
On the Liquefaction of Metals of the Platinum Group

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Phil. Trans. R. Soc. Lond. A 1892 **183**, 629-652

doi: 10.1098/rsta.1892.0016

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XVI. *On the Liquefaction of Metals of the Platinum Group.*By EDWARD MATTHEY, *F.S.A., F.C.S., Assoc. Roy. Sch. of Mines.**Communicated by* SIR G. G. STOKES, *Bart., F.R.S.*

Received March 3,—Read May 5, 1892.

IN the present paper, which is a continuation of a former one which has already been submitted to the Royal Society and has been published in the "Proceedings,"* an attempt is made to ascertain whether liquation occurs in alloys of the rarer metals, notably in those of platinum, with palladium, and with rhodium, and of gold with aluminium.

In the paper communicated to the Royal Society in 1890 upon this subject, I stated that ninety parts of fine gold melted with ten parts of pure platinum, and cast into a spherical mould showed a liquation of the platinum to the centre of the sphere, as shown in Diagram C in that paper.

Subjoined are the full details proving that such liquation occurred.

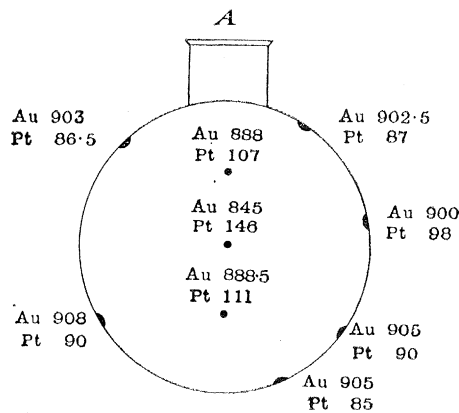
A. Gold 900 parts.
Platinum 100 „

Parts in 1000 of gold :—

Outside.	Intermediate.	Centre.
903	888	845
908	888·5	
905		
902·5		
905		
900		
Average . 903·9		

Maximum difference in the gold between centre and mean of outside, 58·9 per thousand.

* 'Proceedings of the Royal Society,' 1890, vol. 47, pp. 180–186.



In order to prove incontestably this liquation of platinum to the centre of the mass, I again melted together ninety parts of fine gold with ten parts of pure platinum.

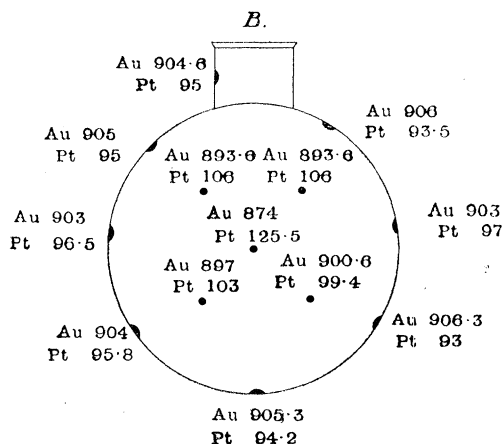
This alloy was melted in a plumbago crucible in the intense heat of an oil furnace, and when melted several times and stirred, was cast into a spherical mould of cast-iron. The weight of the sphere was about 5 kilogs. This, cut into two hemispheres, showed the results given in Diagram B.

B. Gold 900 parts.
 Platinum 100 „

Parts of gold in 1000 :—

Outside.	Intermediate.	Centre.
904.6	893.6	874
905	893.6	
903	897	
904	900.6	
905.3		
906.3		
903		
906		
Average . 904.6		

Maximum difference in the gold between centre and mean of outside, 30.6 per thousand.



The re-arrangement in this instance (*B*) is less than in the case of (*A*).

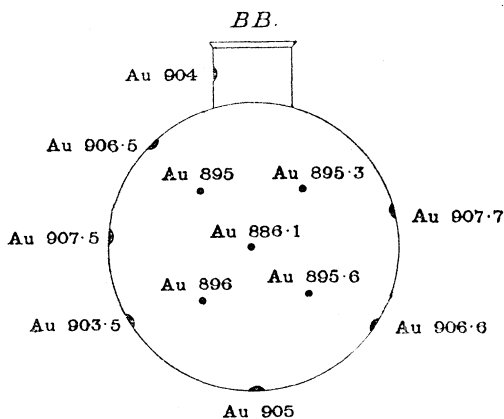
I re-melted this metal, and again made analyses, with a view to determining the amount of the gold at the points indicated on one of the hemispheres obtained (*BB*) and these results go very far to confirm those immediately preceding.

BB. Gold 900 parts.
 Platinum 100 „

Parts of gold in 1000 :—

Outside.	Intermediate.	Centre.
904	895	886.1
906.5	895.3	
907.5	896	
903.5	895.6	
905		
906.6		
907.7		
Average . 905.8		

Maximum difference in the gold between centre and mean of outside, 19.7 per thousand.



Having obtained these castings by melting in a crucible in a wind-oil furnace, I now re-fused this metal (B, BB) by means of the oxyhydrogen flame in a lime furnace at the most intense white heat.

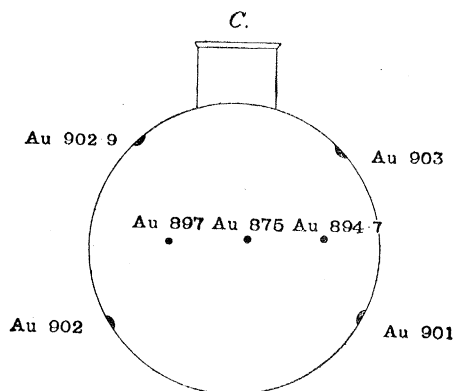
The metal was cast into a spherical mould and divided by cutting into two hemispheres in the usual way. The relative distribution of the gold is shown in diagram C.

