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SPECTRAL STUDIES OF THE EQUILIBRIA IN
AQUEOUS SOLUTIONS OF THE HALO-HYDROXO
COMPLEXES OF PLATINUM (IV)

A THESIS

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PREFACE

This thesis is a report on work done under the direction of Dr. Henry Neumann to whom I am deeply grateful, not only for his able guidance but also for his continuing patience and encouragement without which this work could not have been finished. I wish to thank the members of the reading committee for their help. Thanks are also due to my wife for her assistance.

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SUMMARY

The problem under consideration in this work was twofold; first, to establish the nature of the halo-hydroxo complexes of platinum (IV) existing in aqueous solution and second, to determine the spectral absorption curves of these complexes.

The compounds actually studied were chlorohydroxo and bromohydroxo platينات represented by the general formula $\text{PtX}_{6-n}(\text{OH})_n^{\equiv}$, where X is chloride or bromide and n varies from zero to six.

The chief tool of the investigation was the mole ratio method, which relates changes in some molar property, in this case, spectral absorption, with the changing stoichiometry of the solution. If a series of solutions is made up, each containing the same molar concentration of central ion but with varying ratios of ligand ions to central ion, and if the spectrum of each of these solutions is measured, then the presence of a stable complex will be shown by a change of slope in an absorbancy versus mole-ratio plot at some wavelength. If no such change of slope occurs at any wavelength, the complex of that mole ratio does not, in all likelihood, exist as a stable entity.

The spectra displayed by the halo platينات are of the charge transfer type which are characterized by very large values of the molar extinction coefficient. Consequently, the solutions tested were extremely dilute, 10^{-3} to 10^{-5} M in all platينات. The ligand to central ion mole ratio was varied from zero to six in half-unit steps. The

solutions were acidified with perchloric acid so that the hydrogen ion concentration would remain essentially constant. Pure $\text{Na}_2\text{Pt}(\text{OH})_6$ was used as the primary platinum salt in compounding the solutions, while pure NaCl and NaBr were used as ligand sources. The solutions were equilibrated at 50°C . in a constant temperature bath before making spectral measurements. The latter were made with a Beckman DK recording spectrophotometer in the wavelength region from $200 \text{ m}\mu$ to $350 \text{ m}\mu$, since this is the region where the halo platينات absorb.

The equilibrated solutions of the chloroplatينات were $2.92 \times 10^{-4} \text{ M}$ in platinate and 2.40 M in perchloric acid. The solutions were diluted tenfold for the purpose of spectral measurement. It was established that the equilibria actually measured were those which obtained in the solutions before the dilution. The mole ratio plots of these solutions demonstrated that $\text{PtCl}_6^{=}$, $\text{PtCl}_4(\text{OH})_2^{=}$ and $\text{PtCl}_2(\text{OH})_4^{=}$ are stable species in aqueous solution.

The presence of isosbestic points in the spectra of solutions with Cl/Pt ratios above four, demonstrated the presence of only two species in these solutions. One of these species was known from the spectra to be $\text{PtCl}_6^{=}$. The contribution of this species was subtracted, by a graphical method, from the overall spectrum leaving the spectrum of the other species. The evidence of the mole ratio plots coupled with the virtual constancy of the equilibrium constant for the equilibrium between $\text{PtCl}_6^{=}$ and $\text{PtCl}_4(\text{OH})_2^{=}$ makes certain the assignment of this spectrum to the latter species.

Solid PtCl_4 was prepared and the spectrum of its aqueous solution was recorded. Comparison of this spectrum with the spectra of $\text{PtCl}_6^{=}$ and $\text{PtCl}_4(\text{OH})_2^{=}$ demonstrated that the dissolution reaction was not simply the formation of $\text{PtCl}_4(\text{OH})_2^{=}$. Although this reaction could not be fully elucidated, it was shown that it resulted in a solution in which half the platinum was in the form of $\text{PtCl}_6^{=}$.

Solutions of bromo-platinates were made, each $2.92 \times 10^{-3}\text{M}$ in platinate and 2.40M in perchloric acid. The Br/Pt ratio was varied from zero to six in half unit steps. These solutions were equilibrated at 50°C ., and then diluted one hundred fold for the purpose of recording the spectra. The solutions with a Br/Pt ratio greater than four gave spectra with isosbestic points, which indicated the presence of only two species in these solutions. Comparison of these spectra with the spectrum of pure $\text{PtBr}_6^{=}$ made it plain that one of the species was $\text{PtBr}_6^{=}$. Subtraction of the contribution of $\text{PtBr}_6^{=}$, by a graphical method, from the overall spectra enabled the reconstruction of the spectrum of the second species. The mole ratio plots showed that this second species must be either $\text{PtBr}_4(\text{OH})_2^{=}$ or $\text{PtBr}_2(\text{OH})_4^{=}$. Trial equilibria of each of these species with $\text{PtBr}_6^{=}$ yielded constant equilibrium constants only with $\text{PtBr}_4(\text{OH})_2^{=}$. Consequently the reconstructed spectrum was assigned to $\text{PtBr}_4(\text{OH})_2^{=}$.

The hydrolysis of a solution of $\text{PtBr}_6^{=}$ was followed by recording the change of the spectrum with time. The successive spectra of the hydrolyzing solution displayed isosbestic points and also indicated the

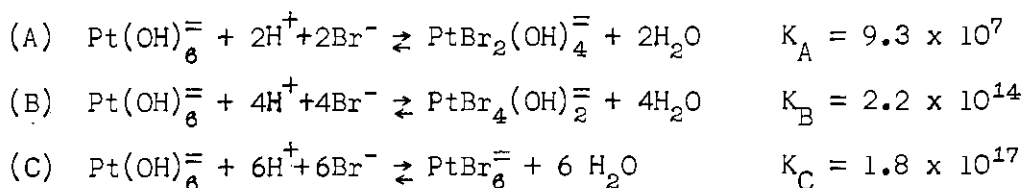
presence of $\text{PtBr}_6^{=}$. Subtraction of the contribution of this species led to the obtention of the spectrum of $\text{PtBr}_4(\text{OH})_2^{=}$. Concentrations of the two species were obtained from the spectra and comparison of these with the times of hydrolysis showed that the kinetics of the reaction were first order reversible with $k + k'$ equal to 0.107 min^{-1} .

Solid PtBr_4 was dissolved in water and its spectrum recorded. The change in the spectrum with time indicated that the dissolution resulted in the formation of $\text{PtBr}_6^{=}$, containing exactly half of the total platinum, followed by the hydrolysis of this $\text{PtBr}_6^{=}$ to $\text{PtBr}_4(\text{OH})_2^{=}$. The kinetics were shown to be apparent first order with k equal to 0.0166 min^{-1} . Comparison of k with $k + k'$ shows that the hydrolysis was acid catalyzed.

A study of the hydrolysis of $\text{PtBr}_6^{=}$ confirmed that it was light catalyzed and that the equilibria obtained were independent of the reaction mechanism.

The bromoplatinate solutions with Br/Pt less than 3.5 contained precipitates of platinic acid. A study of the spectra and stoichiometry of these solutions demonstrated that $\text{PtBr}(\text{OH})_5^{=}$ is not a stable species. Analysis of the mother liquors made possible the estimation of the solubility product constant of platinic acid as 7.3×10^{-4} .

The following equilibrium constants were estimated by comparing various equilibria.



The measurement of the concentration and pH of a solution of sodium platinate enabled the estimation of the hydrolytic constant of sodium platinate as 1.6×10^{-8} and the estimation of the second ionization constant of platinic acid as 6.25×10^{-7} .

CHAPTER I

INTRODUCTION

This work was undertaken for the purpose of applying absorption spectrophotometry to the study of the halo-hydroxo complexes of platinum (IV) existing in aqueous solution. The problems involved were two: first, to establish the nature of the species existing in solution and, second, to assign spectra to the various species. The chlorohydroxo complexes of platinum (IV) were originally selected as the subjects of the investigation because all the members of the series $\text{PtCl}_{6-n}(\text{OH})_n^=$, where n varies from zero to six, had been prepared and isolated either as the free acids or their salts (1). It was initially hoped that the spectrum of each member could be established, and that some useful correlation between spectrum and structure could be established.

Because of difficulties encountered in synthesizing the chloro complexes by the published methods, the bromo complexes were soon substituted for the chloro complexes as objects of study. This substitution also had the advantage that the absorption of the bromo complexes was nearer the visible region of the spectrum. Only after the bromo complexes had been studied were the chloro complexes re-examined.

The history of work bearing on the first problem mentioned above is long. Since the days of Werner, the study of the complexes of platinum has commanded the interests of many chemists. That this interest has been chiefly in synthesis rather than analysis is attested

to not only by the almost awesome variety of such complexes but also by the extreme paucity of information concerning their physical attributes. Obviously, before Werner proposed his theory of secondary valences, there could be no systematic study of complexes in any event. Still, more than a half century later, surprisingly little work has been done concerning the solution chemistry of such well known compounds as the halo-platinates.

It is to be expected that complexes with Pt(IV) as a central atom would be kinetically inert, because of the large loss of crystal field stabilization energy which would be entailed in forming the transition state (2). This expectation is borne out by various studies of exchange and substitution reactions of Pt(IV) complexes (3). It should be particularly noted that hydroxide ion is not a good substitution reagent for platinum (IV) octahedral complexes (4), because of a slow reaction rate. Despite this kinetic inertness, it has long been known that changes take place in the aqueous solutions of halo-platinates, which culminate in the production of precipitates of platinic acid, $\text{H}_2\text{Pt}(\text{OH})_6$ (5,6). The change is due to the slow substitution of halide ligands by hydroxy groups, to a degree dependent on the relative amounts of platinum complex and free halide in the solution. Furthermore, the substitution has always been presumed to be step-wise so that various members of the series $\text{PtX}_{6-n}(\text{OH})_n^-$ may be present in a given solution (3). This premise of step-wise substitution is based on the aforementioned fact that, when X is Cl, all members of the series have been prepared. In the classical work of Miolati (1) all

the members of the series except $\text{PtCl}_3(\text{OH})_3^-$ were prepared. A brief summary (in English) of his work is given by Emeleus and Anderson (7). Very recently, salts containing the $\text{PtCl}_3(\text{OH})_3^-$ ion have been reported (8).

A. Miolati (9) concluded, from conductivity measurements and characterization of precipitated salts, that solutions of PtCl_4 contained the anion $\text{PtCl}_4(\text{OH})_2^-$. Britton and Dodd (10) repeated this study and found that the constitution of an aqueous solution of PtCl_4 could be formally represented as $\text{PtCl}(\text{OH})_3$. Heymann (11) investigated the effect of carbon on the hydrolysis of PtCl_4 and found that all the platinum and three-eighths of the chlorides were adsorbed by the carbon.

Boll and Job (5,6) studied the photochemical hydrolyses of 0.0001 N solutions of H_2PtCl_6 , $\text{H}_2\text{PtCl}_5(\text{OH})$, $\text{H}_2\text{PtCl}_4(\text{OH})_2$, and $\text{H}_2\text{PtCl}_2(\text{OH})_4$, using conductivity measurements, and concluded that the same product was formed in all cases, viz., $\text{H}_2\text{Pt}(\text{OH})_6 \cdot \text{H}_2\text{PtCl}(\text{OH})_5$. Later Boll (12), using the same electrometric method, examined the hydrolysis of PtCl_4 . He found an initial rapid reaction which he attributed to formation of $\text{H}_2\text{PtCl}_4(\text{OH})_2$. This was followed by a second hydrolysis reaction, which proceeded very slowly in darkness, but which could be increased in rate by at least a factor of 100 by use of ultraviolet radiation.

Archibald and Gale (13,14) studied the hydrolyses of K_2PtCl_6 and K_2PtBr_6 and found that both reactions were accelerated by light. Their work will be discussed at greater length in Chapters IV and V of this thesis.

Some observations on the hydrolysis and ligand exchange reactions of $\text{PtCl}_6^{=}$ are included in a recent study of the complexes of several of the platinum group metals (15).

Schmidt and Herr (16), in the course of studying the rate of the isotopic exchange between Br^- and the hexabromo complexes of the platinum metals, made some observations regarding the hydrolysis of the $\text{PtBr}_6^{=}$ ion. They found that the hexabromo complex of platinum is much more susceptible to light catalyzed hydrolysis than are the analogous rhenium, osmium and iridium complexes. They surmised that the hydrolysis might proceed through the formation of a $\cdot\text{PtBr}_5$ free radical.

In all of these studies, even when photochemical effects were important, only substitution reactions were observed.

Many workers have measured the spectra of either $\text{PtCl}_6^{=}$, $\text{PtBr}_6^{=}$, or both. Among these are Samuel and Despande (17), Kirkland and Yoe (18) and Jorgensen (19). Good agreement as to maxima positions and extinction coefficients exists between their results and those obtained in the present investigation.

The spectra of these complexes, and presumably of the halo-hydroxo complexes, consist of two types of bands: low intensity bands in the visible region, and high intensity bands in the ultraviolet region. These latter bands of very strong absorption are generally called "electron transfer" or "charge transfer" bands. The extinction coefficients are, typically, of the order of 1,000 to 10,000 which is considerably greater than the values of 0.1 to 100 which are associated with the d-d transitions of the visible spectra. This high intensity

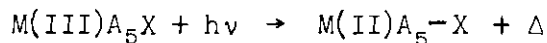
is due not only to the lack of hindering selection rules but also to the large change in polarity between the ground state and the excited state. Since the spectra measured in this research are chiefly of mixtures in which a low intensity band of one complex is obscured by the high intensity band of another, attention will be restricted to the "electron-transfer" spectra.

Although a knowledge of the theory of electron-transfer spectra is not necessary to the resolution of the problems investigated in this work, it will not be amiss to briefly mention a few of the chief expositions of this subject. There is a good, but somewhat dated, review by Rabinowitch (20). Mulliken and Rieke (21) have treated the phenomenon quantum mechanically. Platzman and Frank (22) have proposed an electron well mechanism for the charge transfer. A review of Orgel (23) covers the following subjects: charge-transfer spectra in the crystalline and the gaseous states, the spectra of simple and complex ions in solution, and the photochemical reactions involving charge-transfer. Ballhausen (24) has discussed the problem of the intensities of the bands. Jorgensen (19, 25) has interpreted the spectra of the hexa-halide complexes of Group VIII metals (including $\text{PtCl}_6^{=}$, $\text{PtBr}_6^{=}$, and $\text{PtI}_6^{=}$) in terms of group theory and made band assignments accordingly.

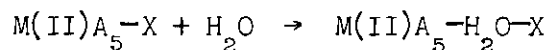
As the term indicates, the characteristic feature of an electron-transfer spectrum is that the absorption of light leads to the transfer of an electron from one part of the system to another. In the particular case of concern, an electron is transferred from the halide ligand to

the platinum. In Jorgensen's analysis (25) the electron transfer band of lowest energy is assumed to be due to the transfer of a π -electron from the ligand to a hole in the 5d shell of platinum. In general the direction and ease of electron transfer can be related to the relative oxidizability of metal ion and ligand. Platinum (IV) is oxidizing in character and the halide ion is reducing. It would be expected that the wavelength of the absorption should vary with the ease with which the ligand is oxidized, i.e., the absorption bands should move to longer wavelengths as the ligand becomes more easily oxidized. This is found to be the case; e.g., the first strong absorption peaks of PtX_6^{2-} are 262 $\text{m}\mu$, 315 $\text{m}\mu$, and 494 $\text{m}\mu$, when X is chloride, bromide and iodide, respectively (25).

Such a transfer is obviously the root of a photochemical oxidation-reduction reaction and, indeed, some charge-transfer absorptions are actually followed by the production of free radicals which can be detected by their subsequent reactions. The surprising fact is that many substances which exhibit strong absorption bands of the electron-transfer type in the ultraviolet region, show no net oxidation-reduction reaction. Adamson and Sporer (26) have shown that, in many cases, the region of light absorption makes little difference in the type of reaction which occurs in the system but that the type, redox or substitution, depends primarily on the oxidizability of the ligands. They proposed a mechanism to explain these facts which has, as a first step, a homolytic separation of ligand from complex in accord with the electron transfer nature of the absorption.



If Δ , representing the excess energy of the system, is small, then the reverse reaction will occur. In this case the transferred electron returns to its original position in the system so that no net chemical reaction occurs. If Δ is large, however, there will be sufficient separation of complex and ligand for interposition of a solvent molecule or other reactive group.



The nature of the net reaction is determined by the fate of $M(II)A_5H_2O-X$. If the return of the electron to the ligand is energetically favorable for this configuration and can occur with high frequency, then $M(III)A_5H_2O$ and X^- will be the products; i.e., aquation will be the net process. Similarly anation will be the net process if an anion plays the role of water in the mechanism. On the other hand, continued separation of the homolytic products may occur, leading to a net oxidation-reduction reaction.

Fortunately one of the systems studied by Adamson and Sporer was the photochemical exchange of Br^- and $PtBr_6^{2-}$. They found the quantum yield to be about 500 for the exchange, while the yield was less than 0.1 for oxidation-reduction.

Although, in the cases of the hydrolyses of $PtCl_6^{2-}$ and $PtBr_6^{2-}$, no net redox reactions take place, Rich and Taube (27) have found evidence that $PtCl_5^{\cdot-}$ is generated, by the action of light on $PtCl_6^{2-}$, in

sufficient amounts to catalyze the exchange between $\text{PtCl}_6^{=}$ and Cl^- . This sensitivity to light is peculiar to the exchange reaction; light does, indeed increase the rate of hydrolysis of $\text{PtCl}_6^{=}$ but the quantum yield is very small. The fact that the reaction rate is influenced by light raises the question as to whether the final equilibrium point is likewise affected. The investigations of Archibald and Gale demonstrated that the equilibrium point is the same whether the hydrolyses proceed via the photochemical path or by a thermal mechanism in the dark. The nondependence of equilibrium on path has also been shown by Schlesinger and Palmateer (28) for the substitution by chloride of bromide in $\text{PtBr}_6^{=}$. These workers studied the relative stabilities of $\text{PtCl}_6^{=}$, $\text{PtBr}_6^{=}$, and $\text{PtI}_6^{=}$ toward substitution by other halide ions and found the order of increasing stability to be $\text{PtCl}_6^{=}$, $\text{PtBr}_6^{=}$, and $\text{PtI}_6^{=}$.

The principal tool used in the present work to extract information from these spectra as to the nature of the platinum complexes was the mole ratio method. This method was devised by Yoe and Jones (29) and, experimentally, consists of measuring the absorbances of solutions in which the concentration of one element of a complex is held constant while the concentration of the other element is varied. For instance, in the case of the system $\text{PtX}_{6-n}(\text{OH})_n^{=}$, the concentration of platinum would be held constant while the concentration of halide would be varied, so that the ratio of halide to platinum would itself be varied in a regular fashion. This varying ratio is then plotted against the changing absorbancy of the solution which, ideally i.e., for very strong complexes, would yield a curve made up of straight

line segments and showing a change of slope at the points where the mole ratio corresponds to a complex actually present in solution. Conversely, the absence of a certain change of slope, in the mole ratio plot, over the entire spectrum is strong evidence that the complex of the corresponding mole ratio does not exist under the experimental conditions. The similarity and difference between this approach and the method of continuous variations are obvious. Several advantages are offered by the mole ratio method. Since the amount of one reactant is held constant, the preparation of solutions is simplified. Fewer solutions are needed to establish the existence or nonexistence of a suspected complex with the mole ratio method than with the method of continuous variations. For complexes of high mole ratios, such as 4:1, 5:1, or 6:1, an error of two per cent in the preparation of solutions or in the estimate of the position of the maximum of a continuous variations plot is sufficient to produce a unit change in the observed mole ratio whereas to produce a unit change utilizing the mole ratio method would require an error of from six to ten per cent. Since the present work leans heavily on the validity of the mole ratio method, it is necessary to establish this validity as quantitatively as possible. Such a foundation has been presented by Meyer and Ayres (30) and a digest of their work is appended to this thesis. Since Meyer and Ayres have been rather stringent in their assignment of tolerances, however, the mole ratio method can be used to determine the stoichiometry of complexes in many cases which do not conform closely to the criteria set forth in their paper.

Since deviations from Beer's law may give rise to false indications of complexes when measurements are made in spectral regions where the absorptivities are changing rapidly with wavelength, it behooves the investigator to proceed cautiously in deducing the presence of complexes from mole ratio plots. In evaluating these it is helpful to know the shape of the various spectral curves throughout the spectral region measured. This knowledge also facilitates the selection of wavelengths which are likely to be productive of information mole ratio plots. Good examples of the application of mole ratio methods can be found in the work of Meyer and Ayres (31) on the platinum (II) -tin (II) chloride system and that of Sundaram and Sandell (32) on the chloro complexes of palladium (II).

Although the mole ratio method establishes the nature of the complexes in solution, which is the first objective of the present work, it does little toward the attainment of the second objective, viz. the assignment of spectra to individual species. This latter objective has been achieved in part, by obtaining the spectrum of one species and using the comparison of this spectrum with the composite spectra of complex mixtures to enable the decomposition of these composite spectra into their component parts. Examples of this method are found in Neumann's (33) study of antimony (V) species in hydrochloric acid solutions, and in Neumann and Cook's (34) study of molybdenum (VI) in hydrochloric acid.

Obtaining the spectrum of a single ionic species is usually difficult, especially, as with the species discussed in the present

work, when the species reacts rapidly with other entities to give a mixture of products. The desired end can sometimes be gained by measuring the spectrum in a solvent where such reactions cannot take place, e.g., in dioxane to avoid hydrolysis. This method presupposes some way of synthesizing a pure solid compound of the desired species. Where this is not feasible, other stratagems must be devised. Since the nature of the latter depend on the specific problem being studied, they will not be discussed in a general fashion in this introduction but will be taken up in the chapters explaining the experimental work.

CHAPTER II

APPARATUS AND REAGENTS

Apparatus

The spectrophotometer used in this work was a Beckman double-beam ratio-recording instrument designated by the manufacturer as Model DK-1. Although the instrument is equipped with various light sources and detectors to enable it to cover the spectral range from 185 μ to 3500 μ , only those components suitable for the 185 μ to 360 μ region will be described here since the experimental spectra were confined to this region. The light source is a hydrogen discharge lamp. Light from this source is chopped at 480 cycles per second and reflected into the monochromator where it is twice dispersed by a thirty degree quartz prism. Monochromatic light from the prism is focused by a simple lens onto a mirror, rotating at 15 cycles per second, which alternately directs the light through the sample cell and reference cell. These cells are made of fused silica and have a one centimeter light path. Light transmitted by either the sample or the reference impinges on a single detector which is, in this case, a photomultiplier tube, which converts it to an a-c voltage. This signal is amplified and transferred to the demodulators. A commutator, synchronized with the rotating mirrors, alternately selects the signal from the sample and reference and sends it to the respective demodulators. The sample demodulator rectifies the sample signal to a d-c voltage which drives the recorder pen.

