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PLATINUM SILVER ALLOYS.

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THE solubility of platinum, when alloyed with silver in nitric acid, may be considered one of the historical facts in the history of the metal, as its announcement by the Graf von Sickingen[1] in 1782, came only forty-six years after the discovery of the element platinum, thus placing it among the earliest known chemical properties. The reasons for and quantitative relations of this solubility have, however, remained unexplained up to the present day, in spite of the numerous attempts on the part of various experimenters. The results of these authors have been conflicting in the extreme, and not only have the later investigators failed to confirm the earlier, but their results in themselves offer no explanation as to the cause of the anomalies. Thus, Clemens Winkler,[2] working with alloys containing percentages of platinum varying from 1 per cent. to 10 per cent., found that the strength of acid used was of small importance, while the weight of residue left, assumed by him to be platinum, was on the average about 66 per cent. of the weight of the original alloy. This percentage varied somewhat irregularly with the strength of acid and percentage of platinum in the alloy, and, in general, decreased with the platinum content of the alloy. John Spiller,[3] on the other hand, investigating alloys of the same range of platinum content, found acid of 1.42 specific gravity to be the best solvent, but records that, even under the most favorable conditions, only 0.75 to 1.25 per cent. of the platinum could be dissolved along with the silver. H. Rose[4] found that, at the most, 10 per cent. went into solution with the silver. N. W. Perry,[5] in a description of an assay method, states that after removing the base metal by cupellation, the platinum could be dissolved completely along with the silver, provided the platinum were alloyed with at least

[1] Muspratt, 4th Ed., 7, p. 255.

[2] Z. anal. Chem. 1874, p. 368.

[3] Pr. Chem. Soc. 13, 118 (1897).

[4] Rose: Handb. Analyt. Chem., 6th Ed., 2, 226.

[5] Eng. Min. J. January, 1879.

twelve times its weight of silver. E. H. Miller,[1] in a comparison of the various wet and assay methods for the determination of platinum, repeated Perry's work and found that, even with a platinum-silver ratio of twenty-seven to one, some platinum remained undissolved. The results in this case were, however, complicated by the presence of iridium and gold in the material experimented on. Later, von den Ropp,[2] in a series of experiments on alloys containing up to 30 per cent. of platinum, found that alloys containing not more than 23 per cent. of platinum could be brought completely into solution by treating them with nitric acid, washing the residue free from nitric acid with water and then treating with hydrochloric acid. Besides this new and positive fact brought out by von den Ropp's work, he also investigated to some extent the black residue left on treating the alloy with nitric acid, and tried the solvent effects of hydrochloric acid, sulphurous acid and ammonia in the order named, the treatment with each reagent being followed with a complete washing of the residue with water, the solutions and wash-waters being kept separate. In this way von den Ropp obtained a series of solutions or colloidal solutions. The cause of the solution of parts of the residue in this way, or the composition of the parts dissolved were, however, not investigated. Finally Krug,[3] in an investigation of the alloys of platinum and copper, found that the residue left on dissolving the alloys in nitric acid, and which he, as well as Winkler and von den Ropp, found to be explosive when heated with organic materials, *i. e.*, filter-paper, consisted of a nitrate. Krug explains the solubility found by von den Ropp (see above), as being merely a reaction of the hydrochloric acid used against this compound giving chlorine which dissolved the platinum. He also advanced the idea that the solutions obtained by von den Ropp with various reagents were simply forms of colloidal platinum. This latter idea will be discussed later in connection with some further solubility experiments. Beside these investigations of the solubilities of the binary alloys of platinum, several papers have been published dealing with experiments on the parting of ternary and even quaternary alloys containing platinum and silver. The results

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[1] School of Mines Quarterly, 17, 26 (1895).

[2] Berlin Dissertation, 1900.

[3] Leipzig Dissertation, 1903.

have in most cases been unsatisfactory, as the problem which, in the case of binary alloys, presented wide inconsistencies in similar work done by different investigators, has in the case of ternary and quaternary alloys become so complicated that it is impossible to decide what variable is responsible for any given set of results. The papers dealing with this phase of the subject will, therefore, not be reviewed in full, but will only be referred to when their results have some direct connection with either our experimental results or conclusions. In a foot-note, reference will be found to some of the more important or recent articles.[1]

As may be seen from the foregoing review, neither the primary fact of why platinum dissolves when alloyed with silver, or the secondary facts as to the quantitative relations of this solution have ever been firmly established. Chemical investigation alone would be enough to settle the latter. It is difficult to see, however, how strictly chemical methods could ever solve the first problem or give the basis on which the results of solution tests could be satisfactorily interpreted. The following investigation was therefore started with the idea of studying the physical properties of the platinum silver alloys and using the results so obtained in the interpretation of a series of solubility tests run in comparison with those of previous investigators.

