE(II) WITH SOLVENT

by

Charles Irvine Sanders

A Dissertation Submitted to the

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I. INTRODUCTION

Substitution reactions of the square planar complexes of platinum, palladium, nickel and gold have been reviewed and summarized by several authors (1, 2, 3, 4). Special interest has been attached to the exchange reactions of these complexes, in particular the exchanges undergone by platinum compounds.

The first study of exchange in platinum(II) complexes was carried out by Grinberg and Filinov (5), who investigated the $[PtBr_4]^=$-Br^{*-} system. A later article by Grinberg (6) on the application of radioactive tracers to the study of complex compounds also dealt with the tetrabromoplatinate(II)-bromide exchange. This exchange was restudied by Grinberg and Shagisultanova (7) in 1955; they found that the degree of exchange depended on the age of the $[PtBr_4]^=$ solutions and inferred that the exchange proceeded through an aquo intermediate. Grinberg et al. (8) showed that the rate of ligand exchange in the $[PdCl_4]^=$-Cl^{*-} and $[PdBr_4]^=$-Br^{*-} systems was faster than that of the corresponding platinum systems and attributed this to more rapid hydrolysis of the palladium compounds rather than any difference in dissociation constants.

Grantham et al. (9) used a tracer method to study the exchange of chloride with $[PtCl_4]^=$. They reported that exchange

with [PtCl$_4$]$^-$ occurred through the first acid hydrolysis and that a direct (chloride independent) exchange occurred with [PtCl$_3$(H$_2$O)]$^-$. It was later shown by Sanders and Martin (10) that the extent of aquation of [PtCl$_3$(H$_2$O)]$^-$ was sufficient to account for the observed "direct" exchange. Elleman et al. (11) investigated the exchange in the [Pt(NH$_3$)Cl$_3$]$^-$-Cl^{*-} system and found that it occurred both by means of an acid hydrolysis equilibrium and by a chloride-independent process. Since the chlorides in the acid hydrolysis product, [Pt(NH$_3$)Cl$_2$(H$_2$O)], are not equivalent, the "chloride-independent" process may have been an acid hydrolysis reaction for which the equilibrium constant was small.

Reishus (12) showed that the kinetics of the exchange of chloride with cis-[Pt(NH$_3$)$_2$Cl$_2$] were first order in the complex but independent of chloride concentration and that the reaction proceeded by means of the first acid hydrolysis. Similarly, the exchange of chloride with the first acid hydrolysis product, [Pt(NH$_3$)$_2$Cl(H$_2$O)]$^+$, occurred by means of the second acid hydrolysis. Adams[1] indicated that at low chloride concentrations, chloride exchange with trans-[Pt(NH$_3$)$_2$Cl$_2$] appeared to go via the first acid hydrolysis.

Rich and Taube (13) studied the exchange of chloride with the tetrachloroaurate(III) ion, which has the same square

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[1]Adams, R., Ames, Iowa. Exchange data. Private communication. 1960.

planar structure as the tetrahaloplatinate(II) and tetra-halopalladate(II) ions. They found that there were two com-ponents in the exchange rate, one first order and the other zeroth order in chloride. It was noted that hydrolysis of the gold complex appeared to be rapid enough to account for the exchange rate which was zeroth order in chloride.

Exchange of ligands in the system $[PtX_4]^=-X^{*-}$, where X was CN^-, I^-, Br^- or Cl^-, was studied by Grinberg and Nikol'skaya (14). They found that the exchange rates de-creased in the order $CN^- > I^- > Br^- > Cl^-$; this is the same order in which the stabilities of the complex ions decrease. Leden and Chatt (15) concluded from studies of equilibria in the $[Pt(C_2H_4)Cl_3]^--X^-$ system that the affinities of several ions for platinum(II) decreased in the order $SCN^- > I^- > Br^- > Cl^- >>$ F^-. This order is the reverse of the order of ion affinities for most metals; however, copper(I), silver(I), cadmium(II) and mercury(II) have the same order as platinum(II). It was suggested that since these metals all have filled inner d-orbitals and chlorine, bromine and iodine have vacant outer d-orbitals, dative π-bonding might occur between the metals and these halides to account for the reverse order in the ion affinities.

Banerjea et al. (16) made kinetic studies of a number of platinum(II) complexes reacting with various nucleophilic reagents and concluded that the reactions fell into two

groups, those first order in complex and zeroth order in attacking reagent, and those first order in both reagent and complex. Reactions in the second category indicated a definite correlation between the reactivity of the reagent and its _trans_ effect, that is, the capacity of a ligand to direct a group entering a complex to the position _trans_ to the original ligand.

Banerjea _et al_. observed that the reactions in the first group had nearly identical rates for several reagents, which indicated that reaction with the reagent was not the rate-determining step. It was suggested that a slow aquation of the complex followed by a rapid reaction with the reagent or an S_{N1} dissociation of the complex followed by rapid reaction with the reagent could explain the observed kinetics.

A mechanism for reactions of square planar complexes in solution was proposed by Banerjea _et al_. and was diagramed by Basolo and Pearson (4) as follows:
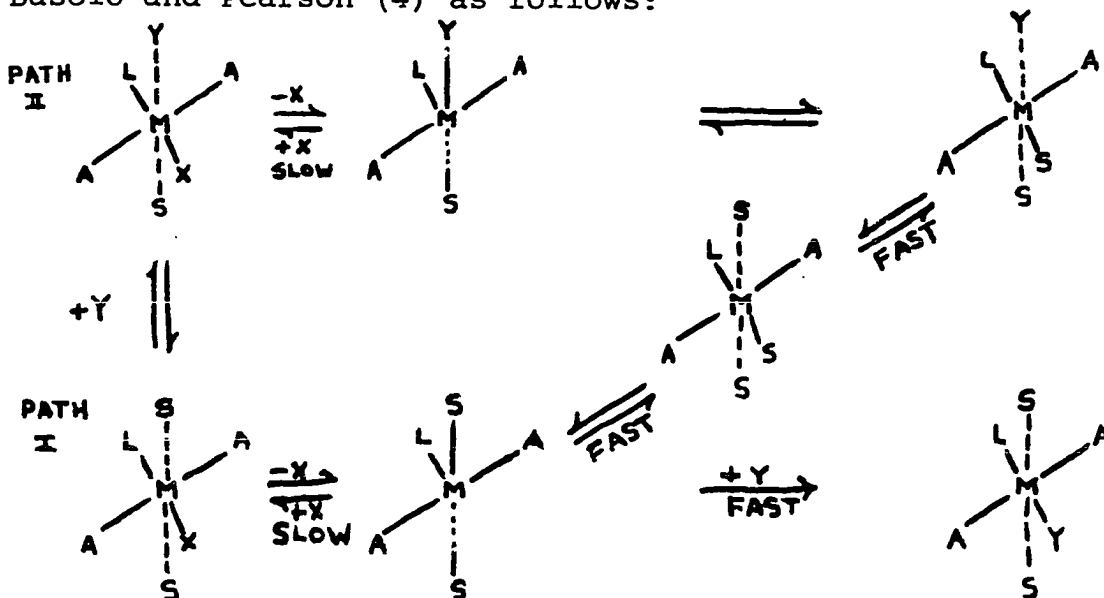
PATH II

PATH I

Path I shows a mechanism for reactions whose rates are independent of the concentration of attacking reagent (Y) and Path II shows a mechanism for cases in which the reaction is first order in Y.

It was felt that a knowledge of the rate of water exchange with the complex $[PtCl_3(H_2O)]^-$ might be useful in establishing a mechanism for square planar substitution reactions. One method for studying the water exchange rate was the use of H_2O^{18} as a tracer.

Taube and his associates have been the most active users of H_2O^{18} for studies of hydration mechanisms. Taube and Hunt (17) studied the exchange of water between the hydrated cations aluminum(III), chromium(III), iron(III), gallium(III), and thorium(IV) and solvent water by mixing solutions of the cation salts with water enriched in O^{18} and determining the isotopic composition of the oxygen in the resulting solvent as a function of time. The composition due to random mixing of normal and heavy water could be predicted. Superimposed on this mixing was a slow dilution of heavy by normal water as the water bound to the cations exchanged with the solvent. The rate and extent of the extra dilution corresponded to the rate and extent of ion hydration. Exchange was complete within three minutes for all of the ions except iron(III) at low acidities and chromium(III). The slow exchange in the low acidity iron(III) solutions was attributed to the presence of

polynuclear hydrolyzed species.

The half-time of exchange for aquated chromium(III) ion was found to be approximately 40 hours at one molar salt concentration, and the coordination number of the ion was found to be approximately six, which confirmed previous observations (18). From the fact that the coordination number was slightly greater than six, Taube and Hunt (17) concluded that the chromic ion displayed a preference for H_2O^{18} over H_2O^{16}.

Further studies on the kinetics of water exchange between aquated chromium(III) ion and solvent were performed by Plane and Taube (19). They reported that the exchange rate was first order in the chromic ion and increased with the concentration of the anion in the solution. The effectiveness of anions for promoting the exchange was in the order NO_3^- > ClO_4^- > Cl^- > Br^-. With Cl^- as the only anion present, the exchange rate was much faster than the formation rate of $[Cr(H_2O)_5Cl]^{++}$. All of the experiments were carried out in acid solution.

Mackenzie and Milner (20) confirmed the conclusions of Plane and Taube concerning the coordination number of six for chromium(III) and concerning the higher concentration of H_2O^{18} in hydration water than in solvent water. However, with no acid added to the solutions they found no specific anion effect but a dependence of the rate of exchange on ionic

strength with no regard to the nature of the electrolyte. The authors also found a higher activation energy than that observed by Plane and Taube and, in the presence of sufficient HCl, a rapid exchange of two oxygens in $[Cr(H_2O)_6]Cl_3$, followed by a slow first order exchange of the other four.

Mackenzie and Milner suggested reactions of the type $[Cr(H_2O)_6]^{+++} + X^- \rightleftharpoons [Cr(H_2O)_5X]^{++} + H_2O$ as a path for the exchange. In nonacidic solutions substitution with OH^- for X^- was assumed to predominate; in acidic solutions the substitution was presumably by other anions, and any specificity of anions was due to steric factors.

Studies on the rate of exchange of water between solvent and the aquated chromium(III) ion in dilute solutions (1.0 to 0.05 molar) were conducted by Hunt and Plane (21). They found that the rate was first order in chromic ion and that the rate constant increased slightly with ionic strength. There was no evidence of anion effects at the concentrations which they used.

The exchange of water between aquated cobalt ions and solvent was studied by Friedman et al. (22). They found that exchange with cobalt(III) and cobalt(II) at $1°$ C. was complete in less than three minutes although it had been expected that the exchange would be slow. Bonner and Hunt (23) suggested that the aquated cobalt(III) ion might indeed be substitution-inert and that the observed exchange of water may be carried

by electron exchange between the aquated cobalt(III) and

cobalt(II) ions. At $0°$ C. in one molar $HClO_4$ the water ex-

change is second order (presumably first order in each cobalt

ion).

Rutenberg and Taube (24) investigated the exchange of

water between the $[Co(NH_3)_5H_2O]^{+++}$ ion and solvent water in

perchloric acid solution. The reaction was found to be first

order in the ion. The authors noted that the rates of sub-

stitution of other groups for water in the cobalt complex sug-

gested that at high concentrations of chloride or sulfate ion

the rate of formation of the corresponding complex ion, i.e.,

$[Co(NH_3)_5Cl]^{++}$ or $[Co(NH_3)_5SO_4]^+$, might exceed the rate of

substitution of water by water. If the rate of substitution

of an anion for water were faster than the water exchange,

this would prove that the primary step in the substitution was

not just an S_{N1} process (loss of water, then reaction). It

was found that even in concentrated sulfate solutions the rate

of anion substitution for water was less than the measured

water exchange rate, but the authors did not consider this

sufficient negative evidence to eliminate the possibility of

S_{N2} substitution. It was possible that under the conditions

tested, S_{N2} exchange of water was faster than S_{N2} replacement

of water by sulfate.