The reference demodulator rectifies the reference signal to a d-c voltage which establishes a constant 100 per cent reference voltage for the recorder. This constant 100 per cent reference voltage is maintained by a slit servo mechanism. The recorder is a continuous, linear strip-chart unit capable of covering the absorbancy range from zero to two. The wavelength scale is capable of variation and, in this work, was usually adjusted so that six inches of strip-chart corresponded to 100 m μ .

The water bath used for this work was the E. H. Sargent constant temperature bath which can maintain a temperature constant within 0.01°C. The temperature is regulated by a mercury switch sensitive to 0.005°C. Three heaters are provided, one intermittent and two continuous.

Reagents

The platinum used was reclaimed from the platinum iridium alloy which is usually used for laboratory ware. The platinum was separated from the iridium by controlled hydrolytic precipitation of the latter metal as the dioxide. This separation, which also serves to remove palladium and rhodium, if present, was carried out as follows:

About one gram of the alloy was dissolved in aqua regia and the resulting solution was evaporated several times with concentrated hydrochloric acid to decompose nitroso compounds. The solution was then diluted to approximately 250 mls and heated to boiling. To the hot solution was added 20 mls of a ten per cent solution of sodium bromate. The solution was then neutralized with a ten per cent solution of

sodium bicarbonate using bromcresol purple as an indicator. Ten more mls of the bromate solution was added and the solution was boiled for five minutes. Sodium bicarbonate was again added to the endpoint of xylene blue. Ten more mls of the bromate reagent was added and the solution was again boiled for 15 minutes. The mixture was then cooled and filtered through a sintered glass funnel using suction. The filtrate contained the platinum. This filtrate was twice evaporated to dryness with concentrated hydrochloric acid to destroy bromate. The platinum was then precipitated with hydrogen sulfide. The metal was filtered off and dissolved in aqua regia. The platinum was then reprecipitated from this solution with formic acid as described in the section dealing with analyses. The precipitated sponge was filtered on paper, washed with 1:50 hydrochloric acid and ignited in a porcelain crucible to gray platinum sponge (35).

Sodium chloride, technical grade, was purified by dissolution in water followed by precipitation brought about by saturating the solution with gaseous hydrogen chloride. This operation was repeated and the sodium chloride thus produced was dried over a Bunsen flame and stored in a glass stoppered bottle.

Reagent grade hydrobromic acid was distilled from red phosphorus before use to free it from traces of free bromine. All other chemicals were commercial materials of reagent grade, and were used without further purification.

CHAPTER III

METHODS OF SYNTHESIS AND ANALYSIS

Syntheses

The following syntheses were performed during the course of this work.

Sodium platinate, $\text{Na}_2\text{Pt}(\text{OH})_6$, was made as follows. A solution of H_2PtCl_6 was made by dissolving about 0.5 g of metallic platinum in aqua regia. Nitrogen compounds were eliminated by several evaporations with concentrated hydrochloric acid. A large excess of sodium hydroxide was added to this solution which was then boiled for two hours. At first a red color developed in the solution. Then a black precipitate was formed to be followed by a green precipitate. The mother liquor at this point was light yellow. The solution was filtered and the residue was washed with water. The green precipitate dissolved in the wash water. The black precipitate is probably PtO_2 . The filtrate was boiled to half its original volume at which point a yellow precipitate was obtained. These crystals were filtered and washed in turn with absolute ethanol and ether until the washings were barely basic to Alkacid test paper. The bright yellow crystals were air dried and stored in a desiccator. The formula was established both by dehydration and by platinum assay (36). The error involved in dehydration is rather large but constant indicating that dehydration is not completed as easily as is generally believed.

Sample Weight	Contained Platinum	Calculated for $\text{Na}_2\text{Pt}(\text{OH})_6$	Weight Loss on Dehydration	Calculated Loss for $\text{Na}_2\text{Pt}(\text{OH})_6$
0.0540 g	0.0330 g	0.0307 g		
0.0568	0.0327	0.0323		
0.0391 g			0.0050 g	0.0061 g
0.0367			0.0046	0.0058

Platinum tetrachloride, PtCl_4 , was prepared as follows. About 0.5 g of platinum metal was dissolved in aqua regia. Nitrogen compounds were expelled by repeated evaporation with concentrated hydrochloric acid. The solution was then evaporated almost to dryness to obtain dark red crystals. These crystals were not analyzed but they probably consist of H_2PtCl_6 with six molecules of water of crystallization (37). These crystals were heated in a stream of dry chlorine for three hours at 275°C to convert them to platinum tetrachloride (38). The composition of the PtCl_4 was established by platinum and chloride assays.

Sample Weight	Pt Found	Cl Found	Pt Calculated	Cl Calculated
0.1362 g	0.0779 g	0.0585 g	0.0788 g	0.0574 g

Platinum tetrabromide, PtBr_4 , was prepared in a manner analogous to that used to prepare PtCl_4 . About 0.5 g of $\text{Na}_2\text{Pt}(\text{OH})_6$ was dissolved in concentrated hydrobromic acid and the resulting solution was evaporated to dryness to give reddish black crystals of bromoplatinic acid. These crystals were not analyzed but were probably $\text{H}_2\text{PtBr}_6 \cdot 9\text{H}_2\text{O}$

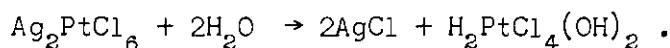
(39). These crystals were heated at 100°C for two hours in an atmosphere of bromine. The resulting dark brown mass probably consisted of PtBr_4 with adsorbed bromine. This product was heated in vacuo at 50°C for three hours to eliminate the excess bromine. The final product was dark red, amorphous and very hygroscopic. Its composition was established as PtBr_4 by platinum and bromide assays.

Sample Weight	Pt Found	Br Found	Pt Calculated	Cl Calculated
0.1412 g	0.0527 g	0.0888 g	0.0534 g	0.0878 g

Attempts were made to prepare the compounds $\text{H}_2\text{Pt}(\text{OH})_6$, $\text{H}_2\text{PtCl}_5\text{OH}$, and $\text{H}_2\text{PtCl}_4(\text{OH})_2$ by the methods described by Miolati (9). Unfortunately, except in the case of platonic acid, insufficient quantities were obtained to establish the compositions. Furthermore, spectral data indicate that the formulations of the partially chlorinated compounds must be held in doubt. The platonic acid, $\text{H}_2\text{Pt}(\text{OH})_6$, was prepared by neutralizing a solution of $\text{Na}_2\text{Pt}(\text{OH})_6$ with acetic acid using methyl orange as an indicator. A fine white precipitate developed which formed a buff colored powder after drying over concentrated sulfuric acid. The composition was checked by platinum assay.

Sample Weight	Pt Found	Pt Calculated for $\text{H}_2\text{Pt}(\text{OH})_6$
0.0464 g	0.0297 g	0.0303 g

An attempt was made to prepare $\text{H}_2\text{PtCl}_4(\text{OH})_2$ by boiling a suspension of Ag_2PtCl_6 in water. According to Miolati (9) the following reaction should take place:



The Ag_2PtCl_6 was obtained from the reaction of AgNO_3 with H_2PtCl_6 . The mother liquor from the boiled Ag_2PtCl_6 was separated from the precipitate and its spectrum recorded but no peaks were shown above 200 μ . It seems unlikely that any such highly chlorinated species as $\text{PtCl}_4(\text{OH})_2^-$ could survive such strongly hydrolyzing conditions.

However, dehydration and dehydrohalogenation of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in vacuo over molten potassium hydroxide yielded an amorphous brown material which, when dissolved in ether, no longer displayed the characteristic spectrum of PtCl_6^- , but, instead, had its main absorption peak at 225 μ . Unfortunately, insufficient material was available for analysis so that the true composition was not known. This was the method used by Miolati (9) to prepare $\text{H}_2\text{PtCl}_5\text{OH}$.

These methods for the synthesis of $\text{H}_2\text{PtCl}_5\text{OH}$ and $\text{H}_2\text{PtCl}_4(\text{OH})_2$ were also applied in an effort to produce the analogous bromo compounds using $\text{H}_2\text{PtBr}_6 \cdot 9\text{H}_2\text{O}$ as a starting material. Here again the solution obtained by boiling Ag_2PtBr_6 and reputed to contain $\text{PtBr}_4(\text{OH})_2^-$ showed no absorption peaks above 200 μ . The attempted dehydration and dehydrohalogenation of $\text{H}_2\text{PtBr}_6 \cdot 9\text{H}_2\text{O}$ in vacuo over molten potassium hydroxide failed. A spectrum of the resulting material dissolved in alcohol showed only the presence of hexabromoplatinic acid.

Analytical Methods

During the course of the work, it was necessary to analyze both solids and solutions for the purpose of determining compositions and concentrations. Some of the solutions were so dilute as to require spectral methods of analysis while, in the case of solids and more concentrated solutions, conventional gravimetric and volumetric methods sufficed. In this latter case platinum was determined gravimetrically as the metal but the mode of reduction depended upon whether or not it was necessary to determine the halide content of the same sample. If a halide assay were not necessary the reduction was performed conventionally with formic acid in a hydrochloric acid solution buffered at a pH of four with sodium acetate (40). If the halide had to be determined in the same sample the following procedure was used. The sample, either solid or solution, was treated with a large excess of solid sodium carbonate in a nickel crucible. The mass was dried, if necessary, and then fused over a Fisher burner. This process converted the platinum halide to a mixture of platinum metal and sodium halide (41). The platinum was separated by filtration through a sintered glass crucible, washed with hot water, dried and weighed. The filtrate was acidified with nitric acid and assayed for halide. If the halide was bromide, Volhardt's method of adding excess silver nitrate and titrating the excess with standard potassium thiocyanate with ferric alum indicator was used (42). A variation of Mohr's method, titration with standard silver nitrate using eosin as an absorption indicator, was used to determine chloride ions (43), since the use of Volhardt's method would have entailed an additional filtration (44).

Very dilute solutions of platinum complexes, 10^{-3} to 10^{-5} molar, were analyzed by converting all the platinum to the hexa-halogenated species and measuring the absorbancy of the solution at an appropriate wavelength. The conversion was brought about by adding a large excess of sodium chloride or sodium bromide to the solution after acidifying, if necessary, with perchloric acid. In the case of $\text{PtCl}_6^{=}$, the absorbancy was measured at $262 \text{ m}\mu$ at which wavelength the molar absorbancy coefficient is 24950. In the case of $\text{PtBr}_6^{=}$, the absorbancy was measured at $315 \text{ m}\mu$ and the molar absorbancy coefficient is 18150. These values for the molar absorbancy coefficients were obtained by measuring the absorbancies of $\text{PtCl}_6^{=}$ and $\text{PtBr}_6^{=}$ solutions at known concentrations at the given wavelengths. The concentration of platinum could then be calculated from the formula:

$$C = \frac{A}{L\epsilon}$$

where C is the molar concentration of platinum,
 A is the absorbancy of the solution,
 ϵ is the molar absorbancy coefficient, and
 L is the length of light path.

CHAPTER IV

OBSERVATIONS ON THE CHLORO-HYDROXO COMPLEXES OF PLATINUM (IV)

Mole Ratio Treatment of Chloro-Hydroxo Complexes

As mentioned in Chapter I, the chloro-hydroxo complexes of platinum (IV) were originally chosen for the study of the relations between spectra and composition but were soon abandoned in favor of the bromo-hydroxo complexes. After the bromo system had been studied, some work was done on the chloro system. This work will be described in this chapter, rather than in chronological sequence, since fewer complexities were encountered with the chloro system and, hence, the operations involved can be more easily explained.

The major purpose was to apply the mole ratio method to the chloride-platinate-water system to determine what members of the series, $\text{PtCl}_{6-n}(\text{OH})_n^-$, where n varies from zero to six, enjoyed a stable existence. Briefly this method consists in measuring the spectral absorbancies of a series of solutions in which the concentration of the central ion of the complex is held constant while the ratio of ligand concentration to central ion concentration is varied in a regular manner. The absorbancies measured at each wavelength are then plotted against the ligand/central ion ratios. If the solutions are at equilibrium, the plot will be a curve made up of straight line segments. The value of the ligand/central ion ratio at which two segments meet, represents the stoichiometry of a stable complex (29).

The necessary solutions were made up in the following manner. A weighed amount of sodium platinate, prepared as described in Chapter III, was dissolved in twenty mls of concentrated perchloric acid, which had been analyzed and found to be precisely 12.00 M. This solution was diluted to about 40 mls with distilled water and allowed to cool. The calculated amount of a standard solution of sodium chloride was then added to adjust the chloride/platinum ratio to the desired value. Finally the solution was made up to 100 mls with distilled water. Each solution contained 2.92×10^{-4} g-atoms of platinum. The chloride/platinum ratio was varied from zero to six in half-unit steps. Each solution was 2.40 M in HClO_4 . This high acid level served two purposes; first, to confine the extent of hydrolysis within a convenient range and, second, to simplify equilibrium calculations by keeping hydrogen ion concentration essentially constant. The prepared solutions were placed in a water bath held at a temperature of $50 \pm 0.1^\circ\text{C}$. This higher temperature was found advantageous because of speedier attainment of equilibrium. The equilibrated solutions were too concentrated to permit direct measurement of spectra using one cm cells. Consequently, aliquots were taken and diluted tenfold with water for spectral measurement. The dilution was made immediately before measurement which was carried out using the Beckman DK spectrophotometer. Every eight to twelve hours a freshly diluted sample was prepared and measured. When consecutive spectra showed identical absorbancies throughout the range from 205 $\text{m}\mu$ to 400 $\text{m}\mu$, it was assumed that equilibrium had been established. Equilibrium was usually established within 48 hours of placing the samples in the bath.

The fact that dilution was necessary before spectral measurement poses a question as to just what equilibrium the measurement represents. If the solution upon dilution underwent further hydrolysis at an appreciable rate, then the measured spectrum would reflect conditions in a solution at room temperature, and having a lower acidity and a smaller concentration of platinum. On the other hand, if the rate of further hydrolysis were slow, then the change taking place between the time of dilution and the time of measurement would be negligible and the spectrum would represent the conditions in a solution at 50°C, having a higher acidity and a higher concentration of platinum. The time necessary to dilute a sample to the proper concentration and record its spectrum on the DK spectrophotometer was between six and seven minutes. As a test, an aliquot of an equilibrated solution was diluted, after which successive samples from this diluted solution were measured one minute after dilution, ten minutes after dilution and twenty minutes after dilution. This test was repeated on several solutions with differing Cl/Pt ratios. In each case the three spectra were identical within the limits of experimental error. The results demonstrate that further hydrolysis in the time between dilution and measurement is indeed negligible and, thus, the spectra obtained represent the conditions in solutions at higher temperature, higher acidity and higher platinum concentration. This conclusion can be reached only if the possibility of a very fast hydrolysis reaction is denied. Admission of such a possibility would, however, not only confute the known kinetic inertness of platinum (IV) complexes (45) but would demand that a small concentration change

(tenfold) should produce a velocity change which would be large (1000 fold) and in a direction opposite to what would be expected from the law of mass action.

In view of the fact that the hydrolysis of platinum salts is affected by light (13), it was also necessary to determine whether varying light conditions would change the position of equilibrium in the halo-platinate solution being considered. To check this point, two series of solutions with varying chloride/platinum ratios were made up. One series was prepared, equilibrated and diluted in ordinary light. The other series was prepared, equilibrated and diluted in red light. Corresponding solutions from each series showed no significant difference in absorption after equilibrium had been reached, although the solutions which were kept in red light came to equilibrium more slowly.

The spectra shown in Figures 1, 2, and 3 are the spectra which were obtained from the tenfold diluted samples of the solutions with varying Cl/Pt ratios, equilibrated at 50°C. The peak at 262 $m\mu$ is prominent for those solutions having a Cl/Pt ratio greater than five. As the relative chloride concentration drops this peak becomes less and less conspicuous, while at the same time, absorption in the region about 217 $m\mu$ becomes more and more important. These two wavelengths, together with 233 $m\mu$ and 250 $m\mu$ were selected for mole ratio plots. These plots are shown in Figure 4. It seems fairly definite from these curves that the species with a Cl/Pt ratio of four exists. There is a good indication that complexes having Cl/Pt ratios of one and two also exist.

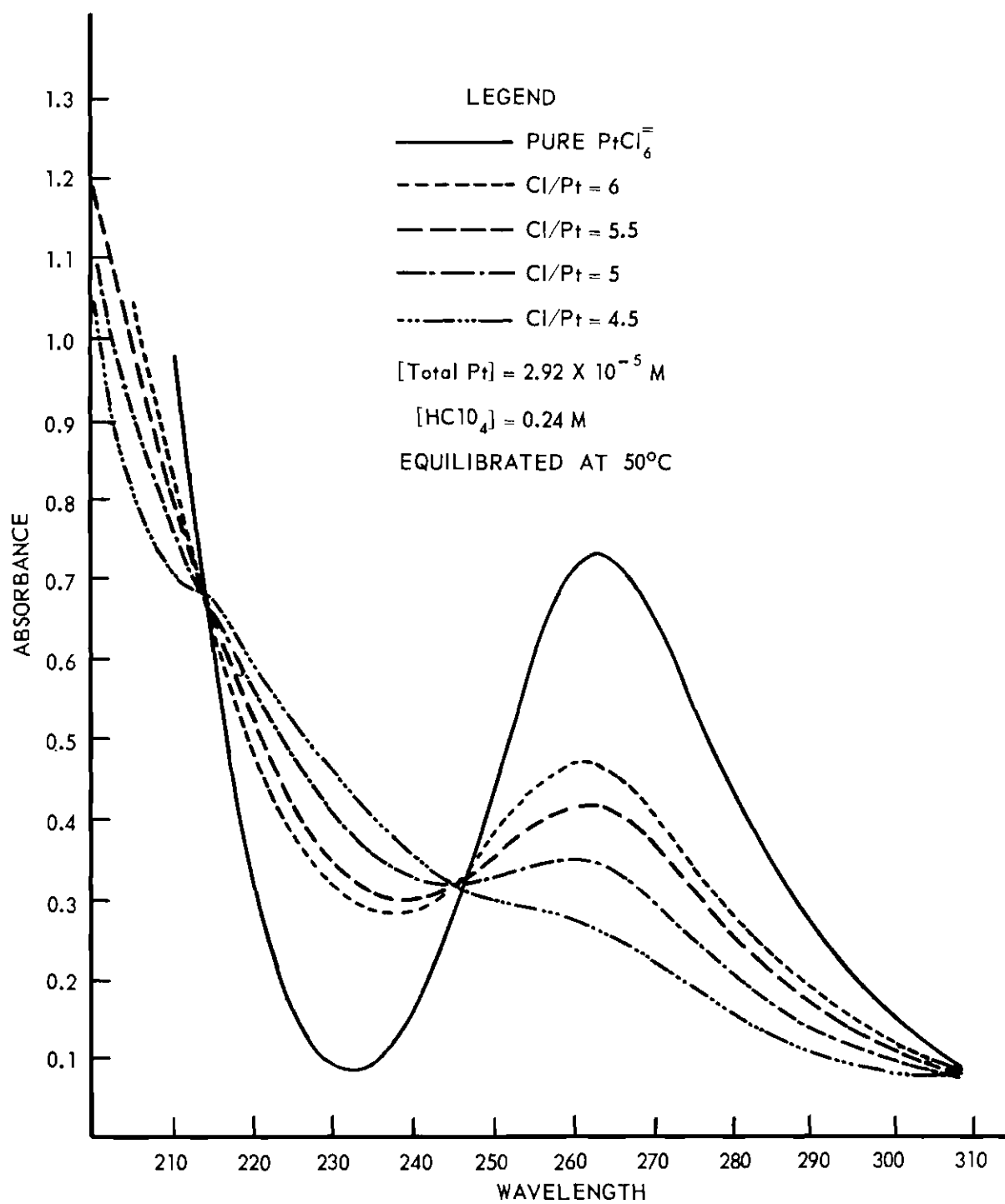


Figure 1. Spectra of Solutions with Varying Cl/Pt Ratios.

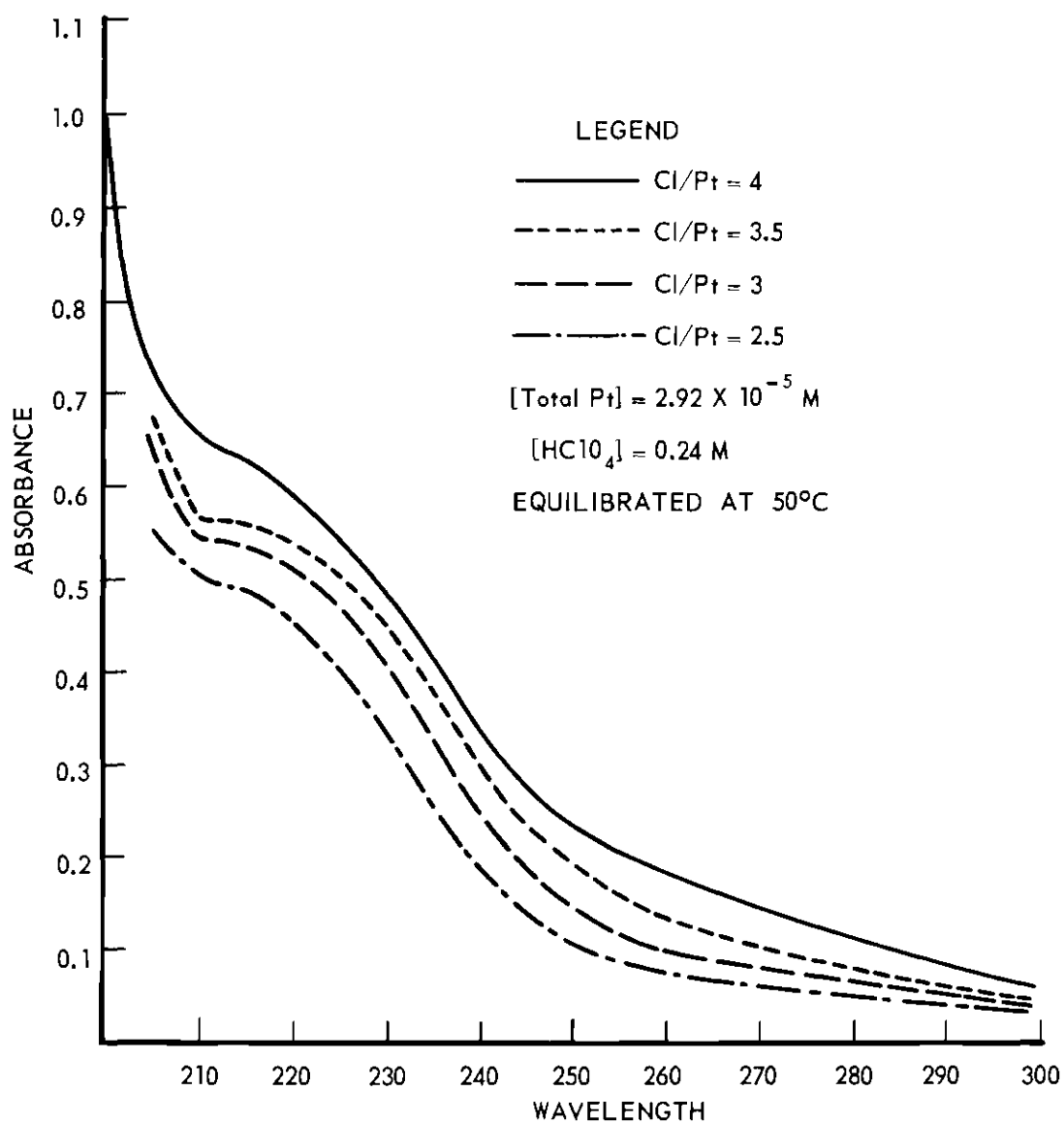


Figure 2. Spectra of Solutions with Varying Cl/Pt Ratios.