The physical properties chosen for investigation were the melting-points and cooling curves, microstructure, specific gravity and electrical conductivity of the different alloys. These, it was felt, would give a sufficiently wide range of properties, so that reliance could be placed on a confirmation of the results of one series by those of another. A careful survey of the literature was made before beginning this study, with very little result. In this connection the assistance obtained from the excellent bibliographies of Howe[2] and Sack[3] should be acknowledged. On cooling curves the only quantitative data which could be found were given by a partial curve published by Heycock and Neville.[4] These

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[1] Carmichael: J. Chem. Ind. **22**, 1324 (1903); Sharwood: Ibid. **23**, 412 (1904); Richards: Analyst, **27**, 265 (1902); Neveu: Ann. Chim. anal. appl. **8**, 161; Hollard and Burtiaux: Ibid. **9**, 287.

[2] Bibliography of the Metals of the Platinum Group. Smithsonian Misc. Collections, Vol. 38, No. 1084.

[3] Bibliographie der Metallegierung, Z. anorg. Chem. **35**, 249 (1903).

[4] Phil. Trans. **189**, A. 25 (1897).

authors investigated alloys containing up to 2 atomic per cent.[1] of platinum (3.55 per cent. by weight) and found that the freezing-point curve rose sharply away from the freezing-point of silver, the alloy containing 2 atomic per cent. of platinum freezing at 990°. Matthiesen,[2] in an account of some experiments on certain platinum silver alloys, refers to the 33 per cent. alloy being at a critical point in electrical resistance. Beyond these references all data that could be found were either inapplicable to the present work or too vague as to percentages of platinum, etc., to be of any use.

EXPERIMENTAL.

The first step was the purification of the materials used and the preparation of alloys of known composition and proved homogeneity, the last two points being questions which had been neglected by previous investigators.

Purification of Materials.—The platinum used was a supposedly chemically pure foil from a foreign maker, but was shown by qualitative analysis, using the method of Mylius and Dietz,[3] to contain iridium. It was, therefore, freed from this by the following purification method.[4] This consisted in dissolving the impure platinum in aqua regia and freeing from nitric acid by repeated evaporations with hydrochloric acid. This hydrochloric acid solution, containing both of the elements in their highest state of oxidation, was then taken to dryness and heated on an electric hot plate for several hours at a temperature of 125°. It was then taken up with hydrochloric acid and water and precipitated by the addition of ammonium chloride and alcohol. The iridium, which had been reduced by the heating to a lower chloride, not being precipitated by the ammonium chloride, passed into the filtrate along with some of the platinum, also reduced. The

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[1] Atomic per cent. may be calculated as follows, for any series of binary alloys A—B:

$$\text{Atomic \% A} = 100\,\frac{\dfrac{\text{weight A}}{\text{atomic weight A}}}{\dfrac{\text{weight A}}{\text{atomic weight A}} + \dfrac{\text{weight B}}{\text{atomic weight B}}}$$

Weight A and B being taken as parts in 100.

Grube: Z. anorg. Chem. 44, 122 (1905).

[2] J. Chem. Soc. 20, 201 (1867).

[3] Ber. 1898, 3137.

[4] Encyclopedia Britt. 9th Ed., 19, 201.

ammonium chlorplatinate was then dried and tested for purity by spreading it out on a glazed paper and examining portions selected from different parts thoroughly under a microscope (80 diameters). In no case, although eight separate portions were examined from each lot, could any salt be detected except the yellow crystals of ammonium chlorplatinate. This salt was then converted to metallic platinum by ignition and washed successively with hydrochloric acid, water, nitric acid and water. The sponge so obtained was either used as such or melted with the oxyhydrogen blowpipe and rolled out into foil.

The silver was guaranteed by a reliable maker to be at least 999 fine, and was used without further purification. As will be shown later, the thermal analysis enabled us to make a check on the purity of the silver by means of a determination of its melting-point.

Preparation of Alloys.—To be used for a preliminary survey of the field, five alloys, weighing 10 grams each, were made, containing approximately 10, 20, 30, 40 and 50 per cent. of platinum. The method of preparation was the same throughout, except that the 40 and 50 per cent. alloys were made from the platinum sponge on account of the greater ease of alloying compared with the foil from which the others were made. In all cases, the silver was first melted in a No. 1 French clay crucible in a small Fletcher furnace. After it was thoroughly melted, the platinum was added piece by piece, if used as foil, or wrapped in an ashless filter-paper, when the sponge was employed. Heating was continued for about five minutes, when the crucible was withdrawn from the furnace and shaken violently until the melt solidified. It was then replaced, and this treatment, melting, holding melted for two to three minutes and then removing and shaking until the button solidified, repeated several times. The crucible was then removed from the furnace and the button allowed to solidify and removed from the crucible. It was then replaced in the crucible in an inverted position and the previous treatment repeated, so that any pieces of platinum which might have sunk to the bottom of the button and so escaped the effect of the several shakings, would come more intimately in contact with the melt. After several such heatings the button was allowed to cool and was cut in half vertically. One of the faces so exposed was then polished and examined with a metallographic microscope for any pieces of unalloyed platinum. If any such were found, the alloy was remelted and the previous treatment repeated until no platinum could be found unalloyed on careful microscopic examination. In cutting the alloys for microscopic examination, considerable difference in their hardness was noted, which will be discussed later in connection with their other physical properties. Before starting the preparation of the alloys, it was feared that the furnace used would not give sufficient heat to melt the alloys of higher platinum content. This fear was, however, without foundation, for using a false top, so that a higher rate of combustion could be used, and also a supplementary blast-lamp of the Waller type, blowing in at the same tuyere hole as the regular blast, it was found that temperatures of 1450° could be reached in the crucible.

