XIV. Researches on the oxymuriatic Acid, its Nature and Combinations; and on the Elements of the muriatic Acid. With some Experiments on Sulphur and Phosphorus, made in the Laboratory of the Royal Institution.\* By H. Davy, Esq. Sec. R.S. Prof. Chem. R.I. F.R.S.E.

## Read July 12, 1810.

THE illustrious discoverer of the oxymuriatic acid considered it as muriatic acid freed from hydrogene; † and the common muriatic acid as a compound of hydrogene and oxymuriatic acid; and on this theory he denominated oxymuriatic acid dephlogisticated muriatic acid.

M. Berthollet, † a few years after the discovery of Scheele, made a number of important and curious experiments on this body; from which he concluded, that it was composed of muriatic acid gas and oxygene; and this idea for nearly twenty years has been almost universally adopted.

Dr. Henry, in an elaborate series of experiments, made with the view of decomposing muriatic acid gas, ascertained that hydrogene was produced from it, by electricity; and he attributed the phænomenon to water contained in the gas.

In the Bakerian lecture for 1808, I have given an account of the action of potassium upon muriatic acid gas, by which more than one third of its volume of hydrogene is produced; and I have stated, that muriatic acid can in no instance be procured

- \* Communicated to the Royal Society at the request of the Managers of the Royal Institution, † Mem. Acad. Stockholm for 1774, p. 94.
  - ‡ Journal de Physique, 1785, p. 325. || Phil. Trans. for 1800, p. 191.

Hh 2

from oxymuriatic acid, or from dry muriates, unless water or its elements be present.

In the second volume of the Memoires d'Arcueil, M. M. GAY LUSSAC and THENARD have detailed an extensive series of facts upon muriatic acid, and oxymuriatic acid. Some of their experiments are similar to those I have detailed in the paper just referred to; others are peculiarly their own, and of a very curious kind: their general conclusion is, that muriatic acid gas contains about one quarter of its weight of water; and that oxymuriatic acid is not decomposable by any substances but hydrogene, or such as can form triple combinations with it.

One of the most singular facts that I have observed on this subject, and which I have before referred to, is, that charcoal, even when ignited to whiteness in oxymuriatic or muriatic acid gases, by the Voltaic battery, effects no change in them; if it has been previously freed from hydrogene and moisture by intense ignition in vacuo.

This experiment, which I have several times repeated, led me to doubt of the existence of oxygene in that substance, which has been supposed to contain it above all others in a loose and active state; and to make a more rigorous investigation than had been hitherto attempted for its detection.

If oxymuriatic acid gas be introduced into a vessel exhausted of air, containing tin; and the tin be gently heated, and the gas in sufficient quantity, the tin and the gas disappear, and a limpid fluid, precisely the same as Libavius's liquor is formed;—it occured to me, that if this substance is a combination of muriatic acid and oxide of tin, oxide of tin ought to be separated from it by means of ammonia. I admitted ammoniacal gas over mercury to a small quantity of the liquor of Libavius;

it was absorbed with great heat, and no gas was generated; a solid result was obtained, which was of a dull white colour; some of it was heated, to ascertain if it contained oxide of tin; but the whole volatilized, producing dense pungent fumes.

Another experiment of the same kind, made with great care, and in which the ammonia was used in great excess, proved that the liquor of Libavius cannot be decompounded by ammonia; but that it forms a new combination with this substance.

I have described, on a former occasion, the nature of the operation of phosphorus on oxymuriatic acid, and I have stated that two compounds, one fluid, and the other solid, are formed in the process of combustion, of which the first, on the generally received theory of the nature of oxymuriatic acid, must be considered as a compound of muriatic acid and phosphorous acid, and the other of muriatic acid and phosphorous acid, and the other of muriatic acid and phosphoric acid. It occured to me, that if the acids of phosphorus really existed in these combinations, it would not be difficult to obtain them, and thus to gain proofs of the existence of oxygene in oxymuriatic acid.

I made a considerable quantity of the solid compound of oxymuriatic acid and phosphorus by combustion, and saturated it with ammonia, by heating it in a proper receiver filled with ammoniacal gas, on which it acted with great energy, producing much heat; and they formed a white opaque powder. Supposing that this substance was composed of the dry muriates and phosphates of ammonia; as muriate of ammonia is very volatile, and as ammonia is driven off from phosphoric acid, by a heat below redness, I conceived that by igniting the product obtained, I should procure phosphoric acid; I therefore introduced some of the powder into a tube of green glass, and

heated it to redness, out of the contact of air by a spirit lamp; but found, to my great surprise, that it was not at all volatile nor decomposable at this degree of heat, and that it gave off no gaseous matter.

The circumstance that a substance composed principally of oxymuriatic acid, and ammonia, should resist decomposition or change at so high a temperature, induced me to pay particular attention to the properties of this new body.

