partially disssolved in a depth of several molecular layers at the surface of the crystallites. The important facts which have been established are (a) the formation of pyrophosphate upon the ignition of precipitated BCP, (b) the slow rate of pyrophosphate formation relative to a macrophase of acid phosphate, and (c) the correlation of the amount of pyrophosphate formed with the observed ratio of Ca to PO_4, as shown by Table I.

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Exchange of Chlorine in Aqueous Systems Containing Chloride and Tetrachloroplatinate(II)[1,2]

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The kinetics of exchange of chlorine has been measured in aqueous solutions containing Cl^-, $[PtCl_4]^=$ and $[PtCl_3(H_2O)]^-$ by the use of Cl^{36}. Addition of $[Pt(NH_3)_4](NO_3)_2$ to the solutions yielded precipitates of $[Pt(NH_3)_4][PtCl_4]$ (Magnus' green or pink salts) and $[Pt(NH_3)_4][PtCl_3(H_2O)]_2$ without fractionation or induced exchange. Exchange occurred by means of the reversible aquation process: $[PtCl_4]^= + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [PtCl_3(H_2O)]^- + Cl^-$, for which $\Delta H_1^\ddagger = 21$ kcal., $\Delta S_1^\ddagger = -8$ e.u., $\Delta H_2^\ddagger = 15$ kcal. and $\Delta S_2^\ddagger = -18$ e.u. In addition to this process one other detectable exchange occurred between Cl^- and $[PtCl_3(H_2O)]^-$ with a rate, $R = k'[PtCl_3(H_2O)]^-$, for which $\Delta H^\ddagger = 25$ kcal. and $\Delta S^\ddagger = 2$ e.u.

Introduction

The exchange of chlorine between chloride ion and the $[PtCl_4]^=$ ion in aqueous solution has been found to proceed with a conveniently measurable rate at room temperatures. The tetrachloroplatinate(II) ion, representative of the square, planar complexes of platinum(II), is inert toward substitution in the sense defined by Taube.[3] Although it has been recognized that water or hydroxide can be substituted for chloride in this ion,[4] it is surprising that for so familiar a system a quantitative treatment of such aquation (or hydrolysis) has not appeared in the literature.

The rate of exchange of a ligand in a complex with its corresponding entity in solution gives very fundamental information about the nature of the species in the solution. The work of Adamson, Welker and Volpe,[5] who observed diverse rate of exchange between cyanide ion and the cyanide ligand in a number of coördination complexes, illustrates the use which can be made of these techniques. Grinberg and Nikol'shaga[6] have studied the exchange in systems with a number of the square platinum(II) complexes. They reported that the exchange rate decreases in order with the ligands: $CN^- > I^- > Br^- > Cl^-$. For the tetrachloroplatinate(II) ion the exchange periods were reported to be long compared to the 38-minute half-life of the Cl^{38} isotope available. The abstract of their work does not mention the possibility of a photo-effect on the rates of exchange, although this effect has frequently been noted in exchange work with related compounds. For example, Adamson and Grunland[7] indicated that the exchange of Br between $[PtBr_6]^=$ and Br^-, undetected in the dark, was exceedingly rapid in light.

Rich and Taube[8] recently have reported studies of the exchange of Cl between $[PtCl_6]^=$ and Cl^- and of the exchange of Pt between $[PtCl_4]^=$ and $[PtCl_6]^=$ with a discussion of the role of Pt^{III}. They had previously described the exchange system $[AuCl_4]^-:Cl^-$.[9] The complex $[AuCl_4]^-$ is closely related to $[PtCl_4]^=$ in that it also exists as the square, coplanar complex.

A number of observations by Flikkema and Hammond[10] have been of great assistance in the interpretation of the results of the present exchange experiments. They found that a chloride ligand of $[PtCl_4]^=$ in its aqueous solution was replaced reversibly by H_2O with a reaction period of a few hours according to the reaction

$$[PtCl_4]^= + H_2O \underset{k_1}{\overset{k_2}{\rightleftharpoons}} [PtCl_3(H_2O)]^- + Cl^- \quad (1)$$

The resulting ion, $[PtCl_3(H_2O)]^-$, is a weak acid which can be titrated by hydroxide with a glass electrode. The extent of aquation can be followed by measuring the acid titer of the solution. Flikkema and Hammond found that the replacement of chloride by water was first order in $[PtCl_4]^=$, and the replacement of water by chloride in the reverse reaction was first order in $[PtCl_3(H_2O)]^-$ and first order in Cl^-. In addition, a second aquation occurred with a much longer period. The formation of $[PtCl_2(H_2O)_2]$ was catalyzed by hydroxide, and the formation of appreciable concentrations of this diaquo-species was accompanied by the formation

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(1) Presented before the Division of Physical and Inorganic Chemistry at the 126th National Meeting of the American Chemical Society, New York, N. Y., September 17, 1954.

(2) Work performed in the Ames Laboratory of the Atomic Energy Commission.

(3) H. Taube, *Chem. Revs.*, **50**, 69 (1952).

(4) J. N. Friend, "Textbook of Inorganic Chemistry," Vol. IX, Part I, 2nd Edition, Charles Griffin and Company, Ltd., London, 1922, pp. 286–288.

(5) A. W. Adamson, J. P. Welker and M. Volpe, THIS JOURNAL, **72**, 4030 (1950).

(6) A. A. Grinberg and L. E. Nikol'shaga, *Zhur. Priklad. Khim.*, **22**, 542 (1949); **24**, 893 (1951), *C. A.*, **45**, 2360h (1951); **47**, 4709a (1953).

(7) A. W. Adamson and J. M. Grunland, THIS JOURNAL, **73**, 5508 (1951).

