

ing another element and his views as to its incorrect atomic weight have led to an extended series of critical studies on this subject. Brauner studied the atomic weight for six years, Norris for nine, Baker and Bennett for thirteen, and the author for ten. We see, therefore, thirty-eight years of experimental work directed to the study of the atomic weight of an element which to-day remains as an element whose elementary character is well established, and which stands with a higher atomic weight than the next element in the horizontal series. While it still remains an exception to the periodic arrangement of Mendeléeff, and so far as its comparison with iodine is concerned, is abnormal, yet in the main points of its chemical behavior and those of its compounds, it properly belongs associated with sulphur and selenium in the sixth group.

The element tellurium still remains, however, an exception to the periodic arrangement of Mendeléeff, its atomic weight being higher than that of iodine. We must hence conclude that either tellurium is abnormal in a direction which has not yet received careful study, or that we do not yet appreciate all of the principles of the periodicity of the elements.

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A STUDY OF THE SOLUBILITY OF POTASSIUM CHLOROPLATINATE.

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The importance of knowing accurately the solubility of a precipitate, in the liquor from which it has been thrown down, if the precipitate is to be used for a quantitative estimation, is apparent to every one. This is the case, in particular, with such substances as potassium chloroplatinate, when this salt is to be used for the determination of the amount of potassium occurring in feldspars and such igneous minerals, where the amount of chloroplatinate which is to be weighed is, generally speaking, comparatively small. The difficulty here encountered is, in a measure, overcome by the methods worked out by Hillebrand¹ and his pupils, who evaporate the solution containing the salt in question, together with the corresponding sodium salt, to dryness and then dissolve out the sodium salt with absolute or eighty per cent. alcohol. The trouble, however, although lessened, is still of the same nature as before, and even under the best conditions some of the potassium salt must be carried into solution, giving a high value to the sodium. With these features of the case in mind, it was thought that it would be of some interest to study the solubility of the potassium chloroplatinate somewhat more carefully than had

¹ Hillebrand, "Analysis of Silicate and Carbonate Rocks," *Bull.* 305, *U. S. Geol. Survey*. Washington: Analysis of Rocks.

hitherto been done, under somewhat similar conditions to those encountered in precipitating this salt from solution in ordinary analytical work. The experiments which have been carried out with this end in view, are described in the following pages.

Bunsen and Kirchhoff¹ were the first to work on the solubility of the chloroplatinate of potassium. They made measurements of its solubility in water, at various temperatures between 0° and 100°. Crookes,² when studying the solubility of thallium salts, determined the solubility of potassium chloroplatinate in water at 15° and 100°. Fresenius³ determined the solubility of this salt in solution of ethyl alcohol and water, which contained 55, 76 and 97.5 per cent. of the alcohol. Gibbs,⁴ while working out the separation of the platinum metals, found that "potassium chloroplatinate is insoluble in strong, cold, aqueous solutions of potassium chloride." Precht⁵ determined the solubility of this chloroplatinate in absolute alcohol and in 96 and 80 per cent. alcohol-water solutions. He also made some very interesting observations on the preparation of the pure salt. Peligot⁶ studied the solubility of the salt in question in solutions of ethyl alcohol and water, and he also made a determination of the solubility in absolute methyl alcohol. No systematic study has been made of the solubility of the chloroplatinate in different concentrations of potassium chloride, nor has the influence of other alcohols been ascertained. It was thought that it would be worth while to obtain some data with regard to both of these points, to somewhat extend the observations mentioned above, and also to ascertain the influence on the solubility of the chloroplatinate of the presence of sodium chloride.

Apparatus.—A constant temperature bath was necessary, in which the solutions could be maintained at a given temperature until they should have attained complete equilibrium. The bath used had a capacity of about 40 liters. It was insulated with a thick coating of felt on the sides, and a thick board of asbestos on the top. It carried the usual arrangement for keeping the solutions constantly agitated, a small hot-air engine of the Hendrici form supplying the motive power for running the stirrer. The bath was supplied with an Ostwald gas regulator, by means of which the temperature could be kept constant, if necessary, within 0.1°.

All burettes and pipettes used were carefully standardized by weighing the water which they delivered.

¹ *Pogg. Ann.*, **113**, 372 (1861).

² *Chem. News*, **9**, 37 (1864).

³ *Anal. Chem. und Pharm.*, **59**, 117.

⁴ *Am. J. Sci.* (2), **31**, 70.

