[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

EQUILIBRIA BETWEEN THE ACIDO- AND AQUO-IRIDIUM PENTAMMINES

BY ARTHUR B. LAMB AND LAWRENCE T. FAIRHALL

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The transformation of the acido cobaltic pentammines into the corresponding aquopentammines, as for instance that of the chloropentammines,

$$[Co(NH_3)_5Cl]^{++} + H_2O \rightleftarrows [Co(NH_3)_5H_2O]^{+++} + Cl^-,$$

has been shown[1] to follow a monomolecular course, and to approach an equilibrium which is affected by changes in concentration in the same way as are the ionization equilibria of the so-called strong electrolytes in water. It was pointed out at that time that this confirmed not only the widely accepted views that ions are hydrated, or in general solvated, and that ionization and hydration are causally related, but also the view that ionization and hydration, at least in part, are stoichiometrically related. It was also shown quantitatively in the same connection that the tendency for an acido group of the complex to be replaced by a water molecule with the addition of a positive charge to the cation and the formation of a free anion, or what may be called the ionizing tendency of the complex in aqueous solution, increases in the order, chloro, bromo and nitrato.

It has long been known that the acido(purpureo)-pentammine salts of iridium undergo in aqueous solution a similar transformation into aquo (roseo) salts. Thus Palmaer,[2] utilizing as a test the insoluble precipitate which roseo salts form with barium dithionate, showed that boiling water on the one hand converts purpureo salts partially into roseo salts, and on the other hand converts roseo salts very largely into purpureo salts. Moreover, while these iridium ammines mimic the corresponding cobalt ammines very closely, they are even more stable, at least toward hot water and hot alkalies. Thus Claus,[3] who first prepared them, observed that they do not give off ammonia even when digested with a concentrated solution of potassium hydroxide, and that when warmed with freshly precipitated silver oxide they give a solution as strongly alkaline as that of any of the caustic alkalies.

It appeared of interest, therefore, to study these ammines in the same way that the cobalt ammines had been studied, in order to ascertain whether the transformations follow a similar course, whether similar equilibria are attained, and whether a change in the central atom of the complex has any effect on the relationships between these equilibria.

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[1] Lamb and Marden, THIS JOURNAL, 33, 1873 (1911).

[2] Palmaer, *Z. anorg. Chem.*, 10, 375 (1895).

[3] Claus, "Beiträge zur Chemie der Platinmetalle," Dorpat, 1854, p. 90.

Preparation of the Ammines.—Metallic iridium was the starting point for preparing these substances; it was converted into sodium chloro-iridate by passing chlorine over a mixture of it with a slight excess of pure sodium chloride, according to the method of Wöhler.[4] This compound was dissolved in water, and the iridium precipitated either as sesqui- or disulfide, depending on the temperature, and this in turn was dissolved in hydrochloric acid to which a few drops of nitric acid had been added. A solution of iridium tetrachloride was thereby obtained, which when heated under pressure with ammonia yielded pentammine iridium chloride.

The dark red solution of iridium tetrachloride must, however, be very carefully evaporated at a temperature below 45°, else the green iridium trichloride, and particularly the insoluble variety of it, is formed in large amount. Various methods of evaporation were tried, such as distillation at low pressures, but the most effective means was found to be evaporation in a vacuum over sticks of potassium hydroxide. Under these conditions, a red, amorphous mass was obtained, which was very soluble in water and reacted satisfactorily with the ammonia solution.

The method of treatment with ammonia was somewhat modified from that of Palmaer. Pure iridium tetrachloride was dissolved in water in a 200cc. salt-mouth bottle, conc. ammonia solution added, and the bottle and its contents cooled to 0° and saturated with ammonia gas. The loosely stoppered bottle and its solution were placed within a larger, wide-mouth bottle, the latter filled to the level of the liquid in the smaller bottle with conc. ammonia solution and covered with a watch glass. The 2 bottles, thus arranged, were then placed in a stout steel bomb and the cover of the latter was effectively sealed by means of a lead and a paper gasket. With such an arrangement it is possible to utilize very high pressures without danger of shattering the inner flask. Since this work was completed, an autoclave similar to this in principle has been described by Kraus.[5]

When everything was in readiness, the whole arrangement was lowered into a bath of boiling water and kept there for about 5 hours. Under these conditions, the dark red tetrachloride is first reduced to the green trichloride with the evolution of some nitrogen (due to the oxidation of the ammonia). The green color of the solution then gradually gives place to a rich sherry color, which denotes more or less complete conversion into the pentammine salt.

When the bomb is opened a small precipitate of iridium trihydroxide mixed with some tri-ammino-trichloride is usually found. This is separated by filtration and the solution slowly evaporated on the steam-bath until the odor of ammonia can no longer be detected. The solution is then acidified with hydrochloric acid, filtered to remove silica, and finally evaporated to dryness on the steam-bath. By the action of heat and the excess of hydrochloric acid, the aquopentammine chloride and aquopentammine hydroxide, originally present, are converted into the more insoluble chloropentammine iridium chloride, and the latter may be washed free from the very soluble tetrammine chloride and ammonium chloride with cold water. The residue is evaporated to dryness and treated with conc. sulfuric acid in sufficient quantity to convert the pentammine chloride into the very soluble chloro sulfate. The insoluble tri-ammine is not affected by the sulfuric acid and is removed by filtration. The chloropentammine iridium chloride is obtained by adding conc. hydrochloric acid to a concentrated solution of the chloro sulfate and is purified by recrystallization from pure water.

The chloro chloride prepared as above served as the starting point for the preparation of the other pentammine compounds of iridium that were studied in this investigation. They were prepared, in brief, by converting chloropentammine iridium chloride

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[4] Wöhler, *Pogg. Ann.*, **31**, 167 (1834).

[5] Kraus, THIS JOURNAL, **39**, 1512 (1917).

into the aquo hydroxide and then adding the corresponding concentrated acid—hydrobromic, nitric, etc. For this purpose, the solution of aquo hydroxide and the concentrated acid used must be cooled to 0° before being mixed, and the filtrations conducted rapidly, using suction. If these conditions are not observed, part of the precipitated aquo salt is lost, on account of its great solubility, and part of it is likely to become converted into the acido salt. The aquopentammine iridium hydroxide was prepared by heating a solution of the chloro chloride in a platinum dish at 100° for several hours with slightly more than the calculated quantity of potassium hydroxide. This is far preferable to the procedure recommended by Palmaer, as it eliminates the possibility of the introduction of silica and its subsequent contamination of the precipitate of aquo salt on acidification. Usually a very small amount of iridium trihydroxide is precipitated during this conversion of the chloro chloride into the aquo hydroxide and this must be separated by filtration before acidification.