Thermal Analysis.—The freezing-points and cooling curves of the alloys were next taken in the Fletcher furnace, the No. 1 French clay crucible holding the alloy being surrounded by a larger crucible to decrease the rate of cooling. The method used was that of direct observation, using a Siemens and Halske galvanometer and a platinum-platinum 10 per cent. iridium thermocouple. The wires for this couple were made with great care in order to insure perfect homogeneity. In fact the platinum iridium was melted and shotted in water four times before the final ingot was cast. The wires were next thoroughly annealed by means of electrical "glowing" to remove any strains from the wire-drawing and were then investigated and found to be thermoelectrically homogeneous. This was done by taking each wire and connecting one end to each of the terminals of the galvanometer by means of two copper wires, the ends of the platinum or platinum alloy wire being contained in an ordinary cold junction bottle. By heating successive places on the wire, it could be shown that the wire itself was homogeneous throughout, or at least that there were no sudden variations in composition. That the wires were not of progressively changing composition was shown by making each end of the wire successively the hot junction and comparing with a second couple. The maximum error found in this way amounted to 2°. This precaution of testing for thermoelectric homogeneity is essential in case it is not desired to make use of more than one junction in a series of determinations of a single point and especially in a Fletcher furnace, where the length of couple heated can not be easily varied to suit the convenience of the operator. The wires of the couple having been annealed and shown to be homogeneous, the couple was next standardized against the boiling-point of pure sulphur, using a Barus boiling-point tube, and against the freezing-point of Kahlbaum's copper. The sulphur used was in the form of crystals from carbon disulphide and was boiled thoroughly to free from any carbon disulphide, either of crystallization or mechanically held. Its boiling-point was taken at 444°.[1] The freezing-point of the copper was taken as 1084°[2] and the determinations were made under a layer of charcoal, the copper being melted under this layer, held melted for some time and also poled with a stick to insure complete reduction. From these points the curve of the couple was calculated, using Holman's logarithmic formula.[3] As a check on the accuracy of this curve, the melting-point of Kahlbaum's antimony was next determined, and in all cases fell within a limit of error of 3° from the temperature of 630° which was taken as the true melting-point.[4] A further check on the accuracy of the standardizing was obtained by the determination of the freezing-point of silver, which was determined in a graphite crucible under a layer of charcoal. This also in every case fell within the 3° limit and formed a very good check on the purity of the silver used in the preparation of the alloys. The melting-point of pure silver free from oxygen was taken as 961°.[5] In taking the melting-points and cooling curves of the alloys themselves it was not possible to use a charcoal cover, as the disturbing influence of oxygen was preferable to any risk of the platinum forming a carbide or taking carbon into solution. It is probable that this influence was of importance only in the alloys of lower platinum content, as with the higher alloys no noticeable spirting took place. Several experimental difficulties arose in these freezing-point and cooling-curve determinations, due largely to the use of such small amounts of alloys as to make the evolution of heat at any one temperature very small. In all

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[1] LeChatelier and Boudouard's "High Temperature Measurements," 2nd Eng. Ed., 296.

[2] Holborn and Day: Am. J. Sci. 11, 145 (1901); 8, 165 (1899).

[3] Holman: Pr. Am. Acad. 31, 234.

[4] Day and Allen: Phys. Rev., Sept., 1904.

[5] Holborn and Day: Am. J. Sci. 11, 145 (1901); 8, 165 (1899).

cases the couple cover was clamped in place so that the end of the couple would come as near as possible to the center of the melt.

Electrical Resistance, Specific Gravity and Ductility.—After the thermal analysis had been finished, the alloys were remelted in crucibles of such a shape that the resulting buttons were in the form of cylinders of approximately 9 mm. diameter. A section was cut from the bottom of each button and reserved for microscopic examination while the remainder of the button was rolled out into tape. The rolling out of the alloys was kindly done for me by Mr. Cohn of the platinum-refining firm of Belais & Cohn, of New York City. From this tape a piece of uniform cross-section was cut out, which was thoroughly annealed and used for the measurement of the electrical resistance. This measurement was done for me on a Wolff bridge, by Mr. A. H. Nelson, of the Department of Physics, to whom I wish to express my thanks.

ELECTRICAL RESISTANCE EXPRESSED IN OHMS PER SQUARE MILLIMETER PER METER.