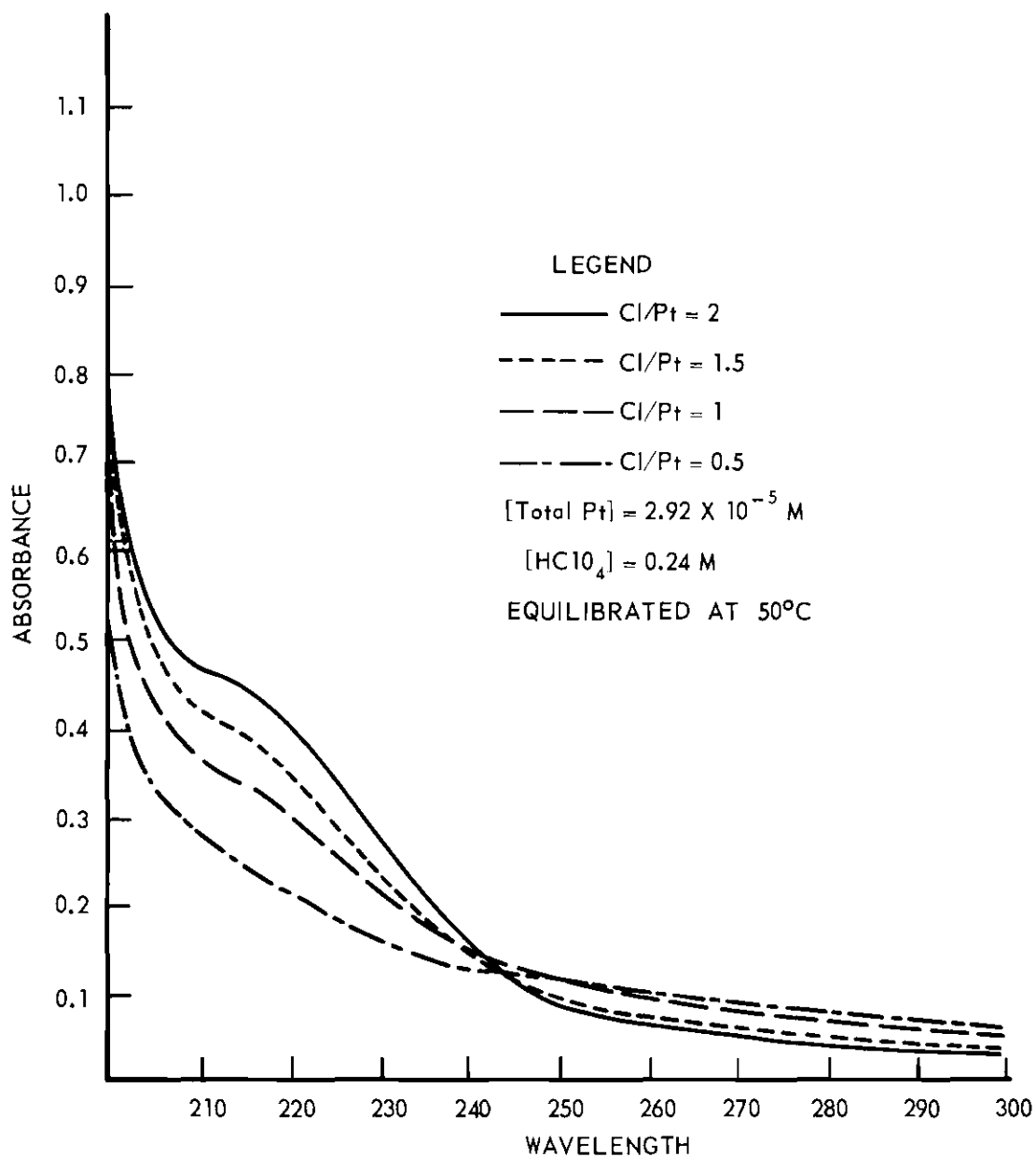


Figure 3. Spectra of Solutions with Varying Cl/Pt Ratios.

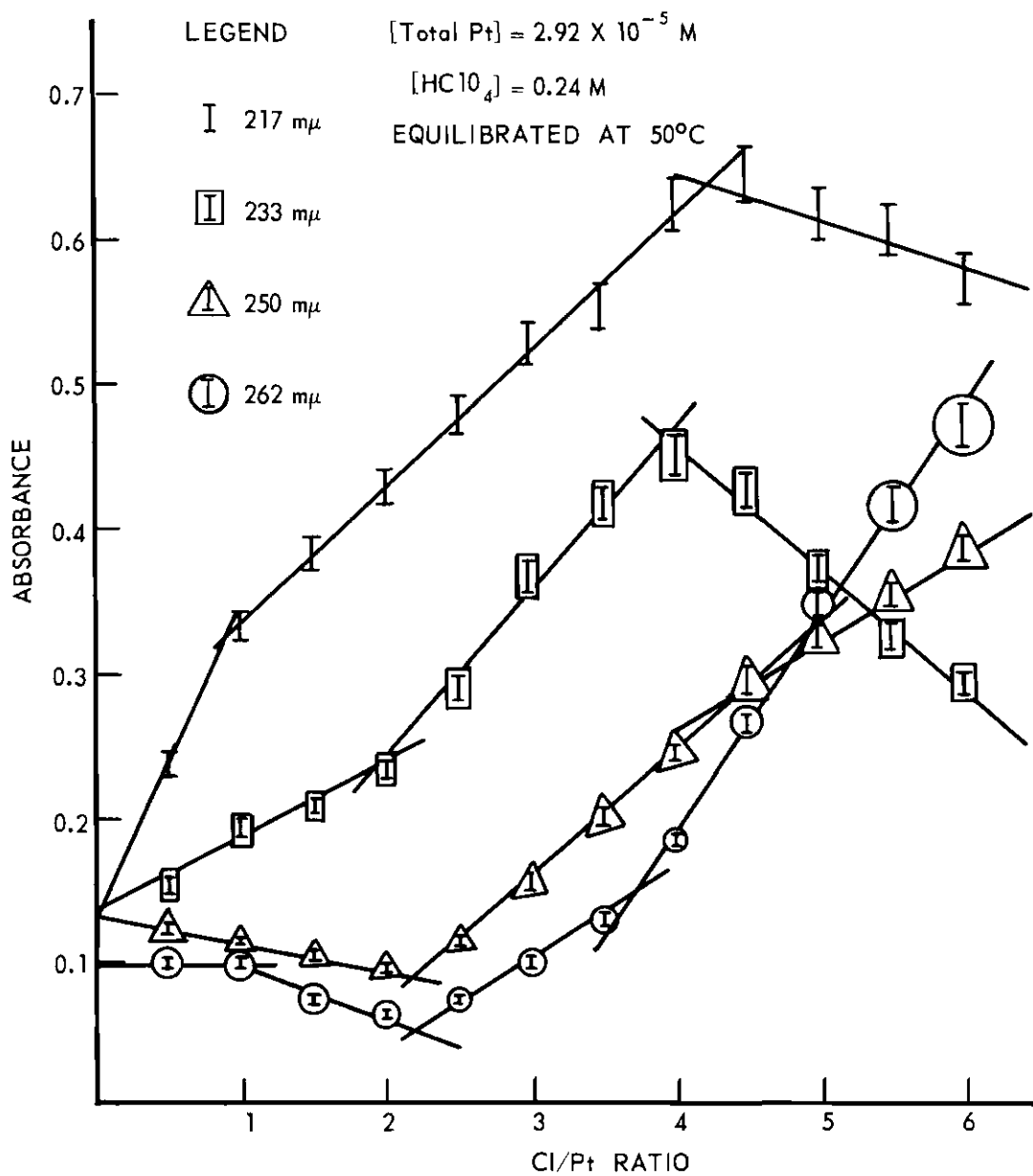


Figure 4. Mole Ratio Plot for Chloroplatinate Complexes.

It will be noted that the spectra of those solutions where $\text{Cl/Pt} \geq 4.5$ show isosbestic points at 214 $\text{m}\mu$ and 245 $\text{m}\mu$. The presence of these points shows a strong probability that there are only two ionic species in these particular solutions which contribute to the absorption at these wavelengths. It is possible, but less probable, that there are more than two absorbing species. The strong absorbance at 262 $\text{m}\mu$ indicates that one of these absorbing species is $\text{PtCl}_6^{=}$ (18).

The spectral absorption of any of these solutions is described at any wavelength, λ , by the formula:

$$A_{\lambda} = C_1 \varepsilon_{1\lambda} + C_2 \varepsilon_{2\lambda}$$

where A_{λ} = absorbance at wavelength λ ,
 C_1 = molar concentration of $\text{PtCl}_6^{=}$,
 C_2 = molar concentration of other species,
 $\varepsilon_{1\lambda}$ = extinction coefficient of $\text{PtCl}_6^{=}$ at wavelength λ ,
 $\varepsilon_{2\lambda}$ = extinction coefficient of other species.

Of these quantities, A_{λ} is known from the spectrum of the solution and $\varepsilon_{1\lambda}$ can be obtained by measuring the spectrum of pure Na_2PtCl_6 in solutions containing high concentrations of chloride ions. Since the sum, $C_1 + C_2$, is equal to the known total concentration of platinum species, then, to obtain a knowledge of the spectrum of the second species, i.e., to determine $\varepsilon_{2\lambda}$, it is only necessary to determine a value for either C_1 or C_2 . One way to estimate C_1 is to assume that, at some wavelength, all of the absorbance can be attributed to

$\text{PtCl}_6^{=}$. Knowing C_1 and ϵ_1 , it is a simple but tedious matter to calculate the absorbance which is due to $\text{PtCl}_6^{=}$ at every wavelength in each spectrum by use of the relationship:

$$C = \frac{A}{L\epsilon}$$

where the meaning of the symbols is as given in Chapter III. Having determined in this manner the contribution of $\text{PtCl}_6^{=}$ to each spectrum, subtraction of it leaves the spectrum of the other absorbing species. A large part of the tedium in this process can be avoided by using a graphical method to obtain the absorbancy values of the second species. The following explanation of this procedure will be considerably more lucid if Figure 1 and Figure 5 are consulted during the reading. Essentially, the total absorbance is plotted versus the fraction of Pt in the form of $\text{PtCl}_6^{=}$ for each solution at any desired wavelength. The result, if Beer's law is obeyed by both compounds, is a straight line which can be extrapolated to determine the absorbancy at which the fraction of Pt in the form of $\text{PtCl}_6^{=}$ is zero, i.e., the absorbancy the solution would have if all the Pt were in the form of the other absorbing species. The first step in plotting is to determine the fraction of Pt in the form of $\text{PtCl}_6^{=}$ for each solution. This can be done approximately by selecting a wavelength at which it can reasonably be assumed that only $\text{PtCl}_6^{=}$ absorbs. In this example, 262 $\text{m}\mu$ was selected as this wavelength. The value of the extinction coefficient of $\text{PtCl}_6^{=}$ at this wavelength is known (18) and, hence, it is a simple matter to calculate the absorbancy at 262 $\text{m}\mu$ of a solution of $\text{PtCl}_6^{=}$ with the

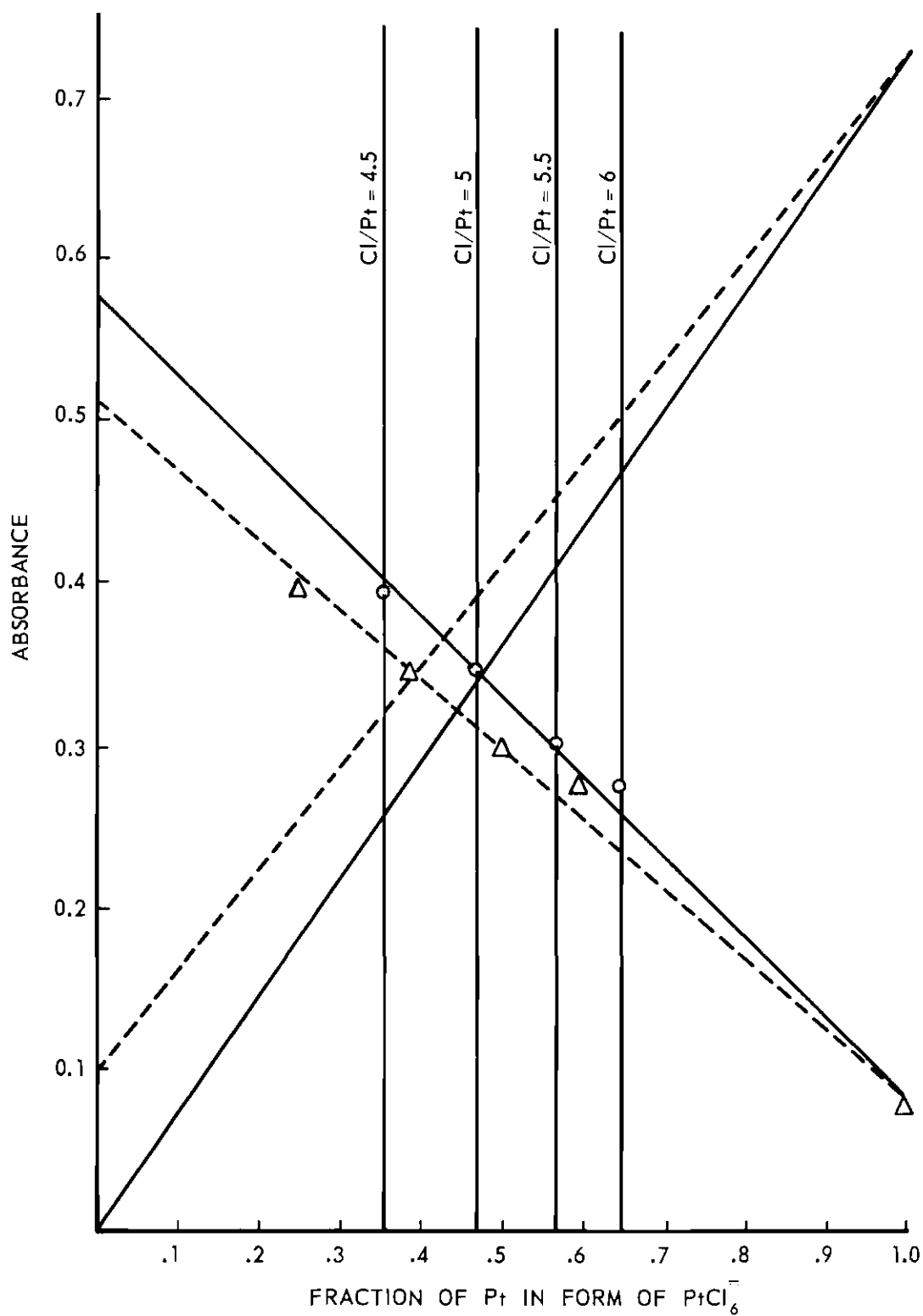


Figure 5. Graphical Method for Reconstructing Spectra.

same total platinum concentration as the solutions being considered, which is 2.92×10^{-5} M. (This is the concentration of the tenfold diluted sample, not of the equilibrated solution.) This absorbancy value is found to be 0.73 which is plotted against the value of 1.0, since all the Pt is in the form of $\text{PtCl}_6^{=}$. This point and the origin, which represents the fact that only $\text{PtCl}_6^{=}$ absorbs at 262 $\text{m}\mu$, determine a straight line. The total absorbancy values at 262 $\text{m}\mu$ of the solutions being tested are then placed on this line. Perpendiculars through these points extended to the x-axis will then give the fraction of Pt in the form of $\text{PtCl}_6^{=}$ present in each solution. These perpendiculars are shown in Figure 5, labelled with the Cl/Pt ratios of the solutions which they represent. The total absorbancy values at any other wavelength are taken from Figure 1 and placed on the proper perpendicular. A line is then drawn through these points and extended to the y-axis. This absorbancy value, where the fraction of Pt in the form of $\text{PtCl}_6^{=}$ is zero, would be the absorbancy, at this wavelength, of a solution of the other absorbing species if all the Pt were in this form, i.e., at a concentration of 2.92×10^{-5} M. Figure 5 shows such a plot for determining the value of the absorbancy at 235 $\text{m}\mu$, which is thus determined to be 0.58. This line and other lines for determining absorbancies were chosen visually. In regions where the absorbance is not changing rapidly with wavelength, the uncertainty involved in this visual judgment is probably less than the experimental error inherent in recording and reading the absorbance. In areas where the absorbance is changing rapidly, the error

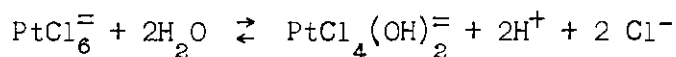
is greater, but not so great as to make the general features of the reconstructed spectrum unreliable.

In the present case, the wavelength which was first selected as one where only $\text{PtCl}_6^{=}$ would absorb, was 290 $\text{m}\mu$, since it was thought reasonable that the other species would have its absorbance maximum shifted to lower wavelengths, and 290 $\text{m}\mu$ was the highest wavelength at which absorbancy differences between the various spectra were sufficiently large to make plotting reasonably definite. The spectrum of the second species reconstructed on this basis showed negative values in the neighborhood of 262 $\text{m}\mu$ with a minimum at that wavelength. This suggested that the assumption about the relative absorptions at 290 $\text{m}\mu$ was a poor one and that 262 $\text{m}\mu$ was a better choice as a wavelength at which the absorbancy could be attributed entirely to $\text{PtCl}_6^{=}$.

However, if all the absorbance at 262 $\text{m}\mu$ be attributed to $\text{PtCl}_6^{=}$, then the calculated concentration of this ion will be too large to fit the known stoichiometry of the solution with a Cl/Pt ratio of 4.5. The calculated fraction of Pt in the form of $\text{PtCl}_6^{=}$ would be 0.35 but the stoichiometry of this solution sets the maximum possible value for this fraction as 0.25. Therefore, some of the absorption at 262 $\text{m}\mu$ must be ascribed to the second species. In order to take this into account, the reference line in Figure 5 must be modified. This was done by assuming that the maximum possible value for $[\text{PtCl}_6^{=}]$, in the solution with Cl/Pt of 4.5, was, indeed, the true value. This is equivalent to assigning a value of 325 to ϵ_2 at 262 $\text{m}\mu$. Using this new reference line (the dotted line in Figure 5), the graphical process

described above was used to obtain the spectrum of the second species depicted in Figure 6. The reconstructed spectrum shows a large peak at 220 $m\mu$ and the suggestion of a shoulder in the neighborhood of 235 $m\mu$. For comparison's sake, the spectrum of a solution of H_2PtCl_5OH , of unknown concentration in ether is also given. The H_2PtCl_5OH was prepared by the method of Miolati (46) but, since the prepared salt was not analyzed, this formula cannot be definitely ascribed. Although the two spectra are similar in the limited range available for comparison, it would seem better to assign the reconstructed spectrum to $PtCl_4(OH)_2^=$ rather than to $PtCl_5OH^=$ because the existence of the former, but not of the latter, is evidenced in the mole ratio plots. It would be enlightening if the spectrum of $PtCl_4(OH)_2^=$ in a nonhydrolytic medium could be compared with the reconstructed spectrum. Unfortunately attempts to prepare such a solution by the method of Miolati failed.

The spectra of Figure 1 and the mole ratio plot of Figure 4 suggest that the solutions with $Cl/Pt \geq 4.5$ contain only $PtCl_6^=$ and $PtCl_4(OH)_2^=$ in equilibrium with each other as expressed in the equation:



and the following equilibrium expression ought to be obeyed:

$$K_4 = \frac{[PtCl_4(OH)_2^=] [H^+]^2 [Cl^-]^2}{[PtCl_6^=]}$$

Water is omitted since its concentration is essentially constant. The H^+ concentration is also large, hence virtually constant, but is

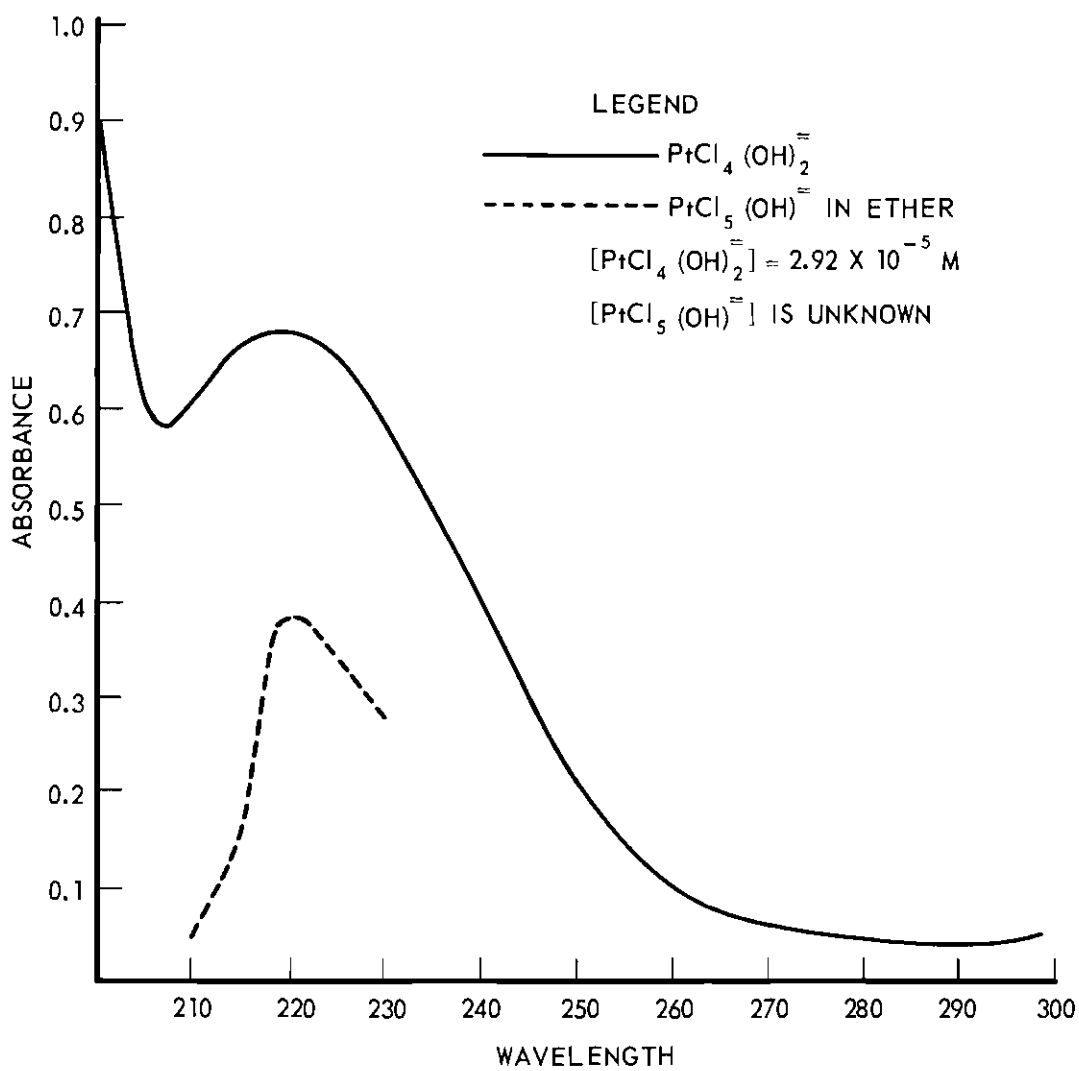


Figure 6. Reconstructed Spectrum of $\text{PtCl}_4(\text{OH})_2^-$.

retained so that later comparisons may be made with the results of other workers. In the table below are the values for the concentrations necessary to calculate K_4 . These values were obtained from known total Pt, Cl and acid concentrations and from the spectra of the solutions assuming that the extinction coefficients of $\text{PtCl}_6^{=}$ and $\text{PtCl}_4(\text{OH})_2^{=}$ at 262 $\text{m}\mu$ are, respectively, 24,900 and 325.