⁵ *Zeit. anal. Chem.*, **18**, 509 (1879).

⁶ *Monit. scient.* (4), **6**, 872 (1892).

The tubes, which contained the solutions while they were in the bath, were of hard glass and had a capacity of about 55 cc. The rubber stoppers used to seal them were boiled in dilute caustic soda for several hours before using, to remove surface impurities.

Two thermometers, A and B, were used in the course of the work, to indicate the temperature of the bath. They were standardized at 0° in a bath of melting ice; again at the transition point of sodium sulphate,¹ 32.383°; and again at 100°.

Preparation of Materials.—The chloroplatinic acid used in preparing the potassium chloroplatinate was prepared as follows: Platinum scrap was boiled for several hours with c. p. concentrated hydrochloric acid, washed with distilled water, and the boiling repeated for about the same length of time with c. p. concentrated nitric acid, to remove surface impurities. After another washing the scrap was dissolved in aqua regia, using only as much of the nitric acid as was necessary to dissolve the platinum. The color of the precipitate formed with the platinum solution and potassium chloride showed that there must have been an appreciable amount of iridium in the platinum scrap. To remove the iridium, advantage was taken of the fact that ammonium chloroiridate is much more soluble in water than ammonium chloroplatinate. 100 parts of water at 20° dissolve only 0.666 part of ammonium chloroplatinate, while 5.00 parts of ammonium chloroiridate will dissolve in 100 parts of water. Accordingly, a somewhat dilute solution of ammonium chloride, that had been once recrystallized, was added slowly, with constant stirring, to the chloroplatinic acid solution, care being taken not to precipitate quite all of the platinum. The ammonium salt thrown down was of a very brilliant yellow color, while the chocolate color of the residue left upon evaporation of the mother liquor, showed that a large part of the iridium had remained behind.

After thoroughly washing the precipitate of ammonium chloroplatinate it was reduced in hydrogen to spongy platinum, and the platinum again dissolved in aqua regia. At this point a slight black residue remained, which would apparently not dissolve in the aqua regia, and which we supposed to be iridium. The solution of the spongy platinum was now precipitated as before with ammonium chloride, the precipitate reduced, the spongy platinum dissolved in aqua regia, and again precipitated with the ammonium chloride. The mother liquor left from this precipitation showed no sign whatever of the presence of iridium, while the residue which was noticed when the first portion of spongy platinum was dissolved did not appear after the second precipitation.

As a further proof of the absence of iridium from the product thus

¹ Richards and Wells, *Proc. Am. Acad. Arts and Sciences*, 38, 434 (1902)

prepared, one-half of the sample was taken and reduced, the spongy platinum dissolved in aqua regia, and again precipitated with ammonium chloride. The precipitate thus obtained was successively recrystallized three times from water. The mother liquors from these recrystallizations were combined with that from the precipitation, and the whole evaporated. However, no indication of iridium appeared in the solution or in the residue.

The final precipitate of ammonium chloroplatinate, which was now assumed to be free from iridium, was reduced, the platinum dissolved in aqua regia, and this was followed by two evaporations, carried almost to dryness, in the presence of an excess of concentrated hydrochloric acid, to remove all traces of nitric acid. Precht,¹ and later Dittmar and McArthur,² and more recently Noyes and Weber,³ have shown how necessary it is to get rid of all the nitric acid, before precipitating with potassium chloride, if a precipitate of known composition is to be obtained. The residue from the final evaporation was taken up with enough water to give a solution containing about 5 per cent. of platinum, and this was added slowly, with constant stirring, to a dilute solution of potassium chloride.

The potassium chloroplatinate prepared in this way was thoroughly washed and carefully dried at a temperature of about 80°. It was kept over anhydrous calcium chloride until used.

From the analysis of several portions of chloroplatinate prepared in different ways, and from solutions of varying dilution, it appears that there is considerable tendency for the precipitate to carry down with it other substances from the solution. This point is receiving some attention in this laboratory. It is enough to say here that the precipitate obtained as above did not contain an appreciable excess of the platinum or of the potassium chloride.

The potassium chloride used in the above preparation, as well as that used directly in making the solubility determinations, was prepared by dissolving Kahlbaum's chemically pure product in distilled water and precipitating this with hydrogen chloride gas, generated by boiling chemically pure hydrochloric acid. The potassium chloride precipitated in this way was twice recrystallized from water, washed, and dried at a temperature of 110°.

The sodium chloride used was prepared in the same manner as the potassium salt.

