

other. They indicate the temperatures of the layers in which they are placed.

Now, if we know the difference of temperatures of two sides of a stratum of a liquid during any time, and the quantity of heat conducted across the stratum during that interval of time, we can calculate the thermal conductivity of the liquid by means of a well-known formula.

The result arrived at by the experiments described, is that the thermal conductivity of water may be taken at from $\cdot 0022$ to $\cdot 00245$ in square centimetres per second.

Some experiments have been made on the thermal conductivity of solution of sulphate of zinc, a solution which happened to be convenient for preliminary trials. The specific heat of solution of sulphate of zinc at different densities, which it is necessary to know for comparison as to thermal conductivity of that liquid with water, has been determined.

Experiments are now being carried on on this subject with the assistance of a grant from the Government Fund of 4,000*l*.

II. "The Preparation in a State of Purity of the Group of Metals known as the Platinum Series, and Notes upon the Manufacture of Iridio-Platinum." By GEORGE MATTHEY. Communicated by F. A. ABEL, C.B., F.R.S. Received March 19, 1879.

In this paper it is not my intention, nor should I be able, to refer generally to the results of work in the various branches of platinum metallurgy carried out by my firm, who, as is well known, have been associated with the development of this special field of industry from its earliest infancy; but I shall confine myself simply to that section of it upon which my personal attention has of late years been specifically concentrated in order to meet and comply with the requisition of the Bureau Internationale des Poids et Mesures, the Section Française de la Commission Internationale du Mètre, and of l'Association Géodésique Internationale (all of them important scientific committees, formed with the object of arriving at an accurate and definite solution of the long agitated question of standard weights and measures), and also at the demand of the French Minister of War, for an alloy the best adapted for the manufacture of the international metre and kilogram standard, and the geodesique rule; and in my endeavour to solve this difficult problem I have had the great advantage of being able to consult those distinguished men, M.M. Henri Sainte Claire Deville and Henri Debray, of Paris, and have also had the

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benefit of the excellent and valued advice of M. Stas, the celebrated Belgian chemist, to all of whom the scientific world owe so much, and to whom I desire to offer my warmest thanks.

In a paper of this kind it would be superfluous for me to enter into any of the already published details concerning the existence and collection of what is known as platinum-dust or mineral. It is sufficient for me to observe that the six metals (of which platinum is the chief) usually found more or less in association in their native state, present characteristics of interest beyond their metallurgical utility, which are, perhaps, worth alluding to *en passant*. It is, for instance, a curious fact that the group should consist of three light and three heavy metals, each division being of approximately the same specific gravity—the heavier being (in round figures) just double the density of the lighter series.

Thus we find osmium, iridium, platinum forming the first division, of the respective specific gravities of 22·43, 22·39, 21·46; whilst ruthenium, rhodium, and palladium are represented by the figures 11·40, 11·36, 11, the average densities of the heavy and light divisions thus being respectively 22·43 and 11·25.

But a more interesting and important classification is what I may designate as a first and second class series, from the more important view of their relative properties of stability. Thus platinum, palladium, and rhodium form the first or higher class, not being volatilizable in a state of oxide; iridium, osmium, and ruthenium forming the second or lower class, their oxides being more or less readily volatilized.

The oxide of iridium is affected at 700 to 800° C., and entirely decomposed at 1,000°, whilst osmic and hyperuthenic acids are volatilized at the low degree of 100°, the latter exploding at 108°. The chlorides of these metals can be sublimed at different temperatures (as also the protochloride of platinum).

I now propose to give a short description of the methods I have employed for preparing the pure platinum and iridium necessary for the manufacture of the alloy, which I call "iridio-platinum," and it is upon the distinguishing characteristics above-mentioned that my method of separation is chiefly founded.

Platinum.