It had no taste nor smell; it did not seem to be soluble, nor did it undergo any perceptible change when digested in boiling water: it did not appear to be acted upon by sulphuric, muriatic, or nitric acids, nor by a strong lixivium of potash. The only processes by which it seemed susceptible of decomposition were by combustion, or the action of ignited hydrat of potash. When brought into the flame of a spirit lamp and made red-hot, it gave feeble indications of inflammation, and tinged the flame of a yellow colour, and left a fixed acid, having the properties of phosphoric acid. When acted on by red-hot hydrat of potash, it emitted a smell of ammonia, burnt where it was in contact with air, and appeared to dissolve in the alkali. The potash which had been so acted upon gave muriatic acid, by the addition of sulphuric acid.

I heated some of the powder to whiteness, in a tube of platina; but it did not appear to alter; and after ignition gave ammonia by the action of fused hydrat of potash.

I caused ammonia, made as dry as possible, to act on the phosphuretted liquor of M.M.GAY LUSSAC and THENARD; and on the sulphuretted muriatic liquor of Dr. Thomson; but no decomposition took place; nor was any muriate of ammonia formed when proper precautions were taken to exclude mois-

ture. The results were new combinations; that from the phosphoretted liquor, was a white solid, from which a part of the phosphorus was separated by heat; but which seemed no further decomposable, even by ignition. That from the sulphuretted liquor was likewise solid, and had various shades of colour, from a bright purple to a golden yellow, according as it was more or less saturated with ammonia; but as these compounds did not present the same uniform and interesting properties, as that from the phosphoric sublimate, I did not examine them minutely: I contented myself by ascertaining that no substance known to contain oxygene could be procured from oxymuriatic acid, in this mode of operation.

It has been said, and taken for granted by many chemists, that when oxymuriatic acid and ammonia act upon each other, water is formed; I have several times made the experiment, and I am convinced that this is not the case. When about 15 or 16 parts of oxymuriatic acid gas are mixed with from 40 to 45 parts of ammoniacal gas, there is a condensation of nearly the whole of the acid and alkaline gasses, and from 5 to 6 parts of nitrogene are produced; and the result is dry muriate of ammonia.

Mr. Cruikshank has shown that oxymuriatic acid and hydrogene, when mixed in proportions nearly equal, produce a matter almost entirely condensible by water; and M. M. Gay Lussac and Thenard, have stated that this matter is common muriatic acid gas, and that no water is deposited in the operation. I have made a number of experiments on the action of oxymuriatic acid gas and hydrogene. When these bodies were mixed in equal volumes over water, and introduced into an exhausted vessel and fired by the electric spark, there was always a deposition of a slight vapour, and a conden-

sation of from  $\frac{1}{10}$  to  $\frac{1}{20}$  of the volume; but the gas remaining was muriatic acid gas. I have attempted to make the experiment in amanner still more refined, by drying the oxymuriatic acid and the hydrogene by introducing them into vessels containing muriate of lime, and by suffering them to combine at common temperatures; but I have never been able to avoid a slight condensation; though in proportion as the gasses were free from oxygene or water, this condensation diminished.

I mixed together sulphuretted hydrogene in a high degree of purity and oxymuriatic acid gas both dried, in equal volumes: in this instance the condensation was not  $\frac{1}{40}$ ; sulphur, which seemed to contain a little oxymuriatic acid, was formed on the sides of the vessel; no vapour was deposited; and the residual gas contained about  $\frac{19}{20}$  of muriatic acid gas, and the remainder was inflammable.

M. M. GAY LUSSAC and THENARD have proved by a copious collection of instances, that in the usual cases where oxygene is procured from oxymuriatic acid, water is always present, and muriatic acid gas is formed; now, as it is shewn that oxymuriatic acid gas is converted into muriatic acid gas, by combining with hydrogene, it is scarcely possible to avoid the conclusion, that the oxygene is derived from the decomposition of water, and, consequently, that the idea of the existence of water in muriatic acid gas, is hypothetical, depending upon an assumption which has not yet been proved—the existence of oxygene in oxymuriatic acid gas.

M. M. GAY LUSSAC and THENARD indeed have stated an experiment, which they consider as proving that muriatic acid gas contains one quarter of its weight of combined water. They passed this gas over litharge, and obtained so much water; but it is obvious that in this case they formed the same

compound as that produced by the action of oxymuriatic acid on lead; and in this process the muriatic acid must loose its hydrogene, and the lead its oxygene; which of course would form water; these able chemists, indeed, from the conclusion of their memoir, seem aware, that such an explanation may be given, for they say that the oxymuriatic acid may be considered as a simple body.

I have repeated those experiments which led me first to suspect the existence of combined water in muriatic acid, with considerable care; I find that, when mercury is made to act upon 1 in volume of muriatic acid gas, by Voltaic electricity, all the acid disappears, calomel is formed, and about .5 of hydrogene evolved.

With potassium, in experiments made over very dry mercury, the quantity of hydrogene is always from 9 to 11, the volume of the muriatic acid gas used being 20.

And in some experiments made very carefully by my brother Mr. John Davy, on the decomposition of muriatic acid gas, by heated tin and zinc, hydrogene equal to about half its volume was disengaged, and metallic muriates, the same as those produced by the combustion of tin and zinc in oxymuriatic gas, resulted.