C. Gold 900 parts.
Platinum 100 „

Parts of gold in 1000 :—

Outside.	Intermediate.	Centre.
902·9	897	875
902	894·7	
901		
903		
Average . 902·2		

Maximum difference in the gold between centre and mean of outside, 27·2 per thousand.



It is evident that the temperature at which the metal is cast, materially affects the extent to which the platinum liquates towards the centre.

In the next experiment, an alloy consisting of pure gold ten parts, and pure platinum ninety parts, was fused together.

This was conducted by melting the two metals in a lime furnace, by means of the oxyhydrogen flame. When the alloy was thoroughly liquid, it was poured into a mould and again melted and cast, to ensure a thorough mixture of the two metals.

The alloy was melted for a third time, and then poured into a spherical mould made of lime. The quantity operated upon was about $5\frac{1}{2}$ kilogs. The sphere showed, when cut into two halves, a brilliant white crystalline structure (D). The gold in the portions of metal removed for examination was very carefully determined by the

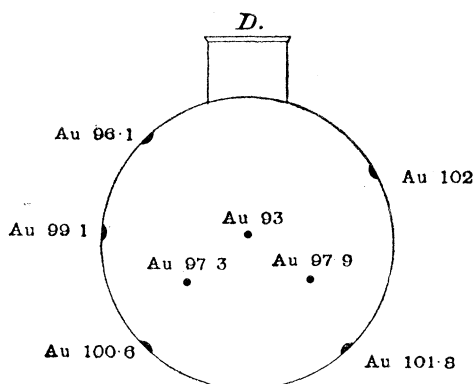
method which will be described subsequently; the platinum will of course be the difference.

D. Gold 100 parts.
Platinum 900 „

Parts of gold in 1000 :—

Outside.	Intermediate.	Centre.
96.1	97.3	93
99.1	97.9	
100.6		
101.8		
102		
Average . 99.9		

Maximum difference in the gold between centre and mean of outside, 6.9 per thousand.



To follow this up : an alloy of gold twenty-five per cent. and of platinum seventy-five per cent. was then made in a similar manner to the alloy D, and the utmost care was taken to ensure a thorough mixture of the two metals. This alloy was also melted in a lime furnace by the oxyhydrogen flame and cast into a spherical lime mould. The sphere weighed between 5 and 6 kilogs., and the alloy was hard and brittle, resembling somewhat one of grey cast-iron.

The following are the results obtained from the hemispheres into which the sphere was divided :—

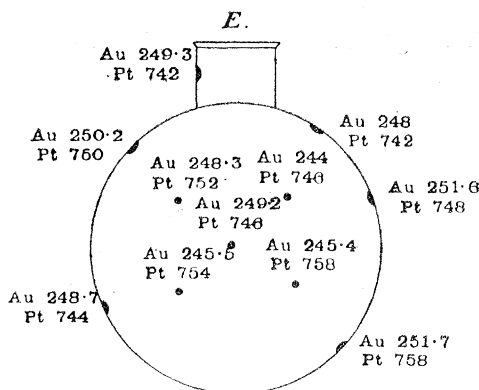
E. Gold 250 parts.
Platinum 750 „

Parts of gold in 1000 :—

Outside.	Intermediate.	Centre.
249·3	245·5	249·2
250·2	245·4	
248·7	248·3	
251·7	244	
251·6		
248		
Average . 249·9		

Maximum difference in the gold between centre and outside, 2·5 per thousand.

Maximum difference in the gold between intermediate and outside, 7·7 per thousand.



It will be observed that in the spheres D and E, in which platinum constitutes the bulk of the mass, the platinum is still driven to the centre. This point requires further investigation ; but it may be pointed out that the same effect occurs in the case of standard silver. The most fusible alloy of the copper-silver series is the one which contains about 650 parts of silver in 1000, and it might, therefore, be expected that the *centre* of an alloy containing more silver than 65 per cent. would be poorer in silver than the outside ; nevertheless, the authorities, LEVOL, ROBERTS-AUSTEN, and in fact, all who have worked with silver-copper alloys know the contrary to be the case. Silver is driven inwards notwithstanding the fact that an alloy poor in silver remains fluid long after the mass as a whole has become comparatively solid. The platinum-gold alloys now in question behave like the silver-copper series.

Palladium-Gold Alloys.

It is not an easy matter to obtain trustworthy assays from alloys of gold and palladium, and this fact first called my attention to the liquation of this metal from gold.

I melted an alloy of ninety parts pure gold with ten parts of pure palladium in a plumbago crucible in a wind-oil furnace (several times to ensure mixture), and then cast this into a spherical mould, which gave a sphere of about 5 kilogs. of the alloy.

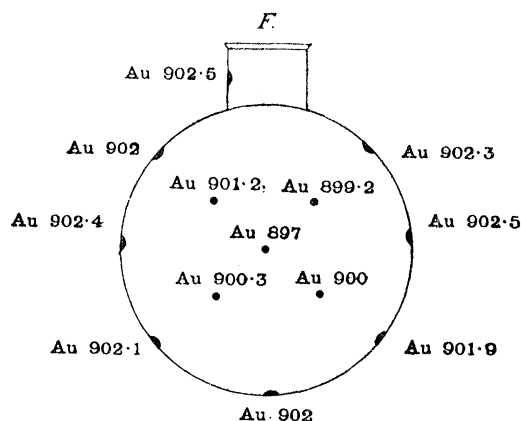
This sphere, which I call F, was cut into halves. The following are the determinations of the gold results from various parts of the hemisphere—the palladium can safely be taken by the difference :—

F. Gold	900 parts.
. Palladium	100 „

Parts of gold in 1000 :—

Outside.	Intermediate.	Centre.
902.5	901.2	897
902	899.2	
902.4	900.3	
902.1	900	
902		
901.9		
902.5		
902.3		
Average . 902.2		

Maximum difference in the gold between centre and mean of outside, 5.2 per thousand.



