Account of a series of experiments, undertaken with the view of decomposing the muriatic acid / [William Henry].

ACCOUNT

OF A

SERIES OF EXPERIMENTS,

UNDERTAKEN WITH THE VIEW OF

DECOMPOSING THE MURIATIC ACID.

BY

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FROM THE

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ACCOUNT, &c.

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MODERN chemistry, notwithstanding its rapid advancement during the few last years, still presents to its cultivators several interesting objects, both of analytic and synthetic inquiry. Among the former, the decomposition of the muriatic and of certain other acids, holds a distinguished place; for our curiosity respecting the nature of these bodies, is strongly excited, by the influence which the discovery would have on the general doctrines of chemical science, as well as on the explanation of individual facts. The theory of the formation of acids, for example, one of the most important parts of the new system of chemistry, must be regarded as incomplete, and liable to subversion, till the individual acids now alluded to have been resolved into their constituent principles. To the best of my knowledge, however, we are not in possession of a single fact that gives the smallest insight into the constitution of the muriatic acid; and the attempts to effect its analysis, can only therefore be directed by the analogy of the decomposition of other bodies, which, from similarity of character, are arranged in the same class.

One of the first objects, in the analysis of a compound body,

should be its complete separation from all other substances, which, by their presence, may tend to introduce uncertainty into the results of the processes that are employed. But it is seldom that a simplicity so desirable can be attained in the objects of chemical research; for, agreeably to a known law of affinity, the last portions of any substance are separated with peculiar difficulty; the force of attraction appearing to increase, as we recede from the point of saturation. In a liquid state, the muriatic acid is a totally unfit subject for analytic experiment; for, in the strongest form under which it can be procured, it still contains a large proportion of water. This watery portion, besides the complexity which it introduces into the results of experiments, prevents any combustible substance that may be applied, from acting on the truly acid part; because that class of bodies, having less difficulty in attracting oxygen from the water than from the acid, will necessarily take it from the former source. The state of gas, therefore, is the only one in which the muriatic acid can become a proper object of analysis.

In the series of experiments on this gas, which I am now about to describe, I employed the electric fluid, as an agent much preferable to artificial heat. This mode of operating enables us to confine accurately the gases submitted to experiment; the phænomena that occur during the process, may be distinctly observed; and the comparison of the products, with the original gases, may be instituted with great exactness. The action of the electric fluid itself, as a decomponent, is extremely powerful; for it is capable of separating from each other, the constituent parts of water, of the nitric and sulphuric acids, of the volatile alkali, of nitrous gas, and of several other bodies, whose components are strongly united. I began, there-

fore, with examining attentively the effects of the electric fluid on the muriatic acid gas, without admixture.*

SECTION I.

On the Effects of Electricity on Muriatic Acid Gas.

When strong electrical shocks were passed through a portion of muriatic acid gas, confined in a glass tube over mercury, the following appearances took place. The bulk of the gas, after 20 or 30 shocks, was considerably diminished; and a white deposit appeared on the inner surface of the tube, which considerably obscured its transparency. In some instances, both the contraction and deposit were much more remarkable than in others. The gas which issued from muriate of soda, soon after the affusion of sulphuric acid, and while the charge was yet warm, exhibited these appearances in an eminent degree. Of this gas, 307 measures were reduced, by 20 shocks, to 227, or were contracted nearly one-fourth. Gas from the same materials, after they had continued working for some hours, was diminished, by similar treatment, only about a twelfth. These effects, therefore, it seemed probable, depended in some measure on the presence of moisture; and I accordingly found, that muriatic acid gas, after more than a week's exposure to muriate of lime, brought into contact with it immediately after cooling from a state of

* The gases submitted to the action of electricity, in the following experiments, were confined in straight glass tubes of various diameters, armed at the sealed end with a conductor of gold, or of platina, but generally of the latter metal. The shocks were as strong as could be given without breaking the tubes, which, notwithstanding every precaution, were often shattered by the force of the explosion. Each measure of gas is equal to the bulk occupied by a grain of mercury.

fusion, was scarcely diminished at all; and that the deposit, though it still occurred, was less copious in quantity. This deposit was not, like corrosive sublimate, soluble in water; but had every property of the less saturated salt, calomel.