Rutenberg and Taube tested the mechanism more directly by

measuring the rate of water exchange in the presence of sul-

fate ion. If the substitution mechanism were S_{N1}, competition between sulfate and water could only decrease the rate of reaction, but if an S_{N2} mechanism held, the rate of reaction, if affected at all, could only increase. (The substitution reaction rate was measured by dissolving O^{18}-labeled $[Co(NH_3)_5H_2O](ClO_4)_3$ in normal water and then sampling the oxygen coordinated to the cobalt at intervals.) An increase in rate could also result from the additional exchange path provided by the equilibrium involved in the formation of the complex ion. The observed effect was a small decrease in rate, which the authors interpreted as strong evidence that the S_{N1} mechanism operates, at least in part.

Stranks and Wilkins (25), in a review article on tracer investigations of mechanisms and structures, stated: "There are very few unambiguous and authentic examples of direct ligand exchange of transition metal complexes in aqueous solution . . . due to the relatively high nucleophilic character, i.e., complexing power, of the solvent water molecules. Kinetic exchange studies of aqueous systems normally reveal either partial or sometimes complete aquation superimposed on the rate of any direct ligand exchange." This thesis study was made to develop some idea of the mechanisms and kinetics of acid hydrolysis in $[PtCl_3(H_2O)]^-$ solutions.

II. EXPERIMENTAL

A. Materials

1. Potassium tetrachloroplatinate(II)

Potassium tetrachloroplatinate(II) was prepared from hexachloroplatinic acid, $H_2PtCl_6 \cdot n\ H_2O$, supplied by the Bram Chemical Company. The platinum was purified of iridium by crystallization of potassium hexabromoplatinate(IV); the bromine complex was converted to potassium hexachloroplatinate(IV) and this was reduced to potassium tetrachloroplatinate(II) with potassium oxalate in the method originally suggested by Vezes (26). The tetrachloroplatinate(II) product was recrystallized from water.

2. Tetraammineplatinum(II) chloride

The compound $[Pt(NH_3)_4]Cl_2$ was prepared by adding aqueous ammonia to a heated solution of $K_2[PtCl_4]$ until the green salt which first appeared dissolved. The solution was boiled to remove excess ammonia and to reduce the volume, and it was then filtered. The filtered solution was added to a salting solution of acetone, ether and alcohol, and $[Pt(NH_3)_4]Cl_2$ precipitated. The salt was filtered, dried in air, and stored in the dark in an ammonia desiccator until used.

3. Water

Water, enriched seven-fold in O^{18} content, was purchased from the Liquid Carbonic Division of the General Dynamics Corporation. After use, the solutions containing water enriched in O^{18} were distilled and the water reused, until repeated dilution reduced the heavy isotope enrichment below twofold.

All normal water used in solutions was tap distilled water which had been redistilled from alkaline permanganate solution.

4. Tetraphenylarsonium acetate

Tetraphenylarsonium acetate, $[As(C_6H_5)_4](C_2H_3O_2)$, was prepared by passing tetraphenylarsonium chloride solution through a Dowex-1 anion-exchange resin in the acetate cycle. The chloride reagent was purchased from the Hach Chemical Company.

5. Radioactive chlorine-36

Chlorine-36, used in the chloride exchange experiment, was obtained in dilute HCl carrier solution from the Isotopes Division, United States Atomic Energy Commission, Oak Ridge, Tennessee. The Cl^{36} isotope decays by a single 0.72 Mev. β-disintegration with a half-life of 3.1×10^5 years. This

long half-life eliminates the need for decay corrections in tracer activity during the exchange experiment.

6. Additional reagents

Additional reagents used were sodium nitrate, silver nitrate, and potassium acetate. All of these materials were reagent grade chemicals sold by the Baker Chemical Company.

B. Equipment

1. Constant temperature bath

A constant temperature bath was used to maintain a temperature of $25° \pm 0.1°$ C. in aging solutions of $K_2[PtCl_4]$. In this bath cooling was provided by a metal coil which carried a constant flow of tap water. Heating was accomplished by a Sargent heater which was regulated by a Precision Scientific electrical control.

2. Analytical equipment

Oxygen isotope-ratio analyses were performed in a Consolidated-Nier isotope-ratio mass spectrometer, Model 21-201. A vacuum oven was used to dry samples for the spectrometer. Oxygen was liberated from the samples by molten $KBrF_4$ or CoF_3 and introduced to the spectrometer, which registered the ratio of ions of mass 34 to ions of mass 32.

All pH determinations were made with a Beckman model "G" pH meter. Shielded electrodes, model 1190-80, were used to perform determinations outside the shielded cabinet. The instrument was standardized against a Beckman or Fisher pH 7 buffer.

In addition to the pH meter, a Machlett Auto-Burette was used in titrations. This device was a self-filling burette calibrated in hundredths of a milliliter. The fine calibration permitted accurate titrations with small volumes of reagent.

3. Geiger-Muller counter

Sample activities were measured with a TCG-1 Geiger-Muller counter manufactured by Tracerlab, Inc. The tube had a dead-time of approximately 200 microseconds and was housed in a lead shield. The pulses from the tube were recorded by a Berkeley decimal scaler, model 100. Samples were backed with cardboard and mounted on an aluminum sample holder placed 7 mm. below the window of the counting tube.

C. Procedures

1. Water exchange

The basic procedures for all of the exchange experiments were the equilibration (aging) of $[PtCl_4]^=$ solutions to

establish a concentration of $[PtCl_3(H_2O)]^-$, dilution of the equilibrium solutions with isotopically-enriched water, precipitation of the platinum species in solution, and analysis of the oxygen in the platinum-containing precipitates.

The equilibrium solutions of high ionic strength were prepared by weighing out the necessary amount of $K_2[PtCl_4]$ and dissolving it in a solution of $NaNO_3$. The concentrations used were 0.02 M $K_2[PtCl_4]$ and sufficient $NaNO_3$ to set the initial ionic strength at 0.636. Solutions of low ionic strength were prepared by dissolving the amount of $K_2[PtCl_4]$ for a 0.02 M solution in water. The solutions were aged at least 24 hours but not more than 48 hours before the exchange experiments were performed.

The aged solutions were mixed thoroughly with equal volumes of isotopically enriched water and aliquots were taken from the diluted solutions at the desired intervals. The platinum species of interest were precipitated from the aliquots of high ionic strength solutions by the addition of dry, powdered $AgNO_3$ with stirring. Precipitation in experiments with low ionic strength solutions was performed by adding a small volume of a concentrated $AgNO_3$ solution or a concentrated solution of $[Pt(NH_3)_4]Cl_2$ to the aliquot with stirring. The "infinity" sample of solvent water was obtained by taking a 1 ml. aliquot from the exchange solution before the final sample was precipitated.

The precipitated platinum salts were filtered on a sintered glass filter without washing and were dried by drawing air through the filter for a short time. The precipitate was then dried under vacuum at room temperature. Analyses for oxygen isotope ratios were performed on the dried samples by H. G. Staley under the direction of Dr. H. J. Svec.

The drying procedures for the samples were tested for reproducibility before adoption as experimental method. In the case of the precipitate with silver, a solution of $K_2[PtCl_4]$ was prepared and aged, diluted with O^{18}-enriched water, allowed to equilibrate for one hour, and treated with $AgNO_3$. The precipitate was divided into four roughly equal portions which were dried in vacuum at room temperature for various lengths of time before analysis. Drying times and analyses of the samples, shown in Table 1, indicated that drying times of 6 hours or more would give reproducible samples. Precipitates were stored overnight or longer in vacuum between filtration and analysis.

The drying of Magnus' salt samples was tested by drying the salt under various conditions of temperature and pressure. Data on conditions and results are shown in Table 2. Drying for 2 hours in vacuum at room temperature appeared to give reproducible dry samples. Precipitates awaiting analysis were stored in a $CaSO_4$ desiccator after the initial vacuum drying.

An attempt was made to determine whether Magnus' salt

Table 1. Data for drying of precipitate with $AgNO_3$

Sample no.	Drying time (hours)	Mole fraction O^{18} x 10^3
1	3.7	3.00
2	6.2	2.49
3	24.9	2.53
4	48.4	2.52

Table 2. Data for drying of Magnus' salt samples

Sample no.	Drying temperature (° C.)	Drying time (hrs.)	Mole ratio N_2/O_2
1A[a]	25	3	3.8
1B[a]	60	3	11.0
1C[a]	60	20	22.1
2[a]	25	20	21.7
3[a]	25	2	8.1
4A[a]	25	2	3.8
4B[a]	25	2	4.4
4C[a]	25	2	3.8
5A[b]	61	24	8.4
5B[b]	61	24	8.4
6[b]	61	48	9.5
7[b]	61	72	9.1

[a]Samples dried in vacuum oven.

[b]Samples dried in oven at atmospheric pressure.

occludes water within the crystal by comparing the infrared spectrum of one sample of the salt prepared under conditions which would assure water in the crystal with the spectrum of another sample prepared so as to exclude water other than occluded water. The sample to contain water was prepared by mixing a solution of $[Pt(NH_3)_4]Cl_2$ with an aged solution of $K_2[PtCl_4]$ to precipitate $[Pt(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][PtCl_3(H_2O)]_2$. This mixture of salts precipitated in the normal green form of Magnus' salt. The sample to be anhydrous was prepared by adding solid $[Pt(NH_3)_4]Cl_2$ to a mixture of equal weights of $K_2[PtCl_4]$ and KCl freshly dissolved in a minimum amount of water. The salt precipitated as a mixture of the pink and green forms.

The salts were filtered, dried in vacuum for two hours, and stored in a desiccator until an infrared spectrum could be taken on a Nujol mull of each sample. The O-H frequencies of the spectra were examined and it appeared that there was some water in both samples, with a slightly greater amount in the salt precipitated from the aged $K_2[PtCl_4]$ solution. The resolution of the infrared spectra was not sufficient to permit any quantitative estimate of the amount of water present. No estimate could be made of the relative amounts of water occluded by the pink and green forms of Magnus' salt (which are thought to have different crystal structures)(27) if water were trapped in the crystals.

In the oxygen analyses of the samples precipitated from one of the high ionic strength solutions there were detected small amounts of nitrogen. It was found by experiment that $NaNO_3$ treated with $KBrF_4$ readily evolved oxygen along with a small quantity of nitrogen. Any nitrates in the platinum-containing precipitates thus could have caused an error in the estimation of the extent of exchange by diluting the oxygen from the water in the samples with normal oxygen. To avoid contamination by nitrate, later experiments employed solutions of low ionic strength (no $NaNO_3$ added) and the $AgNO_3$ precipitating agent was added as a solution rather than as a dry powder.

It was not known whether the addition of silver ion to an aged $K_2[PtCl_4]$ solution precipitated the $[PtCl_4]^=$ and $[PtCl_3(H_2O)]^-$ ions alone, or the $[PtCl_2(H_2O)_2]$ complex in addition to these. The pH of an aged 0.02 M $K_2[PtCl_4]$ solution of low ionic strength, in which the concentrations of $[PtCl_3(H_2O)]^-$ and $[PtCl_2(H_2O)_2]$ were calculated from the equilibrium constants to be 1.16×10^{-2} mole/l. and 8.7×10^{-4} mole/l., respectively, was measured before and after the addition of $AgNO_3$ solution. The addition of the silver caused a rapid decrease in the pH, in one sample from 4.1 to 2.1 and in another sample of the same solution from 4.1 to 1.9. This increase in the acidity of the solution was interpreted as being due to precipitation of all three of the platinum

species, accompanied by release of the acidic protons from the hydrolyzed species. The released acid was titrated but the titration curve obtained did not yield quantitative information due to erratic behavior of the pH meter (caused by the nature of the sampled solution) and precipitation of Ag_2O in the solution being neutralized.

