VI. *On some combinations of Platinum. By* Edmund Davy, *Esq. Professor of Chemistry, and Secretary to the Cork Institution. Communicated by* F. Babington, *M. D. F. R. S.*

Read February 17, 1820.

In my communication to Sir H. Davy, Bart, "On a new fulminating platinum," which has been honoured with a place in the Transactions of the Royal Society,* I stated, that I had obtained some other new compounds of this metal: these have since occupied no inconsiderable portion of my leisure hours, and I now beg leave to lay the results of my inquiry before the Royal Society. A constant attention to other necessary duties, has not allowed me sufficient time to render this investigation so complete as I could have wished; but as I presume the facts are novel, I shall venture to bring them forward in a form, which, though imperfect, may not be wholly destitute of interest.

I. *On a peculiar compound of platinum, obtained from sulphate of platinum, by the agency of alcohol.*

Sulphate of platinum, unlike the other metallic sulphates in general, is, to a considerable extent, soluble in alcohol and in ether; as these fluids are capable, in certain circumstances, of partially or wholly reviving some metallic oxides from their solutions in acids, I wished to try their effects on the sulphate of platinum. Accordingly, I put into a small phial

* Phil. Trans. 1817.

about equal volumes of a strong aqueous solution of the sulphate, and alcohol; and after agitating the mixed fluids, the phial was put aside. Some weeks afterwards, I found the dark colour of the sulphate had entirely disappeared, a dense black substance had subsided, and the supernatant fluid remained colourless and transparent. On opening the phial, an odour similar to that of ether was perceived, the fluid had a strong acid taste, and afforded a copious precipitate with nitrate of barytes. After the black substance had been well washed and dried, a few preliminary experiments, served to show that it was a peculiar compound which had not been noticed. To confirm these results, and procure more of the substance, I repeated the experiment with the sulphate and alcohol. In about two days the fluid assumed a darker tint, the black substance began to precipitate in a finely divided state, and in about a week it had all subsided, leaving the fluid colourless and transparent. I afterwards found that the substance in question may be readily obtained by boiling the sulphate and alcohol* together for a few minutes; it separates in small particles, leaving the supernatant fluid colourless, or with only a slight tinge of yellow. In cases when it is thus procured, a little volatile inflammable fluid, having a peculiar ethereal smell, is also obtained. The substance, after being washed till the water is tasteless and does not affect litmus paper, and dried at a temperature of about 250° Fahrenheit, exhibits the following properties.

* The alcohol used in this experiment, may vary considerably in its strength and quantity, without materially affecting the results. Ether may also be employed as a substitute for alcohol.

2. *Properties of the peculiar compound.*

The substance is of a black colour, and in small lumps, which are soft to the touch, and easily reduced to an impalpable powder. It readily soils the fingers, or paper. It is destitute of lustre. It is tasteless, and apparently unaffected either by cold or hot water. It has a peculiar ethereal smell that is not easily removed, and probably arises from the presence of a little inflammable matter occasioned by the action of the alcohol. It seems to undergo no change by exposure to the air for some time. When it is gently heated, on a slip of platinum or paper, a hissing noise or a feeble explosion is produced, and this effect is accompanied by a flash of red light, and the platinum is reduced. It is insoluble in nitrous, sulphuric, and phosphoric acids, but it dissolves slowly in muriatic acid. It is scarcely affected by chlorine, except moisture be present, when a little muriate is gradually formed. When the powder is put into liquid ammonia, minute globules of air are evolved from it, and after some time it acquires fulminating properties. The quantity of air I have hitherto obtained in this way, has been too small to allow me to ascertain its nature with precision. When the powder is brought in contact with ammoniacal gas, a crackling noise is produced, and it becomes red hot and scintillates; but by this treatment, its external appearance is scarcely altered, though it undergoes a partial decomposition. The powder is immediately decomposed by the agency of alcohol. This fact is shown in an interesting manner by moistening different substances, such as paper, sand, cork, &c. with alcohol, and placing the smallest particle of the powder on them; it hisses, a sufficient degree of heat is produced to reduce and ignite the platinum, and it remains in a state of ignition until the alcohol is consumed. During the agency of alcohol on the powder, acetic acid is produced. This is shown by putting a little of the powder on a paper filter and moistening it with alcohol; a moderate action takes place, and in a few minutes, the odour of acetic acid is very perceptible. In some experiments of this kind, the action, though comparatively feeble at first, has presently increased, the powder has become red hot, and the bottom of the filter completely charred. If two or three grains of the powder are placed in a glass, and a few drops of alcohol added, in about half an hour acetic acid will be produced; and as it evaporates and disappears, it may be successively renewed, at longer or shorter intervals, for some weeks, by occasionally adding a little alcohol.

