

*P H I L O S O P H I C A L*  
*T R A N S A C T I O N S :*

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**X. An account of some experiments on the combinations of different metals and chlorine, &c**

John Davy, Esq.

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X. *An Account of some Experiments on the Combinations of different Metals and Chlorine, &c.* By John Davy, Esq. Communicated by Sir Humphry Davy, Knt. LL.D. Sec. R. S.

Read February 27, 1812.

*Introduction.*

MY brother, Sir HUMPHRY DAVY, appears to me to have demonstrated, in his last Bakerian Lecture, the existence of a class of bodies similar to metallic oxides, and consisting of metals in union with chlorine or oxymuriatic acid.

These combinations are the principal subject of the following pages. I shall do myself the honour of giving an account of the experiments I have made to ascertain the proportions of their constituent parts, and likewise of describing some that have not yet been noticed.

I shall have to relate also the attempts I have made to ascertain the proportions of sulphur in several sulphurets, and the experiments I have performed to estimate the quantity of oxygene in some metallic oxides. The general analogy of definite proportions led me to both these undertakings. This analogy, it will be perceived, I have constantly kept in view, and have had recourse to, both for detecting inaccuracies in my own experiments, and in considering the results of the experiments of others.

As the nomenclature connected with the old hypothesis, respecting oxymuriatic acid, is inconsistent with the new views

of this substance, I shall venture to call the compounds of the metals and chlorine to be treated of, by the names which my brother has proposed for them.

1. *On the Combinations of Chlorine and Copper, &c.*

There are two distinct combinations of chlorine and copper, both of which may be directly made by the combustion of this metal in chlorine gas. When the gas was admitted into an exhausted retort containing copper filings, the filings became ignited, a fixed fusible substance quickly formed, and the interior of the retort soon became lined with a fine yellowish brown sublimate. The former substance evidently contains least chlorine, for when it was heated alone in chlorine gas, it absorbed an additional portion, and was converted into the latter. Hence the fixed compound may, in conformity with the principles of Sir HUMPHRY DAVY's nomenclature, be called cuprane, and the yellow sublimate, cupraneæ.

Cuprane may be procured in several other ways. It may be obtained by heating together copper filings and corrosive sublimate; and it was thus first discovered by BOYLE, who called it resin of copper, from its similitude to common resin. Two parts of corrosive sublimate, and one part of copper filings, I have found the best proportions of the materials.

It may be obtained by boiling copper filings in muriatic acid, or by exposing slips of copper partially immersed in this acid to the atmosphere. In the last instance, I have found the changes connected with the formation of cuprane rather complicated; the copper exposed receives oxygene from the atmosphere, and acid from the ascending muriatic acid fumes, and is thus converted into a green insoluble salt, and this



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absorbing more muriatic acid, slowly passes into the deliquescent muriat, which flowing into the muriatic acid is changed by the action of the immersed copper into cuprane.

M. PROUST, the first modern chemist who examined cuprane, and who is commonly considered as the first discoverer of this compound, found it produced by the action of muriat of tin on muriat of copper; he named it white muriat of copper, and ascertained that a similar substance results from the decomposition of the common deliquescent muriat by heat.

Cuprane, by whatever means prepared, possesses the same properties. It is fusible at a heat just below that of redness, and in a close vessel, or a vessel with a very small orifice, it is not decomposed or sublimed by a strong red heat; but if air, on the contrary, is freely admitted, it is dissipated in dense white fumes. It is insoluble in water. It effervesces in nitric acid. It silently dissolves in muriatic acid, from which it may be separated by the addition of water, which precipitates it unaltered; and it is decomposed by a solution of potash; or by heating it with the fused hydrated alkali: when it affords the orange oxide of copper. Its colour, transparency, and texture appear alone to vary. It is generally opaque, of a dark brown colour, and of a confused hackly texture; but I have obtained it by cooling it slowly after it has been strongly heated, of a light yellow colour, semi-transparent, and crystallized, apparently in small plates.

Cuprane is only very slowly formed by heating cuprane in chlorine gas. The best mode that I have found, of procuring it, is by slowly evaporating to dryness, at a temperature not much above 400 of FAHRENHEIT, the deliquescent muriat of copper. Thus made, it has the same appearance

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and the same properties, as when directly formed. It is of a yellow colour, and pulverulent. Exposed to the atmosphere, it is converted, by the action and absorption of water, into the deliquescent muriat, and its colour, during this alteration, changes from yellow first to white, and lastly to green. It is decomposed by heat; and even in chlorine gas when the experiment is made on a pretty large quantity, part of the chlorine is expelled, and assumes the gaseous state, and cuprane remains.

I have employed the same methods for ascertaining the proportions of the constituent parts of both these combinations. I have separated the copper by iron, and the chlorine by means of nitrat of silver.

A solution of 80 grains of cuprane in nitro-muriatic acid, precipitated by iron, afforded 51.2 grains of copper, well washed, and perfectly dried.

A solution of the same quantity of cuprane in nitric acid, precipitated by nitrat of silver, afforded 117.5 grains of horn silver dried, till it ceased to suffer any loss of weight by exposure to a temperature above 500 FAHRENHEIT.

Since horn silver contains 24.5 per cent. of chlorine,\* 80 grains of cuprane appear to contain 51.2 grains of copper and 28.8 of chlorine. And 100 appear to consist of

36	chlorine
64	copper
<hr/>	
100	

\* This I have ascertained by synthesis; 12 grains of pure silver dissolved in nitric acid, and precipitated with muriat of ammonia, yielded 15.9 grains of fused horn silver. I do not give the particulars of the experiment, which was very carefully made; because the result very nearly agrees with that of KLAPROTH, and of other chemists.



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A solution of 40 grains of cupranea in water, acidulated with muriatic acid, precipitated by iron afforded 18.8 grains of copper.

And a solution of 20 grains of cupranea in water, precipitated by nitrat of silver, afforded 43 grains of horn silver.

Hence 100 of cupranea, omitting the very slight loss, appear to consist of

$$\begin{array}{r}
 53 \text{ chlorine} \\
 47 \text{ copper} \\
 \hline
 100
 \end{array}$$

The deliquescent muriat and the native muriat of copper of Peru, belong to a class of compounds apparently distinct from the preceding combinations of copper and chlorine.