Cl/Pt	$[\text{PtCl}_6^{=}]$ $\times 10^4$	$[\text{PtCl}_4(\text{OH})_2^{=}]$ $\times 10^4$	$[\text{Cl}^-]$ $\times 10^4$	$[\text{H}^+]$	K_4 $\times 10^8$
6	1.73	1.19	2.38	2.4	22.4
5.5	1.46	1.46	1.46	2.4	12.3
5	1.14	1.78	1.04	2.4	9.74
4.5	0.73	2.19	0	2.4	-

The drift in values of K_4 is not unexpected. The values are ultimately dependent on the estimation of ϵ for $\text{PtCl}_4(\text{OH})_2^{=}$. Greater consistency in K_4 could have been obtained by choice of a larger value of ϵ , but would suggest a greater accuracy in the method than is justified. The mole ratio plot is the evidence that $\text{PtCl}_4(\text{OH})_2^{=}$ is the principal hydrolysis product, not the constancy of K_4 .

The only other quantitative data in the literature that can be compared with this work are those of E. H. Archibald (13) and those of Blasius, Preetz, and Schmitt (15). Archibald made a kinetic study of the hydrolysis of K_2PtCl_6 in water, following the reaction by titrimetric determination of the acid generated. The ultimate equilibrium

concentrations of acid in various runs were determined but he made no use of these data in speculation about the composition of the equilibrium mixtures. Blasius, Preetz, and Schmitt (15) made a kinetic study of the exchange of radioactive chlorine between $\text{PtCl}_6^{=}$ and Cl^- in HCl solutions. A net hydrolysis reaction occurred coincident with the exchange, and the distribution of radioactive chlorine at equilibrium was used to calculate the extent of hydrolysis. They did not use their data quantitatively beyond the point of calculating the per cent of hydrolysis in each experiment.

Although it is possible that at equilibrium these solutions are more complicated in composition, it is informative to assume that there is only one other platinum-containing species besides $\text{PtCl}_6^{=}$, and to calculate an equilibrium constant based on this assumption. In the following tabulation these constants are given, along with the pertinent experimental conditions. The constants K_5 , K_4 , and K_3 correspond respectively to the assumption that $\text{PtCl}_5\text{OH}^{=}$, $\text{PtCl}_4(\text{OH})_2^{=}$ or $\text{PtCl}_3(\text{OH})_3^{=}$ is the second species. A dash in the table implies that more HCl is formed (in the case of Archibald's experiments) or more Cl^- released from $\text{PtCl}_6^{=}$ (in the case of the exchange experiments) than can result from the complete hydrolysis of $\text{PtCl}_6^{=}$ to the assumed product.

These results also point to $\text{PtCl}_4(\text{OH})_2^{=}$ as the principal hydrolysis product. The value of K_4 is also similar to that obtained in the spectral experiments. In none of these experiments is the value

Archibald

Initial Conc. K_2PtCl_6	Equilibrium Conc. HCl	$K_5 \times 10^4$	$K_4 \times 10^8$	$K_3 \times 10^{12}$
0.00125 M	0.00374 M	-	-	-
0.00250 M	0.00459 M	-	0.484	0.0147
0.00500 M	0.00690 M	-	0.505	0.0919
0.01000 M	0.00929 M	11.3	0.645	0.293

Blasius, Preetz, and Schmitt

Initial Conc. H_2PtCl_6	Initial Conc. HCl	$K_5 \times 10^4$	$K_4 \times 10^8$	$K_3 \times 10^{12}$
0.0024	0.011	-	15.2	11.4
0.0024	0.047	0.830	8.78	129
0.0037	0.052	0.753	10.2	178
0.0024	0.083	1.69	44.3	2560

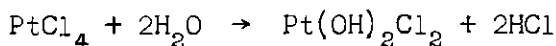
of K_4 established with any great accuracy, but it appears that K_4 does not have a marked temperature dependence.

Since the spectra of the solutions with $Cl/Pt \leq 4$ do not display isosbestic points, at least three species must contribute to the absorbance of these solutions. If the assumptions be made that the extinction coefficients of $PtCl_6^{=}$ and $PtCl_4(OH)_2^{=}$, at 262 $m\mu$, are 24,900 and 325, respectively, and that these two species are the only ones which absorb at 245 $m\mu$, it is possible to reconstruct a series of

spectra by subtracting the contributions of each of these species from the spectra of the solutions with Cl/Pt from three to four inclusive. Figure 3 displays a continuing increase in absorbance between 240 mμ and 300 mμ for the solutions with Cl/Pt ≤ 2.5 , a fact which demonstrates that the assumptions made above are certainly not true for these solutions and are, probably, only approximately true for the solutions with Cl/Pt ratios from three to four. The spectra resulting from this double decomposition do not show any well defined peaks or shoulders which suggests that whatever other species are present have their absorption maxima at wavelengths below 205 mμ.

The Solution Behavior of PtCl₄

As was noted in the introduction, many investigators have studied the nature of PtCl₄ solutions. Miolati (9) concluded that PtCl₄ hydrolyzes to give tetrachloro-dihydroxy platonic acid, basing his conclusion on conductometric titration with alkali and analysis of precipitates obtained from PtCl₄ solutions by addition of silver ion. Britton and Dodd (10) questioned this and proposed that upon first dissolving, PtCl₄ hydrolyzes as follows:

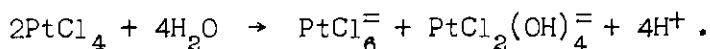


and that, during 24 hours, the hydrolysis proceeds further to give Pt(OH)₃Cl.

Heymann's (11) study of the effect of carbon on the hydrolysis would also indicate that the hydrolysis proceeded to Pt(OH)₃Cl and

$\text{Pt}(\text{OH})_2\text{Cl}_2$. The work described below was undertaken with an eye toward resolving the issue, with the added hope that, if Miolati were correct, the spectrum of $\text{PtCl}_4(\text{OH})_2^-$ would be obtained, thus checking the results of the preceding section.

Solid PtCl_4 was prepared using the method described in Chapter III. The dried compound was analyzed for platinum and chloride contents by the methods given in Chapter III, and the formulation PtCl_4 was thereby demonstrated. A portion of the compound was dissolved in water and the spectrum of the resulting solution was immediately recorded on the Beckman DK spectrograph. Additional spectra of the same solution recorded ten and twenty minutes after the dissolution of PtCl_4 were identical with the original spectrum within the limits of experimental error, a fact which indicates that the species in solution are rather resistant to further hydrolysis. This spectrum of the solution of PtCl_4 is shown in Figure 7 which also shows the spectrum of a 2.92×10^{-5} molar solution with a Cl/Pt ratio of four and the reconstructed spectrum of $\text{PtCl}_4(\text{OH})_2^-$ for the sake of comparison. The concentration of the PtCl_4 solution was found to be 3.02×10^{-5} M by spectroanalysis. It appears clear that the reaction cannot be simply the formation of $\text{PtCl}_4(\text{OH})_2^-$. The very definite shoulder at 262 mμ indicates strongly the presence of PtCl_6^- in the solution. If this be so then the PtCl_6^- must be formed in the process of dissolution of the solid PtCl_4 . A possible reaction consistent with this is:



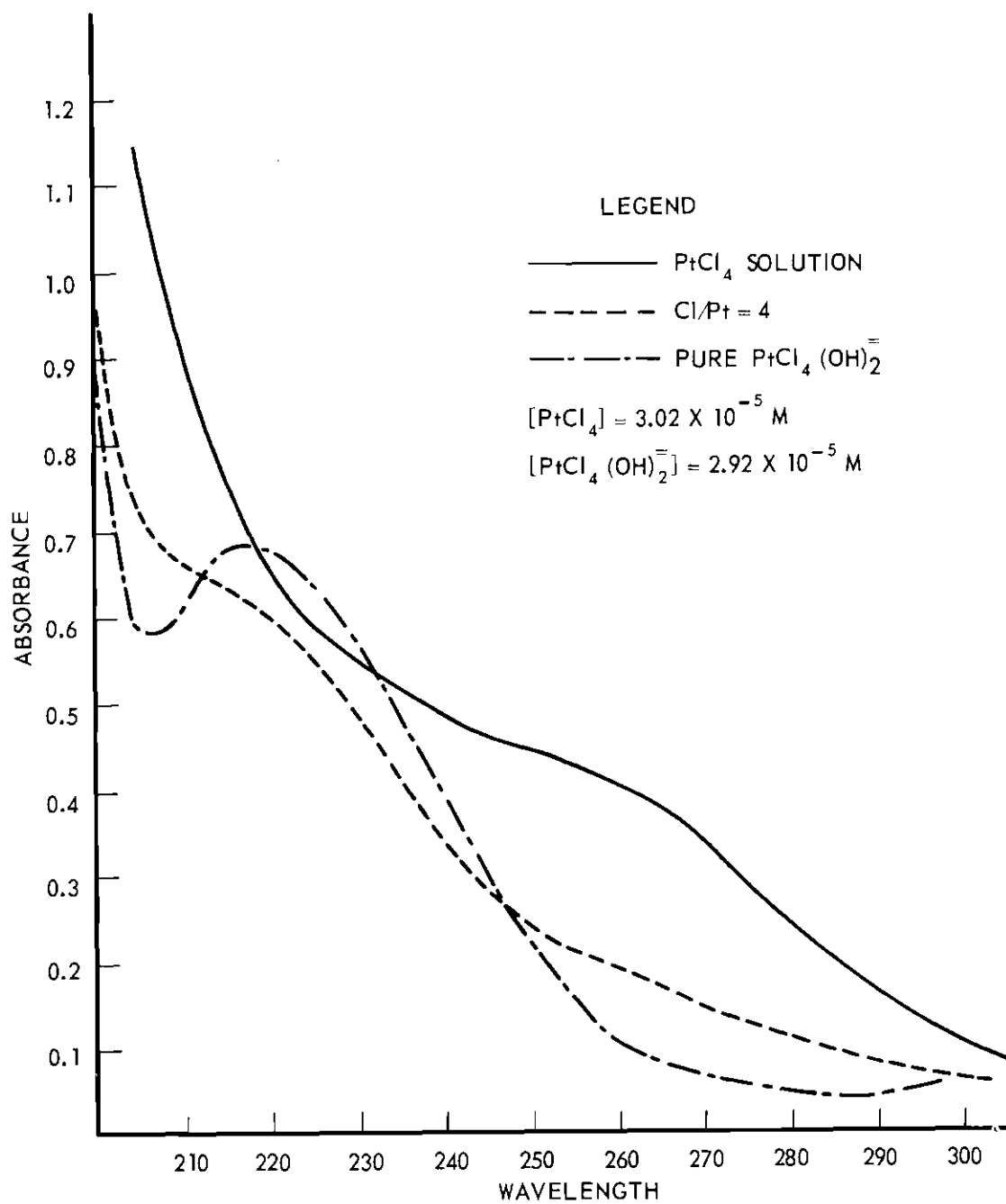


Figure 7. Spectrum of Solution of PtCl_4 .

If all the absorbance of the dissolved PtCl_4 at 262 $\text{m}\mu$ is attributed to $\text{PtCl}_6^{=}$, then the concentration of the latter is $1.53 \times 10^{-5} \text{ M}$, almost exactly half of the total platinum concentration which is $3.02 \times 10^{-5} \text{ M}$.

It is interesting to note that any postulated reaction that leads to retention of all the chlorines in Pt species, regardless of how the chlorines are distributed, leads to two H^+ and one doubly negative Pt species per PtCl_4 dissolved. Hence, any experiments that measure the acidity or that measure the conductivity will not be definitive.

In accord with the postulation of two platinum species in these solutions is the interesting observation of Reed (47) that when a drop of any aqueous solution of PtCl_4 is placed on filter paper a double ring is formed. He attributed this to the presence of two different hydrates with different rates of diffusion.

Falqui (48) has determined that the structure of solid PtCl_4 is that of a cube containing in each corner a PtCl_4 tetrahedron with three of the chlorine atoms resting on three edges of the cube and the fourth chlorine atom directed toward the cube's center. It is not readily apparent how such a structure would break up on dissolution to yield $\text{PtCl}_6^{=}$. Whatever the dissolution reaction is, it appears to end with essentially half of the platinum in the form of $\text{PtCl}_6^{=}$.

CHAPTER V

OBSERVATIONS ON THE BROMO-HYDROXO COMPLEXES OF PLATINUM

Mole Ratio Treatment of Bromo-Hydroxo Complexes

As has been mentioned, this investigation of the bromo-hydroxo complexes, in particular, was undertaken because of difficulties encountered in attempts to synthesize various chloro-hydroxo compounds and because the expected longer wavelength absorption of the bromo complexes would facilitate spectral study. Unfortunately, all the members of the series $\text{PtBr}_n(\text{OH})_{6-n}^-$ have not been isolated. Only those where $n = 0, 4$ and 6 are known in the solid state (49). Therefore, the obvious approach of dissolving pure solid compounds in nonhydrolyzing solvents and measuring their characteristic spectra could not be followed. However, the mole ratio method could be and was applied to the system. Therefore, a series of solutions of varying bromine to platinum ratios was prepared. The platinum concentrations and acidity were held constant throughout the series. The solutions were made up in the following manner. A weighed amount of sodium platinate, prepared as described in Chapter III, was dissolved in twenty mls of 12.00 M perchloric acid. This was diluted to about 40 mls with distilled water and, after cooling, the calculated amount of a standard solution of sodium bromide was added to adjust the bromide/platinum ratio to the desired value. The solution was made up to a volume of 100 mls and allowed to equilibrate in a water bath held at a temperature of 50°C.

The temperature was constant within 0.1°C . The total concentration of all platinum species in each solution was $2.92 \times 10^{-3} \text{ M}$, while the Br/Pt ratio varied from zero to six in intervals of 0.5. All of the solutions were 2.40 M in HClO_4 . These solutions were too concentrated to permit direct measurement of their spectra. Consequently, aliquots were taken and diluted one hundredfold with distilled water for this purpose. The dilution was made immediately before measuring to minimize hydrolysis and the measurement itself was carried out using the Beckman DK spectrophotometer so as to record the spectrum as swiftly as possible after dilution. The spectrum of each solution was measured every eight to twelve hours using a freshly diluted sample until two consecutive spectra showed identical absorbancies throughout the range from $205 \text{ m}\mu$ to $400 \text{ m}\mu$. At this stage it was assumed that equilibrium had been established. Equilibrium was usually established within 48 hours after placing the solutions in the bath.

The same question arises here as in the case of the chloro-hydroxo complexes, that is, whether the spectra represent the equilibria which obtain in the solutions before or after the dilution. In the case of the bromo complexes, the rate of hydrolysis is greater than for the chloro complexes. Even with this greater speed, however, the time of measurement is sufficiently short that the spectra reflect the conditions obtaining in the solutions before dilution.

After 48 hours, a yellow orange precipitate appeared in the solutions of low bromide-platinum ratios, specifically in those in which the Br/Pt ratio was less than three. Some of the precipitate was

taken for analysis. The material was first dried over CaCl_2 , a process which caused a color change from orange to light brown. The dried material was then analyzed by sintering a weighed amount with sodium carbonate, thereby decomposing it to metallic platinum. The sintered mass was leached with water and filtered. The filtrate gave no precipitate with silver nitrate demonstrating the absence of bromide. The residue of platinum was dried and weighed and found to be very close to the theoretical platinum content of $\text{H}_2\text{Pt}(\text{OH})_6$. The only other probable compound which might have precipitated is sodium platinate but this compound is comparatively quite soluble and its platinum content does not correspond to the assay of the material.

Sample Weight	Pt Found	Pt Calculated for $\text{H}_2\text{Pt}(\text{OH})_6$	Pt Calculated for $\text{Na}_2\text{Pt}(\text{OH})_6$
0.0458 g	0.0293 g	0.0299 g	0.0255 g

Obviously these solutions, with precipitates, could not be included with the solutions with higher Br/Pt ratios in the mole ratio plots because of their varying contents of dissolved platinum. These were treated separately as will be explained further in this chapter. The spectra of the solutions with Br/Pt of three or above are shown in Figure 8 and Figure 9. The spectrum of $\text{PtBr}_6^{=}$, at a concentration of 2.92×10^{-5} M, is included in Figure 8 for the sake of comparison. It is obvious that $\text{PtBr}_6^{=}$ is an important species in the solutions with high Br/Pt ratios. The spectrum of $\text{PtBr}_6^{=}$ was obtained as follows.

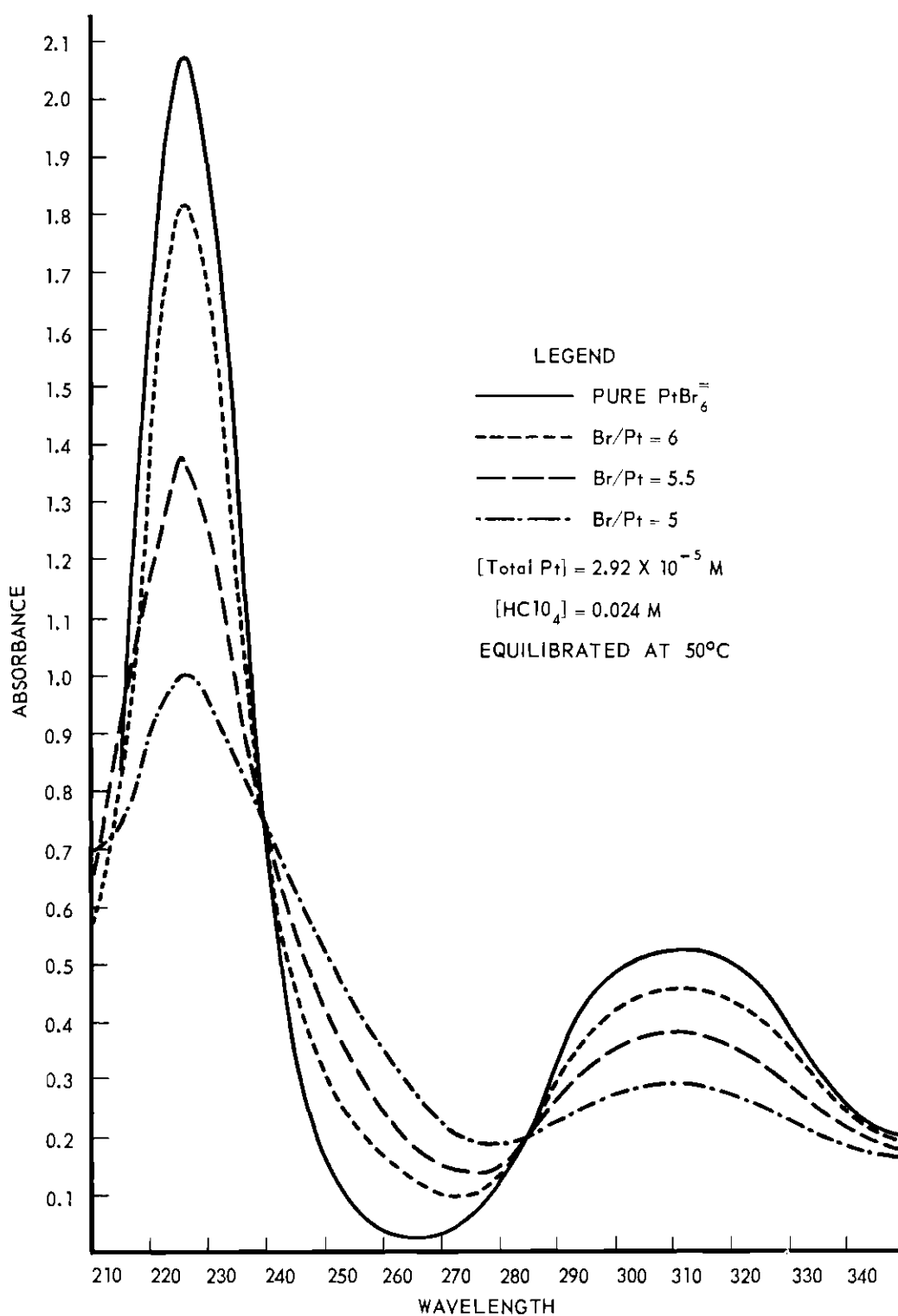


Figure 8. Spectra of Solutions with Varying Br/Pt Ratios.

