

It has been found by later experiments, some of which are still in progress, that with dilution of the solutions much more uniform results may be secured, approaching, in fact, those obtained from the action of weak acids alone.

The cause of the inversion of strong sugar solutions by these heavy salts is undoubtedly to be found in their condition of partial hydrolysis by the solvent. The acid ion in each case is a strong one, while the basic ions are all relatively weak. Indeed, it has been suggested by Walker and Aston¹ that the amount of hydrolysis in solutions of certain salts may be approximately measured by comparing the speed of inversion with that of known amounts of weak acids. The method can be easily applied to a large number of solutions of moderate concentration. Further investigations with special reference to ferrous salts are now in progress.

CHICAGO, DECEMBER, 1895.

MIXED DOUBLE HALIDES OF PLATINUM AND POTASSIUM.

BY CHARLES H. HERTY.

Received November 16, 1895.

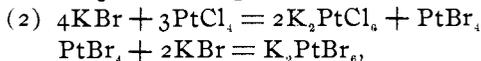
INTRODUCTION.

BY mixing together water solutions of platinum chloride and potassium bromide in the proportion of one molecule of platinum chloride to two molecules of potassium bromide, Pitkin obtained² a compound having the composition represented by the formula $K_2PtCl_4Br_2$.

Two possible explanations were advanced by Pitkin,



a true chemical compound being formed, or



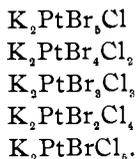
giving thus an isomorphous mixture of K_2PtCl_6 and K_2PtBr_6 . In either case the percentage of the elements remains the same. To determine which of the two explanations is correct, he resorted to fractional crystallization, and from the above solu-

¹ *J. Chem. Soc.*, July, 1895.

² *This Journal*, 1, 472.

tion obtained three successive crops of crystals. Determinations of platinum in each of these showed that they were identical, and he concludes, therefore, that the substance is a chemical compound and not an isomorphous mixture.

In a second paper¹ he described the series



These were prepared by mixing together stated quantities of K_2PtCl_6 and K_2PtBr_6 , dissolving in water and crystallizing. Three successive crops of $\text{K}_2\text{PtCl}_5\text{Br}$ were obtained, showing respectively 36.97, 37.04 and 36.99 per cent. of platinum, again confirming the idea that these substances were true chemical compounds.

In the discussion, which followed the reading of the paper, Dr. Endemann suggested that these substances were most probably isomorphous mixtures.

In a third paper² Pitkin discussed the question of isomorphism and fractional crystallization, upholding his formerly expressed view that the platinum compounds were true chemical compounds. His argument was:

1. In isomorphism "the resulting mixed crystal has a composition dependent on the ratio, one to the other, of the isomorphous salts in solution or the constituents forming these salts."

2. "When two isomorphous salts together in solution are subjected to fractional crystallization, the salts differing in their degree of solubility in the menstruum employed, the crystals first formed will contain relatively a greater amount of the more insoluble salt, while the crystals formed at the end will be correspondingly rich in the more soluble salt."

It is principally upon the second consideration that he bases his claim that the substances are true chemical compounds and not isomorphous mixtures. This claim has been generally accepted and we find in many text books descriptions of the salt $\text{PtCl}_{4.2}\text{KBr}$.

¹ This Journal, 2, 296.

² *Ibid.*, 2, 408.

Quite recently Pigeon¹ has prepared a substance to which he gives the formula $K_2PtCl_2Br_4$. He considers it one of the series previously prepared by Pitkin.

During the past few years I have been constantly occupied with efforts to prepare double halides containing more than one halogen. I have shown² that the double halides of lead and potassium and of antimony and potassium containing more than one halogen are isomorphous mixtures of the double halides containing one halogen. It has seemed desirable, therefore, to repeat the work of Pitkin and determine whether the facts upon which he based his reasoning are correct.

I may state in advance that his analytical results are altogether inaccurate and inadequate. The reasoning which he makes use of to prove that the substances are true chemical compounds, proves beyond doubt, when interpreted by the results which I have obtained, that the substances are isomorphous mixtures.