It is evident from this series of observations, that Scheele's view, (though obscured by terms derived from a vague and unfounded general theory,) of the nature of the oxymuriatic and muriatic acids, may be considered as an expression of facts; whilst the view adopted by the French school of chemistry, and which, till it is minutely examined, appears so beautiful and satisfactory, rests in the present state of our knowledge, upon hypothetical grounds.

When oxymuriatic acid is acted upon by nearly an equal volume of hydrogene, a combination takes place between them, and muriatic acid gas results. When muriatic acid gas is acted on by mercury, or any other metal, the oxymuriatic acid is attracted from the hydrogene, by the stronger affinity of the metal; and an oxymuriate, exactly similar to that formed by combustion, is produced.

The action of water upon those compounds, which have been usually considered as muriates, or as dry muriates, but which are properly combinations of oxymuriatic acid with inflammable bases, may be easily explained, according to these views of the subject. When water is added in certain quantities to Libavius's liquor, a solid crystallized mass is obtained, from which oxide of tin and muriate of ammonia can be procured by ammonia. In this case, oxygene may be conceived to be supplied to the tin, and hydrogene to the oxymuriatic acid.

The compound formed by burning phosphorus in oxymuriatic acid, is in a similar relation to water: if that substance be added to it, it is resolved into two powerful acids; oxygene, it may be supposed, is furnished to the phosphorus to form phosphoric acid, hydrogene to the oxymuriatic acid to form common muriatic acid gas.

None of the combinations of the oxymuriatic acid with inflammable bodies, can be decomposed by dry acids; and this seems to be the test which distinguishes the oxymuriatic combinations from the muriates, though they have hitherto been confounded together. Muriate of potash for instance, if M. Berthollet's estimation of its composition, approaches towards accuracy, when ignited, is a compound of oxymu-

riatic acid with potassium; muriate of ammonia, is a compound of muriatic acid gas and ammonia; and when acted on by potassium, it is decompounded; the oxymuriatic acid may be conceived to combine with the potassium to form muriate of potash, and the ammonia and hydrogene are set free.

The vivid combustion of bodies in oxymuriatic acid gas, at first view, appears a reason why oxygene should be admitted in it; but heat and light are merely results of the intense agency of combination. Sulphur and metals, alkaline earths and acids become ignited during their mutual agency; and such an effect might be expected in an operation so rapid, as that of oxymuriatic acid upon metals and inflammable bodies.

It may be said, that a strong argument in favour of the hypothesis, that oxymuriatic acid consists of an acid basis united to oxygene, exists in the general analogy of the compounds of oxymuriatic acid and metals, to the common neutral salts; but this analogy when strictly investigated, will be found to be very indistinct, and even allowing it, it may be applied with as much force to support an opposite doctrine, namely, that the neutral salts are compounds of bases with water; and the metals of bases with hydrogene; and that in the case of the action of oxymuriatic acid and metals, the metal furnishes hydrogene to form muriatic acid, and a basis to produce the neutral combination.

That the quantity of hydrogene evolved during the decomposition of muriatic acid gas by metals, is the same that would be produced during the decomposition of water by the same bodies, appears, at first view, an evidence in favour of the existence of water in muriatic acid gas; but as there is only one known combination of hydrogene with oxymuriatic acid, one quantity must always be separated. Hydrogene is dis engaged from its oxymuriatic combination, by a metal, in the same manner as one metal is disengaged by another, from similar combinations; and of all inflammable bodies that form compounds of this kind, except perhaps phosphorus and sulphur, hydrogene is that which seems to adhere to oxymuriatic acid with the least force.

I have caused strong explosions from an electrical jar, to pass through oxymuriatic gas, by means of points of platina, for several hours in succession; but it seemed not to undergo the slightest change.

I electrized the oxymuriates of phosphorus and sulphur for some hours, by the power of the Voltaic apparatus of 1000 double plates; no gas separated, but a minute quantity of hydrogene, which I am inclined to attribute to the presence of moisture in the apparatus employed; for I once obtained hydrogene from Libavius's liquor by a similar operation; but I have ascertained, that this was owing to the decomposition of water, adhering to the mercury; and in some late experiments made with 2000 double plates, in which the discharge was from platina wires, and in which the mercury used for confining the liquor was carefully boiled, there was no production of any permanent elastic matter.

As there are no experimental evidences of the existence of oxygene in oxymuriatic acid gas, a natural question arises, concerning the nature of these compounds, in which the muriatic acid has been supposed to exist, combined with much more oxygene than oxymuriatic acid, in the state in which it has been named by Mr. Chenevix, hyperoxygenized muriatic acid.

Can the oxymuriatic acid combine either with oxygene or hydrogene, and form with each of them an acid compound; of which that with hydrogene has the strongest, and that with oxygene the weakest affinity for bases? for the able chemist to whom I have just referred, conceives that hyperoxymuriates are decomposed by muriatic acid. Or, is hyperoxymuriatic acid the basis of all this class of bodies, the most simple form of this species of matter?

The phænomena of the composition and decomposition of the hyperoxymuriates, may be explained on either of these suppositions; but they are mere suppositions unsupported by experiment.