The aquo salts prepared as outlined above were twice purified by dissolving them in water at room temperature, filtering, and re-precipitating with the appropriate concentrated acid, the latter operation being conducted with all reagents at 0°.

The acido salts were prepared from the aquo salts by heating the aqueous solutions of the latter at 100° for some time. As the acido salts are quite insoluble, when the solution is concentrated, they precipitate as rapidly as formed and the crystals may be freed from the last traces of aquo salt by heating at 110° for an hour.

A modified procedure for the preparation of acidopentammine iridium salts was used with marked success in the later part of this investigation. A very concentrated solution of the aquopentammine salt when treated with a saturated solution of the corresponding sodium halide, sodium bromide or iodide, as the case may be, readily passes over to the acido form when heated. Usually the material was heated for a few hours in a small flask suspended in boiling water. The acido salt precipitates under these conditions in a very fine state of subdivision, is easily purified from traces of the sodium salt, and dissolves much more rapidly than the larger crystals obtained by Palmaer's method. This is a decided advantage, for the bromo bromide is soluble to the extent of but 1 part in 352 parts of water, and the iodo iodide to but 1 part in 770, and in both cases the rate of solution of the larger crystals is very slow.

Several analyses established the purity of the bromo- and aquo-bromides. Thus, for the bromo 30.51% of ionic bromine was found, while 30.86% is the calculated amount. Two different samples of the aquo-bromide gave 44.75 and 44.72% of bromine, while 44.74% is the calculated amount. One of these samples analyzed for water gave 3.47% against 3.35% calculated.

Stability of the Iridium Pentammines.—Since Palmaer had shown that to obtain a rapid conversion of acido salt to aquo or *vice versa*, temperatures near the boiling point are required, except in the case of the nitrato salts, it was first necessary to study the stability of these salts under these conditions. For this purpose 0.18 g. of chloropentammine iridium chloride was dissolved in water and the solution made up to 25 cc. This was transferred to a platinum bomb, which was then sealed securely and heated for 10 hours at 100°. The tightness of the seal was demonstrated by the fact that the loss in weight during heating amounted to only 0.02 g. The cold and slightly diluted solution showed a very slight acid reaction toward litmus, requiring two drops of 0.066 N alkali solution for neutralization. Evidently no decomposition had occurred, for otherwise, owing to the free ammonia, the solution would have become alkaline. The slight acidity of the solution was not due to hydrolysis, for a freshly prepared solution of the same salt showed a neutral reaction toward the same litmus solution. It corresponded to 0.2 mg. of hydrogen chloride, and as this substance had been used to precipitate the chloride, traces of it may well have been responsible for the acidity.

Velocity of Transformation

Having assured ourselves of the stability of these salts at 100°, we next investigated the velocity with which the conversion occurs in both directions. To do this we adôpted the methods used successfully with the cobalt ammines,[1] namely, measurement of the rate of change of the electrical conductivity of the solution. Preliminary experiments showed that a stationary equilibrium condition was attained after about 70 hours at 95°, and this temperature was, therefore, chosen for most of our measurements.

Apparatus. The Cell.—Repeated tests showed that with the dilute solutions involved, vessels made even of the most resistant varieties of glass were quite out of the question for accurate measurements at 95° over long periods of time because of the solvent action of the hot solutions. A conductivity cell, shown in Fig. 1, was therefore constructed out of fused quartz.

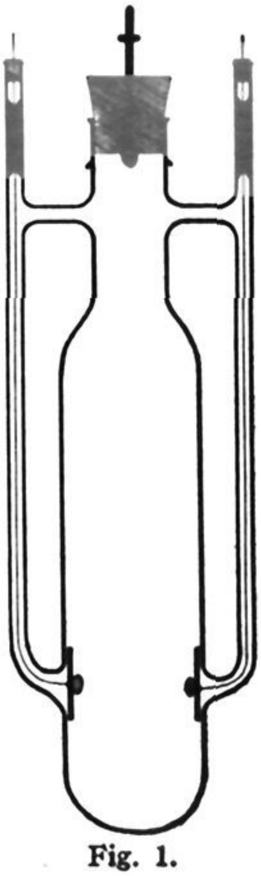
Fig. 1.

The form of the cell is evident from the figure. The electrodes were of heavy platinum foil to which platinum leads had been welded. As the platinum lost its elasticity in the process of welding, this was restored by careful hammering. The electrodes were then sprung into place and were held rigidly by projections or teeth in the walls of the cell. The platinum leads were brought up through the side tubes and cemented into place. The lower part of the capillary tubes, or that part exposed to the water vapor arising from the solution, was cemented with pure caoutchouc dissolved in chloroform. This, when dry, left a thin film of pure rubber covering the lower part of the capillary tube. The remainder of the capillary tube and the tube above it to the extent of 3 or 4 mm. were filled with metallic dental cement and, finally, the wire was firmly supported in place by small rubber stoppers.

Several devices were tried to effect a sealing of the cell, in order to prevent evaporation of the solution of pentammine salt over the long periods during which the cell was maintained at a temperature of 95°. This apparently simple but really most difficult problem was finally solved by the use of an ordinary, carefully selected 1-hole rubber stopper in which a glass plug with an enlargement on its lower end was loosely held. In executing a conductivity measurement, the weighed salt was transferred quantitatively to the weighed quartz cell; pure, redistilled ("conductivity") water was added to a certain mark and the cell again weighed. The rubber stopper was then inserted firmly in the neck and the cell placed in a beaker of water at 95° until its contents had reached a temperature approximately equal to that of the bath. This state was usually attained within 4 or 5 minutes and the cell was then transferred to the thermostat. During this heating and until the solution had reached a temperature of 95°, the glass plug in the rubber stopper was allowed to hang loosely in place, thus allowing the free escape of the heated air in the cell. As soon as thermal equilibrium had been attained, the plug was drawn up firmly into place and the opening thus effectively closed. At the same time the lower part of the stopper was thereby spread out, so that it was compressed against the neck of the cell and provided a further seal. With such an arrangement as this there was no perceptible loss nor change in concentration of the solution due to evaporation.