0.0 per cent. platinum 100.0 " " silver	0.0217
10.39 " " platinum	0.0918
20.59 " " "	0.1814
31.46 " " "	0.2914
37.89 " " "	0.3110
57.05 " " "	not determined

The alloys were then cut into small pieces for further investigation by means of a large pair of shears. In this connection the very interesting qualitative fact may be noticed of the very marked change in ductility and in actual hardness which accompanied the increasing platinum content. This had already been noticed when cutting up the alloys for the different microscopic examinations and the same observations were repeated when the alloys were rolled. Thus the pure silver could be cut and rolled in the manner to be expected from its well-known soft and ductile nature; that is, the hack saw was not appreciably dulled by cutting a button and, in rolling, several passes could be made each time before the button had to be annealed. The 10 and 20 per cent. buttons were very much like it in both of these properties. With the increase of the platinum content up to 30 per cent., however, a marked change was noted in the behavior of the buttons. In cutting, the buttons were much harder and this hardness increased rapidly with the increasing platinum content. Thus, while the 31 per cent. button cut with more difficulty than the lower ones, but was still comparatively soft, the 57 per cent. alloy was, on the other hand, so hard that several saws were broken each time a button had to be cut. This property was still more marked in the case of the rolling, and was shown by the increasing frequency with which the alloys had to be annealed in order to get them to go through the rolls without cracking. The limit of this was reached with the 57 per cent. alloy, which would stand almost no reduction and cracked so badly on the first pass that further rolling and, therefore, the measurement of its electrical resistance, had to be abandoned. Since the object of the investigation was to study simply those properties which would tend to throw some light on the chemical behavior, the question of changes in hardness was followed no further and no attempt was made to check these very rough qualitative results by means of sclerometer measurements.

The alloys having been cut up into small pieces, their specific gravity was measured, using a weighing-bottle, as compared to that of water at 4°, with the following results:

Pure silver	10.61
10.39 per cent. platinum	11.17
20.59 " " "	11.80
31.46 " " "	12.57
37.89 " " "	13.19
57.05 " " "	14.25

Analysis.—In order that the results on the various alloys might be referred to alloys of known composition, the alloys were analyzed by means of the standard parting with sulphuric acid. From the table of results, given below, the necessity of this step is plainly shown and gives some explanation as to the cause of the anomalous results of some previous investigators, who in no case had any further knowledge of the composition of their alloys than that gained from the proportions used in making them up. As in making our alloys the quantities of the metals were weighed exactly for making alloys of 10, 20, 30, 40 and 50 per cent. of platinum, the magnitude of the error even when working carefully in crucibles may be observed, and shows that the composition of the alloys made on charcoal before a blowpipe can only be a matter of conjecture, no matter how carefully the materials may have been weighed. As carried out, the parting differed somewhat in detail from that generally described. In fact the methods as given in most descriptions of the process could not fail to give inaccurate results. One description provides for parting 300 mg. of the alloy for fifteen minutes over a Bunsen burner in a parting flask with 10 cc. of pure concentrated sulphuric acid. The acid was then allowed to cool and decanted into a beaker containing distilled water. The residue was treated as before with 5 cc. of strong sulphuric acid, decanted into the same beaker, and washed till free from acid, adding the washings to the silver sulphate solution. The platinum is then transferred to a small crucible by inverting, dried in an air-bath and weighed. By this means the author, working on an alloy containing over 33 per cent. of platinum, obtained results differing only by 0.1 per cent. on four separate determinations, and states that the platinum was tested for silver, but was found to contain only a minute trace. He further states that the silver may be estimated in the filtrate by the thiocyanate method, or, as in his work, by difference.

In attempting to follow out this method it was found that, even with closely agreeing duplicates, entirely erroneous results were obtained, for the following reasons: (1) In decanting the sulphuric acid solution from the residue platinum passed over with the solution. This platinum was in either a very finely divided or colloidal state, giving a dark color to the solution. The state of division was so fine, that not even by allowing the beaker containing the decanted filtrate to stand on a piece of white paper could any particles be seen as such. That they were present, however, is shown by the fact of their separating, if the solution was allowed to stand over night. And further, the fact that this separation on standing was due to particles already contained in the solution, and not to colloidal platinum or to a precipitate formed by some unnoticed reaction during standing, was shown by taking two portions of the same alloy and parting in the same way with sulphuric acid. One of these solutions was decanted and allowed to stand over night, and in the morning a fine black precipitate was found on the bottom of the containing beaker. The second solution was diluted and filtered, when a black precipitate was found on the filter-paper, and the filtrate on standing threw down no further precipitate. (2) The platinum residue left, always contained some silver. This was less in amount with the lower platinum alloys, but was always a weighable quantity, and in the higher alloys became of very considerable importance. The use of the thiocyanate method for determining the silver in the filtrate was tried, but was not successful, in the presence of the large amounts of sulphuric acid from the solution of the alloy. By precipitating the silver from this acid solution with aluminium foil, dissolving in nitric acid and titrating, better results could be obtained, but the duplicates were not satisfactory.