The deliquescent salt is well understood; and its composition may be inferred, independent of its water, from that of cupranea.

The native muriat is less known, I shall therefore relate the experiments I have made on this interesting mineral.

The specimen I have examined is part of a very fine one, presented to Sir HUMPHRY DAVY by WILLIAM JACOB, Esq. M. P. and deposited in the Museum of the Royal Institution. It consists of muriat and carbonat of copper, of red oxide of iron, and of green coloured quartz. The muriat is partly crystallized; the crystals, from the trials I have made of them, appeared to be pure, and they were, on that account, made the subject of my experiments.

The crystallized muriat dissolves entirely and without effervescence, in all the acids in which I have tried it, and the deliquescent muriat of copper is in each instance formed, and

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a combination of brown oxide of copper with the acid employed.

Heated slowly in a bent luted glass tube, connected with mercury, the native muriat affords water and oxygene gas, and the residue is an agglutinated brownish mass, which dissolves in muriatic acid and gives a greenish precipitate with potash, and is apparently a mixture of brown oxide of copper and cuprane. When the heat is raised rapidly to redness, the water expelled is impregnated with muriatic acid, and muriat of copper. I have obtained from 25 grains of the mineral heated to redness till gas ceased to be produced, just two cubic inches of oxygene. This expulsion of oxygene seems to be owing to the action of chlorine on the brown oxide to form cuprane; and there is, I have ascertained, a similar production of oxygene when heat is applied to a mixture of the deliquescent muriat and brown oxide of copper.

From these results, which perfectly agree with those obtained by eminent chemists on the Continent, who have examined different specimens of this mineral, it appears to be a submuriat of copper, differing in a chemical point of view from the deliquescent salt, merely in containing a smaller proportion of acid.

The following experiments were made with the design of ascertaining the proportions of its constituent parts.

50 grains of the crystals in powder, boiled in a solution of 50 grains of potash, afforded 36.5 grains of brown oxide of copper heated to dull redness.

And 20 grains dissolved in nitric acid, and precipitated by means of nitrat of silver afforded 12.9 grains of dry horn silver.



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Hence, considering the deficiency of weight, as indicating the quantity of combined water, 100 of the native sub-muriat of copper seem to consist of

$$\begin{array}{l} 73.0 \text{ brown oxide} \\ 16.2 \text{ muriatic acid} \\ 10.8 \text{ water} \end{array} = \left\{ \begin{array}{l} 15.8025 \text{ chlorine} \\ .47 \text{ hydrogen.} \end{array} \right.$$

This analysis, allowance being made for difference of theory, nearly agrees with that of KLAPROTH.

M. PROUST, I believe, first discovered an artificial compound similar to the native sub-muriat of copper. He obtained it, in the preparation of the nitro-muriat of copper, and also by a partial abstraction of the acid of the deliquescent muriat, by means of an alkali. I have found that it may be procured in several other ways. It may be made directly by adding the hydrated blue oxide of copper to a solution of muriat of copper; and it may be very readily and economically prepared, by exposing to the atmosphere slips of copper partially immersed in muriatic acid; and it is also produced by the exposure of cuprane to the atmosphere. Its production in the last instance is accompanied with that of the deliquescent muriat; and the formation of both seems to be owing to the absorption of water and oxygene; for cuprane, I have found, though apparently not in the least acted on by dry oxygene gas, is quickly changed when moistened with water and confined in a jar of this gas, and there is a rapid absorption of oxygene.\*

I have not examined all the specimens obtained by these different methods minutely, though sufficiently, I conceive, to

\* I have been informed that submuriat of copper is sometimes found in the neighbourhood of volcanoes, particularly in that of Vesuvius. By means of the above facts, it is evident that its production might be accounted for in such situations.



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ascertain their identity, and their similarity to the native compound. The colour of all of them is greenish white, like that of the native, in a finely divided state. When heated, they all afford water, oxygene gas, and a mixture of cuprane and brown oxide of copper.

I have analysed only the submuriat, precipitated from a solution of muriat of copper, by a weak solution of potash.

50 grains of this, well washed and dried, boiled in a solution of potash, afforded 36.3 grains of dried brown oxide of copper.

And 20 grains dissolved in nitric acid, and precipitated by nitrat of silver, afforded 12.75 grains of dried horn silver. These results differ so little from those obtained with the native, as fairly to permit the conclusion, that the composition of the artificial and native submuriat of copper is the same.

2. *On the Combinations of Tin and Chlorine, &c.*

Tin, like copper, is capable of combining with two different proportions of chlorine. The liquor of Libavius, one of the combinations, is directly formed by the combustion of the metal in chlorine gas; and the other, I find, may be produced by heating together an amalgam of tin and calomel. Thus obtained, it is similar to that which may be procured, by evaporating to dryness, the muriat containing the gray oxide of tin, and fusing the residue in a close vessel. Both are of a gray colour, and of a resinous lustre and fracture, and both inflame, like tin itself, when heated in chlorine gas, and are converted into the liquor of Libavius by the absorption of a fresh portion of chlorine. Hence, as the liquor of Libavius

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contains the largest proportion of chlorine, it may be called stannanea, and the other compound stannane.

Stannane is fusible at a heat below that of dull redness; it bears this temperature, if air be nearly excluded, without undergoing any change; but when subjected to a heat, as strong as glass will bear without being fused, it appears to be, from the slight fume produced, partially decomposed.

It affords the liquor of Libavius when heated with corrosive sublimate, nitre, red oxide of mercury, or with the hyperoxymuriat of potash. In the three last instances, oxide of tin is also formed; and with the hyperoxymuriat, the action is so violent, that inflammation is actually produced.

The liquor of Libavius and aurum musivum are formed when stannane is heated with sulphur.

Stannane, by the action of water, appears to be converted into the insoluble submuriat of tin, and the acidulous muriat.

The stannanea or liquor of Libavius, that I have examined, was made by heating together an amalgam of tin and corrosive sublimate, in the proportions commonly recommended. I have obtained this compound in another way, by treating the concentrated solution of the peroxide of tin in muriatic acid, with strong sulphuric acid; a gentle heat applied to this mixture contained, in a retort, expels the fuming liquor, which may be condensed, as usual, in a cold receiver.