The preparation of this metal to a state of purity is an operation of extreme delicacy. I commence by taking ordinary commercial platinum; I melt this with six times its weight of lead of ascertained purity, and, after granulation, dissolve slowly in nitric acid diluted in the proportion of 1 volume to 8 of distilled water. The more readily to ensure dissolution, it is well to place the granulated alloy in porcelain

baskets such as are used in the manufacture of chlorine gas for holding the oxide of manganese. When the first charge of acid is sufficiently saturated, a fresh quantity should be added until no more action is apparent; at this stage the greater part of the lead will have been dissolved out together with a portion of any copper, iron, palladium, or rhodium that may have been present. These metals are subsequently extracted from the mother-liquors, the nitrate of lead by crystallization, and the remaining metals by well-known methods.

The metallic residue now obtained will be found in the state of an amorphous black powder (a form most suitable for further treatment), consisting of platinum, lead, and small proportions of the other metals originally present—the iridium existing as a brilliant crystalline substance insoluble in nitric acid. After digesting this compound in weak aqua regia, an immediate dissolution takes place of the platinum and lead, leaving the iridium still impure, but effecting a complete separation of the platinum.

To the chloride of platinum and lead after evaporation is added sufficient sulphuric acid to effect the precipitation of the whole of the lead as a sulphate, and the chloride of platinum after dissolution in distilled water is treated with an excess of chloride of ammonium and sodium, the excess being necessary in order that the precipitated yellow double salt may remain in a saturated solution of the precipitant. The whole is then heated to about 80° , and allowed to stand for some days; the ammonio-chloride of platinum will settle down as a firm deposit at the bottom of the vessel, whilst if any rhodium, as is generally the case, is present, the surface liquor will be coloured a rose tint, occasioned by a combination of the salts of the two metals.

The precipitate must be repeatedly washed with a saturated solution of chloride of ammonium and subsequently with distilled water charged with pure hydrochloric acid. This is necessary for its purification. The small quantity of the double salt which will be taken up and held in solution is of course recovered afterwards. Rhodium may still exist in the washed precipitate, which must therefore not be reduced to the metallic state until its separation is completed, and this is best effected by mixing with the dried compound, salts of chloro-platinate and chloro-rhodate of ammonia, bi-sulphate of potash with a small proportion of bi-sulphate of ammonia, and subjecting to a gradual heat brought by degrees up to a dull red in a platinum capsule, over which is placed an inverted glass funnel. The platinum is thus slowly reduced to a black spongy porous condition freed from water, nitrogen, sulphate of ammonia, and hydrochloric acid, the rhodium remaining in a soluble state as bi-sulphate of rhodium and potash, which can be dissolved out completely by digesting in boiling distilled water; a small quantity of platinum will have been taken up in a state of sulphate, but is regained by heating the residue (obtained

on evaporation) to redness, at which heat it is reduced to the metallic condition, the rhodium salt remaining undecomposed.

By the method above described the platinum is freed not only from rhodium, but from all other metals with which it may have been contaminated, and is brought to a state of absolute purity, of the density 21.46, the highest degree obtainable.

Iridium.

In the preparation of this metal when intended to be used for the manufacture of iridio-platinum alloy, I have arrived at freeing it to the utmost possible extent from all its associate metals, except platinum, disregarding the presence of the latter; the proportion of which, once determined, would only form matter of calculation in the final operation of mixing my alloy.

In practice, the purest iridium which can be obtained from its ordinary solution (deprived of osmium by long boiling in aqua regia and precipitated by chloride of ammonium) will almost invariably contain traces of platinum, rhodium, ruthenium, and iron.

I fuse such iridium in a fine state of division with ten times its weight of lead, keeping it in a molten state for some hours, dissolve out the lead with nitric acid, subject the residue to a prolonged digestion in aqua regia, and obtain a crystalline mass composed of iridium, rhodium, ruthenium, and iron, in a condition suitable for my further treatment. By fusion at a high temperature with an admixture of bi-sulphate of potash, the rhodium is almost entirely removed, any remaining trace being taken up together with the iron in a later operation. The iridium so far prepared is melted with ten times its weight of dry caustic potash, and three times its weight of nitre, in a gold pan or crucible; the process being prolonged for a considerable time to effect the complete transformation of the material into iridiate and ruthenate of potash, and the oxidation of the iron; when cold, the mixture is treated with cold distilled water. The iridiate of potash of a blue tinge will remain as a deposit almost insoluble in water, more especially if slightly alkaline, and also the oxide of iron.