Copper wires, non-inductively wound, were soldered to the platinum leads in such a way as to put no strain on the latter, and were attached in turn to small binding posts fitted to the cover of the thermostat. The cell was submerged so that the level of the solution was well below that of the glycerine bath and the neck of the cell was air-jacketed nearly to the rubber stopper. From this point on, however, the neck of the cell was relatively cool. With such an arrangement as this, there was but very little condensation of water in the upper part of the cell, apparently only one or two drops on standing overnight. Nevertheless, the cell was always gently shaken in the bath in order to secure a homogeneous solution before a final measurement was taken.

It should be pointed out that this cell meets three difficult requirements very simply and satisfactorily, namely, no glass or other material soluble in water at 95° is in contact with the solution; platinum electrodes which cannot be sealed by fusion directly into quartz vessels are here held rigidly in place; the cell is very air-tight, and no appreciable evaporation occurs over periods of heating lasting for 3 to 6 days.

Thermostat.—The thermostat for use at 25° in standardizing the conductivity cell, etc., was of the ordinary type; it maintained a temperature of 25.10° to within ±0.002° over long periods of time.

The thermostat for use at 95° was of more special construction. It consisted of a thoroughly lagged agateware vessel of 15 liters capacity filled with glycerol and provided with a lead cover. Glycerol is far superior to oil for a thermostat of this sort, in that vessels after immersion in it are readily cleansed with water. Ethyl benzoate was used as the expanding liquid in the glass regulator, as it not only has an unusually high boiling point, but also is liquid at room temperature, and has a large coefficient of expansion. The heating current was adjusted by an outside rheostat until it was just insufficient to maintain the desired temperature (95°). Regulation was secured by a 20-ohm shunt around this rheostat, which was thrown in and out through the action of the regulator. With the room at normal temperature this gave a temperature cycle of about 0.015° in a period of about 2 minutes, as measured directly in the thermostat liquid. To afford a greater latitude on cold nights an auxiliary automatic cutoff was provided which short-circuited several ohms in the shunt resistance when the temperature of the room dropped to 15°. This thermostat functioned continuously for weeks at a time without interruption or irregularity. The temperature of liquids immersed in it, because of their heat lag, showed no change in temperature discernible on an ordinary Beckmann thermometer graduated to 0.01°.

The conductivity measurements were made on a spirally-wound Kohlrausch bridge, reading to one part in 10,000, which had been calibrated throughout its entire length. The conductance capacity of the quartz cell was determined both at 25° and 95° with a 0.02 *M* solution of potassium chloride which had been recrystallized and fused in platinum. The value 0.2955 was obtained, and redetermination at monthly intervals throughout the duration of the research gave values identical with this within the accuracy of the measurement (±0.0002).

Table I

The Velocity of Transformation of Iridium Pentammine Salts at 95°

Aquo Chloride 0.0047 *M*			Chloro Chloride 0.00256 *M*		
Time Hours	Molecular conductivity Mhos	Velocity constant Mhos/hours	Time Hours	Molecular conductivity Mhos	Velocity constant Mhos/hours
0	(982.0)	...	0	(650.0)	...
0.28	971.5	0.124	1.5	656.7	...
0.42	965.2	0.134	2.8	661.6	...
0.50	963.1	0.127	10.0	674.5	...
0.66	957.0	0.129	50.5	676.1	...
1.0	946.0	0.124	...	(675.0)	...
2.0	912.2	0.128	...	...	...
3.0	882.2	0.130	...	...	...
4.5	849.1	0.125	...	...	...
6.3	815.6	0.124	...	...	...
22.0	697.9	0.116	...	...	...
24.0	693.9	0.114	...	...	...
25.2	690.1	0.116	...	...	...
27.0	688.8	0.112	...	...	...
29.0	680.2	0.133	...	...	...
44.1	676.4	0.107	...	...	...
51.1	674.2	0.122	...	...	...
..	(673.6)	...	...	...	...
	Av.	= 0.122 ± 0.006			
Aquo Bromide 0.00363 *M*			Bromo Bromide 0.00376 *M*		
0	(1034.0)	...	0	(...)	...
2.3	977.0	0.082	0.08	663.3	...
4.0	938.0	0.086	0.58	671.6	...
5.2	914.3	0.086	1.92	682.5	...
8.2	860.5	0.091	9.58	688.0	...
10.0	841.0	0.088	47.15	697.8	...
23.0	754.0	0.082	73.75	698.6	...
25.8	746.0	0.080	...	(702.0)	...
32.2	729.6	0.079	...	...	...
46.2	708.0	0.095[a]	...	...	...
..	(704.0)	...	...	...	...
	Av.	= 0.084 ± 0.004			

TABLE I (*Continued*)

Aquo Iodide 0.00382 M			Iodo Iodide 0.00368 M		
Time Hours	Molecular conductivity Mhos	Velocity Constant Mhos/hours	Time Hours	Molecular conductivity Mhos	Velocity constant Mhos/hours
0	(1028.0)	...	0	(654.5)	...
0.33	1021.0	0.067	0.25	655.5	...
0.67	1013.7	0.069	0.50	656.5	...
1.00	1008.5	0.062	4.33	660.5	...
1.40	1000.5	0.064	17.50	669.7	...
2.67	981.0	0.060	21.33	671.4	...
12.00	863.0	0.055	26.50	673.0	...
16.55	828.7	0.060	29.50	677.8	...
20.0	804.6	0.060	39.50	680.2	...
23.67	784.7	0.060	60.50	681.4	..
48.0	747.1	0.044[a]	348.0	irregular	
60.0	732.6	0.044[a]	...	(690–710)	...
84.66	722.2	0.039[a]	...	...	...
101.0	(719.2)	0.034[a]	...	...	...
	Av.	=0.062 ± 0.003			

Aquo Nitrate 0.00279 M			Nitrato Nitrate 0.00392 M		
Min.			Min.		
0	(985.0)	...	0	(665.0)	...
15.0	964.0[b]	...	4.0	696.4	1.527[b]
75.0	978.0	...	5.0	707.8	1.703[b]
294.0	980.4	...	6.0	713.0	1.603
1092.0	975.5	...	7.0	721.0	1.627
2850.0	976.5	...	8.0	727.8	1.617
3990.0	975.4	...	9.0	734.5	1.609
..	(976.0)	...	10.0	741.3	1.612
..	...	...	15.0	771.8	1.599
..	...	...	25.0	823.1	1.607
..	...	...	30.0	843.1	1.596
..	...	...	35.0	861.1	1.604
..	...	...	40.0	877.0	1.594
..	...	...	45.0	893.3	1.627
..	...	...	55.0	917.2	1.643
..	...	...	75.0	947.0	1.634
..	...	...	90.0	961.3	1.640
..	...	...	195.0	976.5	1.280[b]
..	...	...	...	(989.0)	...
				Av.	1.615 ± 0.012

[a] Omitted in taking the average; some decomposition probably occurred in the aquo iodide.