Grantham et al. (9) showed that the precipitation of Magnus' salt from an aged $K_2[PtCl_4]$ solution containing about 0.01 mole/l. of $[PtCl_3(H_2O)]^-$ resulted in an increase in the hydrogen ion concentration of less than 10^{-4} mole/l. They concluded from this that the amount of the hydrolysis product, $[Pt(NH_3)_4][PtCl_3OH]$, was less than 1% of the total salt precipitated. Grantham et al. stated that analyses of a number of Magnus' salt precipitates indicated that $[Pt(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][PtCl_3(H_2O)]_2$ were precipitated without detectable fractionation. It was assumed, on the basis of Grantham's evidence, that the second hydrolysis product, $[Pt(NH_3)_4][PtCl_2(OH)_2]$, did not precipitate.

2. Chloride exchange

For the chloride exchange experiment, a solution 0.01 M in both $K_2[PtCl_4]$ and KCl was prepared and aged for two days at 25° C. Ten microliters of Cl^{36} tracer solution were added to the aged solution; exchange time was counted from this mixing. Aliquots of the $K_2[PtCl_4]$ solution were withdrawn at

intervals. An equal volume of approximately 0.06 M tetra-
phenylarsonium acetate solution was added to each aliquot and
the resulting solutions were allowed to stand one minute
before filtration to allow nearly complete formation of the
precipitate.

The precipitates were filtered, dried, weighed, mounted
and counted in essentially the same manner as described by
Grantham et al. (9).

3. Titration experiment

The rate of acid hydrolysis of $[PtCl_4]^=$ was measured by
rapid potentiometric titrations of 15 ml. aliquots of a
freshly prepared 0.01 M $K_2[PtCl_4]$ solution at intervals over a
period of 105 minutes following the preparation. The titer of
the solution increased with time due to the formation of
$[PtCl_3(H_2O)]^-$. The base used for the titrations was 0.1040 N
NaOH.

III. TREATMENT OF DATA
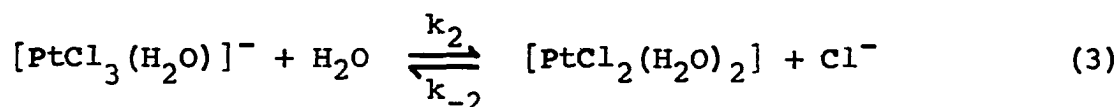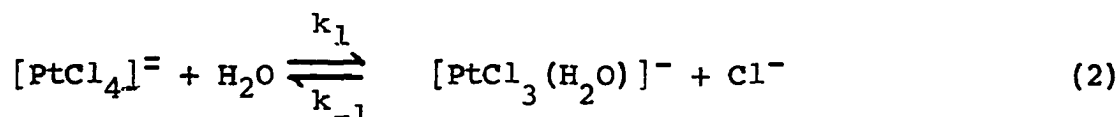
The exchange process of interest in this thesis study is that illustrated by Equation 1.

$$[PtCl_3(H_2O)]^- + H_2O^{18} \rightleftharpoons [PtCl_3(H_2O^{18})]^- + H_2O \qquad (1)$$

The water exchange may be effected by means of acid hydrolysis reactions, by a direct exchange between the platinum species and solvent, or by a combination of these processes.

The exchange was first treated with the assumption that it proceeded only via the acid hydrolysis reactions shown in Equations 2 and 3,

$$[PtCl_4]^= + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [PtCl_3(H_2O)]^- + Cl^- \qquad (2)$$

$$[PtCl_3(H_2O)]^- + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [PtCl_2(H_2O)_2] + Cl^- \qquad (3)$$

in which the k's represent rate constants for the forward and reverse reactions. In the algebraic treatment of this exchange the following symbols were used:

a = the total concentration of platinum in the solution. (All concentrations are given in moles/liter.)

x = the concentration of $[PtCl_3(H_2O)]^-$ in the solution.

y = the concentration of $[PtCl_2(H_2O)_2]$ in the solution.

u = the concentration of O^{18} in $[PtCl_3(H_2O)]^-$.

v = the concentration of O^{18} in $[PtCl_2(H_2O)_2]$.

$\bar{N}_u$ = the mole fraction of O^{18} in $[PtCl_3(H_2O)]^-$.

= u/x

N_v = the mole fraction of O^{18} in $[PtCl_2(H_2O)_2]$.

= $v/2y$

N_w = the mole fraction of O^{18} in the solvent water.

It was assumed that the platinum species shown in Equations 2 and 3 were the only ones present. The concentration of $[PtCl_4]^=$ after the solutions were aged was therefore $(a - x - y)$. Free chloride in the solutions was due to chloride displaced from $[PtCl_4]^=$ by water. Because one chloride was replaced to form the monoaquo species and two to form the diaquo, the concentration of free chloride was $(x + 2y)$. The time rate of change of x could thus be written

$$dx/dt = k_1(a - x - y) - k_{-1}(x)(x + 2y) - k_2(x)$$
$$+ k_{-2}(y)(x + 2y) \qquad (4)$$

Similarly, the rate at which y varies with time could be written

$$dy/dt = k_2(x) - k_{-2}(x + 2y)(y) \qquad (5)$$

If the exchange proceeded only _via_ the acid hydrolyses, the equations expressing the change of u and v with time could be derived from Equations 2 and 3. Thus

$$du/dt = k_1(a - x - y)N_w - k_{-1}(x)(x + 2y)N_u - k_2(x)N_u$$
$$+ k_{-2}(y)(x + 2y)N_v \qquad (6)$$
$$dv/dt = k_2(x)(N_u + N_w) - 2k_{-2}(y)(x + 2y)N_v \qquad (7)$$

From the definitions of N_u and N_v, it may be seen that

$$dN_u/dt = (1/x)(du/dt) - (u/x^2)(dx/dt) \qquad (8)$$

$$dN_v/dt = (1/2y)(dv/dt) - (v/2y^2)(dy/dt) \qquad (9)$$

Substitution of the expressions from Equations 4 and 6 in Equation 8 and collection of terms yielded the equation

$$dN_u/dt = (k_1/x)(a - x - y)(N_w - N_u)$$
$$+ (k_{-2}/x)(y)(x + 2y)(N_v - N_u) \qquad (10)$$

Expressions from Equations 5 and 7 substituted into Equation 9 gave

$$dN_v/dt = (k_2x/2y)(N_u + N_w - 2N_v) \qquad (11)$$

It was not possible to solve Equations 10 and 11 in closed form to obtain N_u and N_v at a given time. The equations could be solved by a point-by-point numerical integration, or they could be put in analytical form with the use of some simplifying approximations and solved analytically. The latter method of solution is presented first.

If the concentration of $[PtCl_2(H_2O)_2]$ was much less than the concentration of $[PtCl_3(H_2O)]^-$, then dN_v/dt was small compared with dN_u/dt, and from Equation 11 it appeared that

$$\tfrac{1}{2}(N_u + N_w) \approx N_v \qquad (12)$$

If N_v in Equation 10 were replaced by the approximation of Equation 12 and y were neglected where compared with x, Equation 10 could be written

$$dN_u/dt \approx (k_1/x)(a - x)(N_w - N_u) + (k_2/2)(N_w - N_u) \qquad (13)$$

For the dilute solutions used, N_w did not change appreciably with time and was assumed constant. It was also assumed that x and y were nearly constant during the exchange experiment. Equation 13 then had the solution

$$\ln[(N_w - N_o)/(N_w - N_u)] = [(k_1/x)(a - x) + k_2/2]t \qquad (14)$$

where N_o and N_u were the values of N_u at time zero and time t, respectively. N_w was taken to be N_∞, the mole fraction of O^{18} in the ligand and solvent water at exchange equilibrium, and Equation 14 could then be written

$$\ln(1 - F) = -[(k_1/x)(a - x) + (k_2/2)]t \qquad (15)$$

where F, the fraction of exchange, was defined by

$$F = (N_u - N_o)/(N_\infty - N_o) \qquad (16)$$

To the extent that the assumptions were valid, the logarithm of (1 - F) was a linear function of the time. The terms relating ln(1-F) and time contained no dependence on N_w, so that ln(1-F) could be calculated at any time without reference to the mole fraction of O^{18} in the solvent.

Equation 15 was used to find the half-time of water exchange in a solution of high ionic strength for which the concentrations and rate constants were

$$a = 1.0 \times 10^{-2} \text{ mole/l.} \qquad k_1 = 0.14 \text{ hr.}^{-1}$$

$$x = 5.4 \times 10^{-3} \text{ mole/l.} \qquad k_{-2} = 230 \text{ hr.}^{-1} \text{ l./mole}$$

$$y = 2.5 \times 10^{-4} \text{ mole/l.}$$

The half-time of exchange via acid hydrolysis in this solution was calculated to be 4.7 hours. In a solution of low ionic

strength, for which the concentrations and rate constants were

$$a = 1.0 \times 10^{-2} \text{ mole/l.} \qquad k_1 = 0.14 \text{ hr.}^{-1}$$

$$x = 5.8 \times 10^{-3} \text{ mole/l.} \qquad k_{-2} = 116 \text{ hr.}^{-1} \text{ l./mole}$$

$$y = 4.4 \times 10^{-4} \text{ mole/l.}$$

the calculated half-time of exchange _via_ acid hydrolysis was 5.5 hours.

To obtain values of N_u and N_v at given times with fewer approximations than were necessary for the analytical solution, Equations 10 and 11 were integrated numerically. Values of x and y at 20 minute intervals were found by simultaneous numerical integration of Equations 4 and 5. The values at zero time were taken to be half the equilibrium values for a 0.02 M $K_2[PtCl_4]$ solution of appropriate ionic strength calculated from K_1 and K_2, the equilibrium constants for the first and second acid hydrolyses (10). A 0.0193 M $K_2[PtCl_4]$ solution with an initial ionic strength of 0.636 was aged and titrated for the purpose of comparing the observed titer with the calculated titer. The observed titer was 1.10×10^{-2} equiv./l.; the calculated titer was 1.16×10^{-2} equiv./l. and the agreement was considered satisfactory. The titer of a 0.02 M $K_2[PtCl_4]$ solution of low ionic strength was also checked by titration. The observed titer was 1.33×10^{-2} equiv./l., which agreed well with the calculated titer of 1.34×10^{-2} equiv./l.

The simultaneous numerical integration of Equations 10

and 11 gave expressions for N_u and N_v of the form

$$N_u = c_1 N_w + c_2 \qquad (17)$$

$$N_v = c_3 N_w + c_4 \qquad (18)$$

where the c's were functions of time. It may be seen from Equations 17 and 18 that the numerical integration, in contrast to the approximate treatment, indicated a relationship between ln (1-F) and time which contained a dependence on N_w.

Values of x, y, c_1, c_2, c_3, c_4 and the rate constants used are given in Table 3 for solutions of low ionic strength and Table 4 for solutions of high ionic strength. The results of the integrations are also presented in graphical form as the three curves in Figure 1. Curve I is the curve calculated for a low ionic strength solution in which [Pt(NH$_3$)$_4$]Cl$_2$ was used as the precipitating agent so that the mole fraction of O^{18} in the precipitate was N_u. The conditions of ionic strength and concentrations were the same as those used in the simplified calculation of N_u presented earlier. The half-time of exchange from Curve I is 6.2 hours.