The mercury by which the muriatic acid was confined, was therefore evidently oxidated; and, to the combination of a part of the gas with the oxide thus produced, the diminution of bulk was doubtless to be ascribed. But it was uncertain from whence this oxygen was derived. It might either result from the decomposition of the acid gas, or of the water chemically combined with it. The following experiments were therefore made, to determine this point.

Experiment 1. Through 1457 measures of muriatic acid gas, 300 electrical shocks were passed. There remained, after the admission of water, 100 measures of permanent gas, (or not quite 7 from each hundred of the original gas,) which, on trial, appeared to be purely hydrogenous.

Exper. 2. Of the gas, dried by muriate of lime, 176 measures received 120 shocks. The residue of hydrogenous gas amounted to 11 measures, or rather more than 6 *per cent.*

These experiments, and other similar ones, made on comparative portions of muriatic acid gas, in its recent state, and after exposure to muriate of lime, convinced me that it was impossible, by this method, wholly to deprive the muriatic gas of water. The recent gas, however, when electrified in smaller quantity than in experiment 1, gave a larger proportion of hydrogenous gas; which shews, that some portion of its moisture was removed, by exposure to muriate of lime. In order, if possible, to procure the gas perfectly dry, another mode of preparing it was resorted to. Alum and common salt were first well

calcined, separately, to expel their water of crystallization, and, being then mixed, were distilled together in an earthen retort. The gas proceeding from these materials, was received over dry mercury; but, though only the last portion that came over was reserved for experiment, it still, after the usual electrization, afforded a product of hydrogenous gas.

In the course of the preceding experiments, I observed that the diminution of the muriatic acid gas stopped always at a certain point, beyond which it could not be carried by continuing the shocks. Gas also, which had been thus treated, when transferred to another tube, and again electrified, did not exhibit any further deposit. It became interesting, therefore, to know, whether the production of hydrogenous gas had a similar limitation; because, the decision of this question would go far towards ascertaining its source. If the evolved hydrogenous gas arose from the decomposition of the acid, it might be expected to be produced, as long as any acid remained undecomposed. But, if water were the origin of this gas, it would cease to be evolved, when the whole of the water contained in the gas had been resolved into its constituent principles.

Experiments 3 and 4. Into two separate tubes, I passed known quantities of muriatic acid gas. Through the one portion, 200 discharges were taken; and through the other, 400. On comparing the quantities of hydrogenous gas produced, it proved to bear exactly the same proportion, in each tube, to the gas originally submitted to experiment. Hence it may be inferred, that the hydrogenous gas, evolved by electrifying the muriatic acid, has its origin, not from the acid, but from the water which is intimately attached to it. The agency of the electric fluid appears also, from the following experiments, to be exerted, not

only in disuniting the elements of water, but in promoting the union of the evolved oxygen with muriatic acid.

Exper. 5. A mixture of common air and muriatic acid gas, in the proportion of 143 of the former to 116 of the latter, was rapidly diminished by electrical shocks; 30 of which reduced the whole to 111.* The remainder consisted of muriatic acid and azotic gases, with a small proportion of oxygenous gas. The deposit formed on the tube was of the same kind as before, but much more abundant.

Exper. 6. The same appearances were occasioned, much more remarkably, by electrifying muriatic acid with oxygenous gas; and the contraction continued, till the mercury rose so as to touch the extremity of the platina conductor. At each explosion, a dense white cloud was seen in the tube, which soon settled on its inner surface, and was of exactly the same chemical composition as the one already described. Nitrous gas and muriatic gas, when electrified together, underwent a similar change.

In order to ascertain whether the mercury by which the gases were confined, in the above experiments, had any influence on their results, they were repeated in an instrument made, purposely for the occasion, by Mr. CUTHBERTSON, of London. It consisted of a glass tube, ground at each end, with the view of receiving two stoppers, each perforated with platina wire, which projected into the cavity of the tube. When the stoppers were in their places, the extremities of the wires were

* This experiment suggests an additional reason, to that already given, for the greater diminution of the first, than of the subsequent portions of muriatic acid gas; for the former may be presumed to have been much more adulterated than the latter, with the atmospherical air of the vessels.

at the distance of about half an inch; and, by properly disposing the apparatus, electrical shocks might be passed, through any gas or mixture of gases, with the contact only of glass and platina.