(8) R. L. Rich and H. Taube, *ibid.*, **76**, 2608 (1954).

(9) R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 1 (1954).

(10) D. S. Flikkema and G. S. Hammond, private communication.

of a visible precipitate, probably by disproportionation, to give platinum metal. Since the reversible aquation of $[PtCl_4]^=$ offers a path for the exchange of chloride, it is of interest to find whether an additional mechanism for the exchange exists.

Experimental

Materials.—Platinum was obtained as the foil from J. Bishop and Co. and as chloroplatinic(IV) acid from the Mallinckrodt Chemical Works. The metal was converted to chloroplatinic(IV) acid by treatment with aqua regia followed by repeated evaporations with hydrochloric acid. K_2PtCl_6 was precipitated by the addition of potassium carbonate and potassium chloride.

Potassium tetrachloroplatinate(II) was prepared by the oxalate reduction of K_2PtCl_6, originally suggested by Vezes.[11] It was found that precipitated platinum served as a very effective catalyst when a K_2PtCl_6 slurry was refluxed with stoichiometric amounts of $K_2C_2O_4$. The effectiveness of the platinum catalyst for this reduction has subsequently been reported by Mikhelis.[12] The product was recrystallized three times and finally precipitated from an acetone-alcohol mixture. A spectroscopic analysis of the salt indicated a trace of Ag, Cu, Pd and a very faint trace of Ir.

$[Pt(NH_3)_4]Cl_2$ was prepared from K_2PtCl_4 by the method of Keller.[13] The chloride was converted to the nitrate by passing its solution through a column of Dowex 1 anion-exchange resin in the nitrate phase. No chloride was detected by the addition of silver nitrate to the $[Pt(NH_3)_4](NO_3)_2$ solutions.

Platinum was normally recovered by a magnesium or formic acid reduction in HCl solution and re-used in the experiments.

Chlorine-36, half-life 4.4 × 10^5 y., decaying by a single 0.72 Mev.-β-disintegration, was the tracer isotope. The radioactive chlorine was obtained from the Isotopes Division, U.S.A.E.C., Oak Ridge, Tennessee, and was carried in dilute HCl. As received, the specific activity was reported to be 0.23 millicuries/g.

Lithium perchlorate which was used to adjust the ionic strength was obtained from G. Frederick Smith Chemical Company. All the water used for the experiments was redistilled from alkaline potassium permanganate solutions.

Other chemicals and reagents were of analytical reagent grade quality and met A. C. S. specifications.

Equipment.—The temperature of the exchange reaction was adjusted by placing the reaction vessels in a water-bath controlled by a mercury thermoregulator to ±0.1°. Exploratory experiments indicated that exchange rates were increased somewhat by light. Therefore, all exchange solutions were contained in glass tubes, 17–18 mm. in diameter, covered by a wrapping of black, opaque tape. The solutions were introduced by means of a pipet through a two-hole stopper. After the last solution was added and shaken gently to mix, the holes were covered with tape, and the tubes were placed in the thermostated water-bath.

The radioactive samples were counted with an end-window Geiger-Müller counter, Model TGC-1 of Tracerlab, Inc. The counter was operated in conjunction with a commercial scaler, Berkeley Instrument Co., Model 100. Samples were mounted on cardboard and placed in a reproducible manner on a shelf at a distance of 7 mm. from the counter window. A self-scattering function of the Cl^{36} activity in $[Pt(NH_3)_4][PtCl_4]$ precipitates was determined empirically over the range of sample thickness employed. The weight of precipitate was chosen in the range of 6.0 to 8.5 mg./cm.^{2}, for which region the variation of the self-scattering function was relatively small.

*p*H measurements were obtained by means of a Beckman Model "G" *p*H meter with an electrode model #290 and adjusted with a standard buffer solution of *p*H 4.

Procedure.—In exchange experiments with *freshly prepared* $[PtCl_4]^=$ solution the HCl tracer solution was added to a standard KCl solution. This tagged chloride solution, after mixing, was added to the reaction tubes in the thermostat. K_2PtCl_4 and $LiClO_4$ crystals were dissolved in a small amount of H_2O and the solution was diluted and mixed in a volumetric flask with a larger amount of H_2O at the bath temperature. The desired quantity of solution was pipetted quickly into the reaction vessel. The time at which solutions were mixed was the zero time for the exchange.

With *aged* solutions of K_2PtCl_4, the desired amounts of KCl, $LiClO_4$, HCl and K_2PtCl_4 were dissolved in water in a volumetric flask and allowed to stand for more than 20 hours. The chloride tracer, always containing less than 2% of the total chloride in less than 0.01% of the total volume, was added from a micropipet. The time at which the tracer was added was the zero time for exchange in this case.

A separate reaction mixture was prepared for each determination of exchange. Under each set of conditions, ten to twenty reaction mixtures were prepared. At various times following the mixing, either a portion of solid $[Pt(NH_3)_4](NO_3)_2$ or its aqueous solution in excess was added to the mixture; and a precipitate began to form within 30 seconds. After five minutes the precipitate was collected on an "S&S Red Ribbon" filter paper supported on a sintered glass disc. The precipitate was washed three times with H_2O, three times with alcohol, and three times with ether. It formed a very fine, evenly distributed deposit on the paper. The samples were dried for at least one hour at 70° and then allowed to cool in the air for at least another hour. To correct for variations in room humidity, which were found to give a detectable effect, tared filter papers were simultaneously carried through the same washing, drying and cooling operations. A statistical study showed that filter paper and weights could be reproduced to about ±01 mg.