Methyl alcohol, free from acetone, was digested for nine hours with a large amount of fresh calcium oxide. It was then distilled. The distillate was treated with a fresh quantity of calcium oxide, and again dis-

¹ *Loc. cit.*

² *Trans. Roy. Soc. Edin.*, **33**, 561 (1887).

³ *THIS JOURNAL*, **30**, 13 (1908).

tilled. That portion coming over at 65.5° was collected and used in these experiments.

The other alcohols, ethyl and isobutyl, were freed from water in a similar manner. Those portions distilling over at 78.4° and 106° , respectively, were used.

These alcohols, after being dehydrated, were carefully protected from the moist air of the laboratory.

The water used in this work was prepared by distilling the ordinary distilled water of the laboratory, after adding a few crystals of potassium permanganate and a few drops of sulphuric acid. As a further indication of its purity, its electrical conductivity was found to be as low as could be expected.

Measurements.—We will first consider the solubility of the salt in water at different temperatures. The method of procedure was as follows: To the tubes were added about 50 cc. of water, and somewhat more chloroplatinate than would dissolve at the particular temperature at which the determination was to be made. It should be stated here that two different determinations were made for every point investigated. The temperature of the bath was now raised to the required point and the thermostat regulated so as to maintain the water at this temperature. The tubes were now attached to the paddles of the stirring apparatus and constantly rotated for from twelve to twenty-four hours. At the lower temperatures, equilibrium is attained very slowly, and in these cases the stirring was continued over night. Several experiments had shown that the solutions would become completely saturated within this time.

In order to determine how much of the chloroplatinate had been dissolved, after the required time had elapsed the stirrer was brought to rest and a test tube raised in the bath, until the top stood just above the water. When the excess of salt had completely settled, which, with the heavy precipitate we are here concerned with, takes place in a very short time, the stopper was removed, and as quickly as possible 25 cc. of the solution were withdrawn with the calibrated pipette, and first transferred to a tared specific gravity bottle and weighed. This procedure was necessary in order to obtain the data required to express the results in terms of grams of salt dissolved in 100 grams of solvent. This solution was then washed into a weighed platinum dish. After evaporating carefully and drying at a low temperature, the dish and residue were weighed. Further drying of the dish and contents was followed by another weighing, and this treatment was repeated until the weight became constant. This process was repeated with 25 cc. of the contents of a second tube, and we thus had two measurements of the solubility

at this particular temperature. The mean of these two determinations gives the values tabulated below.

The results of the determinations of the solubility of the chloroplatinate in water at different temperatures are shown below in Table I.¹ These values represent the amounts of salt, in grains, soluble in 100 grams of water, all weights being reduced to the vacuum standard. For the purpose of this reduction the specific gravity of the chloroplatinate was taken to be 3.54.²

TABLE I.—RESULTS SHOWING THE SOLUBILITY OF POTASSIUM CHLOROPLATINATE IN WATER AT DIFFERENT TEMPERATURES.

Temperature.	Weight of K_2PtCl_6 dissolved.	Temperature.	Weight of K_2PtCl_6 dissolved.
2°	0.4812	59°	2.396
16°	0.6718	68°	2.913
25°	0.8641	78°	3.589
35°	1.132	92°	4.484
48°	1.745		

These results are shown graphically in Plate I, where the temperatures are plotted as ordinates and the weights of chloroplatinate dissolved as abscissae. In order that the results might be compared with those of other observers the amount of salt dissolved for the temperatures 10°, 20°, 30°, etc., taken from the curve in Plate I, are given below, together with those of Bunsen:³

TABLE II.—RESULTS COMPARING THE SOLUBILITY VALUES FOR POTASSIUM CHLOROPLATINATE IN WATER, OBTAINED BY PREVIOUS INVESTIGATORS, WITH THOSE OBTAINED BY THE AUTHORS.