This same metal was now re-melted under the oxyhydrogen flame in a lime furnace, and re-cast into the same spherical iron mould as before, the alloy therefore was at a much higher temperature than in the previous case.

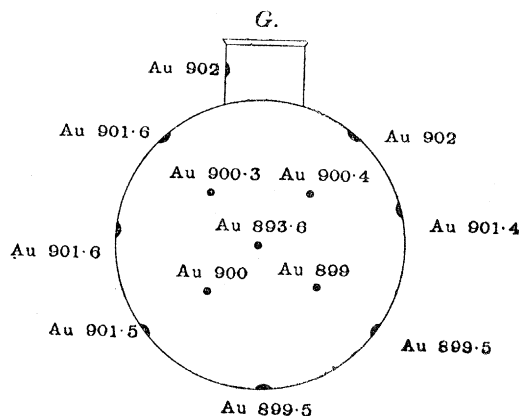
The sphere, which I call G, being cut equally into two, the following are the results from the various indicated portions of the hemisphere :—

G. Gold 900 parts.
Palladium. 100 „

Parts of gold in 1000 :—

Outside.	Intermediate.	Centre.
902	900·3	893·6
901·6	900·4	
901·6	900	
901·5	899	
899·5		
899·5		
901·4		
902		
Average . 901·1		

Maximum difference in the gold between centre and mean of outside, 7·5 per thousand.



It seems therefore clearly demonstrated by these experiments that the metal palladium is driven towards the centre of the mass in alloys of gold and palladium in a similar manner, though not perhaps to the same extent, as platinum-gold alloys, and the experiments shown by the diagrams given prove this fact incontestably.

The methods adopted for the determination of the gold in the respective platinum and palladium alloys were the following :—

In the alloys of gold, 10 per cent., and platinum, 90 per cent. Two carefully weighed portions of the alloys to be analysed were weighed and cupelled with two and three-quarter times their weight of fine silver—in identically the same manner as in conducting the process of gold assaying—one of the resulting buttons being then “parted” in nitric acid, and the other by sulphuric acid. In the first instance, the whole of the platinum dissolves with the silver by employing two distinct treatments

with nitric acid; in the latter, the silver only separates, leaving the whole of the gold and of the platinum together, the proportion of platinum in the alloy being the difference. The two resulting products weighed against each other yield the gold and the platinum. This is a simple but very accurate process, and is the recognised method adopted by the professional assayer when determining gold alloys containing small proportions of platinum.

With each *set* of analyses I employed standards synthetically made with ten parts pure platinum and ninety parts pure gold, by means of which any possible error which might arise was completely checked and controlled.

In the case of the estimation of the gold in the alloys of 90 per cent. platinum, and 10 per cent. of gold, the foregoing process was obviously unavailable, and I was compelled to try several methods in order to obtain trustworthy results. The following, however, proved to be an exceedingly satisfactory process, and was therefore adopted.

Exact weighings of 50 grains each, in duplicate, were taken of each of the portions of the hemispheres removed for examination. These were dissolved in *aqua regia*, evaporated to ensure the elimination of all free acid, and then diluted with distilled water to about 20 c.c. capacity, which was ascertained by experiment to be the best for the complete precipitation of the gold; the gold was precipitated by crystals of pure oxalic acid, washed and weighed. All the duplicate results agreed most satisfactorily. To corroborate these gold results, I precipitated the platinum by means of pure zinc, boiled the precipitated platinum in hydrochloric acid, and after washing and drying weighed the resulting pure platinum. With every set of analyses of metal from their respective spheres, I made up standards synthetically, each of 37.5 grains pure platinum and 12.5 grains pure gold to ensure accuracy, it being practically impossible to extract the whole of the constituent metals within $\frac{2}{100}$ ths per cent. I tried other known processes with a view to obtain absolutely correct results, but I consider that the methods employed were very accurate.

I am confirmed in this view by the experience gained in similar experiments by Mr. W. BETTEL, in a paper contributed to the 'Chemical News,' vol. 56, No. 1452, which is evidently the result of much careful work.

With alloys of gold and palladium it is usual to determine the amount of gold by quartation with pure silver, and parting by nitric acid.

Carefully weighed portions of the alloys are cupelled in pure lead with two and three-quarter times their own weight of fine silver.

These cupelled buttons are laminated and annealed, and then treated by boiling in nitric acid three distinct times. By these means the palladium becomes dissolved, as well as the silver, leaving the pure gold, which, after washing and annealing, is weighed. The difference is, of course, the palladium.

With alloys of gold and palladium, say of gold 90 parts and of palladium 10 parts in the hundred, it is preferable to re-cupel and re-part the gold obtained with a further proportion of fine silver, as sometimes, and where there is as much as 10 per cent. of palladium, the whole of the palladium is not removed in one parting operation.

It is also of importance to work side by side with the portions of metal under examination checks or standards, made of pure gold and pure palladium as nearly to the composition of the alloy to be tested as possible.

The results by this process of quartation are very accurate.

Platinum and Palladium.

The first alloy operated upon in this next series was one of palladium and platinum, in proportions of—

H. Palladium	85 per cent.
Platinum	15 „

To ensure accuracy, the alloy was made from the pure metals in the spongy condition, fused separately, and then alloyed in the foregoing proportions.

The alloy was melted and re-melted in a lime furnace with oxyhydrogen gas, and cast into a mould, to ensure a complete mixture of the two metals.

The alloy was then again remelted, and cast into a lime sphere of about 3 inches diameter. About 4 kilogs. of the alloy was made for this experiment.