After being weighed, samples were mounted on cardboard squares and covered with standard Cellophane sheets. The samples were handled gently and mounted so the deposits remained uniform. Counting times were chosen so that the counting rates above background would have a statistical standard deviation of 1 to 5%. Counting rates were always less than 4000 cts./min. and were corrected for the counter dead-time of 300 μ sec., reported by the manufacturer.

The specific activity of a precipitate, S, was taken as the actual counting rate (corrected for self-scattering to a standard sample thickness) divided by the weight of the chlorine (mg.) present in the sample. S_∞ was the limiting specific activity of the samples which was determined empirically for each set of reaction conditions. The "apparent" fraction of exchange, f, was defined as S/S_∞.

Nature of "Magnus' Salt" Precipitates.—The addition of the cation, $[Pt(NH_3)_4]^{++}$, to a solution with $[PtCl_4]^=$ normally produces very quickly an exceedingly insoluble green precipitate, originally prepared by Magnus,[14] for which the formula $[Pt(NH_3)_4][PtCl_4]$ has been established. Addition of $[Pt(NH_3)_4](NO_3)_2$ to the exchange solutions would therefore be expected to remove effectively the chlorine in $[PtCl_4]^=$ from the solution, and exploratory experiments showed that exchange of chloride with green precipitates was negligible over a period of 15 minutes. The behavior of the $[PtCl_3)H_2O]^-$ ion in these precipitations has not been previously evaluated. Green precipitates were prepared from aged solution containing $[PtCl_3(H_2O)]^-$ and $[PtCl_4]^=$ in a ratio of 3 to 2. The weights of the precipitates frequently were 80% of the weight which would have been observed if all the platinum in anions had been present as $[PtCl_4]^=$ and collected as $[Pt(NH_3)_4][PtCl_4]$. Since the hydrogen ion concentration increase accompanying the precipitation in a solution containing about 0.01 mole/l. $[PtCl_3(H_2O)]^-$ was less than 10^{-4} mole/l., it was evident

TABLE I

ANALYSIS OF PRECIPITATES FROM FRESHLY PREPARED K_2PtCl_4 SOLUTIONS

Substance	Composition, %				
		Calcd. for $[Pt(NH_3)_4^{++}]$ salt of anions			
	Found	$[PtCl_4]^=$	$[PtCl_3(H_2O)]^-$	$[PtCl_3(H_2O)]\cdot[PtCl_3^{--}Cl^-]$	$[PtCl_3(OH)]^-$
Pt (Electrodeposition)	65.3	65.1	64.9	63.1	67.1
Cl (Mohr titration)	23.7	23.6	23.6	22.9	18.3
NH_3 (Micro-Kjeldahl)	11.6	11.3	7.5	11.0	11.7
Other (difference)	−0.6		4.0	2.9	2.9

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(11) M. M. Vezes, *Bull. soc. chim.*, **19**, 879 (1898).

(12) Y. L. Mikhelis, *Zhur. Priklad. Khim.*, **26**, 221 (1953).

(13) R. N. Keller, "Inorganic Syntheses," Vol. II, W. C. Fernelius, Editor, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 250.

(14) G. Magnus, *Pogg. Ann.*, **14**, 242 (1828).

that the amount of the hydrolysis product, $[Pt(NH_3)_4][PtCl_3OH]$, was less than 1% of the total. It appeared, therefore, that the compound $[Pt(NH_3)_4][PtCl_3(H_2O)]_2$ precipitated as a component of the green precipitate and this conclusion was confirmed by analyses. Analyses of a precipitate from a freshly prepared K_2PtCl_4 solution are given in Table I together with the calculated compositions of possible compounds precipitated from aged solutions. It is to be noted that the analysis for ammonia will give the critical differentiation between the most likely components.

A number of precipitates for aged, equilibrium solutions were also analyzed; and the results are given in Table II. The equilibrium values of $[PtCl_4]^=$ and $[PtCl_3(H_2O)]^-$ were calculated from the values of the equilibrium constant given below. The evidence indicated that the two compounds, $[Pt(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][PtCl_3(H_2O)]_2$, were precipitated without detectable fractionation. Infrared spectra of the precipitates from the aged solutions showed strong O–H bands which were not apparent in precipitates from freshly prepared solutions. Additional lines were also present in powder X-ray diffraction photographs of precipitates from aged solutions.

TABLE II

MICRO-KJELDAHL ANALYSIS OF PRECIPITATES FROM AGED K_2PtCl_4–KCl SOLUTIONS

Concn. $[PtCl_4]^=$ (mmole/ml.)	Concn. $[PtCl_3(H_2O)]^-$ (mmole/ml.)	Ammonia, % Found	Ammonia, % Calcd. for mixture
0.0083	0.0000	11.6	11.3
.0085	.0081	10.2	9.5
.0085	.0081	9.2	9.5
.0085	.0081	9.6	9.5
.0040	.0043	9.9	9.4
.0073	.0010	10.8	10.6

On occasions, the precipitates were brown or pink in color. Under a low-power binocular microscope they were observed to consist of the green needles of the typical Magnus' precipitates and very fine pink plates. The pink crystals were apparently similar to those originally described by Jorgensen and Sorensen[15a] and studied by Cox, *et al.*,[15b] and by Drew and Tress.[16] The exact color of the precipitates depended on the relative amounts of the red and green crystals. No crystals of the pink form were ever prepared large enough for single crystal X-ray techniques. However, almost pure pink forms have been prepared from both freshly prepared and aged solutions and analyses and powder diffraction photographs have indicated that pink crystals can be formed from the tetrachloroplatinate(II) ion and the trichloroaquoplatinate(II) ion. It was noted that strikingly different amounts of the two forms would appear in a series of precipitations in which there was no apparent difference in the conditions.