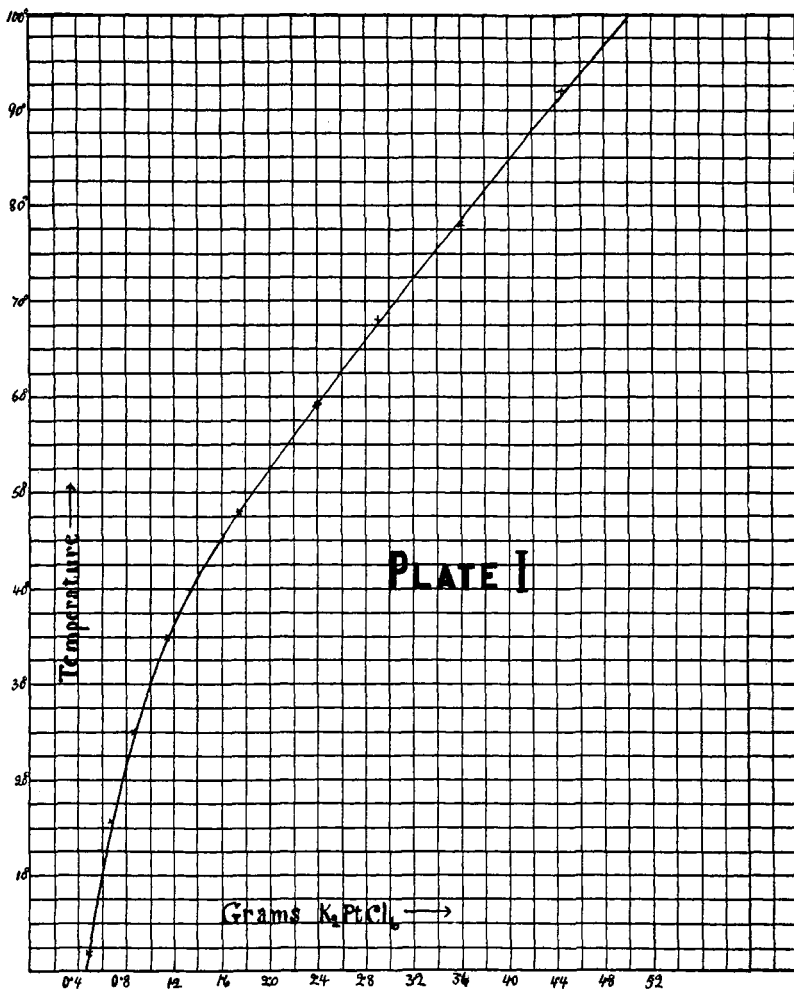
Temperature.	Weight of K_2PtCl_6 dissolved.		Temperature.	Weight of K_2PtCl_6 dissolved.	
	Authors.	Bunsen.		Authors.	Bunsen.
0°	0.4784	0.74	60°	2.444	2.64
10°	0.5992	0.90	70°	3.055	3.19
20°	0.7742	1.12	80°	3.711	3.79
30°	1.000	1.41	90°	4.360	4.45
40°	1.355	1.76	100°	5.030	5.18
50°	1.865	2.17			

¹ It has been pointed out to us by Prof. W. A. Noyes that Dr. Weber found that a solution of potassium chloroplatinate became acid upon boiling. We find that this hydrolysis goes on even at ordinary laboratory temperatures although very slowly, the reaction not being completed within five days. The effect of this reaction upon the solubility appears to be very slight, as a solution of the salt saturated at 95° and maintained at this temperature in contact with the solid phase for 36 hours, upon cooling to 75° gave practically the same value for the solubility as a solution saturated at 75° and not allowed to rise above this temperature. Several of the determinations given in the above table were obtained by approaching the saturation point from both directions. This hydrolytic reaction is being studied further at different temperatures and we hope to have something further to communicate in the near future.

² Landolt-Börnstein-Meyerhoffer, Tabellen.

³ *Loc. cit.*

Crookes¹ states that one part of this chloroplatinate will dissolve in 108 parts of water at 15°, and in 19 parts at the boiling-point of water.



It is at once apparent that the present results show an appreciably lower solubility of the platinum salt in water, particularly at the lower temperatures, than other investigators have found. It seems possible that the salt with which they worked may not have consisted entirely of the chloroplatinate, as Precht,¹ and quite recently Noyes and Weber¹ have shown that it is very difficult to prepare pure chloroplatinic acid. If the nitric acid is to be completely removed by evaporation, this pro-

¹ *Loc. cit.*

cess must be carried out repeatedly, and in the presence of a large excess of hydrochloric acid. Any contamination which resulted from an incomplete removal of the nitric acid would doubtless give high results for the solubility of the chloroplatinate. It is possible, too, that the more complete removal of the iridium in the present instance may also have lowered the solubility slightly.

Before dismissing this point, it should be stated that every care was taken to have the solutions saturated with the chloroplatinate, at the particular temperature at which the experiment was being made, before they were removed from the bath. In some cases they were rotated in the bath for 50 hrs. before being analyzed.