The sphere so produced was afterwards cut, and divided into two hemispheres. The alloy, which had been melted and cast at a temperature of about 2000° C., was decidedly brittle and of a dark grey colour, and the casting was slightly honeycombed from its centre to the tube, or “gate,” through which the metal had been poured into the mould. The alloy was very hard.

In the lower portion of the sphere, shown by the dotted line, the peculiar bluish-purple characteristic of palladium showed itself as a distinct feature.

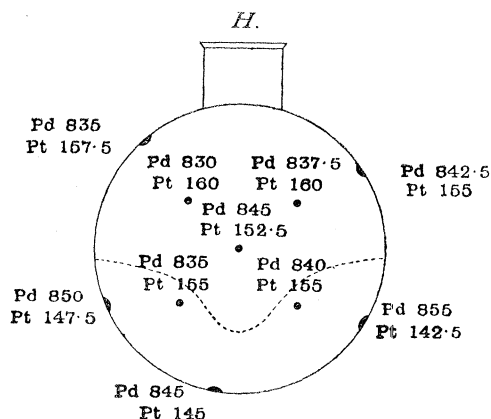
Pieces cut from the places indicated showed the results respectively of palladium and of platinum.

Alloy H. Palladium	850 parts.
Platinum	150 „

Parts in 1000 :—

Outside.		Intermediate.		Centre.	
Palladium.	Platinum.	Palladium.	Platinum.	Palladium.	Platinum.
835	157·5	830	160	845	152·5
850	147·5	835	155		
845	145	840	155		
855	142·5	837·5	160		
842·5	155				
Average .	845·5	149·5	835·6	157·5	

Maximum difference between centre and mean of outside: Palladium, 5 per thousand; Platinum, 30 per thousand



These results distinctly prove that, although there is not much evidence of true "liquation"—that is, rejection of a constituent of an alloy—the palladium does become concentrated by gravity towards the bottom of the "freezing" mass. It is noteworthy that this alloy, when heated to bright redness *in vacuo* by means of a Sprengel pump, did not yield hydrogen. It was, in fact, singularly free from occluded gas.

Following the matter up, the proportions of the same metals were reversed, and an alloy of—

I. Platinum	85 per cent.
Palladium	15 „

was then operated on.

The constituent metals for this alloy were, as in the case of the former one, twice melted in a lime furnace by means of the oxyhydrogen flame, and cast to ensure perfect homogeneity, then re-melted, and cast into a lime sphere of 3 inches diameter.

About 5 kilogs. was the quantity of the alloy made for this experiment.

The alloy, when cut into two hemispheres showed a bright white crystalline structure, not brittle, but tough from the peculiar crystallization, which consisted of interlaced planes.

The casting was perfectly solid, but toward the gate or tube the casting was slightly honeycombed.

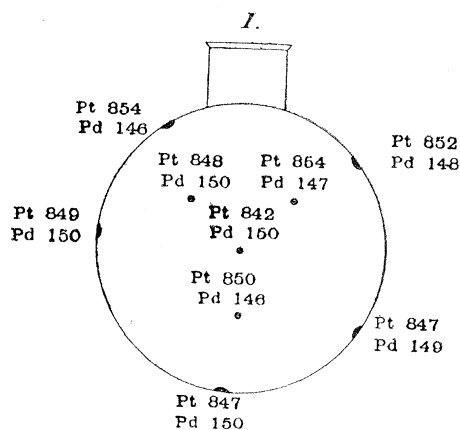
The following proportions of platinum and palladium were found at the points indicated :—

Alloy I. Platinum 850 parts.
Palladium 150 „

Parts in 1000 :—

Outside.		Intermediate.		Centre.	
Platinum.	Palladium.	Platinum.	Palladium.	Platinum.	Palladium.
854	146	848	150	842	150
849	150	854	147		
847	150	850	146		
847	149				
852	148				
Average . 849·8	148·6	850·6	147·6		

Maximum difference between centre and mean of outside :—Platinum, 7·8 per thousand ; Palladium, 1·4 per thousand.



The foregoing results distinctly prove that there is still a slight concentration of palladium at the centre.

H and I.

As the results of the two foregoing alloys were non-malleable, the first being decidedly brittle, I proceeded to investigate this point further by intimately mixing pure sponge platinum and pure sponge palladium in the same proportions as in these two alloys, subjecting the mixed sponge metals to hydraulic pressure in a steel mould, heating them and forging the alloys so heated, in the same manner as with ingot platinum made from sponge platinum. In both cases these alloys, which had been prepared by welding and not fusion, were perfectly tough and malleable, proving that the high temperature necessary for melting these alloys enables them to pass into a crystalline state.

I then melted these two malleable alloys, H and I, by means of the oxyhydrogen

flame in lime crucibles, and allowed them to cool in the crucibles. I employed about 65 grms. for each of these experiments.

Upon examination I found both of these alloys to be malleable, so that the difference between these results, as regards brittleness, is probably to be accounted for by the fact that the slow cooling enables a fine network of crystals to form with resulting toughness.

The process adopted for the determinations in the platinum-palladium series of alloys was the following :—

Of each portion of the alloy to be analysed fifty grain determinations were taken and dissolved in nitrohydrochloric acid and evaporated nearly to dryness, these resulting chlorides re-acidified with hydrochloric acid and again evaporated nearly to dryness.

The re-evaporated chlorides then dissolved up in water and the respective solutions of each determination diluted to about 150 c.c. liquid capacity ; when cold the palladium was precipitated by mercury cyanide. The precipitate thus obtained was allowed to stand for twenty-four hours in a slightly warmed atmosphere, as I have found by experience that the precipitate of palladium cyanide comes down better under these circumstances.

This precipitate, collected on filters, washed, dried, and ignited, gives the whole quantity of pure metallic palladium in the alloy.