The only new and remarkable property, which I have observed the liquor of Libavius to possess, is, its action on oil of turpentine. I was led to make trial of it from an idea of Sir HUMPHRY DAVY, that the combinations of the metals and chlorine might be soluble in oils. In the first experiment, when I poured the fuming liquor into the oil, inflammation immediately took



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place, with violent ebullition and production of dense reddish fumes. I have used other specimens of oil of turpentine, expecting a similar inflammation, but without its occurrence, though there has been in every instance a considerable action. The mixture of the two being made in a retort connected with mercury, no gas was generated, oxide of tin appeared to be formed, and a viscid oil was produced, which, like the fat oils, left a permanent stain on paper, and had little smell or taste, and which, digested with alcohol, imparted something which occasioned a permanent cloudiness on the admixture of water, and an odour to me not unlike that of artificial camphor. The action of the liquor of Libavius on the oil of turpentine is worthy of further inquiry. The preceding account of it, I am aware is very incomplete; but I trust it will serve to call the attention of chemists to a subject so curious.

To discover the proportions of tin, and consequently of chlorine in stannane and stannanea, I have taken advantage of the superior affinity of zinc for chlorine, by means of which the tin is separated in its metallic state.

69.5 grains of stannane, made by heating in a glass tube with a very small orifice, an amalgam of tin with calomel, were, with the exception of two grains of metallic mercury, apparently a mere mechanical mixture, entirely dissolved in dilute muriatic acid. A slip of clean zinc, immersed in this solution decanted from the residual mercury, quickly precipitated the tin in a very beautiful plumose form; and this precipitate collected on a filter, and well washed and dried and fused into one globule under a cover of tallow in a small glass tube, weighed 42 grains.

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As therefore 67.5 grains of stannane contain 42 grains of tin, 100 appear to consist of

$$\begin{array}{r} 62.22 \text{ tin} \\ 37.78 \text{ chlorine} \\ \hline 100.00 \end{array}$$

As stannanea is extremely volatile, it is difficult to weigh it, with perfect accuracy. The mode I adopted, was to pour it into a bottle half full of water, the weight of which was previously ascertained, and to infer the quantity added by the increase of weight.

81.75 grains of stannanea thus weighed in water,\* afforded when decomposed by zinc 34 grains of tin.

Hence 100 of stannanea appear to be composed of

$$\begin{array}{r} 42.1 \text{ tin} \\ 57.9 \text{ chlorine} \\ \hline 100.0 \end{array}$$

I am not acquainted with any analytical method for directly ascertaining the proportion of chlorine in either of the two preceding combinations. Nitrat of silver, when immediately applied, will not answer the purpose, because the oxide of silver is partially reduced by the solution of stannane; and an oxide of tin is thrown down in mixture with the horn silver from the liquor of Libavius.

\* A little muriatic acid was added before the zinc was introduced, to dissolve the oxide of zinc, which, in other similar experiments, I observed was rapidly formed, and which, from the large quantity of hydrogen evolved, appeared to be owing to the decomposition of water, chiefly in consequence of the Galvanic effect of the contact of the two different metals, zinc and tin.



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M. PROUST, to whom we are indebted for very excellent investigations of the different combinations of copper and tin, first discovered a submuriat of tin. He found that a solution of potash precipitated from the solution of muriat of tin this compound, and not the pure gray oxide of tin.

I have obtained it by his method, and all its properties which I have observed, are perfectly agreeable to its supposed composition.

It is decomposed by a red heat. Subjected to distillation in a small bent glass tube connected with mercury, no gas was produced, water containing muriatic acid and muriat of tin was expelled, and a sublimate like stannane was formed, and the fixed residue was gray oxide of tin.

It effervesces violently with nitric acid; and strong sulphuric acid expels from it muriatic acid fumes.

It dissolves without effervescence in the muriatic and acetic and in the dilute, nitric, and sulphuric acids; and all these acid solutions, as they give a black precipitate with a solution of corrosive sublimate, appear to contain the tin in the state of gray oxide.

The complete analysis of this submuriat of tin is difficult. The oxide it contains cannot be accurately separated by potash, nor can nitrat of silver be employed to ascertain the proportion of muriatic acid.

I have found 50 grains of it, dissolved in muriatic acid, to afford, when precipitated by zinc, 31 grains of metallic tin. Now as this submuriat is similar to the submuriat of copper, the analogy being imperfect only in the latter containing the peroxide, and the former the protoxide, it is natural to infer that the proportion of muriatic acid is similar in both. But the

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proportion of muriatic acid in the submuriat of copper is apparently half of that which exists in the muriat; hence, supposing the composition of the submuriat of tin to be similar, 100 of it will consist of

70.4	gray oxide
19.0	muriatic acid
10.6	water
<hr/>	
100.0	

Probability alone can be attached to this estimate. I have not given the calculations by which it was made, as their data are liable to objection.

### 3. *On the Combinations of Iron and Chlorine.*

As there are two oxides of iron, so there are also two distinct combinations of this metal and chlorine. One may be directly formed by the combustion of iron wire in chlorine gas; it is that volatile compound described by Sir HUMPHRY DAVY in his last Bakerian Lecture, which condenses after sublimation in the form of small brilliant iridescent plates. The other, I find, may be procured by heating to redness, in a glass tube with a very small orifice, the residue which is obtained by evaporating to dryness the green muriat of iron; it is a fixed substance requiring a red heat for its fusion; it is of a grayish but variegated colour, of a metallic splendour, and of a lamellar texture. As it absorbs chlorine when heated in this gas, and becomes entirely converted into the volatile compound, and as the volatile compound may likewise be obtained by heating in a glass tube nearly closed, the residue from the evaporation of the red muriat, it is evident that the



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fixed compound contains less chlorine than the volatile, and that the former, consequently, may be called ferrane, and the latter ferranea.

Ferrane dissolves in water and forms the green muriat of iron; but the solution of the whole substance is not complete. There is always left a small and variable quantity of black oxide, which may be considered, on account of its variability, in a state of mechanical mixture, rather than of chemical union with the ferrane.

Ferranea is entirely soluble in water. The solution is identical with the red muriat of iron.

The analysis of both these compounds is easily effected by means of nitrat of silver.