I have endeavoured to obtain the neutralizing acid, which has been imagined to be hyperoxygenised, from hyperoxymuriate of potash. by various modes, but uniformly without success. By distilling the salt with dry boracic acid, though a little oxymuriatic acid is generated, yet oxygene is the chief gaseous product, and a muriate of potash not decomposable is produced.

The distillation of the orange coloured fluid, produced by dissolving hyperoxymuriate of potash in sulphuric acid, affords only oxygene in great excess, and oxymuriatic acid.

When solutions of muriates, or muriatic acid are electrized in the Voltaic circuit, oxymuriatic acid is evolved at the positive surface, and hydrogene at the negative surface. When a solution of oxymuriatic acid in water is electrized, oxymuriatic acid and oxygene appear\* at the positive surface,

<sup>\*</sup> The quantity of oxymuriatic acid in the aqueous solution, is so small, that the principal products must be referred to the decomposition of water. This happens in other instances; the water only is decomposed in dilute solutions of nitric and sulphuric acids.

and hydrogene at the negative surface, facts which are certainly unfavourable to the idea of the existence of hyperoxygenised muriatic acid, whether it be imagined a compound of oxymuriatic acid with oxygene, or the basis of oxymuriatic acid.

If the facts respecting the hyperoxymuriate of potash, indeed, be closely reasoned upon, it must be regarded as nothing more than as a triple compound of oxymuriatic acid, potassium, and oxygene. We have no right to assume the existence of any peculiar acid in it, or of a considerable portion of combined water; and it is perhaps more conformable to the analogy of chemistry, to suppose the large quantity of oxygene combined with the potassium, which we know has an intense affinity for oxygene, and which from some experiments, I am inclined to believe, is capable of combining directly with more oxygene than exists in potash, than with the oxymuriatic acid, which, as far as is known, has no affinity for that substance.

It is generally supposed that a mixture of oxymuriatic acid and hyperoxymuriatic acid is disengaged when hyperoxymuriate of potash is decomposed by common muriatic acid;\* but I am satisfied from several trials, that the gas procured in this way, when not mixed with oxygene, unites to the same quantity of hydrogene, as common oxymuriatic acid gas from manganese; and I find, by a careful examination, that the gas disengaged during the solution of platina, in a mixture

<sup>\*</sup> If hyperoxymuriate of potash be decomposed by nitric or sulphuric acid, it affords oxymuriatic acid and oxygene. If it be acted upon by muriatic acid, it affords a large quantity of oxymuriatic acid gas only. In this last case, the phænomenon seems merely to depend upon the decomposition of the muriatic acid gas, by the oxygene, loosely combined in the salt.

<sup>†</sup> This likewise appears from Mr. CRUICKSHANK's experiments. See Nicholson's Journal, Vol. V. 4to. p. 206.

of nitric and muriatic acids, which has been regarded as hyperoxymuriatic acid, but which I stated some years ago to possess the properties of oxymuriatic acid gas,\* is actually that body, owing its peculiar colour to a small quantity of nitromuriatic vapour suspended in it, and from which it is easily freed by washing.

Few substances, perhaps, have less claim to be considered as acid, than oxymuriatic acid. As yet we have no right to say that it has been decompounded; and as its tendency of combination is with pure inflammable matters, it may possibly belong to the same class of bodies as oxygene.

May it not in fact be a peculiar acidifying and dissolving principle, forming compounds with combustible bodies, analogous to acids containing oxygene, or oxides, in their properties and powers of combination; but differing from them, in being for the most part, decomposable by water? On this idea muriatic acid may be considered as having hydrogene for its basis, and oxymuriatic acid for its acidifying principle. And the phosphoric sublimate as having phosphorus for its basis, and oxymuriatic acid for its acidifying matter. And Libavius's liquor, and the compounds of arsenic with oxymu-

<sup>\*</sup> The platina, I find by several experiments, made with great care, has no share in producing the evolution of this gas. It is formed during the production of aqua regia. The hydrogene of the muriatic acid attracts oxygene from the nitric acid. Oxymuriatic acid gas is set free, and nitrous gas remains in the solution, and gives it a deep red colour. Nitrous acid and muriatic acid produce no oxymuriatic acid gas. Platina, during its solution in perfectly formed aqua regia, gives only nitrous gas and nitrous vapour; and I find, that rather more oxymuriatic acid gas is produced, by heating together equal quantities of nitric acid of 1.45, and muriatic acid of 1.18, when they are not in contact with platina, than when exposed to that metal. The oxymuriatic acid gas, produced from muriatic acid by nitric acid, I find combines with about an equal volume of hydrogene by detonation.

riatic acid, may be regarded as analogous bodies. The combinations of oxymuriatic acid with lead, silver, mercury, potassium, and sodium, in this view would be considered as a class of bodies related more to oxides than acids, in their powers of attraction.

It is needless to take up the time of this learned Society by dwelling upon the imperfection of the modern nomenclature of these substances. It is in many cases connected with false ideas of their nature and composition, and in a more advanced state of the enquiry, it will be necessary for the progress of science, that it should undergo material alterations.