METHOD OF ANALYSIS.

In the analyses of his compounds Pitkin determined platinum alone. These determinations were made by heating the substance with oxalic acid, thoroughly washing the residue and weighing the dried spongy platinum.

Deeming the determination of platinum alone insufficient, I have analyzed all the compounds prepared during this investigation by reduction in hydrogen.

The hydrogen, generated in a Kipp apparatus, was purified by being passed through an acid solution of potassium permanganate, over moist copper carbonate, through alkaline permanganate solution, through water, and finally over calcium chloride, in the order named. The gas was then passed through a combustion tube, about twelve inches in length, in which was placed a porcelain boat containing a weighed quantity of the substance to be analyzed. The combustion tube, constricted at the end, was closely connected with a U tube in turn connected with another U tube, both tubes containing potassium hydroxide solution. Before analysis the dried crystals were finely powdered and thoroughly dried at 110° . After placing in the combustion

¹ *Ann. chim. phys.* [7], 2, 433.

² *Am. Chem. J.*, 15, 81, and 16, 490.

tube the boat containing the substance to be analyzed, all air was driven out by the current of hydrogen. Gentle heat was then applied by means of a Bunsen burner with a winged top attachment. As the reduction proceeded the heating was slowly increased until the flame from the burner almost touched the tube. This was maintained for some time. Finally the flame was removed and the tube allowed to cool, hydrogen passing through for one hour longer in order to remove all traces of hydrochloric or hydrobromic acids. The liquid in the U tubes was then transferred, with thorough rinsing, into a beaker and dilute nitric acid added in excess. The boat containing the metallic platinum and the potassium salts was removed from the tube and the mass thoroughly extracted with water by standing twenty-four hours. The platinum was then filtered in a porcelain Gooch crucible and thoroughly washed with water.

The crucible was then dried for one hour in an air-bath at 110° , heated to redness in a platinum crucible, allowed to cool, and weighed, the platinum being in the form of gray metal. In the filtrate from the platinum and in the neutralized liquid from the U tubes bromine and chlorine were determined by addition of an excess of standard solution of silver nitrate, filtering the precipitated silver halides in porcelain Gooch crucibles, and titrating the excess of silver in the filtrates with a standard solution of ammonium thiocyanate. The crucibles containing the silver salts were dried for three hours at 150° . From the weight of silver used and the weight of silver halides in the Gooch crucibles the weights of bromine and chlorine were calculated. In several cases the neutralized liquid from the U tubes was added to the filtrate from the platinum, the total bromine and chlorine being determined at one time.

In one salt potassium was determined as potassium sulphate by first removing the platinum by electrolysis, then evaporating with sulphuric acid in a weighed platinum dish.

In all of the analytical work vessels were allowed to stay on the balances ten minutes before being weighed. The atomic weights used were: platinum 194.34, potassium 39.03, chlorine 35.37, and bromine 79.76.

The above method of analysis is open to several criticisms.

In the first place the sodium nitrate in the neutralized liquid from the U tubes dissolves a small portion of the precipitated silver salts. In the second place, it is very difficult to remove all of the hydrochloric or hydrobromic acids from the finely divided platinum either by heating or by extraction with water.

In spite of these errors this method would seem to yield much more reliable results than the method of heating with oxalic acid, applicable for determinations of platinum alone.

PREPARATION OF MATERIALS.

The potassium bromide used in this investigation was heated sufficiently high to decompose any potassium bromate present and to drive off any ammonium chloride, repeatedly recrystallized from water, dried, finely powdered, and again thoroughly dried. Potassium chloride was prepared in the same manner.