The method finally adopted was as follows: 300 mg. of the alloy were taken and heated for fifteen minutes in a beaker with 10 cc. of concentrated sulphuric acid on an asbestos pad over a Bunsen burner. This solution was then decanted into a beaker and the alloy broken up by poking the pieces with a stirring rod, and then re-treated for fifteen minutes with 5 cc. more of concentrated sulphuric acid. The solutions were then combined, diluted, filtered through an ashless paper, and washed till entirely free from silver salts. The residue on the paper was then ignited in a porcelain crucible and weighed. This residue was then dissolved in aqua regia and by several treatments with nitric acid, followed by taking the solution gently down almost to dryness most of the free acid was removed, and the free acid that remained was nitric and not hydrochloric. The solution was then diluted somewhat, and the silver precipitated by the addition of common salt in the usual way. The precipitate obtained in this manner was of a reddish yellow color, apparently due to admixed silver chlorplatinate. This precipitate was filtered and washed free from chlorides. It was then dissolved through the paper with dilute ammonia and reprecipitated in the filtrate with nitric acid and a drop or two of hydrochloric acid. It was filtered and weighed in the regular way. It was found that this solution of the impure silver chloride and reprecipitation gave a perfectly white precipitate, while the platinum passed into the filtrate. The strong sulphuric acid solution containing the silver was treated in one of two ways: (1) By diluting to about 900 cc., partly neutralizing and precipitating the silver as sulphide at a temperature of about 90°, filtering, dissolving the sulphide in nitric acid and reprecipitating the silver as chloride, in which form it was weighed. (2) The effect of precipitating the silver as chloride direct in the sulphuric acid solution with common salt, after partly neutralizing with ammonia, was tried with practically the same results as obtained by the first and longer method of procedure. In either case the precipitated silver chloride was washed till the washings gave no test with silver nitrate, while the filtrates were all tested with hydrogen sulphide to be sure that the summations obtained were not due to any balancing of errors. The sulphuric acid used in the parting was tested and found to contain no nitric acid. In some cases, however, unweighable traces of platinum could be found in the filtrate, by means of an examination with a microscope on the concentrated filtrate when tested with ammonium chloride. This was neglected in our work, and no attempt was made to separate it from the silver, which it contaminated, as the amount present was very small.[1] The results follow:

Pt supposed	10.00	20.00	30.00	40.00	50.00
Pt actual	10.39	20.59	31.46	37.89[2]	57.05
Ag retained by Pt	tr.	0.59	0.98	2.24	2.70
Ag in filtrate	89.54	78.62	67.51	59.81	40.26
Summation	99.93	99.80	99.95	99.94	100.01

As may be seen from the previous tables, these results have been used to correct the supposed platinum percentages on the alloys.

Microstructure.—The specimens which had been reserved for the microscopic examination were next prepared for examination and photographing by polishing them successively on rough and smooth Armour emery paper, and on 0, 00, 000 and 0000 Hubert French emery paper. The polishing was finally finished on baize on a rouge board, using carefully washed jewelers' rouge. Etching was done with 1.1 specific gravity nitric acid. For examining and photographing the alloys, a Reichert microscope was used in connection with a Bausch and Lomb photomicrographic

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[1] Recently in a paper published by Delépine (Compt. rend. 142, 631 (1906); abs. J. Chem. Ind. 25, 314 (1906)), it has been claimed that boiling concentrated sulphuric acid will dissolve considerable amounts of platinum on treatment for forty to fifty hours. This is in direct contradiction to other work on the same lines (Conroy: J. Chem. Ind. 22, 465 (1903)) but whether true or not has no application to our experiments where the time of treatment was much less.

[2] The very low platinum content of this alloy can only be explained by the accidental loss of platinum during the preparation, as duplicates show that the figure for platinum as given above is correct, and repeated microscopic examinations of polished sections show that it is homogeneous.

camera, using a Welsbach illumination and an inside illuminator. All photographs were taken at a magnification of 100 diameters.

Results of Thermal Analysis and Microscopic Examination.—Heycock and Neville,[1] in their investigation of a limited portion of the platinum silver cooling curve, found that with increasing platinum content, up to the limit of their investigation, the melting-point rose regularly, their alloy of maximum platinum content (3.55 per cent.) having a melting-point of 990°. In our experiments the alloy containing 10.39 per cent. of platinum was heated to 1200°, and the cooling curve taken from that point. Two evolutions of heat were noticed, the first at 1045–1050° and the second and much larger at 1000°. Owing to the conditions of radiation from the furnace there was always a slight drop of temperature throughout, when operating with weights of alloys as small as 10 grams, and it was not possible to determine whether solidification was complete at 1000° or not. The alloy, when examined under the microscope, was found to consist of crystals set in a ground mass, which was not composite, or at least, which could not be resolved by the highest power available. This is not, however, a positive proof that the ground mass had not frozen out as a eutectic and afterward become simple by segregation, a fact of common occurrence when the eutectic is small in amount. The 20.59 per cent. alloy was heated to 1100°, and on cooling evolved heat strongly at 1085°, and possibly again at 995°, although the indications at the latter point were hardly beyond the experimental error. The microstructure at this point showed large, white dendrites also set in a non-composite ground mass. The 31.46 per cent. alloy was heated to 1300° and a cooling curve taken down to 970°. Marked evolutions of heat took place in the range between 1170° and 1100°. They were, however, very irregular and were different in their exact location in different trials. The examination of the alloys under the microscope showed well-defined crystals of a grayish color set in a dark ground mass. These gray crystals had each a perfectly white silvery core or spine, which offers a clue to the irregularities of the cooling curves. This is, that the rate of cooling was so rapid that the alloy passing through transformation points did not have time to come to equilibrium, and this result is shown both by the microstructure and by the cooling curves. In the cooling curves this is shown