[b] Omitted in taking the average; presumably the temperature had not become fully adjusted.

The results expressed as molar conductivities in reciprocal ohms are collected in Tables I and II, and are shown graphically in Figs. 2 and 3. It can be seen that the points fall closely on smooth curves, and that the curves for the acido and aquo ammines ultimately become closely asymptotic, showing that real equilibrium is established. The very slight overlapping of the curves at equilibrium, barely visible in the graphs, is presumably due to the small quantity of acido ammines (2–4%) usually present in the aquo ammines, which made their solutions appear less concentrated than they really were, and hence gave too low molar conductivities.

TABLE II

VELOCITY OF TRANSFORMATION OF IRIDIUM PENTAMMINE BROMIDES AT 80°

Concentration = 0.00386 *M*

	Aquo Bromide			Bromo Bromide	
Time Hours	Molecular conductivity Mhos	Velocity constant Mhos/hours	Time Hours	Molecular conductivity Mhos	Velocity constant Mhos/hours
0	(875.0)	....	0	(566.8)	....
3.5	859.4	0.0185[a]	2.3	568.0	....
6.0	853.1	0.0154[a]	3.8	569.9	0.0140
17.6	805.0	0.0187	25.3	582.5	0.0154
21.0	797.0	0.0179	28.3	583.6	0.0150
22.0	792.6	0.0183	48.3	586.3	0.0110
25.0	784.5	0.0181	57.5	588.1	0.0102
43.0	739.6	0.0182	70.3	591.3	0.0101
46.0	733.1	0.0183	120.3	601.9	0.0112
54.5	719.4	0.0180	125.3	603.1	0.0116
69.6	699.0	0.0176	175.5	607.3	0.0111
116.2	658.0	0.0177	190.2	609.9	0.0128
163.2	641.5	0.0171	216.0	610.2	0.0116
222.0	632.0	0.0170	238.0	612.2	0.0137
240.0	630.0	0.0175	288.0	612.9	0.0130
283.2	627.6	0.0186	..	(613.0)	....
..	(626.3)	....	..	....	....
	Av.	=0.0179 ±0.0005		Av.	=0.0124 ±0.0015

[a] Omitted in taking the average; presumably the temperature had not become fully adjusted.

At 95° the equilibrium lies near the aquo side for the nitrate, and near the acido side for the chloride, bromide and iodide; at 80°, for the bromide, it lies in a more intermediate position.

Where the change in conductivity is sufficient to justify it, we have computed velocity constants on the assumptions of a monomolecular reaction and a proportionality between the molar conductivities and the relative concentrations of the acido and aquo ammines. These apparent velocity constants, when the equilibrium mixture is taken as the end condition, are actually the sums ($k_1 + k_2$) of the true velocity constants (k_1) of the direct ($\longrightarrow$ acido) and (k_2) of the reverse reaction ($\longrightarrow$ aquo) and should, therefore, have the same numerical value for the reaction either toward aquo or toward acido. It can be seen that a considerable constancy of the velocity constants is secured, and in general that the more favorable to precision are the conditions, the more striking is the constancy. Thus, in the case of the nitrato nitrate changing into the aquo nitrate, the average deviation of the velocity constant is only about 0.8%.

This precise agreement in the case of the acido iridium ammines with the requirements of a monomolecular reaction is entirely in accord with the earlier results obtained with the cobalt ammines,[1] and is quite what would be expected for the reaction $[Ir(NH_3)_5X]^{++} + H_2O \longrightarrow [Ir(NH_3)_5H_2O]^{+++} + Cl^-$ in dilute solution, at least if the reverse reaction is monomolecular, or of negligible speed.

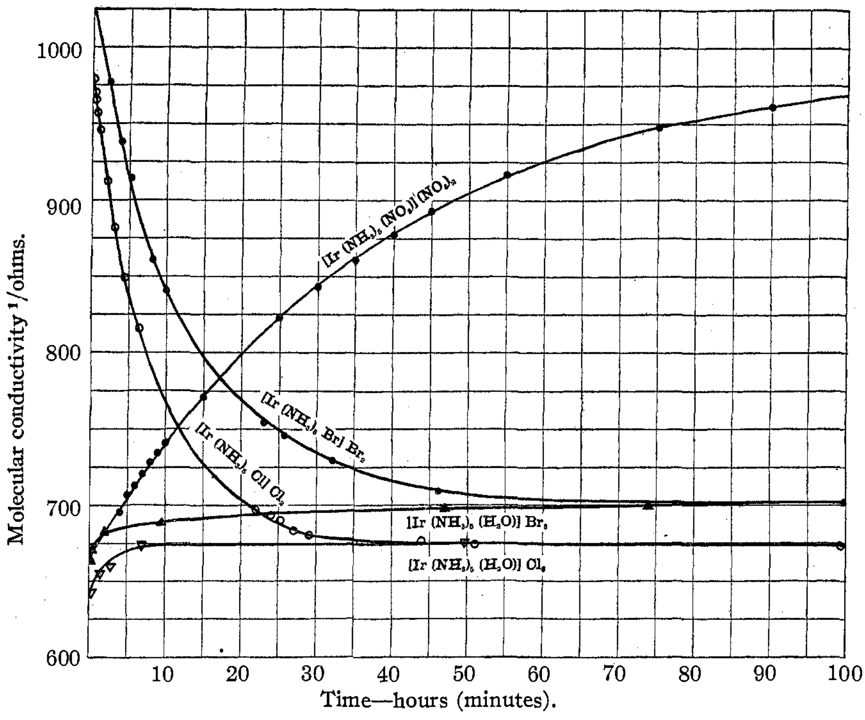

Fig. 2.