This precipitate must be well washed with water charged with a little potash and hypochlorite of soda until the washings are no longer coloured, and then several times with distilled water.

The blue powder is then mixed with water strongly charged with hypochlorite of soda, and allowed to remain for a time cold, then warmed in a distilling vessel, and finally brought up to boiling point until the distillate no longer colours red, weak alcohol acidulated with hydrochloric acid.

The residue is again heated with nitre and potash water charged with hypochlorite of soda and chlorine, until the last trace of ruthenium has disappeared.

Further, to carry out the purification, the blue powder (oxide of iridium) is re-dissolved in aqua regia, evaporated to dryness, re-dissolved in water, and filtered.

The dark-coloured solution thus obtained is slowly poured into a concentrated solution of soda and mixed with hypochlorite of soda, and should remain as a clear solution without any perceptible precipitate, and subjected in a distilling apparatus to a stream of chlorine gas, should not show a trace of ruthenium when hydrochloric acid and alcohol are introduced into the receiver. In this operation the chlorine precipitates the greater part of the iridium in a state of blue oxide, which after being collected, washed, and dried, is placed in a porcelain or glass tube, and subjected to the combined action of oxide of carbon and carbonic acid obtained by means of a mixture of oxalic with sulphuric acid gently heated.

The oxide of iridium is reduced by the action of the gas leaving the oxide of iron intact, the mass is then heated to redness with bi-sulphate of potash (which will take up the iron and any remaining trace of rhodium) and after subjecting it to many washings with distilled water, the residue is washed with chlorine water to remove any trace of gold, and finally with hydrofluoric acid, in order to take out any silica which might have been accidentally introduced with the alkalies employed or have come off the vessels used.

The iridium after calcination at a strong heat in a charcoal crucible, is melted into an ingot, and after being broken up and boiled in hydrochloric acid, to remove any possible trace of iron adhering to it through the abrasion in breaking up, should possess if perfectly pure a density of 22.39; but, as iridium prepared even with the utmost care will still contain minute though almost inappreciable traces of oxygen, ruthenium, rhodium, and possibly iron, the highest density I have yet attained is 22.38.

Alloy of Iridio Platinum.

This compound metal possesses physical properties of great value, forming a beautiful example of the effect of a careful combination of the opposite characteristics of its component parts. Thus, the extreme softness and expansiveness of pure platinum and the brittleness and excessive hardness of pure iridium, produce, by combination in judicious proportions, a perfect and homogeneous alloy, possessing the necessary mean of these properties to render it suitable for many important purposes, amongst others that of the special object to be attained to meet the requirements for an unalterable standard metal, for which it is peculiarly adapted.

In the manufacture of the prototype metres and the geodesique rules (each 4 metres in length) ordered from my firm by the Comité Internationale des Poids et Mesures, the Association Géodésique In-

ternationale, and the French Minister of War, I proceeded in the following manner with the platinum and iridium prepared as described above.

Operating upon a charge of 450 ounces of platinum and 55 ounces of iridium, I commenced by melting these metals together and casting into an ingot of suitable shape, which I then cut into small pieces with hydraulic machinery. After re-melting and retaining in a molten condition under a powerful blast of oxygen and common gas for a considerable time, I re-cast and forged at an intense white heat under a steam hammer, the highly polished surfaces of which were cleaned and polished after each series of blows—when sufficiently reduced it was passed through bright polished steel rollers, cut into narrow strips, and again slowly melted in a properly shaped mould, in which it was allowed to cool. I thus obtained a mass of suitable shape for forging, perfectly solid, homogeneous, free from fissures or air-holes, and with a bright and clean surface at bottom and sides as at top. At the first forging a bar was obtained 35 centims. long, 7·5 wide, 2·5 thick, which weighed—

| | |
|------------------------------|--------------|
| In air | 15·105 grms. |
| In water at 70° F. | 14·405 „ |
| Showing a density at zero of | 21·522 |