It is extremely probable that there are many combinations of the oxymuriatic acid with inflammable bodies which have not been yet investigated. With phosphorus it seems capable of combining in at least three proportions; the phosphuretted muriatic acid of GAY LUSSAC and THENARD is the compound containing the maximum of phosphorus. The chrystalline phosphoric sublimate, and the liquor formed by the combustion of phosphorus in oxymuriatic acid gas, disengage no phosphorus by the action of water; the sublimate, as I have already mentioned, affords phosphorous acid and muriatic acid; and the liquid, I believe only phosphorous acid and muriatic acid.

The sublimate from the boracic basis gives, I believe, only boracic and muriatic acid, and may be regarded as boracium acidified by oxymuriatic acid.

It is evident, that whenever an oxymuriatic combination is decomposed by water, the oxide or acid or alkali or oxidated body formed must be in the same proportion as the muriatic acid gas, as the oxygene and hydrogene must bear the same relation to each other; and experiments upon these com-

pounds will probably afford simple modes of ascertaining the proportions of the elements, in the different oxides, acids, and alkaline earths.

If, according to the ingenious idea of Mr. Dalton, hydrogene be considered as 1 in weight, in the proportion it exists in water, then oxygene will be nearly 7.5; and assuming that potash is composed of 1 proportion of oxygene, and 1 of potassium, then potash will be 48, and potassium \* about 40.5; and from an experiment which I have detailed in the last Bakerian lecture, on the combustion of potassium in muriatic acid gas, oxymuriatic acid will be represented by 32.9, and muriatic acid gas, of course, by 33.9; and this estimation agrees with the specific gravity of oxymuriatic acid gas, and muriatic acid gas. From my experiments, 100 cubical inches of oxymuriatic acid gas weigh, the reductions being made for the mean temperature and pressure, 74.5 grains; whereas by estimation they should weigh 74.6. Muriatic acid gas I find weighs, under like circumstances, in the quantity of 100 cubic inches, 39 grains; by estimation it should weigh 38.4 grains.

It is easy from these data, knowing the composition of any dry muriate, to ascertain the quantity of oxide or of acid it would furnish by the action of water, and consequently the quantity of oxygene with which the inflammable matter will combine.

- \* Supposing potash to contain nearly 15.6 per cent. of oxygene.
- † I have stated in the last Bakerian lecture, that during the decomposition of the amalgam from ammonia, I in volume of hydrogene to z of ammonia is evolved: it is remarkable, that whatever theory of the nature of this extraordinary compound be adopted, there will be a happy coincidence as to definite proportions. If it be supposed that the hydrogene arises from the decomposition of water; then the oxygene that

In considering the dry muriates, as compounds of oxymuriatic acid and inflammable bodies; the argument that I have used in the last Bakerian lecture, to shew that potassium does not form hydrate of potash by combustion, is considerably strengthened; for from the quantity of oxymuriatic acid the metal requires to produce a muriate, it seems to be shewn that it is the simplest known form of the alkaline matter. This I think approaches to an experimentum crucis. Potash made by alcohol, and that has been heated to redness, appears to be an hydrat of potash, whilst the potash formed by the combustion of potassium must be considered as a pure metallic oxide, which requires about 19 per cent. of water to convert into a hydrat.

Amongst all the known combustible bodies, charcoal is the only one which does not combine directly with oxymuriatic acid gas; and yet there is reason for believing that this com-

must be assumed to exist in ammonia, will be exactly sufficient to neutralize the hydrogene, in an equal volume of muriatic acid; or if it be said that ammonium is a compound of 2 of ammonia and 1 of hydrogene in volume, then equal volumes of muriatic acid gas and ammonia will produce the same compound as oxymuriatic acid and ammonium, supposing they could be immediately combined. I once thought that the phænomena of metallization might be explained according to a modified phlogistic theory, by supposing three different classes of metallic bodies: First, The metal of ammonia, in which hydrogene was so loosely combined as to be separable with great ease, and which, in consequence of the small affinity of the basis for water, it had little tendency to combine with oxygene. The second, the metals of the alkalies and alkaline earths, in which the hydrogene was more firmly combined, but in combustion, forming water capable of being separated from the basis. And, thirdly, the metals of the earths and common metals, in which the hydrogene was more intimately combined; producing by union with oxygene, water not separable by any new attractions. The phænomena of the action of potassium and sodium upon muriatic acid, referred to in the text, seem however to overturn these speculations so far as they concern the metals from the fixed alkalies.

bination may be formed by the intermedium of hydrogene. I am inclined to consider the oily substance produced by the action of oxymuriatic acid gas, and olefiant gas, as a ternary compound of these bodies; for they combine nearly in equal volumes; and I find that, by the action of potassium upon the oil so produced, muriate of potash is formed, and gaseous matter, which I have not yet been able to collect in sufficient quantity to decide upon its nature, is formed. Artificial camphor, and muriatic ether, as is probable from the ingenious experiments of M. Gehlen and M. Thenard, must be combinations of a similar kind, one probably with more hydrogene, and the other with more carbon.