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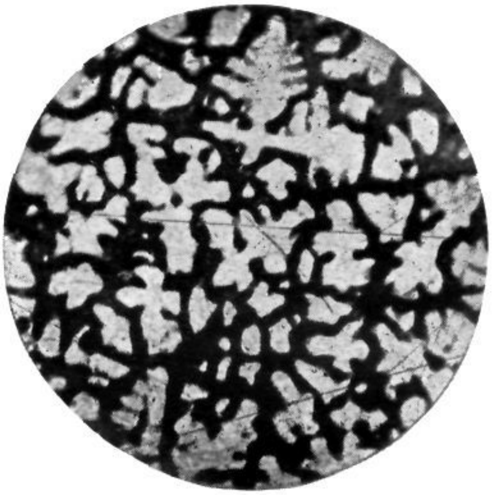
[1] Loc. cit.

by the heat liberations at any one temperature being very small and also confused, owing to heat liberations from two separate causes taking place at the same time in different parts of the button. The most regular of the curves show, however, a consistent evolution of heat at 1160°, and this is taken as probably correct. There are also weak indications at about 1230°. In the microphotographs this is shown by the white core in the centre of the crystals, which disappears when the alloy is remelted and allowed to solidify and cool very slowly in a gas furnace (see photomicrographs). The 37.89 per cent. platinum alloy, while showing much the same characteristics in its microstructure as the 31.46 per cent. alloy, *i. e.*, gray crystals with white centres set in a dark ground mass, gives much sharper heat evolutions during its cooling. These are at 1240°, not very strong but consistent for all curves, and a second at 1170°, which is strongly marked in all curves, and is the most marked evolution for this particular alloy. Unfortunately, the curve was only once continued below 1000°, and in this case was too irregular to be of any value. The 57.05 per cent. alloy was heated to over 1400°, and on cooling gave evolutions of heat at 1240°, 1180° and 1090°. In microstructure it appeared very much like the 37 per cent. alloy.

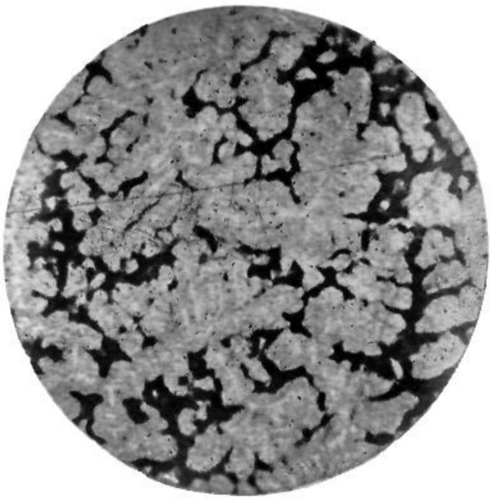
SOLUBILITY TESTS IN NITRIC ACID.

Method of Procedure.—Chemically pure nitric acid was diluted with distilled water and, after cooling, the concentration was adjusted with water to 1.1 specific gravity to within the limit of accuracy of a delicate hydrometer. Three hundred mg. of each of the alloys, cut into small pieces (1 × 2 × 2 mm.) were next weighed out into No. 2 beakers and 25 cc. of the 1.1 acid added to each. These were placed on an electric hot plate and heated rapidly to 70° or 80° and kept at that temperature for an hour, the temperature being observed by means of thermometers. At the end of twenty minutes the alloys were broken up by means of the thermometers, so as to prevent as far as possible the effect of any mechanical coating. After an hour the solutions were removed from the stove and allowed to stand for one and one-quarter hours after diluting to about 75 cc. The solutions were all somewhat colored, those from the 20 and 31 per cent. alloys especially, the order of decreasing intensity of color being 20, 31, 37, 57 and 10. Of these the 20 was almost black and was

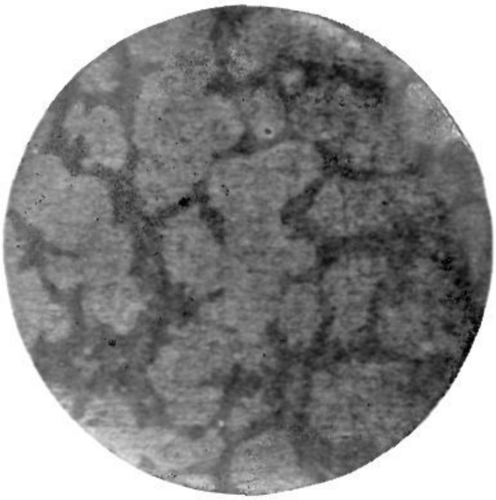


10.39 per cent platinum.
Air cooled.