Results

Aquation Reaction of $[PtCl_4]^=$.—The reversible aquation of $[PtCl_4]^=$ according to reaction 1 affords a mechanism for the exchange between chloride ion and the chloride ligands in the complexes. Since the equilibrium constant and rate constants for this reaction were not available, some experimental determinations of these quantities at 25° were made in order that the role of this process in the total exchange could be evaluated. The following symbols were used for the treatment. Chlorine was only introduced into the system in the form of K_2PtCl_4 or KCl.

a = original concn. of $[PtCl_4]^=$ (before aging)
b = original concn. of chloride ion (before aging)
x = concn. of $[PtCl_3(H_2O)]^-$ at time t
x_∞ = concn. of $[PtCl_3(H_2O)]^-$ at steady state of chemical equilibrium

$$K = \frac{x_\infty(b + x_\infty)}{(a - x_\infty)} = \text{equilibrium constant of reaction 1}$$

Figure 1 shows the titration of a 0.0166 molar K_2PtCl_4 solution which had aged 24 hours and which contained enough $LiClO_4$ to give an ionic strength of 0.318 before aging. The titration indicates the presence of an acid with an ionization constant $K_i \approx 10^{-7}$ and with an equivalence equal to about 60% of the moles of total platinum. The titration curve, indicated by the open circles, was obtained in 30–40 min. during which time additional aquation could occur as the acid was neutralized. A one point titration was made in which the number of equivalents required for the end-point in the complete titration curve were added to a second sample. The *p*H given by the solid point was observed for this case. This result showed that the acid in the one-point titrations was overtitrated. From the number of equivalents which gave the same *p*H in the titration curve, the overtitration is seen to amount to 4.2% in this experiment. With this correction the concentration of acid was calculated from the equivalents of base. The concentration of acid was taken as x_∞, the concentration of $[PtCl_3(H_2O)]^-$. From the observed values of x_∞ the equilibrium constant was calculated to be 0.018 mole/liter at 25°.

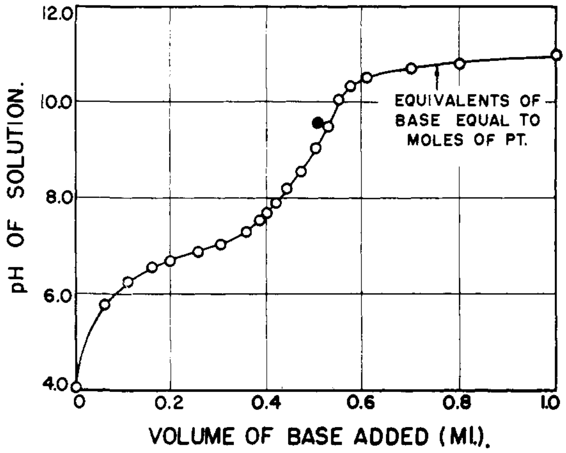

Fig. 1.—Potentiometric titration curve of an aged solution of $[PtCl_4]^=$ with NaOH at 25°; ionic strength equals 0.318; concentration of $[PtCl_4]^=$ before aging = 0.0166; aging time = 48 hr.

Similar titrations at other temperatures yielded the values of K equal to 0.013 at 15° and 0.021 at 30°. From the temperature variation of K, ΔH^0 for the reaction was calculated to be +5100 cal.

From the results of Flikkema and Hammond the rates of the two reactions for equation 1 are given by the expressions

$$R_1 = k_1(a - x);\ R_2 = k_2x(b + x) \qquad (2)$$

where the k's are the specific rate constants. The differential equation for x is

$$dx/dt = R_1 - R_2 = k_1(a - x) - k_2x(b + x) \qquad (3)$$

If x_0 is the value of x at t = 0, the solution of equation 3 is

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[15] (a) S. M. Jorgensen and S. P. L. Sorensen, *Z. anorg. Chem.*, **48**, 441 (1906); (b) E. G. Cox, F. W. Pinkard, W. Wardlaw and G. H. Preston, *J. Chem. Soc.*, 2527 (1932).

[16] H. D. K. Drew and H. J. Tress, *ibid.*, 1586 (1935).

$$\ln\{(x - x_\infty)[x_0 - x_\infty + \sqrt{(b + K)^2 + 4Ka}]/ (x_0 - x_\infty)[x - x_\infty + \sqrt{(b + K)^2 + 4Ka}]\} = -k_2t\sqrt{(b + K)^2 + 4Ka} \quad (4)$$

The aquation of the $[PtCl_4]^=$ ion was followed in a solution prepared by dissolving a weighed quantity of K_2PtCl_4 in H_2O and diluting it in a volumetric flask. At various times after its preparation aliquots were withdrawn from the solution and an amount of NaOH solution sufficient to neutralize 30–60% of the $[PtCl_3(H_2O)]^-$ was added, and the *p*H of the resulting solution was recorded immediately. The actual per cent. of neutralization was taken from the *p*H plot in a complete corrected titration curve. From the equivalents of base added and from the per cent. neutralization was calculated the concentration of $[PtCl_3(H_2O)]^-$ at the time of analysis. The data from one such experiment is illustrated in a plot in Fig. 2. The half-time of the approach toward equilibrium in this experiment was 2.37 ± 0.05 hr. From this value and the equilibrium constant given above, the rate constants for 25° were computed to be: $k_1 = 0.139$ hr.$^{-1}$ and $k_2 = 7.70$ liter moles^{-1} hr.$^{-1}$.