But the reverse transformations, that is, the change of the aquo salts into the corresponding acido salts, should be dimolecular reactions, and yet they too show an equally striking agreement with the requirements of a monomolecular reaction.

These results do not give concordant velocity constants for kinetic equations assuming a slow dimolecular reaction, either between all the aquo ammines and the chloride ions, or for equations assuming a slow reaction between the aquo ammine ions and the chloride ions, in each case, of course, opposed by a monomolecular reaction. Equally poor concordance is obtained assuming a slow monomolecular reaction of the *undissociated* ammine accompanied by its rapid renewal from the ionized ammine present, and opposed by a monomolecular reaction.

There appears, therefore, to be no escape from the conclusion that these slow transformations of aquo into acido ammines are indeed monomolecular reactions. It follows that the combination of the aquo ion with the chloride ion is not the slow and determining change in these reactions; instead, some other slow change is involved, which is monomolecular. In other words, the aquo ammine undergoes a slow internal transformation, the product then reacting rapidly with the chloride ions. This internal transformation may be looked upon as a movement of the water molecule out of the complex, with the result that the affinity of the complex for an electron is greatly increased; or it may be interpreted as the shift of an electron to another position of stability, with the result that a molecule of water is lost, and the affinity of the complex for an additional electron

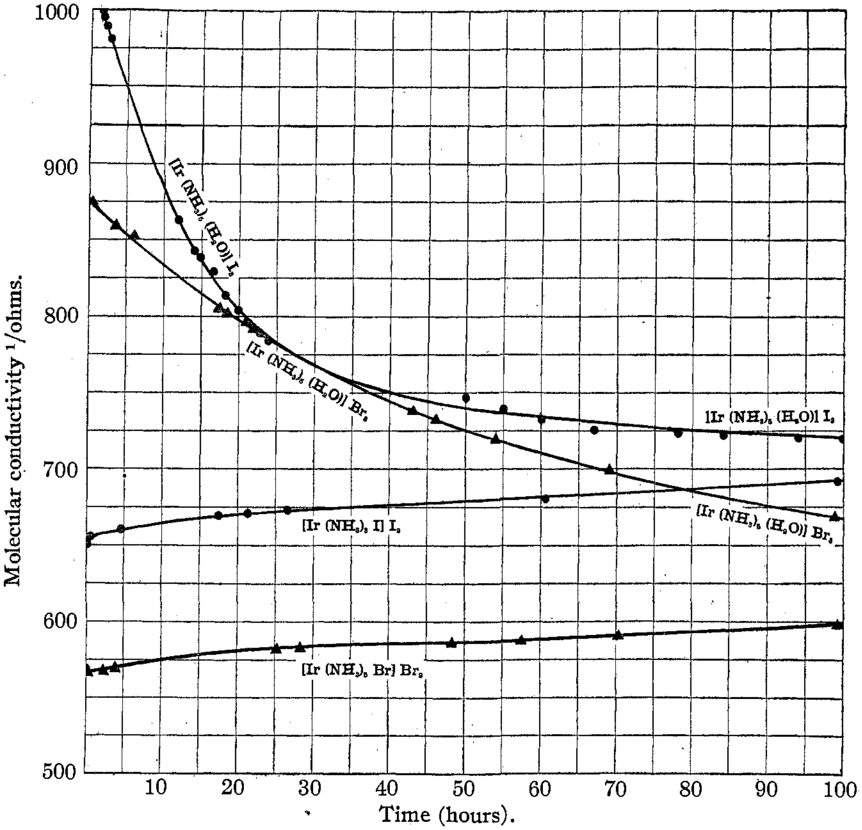

Fig. 3.

is increased. Perhaps an electron, used to hold the water molecule by a non-polar bond, in the sense of Parson and of Lewis, changes its position, and it, or another electron in the complex, at once forms another non-polar union with a chloride ion.

In any case, the satisfactory constancy of these monomolecular velocity constants justifies us in using them to compare the velocities of transformation of the various ammines so far studied. For this purpose the true velocity constants of the direct and reverse reactions (k_1 and k_2) have been calculated from the previously tabulated values of ($k_1 + k_2$), using the equilibrium measurements at these same concentrations given later in this paper. These values, both for the iridium ammines and for the cobalt ammines,[1] all expressed in hours, are given in Table III. In order to compare the iridium with the cobalt ammines at the same temperature, the constants for iridium pentammine bromide at 95° and 80° have been used to compute its constant at 25°, assuming that van't Hoff's familiar equation holds. The constants for the other iridium ammines at 25° have also been computed on the assumption that they have the same temperature coefficient as the bromide, but this assumption is so hazardous that the resulting values can only be considered to show the order of magnitude.

TABLE III
VELOCITIES OF TRANSFORMATION
(Hours)

	Iridium ammines					Cobalt ammines
	95°		80°		25°	25°
	→Acido	→Aquo	→Acido	→Aquo	→Aquo	→Aquo
Chloride	0.118	0.00231	....	....	(0.0000064)	0.0079
Bromide	0.076	0.0081	0.0151	0.0028	0.0000224	0.0234
Iodide	0.054	0.0081	....	....	....	....
Nitrate	0.0475	1.564	....	....	(0.00433)	0.105

It can be seen from this table that the same order exists among the velocity constants for the transformation to aquo among the iridium ammines as among the cobalt ammines, namely, that of the nitrato is greatest, the bromo next, and the chloro smallest. The constant for the nitrato iridium ammine is, however, relatively much greater than that for the nitrato cobalt ammine, at least at high temperatures. The difference may not be so great at 25°. It is also evident from Table III that under similar conditions the acido iridium ammines change very much (about a thousand times) more slowly into aquo ammines than do the acido cobalt ammines.