50 grains of ferrane were put into water: the insoluble residue separated from the solution by decantation; washed, dried, and heated to redness for a minute, previously moistened with oil, weighed 3 grains, and was in the state of the black oxide, being attracted by the magnet. The solution entire, precipitated by nitrat of silver, afforded 102.5 grains of dried horn silver, which indicating 25.1125 grains of chlorine, the proportion of iron, omitting the 3 grains of oxide, appears to be 21.8875. And hence 100 of ferrane seem to consist of

$$\begin{array}{r}
 53.43 \text{ chlorine} \\
 46.57 \text{ iron} \\
 \hline
 100.00
 \end{array}$$

Ferranea is not easily obtained in considerable quantities, I have been obliged in consequence to operate upon small portions. The subject of analysis was procured by sublimation from the residue by evaporation of the red muriat. 20 grains

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of this, in brilliant scales, were weighed in water. The solution, precipitated by nitrat of silver, yielded 53 grains of dried horn silver. Hence 100 of ferranea appear to consist of

64.9	chlorine
35.1	iron
<hr/>	
100.0	

4. *On the Combinations of Chlorine with Manganese, Lead, Zinc, Arsenic, Antimony, and Bismuth.*

I have attempted, by several methods, to obtain more than one combination of these different metals and chlorine, but without success.

I have procured a compound of manganese and chlorine, by evaporating to dryness the white muriat of this metal, and heating to redness the residue in a glass tube, having only a very small orifice. Muriatic acid vapour was produced, and a fixed compound remained, which required a red heat for its fusion, and was not altered by the strongest heat that could be given to it in the glass tube; but was rapidly decomposed when heated in an open vessel, muriatic acid fumes being evolved, and oxide of manganese formed, which was black or red, according to the intensity of the heat applied. The compound of manganese and chlorine is a very beautiful substance, it is of great brilliancy, generally of a pure delicate light pink colour and of a lamellar texture consisting of broad thin plates.

There is not much difficulty in obtaining this compound pure. Iron, with which manganese is commonly contaminated, may be separated by two or three repetitions of the solution of the compound in water, the evaporation to dryness of the



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clear filtered muriat, and fusion of the residue procured by evaporation. Indeed, I think this a good general method for purifying manganese from iron. One of the combinations of the latter metal and chlorine being volatile, heat must separate it from the compound of manganese. And I have thus obtained it so free from iron, that triple prussiat of potash added to its solution in water, gave merely a white precipitate without the slightest tint of blue.

This compound deliquesces when exposed to the atmosphere, and is converted into the white muriat. Like ferrane, it affords a trifling residue when heated with water. The residue is oxide of manganese, white at first, but soon becoming red, and even black; it varies in quantity, according to the exclusion of air in the formation of the combination.

50 grains of the compound dissolved in water, with the exception of 1 grain; this residue was separated by decantation of the fluid, washed, dried, and heated to redness, it was in the state of black oxide. The colourless solution was precipitated by nitrat of silver. The horn silver formed, when dried, was equal to 108 grains. Hence, omitting the 1 grain of mixed oxide, 100 of this compound appear to consist of

54 chlorine

46 manganese

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100

The horn lead that I have analysed, was made by the decomposition of the nitrat of lead by muriatic acid, and it was well washed, dried, and fused in a glass tube with a small orifice. The strongest red heat that I could apply to it, under these circumstances, did not occasion its sublimation.

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50 grains of it that had been fused were dissolved in water. This solution, heated with nitrat of silver, afforded 52.65 grains of dry horn silver. Hence 100 of horn lead appear to be composed of

$$\begin{array}{r} 25.78 \text{ chlorine} \\ 74.22 \text{ lead} \\ \hline 100.00 \end{array}$$

As this compound, when decomposed by an alkali, affords the protoxide of lead, it may be called plumbane.

The butter of zinc I have examined, was obtained by evaporating to dryness the muriat of this metal, and by heating to redness the residue in a glass tube. This compound is not volatile at a strong red heat in a close vessel, it fuses before it acquires a dull red heat, and on cooling it goes through several degrees of consistency, being viscid before it becomes solid.

This compound, when heated with water, affords a small residue of oxide of zinc, which, as in the preceding instances, may be considered as in the state of mechanical mixture.

In consequence of its powerful attraction for water, it is a very deliquescent substance; on this account it is necessary to weigh it in water to avoid error. 49.5 grains of it thus weighed, dissolved entirely in water, with the exception of 1 grain of oxide of zinc, which was separated by decantation and dried and ignited, and its quantity ascertained to be as stated. The solution precipitated by nitrat of silver afforded 99 grains of dried horn silver. Hence, excluding the 1 grain of oxide, 100 of butter of zinc seem to consist of



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50 chlorine

50 zinc

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 100

This compound may be called zincane.

A compound of chlorine and arsenic has been long known, bearing the name of the fuming liquor of arsenic. It may be formed in several ways; by the combustion of arsenic in chlorine gas, by heating in a retort a mixture of arsenic and corrosive sublimate, or of arsenic and calomel, and by the distillation of muriat of arsenic with concentrated sulphuric acid. The old method by means of corrosive sublimate appears best adapted for procuring it in a pure state. About 6 parts of corrosive sublimate to 1 of arsenic are, I find, proper proportions. The mixture of the two substances should be intimate, and the heat applied to the retort for the distillation of the fuming liquor, gentle. When the liquor was not colourless at first, I have purified it by a second distillation.

The fuming liquor of arsenic, it is well known, is decomposed by water. The precipitate produced appears to be merely white oxide of arsenic, for, independent of other circumstances, it does not afford the fuming liquor when heated with strong sulphuric acid.

The fuming liquor, when gently heated, dissolves phosphorus, but it retains on cooling only a very small portion of this substance. The warm solution is not luminous in the dark.

The fuming liquor also, when warm, readily dissolves sulphur; indeed sulphur fused in the liquor seems capable of combining or of mixing with it in all proportions; but on cooling the greatest part of the sulphur is deposited, and assumes

a fine crystalline appearance; the form of the crystals was apparently the octahedron. This deposition seems to be merely sulphur with a little of the fuming liquor between the interstices of the crystals, for the crystals bear washing, and become tasteless superficially, but remain still acid internally, where the water has not penetrated.