A third of the bar was cut off and the larger portion again forged to a length of 95 centims., width 2·5, thickness 2·0, which weighed—

| | |
|------------------------------|--------------|
| In air | 10·814 grms. |
| In water at 60° F. | 10·315 „ |
| Showing a density at zero of | 21·648 |

This was then passed through highly polished rolls until of a length of 4,010 centims. 21 millims. in width, and 5 millims. thick, to which a perfectly rectangular form was subsequently given by drawing it through a series of plates, and thus prepared the rule was in a condition to receive the beautiful polish of which this alloy is susceptible.

After passing it through each hole the metal was annealed by means of a jet of gas and oxygen to a heat just below melting point, and each time throughout after forging, rolling, and drawing was exposed to the action of melted borax, and boiled in concentrated hydrochloric acid to remove any possible trace of adherent iron or other impurity.

A piece cut from the end and presented to the French Academy of Science gave the following results:—

| | |
|-------------------------|---------------|
| Weight in air | 116·898 grms. |
| „ water | 111·469 „ |
| Showing a density of. . | 21·516 |

thus proving that the necessary processes of annealing at a high temperature had caused it sensibly to resume its original density.

The analysis gave—

| | 1. | 2. |
|-----------------|-------------|-------------|
| Platinum | 89·40 | 89·42 |
| Iridium | 10·16 | 10·22 |
| Rhodium | 0·18 | 0·16 |
| Ruthenium | 0·10 | 0·10 |
| Iron | 0·06 | 0·06 |
| | <hr/> 99·90 | <hr/> 99·96 |

From which is deduced:—

| | Proportion. | Density at zero. | Volume. |
|----------------------------------|-------------|------------------|-------------|
| Iridio-platinum, at 10 per cent. | 99·33 | 21·575 | 4·603 |
| Iridium, in excess | 0·23 | 22·380 | 0·010 |
| Rhodium | 0·18 | 12·000 | 0·015 |
| Ruthenium | 0·10 | 12·261 | 0·008 |
| Iron | 0·06 | 7·700 | 0·008 |
| | <hr/> 99·90 | | <hr/> 4·644 |

Density at zero, calculated after No. 1 analysis....21·510

Density at zero, calculated after No. 2 ,, 21·515

thus coinciding perfectly with the practical results obtained.

Messrs. Leon Brunner Brothers, of Paris, who had submitted this material of the géodésique rule to a great number of mechanical experiments, communicated the result of their observations to M. H. Sainte-Claire Deville, thus:—

“ Paris, 27 Août, 1878.

“ MONSIEUR,

“ La division de la règle géodésique, que nous faisons pour l'Association Géodésique Internationale, est terminée depuis quelques jours.

“ Nous avons pensé que vous ne seriez pas mécontent d'apprendre que cette opération a parfaitement réussi, et que c'est au métal que nous attribuons la facilité avec laquelle nous avons pu l'exécuter.

“ Le platine iridié de M. Matthey est incontestablement supérieur au platine ordinaire, pour la confection des règles divisées. Il est exempt de ces pailles qu'on rencontre toujours dans ce dernier, et se laisse polir au charbon. On peut, sans danger, enlever les rébarbes des traits et les conserver très beaux. Le platine ordinaire ne peut-être poli qu'au papier à émeré, et l'on est toujours exposé à gâter la division quand on procède à l'ébarbage. C'est là un inconvénient très-grave.

“ Nous ne pouvons que vous remercier, Monsieur, d'avoir mis à notre disposition un métal qui modifie singulièrement les difficultés

qu'on rencontre dans la fabrication d'une règle géodésique, et nous vous prions de recevoir l'assurance de nos sentiments les plus distingués.

“BRUNNER FRERES.”