One of the greatest problems in œconomical chemistry, is the decomposition of the muriates of soda and potash. The solution of this problem will, perhaps, be facilitated by these new views. The affinity of potassium and sodium for oxymuriatic acid, is very strong; but so likewise is their attraction for oxygene, and the affinity of their oxides for water. The affinities of oxymuriatic acid gas for hydrogene, and of muriatic acid gas for water, are likewise of a powerful kind. Water, therefore, should be present in all cases, when it is intended to attempt to produce alkali. It is not difficult after these views to explain the decomposition of common salt, by aluminous or silicious substances, which, as it has been long known, act only when they contain water. In these cases the sodium may be conceived to combine with the oxygene of the water and with the earth, to form a vitreous compound; and the oxymuriatic acid to unite with the hydrogene of the water, forming muriatic acid gas.

It is also easy, according to these new ideas, to explain

the decomposition of salt by moistened litharge, the theory of which has so much perplexed the most acute chemists. It may be conceived to be an instance of compound affinity: the oxymuriatic acid is attracted by the lead, and the sodium combines with the oxygene of the litharge and with water to form hydrat of soda, which gradually attracts carbonic acid from the air.

As iron has a strong affinity for oxymuriatic acid, I attempted, to procure soda by passing steam over a mixture of iron filings, and muriate of soda intensely heated: and in this way, I succeeded in decomposing some of the salt: hydrogene came over; a little hydrate of soda was formed; and muriate of iron was produced.

It does not seem improbable, supposing the views that have been developed accurate, that by complex affinities, even potassium and sodium in their metallic form, may be procured from their oxymuriatic combinations: for this purpose the oxymuriatic acid should be attracted by one substance, and the alkaline metals by another; and such bodies should be selected for the experiment, as would produce compounds differing considerably in degree of volatility.

I cannot conclude the subject of the application of these doctrines, without asking permission to direct the attention of the Society, to some of the theoretical relations of the facts noticed in the preceding pages.

That a body principally composed of oxymuriatic acid and ammonia, two substances which have been generally conceived incapable of existing together, should be so difficult of decomposition, as to be scarcely affected by any of the agents of chemistry, is a phænomenon of a perfectly new kind.

Three bodies, two of which are permanent gases, and the other of which is considerably volatile, form in this instance, a substance neither fusible nor volatile, at a white heat. It could not have been expected that ammonia would remain fixed at such a temperature; but that it should remain fixed in combination with oxymuriatic acid, would have appeared incredible, according to all the existing analogies of chemistry. The experiments on which these conclusions are founded, are, however, uniform in their results: and it is easy to repeat them. They seem to shew, that the common chemical proposition, that complexity of composition is uniformly connected with facility of decomposition, is not well founded. The compound of oxymuriatic acid, phosphorus, and ammonia, resembles an oxide, such as silex, or that of columbium in its general chemical characters, and is as refractory when treated by common re-agents; and except by the effects of combustion, or the agency of fused potash, its nature could not be detected by any of the usual methods of analysis. Is it not likely, reasoning from these circumstances, that many of the substances, now supposed to be elementary, may be reduced into simpler forms of matter? And that an intense attraction, and an equilibrium of attraction, may give to a compound, containing several constituents, that refractory character, which is generally attributed to unity of constitution, or to the homogeneous nature of its parts?

Besides the compound of the phosphoric sublimate and ammonia, and the other analogous compounds which have been referred to, it is probable that other compounds of like nature may be formed of the oxides, alkalies, and earths, with the oxymuriatic combinations, or of the oxymuriatic

compounds with each other; and should this be the case, the more refined analogies of chemical philosophy will be extended by these new, and as it would seem at first view, contradictory facts. For if, as I have said, oxymuriatic acid gas be referred to the same class of bodies as oxygene gas, then, as oxygene is not an acid, but forms acids by combining with certain inflammable bodies, so oxymuriatic acid, by uniting to similar substances, may be conceived to form either acids, which is the case when it combines with hydrogene, or compounds like acids or oxides, capable of forming neutral combinations, as in the instances of the oxymuriates of phosphorus and tin.

Like oxygene, oxymuriatic acid is attracted by the positive surface in Voltaic combinations; and on the hypothesis of the connection of chemical attraction with electrical powers, all its energies of combination correspond with those of a body supposed to be negative in a high degree.

And in most of its compounds, except those containing the alkaline metals, which may be conceived in the highest degree positive, and the metals with which it forms insoluble compounds, it seems still to retain its negative character.

I shall occupy the time of the Society for a few minutes longer only, for the purpose of detailing a few observations connected with the Bakerian lectures, delivered in the two last years; particularly those parts of them relating to sulphur and phosphorus, which new and more minute enquiries have enabled me to correct or extend.

I have already mentioned that there are considerable differences in the results of experiments, made on the action of potassium, on sulphur and phosphorus, and their combinations with hydrogene, according to different circumstances of the process. I shall now refer to such of these circumstances as I have been able fully to investigate.