It likewise dissolves resin. That which was called rosin was the subject of experiment. The solution was of a blueish green colour; but when gently heated it became brown, and remained so on cooling. The portion of resin the fuming liquor is capable of taking up, is very considerable; when the resin was added in excess, a viscid mixture was formed. The resinous solution was decomposed by water, and the resin was separated apparently unaltered mixed with white arsenic.

The fuming liquor is capable of combining with oil of turpentine and with olive oil. When the mixture was made with either of these oils, there was a considerable elevation of temperature, and a homogeneous colourless fluid was in each instance obtained.

In these and some other properties, the fuming liquor of arsenic is analogous to the fuming compounds of chlorine and sulphur, and chlorine and phosphorus; these too, having the power of dissolving sulphur, and phosphorus, and resin, and of entering into union with the fixed and volatile oils.

It is difficult to ascertain the proportion of the constituent parts of this compound by the ordinary modes of analysis, I have chosen therefore a synthetical method in preference; and from repeated experiments I find that 2 grains of arsenic require for complete conversion into the fuming liquor, 4 cubic inches exactly of chlorine gas.



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The experiments were thus conducted: the arsenic in one piece was put into a small glass retort having a stop-cock, the retort was exhausted, and a known volume of chlorine gas was admitted from a graduated receiver by means of other stop-cocks, and the absorption of chlorine, after the entire conversion of the metal into the fuming liquor, was considered as the proportion condensed by the arsenic.

Now, since 100 cubic inches of chlorine gas weigh just 76.5 grains, 2 grains of arsenic combine with 3.06 grains of chlorine, the weight of 4 cubic inches of the gas. Hence 100 of the fuming liquor appear to consist of

60.48	chlorine
39.52	arsenic
<hr/>	
100.00	

As the fuming liquor gives the white oxide when decomposed by water, arsenicane may be substituted for its old name.

The butter of antimony is a well known substance. That which I have examined was obtained by heating together corrosive sublimate and antimony, or antimony and calomel; and was always purified by a second distillation at a low temperature. The best proportion of corrosive sublimate and the metal for making the compound, I have found to be about  $2\frac{1}{2}$  parts of the former to 1 part of the latter.

The butter of antimony, like arsenicane, is capable, when rendered fluid by heat, of dissolving resin and sulphur, and of combining with the fixed and volatile oils. It affects the oil of turpentine very like the liquor of Libavius; the action is considerable, much heat is produced, and the oil is rendered brown.

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When the butter of antimony is decomposed by a sufficiently large quantity of the hydrosulphuret of potash, that compound is formed which is commonly called the golden sulphur of antimony, and which when decomposed by heat, I have found to afford merely water and sulphuret of antimony.\*

To ascertain the proportion of antimony in the butter of antimony 60.5 grains of this substance colourless and crystallized, weighed in water, were heated in a solution of hydrosulphuret of potash. The whole of the antimony was dissolved, and the hydrosulphuret of potash being in excess, there was no precipitation on cooling. The solution was decomposed by muriatic acid, and the golden sulphur thus thrown down was collected on a filter well washed and dried; heated slowly to redness in a glass tube, steam in plenty was disengaged with very slight traces of sulphur, and sulphuret of antimony remained, which fused into one mass weighed 45 grains. According to the experiments of PROUST, which I have repeated with the same result, sulphuret of antimony contains 74.1 per cent. of metal. Hence 45 grains of sulphuret or the 60.5 of butter of antimony, from which the sulphuret was procured, must contain 33.35 of metal; and considering the remainder 27.15 of the 60.5 as the proportion of chlorine, 100 of the

\* These results appear to me to demonstrate the truth of M. PROUST's opinion, that the golden sulphur is a hydrosulphuretted oxide of antimony. From my experiments the only difference of composition between kermes mineral and the preceding compound, seems to consist in the former containing a smaller proportion of sulphuretted hydrogen than the latter, for I have obtained by the decomposition of kermes mineral, by heat, a compound of sulphuret of antimony and protoxide, and I have converted kermes into the golden sulphur by means of water impregnated with sulphuretted hydrogen.



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butter of antimony seem to consist of

39.58 chlorine

60.42 antimony

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100.00

This compound, as it yields when decomposed by water the submuriated protoxide, may be called antimoniane or stibiane.

A compound of bismuth and chlorine has been long known bearing the name of the butter of bismuth. It is obtained both when bismuth is heated with corrosive sublimate and calomel.  $\frac{2}{1}$  parts of corrosive sublimate to 1 part of metal, I have found good proportions for its preparation. There is some difficulty in procuring it pure and entirely free from the mercury revived; this is most readily effected by keeping the butter of bismuth in fusion, at a temperature just below that at which mercury boils; the mercury slowly subsides and collects in the bottom of the vessel, and this operation continued for an hour or two affords a pure or nearly pure butter of bismuth. Thus prepared, it is of a grayish white colour, opaque, uncrystallized, and of a granular texture. In a glass tube, with a very small orifice, it bears a red heat without subliming.

As a hydrosulphuret of bismuth is produced when the butter of bismuth is heated with the hydrosulphuret of potash, and as this hydrosulphuret, like that of antimony, affords, when decomposed by heat, a sulphuret and water, I have applied the same mode of analysis to this compound as to the last.

55 grains of butter of bismuth were decomposed in a warm solution of hydrosulphuret of potash. The dark brown hydrosulphuret of bismuth thus formed, and not dissolved, was collected on a filter; the hydrosulphuretted solution was

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decomposed by muriatic acid, the slight precipitate of hydro-sulphuret produced was added to the first portion, and the whole was well washed, dried, and heated to redness in a glass tube; the sulphuret of bismuth thus obtained, fused into one mass, weighed 44.7 grains. I had previously ascertained the proportion of metal in this sulphuret, and found it to be 81.8 per cent. 44.7 grains of sulphuret, or 55 grains of the butter, must therefore contain 36.5 grains of bismuth; and hence, 100 of bismuth appear to consist of

33.6	chlorine
66.4	bismuth
<hr/>	
100.0	

The butter of bismuth may be called bismuthane.