It should be noted that the curve in Plate I is a continuous one over the whole range of temperature investigated.

Solutions of Methyl Alcohol and Water.—Solutions of methyl alcohol and water, as solvents, were next tried, the procedure being much the same as in the previous case, except, that here, four parallel determinations were usually made. As the experiments were being carried on very near the temperature of the laboratory, it was thought better, although perhaps not necessary, to filter the 25 cc. of the solution which had been measured out with the pipette, before evaporating. It was found that when the amount of alcohol in the mixture was as high as thirty per cent., reduction of the chloroplatinate to platinum black took place during the evaporation. This method of determination had therefore to be abandoned. In its place we used a colorimetric method as follows: A standard solution of potassium chloroplatinate in pure water was prepared, containing seven grams of the salt per liter of solution. The unknown solution to be determined was poured into a Nessler tube of 100 cc. capacity and distilled to the mark. Using the standard solution as a basis, another solution was prepared in a second tube, which had the same strength of color as the unknown. The volume of the standard solution required to produce this color, multiplied by the amount of chloroplatinate in unit volume, gave the amount of salt in the original unknown. Care was always taken to have the conditions the same in the unknown as in the known solution. For instance, both solutions always contained the same amounts of alcohol or potassium chloride as the case might be; they were also kept at the same temperature, which was a little higher than the temperature at which the determination was being made. It was found that by this method we could detect the presence of 0.0005 gram of potassium chloroplatinate dissolved in 100 cc. of water, or one part of the salt in two hundred thousand parts of water. It is believed that this method gives a degree of accuracy in the determination of a number of points, in particular those dealing with the dilute solutions, that has not hitherto been reached.

With regard to the mixture of ethyl alcohol and water, as well as those of isobutyl alcohol and water, the determinations were carried out in all respects like those described above.

The results for the solubility of potassium chloroplatinate, in various concentrations of methyl, ethyl and isobutyl alcohol and water, are given in Table III. The measurements were all carried out at a temperature of 20°. In the case of isobutyl alcohol and water only two measurements were made, as this alcohol only dissolves to a small extent in water.

In order that these values might be comparable with those obtained by other investigators, the composition of the solutions is expressed in grams of alcohol per one hundred grams of solution, while the amounts of salt dissolved are given in grams per one hundred grams of solvent. As before, all weights are referred to a vacuum.

TABLE III.—RESULTS SHOWING THE SOLUBILITY OF POTASSIUM CHLOROPLATINATE IN SOLUTIONS OF DIFFERENT ALCOHOLS IN WATER.

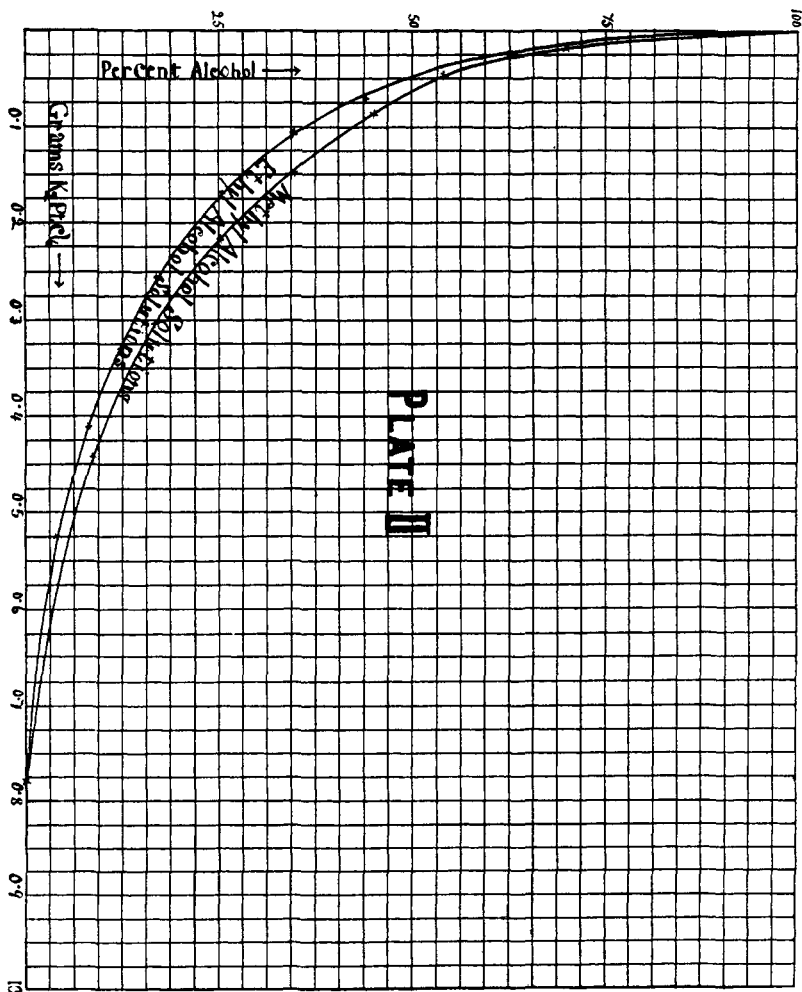
Per cent. of methyl alcohol.	Weight of K_2PtCl_6 in 100 gms. solution.	Per cent. of ethyl alcohol.	Weight of K_2PtCl_6 in 100 gms. solution.	Per cent. of isobutyl alcohol.	Weight of K_2PtCl_6 in 100 grams solution.
0.00	0.7742	0.00	0.7742	0.00	0.7742
8.10	0.4434	3.996	0.5258	8.20	0.625
16.55	0.3050	8.08	0.4122	(saturated)	0.318
25.38	0.2188	12.25	0.3325		
34.58	0.1495	16.51	0.2565		
44.25	0.0877	25.30	0.1698		
54.34	0.0478	34.52	0.1088		
70.42	0.0185	44.16	0.0742		
87.7	0.0061	54.3	0.0356		
100.0	0.0027	64.9	0.0199		
		76.0	0.0131		
		87.7	0.0052		
		100.0	0.0009		