When the powder is boiled in alcohol, it is partially decomposed, and assumes a lighter colour; if it be then thrown on a filter, the odour of acetic acid is soon perceived, and in a few hours the platinum is found reduced and the paper charred. When the powder is mixed with flowers of sulphur, and heated, a sulphuret of platinum is formed of a blue colour. When the powder is heated with phosphorus, there is a brilliant combustion, and a dark grey phosphoret is formed. Oxygen gas does not affect the powder at the common temperature of the air, but by a moderate heat there is a slight combustion, which seems to indicate the presence of a little inflammable matter.

3. *Composition of the peculiar compound.*

In my first attempts to ascertain the nature of the black powder, I was limited to very minute quantities of it; and I made several trials, before I gained any satisfactory evidences of its constitution. I decomposed the powder in long green glass tubes filled with mercury; in such cases, by a gentle heat, the powder became ignited, the reduced platinum amalgamated with the mercury, a little fluid appeared, and some gas was evolved. The fluid reddened litmus, and had an acid taste. The gas rendered lime water turbid, and was in part absorbed by water and by ammonia; and the unabsorbed portion exhibited properties similar to those of nitrogen. These results seemed to prove, that the powder contained acid and inflammable matter; but they were not sufficiently uniform to enable me to place much reliance on them. I then used very small glass retorts, varying in capacity, from $\frac{4}{10}$ to $\frac{7}{10}$ of a cubic inch, and decomposed the powder over pure water and over mercury; but the results were most satisfactory when I operated over mercury. From two experiments of this kind, which I beg briefly to detail, as they very nearly agree, I think I may venture to state the composition of the powder under examination.

Experiment 1. Ten grains of the powder were decomposed in a little retort, over dry mercury, by the heat of a spirit lamp. On the first impression of the heat, gas was disengaged, and shortly after, the interior of the retort assumed a reddish yellow colour (like that exhibited by the vapour of fuming nitrous acid), and small drops of a colourless fluid condensed in the neck of the retort. After the utmost heat of the lamp had been given to the retort, it was suffered to cool, and the results were immediately examined.

(a) Examination of the gas.

The gas remaining in the retort made an ignited piece of wood glow brighter; that which came over (deducting the common air) was $\frac{34}{100}$ of a cubic inch, which diminished to $\frac{25}{100}$ on being transferred to water and agitated. $\frac{20}{100}$ of the unabsorbed gas, on being mixed with an equal volume of pure hydrogen and fired by an electric spark, diminished to $\frac{26}{100}$. Hence, the unabsorbed portion of gas contained more oxygen than could have been furnished from the common air of the retort.

From other experiments, the gas absorbed by water was found to be carbonic acid; it rendered lime water turbid, was absorbed by ammonia, and again disengaged by muriatic acid.

(b.) Examination of the fluid.

The fluid which rose in the neck of the retort reddened litmus paper, and resembled the nitrous acid in odour, colour, and taste. It acted upon the mercury in contact with the retort, and when washed out by pure water, the solution did not affect the nitrate of barytes, or silver.

(*c.*) The platinum was perfectly reduced, and its particles formed a loosely coherent mass, which could not be removed until the bulb of the retort was broken. It weighed $9\frac{5}{8}$ grains, and suffered no diminution on being again heated to redness in a platinum cup.