Among the preceding combinations of the metals and chlorine, there is a surprising difference in respect to volatility and fusibility. Iron and manganese, two difficultly fusible metals, form with chlorine readily fusible compounds, and a combination of the former metal and chlorine is even volatile; the compounds of tin and chlorine, and of chlorine and antimony, are very volatile substances, though the metals themselves are fixed at very high temperatures; on the contrary, the combinations of chlorine with bismuth, zinc, and lead, do not exceed in fusibility; indeed are not quite so fusible as the metals themselves. I can offer no explanation of these phenomena.

Another singularity attending the liquid fuming compounds of chlorine, such as the liquor of Libavius, the fuming liquor of arsenic, and the oxymuriats of sulphur and phosphorus, is, that they do not become solid at low temperatures. I have



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reduced, by means of a mixture of snow and muriat of lime, the temperature of all these substances 20 degrees below the zero of FAHRENHEIT's thermometer, but without affecting their liquidity.

The influence of atmospheric air on the compounds of the metals and chlorine at high temperatures is curious, and worthy of particular attention. The combinations of chlorine with lead, zinc, copper, and bismuth, appear to be volatile in open vessels, and fixed in closed ones. How moist air operates in these instances, it is difficult to say. In other cases, where it evidently acts chemically, the changes explain themselves; thus, when the compounds of iron and chlorine and of manganese and chlorine are heated in the open air, hygrometrical water of the atmosphere seems to be decomposed, as muriatic acid fumes are produced, and oxides of the metals formed. Probably the volatility of the other compounds is connected with similar circumstances. This action of moist air has hitherto been much neglected; it is certainly worthy of being more fully inquired into, both in a theoretical and practical point of view. Its importance in practice is exemplified in the reduction of horn silver, and in the formation of several of the compounds of chlorine and the metals; if moist air be admitted in these operations, the silver will be lost, and the compounds not formed.

Guided by analogy, I have been led to try whether the muriat of magnesia, which is readily decomposed by heat in the open air, would not, when the air was excluded, by introducing it into a glass tube with a very small orifice, afford a permanent compound. The result was agreeable to my expectations; I obtained, by strongly heating the muriat for a

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quarter of an hour, a substance like enamel in appearance, being semi-fused, and which appeared to be a mixture of magnesia and the true compound of magnesium and chlorine, for heated with water magnesia was separated, and a muriat of magnesia formed.

5. *On the Relation between the Proportion of Oxygene and Chlorine in Combination with several Metals.*

Errors being very common in chemical analyses, even in those conducted most skilfully and carefully, all possible means should be taken to discover them; and no means, I think, promise to be more effectual for this purpose, than the general analogy of definite proportions. From a great variety of facts, it appears that oxygene and chlorine combine with bodies in the ratio of 7.5 to 33.6. With 1 part by weight of hydrogen, for example, 7.5 of oxygene unite to form water, and 33.6 of chlorine unite with the same proportion to produce muriatic acid gas. To judge therefore of the accuracy of the analyses of the preceding combinations of the metals and chlorine, it is only necessary to compare them with the analyses of the oxides of the same metals. If the two agree, there will be reason to consider them both correct, but should they disagree, there is equal reason for supposing one or both of them to be wrong.

Thus, as the orange oxide of copper is analogous to cuprane and the brown oxide to cuprane, the oxygene and chlorine should be to each other in these compounds as 7.5 to 33.6. And from comparison of my analysis, with those of Mr. CHENEVIX and M. PROUST, it appears, that in the two first, copper being as 60, the oxygene is to the chlorine as 7.79, instead of 7.5 to



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33.77, instead of 33.6; and in the two last as 7.5 to 33.6, or as 15 to 67.2. Coincidences as near as might be reasonably expected.

There is not the same agreement between M. PROUST's analyses of the oxides of tin and the preceding ones of the combinations of this metal and chlorine. This discordance induced me to repeat my analyses, and obtaining the same result as at first, I directed my attention to the oxides of tin, and made the following experiments to ascertain the proportion of their constituent parts.

42.5 grains of tin, which had been precipitated from the muriat of this metal by zinc, were heated with nitric acid in a platina crucible, and slowly converted into peroxide; the acid and water were driven off by gentle evaporation at first, and afterwards by a strong red heat continued for a quarter of an hour. The peroxide thus produced was of a light yellow colour, and being very gradually dried, it was semi-transparent, and hard enough to scratch glass; it weighed 54.25 grains. Hence, as 42.5 grains of tin acquire, on conversion into peroxide, 11.75 grains of oxygene, this oxide appears to contain 21.66 per cent. of oxygene, just the quantity found in the native oxide by KLAPROTH, instead of 28, the proportion stated by PROUST.

M. BERTHOLLET, jun. has shewn that M. PROUST's estimate of 20 per cent. of oxygene in the protoxide is incorrect. To ascertain the true proportion, 20 grains of tin were dissolved in strong muriatic acid in a retort connected with a pneumatic apparatus, and without the assistance of heat; 16 cubic inches of hydrogen gas were produced. (Barom. 30, thermom. 60) as the production of this quantity of hydrogen indicates an

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absorption of oxygene by the tin equivalent to 8 cubic inches, or (as 100 cubic inches weigh 34.2 grains) to 2.736 grains, the protoxide of tin appears to contain 11.99 per cent. of oxygene.

These analyses of the oxides, compared with those of the combinations of tin and chlorine, are found very nearly to agree. The ratio of oxygene to chlorine in the two first similar compounds, the tin being as 55, is as 7.5 to 33.4; and in the two last, viz. the peroxide and the liquor of Libavius, as 7.6 to 33.5, or as 15.2 to 67.

As the black oxide of iron is formed by the decomposition of ferrane by a solution of potash, and the red oxide by that of ferranea, it is evident that these oxides and combinations of iron and chlorine should coincide in the proportions of their constituent parts. This appears from the analyses\* of Dr. THOMPSON to be nearly the case, for iron being as 29.5, the oxygene is to the chlorine in the black oxide and ferrane as 8 instead of 7.5 to 33.6; and in the two others as 8 to 33.6, or as 13.2 to 55.5. Here the agreement is less than in other instances; but this is not surprising considering the different estimates of the proportions of oxygene in the oxides of iron, and the difficulty of ascertaining them correctly.