Exper. 7. In this tube I electrified the muriatic acid gas, and then admitted to it an infusion of litmus. The sudden destruction of its colour evinced the formation of oxygenated muriatic acid. Not the smallest deposit appeared on the tube.

Experiments 8 and 9. The same phænomenon took place, when an infusion of litmus was brought into contact with a mixture of common air and muriatic acid, and of oxygenous gas and muriatic acid, after electrization in this instrument; oxygenated muriatic acid being produced in both cases.

The above facts prove, that the combination of oxygen with muriatic acid, in these experiments, is not occasioned by a predisposing affinity in the mercury to combine with oxygenated muriatic acid; but that the electric fluid serves actually as an intermedium, in combining the muriatic acid with oxygen.

From the relation of these experiments it appears, that not the smallest progress had been made by them, towards the decomposition of the muriatic acid. I resolved, therefore, to attempt its analysis, in a similar manner, with the aid of combustible gases.

SECTION II.

Effects of electrifying the Muriatic Acid Gas with inflammable Substances.

In a memoir read before the Royal Society, and inserted in their Transactions for 1797, I have shewn, that when electrical

shocks are passed repeatedly through a confined portion of carbonated hydrogenous gas, the water held in solution by the gas, is decomposed by the carbon, which forms a constituent part of it; that carbonic acid is formed; and an addition made, of hydrogenous gas. Hence, the bulk of the carbonated hydrogen gas is considerably enlarged by this process; which shews, by its results, that the affinity of carbon for oxygen, is rendered much more powerful and efficient by the electric fluid. I have since found, that other oxygenated substances are decomposed, by electrifying them with carbonated hydrogen gas. Nitrous gas, for example, is speedily destroyed by this process, and carbonic acid and azotic gases are obtained.

Every attempt to decompose the muriatic acid, must be founded on the presumption that it is an oxygenated substance; and those bodies promise to be the most successful agents, that possess a strong affinity for oxygen. Now, of all known bodies, charcoal most strongly attracts oxygen; and I have, therefore, repeatedly attempted the destruction of this acid, by passing it over red-hot charcoal. But, in a series of experiments, which I made some time since, with this view, in conjunction with Mr. RUPP, we soon found reason to be dissatisfied with the difficulty and uncertainty of this process. An immense production of hydrogenous gas took place; but it was not easy to determine whether it had its origin from real acid, or from water. Our experiments, however, though insufficient to furnish decisive proof, induced us to believe that it had the latter origin.

It next occurred to me, that the comparative affinities of the muriatic radical, whatever it may be, and of charcoal, for oxygen, would be elegantly and satisfactorily ascertained, by electrifying together the carbonated hydrogen and muriatic gases. If the

muriatic acid be capable of decomposition by carbon, it might be expected to be destroyed by this process; and the exact quantity of acid decomposed, and the nature and quantity of the products, would thus be easily determined. I electrified, therefore, the muriatic acid and carbonated hydrogen gases, with the most scrupulous attention to the phænomena and results. That the electric fluid might not be misapplied, in decomposing the water of the carbonated hydrogen gas, it was kept more than a week, before use, over quick lime, introduced to it while yet hot.

Exper. 10. Of this carbonated hydrogenous gas, 186 measures were expanded, by 130 shocks, to 211; that is, the gas was increased about $\frac{1}{8}$ its bulk.

Exper. 11. Of the same gas, 84 measures were mixed with 116 of muriatic acid gas, dried by muriate of lime. By 120 shocks, the mixture was a little dilated. After the admission of a drop or two of water, there remained 91 measures; *i. e.* the addition of permanent gas was 7 measures, or about as much as might have been expected from the muriatic gas alone.

Exper. 12. Eighty-three measures of dry carbonated hydrogenous gas, with 89 of muriatic acid gas, received 200 shocks. The permanent residue, after the admission of water, was 101 measures: the addition, therefore, amounted to 18. Of the added 18, 6 may be accounted for by the decomposition of the water of the muriatic gas, and 10 by that of the carbonated hydrogenous gas. There remain, therefore, only 2 measures that can be supposed to be produced from the muriatic acid gas; a quantity too small to afford grounds for supposing them to arise from decomposed acid.