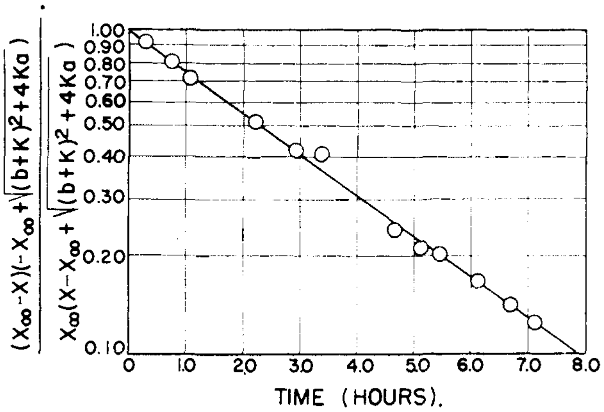

Fig. 2.—Aquation of $[PtCl_4]^-$ *versus* time at 25°; initial concentration of $[PtCl_4]^-$ = 0.0166; ionic strength = 0.318.

Exchange in Freshly Prepared $[PtCl_4]^=$ Solutions.—The extent of exchange was followed in freshly prepared K_2PtCl_4 solutions with high chloride concentrations so that only a small fraction of the platinum would be converted to $[PtCl_3(H_2O)]^-$ when the first aquation equilibrium was established. The courses of two of the actual exchange reactions are shown in Fig. 3. The plots of this figure show that any separation-induced exchange was less than 2 to 4%, a feature which was also apparent in the other experiments.

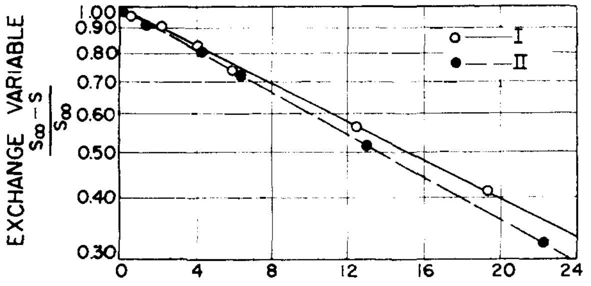

Fig. 3.—Exchange in freshly prepared $[PtCl_4]^-$ solutions at 25°; ionic strength = 0.318; I, a = 0.166, b = 0.268; II, a = 0.0415, b = 0.0638.

The figure also shows that a single exponential function describes the exchange variable $(1 - f)$ over the range of the observations. A summary of the results under various initial concentrations is given in Table III. It is to be noted that the half-time of the exchange in these experiments was nearly independent of the concentration variables.

TABLE III

EXCHANGE EXPERIMENTS WITH FRESHLY PREPARED SOLUTIONS OF K_2PtCl_4 AT 25°, IONIC STRENGTH = 0.318

Concn.^{a} Cl^- b	Concn.^{a} $[PtCl_4]^-$ a	Concn.^{a} $[PtCl_3(H_2O)]^-$ x_∞	$t_{1/2}$, hr. Calcd.	$t_{1/2}$, hr. Obsd.
0.268	0.0166	0.0010	16.8	15.3
.134	.0083	.0010	16.9	15.2
.0938	.0166	.0025	13.1	13.2
.0638	.0042	.0016	15.0	13.8

^{a} Concentrations expressed in moles/l.

For the treatment of the exchange experiments the following additional symbols were defined.

u = atoms of Cl^{36} in $[PtCl_4]^=$ per ml. of soln.
v = atoms of Cl^{36} in $[PtCl_3(H_2O)]^-$ per ml. of soln.
w = atoms of Cl^{36} in Cl^- per ml. of soln.
$I = u + v + w$ = total radioactive atoms per ml.
$S_u = u/4(a - x)$; specific activity of $[PtCl_4]^=$
$S_v = v/3x$; specific activity of $[PtCl_3(H_2O)]^-$
$S_w = (I - u - v)/(b + x)$; specific activity of Cl^-.

The apparent fraction of exchange, *f*, taken as the ratio S/S_∞ for the precipitate is given by the expression

$$f = (u + v)/(u_\infty + v_\infty) \quad (5)$$

If the only exchange occurs by means of the reversible aquation of $[PtCl_4]^=$, the following rate equations apply

$$du/dt = -4R_1S_u + R_2(3S_v + S_w) \quad (6)$$
$$dv/dt = 3R_1S_u - 3R_2S_v \quad (7)$$

Using the rate expressions in (2), these equations become

$$du/dt = -k_1u + k_2v(b + x) + k_2x(I - u - v) \quad (8)$$
$$dv/dt = 3k_1u/4 - k_2v(b + x) \quad (9)$$

If $x < a$, $v < u$ and $dv/dt \approx 0$, then the differential equation for u becomes

$$du/dt = -k_2(x + K/4)u + k_2xI \quad (10)$$

To approach isotopic equilibrium, each of the four chlorides must be replaced by H_2O which in turn is replaced by chloride; *i.e.*, the reverse aquation must occur at least four times for each complex. Consequently, a major portion of the exchange occurs very close to the steady state of chemical equilibrium. If x in equation 10 is replaced by the constant, x_∞, a single exponential component for the exchange will have a half-time of

$$t_{1/2} = (\ln 2)/k_2(x_\infty + K/4) \quad (11)$$

The half-times calculated by this procedure are included in Table III. It is noted that, as equation 11 predicts, the experimental half-time changed very slightly with large changes in the concentra-

TABLE IV

EXCHANGE EXPERIMENTS WITH AGED SOLUTIONS OF K_2PtCl_4[a]