The yellow oxide of lead and the white oxides of antimony, bismuth, zinc, and arsenic are formed, when the combinations of these metals and chlorine are decomposed by a solution of potash. But on comparison with the best analyses of the oxides, there is not, excepting in the case of zinc and arsenic, that coincidence of proportions which might be expected. Zinc being as 34.5, the oxygene in the oxide from the analysis

\* NICHOLSON'S Journal, Vol. XXVII. p. 375.



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of PROUST, is to the chlorine as 7.5 to 34.4; and the arsenic being as 21.9, the oxygene, from the analysis of the same chemist, is to the chlorine as 7.3 to 33.6. The analyses of the oxides of the other metals being at variance with those of the chlorine combinations, I was induced to make the following experiments, with the hope of discovering the cause of the difference.

100 grains of lead, which had been precipitated from the nitrat of lead by zinc, were dissolved in nitric acid and thrown down by carbonat of potash. This precipitate of carbonat of lead was well washed and dried and heated to dull redness for a quarter of an hour in a platina crucible; by this treatment all the carbonic acid was expelled; the remaining yellow oxide weighed 107.7 grains, and it dissolved in muriatic acid without effervescing, and without affording any residue of brown oxide. Hence the yellow oxide of lead appears to contain 7.15 per cent. of oxygene. And this proportion of oxygene in the oxide compared with that of chlorine in plumbane, lead being as 97.2 appears to be in the ratio of 7.5 to 33.8, instead of that of 15.6 the estimate of KLAPROTH, or of 11.2 the estimate of Dr. THOMPSON to 33.8. KLAPROTH might have been misled by considering the hydrated oxide as a true white oxide free from water.

According to M. PROUST the peroxide of antimony contains 23 per cent. of oxygene, and the protoxide 18.\* I have repeated this chemist's experiments; my results, in which the peroxide is concerned, agree with his; but there is not the same concordance in those relating to the protoxide. The protoxide I used was either prepared by the decomposition of

\* Journal de Physique, Tom. LV.

the butter of antimony, or of the sulphat, by a boiling solution of carbonat of potash. This oxide, in its purest state, I have always found as M. PROUST describes it, of a light fawn colour before fusion, and afterwards in mass of a gray colour, and of a radiated crystalline texture. 100 grains of it that had been fused were heated in the state of powder with strong test nitric acid in a platina crucible, when nitrous gas ceased to be produced, the excess of nitric acid was expelled by a gentle heat, and the oxide was heated to dull redness, the increase of weight after this, was equal to 10.4 grains; nitric acid was again added and the process repeated, but without any alteration of weight being produced. Hence as the peroxide contains 23 per cent. the protoxide seems to contain 15 per cent.; which proportion of oxygene very nearly agrees with that of chlorine in the butter of antimony, for antimony being as 42.5, the former is to the latter as 7.5 to 34.6, instead of 33.6. I put some confidence in this estimate of the proportion of oxygene in the protoxide, not only on account of its agreement with the analysis of the butter of antimony, but because it was confirmed on the repetition of the experiment.

KLAPROTH concludes from his experiments, that the oxide of bismuth, prepared by means of nitric acid, contains 17.7 per cent. of oxygene, and in consequence this oxide has been considered distinct from that which is formed by direct calcination of the metal, and which contains a much smaller proportion. But there is reason to believe that this difference does not really exist, and that there is only one known oxide of bismuth, and that KLAPROTH's oxide was an hydrated oxide; for I have found that 100 grains of bismuth, converted by nitric acid into oxide, precisely in the same manner as the



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protoxide of antimony was more highly oxidated, gained only 11.1 grains. KLAPROTH did not heat his oxide to redness, and hence apparently the discordance. From the above result, which I have confirmed by repetition of the experiment, oxide of bismuth seems to contain 10 per cent. of oxygene and bismuth being as 67.5, the oxygene in the oxide is to the chlorine in the butter of bismuth, as 7.5 to 34.2.

6. *On the Relation between the Proportion of Sulphur in the Sulphurets, and the Proportion of Chlorine in some of the Combinations of Chlorine and the Metals.*

The last section afforded proofs of the useful application of the general analogy of definite proportions in correcting the results of chemical analyses. In the present section, it is my intention to pursue a little further, the plan that I have adopted in the preceding, and to apply another test to the analyses of the combinations of the metals and chlorine, by comparing some of them with the combinations of the same metals and sulphur.

I was first led to examine the sulphurets of tin on a different account. Aurum musivum, it has been observed, is formed when stannane is heated with sulphur. According to M. PROUST, this substance is a sulphuretted oxide of tin. Were this opinion correct, an argument might evidently be deduced from it, in favour of the existence of oxygene in chlorine. To satisfy myself respecting this, I endeavoured to ascertain whether any sulphureous acid gas is produced by the decomposition of aurum musivum by heat, as it is commonly asserted. I heated to redness in a bent luted green glass tube connected with a pneumatic mercurial apparatus about 20 grains of

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aurum musivum, prepared by the decomposition of stannane with sulphur, no more gas was produced than the expansion by heat occasioned, sulphur sublimed, and a gray sulphuret of tin remained. These results I have several times obtained, and not only with aurum musivum prepared as the preceding, but with some also made according to Woulfe's process. As no sulphureous acid gas was produced, and as sulphur sublimed, it may be concluded that aurum musivum differs merely from the gray sulphuret in containing a larger quantity of sulphur. My next object was to ascertain the exact proportion of sulphur in both these sulphurets, for the sake of comparison with the combinations of tin and chlorine.

100 grains of tin in a finely divided state, as precipitated from the muriat of this metal by zinc, were heated in a glass tube intimately mixed with sulphur, the combination of the two was accompanied with vivid ignition, the sulphuret formed weighed 127.3 grains, and broken, it appeared perfectly homogeneous; it was pounded, and again heated with sulphur; but the excess of sulphur being expelled, the fused sulphuret had not increased in weight. The second time I made this experiment, I obtained the same result.

50 grains of aurum musivum, purified from mixed sulphur by exposure in a close vessel to a dull red heat, were decomposed by a bright red heat in a small green glass tube nicely weighed, and having only a very small orifice; the loss of sulphur, by conversion into the gray sulphuret, was equal to 9.3 grains. Hence, as 40.7 grains of gray sulphuret contain 8.72 grains of sulphur, 50 grains of aurum musivum appear to contain 18.02 grains.