Equilibrium Measurements

The limiting values of the molar conductivities to which the above velocity curves approach asymptotically can be used to compute the concentrations of aquo and acido salt in the equilibrium. This method is, however, in the first place, dependent on the assumption of precise proportionality between concentration and molar conductivity and, in the second place, is subject to errors of extrapolation to zero time. It has, therefore, appeared desirable to determine the equilibrium concentrations of the aquo and acido ammines by the direct analysis of chilled samples. For this purpose, we have adopted the same method, depending on the non-precipitability by silver nitrate of the acido halogen, as was used with the cobalt ammines.[1]

When silver nitrate is added in excess to a mixture of halogeno and aquo ammine, the excess weight of silver halide precipitated over that which would have been formed had no aquo salt been present, is a measure of the amount of aquo salt present.

If a is the weight of pure ammine initially present, w the weight of silver halide precipitated, A the molecular weight of the initial pure ammine, and AgHal the molecular weight of the silver halide, then

$$\%\ \text{aquo} = 100\left[\frac{w}{a}\left(\frac{A}{\text{AgHal}}\right) - 2\right].$$

If the original ammine was not pure, but contained a fraction c of acido and $1-c$ of aquo, and if P and R are, respectively, the molecular weights of the acido and aquo salts, then

$$\%\ \text{aquo} = 100\left[\frac{w}{a}\left(\frac{P}{\frac{P}{R}(1-c) + c\text{AgHal}}\right) - 2\right].$$

Since the decomposition of the iridium ammines is less rapid, the extremely sudden cooling of the equilibrium mixture which was necessary in the case of the cobalt ammines could be omitted here. However, the flasks containing the equilibrium mixture were chilled by plunging in ice water, and less than a minute was required to bring their contents to room temperature.

While special precautions for cooling the solution were unnecessary, the solutions were so dilute (0.001 to 0.016 M) and their volumes were so small (90 cc.), that extreme accuracy was required in the analyses. Thus, to secure a precision of 0.1% in the relative amounts of acido and aquo salts in the solution, it was necessary to determine the halogen present to within $\pm 1 \times 10^{-7}$ gram molecules ($\pm$0.008 mg. Br) in the case of the most dilute solutions, and to $\pm 16 \times 10^{-7}$ gram molecules ($\pm$0.15 mg. Br) in the case of the most concentrated solutions. These requirements quite precluded any gravimetric method of determination. Fortunately, however, McLean and Van Slyke[6] have described a new and accurate method for the volumetric determination of small quantities of halogens, to which we have resorted.

Several modifications of this method were found necessary in order to attain the accuracy required for our analyses.

In the first place, weight burets with a counterpoise were substituted for volumetric ones.

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[6] McLean and Van Slyke, THIS JOURNAL, 37, 1128 (1915).

In the second place, the caprylic acid recommended by Van Slyke as a coagulant was found to have little merit for the small quantity of silver halide with which we worked. Instead, practically all of the halide could be coagulated readily enough by a little careful manipulation, and in any case we always found it necessary to refilter the first third of the filtrate. The precipitate was then well washed with a little dilute solution of ammonium nitrate.

Third, the buffer-indicator solution was added only *after* the silver iodide had been coagulated as completely as possible. It is important that the buffer solution be added after practically all the silver nitrate has been precipitated, and not at the beginning, as recommended by McLean and Van Slyke.

Fourth, it was found necessary in general to avoid having much silver iodide present, on account of its known great tendency to occlude silver nitrate. Besides, a large quantity of silver iodide seriously interferes with the end-point, and must be removed by filtration before the buffer-indicator solution is added. This must always be done in the case of the analysis of iodides, in spite of McLean and Van Slyke's statement to the contrary.

Fifth, the buffer-indicator solution was found to age rapidly, particularly in hot weather. Small quantitites, therefore, of the sodium-nitrite–trisodium-citrate solution were made up as required, and pure, fresh starch paste added to it.

Sixth, the sharpness of the end-point was found to vary decidedly with the proportions taken, and with the amount of nitric acid present, so blank tests with the identical amounts and concentrations of the solutions were made, and the weight of the potassium iodide solution required to produce the standard end-point was ascertained, and a correction for it applied. This usually amounted to about 0.062 g.

Seventh, the temperature during titration also has an important effect on the delicacy of the end-point. Thus, whereas in a given solution at 0° one drop of the potassium iodide produced the standard shade, 2 drops were required at 20°, and 3 drops at 31°. The color obtained at 0° largely disappeared on warming the solution to room temperature. The temperature was, therefore, kept carefully constant during the blank and the definitive titrations.

With these modifications and precautions this method lends itself admirably to the accurate determination of small amounts of halides in solution. Thus, analyses of duplicate samples drawn from the same flask usually agreed to within a few milligrams of the potassium iodide solution, or to within about 0.2% of aquo salt in an average sample of a mixture of ammines.

As a further check on the accuracy of the method, a sample of potassium bromide was carefully purified and dried, and an approximately 0.02 *M*

TABLE IV

ANALYSIS OF A KNOWN POTASSIUM BROMIDE SOLUTION BY A MODIFIED McLEAN-VAN SLYKE METHOD

Wt. of sample G.	Wt. of Bromine Taken G.	Wt. of Bromine Found G.	Diff. Mg.
18.635	0.031184	0.031204	+0.020
17.972	0.030074	0.030037	−0.037
17.516	0.029312	0.029365	+0.053
18.055	0.030214	0.030274	+0.060
		Av. difference	+0.024
		Av. deviation	±0.033

solution made up, containing 1.6734 g. of bromine per 1000 g. of solution weighed in the air. Samples of this solution were then analyzed, according to the above method, with the results shown in Table IV.

It can be seen that the results were very concordant, their average differing only by 0.02 mg. from the known value, and the average individual deviation being only 0.03 mg. This degree of accuracy would afford a precision of 0.3% in the relative amounts of acido and aquo ammines in the most dilute, and of 0.02% in the most concentrated solutions of ammines which we have studied.