Curve II of Figure 1 is for a low ionic strength solution in which the precipitating agent was AgNO$_3$. The observed mole fraction of O^{18} in the precipitate, N_c, was due to u and v, and was taken to be expressed by

$$N_c = (x N_u + 2y\, N_v)/(x + 2y) \qquad (19)$$

The half-time of exchange from Curve II is 4.5 hours.
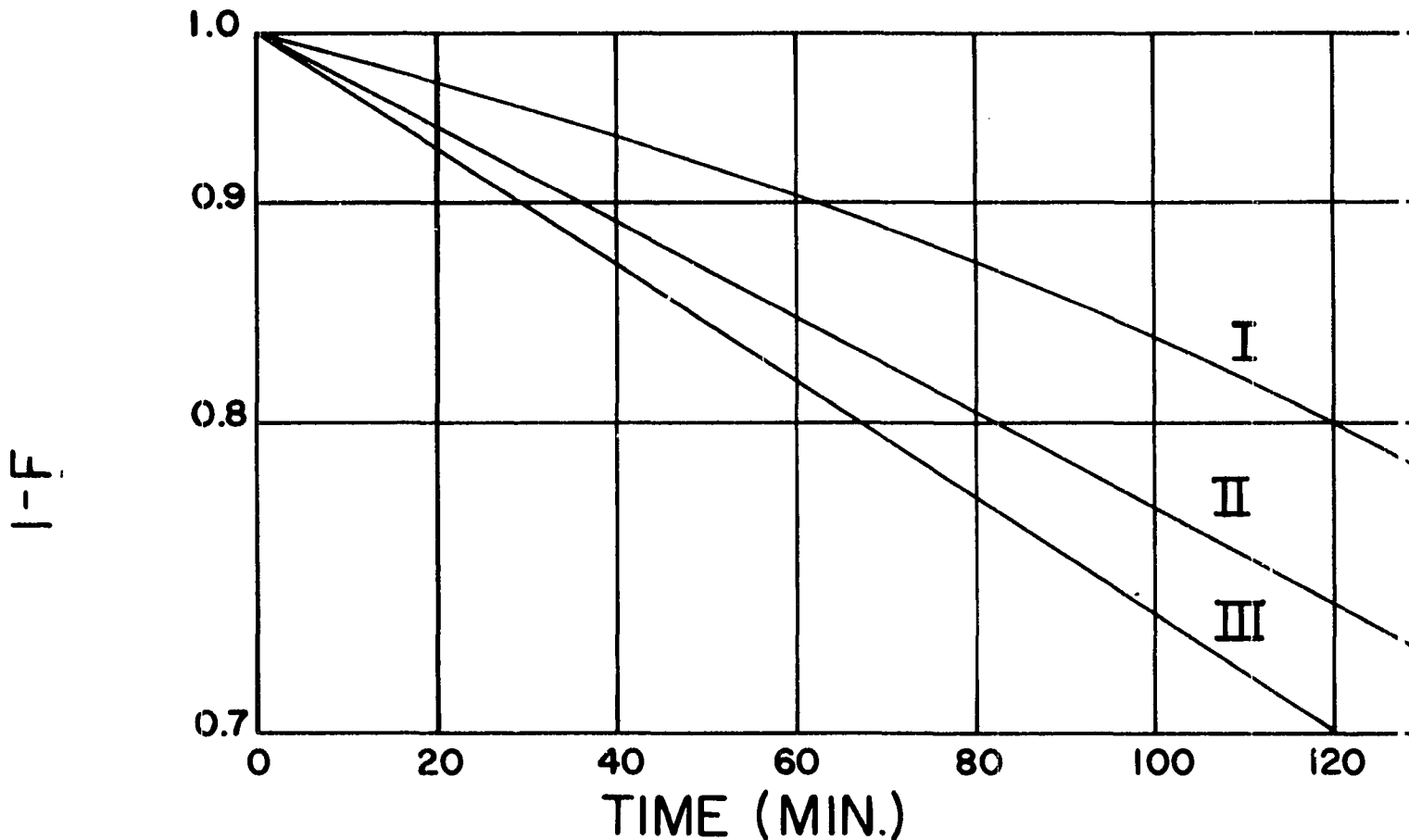
Curve III was calculated for a solution of high ionic

Figure 1. Semilogarithmic plot of exchange data curves calculated from numerical integration results. Curve I: $N_{\infty} = 0.00359$ [Pt(NH$_3$)$_4$]Cl$_2$ used as precipitating agent, low ionic strength (Expt. IV, Table 6). Curve II: $N_{\infty} = 0.00894$, pptng. agent = AgNO$_3$, low ionic strength (Expt. I, Table 6). Curve III: $N_{\infty} = 0.00413$, pptng. agent = AgNO$_3$, high ionic strength (Expt. III, Table 5)

Table 3. Calculated exchange data for low ionic strength solutions[a,b]

Time (min.)	x $\times 10^3$	y $\times 10^3$	c_1 $\times 10^2$	c_2 $\times 10^3$	c_3 $\times 10^2$	c_4 $\times 10^3$
0	5.805	0.435	0	1.961[c]	0	1.961[c]
20	5.806	0.547	2.98	1.903	25.81	1.455
40	5.834	0.626	6.36	1.837	36.35	1.248
60	5.879	0.680	9.85	1.768	42.42	1.129
80	5.935	0.717	13.33	1.700	46.60	1.047
100	5.997	0.742	16.73	1.633	49.82	0.984
120	6.061	0.759	19.99	1.569	52.49	0.932

[a]Approximate ionic strength 0.03 (no added salt).

[b]Initial concn. of $[PtCl_4]^=$ = 0.01 M. Rate constants: k_1 = 3.83 $\times$ 10^{-5} sec.$^{-1}$, k_2 = 3.22 $\times$ 10^{-5} sec.$^{-1}$, k_{-1} = 1.28 $\times$ 10^{-3} sec.$^{-1}$ l./mole, k_{-2} = 3.22 $\times$ 10^{-2} sec.$^{-1}$ l./mole.

[c]Spectroscopic analysis of water used in experiments.

Table 4. Calculated exchange data for high ionic strength solutions[a,b]

Time (min.)	$x \times 10^3$	$y \times 10^3$	$c_1 \times 10^2$	$c_2 \times 10^3$	$c_3 \times 10^2$	$c_4 \times 10^3$
0	5.446	0.247	0	1.961[c]	0	1.961[c]
20	5.433	0.360	3.66	1.889	45.57	1.067
40	5.470	0.415	8.43	1.796	49.48	0.991
60	5.528	0.440	13.12	1.704	52.06	0.940
80	5.593	0.453	17.58	1.616	54.40	0.894
100	5.658	0.458	21.77	1.534	56.64	0.850
120	5.721	0.461	25.68	1.457	58.81	0.808

[a]Approximate ionic strength of 0.318 attained by addition of $NaNO_3$.

[b]Initial concn. of $[PtCl_4]^= $ - 0.01 M. Rate constants: k_1 = 3.86 x 10^{-5} sec.$^{-1}$, k_2 = 3.44 x 10^{-5} sec.$^{-1}$, k_{-1} = 2.58 x 10^{-3} sec.$^{-1}$ l./mole, k_{-2} = 6.39 x 10^{-2} sec.$^{-1}$ l./mole.

[c]Spectroscopic analysis of water used in experiments.

strength for which the precipitating agent was $AgNO_3$ and N_C depended on u and v as for Curve II. From Curve III the half-time of exchange appears to be 3.8 hours. The approximate treatment of the same data as were used for Curve III gave a half-time of 4.7 hours.

The exchange of water between $[PtCl_3(H_2O)]^-$ and solvent may be a direct exchange, in which case the reaction is illustrated by Equation 1, with the rate constants k_W and k_{-W} for the forward and reverse reactions. The symbols used in the algebraic treatment of the direct exchange were the same as those used for the treatment of the exchange _via_ acid hydrolysis.

From Equation 1 it may be seen that

$$du/dt = k_W(x)(N_W) - k_{-W}(x)(N_u) \tag{20}$$

If there was no isotope effect, $k_W = k_{-W}$, and Equation 20 had the form

$$du/dt = k_W(x)(N_W - N_u) \tag{21}$$

If x remained constant during the exchange or if the water exchange were rapid compared with acid hydrolysis, then it may be seen from Equation 8 that

$$dN_u/dt = (1/x)(du/dt) \tag{22}$$

Substitution of the expression for du/dt from Equation 21 into Equation 22 gave

$$dN_u/dt = k_W(N_W - N_u) \tag{23}$$

Equation 23 was integrated to give

$$\ln[(N_w - N_0)/(N_w - N_u)] = \ln[1/(1 - F)] = k_w t \qquad (24)$$

if $N_w = N_\infty$.

If there were an isotope effect and k_w were not equal to k_{-w}, then

$$dN_u/dt = k_w(N_w) - k_{-w}(N_u) \qquad (25)$$

Equation 25 has the solution

$$N_u = N_0\, e^{-k_{-w}t} + (k_w/k_{-w})N_w[1 - e^{-k_{-w}t}] \qquad (26)$$

In this case, N_∞ would not be equal to N_w but rather would be equal to $(k_w/k_{-w})N_w$. Then the fraction of exchange is expressed as a function of time by

$$\ln[1/(1 - F)] = k_{-w}t \qquad (27)$$

If the direct exchange is considered for the case in which there was no isotope effect but x did change appreciably during the course of the exchange, Equation 8 expresses the change of N_u with time. Substitution of the expressions for du/dt from Equation 21 and for dx/dt from Equation 4 into Equation 8 yielded

$$dN_u/dt = k_w(N_w - N_u) - N_u[(k_1/x)(a - x - y)$$

$$- k_{-1}(x + 2y) - k_2 + k_{-2}(y/x)(x + 2y)] \qquad (28)$$

To obtain the rate constants for the acid hydrolyses, the rate of acid hydrolysis of $[PtCl_4]^=$ was measured by titrating the hydrolysis product, $[PtCl_3(H_2O)]^-$. The rates of the acid hydrolyses of $[PtCl_4]^=$ and $[PtCl_3(H_2O)]^-$ were measured by a chloride exchange experiment, since the chloride exchange

occurs via the acid hydrolyses. Knowledge of the acid hy-drolysis rate of $[PtCl_4]^=$ permitted calculation of the acid hydrolysis rate of $[PtCl_3(H_2O)]^-$ from the exchange data.

The following additional symbols were defined for the treatment of the chloride exchange:

p = atoms of Cl^{36} in $[PtCl_4]^=$ per ml. of solution.

q = atoms of Cl^{36} in $[PtCl_3(H_2O)]^-$ per ml. of solution.

r = atoms of Cl^{36} in $[PtCl_2(H_2O)_2]$ per ml. of solution.

s = atoms of Cl^{36} in Cl^- per ml. of solution.

I = $p + q + r + s$ = total radioactive atoms per ml.

S_p = specific activity of $[PtCl_4]^= = p/4(a - x - y)$.

S_q = specific activity of $[PtCl_3(H_2O)]^- = q/3x$

S_r = specific activity of $[PtCl_2(H_2O)_2] = r/2y$

S_s = specific activity of $Cl^- = x/(b + x + 2y)$

$\quad = (I - p - q - r)/(b + x + 2y)$.

If exchange of chloride occurred only via the reversible acid hydrolysis of $[PtCl_4]^=$ and $[PtCl_3(H_2O)]^-$, the following rate equations applied under conditions of chemical equilibrium:

$$dp/dt = -4 R_1 S_p + 3 R_1 S_q + R_1 S_s \tag{29}$$

$$dq/dt = 3 R_1 S_p - 3 R_1 S_q - 3 R_2 S_q + 2 R_2 S_r + R_2 S_s \tag{30}$$

$$dr/dt = -2 R_2 S_r + 2 R_2 S_q \tag{31}$$

In Equations 29 through 31, R_1 is the equilibrium rate of acid hydrolysis of $[PtCl_4]^=$ and R_2 is the equilibrium rate of

acid hydrolysis of $[PtCl_3(H_2O)]^-$.