The ratio in which sulphur combines with bodies is to that



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in which oxygene and in which chlorine combines, as 15 to 7.5 and 33.6. This appears from the proportions of the constituent parts of sulphuretted hydrogene and sulphureous acid gas, for I have found 100 cubic inches of the former to weigh 36.64 grains, and 100 of the latter 68.44 grains. In the comparison, therefore, between the sulphurets of tin and the combinations of this metal and chlorine, 15 by weight of sulphur are equivalent to 33.6 of chlorine. And the tin being as 55, it appears from the analysis of the gray sulphuret and stannane, that the sulphur is to the chlorine as 15 exactly to 33.4; and from the analysis of the other two compounds, aurum musivum and the liquor of Libavius, as 15.5 to 33.5, or as 31 to 67.

The proportions of sulphur in the two sulphurets of iron, do not accord with the proportions of oxygene in the oxides, or of chlorine in the chlorine combinations; but I am yet ignorant of the cause of this difference.

100 grains of lead, heated with sulphur in a glass tube, afforded, in two trials, 115.5 grains of fused sulphuret. Hence lead being as 97.2, the sulphur is to the chlorine in the respective combinations as 15.09 to 33.8.

Sulphuret of antimony contains 25.9 per cent. of sulphur. Hence antimony being as 42.5, the sulphur in the sulphuret is to the chlorine in the butter of antimony, as 14.86 to 34.6.

100 grains of bismuth heated with sulphur afforded 122.3 grains of sulphuret. Hence bismuth being as 67.5, the sulphur is to the chlorine as 15.08 to 34.2.

In the following table, the proportions are collected in which chlorine, sulphur, and oxygene combine with several metals; the numbers representing the metals are kept constantly the same, for the greater facility of comparison.

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Copper	60	+	32.77	chlorine	= cuprane.
		+	67.20	ditto	= cupraneæ.
		+	7.79	oxygene	= orange oxide.
		+	15.00	ditto	= brown oxide.
Tin	55	+	33.40	chlorine	= stannane.
		+	67.00	ditto	= stannaneæ.
		+	15.00	sulphur	= gray sulphuret.
		+	31.00	ditto	= aurum musivum.
		+	7.50	oxygene	= protoxide.
Iron	29.5	+	15.20	ditto	= peroxide.
		+	33.60	chlorine	= ferrane.
		+	55.50	ditto	= ferraneæ.
		+	8.00	oxygene	= black oxide.
Manganese	28.4	+	13.20	ditto	= red oxide.
		+	33.60	chlorine.	
Lead	97.2	+	33.80	chlorine	= plumbane.
		+	15.09	sulphur	= sulphuret.
		+	7.50	oxygene	= yellow oxide.
Zinc	34.5	+	34.40	chlorine	= zincane.
		+	7.50	oxygene	= oxide.
Arsenic	21.9	+	33.60	chlorine	= arsenicane.
		+	7.30	oxygene	= white oxide.
Antimony	42.5	+	34.60	chlorine	= antimonane.
		+	14.86	sulphur	= sulphuret.
		+	7.50	oxygene	= protoxide.
Bismuth	67.5	+	34.20	chlorine	= bismuthane.
		+	15.08	sulphur	= sulphuret.
		+	7.50	oxygene	= oxide.



7. *On the Action of muriatic Acid on some Combinations of Chlorine and Metals.*

Sir HUMPHRY DAVY has pointed out in a great variety of instances, the existence of an analogy between chlorine and oxygene. He has shewn that the former, united with certain inflammables, constitutes, like the latter, acid compounds; and combined with metals, as it has already been observed, substances similar in many respects to metallic oxides.

I have kept this analogy in view in my inquiries, and directed by it in my experiments, I have obtained some results which appear to me to coincide with it.

Thus having been led to try the action of muriatic acid on different combinations of the metals and chlorine, I have found many of them capable of uniting with this acid, and of forming compounds not dissimilar to some of those consisting of acids and metallic oxides.

Corrosive sublimate, stannane, cuprane, and the combinations of chlorine with antimony, zinc, lead, and silver are all soluble in different degrees in muriatic acid.

Corrosive sublimate, which is but sparingly soluble in water, and still more sparingly in the sulphuric and nitric acids, is, I have ascertained, very readily soluble in muriatic acid. 1 cubic inch of the common strong acid takes up about 150 grains of this substance, and when gently heated, a quantity far more considerable, about 1000 grains. The compound thus formed solidifies on cooling into a crystalline fibrous mass of a pearly and brilliant lustre. It is decomposed by heat, the acid being first expelled, and when exposed to the atmosphere, it efflo-

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resces and appears to lose its acid, for afterwards analysed, it is found to be pure corrosive sublimate.

When I first tried the action of muriatic acid on the different combinations of chlorine already mentioned, I was not aware that KLAPROTH had before observed the solubility of horn silver in this acid, and Mr. CHENEVIX that of cuprane. Horn silver, cuprane, and horn lead are precipitated from muriatic acid, unaltered by water. Both the hot saturated solutions of the two last compounds deposit crystals on cooling; those, from the solution of the former, are of an olive green colour and of a prismatic form, and consist of cuprane and muriatic acid; those from the latter, are small white brilliant plates.

Finding the combinations of the metals and chlorine, so generally soluble in liquid muriatic acid, I expected that some of them might absorb muriatic acid gas; but none that I have tried have possessed this property, not even the liquor of Libavius. Indeed this is not singular, for water is necessary to the composition of many saline bodies, neutral carbonat of ammonia and nitrat of ammonia, for instance, cannot be formed without the presence of water. Neither is the precipitation of cuprane, horn silver, and horn lead from muriatic acid by water extraordinary; there are several salts containing metallic oxides which are liable to the same change, the oxides having less affinity for the acid, than water has.

The action of muriatic acid on the combinations of the different metals and chlorine will, I have little doubt, afford, when more minutely investigated, explanations of many phenomena which are not yet well accounted for. Before I conclude, I shall mention only one instance to which it already appears



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to be applicable. M. PROUST has observed the decomposition of calomel by boiling muriatic acid, and its conversion into corrosive sublimate and running mercury. Now calomel being insoluble in muriatic acid, these changes evidently appear to be owing to the strong attraction of the acid, for corrosive sublimate, which has been already shewn to exist.