Great difficulty was experienced in the preparation of pure chloroplatinic acid. This was unexpected, as previous investigators make no mention of any great difficulty. The purest specimens sent out by the manufacturers showed, on reduction in hydrogen, a coating of ammonium chloride on the combustion tube after raising the heat considerably. The substance was then prepared by dissolving platinum in aqua regia and evaporating repeatedly with hydrochloric acid. Still ammonium chloride was found after reduction with hydrogen. The constant appearance of ammonium chloride led to the hypothesis that some nitrogen compound might be present in the hydrogen used, and on coming into contact with the platinum black, in the presence of hydrogen and hydrochloric acid, might be converted into ammonium chloride. To test this point hydrogen was prepared from strictly pure zinc and the purest sulphuric acid which could be obtained. This hydrogen was then purified by Phillips' method.¹ Still ammonium chloride appeared after reduction of the platinum compounds.

The next explanation which suggested itself was the presence of some trace of the compound $2\text{NOCl} \cdot \text{PtCl}_4$, formed during the treatment with aqua regia. To eliminate this possible source of error, chloroplatinic acid was prepared by the method recommended by Pigeon,² in which no nitric acid is used. This

¹ *Am. Chem. J.*, 16, 165.

² *Ann. chim. phys.* [7], 2, 495.

method consists in precipitating the platinum as ammonium platinichloride, reducing this at a low temperature in hydrogen, and treating the finely divided platinum with hydrochloric acid and chlorine in a large flask, the chlorine being replenished as rapidly as it is taken up by the platinum.

A specimen prepared in this way also yielded ammonium chloride. While repeating this method of preparation an accident showed its unfitness for the purpose. According to directions a portion of the ammonium platinichloride had been reduced in hydrogen at a temperature just sufficient for the reduction, and the ammonium chloride evolved driven from the tube. Accidentally the temperature was considerably raised. Immediately quite a large deposit of ammonium chloride was formed on the combustion tube, showing that platinum black occludes ammonium chloride in quite large quantity. Efforts were made to remove all of the occluded ammonium chloride by prolonged heating in hydrogen but this proved very unsatisfactory. This method of Pigeon's is therefore unfit for use and there is little doubt but that the substances with which he conducted his thermochemical experiments were largely contaminated by ammonium platinichloride. A second method of Pigeon's was then tried. This consists in passing a current of chlorine gas through an emulsion of ammonium platinichloride and hot water. Nitrogen is given off and chloroplatinic acid formed, but on reduction in hydrogen ammonium chloride was again deposited. Finally, at the suggestion of Dr. H. N. Morse, of Johns Hopkins University, ammonium platinichloride was intimately mixed with pure oxalic acid and the mass heated to redness. A residue of spongy platinum was obtained which gave only a slight deposit of ammonium chloride on being heated in hydrogen. The platinum thus prepared was converted into chloroplatinic acid by treatment with chlorine and hydrochloric acid. The hydrochloric acid was prepared by heating concentrated chemically pure hydrochloric acid and passing the liberated gas into freshly distilled water. The chloroplatinic acid thus prepared still yielded a slight deposit of ammonium chloride.

Further attempts were made to purify this by cooling the solution, in the hope that the ammonium platinichloride would sepa-

rate from the solution, but this failed. Finally a current of chlorine gas was passed through a portion of this chloroplatinic acid solution for some time. The product still yielded a slight quantity of ammonium chloride on reduction in hydrogen. However, it was considered sufficiently pure for the purposes of the investigation and accordingly was used. All of the above processes were carried out in a room as free from ammonium chloride as was practicable.

The amount of platinum in the water solution of the chloroplatinic acid was determined by electrolysis.

One cc. solution = 0.08956 gram of platinum.

The use of chloroplatinic acid for determining potassium suggests that in addition to the precautions, already taken by the Association of Official Agricultural Chemists, of working in a room other than the general laboratory, more care should be taken in regard to the absence of ammonium platinichloride from the chloroplatinic acid as first sent out by the manufacturers.

METHOD OF WORK.