Experiment 2. Ten grains of the same powder as that used in the first experiment, afforded by its decomposition $9\frac{5}{8}$ grains of platinum, a little fluid agreeing in its properties with that noticed in the former experiment, and $\frac{34}{100}$ of gas, which was examined in a different manner from that of Experiment 1. The gas remaining in the retort, was treated with pure nitrous gas; red fumes were produced, and the absorption was so great that the mercury presently rose near the bulb of the retort, and was still rising, when its neck was intentionally broken to secure the platinum. Hence, it seems the gas in the retort was oxygen.

The gas that came over was first treated with lime-water; an immediate turbidness was produced, and increased by agitation, and $\frac{9}{100}$ of the gas were absorbed. To the residual gas, nitrous gas was added, which occasioned a considerable absorption; and the remaining gas, which exhibited the properties of nitrogen, was principally derived from the common air of the retort. By adding a little diluted muriatic acid to the turbid fluid, it immediately became transparent, and the absorbed carbonic acid was slowly disengaged, and the mercury was studded with innumerable little globules of it.

From these experiments, 100 grains of the black powder appear to contain 96·25 platinum.

96·25	platinum.
3·75	nitrous acid, a little oxygen, and a minute portion of carbon.
10·000	

Though the powder was dried at a heat considerably above 212°, it may contain water; and if this is the case, its composition may be differently stated, as deduced from the foregoing experiments:

96·2500	platinum.
0·1200	oxygen.
0·0106	carbon.
3·6194	nitrous acid and water.
100·0000	

4. *Observations, &c. on the peculiar compound.*

From the preceding experiments, the black powder obtained by the agency of alcohol on the sulphate of platinum, appears to consist almost solely of platinum, with a little oxygen, and the elements of the nitrous acid. The very minute portion of carbonaceous matter it contains, is probably accidental. If the constitution of the powder is such as I have stated, a doubt may arise whether it can be considered as a definite compound; but its solubility in the muriatic acid, the facility with which it combines with sulphur, and resists the action of a strong solution of potash at a boiling heat, and its acquiring fulminating properties in liquid ammonia, are all circumstances which favour the notion of its being a true chemical compound. It seems rather doubtful, whether the powder can be regarded as a sub-nitrate of platinum, or a combination of platinum with oxygen and nitrogen, in a different state from that in which they co-exist in the nitrous acid. On the idea that the powder is a compound of the metal with a little oxygen and nitrous acid, something may be said on the mode of its formation, and on the more remarkable properties it exhibits.

From the manner in which the sulphate of platinum is formed, (namely, by the agency of nitrous acid on the hydrosulphuret of platinum) there can be no difficulty in accounting for the presence of a small portion of nitrous acid in it; and my experiments incline me to the opinion, that it is scarcely possible to separate the last portions of nitrous acid from the sulphate, without entirely decomposing it. That the quantity of nitrous acid in the sulphate must, however, be very limited, appears from this circumstance, that the addition of a little nitrous acid to the sulphate, entirely prevents the formation of the black powder, though successive portions of alcohol be added, and the whole boiled for a considerable time.

When sulphate of platinum, containing a little nitrous acid, is treated with alcohol, a mutual action takes place; slowly at the common temperature of the air; but rapidly by the assistance of heat: the sulphuric acid being united to the oxide of platinum by a weak affinity, seems to form a new combination with the alcohol, whilst the oxide combines with the portion of nitrous acid present, to form the black powder. In certain cases, as is well known, alcohol separates salts from their aqueous solutions, in consequence of a stronger affinity for the water in which they are dissolved; but in this instance, the agencies of alcohol and of nitrous acid, are probably concerned in separating the sulphuric acid from the sulphate.