If the concentration of $[PtCl_2(H_2O)_2]$ was much less than the concentration of $[PtCl_3(H_2O)]^-$, then dr/dt was much smaller than dq/dt and dp/dt. Under these conditions it appeared from Equation 31 that $S_r \approx S_q$ and

$$r \approx (2y/3x)q \qquad (32)$$

The second acid hydrolysis rate was related to the first by the natural parameter β, defined by

$$\beta R_1 = R_2$$

When r and R_2 in Equations 29 and 30 were replaced by the expressions of Equations 32 and 33, the resulting equations could be rearranged to give

$$(1/R_1)(dp/dt) + p[1/(a - x - y) + 1/(b + x + 2y)]$$
$$+ q[(1 + 2y/3x)/(b + x + 2y) - 1/x] = I/(b + x + 2y) \qquad (34)$$

$$(1/R_1)(dq/dt) + q[1/x + \beta(1 + 2y/3x)/(b + x + 2y) + \beta/3x]$$
$$+ p[\beta/(b + x + 2y) - 3/4(a - x - y)] = \beta I/(b + x + 2y) \qquad (35)$$

The solutions for these simultaneous linear differential equations were

$$p = p_\infty + A_1 e^{\alpha_1 t} + A_2 e^{\alpha_2 t} \qquad (36)$$

$$q = q_\infty + B_1 e^{\alpha_1 t} + B_2 e^{\alpha_2 t} \qquad (37)$$

where p_∞, q_∞, A_1, B_1, A_2, B_2, α_1, α_2 were determined by a, b, I, k_1, β, K_1 and K_2.

If the separation procedure precipitated $[PtCl_4]^=$ and $[PtCl_3(H_2O)]^-$ without fractionation, the activity of the

precipitate was a measure of the quantity (p + q). The fraction of exchange, F, at a given time was taken as the activity per mg. of precipitate from the aliquot selected at the given time divided by the activity per mg. of precipitate in a sample taken at infinite time (a period greater than ten times the half-time of exchange). The relation between F and (p + q) was

$$F = (p + q)/(p_\infty + q_\infty) \tag{38}$$

Combination of Equations 36, 37 and 38 gave the convenient expression

$$(1 - F) = c_1 e^{\alpha_1 t} + c_2 e^{\alpha_2 t} \tag{39}$$

By a trial and error method, a value of β was found which would produce good agreement between the exponential functions of Equation 39 and the observed values of (1 - F). This value of β was then used to calculate k_2 from k_1 and the appropriate concentrations.

IV. RESULTS AND DISCUSSION

The rate constants for the acid hydrolyses of $[PtCl_4]^=$
and $[PtCl_3(H_2O)]^-$ in solutions of low ionic strength were
measured in connection with the present thesis study. The
value for k_1 of 3.83×10^{-5} sec.$^{-1}$ was determined by a
titration experiment. A graph of titer vs. time, showing the
results of the experiment, is presented as Figure 2. The
blank titer of 0.02 ml. was not subtracted from the aliquot
titers and as a consequence the curve of Figure 2 does not
pass through zero titer at zero time.

The rate constant for the acid hydrolysis of $[PtCl_3(H_2O)]^-$,
k_2, was measured by means of a chloride exchange experiment.
The exchange data, which are presented in Figure 3, were used
to find a value of β as described earlier. The best value
of β was found to be 1.12, and this result was used to cal-
culate a value for k_2 of 3.22×10^{-5} sec.$^{-1}$

The rate constant k_1 for solutions of high ionic strength
was determined by Grantham et al. (9) by a titration experi-
ment. They found a value of 3.86×10^{-5} sec.$^{-1}$ for k_1.
Grantham et al. had neglected the acid hydrolysis of
$[PtCl_3(H_2O)]^-$ in determining k_2 by a chloride exchange experi-
ment and as a consequence calculated a value which was too
high. Their chloride exchange data were used in the more
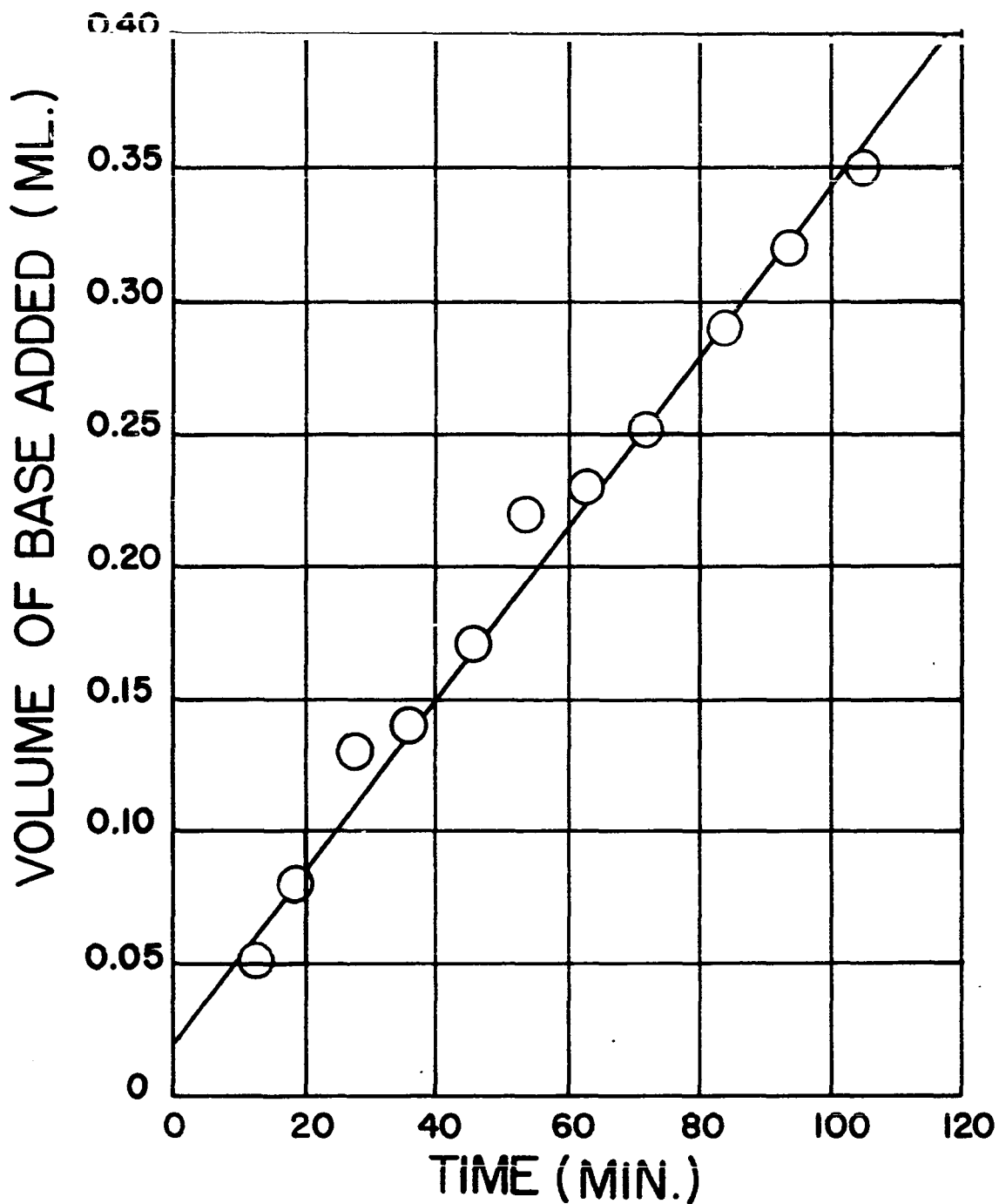rigorous treatment to find values of β and k_2. The value of

Figure 2. Graph of titer vs. time for a freshly prepared
0.01 M solution of $K_2[PtCl_4]$. Aliquot volume
= 15 ml. Base = 0.1040 N NaOH. No blank correc-
tion made. Value of k_1 found = 3.8 x 10^{-5} sec.$^{-1}$
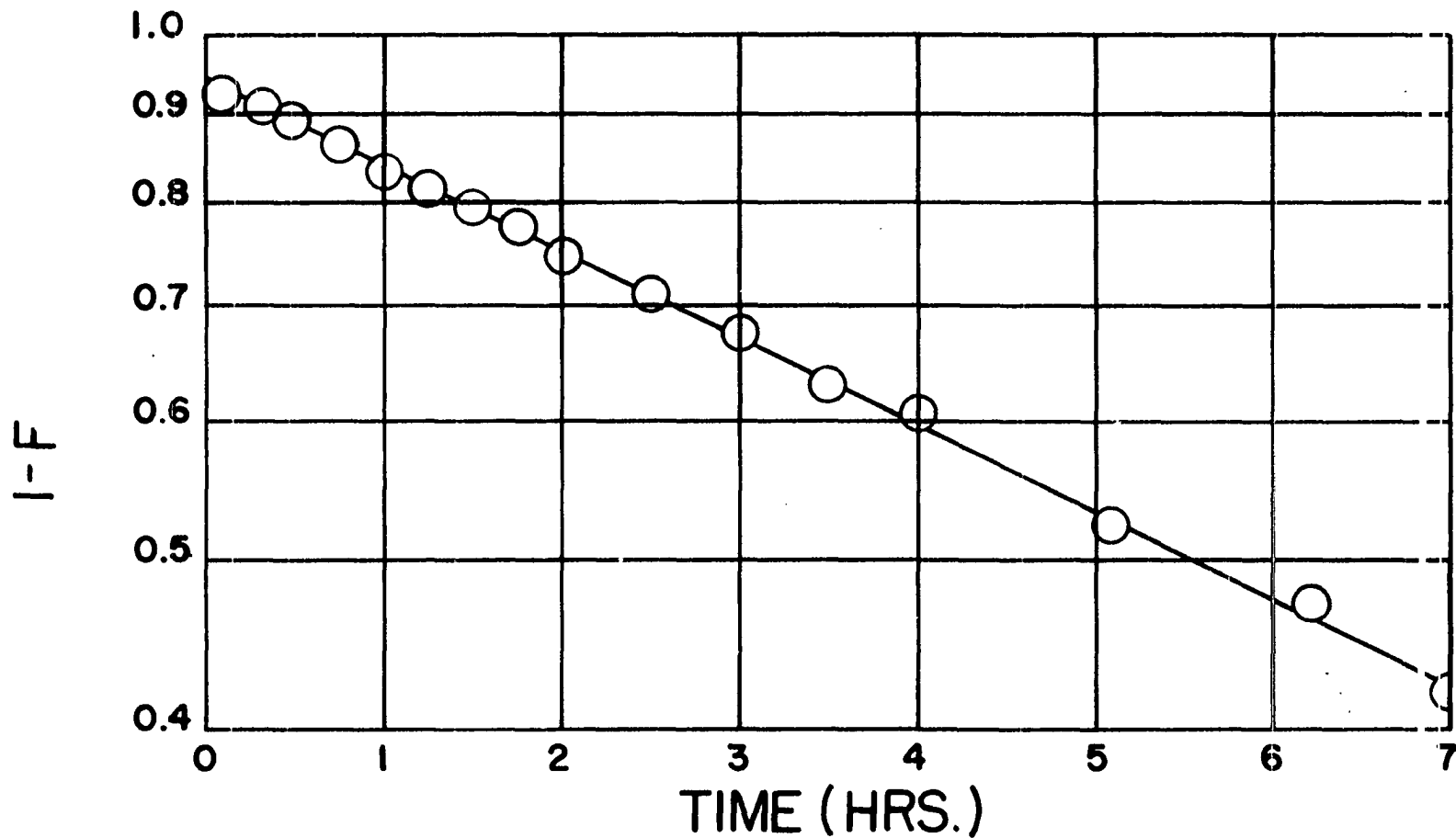
Figure 3. Semiloarithmic plot of data for chlorine exchange in aged $K_2[PtCl_4]$ solution. a = 0.01, b = 0.01. Value of k_2 found = 3.2 x 10^{-5} sec.$^{-1}$

the rate constant found from the results of six experiments by Grantham et al. was 3.44×10^{-5} sec.$^{-1}$ with a standard deviation of 5.3×10^{-6} sec.$^{-1}$

Experimental conditions and results for the exchange of H_2O between solvent and $[PtCl_3(H_2O)]^-$ are presented in Tables 5 and 6. The exchange data are also presented in the form of semilogarithmic plots of $(1 - F)$ vs. time in Figures 4 and 5.