If the substances obtained by Pitkin are true chemical compounds it seems only natural to suppose that they could be reproduced under at least some slight variation in the original proportions of the substances used in their preparation. To determine this point four solutions were prepared, using the same amount of platinum solution in each. In one a definite quantity of potassium bromide was used. In the other three arbitrarily taken portions of the potassium bromide were replaced by equivalent quantities of potassium chloride. To prepare $K_2PtCl_4Br_2$, Pitkin used two grams platinum chloride and 1.404 grams of potassium bromide. These are the quantities required by using the atomic weights: platinum 197.18, chlorine 35.46, bromine 79.95, and potassium 39.13. More recent determinations of the atomic weight of platinum give the figure 194.34. The above quantities therefore evidently do not give the proportion $PtCl_4 : 2KBr$. However I have endeavored to meet this point by using 1.404 grams of potassium bromide and 12.99 cc. of the platinum solution = 1.163 grams of platinum, conforming thus to the proportion $PtCl_4 : 2KBr$ according to the atomic weights used by Pitkin.

In the replacement of potassium bromide by potassium chloride the more recent atomic weights were used. Potassium 39.03, chlorine 35.37, and bromine 79.76.

The quantities of the various substances actually used in the four experiments were :

TABLE I.

	H ₂ PtCl ₆ Sol. cc.	H ₂ O. cc.	KBr. Grams.	KCl. Gram.
A	12.99	57.00	1.404
B	12.99	57.00	1.200	0.1278
C	12.99	57.00	1.000	0.2531
D	12.99	57.00	0.800	0.3784

When the two solutions in each case were first mixed a small quantity of a light yellow precipitate was thrown down. On boiling with an inverted condenser all dissolved, the solutions becoming dark red. After cooling bright red octahedral crystals separated in each case, growing slightly lighter in color from A to D. The crystals were prepared for analysis as described above. On analysis the following results were obtained :

TABLE II.

	Pt. Per cent.	Cl in dis- tillate. Per cent.	Br in dis- tillate. Per cent.	Cl in resi- due. Per cent.	Br in resi- due. Per cent.	Total Cl. Per cent.	Total Br. Per cent.
A ..	34.93	23.19	4.47	4.74	18.12	27.93	22.59
B ..	35.90	24.91	2.03	6.19	15.47	31.10	17.50
C ..	36.46	26.02	1.04	7.58	12.93	33.60	13.97
D ..	37.07	26.73	0.31	8.41	11.44	35.14	11.75

TABLE III.

	Calculated for K ₂ PtCl ₄ Br ₂ .	A.	B.	C.	D.	Calculated for K ₂ PtCl ₅ Br.
Pt per cent.	33.89	34.93	35.90	36.46	37.07	36.74
Cl " "	24.67	27.93	31.10	33.60	35.14	33.43
Br " "	27.82	22.59	17.50	13.97	11.75	15.08
Atomic ratio						
Pt : (Cl + Br)		1 : 5.97	1 : 5.95	1 : 6.00	1 : 5.98

From these results it is evident that four substances have been prepared, each differing in composition from the two nearest members of the series described by Pitkin, K₂PtCl₄Br, and K₂PtCl₅Br.

Furthermore the crystals show a variation in composition in

accord with the variation in composition of the solutions from which they formed. (See Table I). Yet in all four substances the atomic ratio of platinum to chlorine and bromine combined is practically 1:6. Again, if we assume C to be an isomorphous mixture of K_2PtCl_6 and K_2PtBr_6 , then 33.60 per cent. of chlorine requires 30.77 per cent. of platinum, while 13.97 per cent. of bromine requires 5.68 per cent. of platinum, giving the total per cent. of platinum required by this assumption 36.45. There was actually found 36.46 per cent.

In the hope of gaining some light upon the nature of these substances, separate determinations of chlorine and bromine were made in the portion which passed off in the current of hydrogen and in the portion combined with potassium in the residue. No definite conclusion on this point can be drawn from the results, except that a portion of the hydrobromic acid liberated decomposed a portion of the potassium chloride, setting free hydrochloric acid. Thermochemical considerations lead us to expect this as has been pointed out already by Pigeon. The results in Table III seem to show that the substances are isomorphous mixtures.