Temp., °C.	Concn.[b] of Cl^- before aging b	Concn.[b] of $[PtCl_4]^-$ before aging a	Calcd. concn.[b] of $[PtCl_3(H_2O)]^-$ x	Aging time, hr.	pH[c]	$t_{1/2}$, hr.[d] Obsd.	$t_{1/2}$, hr.[d] Calcd.	β (R'/R)
25.0	1.000	0.016	0.0003	48		15.0	19.2	
	0.268	.0166	.0010	25		19.0	17.1	
	.134	.0083	.0010	192	5.59	14.2	17.4	
	.134	.0083	.0010	48	4.86	15.2	17.4	
	.134	.0083	.0010	21	3.07	14.8	17.4	
	.134	.0083	.0010	20	2.02	14.2	17.4	
	.134	.0083	.0010	19	0.81	15.3	17.4	
	.094	.0166	.0026	25		11.7	13.7	0.17
	.075	.0166	.0031	23	5.41	9.2	12.9	.42
	.065	.0166	.0035	23	2.01	9.8	12.5	.27
	.050	.0166	.0042	21		7.5	11.4	.56
	.040	.0166	.0048	25	2.01	8.0	11.1	.36
	.025	.0166	.0061	23		5.1	10.1	.95
	.025	.0166	.0061	25	2.02	6.5	10.1	.50
	.025	.0042	.0017	20	5.43	12.2	20.1	.58
	.010	.0166	.0083	22	4.72	3.5[e]	8.9	
	.010	.0166	.0083	192	4.40	4.1	8.9	1.01
	.010	.0166	.0083	23	4.39	4.4[f]	8.9	0.94
	.010	.0166	.0083	68	4.31	4.3	8.9	.98
	.010	.0166	.0083	20	2.04	4.8	8.9	.80
	.010	.0166	.0083	22	0.68	4.2	8.9	1.00
	.010	.0083	.0046	24	3.44	6.3	14.3	1.08
	.010	.0042	.0025	42		5.6	18.1	2.80
30.0	.134	.0083	.0011	23	2.03	8.9		
	.075	.0166	.0035	22	4.00	5.6	6.7	0.18
	.025	.0166	.0066	22	4.57	2.9	5.4	0.79
	.010	.0166	.0088	22	4.31	2.1	4.9	1.12
	.010	.0166	.0088	22	2.02	2.2	4.9	
15.0	.134	.0083	.0007	25	2.05	55.5		
	.075	.0166	.0024	22	5.58	35.3	40.9	0.15
	.025	.0166	.0050	21	5.01	18.7	29.4	.55
	.010	.0166	.0072	21	4.60	14.3	24.8	.58
	.010	.0166	.0072	22	2.06	14.8	24.8	

[a] Ionic strength of solution before aging adjusted to 0.318 by addition of $LiClO_4$ when possible. [b] All concentrations expressed in units of moles/liter. [c] If not given, the pH was fixed by the ionization of the $[PtCl_3(H_2O)]^-$, *i.e.*, *ca.* 4–5.5. [d] Half-time calculated on the basis that all the exchange occurs by means of the aquation of $[PtCl_4]^-$ (reaction 1). [e] In diffuse laboratory light. [f] Special purification to remove possible Ir impurity.

tion variables. The direction of the actual changes is indicated in the calculated values and the actual agreement to within 10% indicates that the reversible equation, equation 1, accounts satisfactorily for the observed exchange under these conditions. Exchange by a second-order process was therefore not detected.

Exchange in Aged $[PtCl_4]^=$ Solutions.—When the exchange was followed in aged solutions of $[PtCl_4]^=$, the initial chloride concentration was varied over a wide range so that the fraction of platinum present as $[PtCl_3(H_2O)]^-$ varied from 2 to 60%. Plots of four experiments in Fig. 4 show that for this situation the extent of very rapid or of separation-induced exchange was less than 4%. Over the region for $0 < f < 0.8$, which could be followed, a single exponential component described all the exchanges satisfactorily. The experimental conditions and the resultant half-times from the semi-logarithmic plots for individual experiments have been included in Table IV. A number of the experiments were checked one or more times to be certain that reproducible systems were being studied; and in general, most the half-times which were checked have agreed to within ±5%. Isolated cases were observed in which one or two of a group of similar experiments gave widely divergent half-times. Such results may have reflected the effect of an impurity in those experiments, which was capable of producing the type of catalysis described by Rich and Taube.[7]

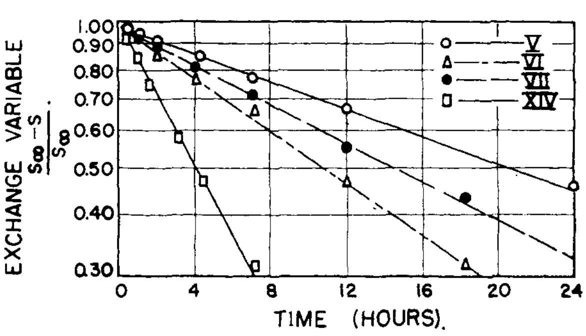

Fig. 4.—Exchange in aged solution of $[PtCl_4]^-$ and Cl^- at 25°; ionic strength = 0.318; V, a = 0.0166, b = 0.268; VI, a = 0.083, b = 0.134; VII, a = 0,166, b = 0.094; XIV, a = 0.0166, b = 0.01.