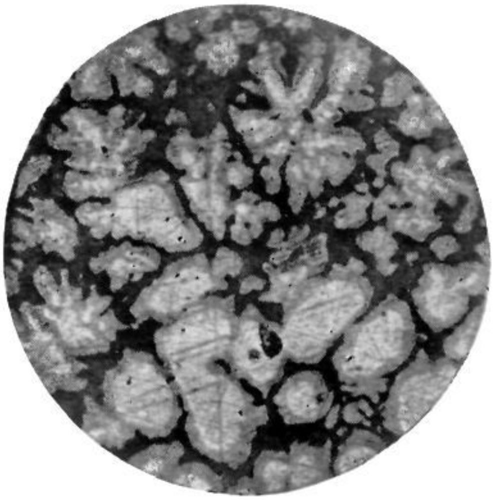
20.59 per cent. platinum.
Air-cooled.



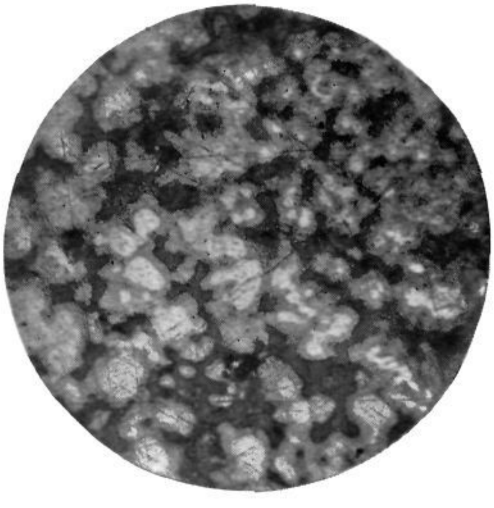
31.46 per cent. platinum.
Air-cooled.



31.46 per cent. platinum.
Furnace-cooled.



37.89 per cent. platinum.
Air cooled.



57.05 per cent. platinum.
Air-cooled.

opaque, the remainder rapidly shaded down in color to the 10, which was almost colorless. The solutions were then filtered through 7 cm. ashless filter-papers, when it was found that the filtrates bore the same color relation as the original solutions. On attempting to wash the precipitates with distilled water, they washed through the paper readily and acted in the manner common to all colloidal precipitates. The filtrates and wash solutions were therefore combined and the residues salted out with sodium nitrate free from chloride. After standing they were filtered through the same filter-paper as before, and on washing with 1 per cent. nitric acid (*i. e.*, 1 cc. of 1.42 acid in 100 of water) it was found that they could be washed free from silver without loss from the formation of any colloidal precipitate. After ignition in porcelain crucibles they were weighed, dissolved in aqua regia and the silver contained determined as in the case of the analysis of the alloys. During the ignition, slight explosions due to the precipitate reacting with the filter-paper could always be noticed. The results follow, the one given for the 31.46 per cent. alloy being determined on the alloy in the rapidly cooled state.

Per cent. Pt in alloy	10.39	20.59	31.46	37.89	57.05
" " residue	3.86	8.58	36.59	49.13	65.16
" " Ag in residue	0.27	1.81	12.09	13.64	12.19
" " Pt in residue	3.59	6.77	24.50	35.49	52.97

Evidently, from the foregoing any ratio of platinum and silver which will allow of complete solution of both in nitric acid of 1.1 specific gravity must lie within considerably closer ranges than those investigated above. A further series of alloys was therefore made in order to test further for this point. These alloys were made in the same way as the previous set and were examined microscopically for homogeneity. Parting tests were conducted as before with nitric acid of 1.1 specific gravity, except that the silver content of the residues was not determined, as the object was to find a completely soluble ratio, or failing that the most nearly soluble ratio to test the process as a means for analytical separation. Since Miller's[1] work had shown that with a platinum content of 4 per cent, some residue was left, the alloys below that point were investigated thoroughly. Besides these, alloys were

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[1] Loc. cit.

made at ratios selected by means of the cooling curves and certain alloys were selected arbitrarily in order that the solubility results might not have to be interpolated except over very narrow ranges. The results follow, those for the 31.46 per cent. alloy in this case being on the very slowly cooled alloy.

Per cent. Pt in alloy....	0.50	1.00	2.00	3.00	4.00	5.00	
" " residue.........	0.42	0.85	1.74	2.19	2.98	3.56	
" " Pt in alloy....	13.00	14.00	15.00	16.00	18.00	25.00	31.46
" " residue.........	3.33[1]	4.26	4.32	4.55[1]	4.54[1]	16.62	38.58

In these tests as well as those of the previous series the formation of colloidal platinum was very marked, especially with the alloys near to 20 per cent. of platinum. When this had been completely removed by means of ammonium nitrate and heat, the solutions were still colored, but this coloration was very slight and no further separation took place in solutions containing considerable ammonium nitrate and nitric acid, even on standing several days.