To obtain the platinum from the mother liquors, from which the palladium cyanide had been precipitated, these solutions were in each determination evaporated to about 30 c.c. capacity, and the platinum was then precipitated by ammonium chloride.

The precipitate of the double salt of platinum ammonium chloride was then collected on filters, dried, ignited, and weighed, the result being pure platinum.

The small proportion of platinum remaining in the mother liquors was precipitated by means of pure metallic zinc as metallic platinum, which, washed and digested in weak hydrochloric acid, was collected, ignited, and weighed, the results being added to those obtained by the ammonium chloride precipitation.

All these results were checked by standards of pure palladium and of pure platinum in the proportion of—

Palladium	85	}	in the case of the alloys marked H.
Platinum	15		

and also of—

Platinum	85	}	in those marked I.
Palladium	15		

the results of which confirmed the accuracy of the process employed.

Platinum and Rhodium.

Much attention has lately been drawn to an alloy of pure platinum, with 10 per cent. of rhodium, which has become important from the excellent service it has rendered in the determination of high temperatures. The alloy of platinum with 10 per cent. of rhodium is used with pure platinum as a thermo-couple, and it is, therefore, interesting to be able to set at rest any doubt which might arise as to this alloy being uniform in composition when melted and drawn into wire.

For this purpose I prepared an alloy, J, of :—

Platinum	90 per cent.
Rhodium	10 „

by fusing together in a lime furnace by the oxyhydrogen gas flame pure melted platinum with pure melted rhodium in the above proportions.

About one and a half kilogs. of this alloy was made, and after three times melting and casting, the alloy was re-melted and poured into a lime sphere of two inches diameter.

Upon cutting the sphere into hemispheres I found that a beautiful white malleable alloy was the result, with very slight evidence of shrinkage, care being taken to provide against this by an extra long gate or pour.

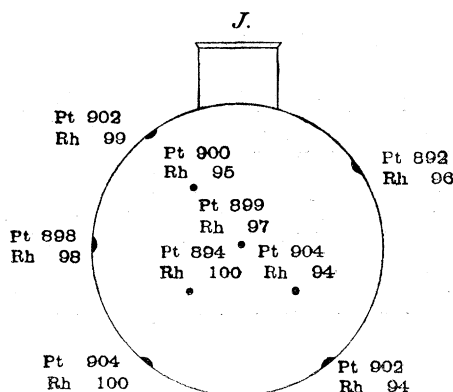
The following are the proportions of platinum and rhodium found by analysis at the points indicated :—

Alloy J. Platinum	900 parts.
Rhodium	100 „

Parts in 1000 :—

Outside.		Intermediate.		Centre.	
Platinum.	Rhodium.	Platinum.	Rhodium.	Platinum.	Rhodium.
902	99	900	95	899	97
898	98	894	100		
904	100	904	94		
902	94				
892	96				
Average .	899·6		97·4		

Maximum difference between centre and mean of outside :—Platinum ·6 per thousand; Rhodium, ·4 per thousand.



This result proves that the alloy is not subject to liquation, and fully justifies the high opinion that H. LE CHATELLIER and ROBERTS-AUSTEN have formed as to its suitability for thermometric measurements.

The process adopted for the separation and determination of the rhodium and platinum in this alloy is one that I have found by experience to be exceedingly accurate if conducted with care. (It is described by TURNER, 'Elements of Chemistry,' 5th Ed., 1834, p. 652.)

Fifty grains of each determination were dissolved in nitrohydrochloric acid, and evaporated to dryness. The dry chlorides were then dissolved up in a warm solution of sodium chloride, and again evaporated to dryness. The resulting dry mass was then taken from the evaporating dishes and triturated in a porcelain mortar, from which each determination was then transferred to closed flasks, and digested in absolute alcohol in a very slightly warmed atmosphere for 24 hours, the bottles being shaken from time to time.

At the end of this period the whole of the platinum chloride is taken up in solution by the alcohol, and the rhodium chloride left combined with the sodium chloride as a double salt of rhodium and sodium chloride insoluble in alcohol. This latter salt was washed with alcohol to remove all platinum chloride, and then dissolved in water.

From this solution the metallic rhodium was obtained by direct precipitation with pure zinc, washed digested in weak hydrochloric acid, collected, dried, ignited, and weighed.

The platinum from the alcoholic chlorides when evaporated and re-dissolved in water was determined by precipitation with ammonium chloride and pure zinc, as in the palladium-platinum series, and weighed as metallic platinum.

With these analyses accurately weighed portions of pure rhodium and pure platinum, in the proportions of platinum 900, and rhodium 100 parts, were dissolved and treated as standards to ensure accuracy in the results of the analyses.

It will be observed that, in some cases of members of the platinum group, the results of the analyses add up in excess of 1000.

This is to be explained by the exceptional difficulty which attends the accurate determination of the metals of this group.

Gold and Aluminium.

The interest of the problems connected with the liquation of alloys of the rare and precious metals, suggested the desirability of investigating the behaviour of a metal with a very high specific gravity alloyed with a metal with a very low one.

For this purpose gold, which has a specific gravity of 19·3, and aluminium, whose specific gravity is 2·6, were selected.

In order to show an absolute contrast, two alloys were adopted, viz.: —

K. Aluminium 90 parts,
Gold 10 „

and

L. Gold 90 parts.
Aluminium 10 „

The alloy K was the first one experimented with. The ten parts of gold were first melted in a crucible, and the 90 parts of aluminium gradually introduced, the alloy being stirred as each portion of aluminium was added. When the whole quantity of aluminium had been added to the melted gold, the crucible was withdrawn from the fire, the contents thoroughly stirred and cast into a spherical mould. This alloy was white and tough, but the fracture at the lower part of the hemisphere exhibited a purple-pink mottled appearance, of which more will be said subsequently.