It may be seen from Tables 5 and 6 that the mole fraction of O^{18} observed in the sample approached but never equaled the mole fraction of O^{18} in the solvent, even in samples which had exchanged for five hours. Also, the fraction of exchange appeared to undergo an initial rapid increase, after which it increased slowly to a value not greater than 0.85.

This apparent failure to attain equilibrium might have been an effect due to the difference in the methods of analyzing the Magnus' salt precipitates and the solvent. If this were the case, a better value for N_∞ than N_w would have been the mole fraction of O^{18} in a sample taken after a long time of exchange. Figures 6 and 7 are graphs of the exchange data calculated on the basis that N_∞ was the mole fraction of O^{18} in the last sample of each experiment. These data for solutions in which the precipitate was Magnus' salt are presented also in Table 7.

The fractions of exchange were also calculated with the assumption that the water exchange was rapid and the samples

Table 5. Data for solutions of high ionic strength[a,b]

Expt. no.	Mole fraction O^{18} in sample	Mole fraction O^{18} in solvent	1 - F	Exchange time (Min.)
I	0.00396	0.00877	0.706	2
	0.00424		0.665	8
II	0.00288	0.00497	0.694	10
	0.00320		0.588	20
	0.00331		0.551	40
	0.00333		0.545	80
III	0.00253	0.00413	0.737	4
	0.00270		0.659	15
	0.00276		0.631	60
IV	0.00230	0.00286	0.622	30
	0.00237		0.544	60
	0.00239		0.522	180
	0.00236		0.556	300

[a]Approximate ionic strength 0.318 attained by addition of NaNO$_3$. a = 0.01, x $\approx$ 0.005, y $\sim$ 0.0004.

[b]Solid AgNO$_3$ used for precipitations.

Table 6. Data for solutions of low ionic strength[a]

Expt. no.	Mole fraction O^{18} in sample	Mole fraction O^{18} in solvent	1 - F	Exchange time (min.)
I[b]	0.00472	0.00894	0.605	3.5
	0.00517		0.540	10
	0.00556		0.484	25
	0.00604		0.415	45
II[b,c]	0.00382	0.00503	0.394	2
	0.00403		0.326	9
	0.00430		0.238	20
	0.00441		0.202	36
	0.00403		0.326	60
	0.00367		0.443	90
	0.00385		0.384	120
	0.00393		0.358	180
III[b]	0.00301	0.00365	0.379	2
	0.00333		0.189	20
	0.00332		0.195	40
	0.00332		0.195	80
IV[d]	0.00314	0.00359	0.276	4
	0.00333		0.160	20
	0.00336		0.141	40
	0.00338		0.129	60
V[d]	0.00687	0.00952	0.351	1.5
	0.00776		0.233	3
	0.00817		0.180	8
	0.00836		0.153	180

[a]Approximate ionic strength 0.03 (no added salt). a = 0.01, x ≈ 0.006, y ≈ 0.0006.

[b]Samples precipitated with $AgNO_3$ solution.

[c]Samples dried 3 wks. before analysis. Less Ag added than in Expts. I and III.

[d]Samples precipitated as Magnus' salt.
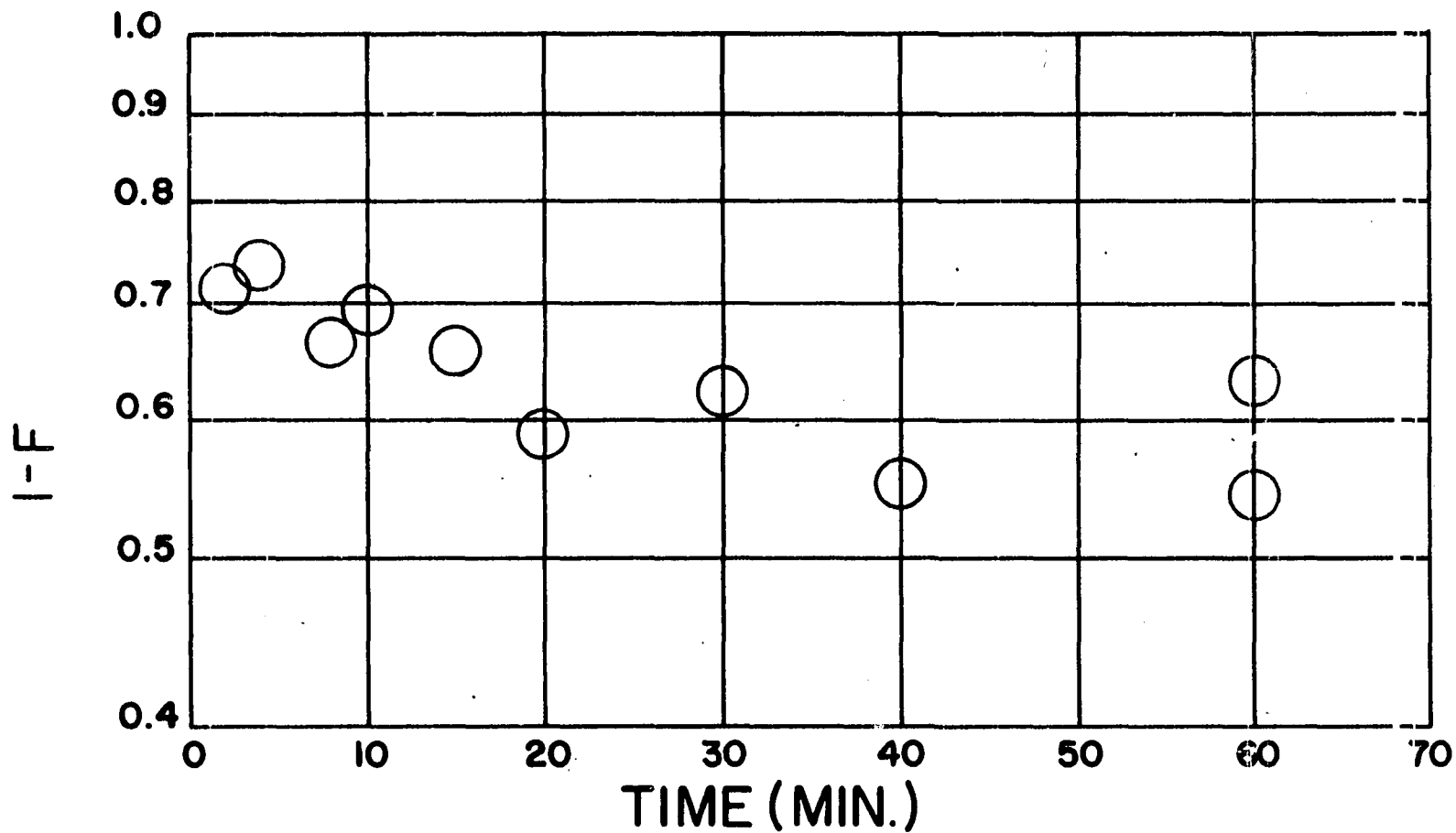
Figure 4. Semilogarithmic plot of data from experiments with solutions of high
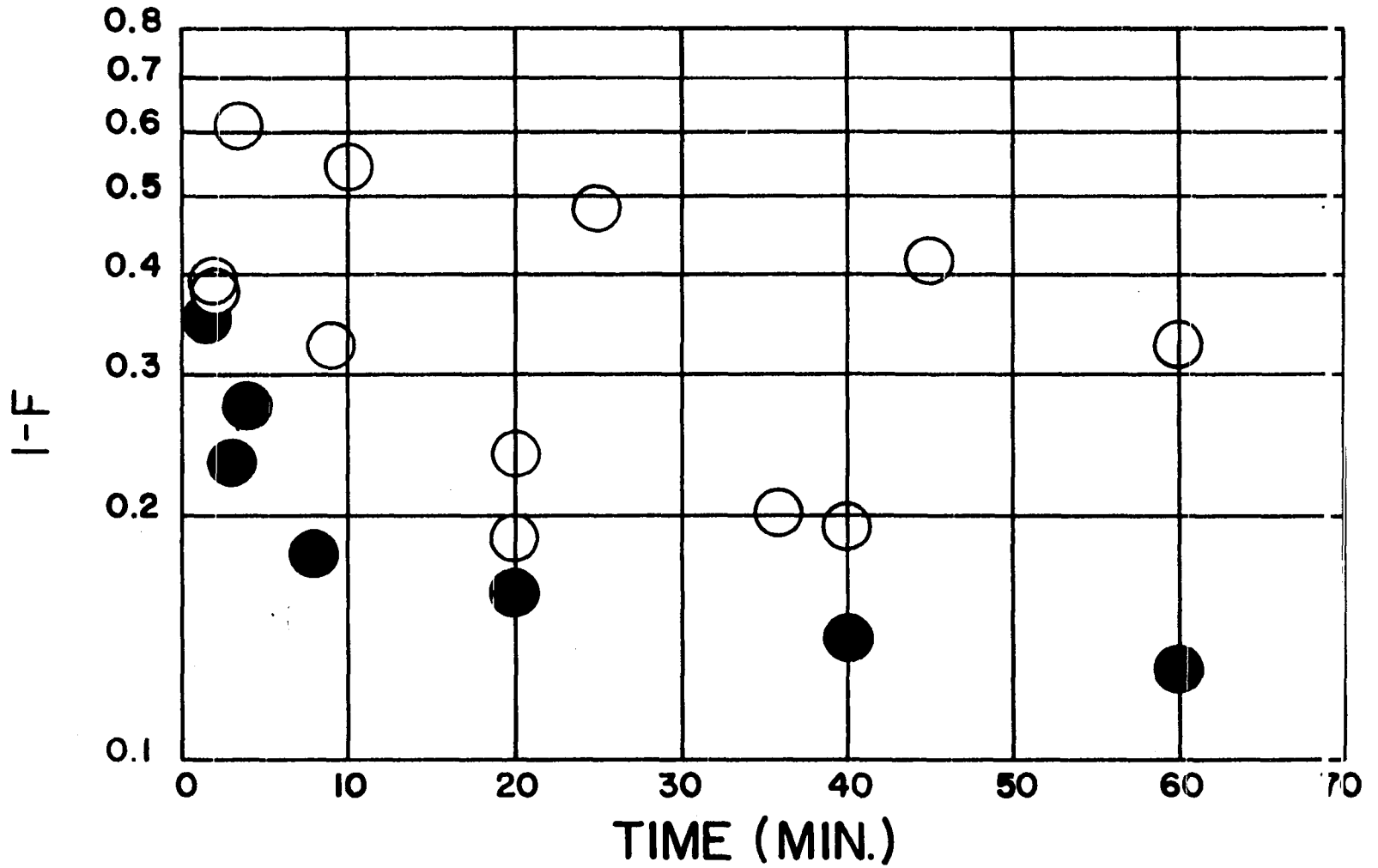ionic strength. All precipitations with AgNO₃ (Table 5)