TABLE IV.

Values showing the solubility of potassium chloroplatinate in mixtures, made up of even percentage values by weight of water and alcohol. For the sake of comparison, Peligot's results for ethyl alcohol mixtures are given in the last column.

Per cent. of alcohol by weight.	Weight of K_2PtCl_6 in 100 gms. of solution.		
	Methyl alcohol mixtures.	Ethyl alcohol mixtures.	Peligot's results, ethyl alcohol mixtures.
0.00	0.7742	0.7742	0.75
5.00	0.535	0.491	...
10.00	0.412	0.372	0.5
20.00	0.2642	0.218	0.35
30.00	0.1831	0.134	0.28
40.00	0.1165	0.076	0.14
50.0	0.0625	0.0491	0.12
60.0	0.0325	0.0265	0.08
70.0	0.0182	0.0128	0.06
80.0	0.0124	0.0085	0.05
90.0	0.0038	0.0025	0.02
100.0	0.0027	0.0009	

These results are shown graphically in Plate II, the per cent. of alcohol being plotted as ordinates and the amounts of salt dissolved in grams, as abscissae. From this curve the above results (Table IV) are taken for the round concentrations.



A glance at the curves in Plate II shows, at once, that the solubility of the salt in the alcohol water solutions varies in a regular manner with the amount of alcohol present, decreasing gradually as the per cent. of alcohol increases. It should be noted, too, that it is appreciably more soluble in the methyl alcohol solutions than in those of ethyl alcohol. This is true also of the pure alcohols, for the absolute methyl alcohol

dissolves about six times as much salt as the absolute ethyl alcohol. This shows that a more complete precipitation of the chloroplatinate is obtained by using ethyl alcohol than methyl.

Attention should also be drawn to the considerable difference between the solubility of the chloroplatinate in 90 per cent. alcohol and in absolute alcohol. The removal of the last 10 per cent. of water lowers the solubility seven times. This shows the importance of using absolute alcohol in the precipitation of this salt. When sodium chloroplatinate is also present, however, it appears from Morozewicz's¹ work, that solutions containing over 80 per cent. alcohol decompose the sodium salt, precipitating sodium chloride.

Potassium and Sodium Chloride Solutions.—The solubility of the chloroplatinate in solutions of sodium and potassium chloride was next examined. These solutions were prepared by weighing out a certain amount of dry salt, making up to a definite volume, and subsequently diluting this standard by means of carefully calibrated pipettes. The determination of the amount of salt (chloroplatinate) which had passed into solution, was made by the colorimetric method. These determinations were, however, in the case of the sodium chloride solutions, always checked in the following manner. When the solutions were first made up, the amount of platinum salt added, as well as the volume of the solution, was carefully determined. When the solutions were ready to analyze, they were taken from the bath, the stopper removed, and the whole quickly filtered through a previously weighed Gooch crucible, the residue of the chloroplatinate being washed into the crucible with absolute alcohol, this, serving at the same time to wash the mat of the crucible. After carefully drying the crucible and contents, they were weighed. This method gave results which were in close agreement with those obtained by the colorimetric method.