The able researches of Dr. Thomson have shewn that sulphur, in its usual state, contains small quantities of acid matter; and though, in my first experiments, I conceived that by employing chrystalized native sulphur, which had been recently sublimed in nitrogene, I should avoid the presence of any foreign matter, yet I am inclined to believe that this is not the case; for by subliming some similar sulphur in nitrogene, I find that litmus paper placed in the upper part of the retort is slightly reddened.

When potassium is made to unite with sulphur, if the retort employed is not lined with sulphur, some of the potassium is destroyed by acting upon the glass; and when large quantities of sulphur are used, it is very difficult to decompose the whole of the sulphuret of potassium by an acid: sulphuretted hydrogene likewise is soluble in muriatic acid; and this circumstance led me to under-rate the quantity of sulphuretted hydrogene given off in experiments of this kind.\*

In acting upon sulphuretted hydrogene by potassium in my early experiments, I used large quantities of the gas and of the metal; and in these cases I have reason to believe that the violence of the combustion, occasioned the decomposition

\* This circumstance has been pointed out by M. M. GAY LUSSAC and THENARD; in a paper printed in the Journal de Physique for December, in which these gentlemen endeavour to shew that, whether potassium has been acted upon by large or small quantities of sulphur, and under all circumstances, it evolves a quantity of gas exactly equal to that which it produces by the action of water. I have been able to gain no results so precise on this subject. I have in another place (the same journal in which their memoir has appeared) offered some observations on their enquiries.

of a considerable quantity of the gas; and, in consequence, led me to form erroneous conclusions concerning the nature of this curious operation.

In all late experiments in which sulphur, or sulphuretted hydrogene were concerned, I have used muriatic acid saturated with sulphuretted hydrogene over mercury. I have employed sulphur distilled from iron pyrites in vacuo, which did not in the slightest degree affect litmus paper, and I have combined it with potassium in retorts of green-glass, or plate-glass lined with sulphur and filled with very pure nitrogene or hydrogene. In making potassium act upon sulphuretted hydrogene, I have employed the gas only in the quantities of from 1 to 2 cubical inches, and have made the combination in narrow curved tubes of green glass over dry mercury. With all these precautions, and after having made a great number of experiments. I am not able to gain perfectly uniform results. Yet there is a sufficient correspondence between them to enable me to form conclusions, which I may venture to say cannot be far from the truth.

When 1 grain of potassium, which would give by the action of water about 1 cubical inch and  $\frac{1}{16}$  of hydrogene is made to act upon about half a grain of sulphur, some sulphur sublimes during the combination, which always takes place with heat and light, and from  $\frac{1}{14}$  to  $\frac{1}{10}$  of a cubical inch of sulphuretted hydrogene is evolved. The compound acted on by muriatic acid, saturated with sulphuretted hydrogene, affords from  $\frac{9}{10}$  to  $\frac{11}{10}$  of a cubical inch of pure sulphuretted hydrogene.

When more sulphur is used so as to be from twice to ten times the weight of the potassium, the quantity of sulphuretted hydrogene evolved by the action of the acid, is from  $\frac{7}{10}$  to  $\frac{9}{10}$ ; but if heat be applied to the combination, so as to drive off the superfluous sulphur, the quantity of gas collected is very little inferior to that produced from the combination in which a small proportion of sulphur is used; and I am inclined to believe, from the phænomena presented in a great number of experiments, that sulphur and potassium, when heated together under common circumstances, combine only in one proportion, in which the metal is to the sulphur nearly as 3 to 1 in weight; and in which the quantities are such that the compound burns into neutral sulphate of potash.

When a grain of potassium is made to act upon about 1.1 cubical inches of sulphuretted hydrogene, all the hydrogene is set free, and a sulphuret of potassium containing one fourth of sulphur is formed, exactly the same as that produced by the immediate combination of sulphur and the metal.

When sulphuretted hydrogene is employed in larger quantities, there is an absorption of this gas, and a volume is taken up about equal to the quantity of hydrogene disengaged, and a compound of sulphuretted hydrogene and sulphuret of potash is formed, which gives sulphuretted hydrogene by the action of an acid, nearly double in quantity to that given by the sulphuret of potassium.

From a number of experiments I am inclined to believe that potassium and phosphorus, in whatever quantities they are heated together, combine only in one proportion, a grain of potassium requiring about  $\frac{3}{8}$  of a grain of phosphorus to form a phosphuret; which when acted upon by muriatic acid, produces from  $\frac{8}{10}$  to  $\frac{10}{10}$  of a cubical inch of phosphuretted hydrogene.

Half a grain of potassium decomposes nearly three cubical inches of phosphuretted hydrogene, and sets free rather more than four cubical inches of hydrogene; and the phosphuret formed seems to be of the same kind as that produced by direct combination of the metal with phosphorus.