Figure 5. Semilogarithmic plot of exchange data from experiments with low ionic strength solutions (Table 6). Open circles = precipitation with $AgNO_3$. Filled circles = precipitation as Magnus' salt (Table 6)
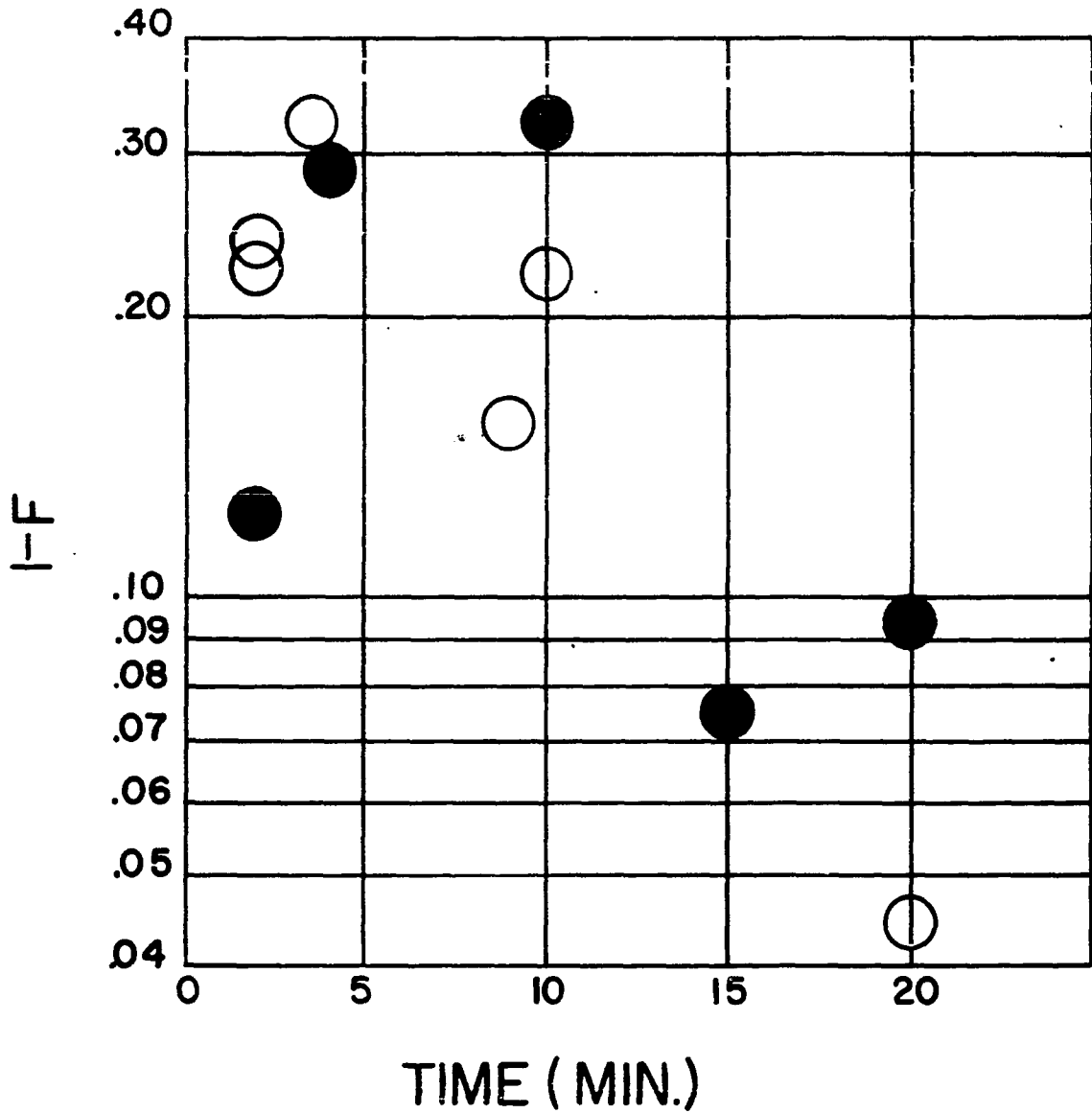
Figure 6. Semilogarithmic plot of exchange data from experiments in which $AgNO_3$ was used for precipitations. Value of N_∞ from last sample of each experiment. Open circles = high ionic strength solns. (Table 5). Filled circles = low ionic strength solns. (Expts. I-III, Table 6)
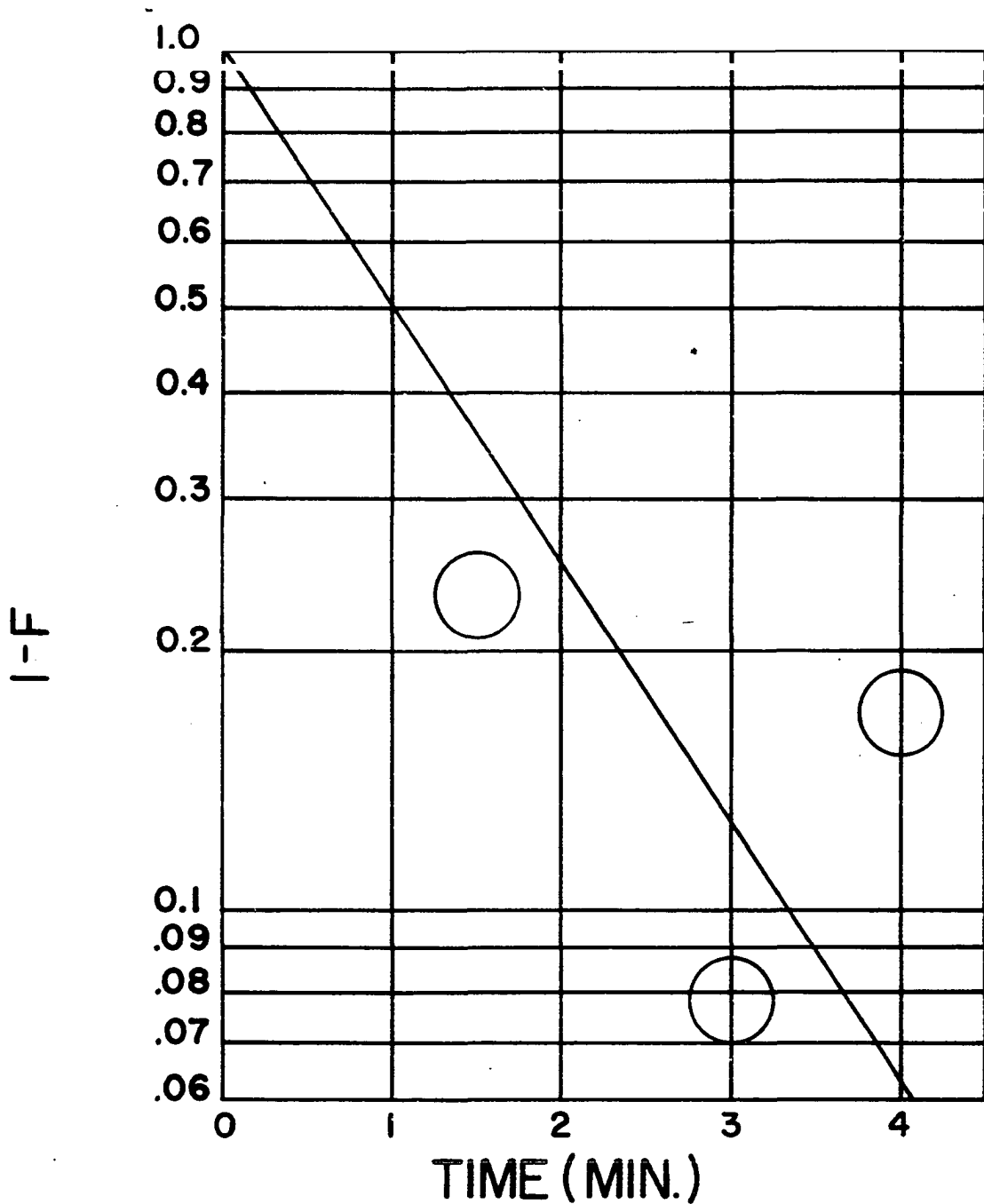
Figure 7. Semilogarithmic plot of exchange data from experiments in which samples were precipitated as Magnus' salt. Value of N_∞ from last sample of each experiment. Low ionic strength solutions (Expts. IV, V, Table 6)

Table 7. Comparison of data calculated from different values of N_∞

Expt. no.	Mole fraction O^{18} in sample	(1 − F) with N_∞ from last sample	(1 − F) with N_∞ from mixture	Exchange time (min.)
IV[a]	0.00314	0.169	0.248	4
	0.00333	0.035	0.127	20
	0.00336	0.014	0.108	40
	0.00338	0.0	0.096	60
	0.00353	--	0.0	∞
V[a]	0.00687	0.232	0.324	1.5
	0.00776	0.078	0.201	3
	0.00817	0.030	0.145	8
	0.00836	0.0	0.117[b]	180
	0.00922	--	0.0	∞

[a]For experimental conditions, see Table 6.

[b]N_∞ = 0.00921 for this sample, since final mixture was 2.1 ml. of precipitating reagent plus 49 (rather than 50) ml. of $K_2[PtCl_4]$ solution.

were equilibrating with a mixture of the water from the exchange solution and the water carrying the precipitating agent. Thus N_{∞} was lower than N_w. The exchange data calculated on this basis are presented in Table 7.

At the beginning of this study, it was thought that the exchange of water might be relatively slow and that the major portion of the exchange might occur _via_ acid hydrolysis. This prediction seemed to be borne out by the exchange data obtained from experiments with solutions of high ionic strength. After a rapid initial exchange, which was attributed to the exchange of water in the hydration spheres of the silver ions used for precipitation, the exchange appeared to proceed slowly toward equilibrium.

To eliminate the effects of the initial exchange, calculations of the fraction of exchange were based on the fraction of the sample water complexed to platinum. It was assumed that in the first exchange sample, which was usually obtained after an exchange time of one to three minutes, the water complexed to platinum had undergone negligible exchange and had the isotopic composition of normal water but the other water in the sample (complexed to silver) had equilibrated completely with the solvent water. Thus the observed mole fraction of O^{18} in the sample, N_c, was related to f, the fraction of water complexed to platinum, by

$$(1 - f)N_w + (f)N_o = N_c \tag{40}$$

The value of f was found to be about 0.7 from two experiments. With a value for f, Equation 40 was used to calculate the mole fraction of O^{18} in water complexed to platinum, and the calculated mole fraction was in turn used to calculate the fraction of exchange.

When it was discovered that samples from high ionic strength solutions were contaminated with NO_3^-, work was begun on experiments with solutions of low ionic strength. The same procedure was used to estimate f. It was found, however, that f varied from 0.6 to 0.4.

The hypothesis that exchange of water of hydration on silver accounted for the observed rapid initial exchange was tested with an experiment which reversed the procedure used for precipitation in the exchange experiments. The amount of $AgNO_3$ normally used for precipitation (0.34 gm.) was dissolved in 50 ml. of water enriched three-fold in O^{18} and the solution was allowed to stand for 4 minutes. Then 0.21 gm. of dry powdered $K_2[PtCl_4]$ was added and the precipitate was filtered, dried and analyzed. Oxygen was found in the precipitate and it had a mole fraction of O^{18} of 0.00200. The isotopic abundance of O^{18} is 0.00204.

If the silver were hydrated, it should have had bound to it water with a mole fraction of O^{18} of 0.00573. Evidently the source of the oxygen in the precipitate was NO_3^- ion, and even in solutions of low ionic strength nitrate contamination

was present if $AgNO_3$ were used as the precipitating agent.

Variation in the amount of nitrate contamination could have been responsible for the scattering of the oxygen analysis data, and the presence of nitrate may have prevented the sample analysis from agreeing with the solvent analysis.

It was also found that addition of $AgNO_3$ to aged $K_2[PtCl_4]$ solutions apparently precipitated all of the platinum species in addition to Cl^-. The amount of $AgNO_3$ which had been used to precipitate the exchange samples was expected to precipitate only $[PtCl_4]^=$, $[PtCl_3(H_2O)]^-$, and Cl^-. Therefore the number of moles of Ag^+ added was $2(a - x - y) + x + (x + 2y)$ or $2a$. Since in actuality $[PtCl_4]^=$, $[PtCl_3(OH)]^=$, $[PtCl_2(OH)_2]^=$, and Cl^- precipitated, the amount of Ag^- that should have been added was $2(a - x - y) + 2x + 2y + (x + 2y)$ or $(2a + x + 2y)$ moles. The fact that the amount of Ag^+ added was insufficient for the complete precipitation of all possible species meant that fractionation in precipitation of the oxygen-containing species could have occurred. If fractionation did occur, the relation of the sample analysis to u and v was unknown.