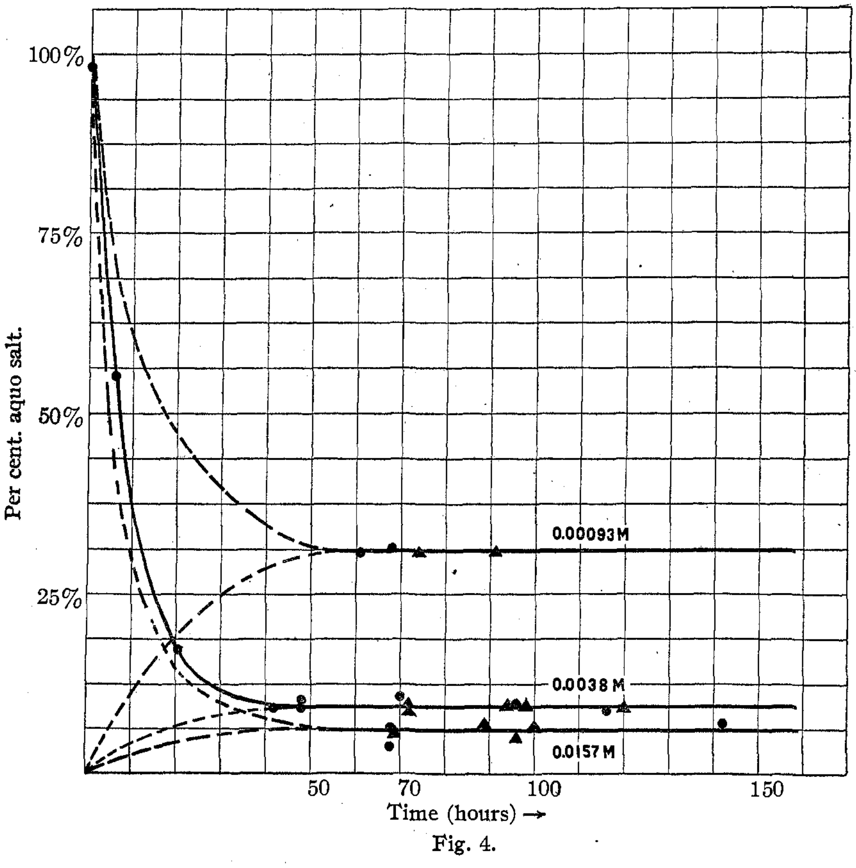

Fig. 4.

The solutions for the equilibrium determinations were prepared by weighing out the dry salt into a dry quartz flask, adding the necessary amount of conductivity water, heating to 95° in a water-bath, sealing hermetically as in the conductivity measurements, and placing in the accurately regulating thermostat at 95° above mentioned. Preliminary experiments showed that here, too, glass vessels gave wholly unreliable results. Numerous determinations were made on the chloro, bromo, and iodo equilibria at 3 concentrations. A few determinations of the bromo equilibrium were made at 80°. In all cases the equilibria were approached from both sides.

The analytical results obtained for the bromo and aquo bromide equilibrium, as typical, are shown graphically in Fig. 4. It can be seen that the points lie on curves closely resembling the corresponding curves obtained in the conductivity measurements. Equilibrium is evidently attained in about 40 hours.

The analytical results obtained after the equilibria had been established (the periods of heating varying from 50 to 100 hours) have been averaged, and the averages assembled in Table V. The percentages obtained in the equilibria reached from the two sides are listed separately. The number of determinations used in obtaining the average, and the average deviation of these results from the average are also listed, so that an estimate of the accuracy can be made.

TABLE V

EQUILIBRIUM MEASUREMENTS ON IRIDIUM PENTAMMINE SOLUTIONS

Temp. = 95° Δ = Average deviation from average

% = Percentage of aquo

Ammine	Total concentration M	From aquo %	Δ	No. of det's.	From acido %	Δ	No. of det's.	Mean %	From velocity %
	0.0157	2.7	0.5	4	3.2	0.7	4	3.0	
Chloride......	0.0038	4.4	0.4	2	4.6	0.6	3	4.5	6.0
	0.00093	27.5	1.1	2	24.7	0.6	2	26.1	
	0.0157	6.2	0.8	4	5.9	1.3	3	6.0	
Bromide......	0.0038	9.6	0.2	6	9.6	0.6	6	9.6	9.6
	0.00093	30.9	0.1	2	30.7	0.5	2	30.8	
	0.0157	6.3	0.7	2	(6.4)	0.6	2	6.3	
Iodide........	0.0038	13.1	0.9	3	(5.1)	0.9	5	13.1	13.0
	0.00093	47.5	0.9	3	(18.1)	1.2	4	47.5	
Temp. = 80°									
Bromide......	0.00385	12.8	1.0	2	12.5	0.6	2	12.6	14.7

These results show: (a) that closely identical and reproducible values for the concentrations of the aquo and acido ammines at equilibrium are obtained, independent of the time, *and of the direction from which equilibrium is reached;*[7] (b) that the relative concentration of aquo ammine in every case increases greatly with the dilution; (c) that at the same concentration the equilibria are all displaced away from the aquo, as compared with the corresponding cobalt ammines; thus, at equilibrium the chloro- and

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[7] The aquo-iodo equilibrium was the only exception to this. Here, in spite of the repeated and painstaking purifications, the results obtained from the iodo-iodide were much lower than from the aquo iodide. In every case a brownish, amorphous precipitate developed. It was very small in amount in the solutions from the aquo iodide, but was pronounced in those from the iodo iodide, particularly in the more concentrated ones. A plausible explanation is that this substance was the insoluble and undissociated tri-iodo-tri-ammine.

bromocobaltic pentammine solutions contain 72 and 98% of aquo ammine, respectively, at 0.01–0.02 *M* total concentration and 70°: the relative positions of the chloro and bromo equilibria are, however, the same; (d) that with decreasing temperature the equilibria shift toward the aquo and thus tend to resemble more closely the corresponding equilibria among the cobalt ammines.

The compositions of the equilibrium mixtures of the 0.0038 *M* solutions have also been computed from the limiting values approached by molecular conductivities of these solutions. It can be seen that a close agreement is obtained in the case of the bromo and iodo ammines, and an approximate agreement in the case of the chloro ammine.

The Equilibrium Constant

The equilibrium between aquo- and chloro-pentammine cobaltic chloride was found[1] to follow quite closely the equation, $[C_R \times C_{Cl^-}]^{0.73}/C_P = K_1$, where C_R and C_P represent the total concentration of aquo and chloro salts. This equation is identical with the Storch-Bancroft equation which applies so closely to the ionization of aqueous solutions, except that all the aquo and chloro ammine molecules were considered as active in the equilibrium, rather than only the ionized fraction of these molecules. A still better agreement was obtained with the wholly empirical equation $[C_R \times C_{Cl^-}]^{0.46}/C_P = K_2$. These same equations have been tested with the above data on the aquo- and bromopentammine iridium bromides, since these data appear to be the most trustworthy. With an exponent of 0.84 for K_1 and 0.68 for K_2 the following values of the constants were obtained.