The specific gravity of this alloy was 2·89. The sphere was then cut into two equal halves from top to bottom. About 1 kilog. of the alloy was employed for this experiment.

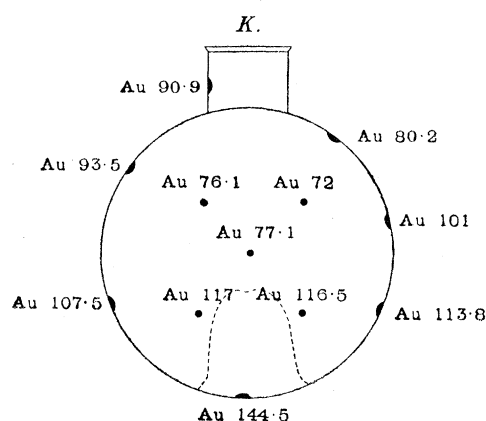
Alloy K. Aluminium 900 parts.
Gold 100 „

Parts in 1000 of gold—

Outside.	Intermediate.	Centre.
90·9	76·1	77·1
93·5	72	
107·5	117	
144·5	116·5	
113·8		
101·0		
80·2		
Average . 104·4		

Maximum difference in the gold between centre and mean of outside, 27·3 per thousand.

Maximum difference in the gold between centre and mean of bottom of casting, 67·4 per thousand.



The above figures show the proportion of gold found by analysis at the different points of the hemisphere K. The result is a complex one, a rich alloy of gold and aluminium falls to the bottom of the mass by gravity, about 8 per cent. remaining in solution, and, on freezing, the gold becomes concentrated externally from the mother liquor.

The alloy L, of gold 90 per cent. and aluminium 10 per cent., was then made by first melting the gold and subsequently adding the 10 per cent. of aluminium, well stirring, and casting into a similar spherical mould as with the other alloy (K).

This alloy was very fluid, its fracture hard, white, crystalline, and very brittle. The whole of the interior, when the sphere was cut in two halves from top to bottom, showed purple-pink spots throughout; but from the bottom of the hemisphere to the centre a pyramidal cone of white crystalline metal showed itself distinctly through the mass, in the direction shown by the dotted line. Its specific gravity was 11.96.

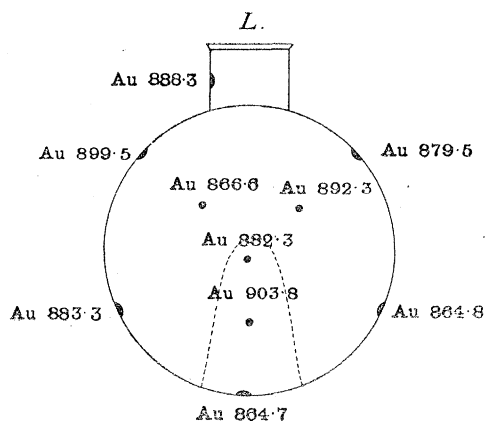
About $4\frac{1}{2}$ kilogs. were employed for this experiment.

Alloy L. Gold	900 parts.
Aluminium	100 ,,

Parts in 1000 of gold :—

Outside.	Intermediate.	Centre.
888.3	866.6	882.3
899.5	892.3	
883.3	903.8	
864.7		
864.8		
879.5		
Average . 880		

Maximum difference in the gold between centre and mean of outside, 2.3 per thousand.



The above are the proportions of gold found at the different points of the hemisphere.

It will be evident that the cooling of the alloy has been attended with much re-arrangement, but it is difficult to say that there has been true liquation or concentration of any given constituent of the alloy, as the mass seems to be a congeries of complex alloys of aluminium and gold.

The beautiful rose-purple alloy of aluminium and gold, prepared in accordance with Professor ROBERTS-AUSTEN'S instructions in 'Nature,' June 21, 1891—viz., 786 parts of pure gold and 214 parts of aluminium—were melted together, thoroughly mixed, and cast into a 3-inch sphere.

This alloy, which I call M, is extremely brittle, but the beauty of its magnificent fracture was most striking; and the purple-pink appearances in the fractured spheres K and L are evidently reproductions of this alloy in some other proportions. Evidences of this colouring have been alluded to as showing in the alloys K and L.

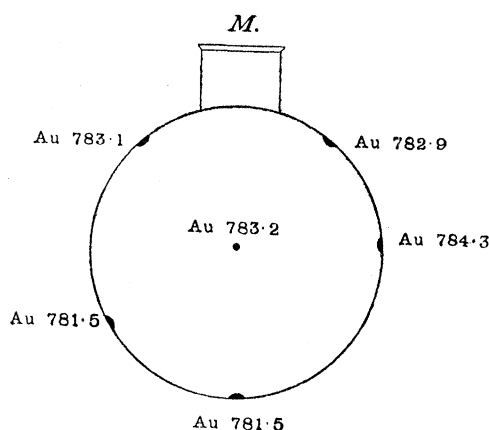
Trials made from various parts of the sphere, when broken up, showed proportions of gold as under.

Alloy M. Gold	786 parts.
Aluminium	214 ,,

Parts in 1000 of gold :—

Outside.	Centre.
783.1	783.2
781.5	
781.5	
784.3	
782.9	
Average	782.6

Maximum difference in the gold between centre and mean of outside, '6 per thousand.



This result is of special interest. The alloy has a composition which corresponds to the formula Al_2Au , the constituent metals therefore exist in atomic proportions; it would appear to be a true chemical compound. There is little or no evidence of liquation, the maximum difference between any two assays being only 2.8 parts in a thousand. As this is the most highly coloured alloy yet known, the simple atomic relations between its constituents is of much theoretical importance. It would appear to be as uniform in its composition as any alloy known.

Several methods were tried for the determination of the gold in these various alloys of gold and aluminium.

Cupellation with excess of lead to remove the aluminium proved quite useless.