If, according to Mr. Dalton's ideas of proportion, the quantity in which sulphur enters into its combinations were to be deduced from its union with potassium, in which it seems to form about \( \frac{1}{4} \) the weight of the compound, the number representing it would be 13.5. I have lately weighed sulphuretted hydrogene, and sulphureous acid gas, with great care: the specific gravity of the first at mean temperature and pressure, from my experiments, is 10645, which differs very little from the estimation of Mr. Kirwan: that of sulphureous acid gas I find is 20967. Sulphuretted hydrogene, as I have shown, contains an equal volume of hydrogene; and on this datum the number representing sulphur is 13.4. I have never been able to burn sulphur in oxygene without forming sulphuric acid in small quantities; but in several experiments I have obtained from 92 to 98 parts of sulphureous acid from 100 of oxygene in volume; from which I am inclined to believe, that sulphureous acid consists of sulphur dissolved in an equal volume of oxygene; which would give the number as 13.7\* nearly, considering the acid gas as containing 1 pro-

In the last Bakerian lecture, I have estimated the specific gravity of sulphuretted

<sup>\*</sup> The estimation from the composition of sulphuretted hydrogene, must be considered as most accurate, and that from the formation of the sulphuret of potassium as least accurate: for it was only by combining sulphur and potassium in small proportions, and ascertaining in what cases uncombined sulphur could be distilled from the compound, that I gained my conclusions concerning the composition of the sulphuret of potassium.

portion of sulphur, and 2 of oxygene; and these estimation do not differ from each other materially.

I have made several experiments on the combustion of phosphorus in oxygene gas. From the most accurate, I am inclined to conclude that 25 of phosphorus absorb in combustion about 34 of oxygene in weight; and considering phosphoric acid as composed of 3 proportions of oxygene and 1 of phosphorus, the number representing phosphorus will be about 16.5, which is not very remote from the number that may be deduced from the composition of phosphoret of potassium.

The numbers which represent the proportions in which sulphur and phosphorus unite with other bodies, are such, as do not exclude the existence of combined portions of oxygene and hydrogene in their constitution; but it may be questioned, whether the opinion which I formed, that the inflammable gas disengaged from them by electricity, is necessary to the peculiar form in which these bodies exist, is not erroneous. Phosphorus, as I have stated in the last Bakerian lecture, is capable of forming a solid hydruret: and a part of the sulphur distilled from iron pyrites, is usually of a soft consistence, and emits the smell of sulphuretted hydrogene, and probably contains that body. It is not unlikely, that in all cases, phosphorus and sulphur contain small quantities of the hydrurets of phosphorus and sulphur; and the production of a minute portion of sulphuric acid in the slow combustion of sulphur, is pro-

hydrogene at 35 grains, the 100 cubical inches, which was not far from the mean, between the estimations of Mr. Kirwan and Mr. Thenard. According to this last experiment, sulphuretted hydrogene is composed of 1 proportion of hydrogene, represented by 1, and 1 of sulphur represented by 13.4

bably connected with the production of water. Though the pure oxides of sulphur and phosphorus have never been obtained, yet from the doctrine of definite proportions, these bodies ought, under certain circumstances, to be formed. And I am inclined to believe, that they sometimes exist in minute quantities, in common phosphorus and sulphur, and with hydrogene, give to them their variable properties.

The colours of different specimens of phosphorus, as well as of sulphur, differ considerably; the red colour of phosphorus as it is commonly prepared, is probably owing to a slight mixture of oxide. Common roll sulphur is of a very pale yellow, the Sicilian sulphur of an orange colour, and the sulphur distilled from iron pyrites in vacuo, which arose in the last period of the process, of a pale yellowish green colour. All the late experiments that I have made, as well as my former researches, induce me to suspect a notable proportion of oxygene in Sicilian sulphur, which is probably owing to the presence of oxide of sulphur, which may give rise to sulphuric acid in distillation, or to sulphuric acid itself.

Conceiving that if definite proportions of oxygene and hydrogene existed in sulphur and phosphorus, they ought to be manifested in the agency of oxymuriatic acid gas on these bodies, I made some experiments on the results of these operations. In the first trial, on the combination of sulphur with oxymuriatic acid gas, I employed 5 grains of roll sulphur, and admitted the gas into the exhausted retort, from a vessel in which it had been in contact with warm water: in this case more than a half a cubical inch of oxygene gas, and nearly two cubical inches of muriatic acid gas, were produced. Suspecting in this instance, that aqueous vapour had been

decomposed, I employed cold water in the next experiment, and dried the gas by muriate of lime; in this case, though Sicilian sulphur was used, no oxygene gas was evolved; and not a half a cubical inch of muriatic acid; the quantity was the same as in the last experiment; and it was found, that between 16 and 17 cubical inches of oxymuriatic acid gas disappeared; the whole of the sulphur was sublimed in the gas, and the liquor formed, was of a tawney orange colour.

No oxygene was expelled during the combustion of phosphorus in oxymuriatic acid gas, nor could I ascertain that any muriatic acid had been formed; 3 grains of phosphorus were entirely converted into sublimate, by the absorption of about 23 cubical inches and a half of the gas.

It would seem from these quantities, that the sulphuretted liquor formed by subliming sulphur in oxymuriatic acid gas, consists of 1 proportion of sulphur, represented by 13.5, and 1 of oxymuriatic gas represented by 32.9, and that the phosphoric sublimate must be composed of 3 portions of oxymuriatic gas, represented by 98.7, and 1 of phosphorus represented by 16.5