TABLE VI

EQUILIBRIUM CONSTANTS OF THE BROMO-AQUO BROMIDE EQUILIBRIUM

Conc. of ammine	K_1	K_2
0.0157	0.0078	0.0059
0.0038	0.0053	0.0034
0.00083	0.0083	0.0063

K_1 and K_2 exhibit an approximate constancy.

Other equations, particularly those using the concentrations of the aquo and bromo ions, were tested, the ionization[8] being computed from Lewis

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[8] In the expectation of obtaining data useful for this purpose by direct measurements on the ammines, the conductivities of bromopentammine iridium bromide solutions of various concentrations at 95° were measured. The results are given in Table VII. It was found that they agreed excellently with the requirements of the Storch-Bancroft equation, when λ_0 was taken as 821 mhos, K as 4.66×10^{-6}, and n as 1.53. This is shown by the excellent agreement of the values of λ computed from this equation with those directly observed (Cols. 2 and 3). The percentage dissociations computed from these values of λ are given in Col. 4. Since, however, similar measurements were not available for the aquo ammines, it seemed more legitimate to use the directly comparable data of Lewis, mentioned above.

and Randall's data[9] for lanthanum nitrate and barium chloride, respectively, assuming that the ionization in these mixtures is the same as in a pure solution of the same total ion concentration; but less satisfactory constants were obtained. In general, then, we may say that the iridium and cobalt ammines appear to conform to similar mass-law equations.

TABLE VII

CONDUCTIVITIES OF SOLUTIONS OF BROMOPENTAMMINE IRIDIUM BROMIDE

Temp. = 95° $K = 4.66 \times 10^{-6}$ $n = 1.53$

	Molar conductivity		
Conc. Millimoles	Obs. Mhos	Calc. Mhos	Dissociation %
9.618	600	596.7	73.1
3.763	660	661.0	80.4
1.457	712.5	712.5	86.8
0.482	755	755.3	92.0
0	(821)	...	..

More rigorous computations do not appear profitable at present for two reasons: first, the precision of the data does not justify them; second, in all probability, at high dilutions these ammines are considerably hydrolyzed, the aquo certainly more so than the acido. Any hydrolyzed ammine will be withdrawn from the equilibrium, and as it will be largely aquo ammine and will appear as such in the analysis, the results will be vitiated to this extent, and in general the percentage of aquo will appear too large, particularly at high dilutions. The percentages of aquo ammines at the highest dilution do indeed appear to be too large.

Summary

1. Palmaër's methods for the preparation of iridium pentammine salts have been somewhat modified in the interest of convenience and purity.

2. Chloropentammine iridium chloride has been shown to undergo no appreciable decomposition in aqueous solutions at 100°.

3. The velocities of transformation of chloro-, bromo-, iodo- and nitratopentammines into the corresponding aquo ammines, and *vice versa*, have been measured at 95°, and in the case of the bromo ammines, at 80°. All of these transformations have been found to follow the course of a monomolecular reaction, and their velocity constants have been found to have the same relative magnitudes as do the corresponding constants of the cobalt ammines.

4. The equilibria reached in these transformations have been investigated analytically. For this purpose, the method of McLean and Van Slyke for the volumetric determination of small amounts of halogens has been carefully studied, and has been further refined. The values for the equilibrium concentrations thus ascertained have been found to be in

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[9] Lewis and Randall, THIS JOURNAL, **43**, 1112 (1921).

substantial agreement with those computed from the velocity measurements, and similar to those of corresponding equilibria among the cobalt ammines. They are all, however, markedly displaced away from the aquo, as compared with the corresponding cobalt ammines.

5. The values for the concentrations found in the bromo bromide equilibrium, and these are our most trustworthy data of this kind, have been shown to agree reasonably well with the requirements of an empirical equation similar to that found for the cobalt ammines.

6. The conclusion has, therefore, been drawn that, while the exchange of the central cobalt atom for an iridium atom in the ammines studied has produced a general shift in the velocity and equilibria constants, it has produced no relative displacements.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MINNESOTA]

A METHOD FOR THE QUANTITATIVE SEPARATION OF BERYLLIUM AND URANIUM

BY PAUL H. M.-P. BRINTON AND REUBEN B. ELLESTAD

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The separation of beryllium from uranium is not often required in analyses, as the 2 elements seldom occur together. In a few minerals,[1] however, both elements occur, and in the course of an investigation by one of us it became necessary to find an accurate method for the determination of beryllium and uranium in mixtures of the two. Search through the literature showed that the problem had received but little attention.

In the exhaustive paper of Kern[2] on the separation of uranium from a great number of elements no mention is made of beryllium; nor is this element considered in Brearley's book.[3] Schoeller and Powell[4] describe a method for the separation of uranium from iron, titanium, cobalt, nickel, manganese, zinc, beryllium and the alkaline earth elements, by pouring the boiling solution containing these elements into hot sodium carbonate solution, boiling, diluting, and again boiling. However satisfactory this method may be for the separation of uranium from the other elements, we found it inaccurate for the separation from beryllium, as the precipitation of beryllium was incomplete, and the basic carbonate was contaminated by uranium. Approximate results may sometimes be obtained by this compensation of errors, but the method cannot be regarded as reliable.

Wunder and Wenger[5] proposed the precipitation of uranium as $UO_4.2H_2O$ by hydrogen peroxide as a method of separating uranium from beryllium. With pure solutions and using hydrogen peroxide prepared with elaborate precautions to eliminate impurities,

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[1] Duparc, Sabot and Wunder, *Bull. soc. franç. mineral.*, **36**, 5 (1913).

[2] Kern, THIS JOURNAL, **23**, 685 (1901).

[3] Brearley, "The Analytical Chemistry of Uranium," Longmans, **1903**.

[4] Schoeller and Powell, "The Analysis of the Minerals and Ores of the Rarer Elements," Griffin and Co., **1919**, p. 185.

[5] Wunder and Wenger, *Z. anal. Chem.*, **53**, 371 (1914).