The vivid action of ammoniacal gas on the powder, may be referred to the mutual energy with which the alkaline gas, and loosely combined nitrous acid in the powder, act upon each other. I found by experiment, that ammoniacal gas is absorbed in this instance; thus, 3 grains of the powder were placed in a graduated glass receiver, and filled with dry mercury. 2·3 cubic inches of ammoniacal gas, containing only $\frac{1}{100}$ impurity, were let up into the receiver: an immediate action took place, the powder became ignited, and after two hours, $\frac{3}{10}$ of a cubic inch of the gas were absorbed; recently boiled pure water, whilst yet hot, was let up into the receiver, and the residual gas was all absorbed, except a small globule, which did not exceed the original impurity in the ammonia.

The action of alcohol on the powder is curious, and is connected with the decomposition of both substances. When the powder is brought in contact with the vapour of alcohol, at the common temperature of the air, there is an immediate chemical action; the heat generated is sufficient to reduce and ignite the metal, and to continue it in a state of ignition, until the alcohol is consumed. In this case, the acid first noticed by Sir H. DAVY, (in his beautiful experiment of the ignited platinum wire, and since, more fully examined by Mr. DANIELL), is produced. In other instances, the acetic acid, as has been mentioned, is formed. It would be premature to speculate on the uses to which this powder may be applied, but from its peculiar properties, there is reason to think it will admit of some useful applications. I have already employed it as an easy means of affording heat and light. To produce heat, it is only necessary to moisten any porous substance, such as sponge, cork, cotton, asbestos, sand, &c. with alcohol or whiskey, and to let a particle of the powder fall on the substance so moistened; it instantly becomes red hot, and remains so until the spirit is consumed; nor is the ignited metal extinguished by exposure to the atmosphere, or by blowing the breath on it; on the contrary, partial currents of air only make it glow brighter. The heat produced in this way, may be accumulated to a considerable extent, by increasing the quantity of the materials employed. I have also constructed a tinder box, to procure immediate light by means of the powder. It consists of two small phials placed in a japanned box, and some sulphur matches tipped with phosphorus. One of the phials contains the powder; the other, alcohol. The stopper of the phial containing the alcohol, has a bit of sponge inserted in a small aperture at the bottom of it. When a light is wanted, it is only necessary to shake the bottle so as to moisten the sponge with the alcohol, take out the stopper, and put the smallest particle of the powder on the moistened sponge; it instantly becomes red hot, and will readily kindle one of the matches. This mode of igniting a metal seems to be quite a new fact in the history of chemistry; but the means of keeping it in a state of ignition, is only another illustration of the facts previously pointed out by Sir H. DAVY, in his late valuable researches, which have thrown so much light on the philosophy of flame, and led to such very interesting, important, and unexpected results.

5. On the effects of sulphate of platinum upon gelatine.

When an aqueous solution of sulphate of platinum is added to any solution of gelatine, such as isinglass, size, or glue, a precipitate occurs, and all the sulphate is separated in union with the gelatine; or if a minute portion remain, it is precipitated on boiling the fluid. This precipitate, whilst in a moist state, is of a brown colour, and has some degree of tenacity; but when well washed and dried at a temperature a little above the boiling point of water, its colour changes to a jet black; it becomes hard and brittle, and has a resinous lustre. It is not decomposed by being boiled in water or in weak alkaline solutions. When it is gently heated by a spirit lamp on a slip of platinum, a violent action is produced, and a dense white vapour is exhaled, in which the odour of sulphureous acid is perceptible, the substance becomes ignited, and is presently decomposed, leaving the reduced platinum in small grains.

When this compound is decomposed by heat in close vessels over water or mercury, it yields a grey sulphuret of platinum,* nitrogen, sulphureous, carburetted hydrogen and carbonic acid gases, carbonate of ammonia, and an oily-like fluid. This compound of sulphate of platinum and gelatine, when dried at a heat just above that of boiling water, afforded, by its decomposition in two experiments, half its weight of platinum; and if my former statement of the composition of sulphate of platinum is correct, 100 grains of the above compound will consist of about