Because the experiments with $AgNO_3$ as the precipitating agent carried the possibility of error due to nitrate contamination and due to inexact knowledge of the composition of the precipitate, experiments were begun with Magnus' salt as the precipitate. The results of the latter experiments

appeared to be more reproducible than results obtained using
$AgNO_3$ as the precipitating agent. However, as noted earlier,
it was observed that the precipitate analyses, even after long
exchange times, did not show the same mole fraction of O^{18} as
the solvent analyses.

A possible explanation for the difference between solvent
and precipitate analyses was the difference in the size of the
samples analyzed. The precipitates contained about 3 mg. of
oxygen, whereas the solvent sample contained about 900 mg. of
oxygen. A small amount of contamination from air or some
other source of oxygen would have been much more significant
in the precipitate analysis than in the solvent analysis.

A means by which the analytical samples could have be-
come contaminated was provided by the techniques used for
obtaining oxygen from the samples for analysis. Oxygen was
obtained from the solvent by vacuum distilling the water
into an outgassed sample of CoF_3 which was at liquid nitro-
gen temperature and then warming the water and CoF_3 to slight-
ly above room temperature. Oxygen was released from the
precipitates by pouring the solid samples into a tube con-
taining outgassed CoF_3 and heating the mixture to about 450°
C. During the outgassing of the CoF_3 the temperature was not
uniform throughout the reaction tube and material blown on
the walls by the outgassing was not thoroughly freed of
gaseous impurities. Addition of Magnus' salt to the tube

might then mechanically carry the impure CoF_3 from the walls to the hot reaction zone, and when the mixture was heated oxygen from the precipitate could be diluted with oxygen from the CoF_3. It was found by the analyst that higher reaction and outgassing temperatures for samples of Fe_2O_3 enriched in O^{18} resulted in higher O^{18}/O^{16} ratios. Outgassing temperature was not a problem with the water samples since oxygen evolution took place near room temperature.

It was assumed in treating the data that the observed analysis of the O^{18} content of the precipitate differed from the true value by an amount proportional to the difference in O^{18} content between the sample and normal water. The constant of proportionality was determined by the difference in the analyses of the O^{18} contents of the solvent and the samples with long exchange times. This assumption was equivalent to treating the analysis of the sample at long exchange time as N_{∞} and the analyses of the samples at shorter times as N_u in the calculation of F by Equation 16.

A variable in the exchange experiments in addition to the mole fraction of O^{18} was the sampling time. Although the precipitations and filtrations were conducted as reproducibly as possible, there was an unavoidable error in the timing of the precipitation due to the fact that Magnus' salt did not precipitate immediately when solutions of $K_2[PtCl_4]$ and $[Pt(NH_3)_4]Cl_2$ were mixed. The first visible precipitation

occurred about 0.1 minute after the mixing. In spite of the possibilities for experimental error, it was felt that the experiments in which the samples were precipitated as Magnus' salt showed good evidence for the rapid exchange of H_2O between $[PtCl_3(H_2O)]^-$ and solvent. As shown in Figure 7, the apparent half-time of the exchange was approximately one minute. In the absence of knowledge of any isotope effect on the exchange, Equation 35 was presumed to describe the reaction. For a half-time of exchange of one minute, the rate constant, k_w, had the value 1.2×10^{-2} sec.$^{-1}$

In this case, the exchange of water between the solvent and the aquo-complex by means of the acid hydrolysis was insignificant compared with the exchange by a direct process. The problem was then to postulate a mechanism for substitution reactions in the square planar platinum(II) complex which would account for the rapid direct exchange.

The mechanism which is thought to be the most likely for the acid hydrolysis of $[PtCl_4]^=$ in aqueous solutions is illustrated in Figure 8a. This mechanism takes account of the fact that the square planar compexes in aqueous solution may have distorted octahedral configurations with the groups on the axial positions labile (4). The transition state is a five-coordinated species which probably has approximately a trigonal bipyramidal configuration. The exchange of water between $[PtCl_3(H_2O)]^-$ and solvent can occur by an exactly
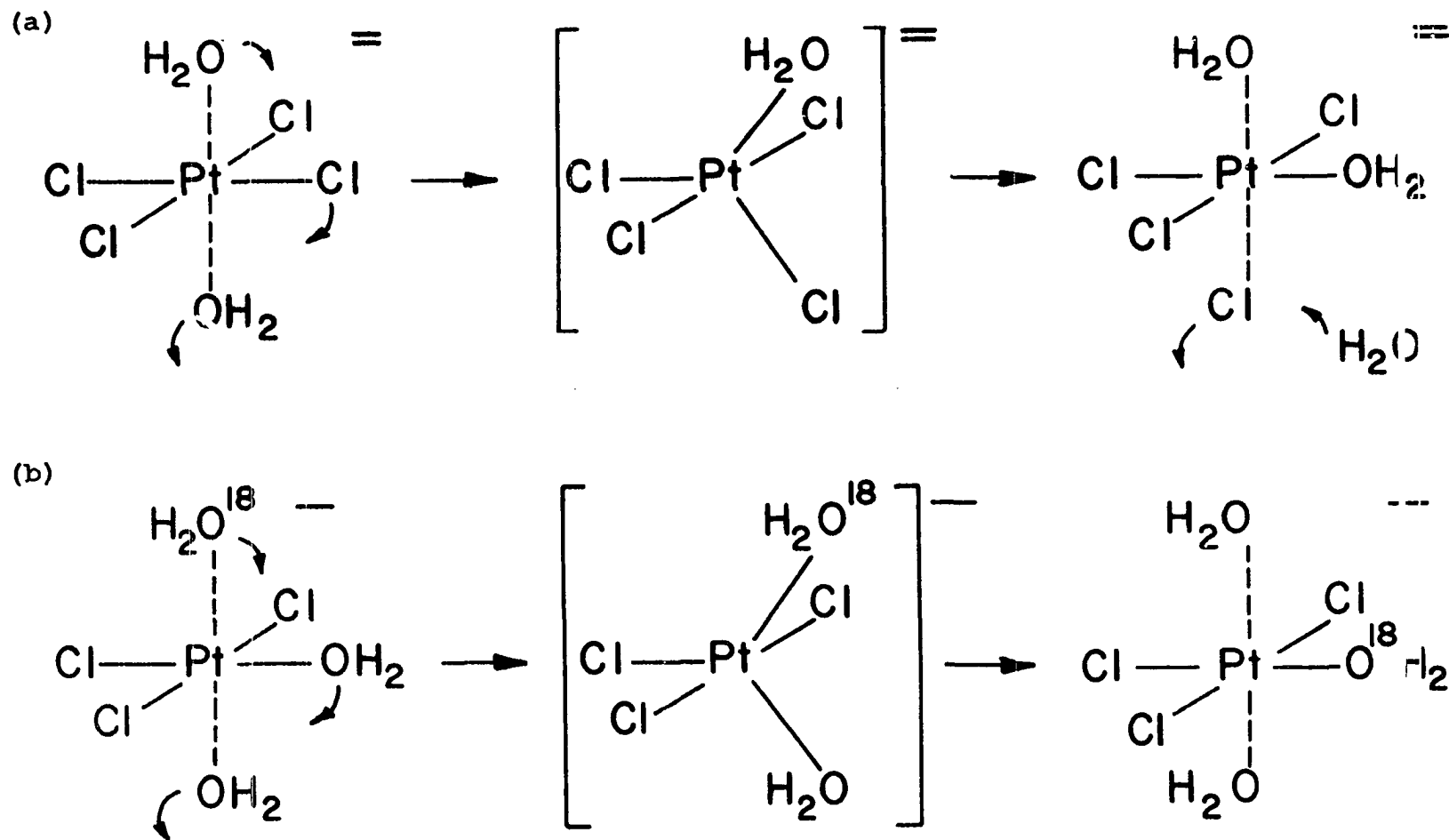
Figure 8. (a) Mechanism of acid hydrolysis of $[PtCl_4]^=$

(b) Mechanism of exchange of water between $[PtCl_3(H_2O)]^-$ and solvent

similar mechanism, as shown in Figure 8b.

In the above mechanism, the forward acid hydrolysis re-
action is essentially an internal rearrangement, with the
charge on the complex remaining constant until the substitu-
tion (in this case of chlorine by water) is complete. Thus it
would be expected that a change in the ionic strength of the
solution would not affect the reaction rate. It was found
that the rate constants for the acid hydrolyses of $[PtCl_4]^=$
and $[PtCl_3(H_2O)]^-$ showed no dependence on ionic strength,
within the limits of experimental error. On the other hand,
the reactions which reverse the acid hydrolyses are the
attack of Cl^- on the platinum species and would be expected
to be aided by an increase in ionic strength. It was found
that the rates of the reverse reactions increased with in-
creased ionic strength.

Basolo et al. (28) reported that the order of decreasing
susceptibility to replacement by pyridine in aqueous solution
of different X groups in the $[Pt(dien)X]^+$ series (where dien =
diethylenetriamine) was $NO_3^- > Cl^- > Br^- > I^- > N_3^- > SCN^- >$
$NO_2^- > CN^-$. This order paralleled the general order of in-
creasing ligand stability toward replacement for platinum(II)
complexes (4, 15). Since the rate constant for the replace-
ment of water by water, k_w has a value of 1.2×10^{-2} sec.$^{-1}$,
which is greater than the rate constant for the replacement of
chloride by water, $k_2 = 3.2 \times 10^{-5}$ sec.$^{-1}$, and H_2O ligand

probably should fall in the replacement series between Cl⁻ and
NO_3^-.

The fact that the rate of water exchange is measurable
means that, by definition, $[PtCl_3(H_2O)]^-$ is inert as regards
water exchange. The ligand water is not in labile equilibrium
with solvent as postulated in some mechanisms, such as the
"dissociation" mechanism through a square pyramid intermediate
proposed by Basolo and Pearson (4).

The work reported in this thesis has yielded some useful
information about substitution reactions of $[PtCl_4]^=$ and its
acid hydrolysis products. The work has also suggested some
areas for future exploration.

The first line of investigation probably should lie in
the direction of analytical studies. Although Magnus' salt is
a good sampling precipitate, it would be useful to obtain a
reagent which causes immediate precipitation of a salt with a
definite composition when added to a solution containing
$[PtCl_3(H_2O)]^-$.

Studies on the techniques of isotope ratio determination
are in progress. Very precise and accurate isotope analyses
would permit the exploration of some fields in addition to
the water exchange. For example, it would be interesting to
look for isotope effects on the rate of water exchange or the
possibility of concentration of one of the oxygen isotopes in
the platinum aquo complexes.

Further study of the chlorine exchange between $[PtCl_4]^=$ and Cl^-, or $[PtCl_3(H_2O)]^-$ and Cl^-, is in order. It would be of interest to compare the energies of activation for these systems with the activation energies of the chloroammine-complexes of platinum(II). Effects of chloride concentration and ionic strength on the chloride exchanges might also yield some information of interest.

V. SUMMARY

There is a rapid exchange of water between $[PtCl_3(H_2O)]^-$ and solvent. This exchange occurs by means of a direct process and appears to have a half-time of about one minute.

The rates of the acid hydrolyses of $[PtCl_4]^=$ and $[PtCl_3(H_2O)]^-$, as measured by the chloride exchange reaction, are not affected by a ten-fold change in ionic strength. The rates of the reverse reactions are increased by increased ionic strength.

The water exchange and acid hydrolysis rate data are interpreted in terms of a mechanism involving a five-coordinated trigonal transition state.

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VII. ACKNOWLEDGEMENTS