TABLE V.—RESULTS SHOWING THE SOLUBILITY OF POTASSIUM CHLOROPLATINATE IN SOLUTIONS OF POTASSIUM AND SODIUM CHLORIDE.

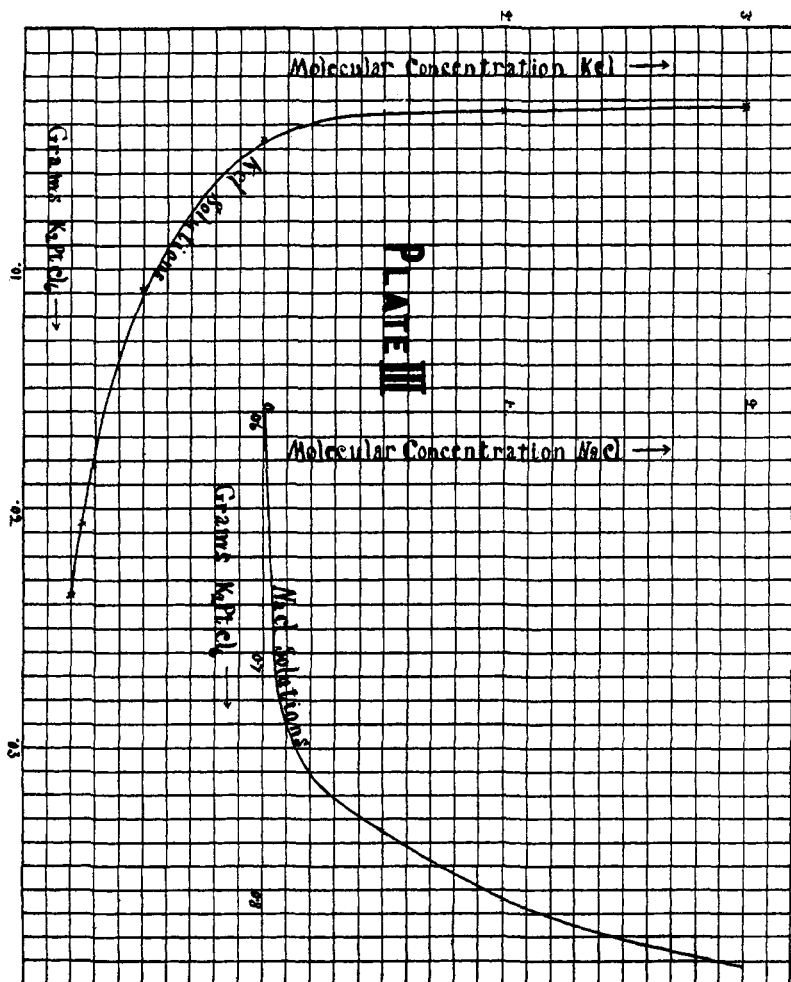
Concentration of KCl solutions.	Weight of K_2PtCl_6 in 100 gms. of solution.	Concentration of NaCl solutions.	Weight of K_2PtCl_6 in 100 gms. of solution.
0.000	0.7742	0.000	0.672
0.200	0.0236	0.050	0.700
0.250	0.0207	0.100	0.729
0.500	0.0109	0.250	0.758
1.000	0.0046	0.500	0.775
2.000	0.0045	0.750	0.791
3.000	0.0043	1.000	0.805
4.000	0.0042	2.000	0.834
Saturated	0.0034		

The results obtained with the sodium and potassium chloride solutions, are shown in Table V. The concentrations are expressed in terms of

¹ *Chem. Abst. Am. Chem. Soc.*, 1, 972.

gram molecules per liter. The measurements were carried out at 20° in the case of the potassium chloride solutions, and in the case of the sodium chloride solutions at 16° .

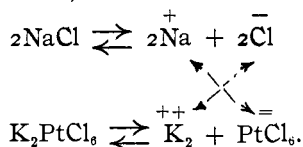
These results are shown graphically in Plate III, the concentrations of the solutions, as regards potassium and sodium chloride, being plotted as ordinates and the amounts of chloroplatinate dissolved as abscissae.