56·11	oxide of platinum,
20·02	sulphuric acid,
23·87	gelatine and water.
100·00	

6. *On the sulphate of platinum, as a test for gelatine.*

As I found that minute quantities of gelatine in solution, were readily detected by the sulphate of platinum, I made some experiments to ascertain the efficacy of this substance as a test for gelatine, and I am inclined to think it merits a decided preference over the re-agents at present used by chemists for this purpose. The best known substances for detecting the presence of gelatine are, I presume, those which contain the tanning principle, as the infusions of oak-bark, nutgalls, catechu, &c. And a variety of gelatine, isinglass, (as is well known), is employed to ascertain the quantity of

* In the "Annales de Chimie," &c. Tome V., M. VAUQUELIN treats of the sulphuret of platinum as a new compound which he had formed; but I published an account of it in the Philosophical Magazine, in the year 1812.

tanning principle in different astringent substances; but for this purpose, as Sir H. DAVY has shown,* many precautions are necessary; and from his experiments it appears that tannin may exist in a state of combination, in which its presence cannot be made evident by means of a solution of gelatine. I have made several comparative experiments on the efficacy of those astringent infusions, and of the sulphate of platinum, as tests for gelatine; and I think I may venture to conclude, that the sulphate is a test of superior delicacy, and more certain in its operation. Thus, in cases where the gelatine was in very minute quantity, or in a very diluted state, when no effect was produced by strong infusions of oak-bark, nutgalls, or catechu, there was an immediate precipitate on adding sulphate of platinum. In instances also, when the quantity of gelatine was too minute to be readily detected by simply adding the sulphate, the effect was immediately produced on boiling the fluid.

The effects of sulphate of platinum on solutions of the different varieties of gelatine, as isinglass, glue, and size, appear to be precisely similar, and the precipitates obtained in such cases, seem to be uniform in their properties and composition; nor are they affected by the presence of any of the mineral acids in excess. The operation of astringent infusions, as oak-bark, nutgalls, and catechu, on solutions of the different varieties of gelatine, is not uniform. According to Sir H. DAVY, catechu contains a much larger quantity of the tanning principle than oak-bark; yet I found that an infusion of it produced no precipitate in solutions of size, of different degrees of concentration. The size I employed was

* Phil. Trans. 1803.

such as paper-hangers use; it had been recently prepared, and was, previous to its being dissolved in water, in the form of a tremulous jelly. The sulphate of platinum occasions, after a short time, a brown precipitate in astringent infusions; but this substance I have not examined.

7. *On a grey oxide of platinum.*

In the course of my experiments to ascertain the composition of fulminating platinum, I treated it with nitrous acid, and thus procured, as I have elsewhere stated, a grey oxide of platinum, which has not yet been described. It may be obtained by adding strong nitrous acid to fulminating platinum, boiling it to dryness, and exposing the dry mass to a heat just below redness, so as to expel all the nitrous acid. The oxide of platinum remains. It is to be finely pulverized and boiled, first in pure water, and then in a weak solution of caustic alkali to separate the last portions of acid, which adhere with great tenacity to it. It is now to be well washed and dried at a heat not exceeding that of boiling mercury. I have usually made the experiment in a platinum crucible on a hot sand bath. The oxide thus prepared exhibits the following properties.

8. *Properties and composition of the grey oxide of platinum.*

Its colour is da:k iron grey. It has the metallic lustre. It is sufficiently hard to cut brass, which it polishes, and when the polished surface is rubbed a little with the oxide, a delicate coating of platinum remains. It does not touch steel. It is not affected by cold or hot water, nor by the nitrous, sulphuric, or phosphoric acid at a boiling heat. It is insoluble in nitro-muriatic acid, and in cold muriatic acid, but it slowly dissolves in this last acid by the assistance of heat. It is not acted upon by a strong solution of the fixed alkalies. When the oxide is put into liquid ammonia, minute globules of air are evolved from it, but the quantity has been too small to admit of being examined; probably it is common air, as the oxide appears to undergo no change by being kept for some weeks in ammonia. When heated with sulphur, the oxide yields sulphureous acid gas and a grey sulphuret of platinum. When mixed with zinc filings and heated, the oxide is decomposed with vivid ignition, and white oxide of zinc is formed.