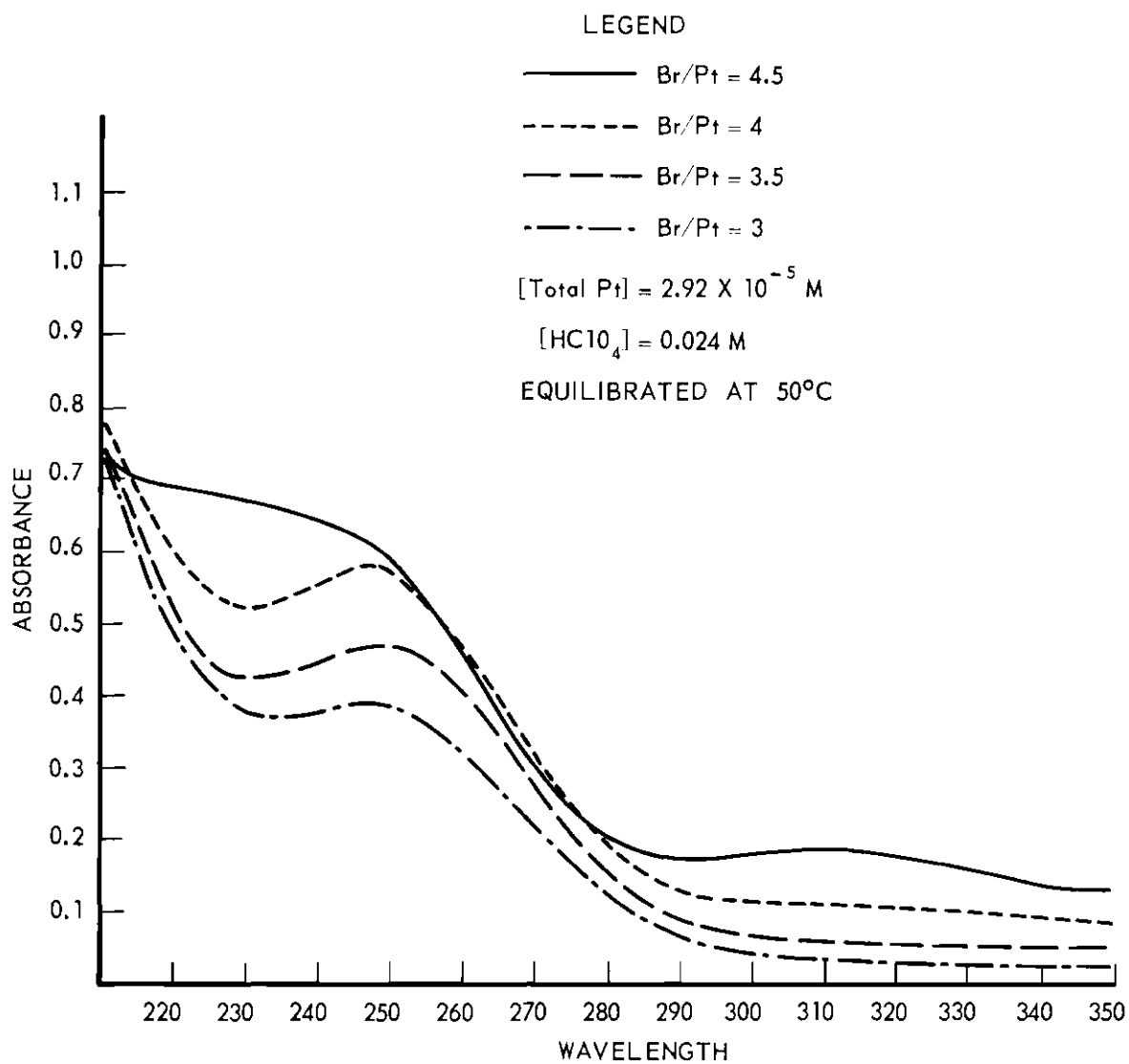


Figure 9. Spectra of Solutions with Varying Br/Pt Ratios.

Two different samples of $\text{Na}_2\text{Pt}(\text{OH})_6$, one weighing 0.0922 grams and the other 0.0999 grams, were taken. One sample was dissolved in 80 mls of 5M NaBr and 20 mls of concentrated HClO_4 . The other sample was dissolved in 20 mls of 5M NaBr, 60 mls of H_2O and 20 mls of concentrated HClO_4 . Both samples were equilibrated at 50°C . Aliquots of 10 mls were taken from each solution, diluted to 100 mls, and the spectra of the diluted solutions were measured on the DK spectrophotometer. The two spectra were identical within the limits of experimental error indicating that these solutions contain only one absorbing species, namely PtBr_6^- . The spectrum shows a large peak at $315 \text{ m}\mu$ with a definite shoulder at $360 \text{ m}\mu$, an absorbance minimum at $267 \text{ m}\mu$ and a very large peak at $225 \text{ m}\mu$.

Figure 10 shows a mole ratio plot of absorbancies at several selected wavelengths versus Br/Pt ratio. The plot indicates that the species $\text{PtBr}_4(\text{OH})_2^-$ enjoys a considerable degree of stability in solution while $\text{PtBr}_5(\text{OH})^-$ does not. Since isosbestic points are not present in all the curves, it would seem that at least one other species than PtBr_6^- and $\text{PtBr}_4(\text{OH})_2^-$ must be present in those solutions where $\text{Br/Pt} \leq 4.5$.

Those solutions where $\text{Br/Pt} \geq 5$ do show isosbestic points at $285 \text{ m}\mu$ and $240 \text{ m}\mu$ and it is reasonable to suppose that their spectra are composites of the spectrum of PtBr_6^- and the spectrum of $\text{PtBr}_4(\text{OH})_2^-$, since the latter species is stable according to the mole ratio plots.

By subtracting the known spectrum of PtBr_6^- from these composite spectra, it should, then, be possible to obtain the spectrum of the

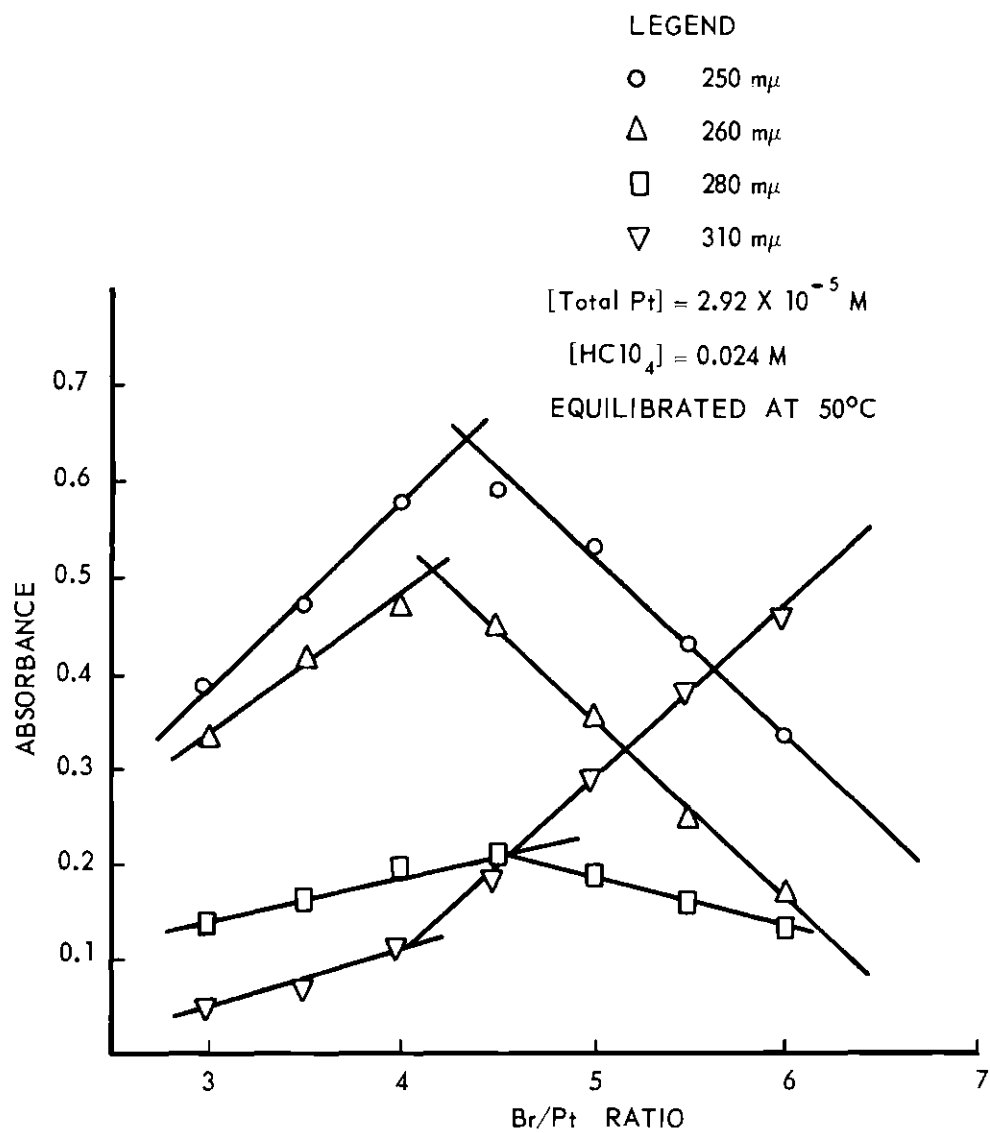


Figure 10. Mole Ratio Plots of Bromoplatinate Solutions.

putative $\text{PtBr}_4(\text{OH})_2^-$. The method is completely analogous to that used in the case of the chloro-hydroxo complexes, which was described in Chapter IV. First the concentration of PtBr_6^{2-} in each solution was calculated on the assumption that this ion was the only absorber at a wavelength of 315 $\text{m}\mu$. These concentrations were used in the graphical method to reconstruct the spectrum of $\text{PtBr}_4(\text{OH})_2^-$. This spectrum showed negative absorption values in the vicinity of 225 $\text{m}\mu$. Consequently, reconstruction was repeated using this wavelength as one at which only PtBr_6^{2-} absorbs. However, the concentration of PtBr_6^{2-} which was calculated for the solution where Br/Pt is 4.5, is forbidden by the known stoichiometry of this solution. The calculated concentrations of $0.97 \times 10^{-3} \text{ M}$ for PtBr_6^{2-} and $1.95 \times 10^{-3} \text{ M}$ for $\text{PtBr}_4(\text{OH})_2^-$ would require a $13.52 \times 10^{-3} \text{ M}$ concentration of bromide to satisfy the ligand requirements, while the actual bromide concentration of this solution is only $13.14 \times 10^{-3} \text{ M}$. Therefore, it became necessary to select some other means for estimating the concentrations of PtBr_6^{2-} in the solutions. This was done by assuming that the concentration of PtBr_6^{2-} in the solution where Br/Pt equals 4.5, is equal to the maximum concentration permitted by the stoichiometry, i.e., one fourth of the total platinum concentration. This assumption established a new line for the graphical method, as shown in Figure 11 for the wavelength of 225 $\text{m}\mu$. Use of the graphical method with this new base line enables the reconstruction of the spectrum of $\text{PtBr}_4(\text{OH})_2^-$ shown in Figure 12. The spectrum, which can be tentatively attributed to $\text{PtBr}_4(\text{OH})_2^-$ shows a maximum at 245 $\text{m}\mu$.

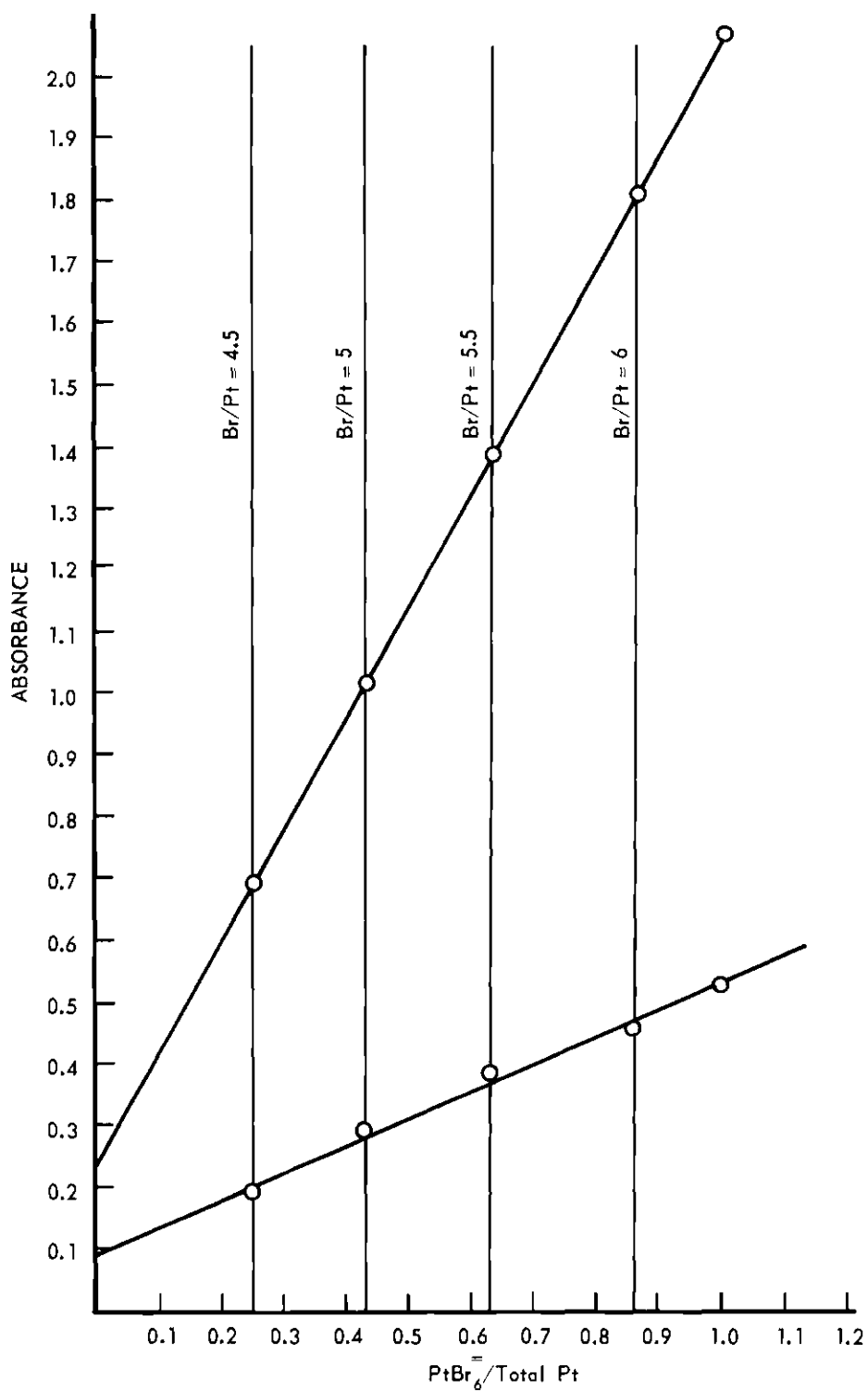


Figure 11. Absorbance Composition Plot for $\text{PtBr}_6\text{-PtBr}_4(\text{OH})_2^{\equiv}$ Solutions. Base Line at 225 μ .

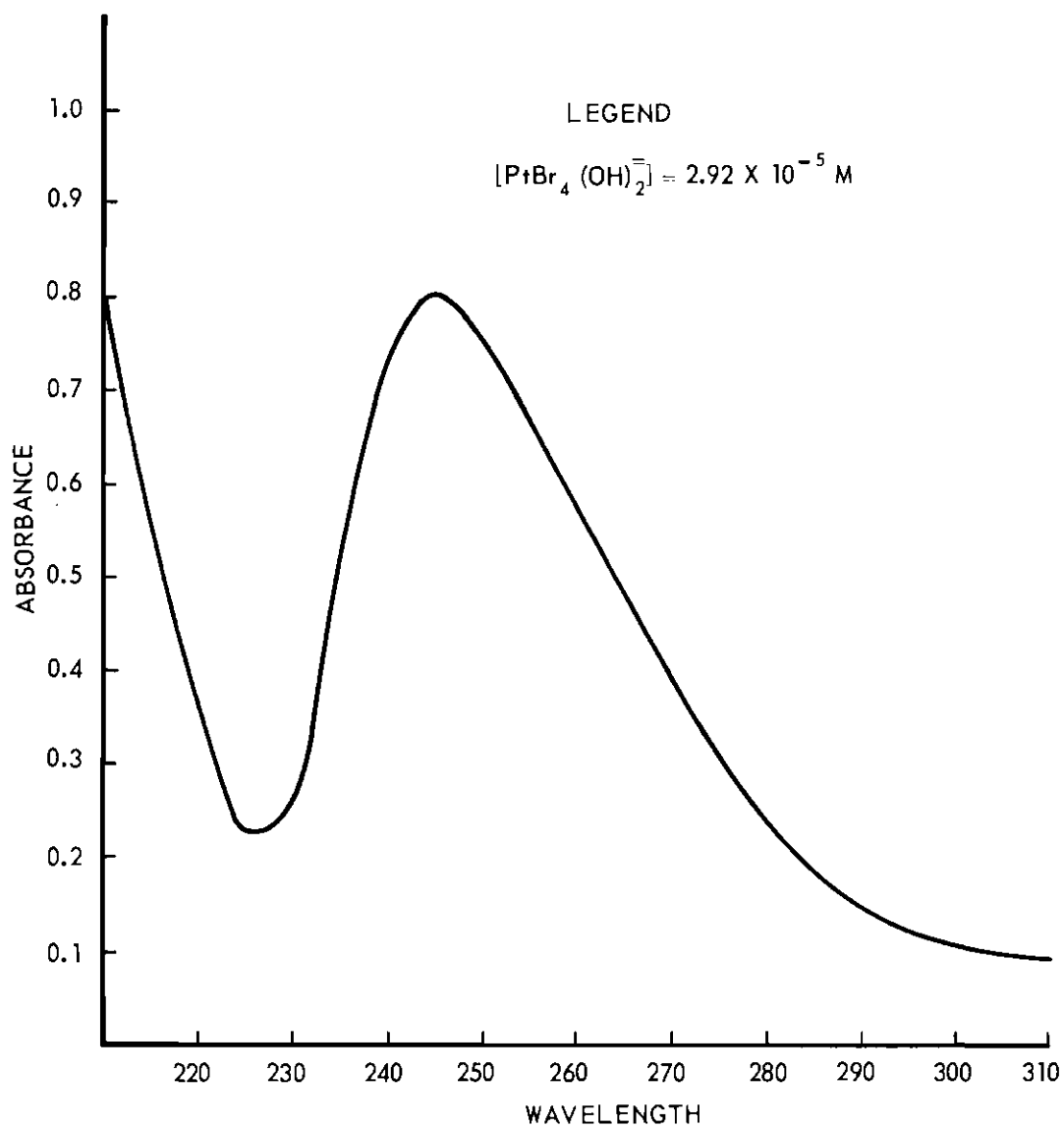
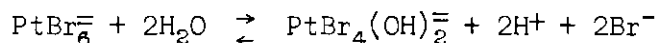


Figure 12. Spectrum of $\text{PtBr}_4(\text{OH})_2^-$.

It should, then, be possible to use the data to calculate an equilibrium constant for the equilibrium:



which is described by the expression:

$$K_e = \frac{[\text{PtBr}_4(\text{OH})_2^-] [\text{Br}^-]^2 [\text{H}^+]^2}{[\text{PtBr}_6^-]} .$$

Since, in the case of the solutions used to establish the mole ratio plots, the concentration of water is essentially constant, it has been incorporated with K_e . The data necessary for calculating K_e are tabulated below. The values of $[\text{PtBr}_6^-]$ were obtained by comparing the absorbancies at 225 μ with Figure 11, which relates absorbance with composition. Values of $[\text{PtBr}_4(\text{OH})_2^-]$ were obtained by difference and values of $[\text{Br}^-]$ by calculation from the values of the concentrations of the platinum species and the known amounts of total bromide in various solutions.

Br/Pt	$[\text{PtBr}_6^-]$ $\times 10^3$	$[\text{PtBr}_4(\text{OH})_2^-]$ $\times 10^3$	$[\text{Br}^-]$ $\times 10^3$	$[\text{H}^+]$	K_e $\times 10^7$
6	2.51	0.41	0.82	2.40	6.3
5.5	1.84	1.08	0.70	2.40	16.6
5	1.25	1.67	0.42	2.40	13.6

These constants are, of course, those which define the extent of hydrolysis at 50°C. The agreement among the values is reasonably good and indicates that the postulated equilibrium and the assignment of the spectrum in Figure 12 to $\text{PtBr}_4(\text{OH})_2^-$ are correct.

Hydrolysis of the Hexabromoplatinate Ion

As has been pointed out, solutions of bromoplatinate, when diluted for the purpose of recording spectra, were quite prone to hydrolyze. Errors arising from this hydrolysis could be held small by recording the spectra as swiftly as possible. This hydrolysis, in itself, however, was productive of further data concerning the spectrum of $\text{PtBr}_4(\text{OH})_2^-$.

A solution containing platinum and bromide in one to six ratio was made up and allowed to equilibrate as usual. This solution had a total platinum concentration of 2.92×10^{-3} M and a perchloric acid concentration of 2.40 M. A one ml aliquot was then diluted to 100 mls and the spectrum of the resulting solution was recorded at various time intervals until the rate of hydrolysis slowed to such an extent that any change in the spectrum fell within the experimental error involved in recording it. The series of spectra thus obtained is shown in Figure 13.* The most noteworthy feature of the spectra is the appearance of three well-defined isosbestic points at 214 $\text{m}\mu$, 242 $\text{m}\mu$ and 284 $\text{m}\mu$ which correspond closely to the isosbestic points discovered in the spectra of solutions of varying concentrations of bromide ion where the Br/Pt ratio is 4.5 or

*A very similar experiment and series of spectra are reported by G. Schmidt and W. Herr (16). In their experiment K_2PtBr_6 was dissolved in 0.5 M H_2SO_4 , and the absorption spectrum measured from 250 $\text{m}\mu$ to 500 $\text{m}\mu$. The spectra were merely reported, and no conclusions were drawn.