With the provision that $R_1 = R_2 = R$, a constant, equations 6 and 7, which are valid if exchange occurs only by the means of equation 1, can be written in the form

$$(1/R)(\mathrm{d}u/\mathrm{d}t) = -u/(a - x) + v/x + (I - u - v)/(b + x) \qquad (12)$$

$$(1/R)(\mathrm{d}v/\mathrm{d}t) = 3u/4(a - x) - v/x \qquad (13)$$

The solutions for these simultaneous linear differential equations are

$$u = u_\infty + A_1e^{-\alpha_1 t} + A_2e^{-\alpha_2 t} \qquad (14)$$

$$v = v_\infty + B_1e^{-\alpha_1 t} + B_2e^{-\alpha_2 t} \qquad (15)$$

where u_∞, v_∞, A_1, A_2, B_1, B_2, α_1, α_2 are functions of the concentration variables (constant for any one set of exchange experiments). If the separation procedure precipitates $[PtCl_4]^=$ and $[PtCl_3(H_2O)]^-$ without fractionation, the equation giving the function f is

$$(1 - f) = - C_1e^{-\alpha_1 t} - C_2e^{-\alpha_2 t} \qquad (16)$$

Values of the parameters in equation 16 were computed for each set of conditions. Although equation 16 contains two exponential components, semi-logarithmic plots of the functions in the region $0 < f < 0.8$ were not distinguishable from single component exponential functions. Indeed, in a number of experiments (but not all) the single period agreed to within a few per cent. with the longer period exponential component. Therefore, the half-times obtained from the slopes of the calculated semi-logarithmic plots are given as the calculated $t_{1/2}$ in Table IV. In the series of experiments performed at a *p*H of 4.0–5.5 (in which no acid in addition to the carrier had been introduced), it was noted that if the concentration of $[PtCl_3(H_2O)]^-$ was less than 15% of $[PtCl_4]^=$, the calculated and observed half-times agreed to *ca.* 10%. Apparently, in this range the simple aquation mechanism accounts for the exchange. However, as the Cl^- concentration was decreased further so that a greater fraction of the platinum existed as the aquo-complex, the observed half-times became much less than the calculated values. Under these conditions the simple aquation did not account for the exchange and an additional path for exchange between Cl^- and $[PtCl_3(H_2O)]^-$ was required.

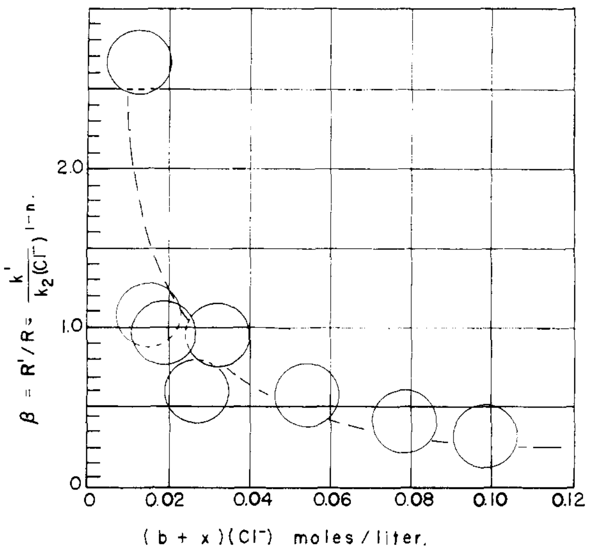

Fig. 5.—Ratio of exchange rate of $[PtCl_3(H_2O)]^-$ to the equation rate of $[PtCl_4]^=$ *vs.* chloride concentration at 25°; ionic strength = 0.318.

Exchange between Chloride and Trichloroaquoplatinate(II).—Flikkema and Hammond[9] indicated that the second aquation, or the substitution of Cl^- by H_2O to form $[PtCl_2(H_2O)_2]$, was too slow to provide the observed exchange rate. The additional exchange was considered to occur as a reaction of the form

$$[PtCl_3(H_2O)]^- + Cl^{-*} \xrightarrow{R'} [PtCl_2(H_2O)Cl^*]^- + Cl^- \qquad (17)$$

Under the steady-state conditions of chemical equilibrium, R' was taken to be a constant. The rate equation, (12), for u remained unchanged by the introduction of this reaction. However, an additional term in the rate equation for v was required so that equation 13 was replaced by

$$\mathrm{d}v/\mathrm{d}t = R[3u/4(a - x) - v/x] + R'[(I - u - v)/(b + x) - v/3x] \qquad (18)$$

The simultaneous differential equations, (12) and (18), have solutions of the same form as the expressions in (14) and (15). Consequently, for each set of experimental conditions the parameters of these solutions were calculated as a function of the natural parameter, $\beta = R'/R$. For possible values of β the calculated semilogarithmic plots of the function $(1 - f)$ were nearly straight lines over the region $0 < f < 0.8$. A value of β for each set of experimental conditions was selected by trial and error which would give the observed slope (or half-time) of the $\log(1 - f)$ function. Values of β for a series of experiments in the *p*H range of 4.0–5.5 are shown in Fig. 5. If the rate of this additional exchange process is assumed to have the form

$$R' = k'[PtCl_3(H_2O)^-][Cl^-]^n \qquad (19)$$

then β will be given by the expression

$$\beta = R'/R = k'/k_2(b + x)^{1-n} \qquad (20)$$

It can be seen from Fig. 5 that the points lie along the curve which is a plot of the function $1/[(b + x)]$. The value of n is therefore zero, and the exchange of $[PtCl_3(H_2O)]^-$ with chloride is first order in the concentration of the complex and independent of chloride. The best value of k' for this first-order exchange reaction taken from all the data was 0.16 hr.$^{-1}$. It is approximately equal to k_1, the first order rate constant for the aquation of $[PtCl_4]^=$.

Effect of Hydrogen Ion.—In a number of experiments the hydrogen ion was increased by replacing a portion of the lithium perchlorate by perchloric acid. Higher values of *p*H than those given by the normal ionization of the $[PtCl_3(H_2O)]^-$ were not used because the second aquation is base catalyzed, and precipitates form fairly rapidly in basic solutions. In all the solutions studied, therefore, the hydrogen ion dissociation of $[PtCl_3(H_2O)]^-$ was one per cent. or less. From the observed halftimes of the exchange with varying *p*H, it appears that the aquation process, equation 1, and the exchange of $[PtCl_3(H_2O)]^-$, equation 17, are substantially independent of hydrogen ion activity.