In the year 1876 the suggestion was made to supersede the rectangular form by a tubular one, and I was requested to produce one of the following dimensions: Length, 1,002 centims.; exterior diameter, 37 millims.; interior diameter, 35 millims.; with rounded ends, one having an extension of small tube 4 millims. exterior diameter, 2 millims. interior diameter, 40 millims. long, which I did by the system of tube making with autogenous joints adopted by me with excellent results for the last 20 years, employing for the purpose an alloy prepared as above described. These proved to be so satisfactory that I have since made others, both round and square, of various dimensions, as lately shown at the Paris Exhibition.

Iridio-platinum alloy has now been proved to possess the following among many advantages for standard rules and weights:—

It is almost indestructible, has extreme rigidity, especially in the tube form, and a most beautifully polished surface can be obtained upon it; its coefficient of elasticity is very great, whilst for standard weights its high density is a valuable quality, and for these I should indeed recommend an alloy of not less than 20 per cent. of iridium. I lately made at the request of M. H. Sainte-Claire Deville a cylinder 40 millims. by 40 millims. of such an alloy, which showed by analysis the following proportions):—

| | |
|-----------------|---------|
| Platinum | 80·6600 |
| Iridium | 19·0786 |
| Rhodium | ·1220 |
| Ruthenium | ·0460 |
| Iron | ·0980 |

100·0046

and gave the density of 21·614.

With such a high density its coefficient of elasticity is 22·200000, one of the highest known, whilst its malleability and ductility are almost without limit.

The volume of the kilogram thus prepared is only 46·266 cub. centims., it displaces 2·267 cub. centims. less than the kilogram of the archives of France, and on this account, as on many others, is of course preferable.

The results I have arrived at in preparing alloys of higher grades, viz., 25—30—40 and 50 per cent. of iridium, are as follows:—

The alloy of 20 per cent. iridium is, as I have stated already, malleable and ductile.

25 per cent. can only with great difficulty and waste be worked

into sheet and wire when heated at low temperature. 30 per cent. and 40 per cent. with great difficulty only at a temperature little less than melting point, being brittle when cold, but with a grain of great beauty and fineness.

50 per cent. I have as yet failed to work up into forms other than castings beyond what I can effect by pressure when in a semi-fused condition.

The general results of my work on this alloy would lead me, therefore, to make the following recommendations.

For the manufacture of standard rules to use an alloy of not less than 85 per cent. platinum and 15 per cent. iridium, adopting the tubular form.

For the standard weights to use an alloy of not less than 80 per cent. platinum and 20 per cent. iridium, adopting the form now generally made.

Finally, following the expression of the great French chemist, M. Dumas, I hope by these labours "d'avoir enriché l'outillage scientifique d'un alliage doué des propriétés précieuse."

III. "On the Reversal of the Lines of Metallic Vapours." No. VI. By G. D. LIVEING, M.A., Professor of Chemistry, and J. DEWAR, M.A., F.R.S., Jacksonian Professor, University of Cambridge. Received March 27, 1879.

The experiments described in the following communication were made with the electric arc, and in lime crucibles,* or in crucibles of a highly calcareous sandstone, kindly supplied to us by Messrs. Johnson, Matthey, and Co., as described in our fourth communication on this subject; but for some of them we used, instead of a galvanic battery, a magneto-electric machine producing a much more powerful current and a much longer arc. The experiments with this machine were made, through the kindness of Dr. Tyndall, at the Royal Institution, and we are indebted to Messrs. Siemens both for the working of the machine and for sparing to us the services of a skilled engineer, in

* In our first paper on this subject, communicated in February, 1878, when referring to the experiments of Lockyer and Roberts ("Proc. Roy. Soc.," xxiii), we mentioned that they employed the combined action of a charcoal furnace and an oxyhydrogen blowpipe, but omitted to mention that they used a lime chamber after the model of Stas. Referring to fig. 1 in our communication of February 12, 1879, where the use of an oxyhydrogen blowpipe in a lime block is represented, we disclaim any novelty in the use of lime; the difference between our experiments and theirs consisting in this, that we use the continuous spectrum from the hot walls of our crucible, instead of an external independent source of light, as a background against which the absorbent action of the vapours is seen, in the same way as we had previously used iron tubes, and now use the electric arc.