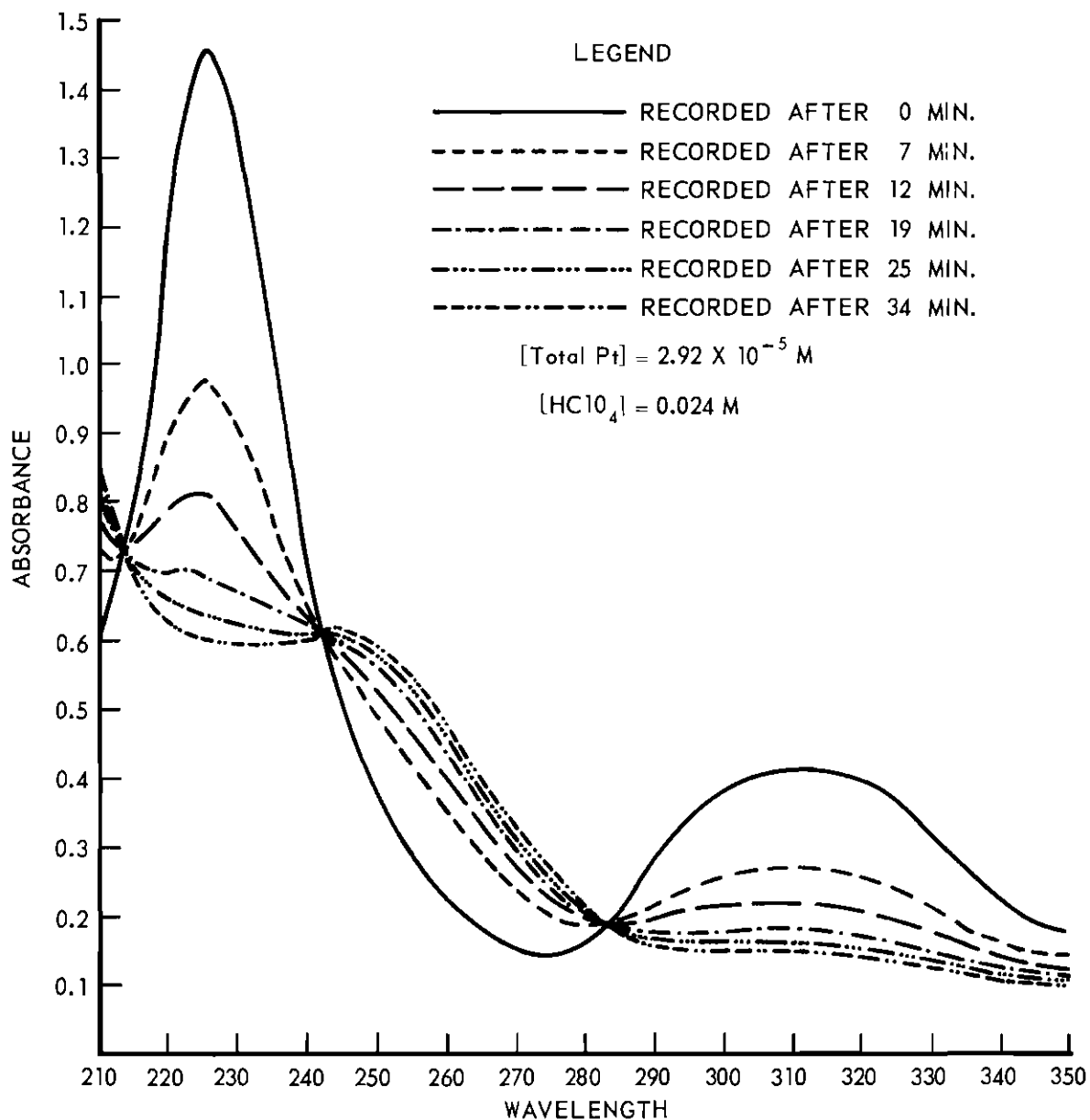


Figure 13. Hydrolysis of $\text{PtBr}_6^{=}$.

greater. As before, it can be concluded that these solutions contain $\text{PtBr}_6^{=}$ and one other species which is probably $\text{PtBr}_4(\text{OH})_2^{=}$. Therefore, a comparison of these spectra of a solution undergoing hydrolysis with the spectrum of a solution having $\text{PtBr}_6^{=}$ as the only absorbing species, makes possible the reconstruction of the spectrum of the other absorbing species present in the hydrolyzing solution. This was done using the methods already described and the resulting reconstructed spectrum is shown in Figure 14. Figure 14 also shows the spectrum obtained from the solutions having a Br/Pt ratio of 4.5 or more. Comparison shows some differences. The peak is shifted to longer wavelengths and the absorbance is less for the spectrum obtained from the hydrolyzing $\text{PtBr}_6^{=}$. This difference probably demonstrates a small contribution to the absorbance by a third species in the solutions used for the mole ratio method. However, there is sufficient agreement between the spectra that it can reasonably be assumed that Figure 14 represents the spectrum of $\text{PtBr}_4(\text{OH})_2^{=}$, keeping in mind the evidence of the mole ratio plots. The evidence thus suggests that hydrolysis of $\text{PtBr}_6^{=}$ proceeds to an equilibrium with $\text{PtBr}_4(\text{OH})_2^{=}$ under these conditions.

Archibald and Gale (14) examined the hydrolysis of K_2PtBr_6 at 20°C by dissolving the salt in water and following the reaction by titrating the acid formed. In their experiments the initial $\text{PtBr}_6^{=}$ concentration varied from 5.0×10^{-4} M to 1.00×10^{-2} M. In the absence of light observable hydrolysis did not occur until after several days. When the solutions were irradiated with a 300 watt lamp they obtained curves like that depicted below when solution acidity was plotted versus

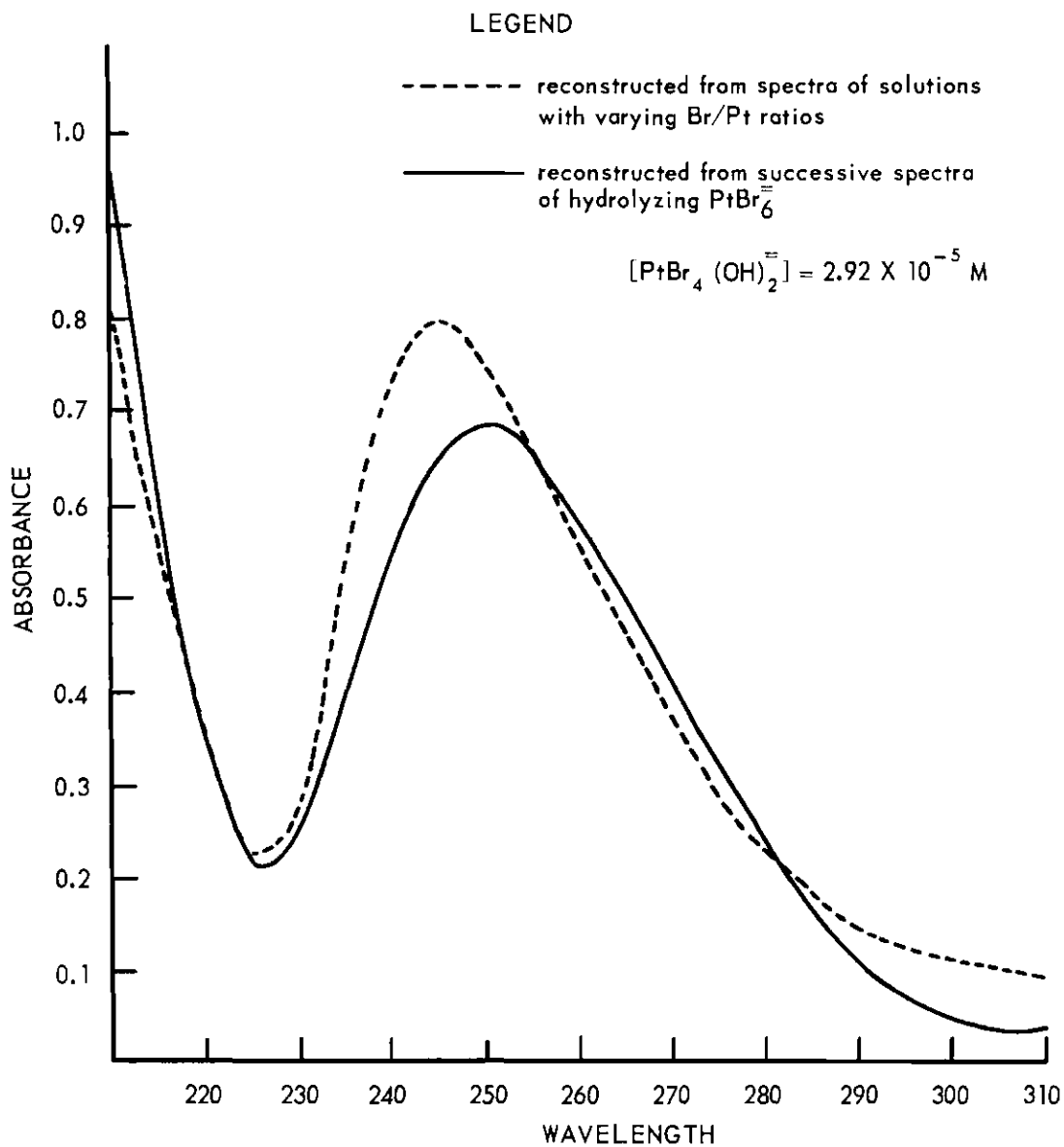
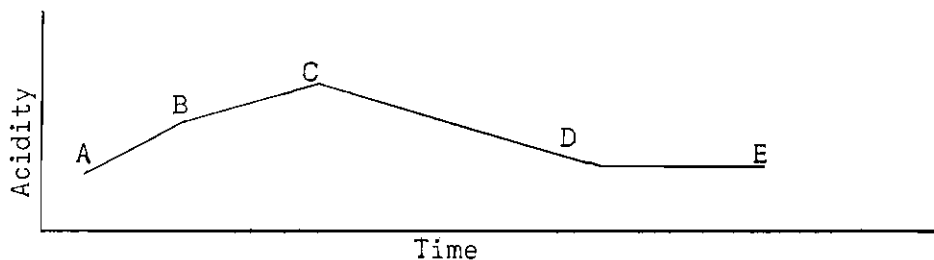


Figure 14. Spectra of $\text{PtBr}_4(\text{OH})_2^{2-}$.



time. In general the maxima occurred at 400-500 minutes. A maximum is observed only in a light catalyzed reaction. Somewhat similar observations were made in the course of the present work. Figure 15 shows the absorbancies of five solutions of H_2PtBr_6 plotted versus time. All the solutions were initially $5.43 \times 10^{-5} \text{ M}$ in PtBr_6^- and $2.5 \times 10^{-3} \text{ M}$ in NaBr . Curve number four illustrates the hydrolysis of a solution prepared and kept in red light. The typical minimum is not shown. All the other solutions were light catalyzed. The rates vary considerably, perhaps due to variations in temperature and light since the solutions were prepared on different days.

The solution whose hydrolysis is represented by the spectra of Figure 13 does not, however, show a maximum in the extent of hydrolysis but proceeds steadily to the equilibrium value. This particular solution was exposed to ordinary light throughout the hydrolysis, so that the lack of a maximum must be ascribed to some other cause. That which immediately comes to mind is acid catalysis during some stage of the hydrolysis, since this solution was 0.024 M in HClO_4 , while the solutions of Archibald and Gale, as well as the solutions of Figure 15, contained no acid except that generated by the reaction.

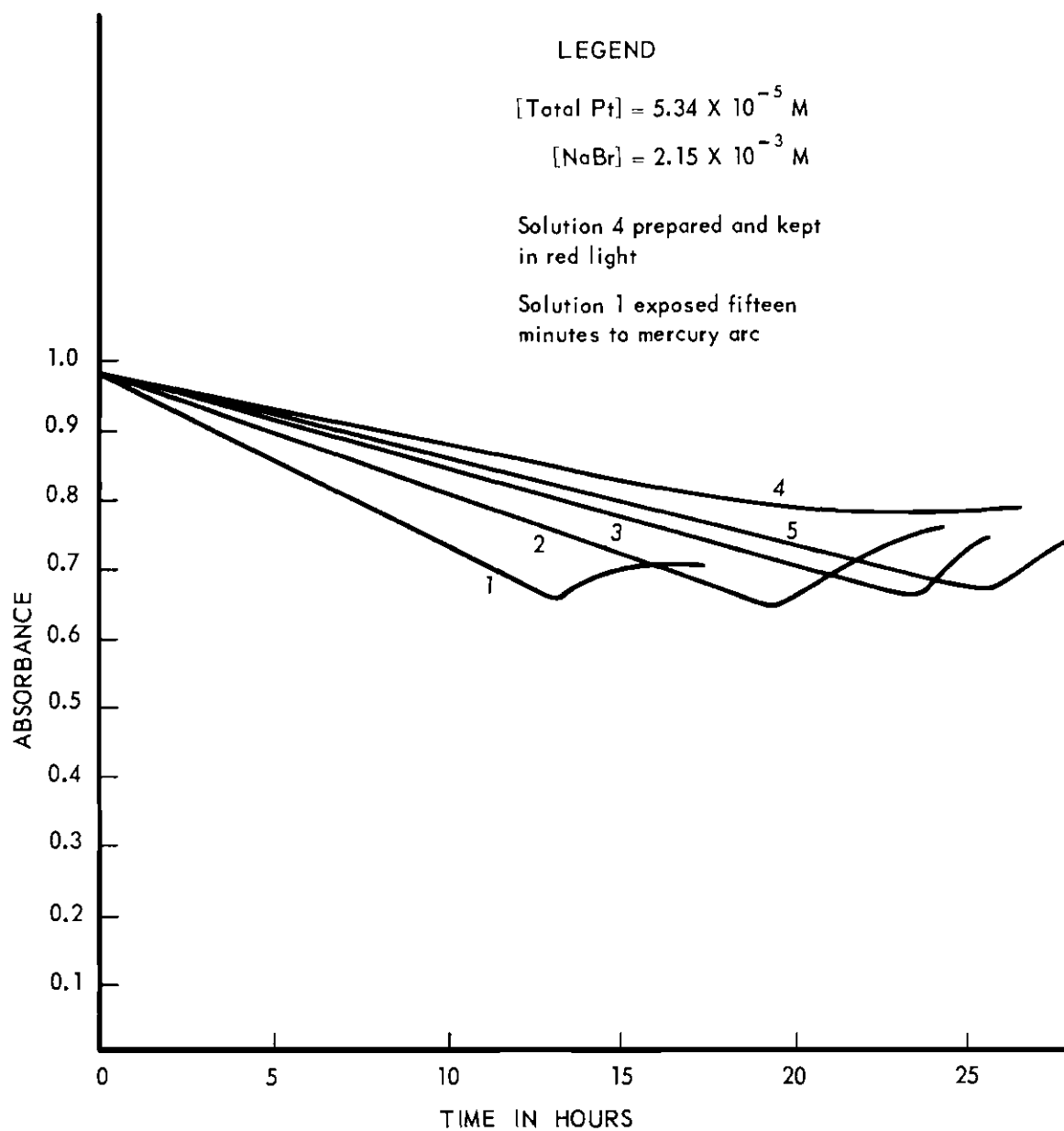
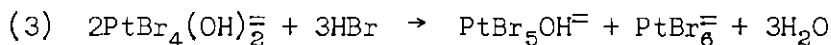
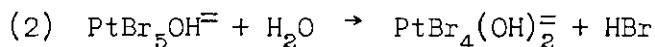
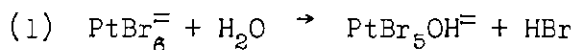


Figure 15. Absorbance Variation of $\text{PtBr}_6^=$ with Time at 312 mμ.

Archibald and Gale explained their curves by postulating the following series of reaction:



where (2) is considered responsible for the maximum at C. In the light of the present work there is no evidence for the presence of $\text{PtBr}_5(\text{OH})^{=-}$. Further evidence on this point can be obtained by treating their equilibria data in the same way as was done earlier for the chloro system. The only data from the present work which would be fairly comparable would be that inferred from the completely hydrolyzed solution of $\text{PtBr}_6^{=2-}$, which has reached equilibrium at room temperature. By use of the equilibrium absorbance at 225 $\text{m}\mu$ from Figure 13, and the composition-absorbance curve of Figure 11, values of K_5 , K_4 and K_3 can be calculated. The results of this comparison are as follows:

Archibald and Gale (14)

Initial $\text{K}_2\text{PtBr}_6^{=2-}$ Concentration	HBr Concentration at Equilibrium	$K_5 \times 10^6$	$K_4 \times 10^{12}$	$K_3 \times 10^{18}$
$10 \times 10^{-4} \text{ M}$	$1.10 \times 10^{-4} \text{ M}$	-	1.8	1.0
$25 \times 10^{-4} \text{ M}$	$1.60 \times 10^{-4} \text{ M}$	2.5	1.5	1.7
$50 \times 10^{-4} \text{ M}$	$1.88 \times 10^{-4} \text{ M}$	1.8	2.3	4.7
$100 \times 10^{-4} \text{ M}$	$2.61 \times 10^{-4} \text{ M}$	2.4	6.8	30
From Spectral Data		2.3	5.3	20

On the basis of the trends in the values of the K 's, $\text{PtBr}_3(\text{OH})_3^-$ can be eliminated from consideration as the hydrolysis product, but no choice is possible between $\text{PtBr}_5(\text{OH})^-$ and $\text{PtBr}_4(\text{OH})_2^-$. Since the mole ratio plot gives evidence of $\text{PtBr}_4(\text{OH})_2^-$ but not of $\text{PtBr}_5(\text{OH})^-$, the former is believed to be the product. The reconstructed spectrum of Figure 14 is thus attributed to $\text{PtBr}_4(\text{OH})_2^-$. The differences in the two spectra of Figure 4 may be within the experimental error of the methods used for reconstruction, or may result from the fact that $\text{PtBr}_4(\text{OH})_2^-$ has two isomeric forms, which may be present in varying fractions in the two experiments.

One unexplained difficulty remains. Comparing the value of K_e at 50°C with K_4 , it is seen that K_e has a value of about 1×10^{-6} at 50°C (in 2.40 M HClO_4) as compared to a value of about 5×10^{-12} at room temperature (in 0.024 M HClO_4). This seems to be an unusually large difference, even though both temperature and activity differences exist, especially since the chloro system shows only a small difference for corresponding conditions.

A kinetic expression can be derived for the hydrolysis described by the spectra of Figure 13, by comparing the time elapsed with the concentrations of PtBr_6^- and $\text{PtBr}_4(\text{OH})_2^-$, the latter two data being calculated from the spectral absorption at 315 μ and the known total platinum concentration. Trials of various possibilities showed that only by treating the hydrolysis as a first order, reversible reaction could constancy of the velocity constants be obtained. The values obtained are as follows:

Time After Dilution	$k + k'/2.303$
7 minutes	$0.0452 \text{ minutes}^{-1}$
12	0.0467
19	0.0459
25	0.0453
34	0.0499

k and k' are, respectively, the velocity constants for the forward and reverse reactions. That the reverse reaction appears first order, rather than third order as would be expected from the molecularity, indicates that the contribution of k' to $(k + k')$ must be small.

The spectra of hydrolyzing PtBr_6^- , obtained by Schmidt and Herr (16) can be used to estimate a value for $k + k'/2.303$ for a solution of PtBr_6^- which is 0.5 M in H_2SO_4 . This value turns out to be 0.06 min^{-1} which is close to the values obtained during this investigation.

The Solution Behavior of Platinum Tetrabromide

Solid platinum tetrabromide was prepared by the method described in Chapter III. The prepared compound was assayed for platinum and bromine to establish its composition. The compound was stored in a desiccator over concentrated sulfuric acid because of its extreme hygroscopicity.

An unknown amount of PtBr_4 was added to 100 mls of water. The compound dissolved quickly and its spectrum was measured immediately on the Beckman DK spectrophotometer.

Successive spectra of the same solution were recorded at short intervals. The spectra thus obtained displayed large peaks at 315 $m\mu$ and 225 $m\mu$ as well as isosbestic points at 212 $m\mu$, 248 $m\mu$ and 277 $m\mu$. The isosbestic points were not well defined as compared with those shown by the successive spectra of hydrolyzing $\text{PtBr}_6^{=}$ and might better be described as isosbestic regions. These spectra are shown in Figure 16.

After the spectra were recorded, a portion of the solution was analyzed for total platinum concentration by adding it to a solution containing a large excess of bromide ions and perchlorate ions and measuring the absorption of the solution at 315 $m\mu$. By this means the total platinum concentration in the solution was found to be 7.5×10^{-5} M.

The peaks at 225 $m\mu$ and 315 $m\mu$ are almost certain proof that one of the species present in the solution of PtBr_4 is $\text{PtBr}_6^{=}$. Furthermore, its appearance in the solution is immediate upon the dissolution of PtBr_4 . The correspondence of the isosbestic points in these spectra with the points found in the spectra of solutions with varying Br/Pt ratios also demonstrates the presence of $\text{PtBr}_4(\text{OH})_2^{=}$. If $\text{PtBr}_6^{=}$ and $\text{PtBr}_4(\text{OH})_2^{=}$ are assumed to be the only absorbing species at 315 $m\mu$, then, it can be calculated from the absorbance shown by the initial spectrum of the dissolved PtBr_4 that exactly half of the platinum is initially in the form of $\text{PtBr}_6^{=}$. The succeeding spectra record the hydrolysis of this $\text{PtBr}_6^{=}$ to $\text{PtBr}_4(\text{OH})_2^{=}$. Therefore, PtBr_4 , upon dissolution, breaks up into $\text{PtBr}_6^{=}$ and some other ion. It is reasonable to assume that the structure established by M. Falqui (48), for PtCl_4 , also holds true for PtBr_4 . As in the case of PtCl_4 , it is

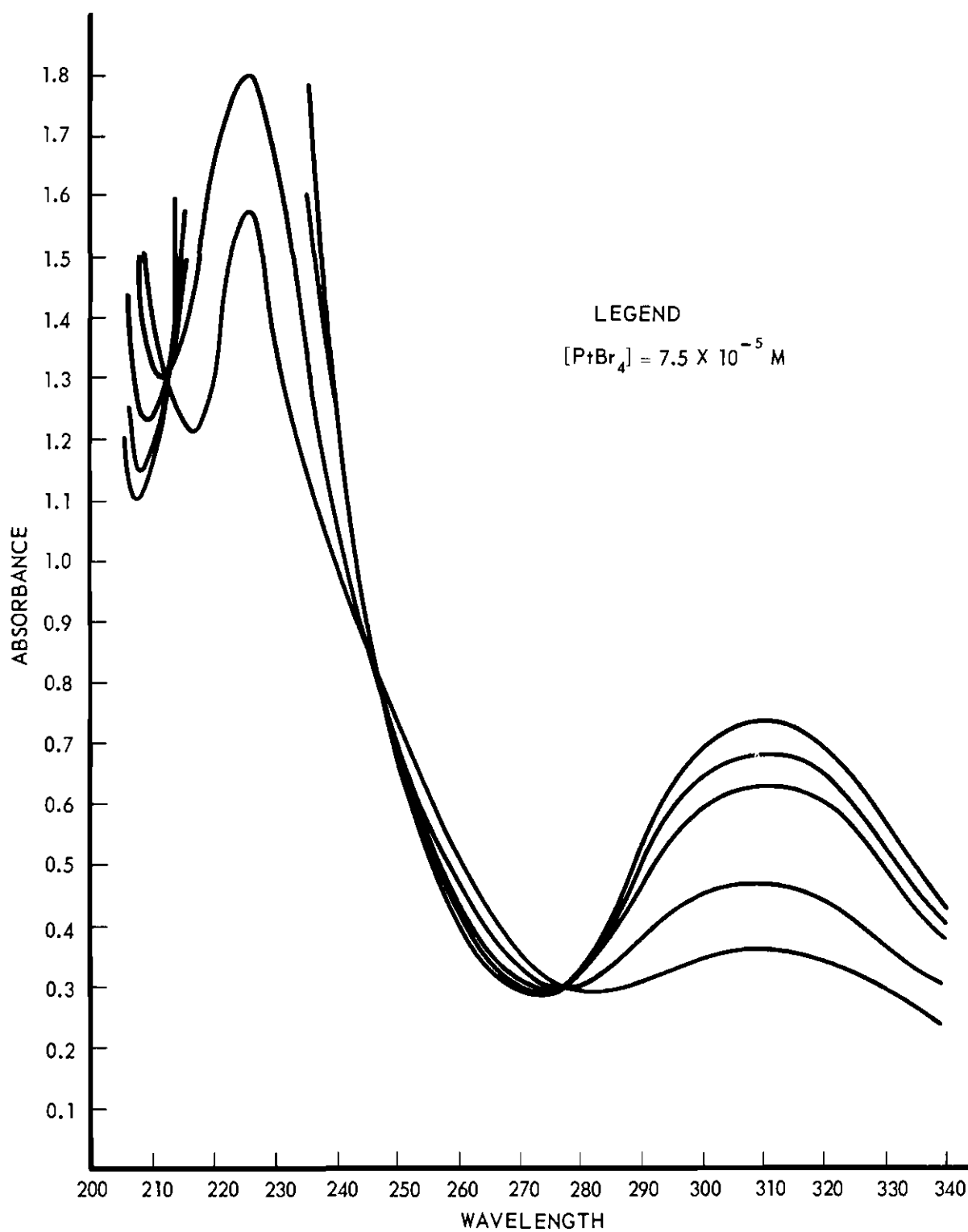


Figure 16. Hydrolysis of PtBr_4 Solution.

not readily discernible how this structure would break up to yield $\text{PtBr}_6^{=}$, but whatever the dissolution reaction is, it leads to the appearance of half the platinum in the form of $\text{PtBr}_6^{=}$. In any event, it appears that the spectra obtained by dissolving PtBr_4 in water can be explained by postulating a primary decomposition into $\text{PtBr}_6^{=}$, and some other unknown species, followed by hydrolysis of the $\text{PtBr}_6^{=}$ to form $\text{PtBr}_4(\text{OH})_2^{=}$.