When the oxide is mixed with borax, and exposed to a strong red heat before the blowpipe, it forms a black glass, which becomes of a lighter colour on urging the heat to whiteness, and the oxide appears to be reduced. If the oxide is mixed with powdered glass and fused, a glass is obtained of a dull brown colour. The oxide is readily reduced by moistening it with oil of turpentine, and heating it moderately; or by exposing it to a dull red heat in the atmosphere; but it requires a strong red heat to reduce it in close vessels. Some of the oxide which had been well dried, first on a hot sand bath, and then exposed to a heat just below redness, on a slip of platinum, was decomposed in very small green glass retorts, over mercury. In two experiments in which I used 7 grains of the oxide, I obtained in each instance 6 grains of platinum, and 2·1 cubic inches of oxygen, the thermometer being at 60° and barometer 30°. I found also in the necks of the retorts, a slight trace of a fluid that reddened litmus paper, and had an odour similar to that of nitrous acid. Now, if

6 grains of platinum combine with 2·1 cubic inches of oxygen, 100 grains will take 34 cubic inches; and calculating from Sir H. Davy's statement, that 100 cubic inches of oxygen weigh 34 grains, the grey oxide of platinum will be found to consist of

100 platinum	or per cent, of	89·366	platinum,
11·9 oxygen		10·634	oxygen.
		100·000	

It will be readily seen, that I have here deduced the composition of the grey oxide from the actual quantity of oxygen and metal obtained in the experiments; and this mode of analysis seems liable to little objection, and can very rarely be resorted to, in ascertaining the composition of metallic oxides. On comparing my previous experiments upon the grey oxide, with the above results, I am most inclined to place confidence in the latter. There is, indeed, a near coincidence between them, and the difference, which is only about one per cent, may be referred to the presence of a little more acid in my first experiments. The grey oxide is insoluble in aqua regia, a fact which seems to add additional support to Sir H. Davy's opinion respecting the action of aqua regia on platinum.* This menstruum, according to Sir H. Davy, does not oxidate platinum, but merely causes its combination with chlorine. Now, if the metal were oxidated previous to its solution, the oxygen, there is reason to think, would be derived from the nitrous acid, and the grey oxide formed by this acid, be produced, which can scarcely

* Journal of Science and the Arts, Vol. I.

be the case, as it is insoluble in aqua regia. Add to this, the fact, that by evaporating a common solution of platinum to dryness, no nitrate can be obtained, but only a muriate, or a compound of the metal and chlorine.

If, according to the statements of Professors VAUQUELIN and BERZELIUS, the black oxide of platinum contains about 15 per cent. of oxygen, the grey oxide may be considered as the protoxide, containing 1 proportion, and the black oxide $1\frac{1}{2}$ proportion of oxygen; and the number representing the element or proportion in which platinum combines with bodies will be 126, taking Sir H. DAVY's number 15, to represent the proportion in which oxygen unites with bodies.

Mr. COOPER states the black oxide of platinum to consist of 100 platinum, with only 4·317 of oxygen;* but he has, I think, considerably under-rated the oxygen in it. On repeating his experiments on a small scale, I obtained results different from those he has stated. Thus, he says the powder obtained from the muriate of platinum by a neutral solution of mercury, is a compound of calomel and the protoxide of platinum; but by decomposing this powder in a little retort over mercury, I found the neck of the retort partially lined with metallic mercury; and this fact alone, I think, is sufficient to awaken suspicion as to the accuracy of his results. Mr. COOPER, I presume, used a nitrate of mercury to decompose the muriate of platinum, but he seems to have overlooked the nitrous acid in stating his results.

The chemical history of platinum, is far from being complete. The great want of uniformity in the statements of

* Journal of Science and the Arts, Vol. III.

chemists respecting the composition of the known compounds of this valuable metal, and the circumstance of their not harmonizing with the doctrine of definite proportions, prove the necessity of submitting them to a more rigid examination; and this could not be done without rendering our information on the subject more accurate and extensive.

Cork Institution,
Sept. 1, 1819.