As previous investigators had found that the amount of residue varied with the strength of acid used, a further series was run, using nitric acid of 1.40 specific gravity as a solvent. The method of procedure was the same as that of the previous series, the results being as follows:

Per cent. Pt in alloy	0.50	1.00	2.00	3.00	4.00	5.00	10.00	
" " residue.....	0.22	0.42	1.09	1.81	2.42	2.62	4.53	
" " Pt in alloy	13.00	14.00	15.00	16.00	18.00	20.00	25.00	30.00
" " residue.....	5.79	4.97	7.93	11.54	11.65	13.94	20.66	29.29

The foregoing results show clearly the impossibility of separating platinum from gold, iridium, etc., when alloyed with silver by means of one parting with nitric acid, and also the fallacy of assay methods, such as Perry's, based on this supposed separation. The questions as to the explanation of the solubilities are, however, more complex. From the results of etching tests made on the stage of the microscope it is apparent that the reaction of the alloy with the nitric acid is a double one, part tending to give solution of the alloy and part tending to produce the explosive nitro compound, well-known as one of the products of this reaction. This in itself would explain many of the differences shown by the work of various investigators working on alloys of

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[1] Average of two figures.

the same composition. A second cause enters in, however, which is probably the more important. It is as follows: From the thermal data and microstructure it may be seen that the alloys consist of a series of solid solutions, having several reaction or transformation temperatures where the crystals already separated out react with the molten part of the alloy. On account of the high melting-point of these alloys, the cooling through these ranges is always so rapid that these reactions are never complete and the final alloy consists of a variety of products upon whose individual solubilities depend the solubility of the alloy as a whole.

Attempts were made to isolate the different components of the alloys by means of solution with various reagents. These were, however, all futile, as it was not possible to find in the time at our disposal, any reagent which would give a complete solution of one constituent without attack on the remainder of the alloy. In the course of this work the 37.89 and 57.05 per cent. platinum alloys were remelted and quenched in cold water from the molten state, and polished slips were submitted to the action of nitric acid of 1.2 specific gravity in the cold for a period of about ten days, the object being to isolate the constituent first to freeze out. The acid was changed frequently and the products of the reaction were removed by washing by decantation with cold water. The slips of alloy, even after being so disintegrated that they felt apart on being pressed with a stirring rod, retained their bright appearance, showing that one constituent at least was apparently unattacked by the acid. In no case was it possible, however, to carry the treatment so far that standing in fresh acid for twenty-four hours gave no attack, as shown by the presence of silver in the solution. Whether this was due to some attack on the apparently insoluble constituent or to the continued solution of undissolved ground mass could not be determined. The residues were finally washed thoroughly and examined under a microscope when they were found to consist of grains which were apparently unattacked. Analysis of these grains while, sufficiently concordant to point to a definite platinum silver compound, did not justify the assignment of a formula. Coupled with the marked and increasing hardness and brittleness of the alloys containing more than 30 per cent. of platinum, which properties are lacking in both of the metals forming the alloys and persist even in the annealed samples, we are led to conclude that a platinum silver compound crystallizes out which reacts against the liquid during solidification, giving a soluble or partially soluble product, which in turn further reacts or is transformed. The explanation of the abnormal solubilities of these alloys and of the widely differing results of the different investigators therefore lies in the presence of varying amounts of these constituents, depending both upon the composition and rate of cooling of the alloy.

CONCLUSIONS.

(1) The separation of platinum from gold, iridium, etc., in one operation by means of alloying with silver and parting with nitric acid is impossible.

(2) Analytical results on platinum silver alloys, based on parting with concentrated sulphuric acid, are incorrect for alloys containing 20 per cent. or more of platinum, unless correction is made for the undissolved silver remaining with the platinum.

(3) The existence of platinum silver compounds is probably the explanation of the irregular results obtained in parting with nitric acid.

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THE INSOLUBLE CHROMICYANIDES.[1]

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As the potassium salt of hydrochromicyanic acid was used to precipitate the others, the methods of preparing the salts were first considered.

In 1903 L. O. Beatty investigated the method of preparation of potassium chromicyanide, and found that the methods of Böckmann,[2] Stridsberg,[3] Kaiser[4] and Christensen[5] did not give

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[1] Read at the May Meeting of the New York Section of the American Chemical Society.

[2] Traité de Chimique Organique, J. Liebig, Vol. I, p. 174; Gmelin's "Handbook of Chemistry," Vol. VII, p. 420; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 1864, Vol. XVII, p. 302.

[3] Jahresb. 1864, Vol. XVII, p. 304; N. Arch. ph. nat. XXII, p. 151.

[4] Ann. Chem. Pharm. III suppl., p. 163; Gmelin Handb. 4