Any differences, such as the shift of isosbestic points, then, between the spectra of hydrolyzing PtBr_4 and the spectra of hydrolyzing $\text{PtBr}_6^{=}$ must be due to the presence of a third species in the former case and/or the presence of HClO_4 in the latter case. There are other differences between the two cases. With PtBr_4 , the rate of hydrolysis is much slower and the kinetics do not indicate reversibility as they do in the case of $\text{PtBr}_6^{=}$. Both hydrolyses are first order. The table gives the rate constants for the hydrolysis of PtBr_4 . The average value of k is 0.0166 min^{-1} . For comparison, $k + k'$, the overall rate of reaction for the hy-

Time	$k/2.303$
3 minutes	$0.0073 \text{ minutes}^{-1}$
9	0.0067
24	0.0081
42	0.0075
62	0.0062

drolysis of $\text{PtBr}_6^{=}$ is 0.1070 min^{-1} . Since the hydrolysis of $\text{PtBr}_6^{=}$ is undoubtedly the rate-determining step after the initial dissolution of PtBr_4 , the

difference in rates is almost certainly due to the difference in acidities. The evidence is strong, therefore, that the hydrolysis of PtBr_6^- is acid catalyzed. It should be noted that solutions of PtBr_4 in 0.24 M HClO_4 do not display isosbestic points.

Solutions of Bromo-Hydroxo Platinates in Equilibrium
with Solid Platinic Acid

It will be recalled that, in the experiment designed to obtain spectra of bromoplatinate solutions with varying mole ratios of bromide to platinum, precipitates of $\text{H}_2\text{Pt}(\text{OH})_6$ developed in those solutions where the bromide to platinum ratio was equal to or less than 2.5. The mother liquors were assayed for total platinum content by adding to them a large excess of bromide ions and measuring the spectra of the solutions thus obtained. The figures obtained in this manner are given below:

Exp. No.	Original Br/Pt	Bromine in Mother Liquor	Platinum in Mother Liquor
1	0	0	0.127×10^{-3}
2	0.5	1.46×10^{-3}	0.910×10^{-3}
3	1	2.92×10^{-3}	1.515×10^{-3}
4	1.5	4.38×10^{-3}	2.081×10^{-3}
5	2	5.84×10^{-3}	2.400×10^{-3}
6	2.5	7.30×10^{-3}	2.900×10^{-3}

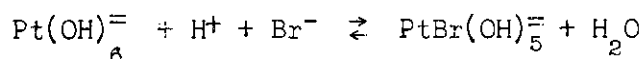
Since a precipitate of $\text{H}_2\text{Pt}(\text{OH})_6$ was in contact with each of the mother liquors, the concentration of $\text{Pt}(\text{OH})_6^-$ in the mother liquors

is known to be constant and equal to 0.127×10^{-3} M. The concentration of platinum species containing bromine can then be obtained by subtracting this value from the values for the total platinum content of the various mother liquors. The concentrations of brominated platinum species thus obtained are:

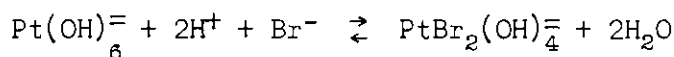
Exp. No.	B Total Bromine	A Brominated Platinum	Ratio = B/A
2	1.46×10^{-3}	0.783×10^{-3}	1.84
3	2.92×10^{-3}	1.388×10^{-3}	2.10
4	4.38×10^{-3}	1.954×10^{-3}	2.24
5	5.84×10^{-3}	2.273×10^{-3}	2.57
6	7.30×10^{-3}	2.773×10^{-3}	2.64

Since the total bromine contains some free bromide, the ratio B/A provides an upper limit to the average number of bromides bound per platinum. The data suggest that $\text{PtBr}_2(\text{OH})_4^=$ is an important species in these solutions, and that $\text{PtBr}(\text{OH})_5^=$ must also be present in Experiment 2.

Further insight into the composition of these solutions can be obtained by making some assumptions which can be tested experimentally. First, assume that $\text{PtBr}_2(\text{OH})_4^=$ and $\text{PtBr}(\text{OH})_5^=$ are the only brominated species involved. The equilibria are:



and



with equilibrium constants

$$K_1 = \frac{[\text{PtBr}(\text{OH})_5^{=1-}]}{[\text{Pt}(\text{OH})_6^{=2-}] [\text{Br}^-]} ,$$

$$K_2 = \frac{[\text{PtBr}_2(\text{OH})_4^{=2-}]}{[\text{Pt}(\text{OH})_6^{=2-}] [\text{Br}^-]^2} .$$

Let C_o = concentration of total platinum

and L_o = concentration of total bromide.

Thus $C_o = [\text{Pt}(\text{OH})_6^{=2-}] + [\text{PtBr}(\text{OH})_5^{=1-}] + [\text{PtBr}_2(\text{OH})_4^{=2-}]$

and $L_o = [\text{Br}^-] + [\text{PtBr}(\text{OH})_5^{=1-}] + 2[\text{Pt}(\text{OH})_4\text{Br}_2^{=2-}] .$

For convenience define:

$$F_1 = L_o - C_o + [\text{Pt}(\text{OH})_6^{=2-}]$$

$$F_2 = 2C_o - L_o - 2[\text{Pt}(\text{OH})_6^{=2-}]$$

$$P = K_1 [\text{Pt}(\text{OH})_6^{=2-}] - 1 .$$

From the equilibrium constants and defined quantities, algebraic manipulation gives

$$\frac{F_1}{F_2} = \frac{1}{P} + \frac{K_2 [\text{Pt}(\text{OH})_6^{=2-}]}{P^2} F_2 .$$

C_0 , L_0 , F_1 , and F_2 are known for each experiment and are tabulated below:

Exp. No.	C_0 $\times 10^3$	L_0 $\times 10^3$	F_1 $\times 10^3$	F_2 $\times 10^3$	F_1/F_2
1	0.127				
2	0.910	1.46	0.677	0.166	6.39
3	1.515	2.92	1.532	-0.144	-10.63
4	2.081	4.38	2.426	-0.472	- 5.13
5	2.400	5.84	3.567	-1.294	- 2.76
6	2.900	7.30	4.527	-1.754	- 2.54

Negative values of F_2 are physically meaningful, merely implying that $[\text{Br}^-] > [\text{PtBr}(\text{OH})_5^-]$.

A plot of F_1/F_2 versus F_2 provides a test of the assumptions. This plot is shown in Figure 17. Since the plot does not yield a straight line, the assumptions cannot be valid for all the solutions.

If the assumptions have any validity it will be in the experiments in which L_0 is the smallest. If the assumptions apply to Experiments 2 and 3, the straight line through the corresponding points can be used to yield the following conclusions: Since a line through the first two points of the plot has a Y-intercept of -1,

$$P = K_1[\text{Pt}(\text{OH})_6^-] - 1 \approx -1.$$

This shows that $K_1[\text{Pt}(\text{OH})_6^-]$ is much smaller than +1, and that $[\text{PtBr}(\text{OH})_5^-]$ must be small. If the first two points are assumed true,

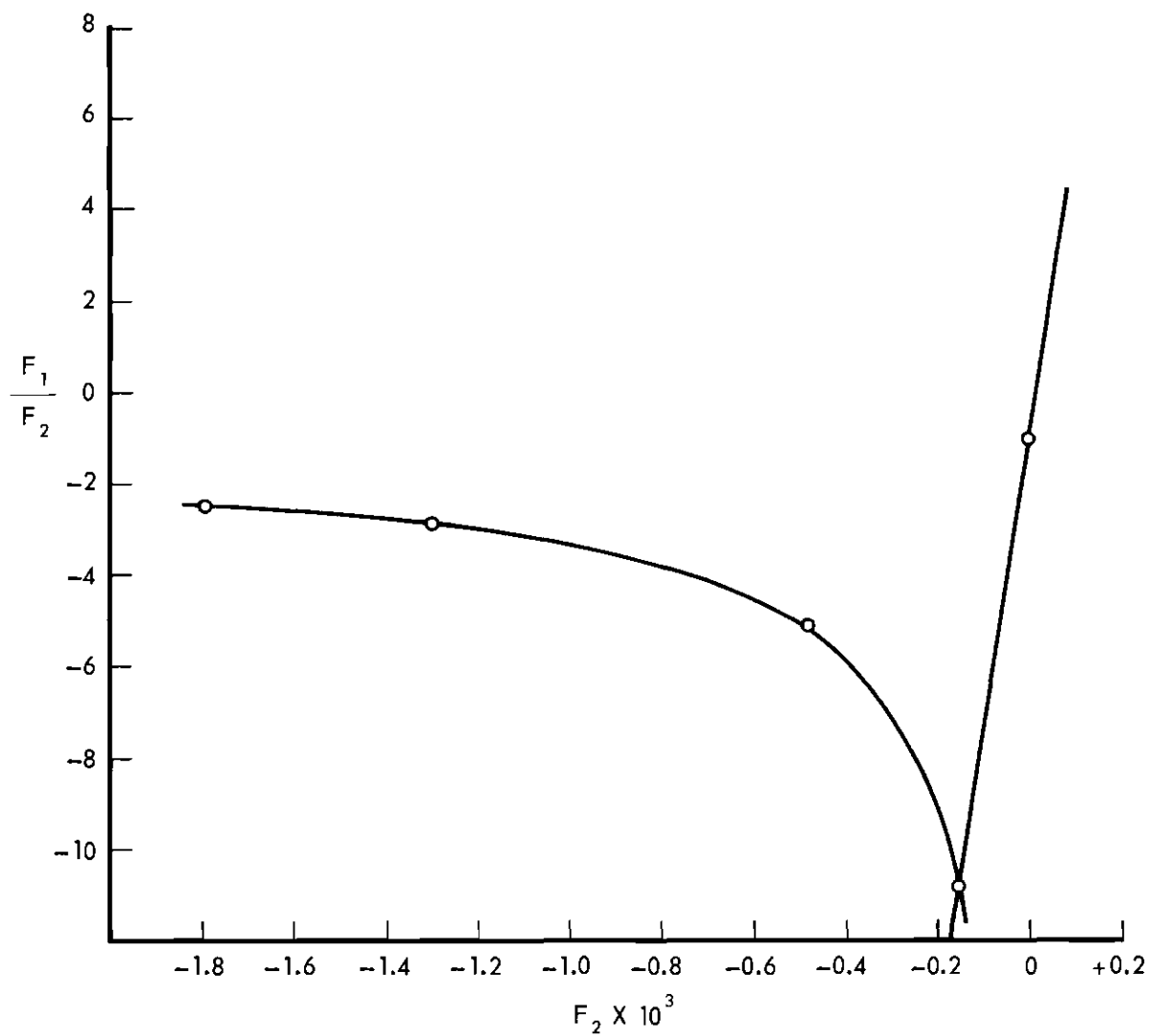


Figure 17. Test Plot for Low Br/Pt Equilibria.

then, from the slope, it is found that:

$$\frac{K_2[\text{Pt}(\text{OH})_6^-]}{P^2} = 68 \times 10^3 .$$

Therefore, if $P = -1$,

$$K_2 = 5.35 \times 10^8 .$$

Noting that $[\text{PtBr}(\text{OH})_5^-]$ is small, and that the mole ratio plots for both the chloro- and bromo-systems show no evidence of $\text{PtX}_3(\text{OH})_3^-$, it will next be assumed that only $\text{PtBr}_2(\text{OH})_4^-$ and $\text{PtBr}_4(\text{OH})_2^-$ are species of consequence, besides $\text{Pt}(\text{OH})_6^-$, in Experiments 3 - 6. The following expressions for their concentrations can be derived:

$$[\text{PtBr}_2(\text{OH})_4^-] = \frac{1}{2}\{4C_0 - L_0 - 4[\text{Pt}(\text{OH})_6^-] + [\text{Br}^-]\}$$

$$[\text{PtBr}_4(\text{OH})_2^-] = \frac{1}{2}\{L_0 - 2C_0 + 2[\text{Pt}(\text{OH})_6^-] - [\text{Br}^-]\} .$$

These expressions, together with the expression:

$$K_2 = \frac{[\text{PtBr}_2(\text{OH})_4^-]}{[\text{Pt}(\text{OH})_6^-] [\text{Br}^-]^2} = 5.35 \times 10^8$$

can be used to obtain the following values for $[\text{PtBr}_2(\text{OH})_4^-]$, $[\text{PtBr}_4(\text{OH})_2^-]$, and $[\text{Br}^-]$. K'_e is defined by the expression:

$$K'_e = \frac{[\text{PtBr}_4(\text{OH})_2^-]}{[\text{PtBr}_2(\text{OH})_4^-] [\text{Br}^-]^2} .$$

Exp. No.	$[\text{Br}^-]$ $\times 10^3$	$[\text{PtBr}_2(\text{OH})_4^{=}]$ $\times 10^3$	$[\text{PtBr}_4(\text{OH})_2^{=}]$ $\times 10^3$	K'_e $\times 10^{-8}$
2	0.115	0.894	-0.221	-0.187
3	0.143	1.388	0.00005	0.00018
4	0.159	1.798	0.157	0.035
5	0.159	1.705	0.568	0.132
6	0.171	1.981	0.791	0.137

The lack of constancy in K'_e demonstrates that the assumption that $\text{PtBr}_2(\text{OH})_4^{=}$ and $\text{PtBr}_4(\text{OH})_2^{=}$ are the only brominated species is invalid although it may be a good approximation for Experiments 5 and 6.

A similar treatment based on the assumption that $\text{PtBr}_2(\text{OH})_4^{=}$ and $\text{PtBr}_3(\text{OH})_3^{=}$ are the only brominated species leads to equilibrium constants which are not constant and must be rejected.

It can be concluded that no equilibrium, involving only two brominated platinum species, can satisfactorily describe all the solutions. Figure 18 shows the spectra of these solutions normalized to a total platinum concentration of 2.92×10^{-3} M, while Figure 19 shows the spectra of these same solutions normalized to a brominated platinum concentration of 2.92×10^{-3} M. It would appear from these spectra that the solution of Experiment 2 is quite different from the others. It is to be noted that the analyses for total Pt and total Br of this solution demand that some less brominated species than $\text{PtBr}_2(\text{OH})_4^{=}$ must be present. It is likely that the solutions of Experiments 5 and 6 can be adequately represented by an equilibrium among the three species,

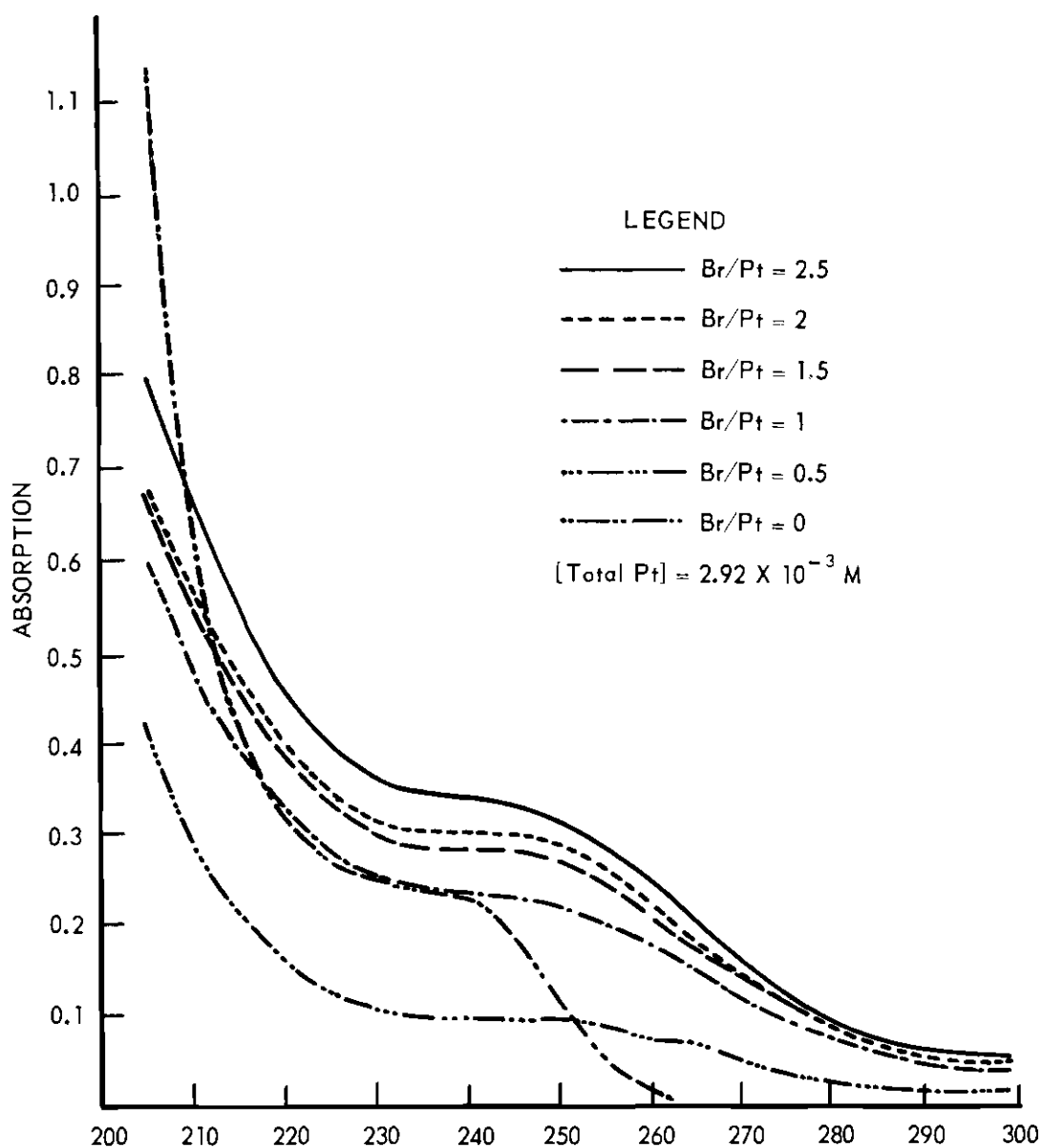


Figure 18. Spectra of Mother Liquors Normalized to Constant Pt Content.

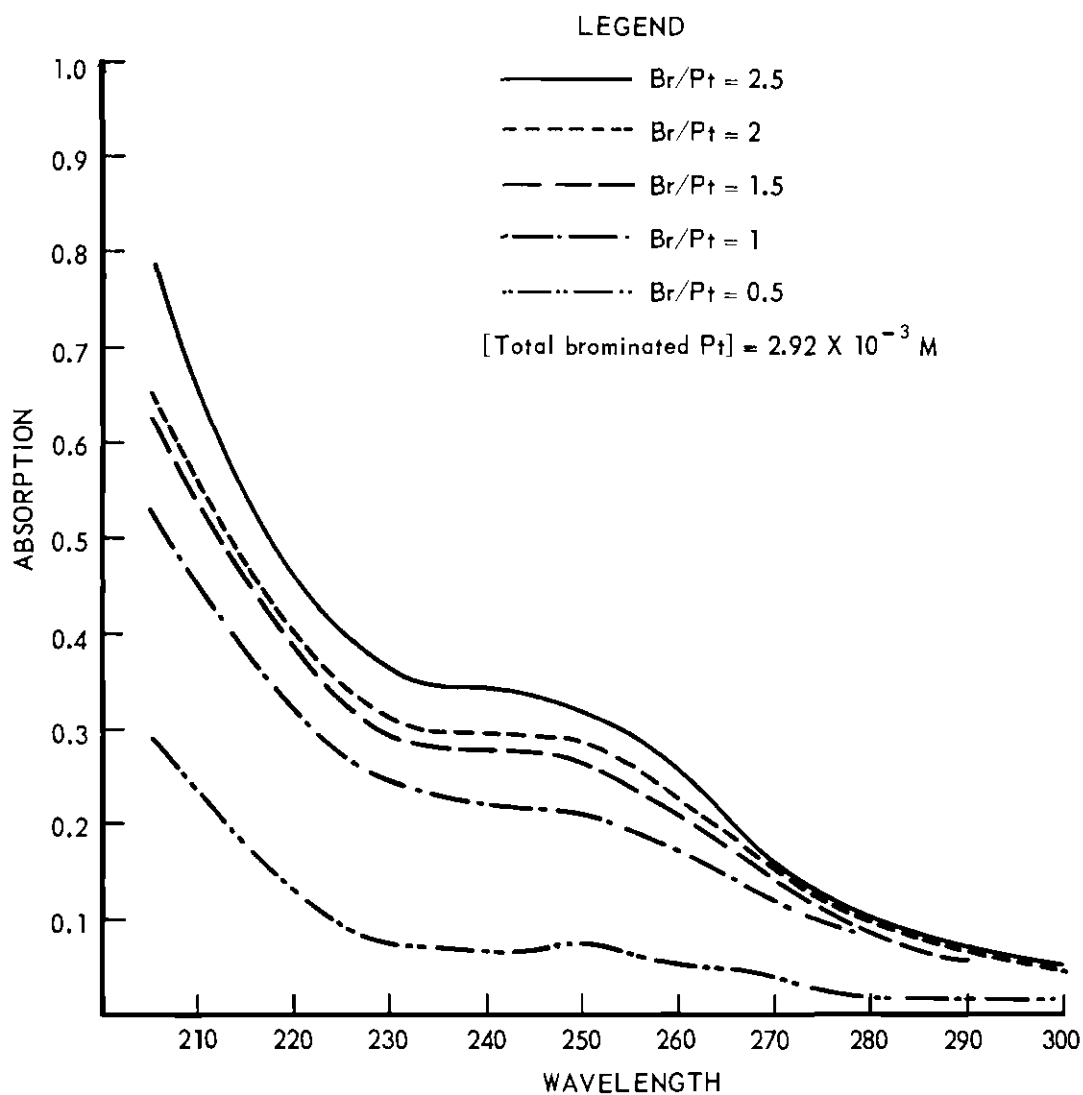


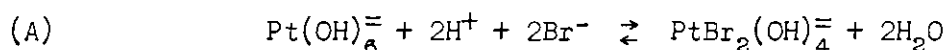
Figure 19. Spectra of Mother Liquors Normalized to Constant Brominated Pt Content.