If we consider the potassium chloride solutions, we see that the amount of salt dissolved diminishes rapidly as the concentration of the potassium chloride increases, until we reach a concentration of about one gram molecule per liter. From this point on, the increase in the concentration of the potassium chloride has very little effect upon the amount

of chloroplatinate dissolved. This is surely what we would expect. Potassium chloride being, in its aqueous solution, a strongly ionized salt, we have here a high concentration of the potassium ion; in this case the one common to both salts. This will prevent the dissociation of the chloroplatinate, and therefore very little will go into solution. Apparently, by the time we have reached a concentration of about one gram molecule per liter, with regard to potassium chloride, equilibrium is practically established between the potassium chloride undissociated and the potassium and chlorine ions, as the addition of more chloride has little effect on the solubility of the chloroplatinate.

In the case of the sodium chloride solutions, we see that the amount of chloroplatinate dissolved increases as the amount of sodium chloride present increases. This increase is rapid at first, but after a concentration of 0.05 gram molecules of sodium chloride is reached, we see from Plate III that this increase is much smaller and very nearly proportional to the increase in concentration of the sodium chloride. The equilibrium is here between the ionized potassium chloride formed and the dissociated potassium chloroplatinate, thus:



The more dissociated sodium chloride there is present, the more sodium ions there are to unite with the PtCl_6 ions to form undissociated sodium chloroplatinate, and therefore the greater will be the amount of potassium chloroplatinate which will dissolve. This being the case, that portion of the sodium chloride which is dissociated will be largely instrumental in causing the potassium chloroplatinate to dissolve. And this is what we find to be the case. The first portion of sodium chloride added to pure water has a greater effect than later portions, as it almost entirely dissociates, while the same amount added to a concentrated solution has almost no effect.

If we compare the solubility of the chloroplatinate in potassium chloride solutions, with its solubility in the water-alcohol solutions, we see that about the same amount of the platinum salt is dissolved by a solution of potassium chloride containing two gram molecules per liter, as by a water-alcohol solution containing ninety per cent. of alcohol. If then, platinum was being precipitated from a solution, and not potassium, a more complete precipitation of the platinum would be obtained by adding a saturated solution of potassium chloride than by adding absolute alcohol.

The work described in the foregoing pages shows that:

(1) Small amounts of potassium chloroplatinate in solution can be estimated colorimetrically with considerable accuracy. This will be true of any salt which gives the PtCl_6 anion, provided the color of the cation is not such as to interfere.

(2) The chloroplatinate is less soluble in solutions of ethyl alcohol and water than in water solutions of either methyl or isobutyl alcohol. Only 0.0007 gram of the salt dissolves in 100 cc. of ethyl alcohol at 20° .

(3) The solubility of the chloroplatinate in potassium chloride solutions decreases with the increase in concentration of the potassium chloride, until a concentration of one gram molecule per liter is reached. Beyond this point, increasing the concentration of the potassium chloride has practically no effect.

(4) The solubility of the chloroplatinate in solutions of sodium chloride, increases rapidly until a concentration of 0.05 gram molecules per liter is reached. For more concentrated solutions the increase in solubility is small and almost proportional to the increase in concentration of the sodium chloride.

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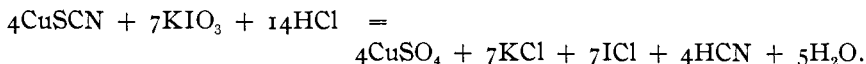
ON A VOLUMETRIC METHOD FOR COPPER.

BY G. S. JAMIESON, L. H. LEVY AND H. L. WELLS.

Received February 26, 1908.

The process to be described is based upon the titration of cuprous thiocyanate with potassium iodate solution in the presence of a large excess of hydrochloric acid. This method of titrating a number of reducing substances, such as free iodine, iodides, arsenites and antimonites, in a very satisfactory manner, is due to L. W. Andrews.¹ The reaction depends upon the formation of iodine monochloride and the disappearance of the iodine color imparted to an immiscible solvent, such as chloroform or carbon tetrachloride.

We find that cuprous thiocyanate is oxidized by iodine chloride sharply and quantitatively with the formation of cupric salts, sulphuric and hydrocyanic acids, according to the equation



This oxidation is similar to that obtained in Parr's method² for the titration of CuSCN by means of potassium permanganate solution, but we consider the iodate titration far preferable to the latter in simplicity and accuracy.

To show the applicability of the Andrews method to the titration of

¹ THIS JOURNAL, 25, 756 (1903).

² *Ibid.*, 22, 685 (1900).