The removal of the aluminium by digestion in hydrochloric acid, and collecting the residual gold did not yield satisfactory results.

The process adopted, therefore, was as follows :—

Accurately weighed portions of fifty grains each of the alloys under examination were fused with litharge, under a flux of potassium carbonate and borax with a small proportion of powdered charcoal, and the resulting slag re-fused with a further small quantity of litharge and powdered charcoal.

The lead buttons containing all the gold (the aluminium having combined with the fluxes employed) were cupelled, and the resulting gold cupelled with silver and parted with nitric acid in the usual manner. All these determinations were worked with checks or standards of fine gold and pure aluminium.

This process for the determination of gold was employed for every one of the foregoing aluminium-gold alloys.

Conclusions.

I regret that time has not enabled me to examine more members of each particular series of alloys, so as to present results in fuller detail; in fact, the silver-copper series is the only one upon which anything like exhaustive work has been done. No doubt, in every series of alloys there is one definite alloy which would yield a uniform

mass on cooling, and it is known that in the silver-copper series this alloy (LEVOL'S) contains 718 parts of silver per thousand. It is not certain, however, that this is the *eutectic* alloy of the series—that is, the one with the lowest melting point—but it is well known that when silver-copper alloys which contain more silver than 718 parts per thousand are cooled, the centre of the solidified mass is richer than the exterior. This is the case with standard silver for instance, which contains 925 parts of silver per thousand, and it is safe to conclude that an alloy rich in copper is the first to fall out from the mass, and that this alloy sets round the inner surface of the mould, driving a still fluid alloy—rich in silver—to the centre. The general rule in the present results, seems to be that *in the cooling of a fluid mass of two united metals, an alloy rich in the more fusible constituent of the mass falls out first driving the less fusible constituent to the centre.* The gold-platinum alloys (A, B, C, D, and E) seem to be always rich in gold externally.

It is remarkable that the metals of the platinum group do not show much liquation among themselves, but, on the other hand, when gold is united to the members of the platinum group there is evidence of liquation.

The gold-palladium one (F), follows the above rule.

There is evidence that the alloy E, containing 750 parts of platinum and 250 of gold, is near the composition of a true compound, as it shows but little sign of liquation, and is, moreover, hard and brittle, differing materially from the rest of the series. The purple alloy of gold and aluminium M, AuAl_2 , is almost certainly a true chemical compound, the solidified mass being as nearly uniform in composition as may be. The uniformity of the alloy (J) of platinum with 10 per cent. of rhodium is of much interest in view of the important part which the alloy is playing in pyrometric work.

Conducting the experiments, the results of which are embodied in the present paper, has been very laborious, and although, as already stated, no complete series of the alloys of any two metals has been examined, quite sufficient data have been collected to afford valuable guidance to the metallurgist, who will now know what behaviour may be expected from the other members of the groups of the alloys in question. The gold-platinum series of alloys are of industrial importance, as native gold is so often associated with platinum, and it is somewhat surprising to find that assays made on pieces of metal cut from the exterior of an ingot cannot be trusted to represent the composition of the mass. The aim of the investigation has been to show that notwithstanding the great difficulty which attends the preparation of alloys of metals with very high melting points, it is possible to elicit from them the same kind of information which has proved to be so useful in the case of the more ordinary and tractable alloys.

Methods adopted for the Analysis of the several Alloys Experimented upon.

(Added June 13, 1892.)

For alloys of gold 100, and platinum 900 parts.—Two carefully weighed portions of the alloys to be analysed were weighed and cupelled in pure lead with two and three-quarter times their weight of pure silver, in identically the same manner as in conducting the process of gold assaying; one of the buttons so obtained was then, after lamination and annealing, parted in nitric acid, which by two distinct treatments removes the whole of the silver and the platinum, leaving the gold in a pure state, which, when washed, annealed and weighed accurately, gives the proportion of pure gold in the alloy.

The other button, after being laminated and annealed in precisely the same way, was parted in sulphuric acid, which removes the silver only, leaving the whole of the gold and the platinum intact. By weighing the gold obtained by parting in nitric acid against the gold and platinum left by the sulphuric acid parting, the proportion of platinum obtained is the difference. This is a simple but very accurate method, and is universally recognised and employed by professional assayers when determining alloys of gold containing platinum. By working checks or standards of gold and platinum, made synthetically of platinum ten and gold ninety parts, any error which might arise is completely checked and controlled.

In the case of the alloys of platinum 900, and gold 100 parts, the foregoing process was obviously unavailable. After many different experiments, the following method was one which I found to be accurate and trustworthy; and duplicate analyses, each on 50 grains of metal, were carefully made by this process on each of the portions of the hemispheres removed for examination.

Exact weighings of fifty grains each were taken of each of the alloys under examination and treated with an excess of nitrohydrochloric acid, which gradually dissolved the whole. The resulting solutions of platinum-gold chloride were then evaporated nearly to dryness to ensure the elimination of all free acid, so as to obtain perfectly neutral solutions. These chloride solutions were then diluted with distilled water to about 20 cub. centims. capacity, a degree of strength which was ascertained by experiment to be the best for ensuring complete precipitation of the gold. The metallic gold was thrown down by means of crystals of oxalic acid and was carefully washed, dried, and weighed.

From the mother liquors the metallic platinum was then precipitated by means of pure metallic zinc, and the resulting precipitated platinum was thoroughly washed, and boiled in diluted hydrochloric acid. The platinum thus purified was then washed, dried, and weighed.

Side by side, with each set of analyses, standards synthetically prepared were used, each of 37·5 grains pure platinum and 12·5 grains pure gold. This was

necessary to ensure accuracy, as in practice it is found impossible to obtain the whole of the constituent metals from these alloys within $\frac{2}{100}$ ths per cent.