$\text{Pt}(\text{OH})_6^{=}$, $\text{PtBr}_2(\text{OH})_4^{=}$ and $\text{PtBr}_4(\text{OH})_2^{=}$; but the solutions of Experiments 3 and 4 are more complex and it is possible that $\text{PtBr}_3(\text{OH})_3^{=}$ may be significant. However, there is no simple way to test this hypothesis.

The value of K_2 , 5.35×10^8 , which was calculated from the straight line of Figure 17, is that which is defined by the expression:

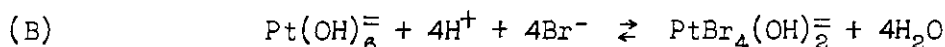
$$K_2 = \frac{[\text{PtBr}_2(\text{OH})_4^{=}]}{[\text{Pt}(\text{OH})_6^{=}] [\text{Br}^-]^2}.$$

Since the acid concentration of all the solutions was 2.40 M, then the equilibrium constant, K_A , for the following equation can be calculated:



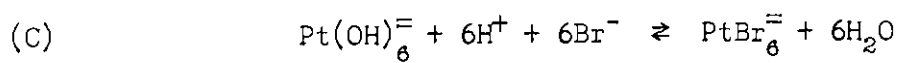
$$K_A = \frac{[\text{PtBr}_2(\text{OH})_4^{=}]}{[\text{Pt}(\text{OH})_6^{=}] [\text{H}^+]^2 [\text{Br}^-]^2} = \frac{5.35(10^8)}{5.76} = 9.3 \times 10^7.$$

K_A and the values of K'_e for Experiments 5 and 6, as defined in page 71, can then be used to calculate a value of K_B for this equation:



$$K_B = \frac{[\text{PtBr}_4(\text{OH})_2^{=}]}{[\text{Pt}(\text{OH})_6^{=}] [\text{H}^+]^4 [\text{Br}^-]^4} = \frac{K_A K'_e}{[\text{H}^+]^2} = 2.2 \times 10^{14}.$$

K_B and the values of K_e , as defined on page 53, can be used to calculate a value of K_C for the equation:



$$K_C = \frac{[\text{PtBr}_6^{=-}]}{[\text{Pt}(\text{OH})_6^{=+}] [\text{H}^+]^6 [\text{Br}^-]^6} = \frac{K_B}{K_e [\text{H}^+]^2} = 1.8 \times 10^{17}.$$

CHAPTER VI

MISCELLANEOUS OBSERVATIONS

During the course of this work some few miscellaneous data were gathered which, while not particularly germane to the primary project, are of sufficient interest to warrant recording.

Some of the sodium platinate, $\text{Na}_2\text{Pt}(\text{OH})_6$ prepared as described in Chapter II, was dissolved in water and the pH of the resulting solution was measured. A solution which was 4.34×10^{-3} M in $\text{Na}_2\text{Pt}(\text{OH})_6$ had a pH of 9.92. If it be assumed that the second dissociation constant of $\text{H}_2\text{Pt}(\text{OH})_6$ is much smaller than the first, then the former is equal to 6.25×10^{-7} and the hydrolytic constant of $\text{Na}_2\text{Pt}(\text{OH})_6$ is equal to 1.61×10^{-8} .

In the work with solutions of low Br/Pt ratios, it was demonstrated that the mother liquors in contact with solid $\text{H}_2\text{Pt}(\text{OH})_6$ were 0.127×10^{-3} M in $\text{Pt}(\text{OH})_6^-$. Since these same mother liquors were 2.4 M in HClO_4 it follows that the solubility product constant of platinic acid is about 7.3×10^{-4} .

In an attempt to find a nonaqueous solvent for solid $\text{H}_2\text{PtBr}_6 \cdot 5\text{H}_2\text{O}$ the following facts were observed. Alcohol, ether and dioxane reduce the Pt(IV) to Pt(II) and, eventually, to Pt (0). The compound is insoluble in carbon disulfide, carbon tetrachloride, nitromethane and dimethyl formamide. Concentrated sulfuric acid and glacial acetic acid react with H_2PtBr_6 to give yellow insoluble compounds.

CHAPTER VII

CONCLUSIONS

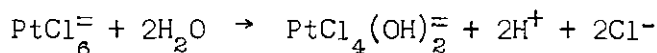
The hydrolysis reactions of the chloro- and bromo-platinates are light catalyzed. In each case the composition of the solution at equilibrium is the same whether equilibrium is obtained photochemically or by way of a thermal mechanism in the dark. The hydrolysis of hexabromoplatinate to tetrabromoplatinate is catalyzed by acid, in addition to the catalysis by light. At an acid concentration of 2.40 M the kinetics of hydrolysis show a first-order behavior without appreciable complication by the reverse reaction. The apparent first-order rate constant for the hydrolysis is 0.017 min^{-1} .

Application of the mole ratio method to both the chloro- and bromo- systems indicates that the anions of the types PtX_6^- , $\text{PtX}_4(\text{OH})_2^-$, and $\text{PtX}_2(\text{OH})_4^-$ are stable in aqueous solution. The solubility studies show that $\text{PtBr}(\text{OH})_5^-$ is not a species of consequence in solutions with low Br/Pt ratios. Such solutions probably contain $\text{PtBr}_4(\text{OH})_2^-$, $\text{PtBr}_2(\text{OH})_4^-$, $\text{Pt}(\text{OH})_6^-$, and, perhaps, $\text{PtBr}_3(\text{OH})_3^-$.

It has been possible to reconstruct the spectra of $\text{PtCl}_4(\text{OH})_2^-$ and $\text{PtBr}_4(\text{OH})_2^-$. The former is shown in Figure 6; the latter in Figure 14.

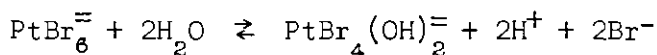
Solid PtCl_4 reacts with water in such a way that half of the platinum is found in the form of PtCl_6^- . PtBr_4 reacts in a completely analogous fashion.

At constant hydrogen ion concentration, the equilibrium constant for the reaction:



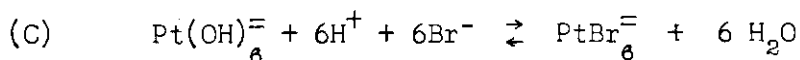
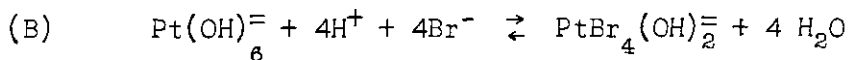
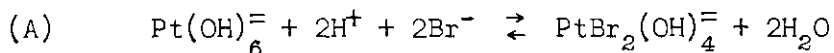
is approximately 1.5×10^{-7} at 50°C , and with platinate concentrations of 10^{-4} M.

At constant hydrogen ion concentration, the equilibrium constant for the reaction:



is approximately 2×10^{-7} at 50°C , and with platinate concentrations of 10^{-3} M. It is approximately 1×10^{-8} at 20°C , and with platinate concentrations of 10^{-5} M.

Equilibrium constants have been estimated for the following reactions:



$$K_A = 9.3 \times 10^7$$

$$K_B = 2.2 \times 10^{14}$$

$$K_C = 1.8 \times 10^{17} .$$

The solubility product constant of platinic acid is approximately 7.3×10^{-4} . The second dissociation constant for the acid is about 6.3×10^{-7} .

The hydrolytic constant of $\text{Na}_2\text{Pt}(\text{OH})_6$ is about 1.6×10^{-8} .

CHAPTER VIII

RECOMMENDATIONS

The following work should be undertaken to further the knowledge of the chemistry of halo-platinates:

A kinetic study of the hydrolysis of PtBr_6^- should make possible some conclusions as to the nature of the mechanism involved.

An extension of the mole ratio method to fluoro- and iodo-platinates would be of interest. The former case might require work in the vacuum ultra-violet and would certainly require some experimental ingenuity to circumvent the difficulties of working with fluoride solutions. Work with the iodo-platinates would, of course, involve the problem of auto-oxidation and reduction.

A re-investigation of solutions with low bromide to platinum ratios should be made by selecting working concentrations such that the precipitation of platinic acid will be avoided.

The spectra of PtCl_4 and PtBr_4 should be examined in non-aqueous solvents.

The data found in the course of this work should be used to investigate the nature of halo-platinate species extracted from aqueous solutions into organic solvents.

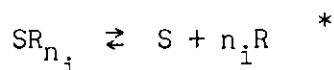
The solubility product constant of platinic acid should be quantitatively determined.

Since, in general, the nature of dissolution reactions has received little attention, it would be worthwhile to investigate this phenomenon by use of metals which form kinetically inert complexes.

APPENDIX

The following mathematical treatment and the conclusions drawn therefrom are a digest of the work of A. S. Meyer, Jr., and G. H. Ayres (30).

Consider the general case where R reacts with S to form N consecutive complexes. Let the i^{th} complex be designated by SR_{n_i} and its concentration by $[SR_{n_i}]$. For the reaction:

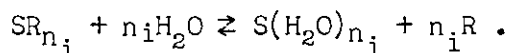


the dissociation constant, k_{n_i} , is:

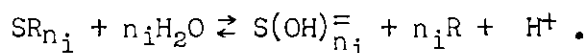
$$k_{n_i} = \frac{[S] [R]^{n_i}}{[SR_{n_i}]} .$$

The values, n_0 , n_1 , n_N represent a sequence of increasing integers corresponding to the stoichiometry of the complexes formed. For a complex of the type $S_p R_g$, $n_i = 8/p$. Let the first member of the series

*It should be remarked that, although Meyer and Ayres write the general equation in this form, the reactions are generally of the type:



In the case of the present work the equation would be:



The H_2O molecules can be ignored since the concentration of water is essentially constant. However, the experiments must be performed at constant hydrogen ion concentration to make the treatment valid for the work reported in this thesis.

of complexes, SR_{n_0} be represented simply by S . The dissociation constant for this complex is set equal to one. If the absorbances at a given wavelength are measured for a series of solutions whose total molar concentration of S is M , and of R is yM , and the absorbance values are plotted against y , the shape of the curve will be determined by the stoichiometry and dissociation constants of the complexes formed and by the concentration, M , of these solutions.

For an ideal system, the influence of dissociation can be neglected and, when the value of y corresponds to the mole ratio for the formation of one of the complexes SR_{n_j} , (where $n_j < n_N$) the concentration of this complex will be equal to M and the absorbance A will be equal to Mba_{n_j} , where b is the optical path length and a_{n_j} is the absorptivity of the complex. Similarly, when $y = n_{j+1}$, $A = Mba_{n_{j+1}}$. For intermediate values of y the absorbance is given by the equation:

$$A(y)_{n_j \leq y \leq n_{j+1}} = Mb \left[a_{n_j} + (y - n_j) \frac{a_{n_{j+1}} - a_{n_j}}{n_{j+1} - n_j} \right]_{n_j \leq y \leq n_{j+1}}.$$

For the complex of highest mole ratio, SR_{n_N} , the absorbance will be given by:

$$A(y)_{y \geq n_N} = Mb [a_{n_N} + a_R(y - n_N)]_{y \geq n_N}.$$

The entire curve may be represented by summing over j to yield:

$$A(y) = \sum_{j=0}^N Mb \left[a_{n_j} + (y - n_j) \frac{a_{n_{j+1}} - a_{n_j}}{n_{j+1} - n_j} \right] \quad n_j \leq y \leq n_{j+1} + Mb[a_{n_N} + a_R(y - n_N)] \quad y \geq n_N$$

Therefore, for this ideal case, $A(y)$ is a continuous curve made up of straight line segments. Changes of slope may be observed at any mole ratio of one of the complexes formed. A change of slope will be found at $y = n_j$ unless:

$$\text{Slope 1} = \frac{a_{n_j} - a_{n_{j+1}}}{n_j - n_{j+1}} = \frac{a_{n_{j+1}} - a_{n_j}}{n_{j+1} - n_j} = \text{Slope 2}.$$

While this may be true for some wavelengths, it is unlikely to be true over a wide wavelength region. Therefore, the absence of change of slope over the entire measurable spectrum is strong evidence that a complex of such ratio does not exist.

If the complex is much dissociated, the mole ratio plot shows no sharp break, but only a gradual change of slope approaching asymptotically a constant absorbance at high mole ratios. The technique may then be modified by making measurements on several solutions whose mole ratios lie between that of the complex under consideration and the preceding and following complexes. The dissociation will be lowered in these ranges by buffer action. If an appropriate relationship is obtained between the concentration and the dissociation constants, the system will approach ideality in these regions, and the stoichiometry of the complex may be obtained by extending the straight-line portions of the curve until they intersect. The absolute value of the relative error

introduced will be equal to $(A_{\text{ideal}} - A_{\text{dissociated}}) / A_{\text{ideal}}$ which will be shortened to $\Delta A/A$. By making the approximation that only the principal component and adjacent complexes contribute to the absorption, it can be calculated that:

$$\Delta A/A = F - f_{n_{j-1}} \frac{a_{n_{j-1}}}{a_{n_j}} - f_{n_{j+1}} \frac{a_{n_{j+1}}}{a_{n_j}}$$

where f_j is the fraction of M in the form of the j^{th} complex and F is the fraction of M dissociated. When the value of the absorptivity of SR_{n_j} is greater than that of either of the adjacent complexes, the error of measurement cannot exceed the fraction dissociated. By expressing the above equation in terms of the slopes of the intersecting segments and assuming $[R]$ equal to zero, the following expression can be arrived at:

$$\Delta A/A = \frac{F(n_{j+1} - n_j)(n_j - n_{j-1})}{(n_{j+1} - n_{j-1})} \frac{\text{Slope 1} - \text{Slope 2}}{a_{n_j}}.$$

This indicates that, for cases where the change of slope is small, extensive dissociation may be tolerated but, since such cases represent wavelengths for which slight evidence for the existence of a complex will be observed, they are of little interest.

For the case where one or both of the adjacent complexes absorbs more than the intermediate complex, it is assumed that F equals the experimental error. Since the latter is of the order of one per cent

when using a Beckman spectrophotometer, then a maximum dissociation of one per cent can be taken as a limiting value. By using this value and by assuming that only four complexes contribute to the absorbance, the mathematical relationship between $[R]$ and the dissociation constants can be manipulated to yield the following:

$$\frac{k_{n_{j+1}}}{k_{n_j}} >> 600 \frac{k_{n_j}}{k_{n_{j+1}}} .$$

The above value represents the minimum ratio between the successive step-wise dissociation constants which will allow the extrapolation method to be applied.

BIBLIOGRAPHY

1. Duval, Clement, Nouveau Traité de Chimie Minérale, Paul Pascal, Editor, Paris, Masson et Cie., 1958, Vol. XIX, pp. 750-1.
2. Basolo, F., and R. Pearson, Mechanisms of Inorganic Reactions, New York, John Wiley and Sons, 1958, pp. 108-9.
3. Taube, H., "Rates and Mechanisms of Substitution in Inorganic Complexes in Solution," Chemical Reviews, 50, (1952), pp. 77, 81, 115.
4. Pearson, R., "The Nature of Substitution Reactions in Inorganic Chemistry," Journal of Physical Chemistry, 63, (1959), p. 325.
5. Boll, M., and P. Job, "Cinétique photochimique des acides chloroplatiniques en solution très étendue," Comptes rendus des séances de l'Académie des Sciences, 154, (1912), pp. 881-2.
6. Boll, M., and P. Job, "Hydrolyse photochimique des solutions très étendues d'acides chloroplatiniques," Ibid, 155, (1912), p. 826.
7. Emeleus, H. J., and J. H. Anderson, Modern Aspects of Inorganic Chemistry, Second Edition, New York, D. Van Nostrand Co., 1952, pp. 197-8.
8. Babaeva, A. V., and N. I. Ushakova, "Platinum Tetraamine Salts of Trichlorotrihydroxy-platinic Acid," Zhurnal Neorganicheskoi Khimii, 7, (1962), p. 487; Chemical Abstracts, 56, p. 15142d.
9. Miolati, A., "Über das Platintetrachlorid," Zeitschrift für anorganische Chemie, 22, (1900), p. 445.
10. Britton, H. T. S., and E. N. Dodd, "Electrometric Studies of the Precipitation of Hydroxides. Part XII. The Reaction of Sodium Hydroxide in Solution and a Note on the Reaction of Potassium Cyanide on Platinic Chloride," Journal of the Chemical Society, London, 1933, (1933), pp. 1429-31.
11. Heymann, V. E., "Über die Einwirkung von Kohle auf geloste Schwermetalle, insbesondere auf Platinchlorid," Zeitschrift für anorganische und allgemeine Chemie, 207, (1932), pp. 251-6.
12. Boll, M., "Comportement des solutions très étendues d'acide chloroplatinique en obscurité complet aux températures diverses," Comptes rendus des séances de l'Académie des Sciences, 168, (1919), p. 1108.

13. Archibald, E. H., "The Hydrolysis of Platinum Salts. Part I. Potassium Platinichloride," Journal of the Chemical Society, London, 117, (1929), pp. 1104-20.
14. Archibald, E. H., and W. A. Gale, "The Hydrolysis of Platinum Salts. Part II. Potassium Platinibromide," Ibid, 121, (1922), pp. 2849-57.
15. Blasius, E., W. Preetz and R. Schmitt, "Untersuchung des Verhaltens der Chlorokomplexe der Platinelemente in Lösung und an Anionenaustauschern," Journal of Inorganic and Nuclear Chemistry, 19, (1961), pp. 115-32.
16. Schmidt, G., and W. Herr, "Zur Kinetik des Br-Isotopenaustausches zwischen (MeBr_6^-) , $(\text{Me}=\text{Re, Os, Ir oder Pt})$ und Br^- -Ionen," Zeitschrift Naturforschung, 16a, (1961), pp. 748-52.
17. Samuel, R., and A. R. R. Despande, "Absorptionsspektren komplexer Salze der Metalle Cr, Mn, Ru, Rh, Po, Re, Os, Ir und Pt," Zeitschrift für Physik, 80, (1933), pp. 395-401.
18. Kirkland, J. J., and J. H. Yoe, "Ultra-Violet Spectrophotometric Determination of Platinum," Analytica Chimica Acta, 9, (1953), p. 441.
19. Jorgensen, C. Klixbull, "Complexes of the 4d- and 5d- Groups. II. Crystal-Field and Electron-Transfer Spectra of Ruthenium (II) and (III), Iridium (IV) and Platinum (IV)," Acta Chemica Scandinavica, 10, (1956), p. 518.
20. Rabinowitch, E., "Electron Transfer Spectra and Their Photochemical Effects," Reviews of Modern Physics, 14, (1942), pp. 112-21.
21. Mulliken, R. S., and C. A. Rieke, "Molecular Electronic Spectra, Dispersion and Polarization. Theoretical Interpretation and Computation of Oscillator Strengths and Intensities," Reports of Progress in Physics, 8, (1941), p. 231.
22. Platzman, R., and J. Franck, "Theory of Absorption Spectra of Halide Ions in Solution," Zeitschrift für Physik, 138, (1954), pp. 411-31.
23. Orgel, L. E., "Charge Transfer Spectra and Some Related Phenomena," Quarterly Reviews, 8, (1954), p. 422.
24. Ballhausen, C. J., "Intensities of Spectral Bands in Transition Metal Complexes," Progress in Inorganic Chemistry, 2, (1960), p. 251.

25. Jorgensen, C. Klixbull, "Electron Transfer Spectra of Hexahalide Complexes," Molecular Physics, 2, (1960), pp. 309-22.
26. Adamson, A. W., and A. H. Sporer, "Photochemistry of Complex Ions. I. Some Photochemical Reactions of Aqueous PtBr_6^- , $\text{Mo}(\text{CN})_6^{4-}$ and Various Co (III) and Cr (III) Complex Ions," Journal of the American Chemical Society, 80, (1958), p. 3865.
27. Rich, R. L., and H. Taube, "Catalysis by Pt (III) of Exchange Reactions of PtCl_4^- and PtCl_6^- ," Ibid, 76, (1954), p. 2608.
28. Schlesinger, H. I., and R. E. Palmateer, "Studies on Complex Ions. III. The Relative Stabilities of the Halogenoplatinates," Ibid, 52, (1930), pp. 4316-31.
29. Yoe, J. H., and A. L. Jones, "Colorimetric Determination of Iron with Disodium 1,2 dihydroxybenzene 3,5 disulfonate," Industrial and Engineering Chemistry, Analytical Edition, 16, (1944), p. 111.
30. Meyer, A. S., and G. H. Ayres, "The Mole Ratio Method for Spectrophotometric Determination of Complexes in Solution," Journal of the American Chemical Society, 79, (1957), pp. 49-53.
31. Meyer, A. S., and G. H. Ayres, "The Interaction of Platinum (II) and Tin (II) Chlorides," Ibid, 77, (1955), p. 2671.
32. Sundaram, A. K., and E. B. Sandell, "Chloro Complexes of Palladium (II) in Solution," Ibid, p. 855.
33. Neumann, H. M., "Antimony (V) Species in Hydrochloric Acid Solution," Ibid, 76, (1954), p. 2611.
34. Neumann, H. M., and N. Cook, "Species of Molybdenum (VI) in Hydrochloric Acid," Ibid, 79, (1957), p. 3026.
35. Hillebrand, W. F., G. E. F. Lundell, H. A. Bright and J. I. Hoffman, Applied Inorganic Analysis, Second Edition, New York, John Wiley and Sons, 1953, p. 376.
36. Duval, op. cit., p. 781.
37. Ibid, p. 748.
38. Mellor, J. W., Comprehensive Treatise on Inorganic and Theoretical Chemistry, New York, Longmans Green and Co., 1931, Vol. XVI, p. 292.
39. Duval, op. cit., p. 753.

40. Hillebrand et al., op. cit., p. 378.
41. Ibid, p. 726.
42. Ibid, p. 207.
43. Ibid, p. 733.
44. Rosanoff, M. A., and A. E. Hill, "A Necessary Modification of Volhardt's Method for the Determination of Chlorides," Journal of the American Chemical Society, 29, (1907), p. 269.
45. Basolo and Pearson, op. cit., p. 106.
46. Miolati, A., and I. Bellucci, "Über die Pentachlorplatinsäure," Zeitschrift für anorganische Chemie, 26, (1901), pp. 210-21.
47. Reed, L., Chemical News and Journal of Industrial Science, 67, (1893), p. 261.
48. Falqui, M., "Struttura cristallina di alcuni alogenuri di elementi dell'ottavo gruppo. Nota II. La Struttura cristallina del cloruro platinico," Annali di Chimica applicata, Roma, 48, (1958), pp. 1160-7.
49. Duval, op. cit., pp. 753-4.

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