Effect of Variation of Temperature.—Table IV also contains the results of experiments at 15 and 30°. Values of k_1 and k_2 were calculated for each of these temperatures from the half-times of exchange in the set of experiments with highest chloride concentration. The assumption was employed that under these conditions the exchange occurred only by the reversible aquation of $[PtCl_4]^=$, equation 1. From these values of k_1, the values of K, and from the exchange half-times of the set of experiments with the lowest chloride concentration were calculated the magnitudes of k'. The results have been collected in Table V which also includes the indicated $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for activation based on the assumption of a transmission coefficient of unity.

TABLE V

VARIATION OF RATE CONSTANTS WITH TEMPERATURE

Temp., °C.	k_1, hr.$^{-1}$	k_2 l. hr.$^{-1}$ moles^{-1}	k', hr.$^{-1}$
15	0.043	3.2	0.033
25	0.14	7.7	0.16
	(0.16)[a]	(8.7)	(0.11)
30	0.28	13	0.28
$\Delta H^\ddagger$, kcal.	21	15	25
$\Delta S^\ddagger$, e.u.	−8	−18	+2

[a] The values in parentheses for 25° were calculated in the same manner as the values for 15 and 30°, and reflect the difference between the calculated and observed half-times given in Table IV for this experiment with $a = 0.0083$ and $b = 0.134$.

Discussion

In summarizing the behavior of the platinum(II) species which have been indicated by these experiments, it is of interest to make comparisons with the observations and conclusions of Rich and Taube[8] to the gold(III) system. The corresponding ions of the two systems have the same electron configurations and the striking differences in properties reflect the difference of one unit in the nuclear charge of the central atom.

Exchange in the gold system occurs approximately 200 times faster than in the platinum system under comparable temperatures and concentrations. In addition, the exchange occurs by fundamentally different processes. A large fraction of the exchange of $[AuCl_4]^-$ involves the chloride ion in an SN2 process. This mechanism was not evident for the $[PtCl_4]^=$ and must contribute less than 10% of the total exchange in 0.27 molar chloride concentrations. The additional coulomb barrier of the double charge of the anion may be responsible for this difference.

Aquation of $[PtCl_4]^=$ yields the species $[PtCl_3(H_2O)]^-$, which functions as a weak acid according to the equation

$$[PtCl_3(H_2O)]^- \rightleftarrows [PtCl_3(OH)]^= + H^+;\ K_i = 10^{-7} \qquad (21)$$

The fact that there is no evidence of the $[AuCl_3(H_2O)]$ species would be consistent with the difference in the standard free energy of ionization of −12 kcal. that normally occurs for differences of one unit formal charge on the central atom of an oxygen acid.[17] For $[AuCl_4]^-$ the ΔF^0 for the hydrolysis reaction

$$[AuCl_4]^- + H_2O \rightleftarrows [AuCl_3(OH)]^- + H^+ + Cl^- \qquad (22)$$

is *ca.* + 6.8 kcal.; ΔF^0 for the similar process for $[PtCl_4]^=$, which is the sum of the aquation and ionization steps, is +11.8 kcal. According to the concepts of Latimer and Jolly,[18] the entropy change in the two systems should be nearly equal. This difference in ΔF^0 of 5 kcal. corresponds to the effect of the central atom charge on the M–OH and M–Cl bond energy difference.

From the values of $\Delta F^0 = +2.4$ kcal. and $\Delta H^0 = +5$ kcal., given by the measurements of the equilibrium constant for the aquation of $[PtCl_4]^=$, equation 1), the entropy of aquation is calculated to be +9 e.u. This value is in good agreement with the prediction following the treatment of Latimer and Jolly.[18]

In low concentrations of the $[PtCl_3(H_2O)]^-$ ion the aquation process accounts satisfactorily for the observed exchange rate. It is impossible to distinguish between an SN1 process and an SN2 process involving the solvent. One can conclude, however, that if the SN1 process occurs, the activated species reacts exclusively with H_2O, rather than Cl^-. With $[AuCl_4]^-$ the exchange occurred more rapidly than the hydrolysis. Therefore, Rich and Taube concluded that: either (1) the chloride independent exchange included a contribution from an SN1 mechanism, or else (2) the $[AuCl_3OH]^-$ exchange chloride ligands rapidly with the chloride. In case alternative 2 were correct, the relative exchange rate for $[AuCl_3(OH)]^-$ is much greater than for the corresponding $[PtCl_3(H_2O)]^-$ species for which k' approximately equalled k_1. Insofar as the exchange of $[PtCl_3(H_2O)]^-$ appears to occur much more rapidly than the aquation of this species, an SN1 mechanism is required. The chloride ion can apparently compete effectively with the solvent in entering the uncharged transition species. Since the SN1 process occurs for exchange of chloride by $[PtCl_3(H_2O)]^-$, it seems reasonable that the aquation of $[PtCl_4]^=$ may involve a similar process in which addition of chloride is prevented by the coulomb repulsion. Energies of activation given by the rate constants k_1 and k' are rather high; however, the entropies of activation are normal in contrast to the very low energy and low entropy of activation for the first-order exchange rate constant in the $[AuCl_4]^-$ system found by Rich and Taube. The entropy of activation of −17 e.u. for the replacement of the H_2O in $[PtCl_3(H_2O)^-]$ by Cl^- appears normal for a case in which species with like charges react.

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