Pitkin's principal argument in support of the idea that the substances obtained by him were true chemical compounds is that the successive crops of crystals obtained from a solution of platinum chloride and potassium bromide are identical. Three successive crops were analyzed by him and gave the per cents. of platinum respectively, 34.22, 34.70, and 34.39. No determination of bromine or chlorine was made. To test this point more thoroughly the mother liquors from A, B, C, and D above were evaporated to about one-half of the previous volume and allowed to crystallize. Crystals were obtained in each case closely resembling the first crops obtained from the respective solutions. These crystals, designated A', B', C', and D', gave on analysis:

TABLE IV.

	Pt. per cent.	Cl. per cent.	Br. per cent.	Atomic ratio. Pt : (Cl+Br).
A'.....	33.48	25.37	26.26	1 : 6.08
B'.....	34.10	26.14	25.58	1 : 6.04
C'.....	35.27	28.30	22.25	1 : 5.95
D'.....	36.10	31.63	17.09	1 : 5.97

Potassium was determined in A'. There was found 13.59 per cent.

Finally the mother liquors from A', B', C' and D' were allowed to evaporate spontaneously until all water had passed off. A third crop of crystals was thus obtained in each case. These crystals closely resembled the former crops in regard to crystal form, but were much darker in color. They were designated A'', B'', C'' and D''.

A slight odor of hydrochloric or hydrobromic acid was noticed in each vessel when the evaporation was complete. On analysis the substances gave the following :

TABLE V.

	Pt. per cent.	Cl. per cent.	Br. per cent.	Atomic ratio. Pt : (Cl + Br).
A''.....	32.76	20.53	33.14	I : 5.91
B''.....	32.88	22.30	31.36	I : 6.05
C''.....	34.35	26.44	24.21	I : 5.95
D''.....	35.09	28.01	22.20	I : 5.93

By combining Tables II, IV and V it will readily be seen that the successive crops of crystals obtained from a solution are by no means identical, thus :

TABLE VI.

	Pt. per cent.	Cl. per cent.	Br. per cent.
A.....	34.93	27.93	22.59
A'.....	33.48	25.37	26.26
A''.....	32.76	20.53	33.14
B.....	35.90	31.10	17.50
B'.....	34.10	26.14	25.58
B''.....	32.88	22.30	31.36
C.....	36.46	33.60	13.97
C'.....	35.27	28.30	22.25
C''.....	34.35	26.44	24.21
D.....	37.07	35.14	11.75
D'.....	36.10	31.63	17.09
D''.....	35.09	28.01	22.20

If these results be arranged according to the per cent. of platinum, it will be seen that twelve substances have been prepared, each varying from the calculated per cents. for $K_2PtCl_4Br_2$ or K_2PtCl_6Br , yet approaching these more nearly than any of the

other members of the series prepared by Pitkin. In all of the twelve the atomic ratio of platinum to chlorine and bromine combined, allowing for error in the analytical work, is practically 1 : 6, which is required if the substances are isomorphous mixtures :

TABLE VII.

	Pt. per cent.	Cl. per cent.	Br. per cent.	Atomic ratio Pt: (Cl + Br).
A''	32.76	20.53	33.14	1 : 5.91
B''	32.88	22.30	31.36	1 : 6.05
A'	33.48	25.37	26.26	1 : 6.08
B'	34.10	26.14	25.58	1 : 6.04
C''	34.35	26.44	24.21	1 : 5.95
A	34.93	27.93	22.59	1 : 5.97
D''	35.09	28.01	22.20	1 : 5.93
C'	35.27	28.30	22.25	1 : 5.95
B	35.90	31.10	17.50	1 : 5.95
D'	36.10	31.63	17.09	1 : 5.97
C	36.46	33.60	13.97	1 : 6.00
D	37.07	35.14	11.75	1 : 5.98

In addition to these, five other compounds were prepared. In these platinum was determined by electrolysis.

The per cents. of platinum found in these were 35.05, 34.94, 34.43, 34.00, and 33.26.

Pitkin relied upon analytical data in which no attention was paid to a variation of one-half per cent. and in one case one per cent. in the amounts of platinum present in different substances. Such were considered identical. By an inspection of Table VII it will be seen that such a variation in the platinum means so great a variation in the chlorine and bromine that it is impossible to consider such substances identical.