I tried other known processes for these determinations, but none gave such accurate results ; and in this view I am confirmed by Mr. W. BETTEL whose paper in the 'Chemical News,' vol. 56, No. 1452, shows that he has devoted much patient attention to the subject.

The method of analysis adopted in the case of the alloys of gold 900 and palladium 100 parts, consisted in removing the palladium by the process of "quartation" with fine silver. Carefully weighed portions of the alloys under examination were cupelled in pure lead with two-and-three-quarter times their weight of fine silver. Each cupelled button so produced was then laminated, annealed, and treated with and "parted" by boiling in nitric acid three distinct times. By these means the palladium is dissolved out as well as the silver, the gold being left. The resulting gold, after being washed and annealed, was again cupelled in lead with a further proportion of two-and-three-quarter times its weight of fine silver, and again parted by boiling in nitric acid three distinct times, to ensure the removal of the whole of the palladium, the gold so obtained after being washed, annealed, and weighed, yielding the percentage of pure gold in the alloy. The proportion of palladium was then found by the difference

To ensure accuracy, checks or standards, made up of pure gold 900 parts and palladium 100 parts, were worked side by side with all the analyses made.

All the results by this process are trustworthy and accurate.

The process adopted for the determinations of the platinum and palladium in the series of alloys made of these metals was as follows :—

Of each portion of the alloy to be analysed, accurately weighed portions of 50 grains each were attacked by nitrohydrochloric acid, which gradually dissolved the whole of the alloy under digestion. The resulting chlorides were then carefully evaporated nearly to dryness, then re-acidified with hydrochloric acid, and again evaporated almost to dryness. These re-evaporated chlorides were then dissolved in distilled water, and the respective solutions of each analysis were diluted to a volume of about 5 ounces, and allowed to become quite cold.

Cyanide of mercury was then added in slight excess to precipitate the palladium, and the whole allowed to remain for twenty-four hours in a warm atmosphere, experience showing that this precipitate of palladium cyanide comes down better under these circumstances. At the end of this time the precipitate of palladium cyanide was collected on filters, washed, dried, ignited, and weighed as pure palladium.

The whole contents of the palladium in the alloys is precipitated by these means.

To obtain the platinum from the mother liquors, from which the palladium had been removed, they were evaporated to a capacity of about 30 cub. centim. Ammonium chloride was then added, and the platinum precipitated as the double salt of platinum-

ammonium chloride. This precipitate was then carefully collected on filters, dried, ignited, and weighed, the result being pure platinum.

The small proportion of platinum remaining in the mother liquors was precipitated by means of pure metallic zinc as metallic platinum, which, when washed and digested in diluted hydrochloric acid, was collected, ignited, and weighed, the results being added to those obtained by the ammonium chloride precipitation. All these results were checked by standards of pure palladium and pure platinum in the proportions of—

Palladium	85	} in the case of the alloys marked H,
Platinum	15	

and of—

Platinum	85	} in those marked I,
Palladium	15	

and the results obtained by analysing these standards confirmed my views as to the accuracy of the process employed.

Alloy J. Platinum	90 parts.
Rhodium	10 „

The process adopted for the separation and determination of the rhodium and platinum in this alloy is one that I have found by experience to be exceedingly accurate if conducted with care. (It is but little known, although it was described many years ago in TURNER'S 'Elements of Chemistry, 5th edition, 1834, page 652.)

Fifty grains of each of the alloys under examination were dissolved in nitrohydrochloric acid, and evaporated to dryness. The dry chlorides were then dissolved in a warm solution of sodium chloride, and again evaporated to dryness. The resulting dry mass was then taken from the evaporating dishes and triturated in a porcelain mortar, from which the mass was then transferred to closed flasks and digested in absolute alcohol in a slightly warm atmosphere for 24 hours, the bottles being shaken from time to time. At the end of this period the whole of the platinum chloride is taken up in solution by the alcohol, and the rhodium chloride is left combined with the sodium chloride as a double chloride of rhodium and sodium insoluble in alcohol. This latter salt was washed with alcohol to remove any platinum chloride, and then dissolved in water. From this solution the metallic rhodium was obtained by direct precipitation with pure zinc; it was washed, digested in weak hydrochloric acid, collected, dried, ignited, and weighed.

The alcoholic chlorides containing the platinum chloride were evaporated and re-dissolved in distilled water. The platinum was then thrown down by means of

ammonium chloride and by pure zinc, as in the palladium-platinum series, and weighed as metallic platinum.

In these analyses, accurately weighed portions of pure rhodium and pure platinum, in the proportions of platinum 900, and rhodium 100 parts, were dissolved and treated as standards to ensure accuracy in the results of the analyses.

In the case of the gold-aluminium alloys, several methods were tried for the determination of the gold in these various alloys, direct cupellation with lead, and the removal of the aluminium by dissolution in hydrochloric acid, but neither yielded satisfactory results. The process adopted, therefore, was to ascertain accurately the proportion of gold in the various portions of the alloys removed for analysis by the following method, the aluminium being found by the difference.

Determinations of 50 grains each from the various portions of the alloys removed for examination were carefully fused in small clay crucibles with litharge under a flux of borax and potassium carbonate, with a small proportion of powdered charcoal. The button of lead so obtained was removed, and the slag re-fused with a further small quantity of litharge and powdered charcoal. The resulting lead buttons were then cupelled, and yielded the gold contained in the alloy (the whole of the aluminium having combined with the fluxes employed). The gold so obtained was then cupelled in pure lead with two-and-three-quarter times their weight of fine silver, and parted in nitric acid. The gold thus purified was washed, dried, annealed, and weighed.

This process for the determination of the gold was employed for every one of the aluminium gold alloys.

All these analyses were checked by means of synthetical standards made up of gold and aluminium in the same proportions as in the alloys for examination.