From the above evidence there seems little doubt but that the substances are isomorphous mixtures. To test the point still further a large portion of A was dissolved in hot water; on cooling, crystals quite similar to A separated. These were dried and designated X. The analytical results are placed side by side with those of A for convenience in comparing the two.

TABLE VIII.

	Pt. per cent.	Cl. per cent.	Br. per cent.	Atomic ratio Pt: (Cl + Br).
A	34.93	27.93	22.59	1 : 5.97
X	35.48	29.96	18.80	1 : 5.93

By recrystallization the first crop obtained was thus evidently richer in the more insoluble compound, K_2PtCl_6 . This would be expected in the case of an isomorphous mixture of two substances differing in their degree of solubility.

Further evidence of the mixed nature of the substances was obtained by placing a considerable quantity of the substance X in a well fitting glass stoppered bottle, pouring upon the finely powdered substance a quantity of water quite insufficient for complete solution in the cold, placing the stopper in the bottle and shaking thoroughly several days. After being shaken for a short time and the undissolved portion allowed to settle, it was found that instead of the homogeneous powder, originally present in the bottle, two distinct layers were now present, one a dark red, the other a light yellow. Evidently the water had dissolved the more soluble red bromide to a larger extent than the less soluble yellow chloride. After four days the liquid was filtered from the undissolved residue. This residue was thoroughly dried, powdered, and intimately mixed and labelled Y. Its analysis, compared with the original substance X showed

TABLE IX.

	Pt per cent.	Cl per cent.	Br per cent.	Atomic ratio. Pt : (Cl + Br).
X	35.48	29.96	18.80	1 : 5.93
Y	35.87	30.98	17.80	1 : 5.96

confirming thus the idea that the more soluble bromide had dissolved to a larger extent than the less soluble chloride.

SUMMARY.

Four lines of evidence have thus been adduced, all pointing to the conclusion that the double halides of platinum and potassium containing more than one halogen are isomorphous mixtures of different double halides containing only one halogen :

1. The formation of a series of substances varying in composition approximately as the variation in the composition of the solutions from which they crystallized. None of these substances correspond to the formulas proposed by Pitkin, but all show an approximate atomic ratio, platinum to chlorine and bromine, of 1:6. Fifteen other substances, all varying in composition, have been prepared ; in ten of these the atomic ratio of platinum

to chlorine and bromine was found to be practically 1 : 6, in the other five platinum alone was determined.

2. The successive crops of crystals obtained from a water solution of chloroplatinic acid and potassium bromide are not identical, but show gradually increasing proportions of the more soluble potassium platinibromide and correspondingly decreasing proportions of the less soluble potassium platinichloride.

3. On recrystallizing from water one of the substances under examination, the first crop of crystals is not identical with the original substance but is a product richer in chlorine and correspondingly poorer in bromine. This is to be expected on recrystallizing an isomorphous mixture of two substances differing in degree of solubility.

4. On treating one of the substances obtained with a quantity of water insufficient for complete solution, the more soluble bromide was dissolved from the mass to a greater extent than the less soluble chloride. This was confirmed both by the appearance of the insoluble residue and its analysis.

At the beginning of this investigation Mr. Henry Hillyer, Jr., a student in this laboratory, was associated with me in the work. His sad death at his home in Augusta, Ga., on April 4, 1895, terminated this association. I desire to here pay tribute to his rare qualifications as an investigator and to the manliness which characterized his every act.

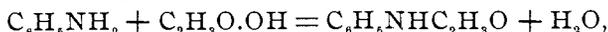
UNIVERSITY OF GEORGIA.
NOVEMBER 9th, 1895.

THE QUALITATIVE EXAMINATION OF ACETANILID.

BY CHARLES PLATT.

Received November 22, 1895.

IN view of the deficiency in the analytical literature of the acid anilids the following tests may prove of interest. The formation of acetanilid, or phenylacetamid, $C_6H_5NHC_2H_5O$, from anilin and glacial acetic acid



and the corresponding formation from anilin and acetyl chloride