Exper. 13. Dry carbonated hydrogenous gas 132 measures,
mixed with dry muriatic gas - 108
240
by 200 shocks, expanded to - 268

Part of this gas was then transferred to another tube, and the proportion of permanent gas ascertained. Through the remainder, 150 additional shocks were passed, before the amount of the gas thus evolved was determined. In both, it bore exactly the same proportion to the original gas; which shews, that by continuing the electrization, no further effects were produced.

A great variety of similar experiments convinced me, that by electrifying together the carbonated hydrogenous and muriatic gases, not the smallest progress was made towards the decomposition of the latter. All that was thus effected, consisted in the decomposition of the water of the two gases, by the carbon of the combustible gas; and, when this was completely accomplished, no further effect ensued from continuing the electrization. The generation of carbonic acid was proved, by the following experiment.

Exper. 14. To a mixture of carbonated hydrogen and muriatic gases, after having received above 100 shocks, a drop of water was admitted, which absorbed the muriatic acid. The liquid was then taken up by blotting-paper; and the residuary gas, being transferred into another tube, was brought into contact with a solution of pure barytic earth. The precipitation of this solution, evinced the presence of carbonic acid.

It was desirable, however, that the effects should be ascertained, of electrifying together pure muriatic acid and pure carbonated hydrogenous gas, both perfectly free from water. Now,

from the experiments related in the first Section, it appears highly probable, that a complete purification from moisture is produced, in both gases, by the action of the electric fluid; all the water they before contained being thus decomposed. In the following experiments, therefore, the two gases were separately electrified, before they were submitted to this process conjointly.

Exper. 15. To a portion of muriatic acid, diminished by the action of electricity from 144 to 121 measures, 27 measures of carbonated hydrogenous gas, expanded as far as possible, were added, and 200 shocks passed through the mixture. The addition of permanent gas amounted to 14 measures; 10 of which may be traced to the muriatic acid, and were evolved by its separate electrization. The remaining 4 measures, which remain to be accounted for, are too small a quantity to be ascribed to the decomposition of the acid.

Exper. 16. To a quantity of carbonated hydrogenous gas, which had received 400 shocks, and occupied the space of 212 measures, I added 232 of muriatic acid, through which 200 shocks had previously been passed. The electrization of the mixture was next continued, till 800 discharges had taken place. On examining the mixture of gases, during this operation, no change whatever took place; and, after its close, no more muriatic acid had disappeared, than would have been deficient after the first electrization; nor was there any further production of permanent gas.

Exper. 17. The same result was obtained, by electrifying together 280 measures of carbonated hydrogenous gas, previously expanded by 600 shocks, and 114 of muriatic acid, after 400 shocks. The additional discharge, through this mixture,

of 1000 shocks, did not evince the smallest progress towards the decomposition of the muriatic acid.

Exper. 18. In the naturally moist state of these gases, it follows, from the 14th experiment, that carbonic acid is produced by electrifying them in conjunction. It appeared to me of some importance to ascertain whether, after a previous decomposition of their moisture, carbonic acid would continue to be generated. But the electrified carbonated hydrogenous gas itself contains carbonic acid, which, unless removed, would render the result of the experiment undecisive. This was accomplished by passing up, to a portion of electrified gas, a bubble or two of dry ammoniacal gas, which, uniting with the carbonic acid, would condense any portion of it that might be present. The remainder was transferred into another tube; and, to this carbonated hydrogenous gas, perfectly deprived both of moisture and carbonic acid, muriatic acid gas, previously electrified, was added, and electrical shocks were passed through the mixture. A drop of water was then admitted; and the residuary gas, after having been dried, was transferred into another tube. On passing up barytic water, not the smallest trace of carbonic acid could be discovered.

From the preceding experiments, the following conclusions may be deduced.

1. The muriatic acid gas, in the driest state in which it can be procured, still contains a portion of water. From a calculation founded on the experiments described in the first section, the grounds of which are too obvious to require being stated, it follows, that 100 cubical inches of muriatic gas, after exposure to muriate of lime, still hold in combination 1.4 grain of water.

2. When electrical shocks are passed through this gas, the

watery portion is decomposed. The hydrogen of the water, uniting with the electric matter, constitutes hydrogenous gas, and the oxygen unites with the muriatic acid; which last, acting on the mercury, composes muriate of mercury.

3. The electric fluid serves as an intermedium, in combining oxygen with muriatic acid.

4. The really acid portion of muriatic gas does not sustain any decomposition by the action of electricity.

5. When electric shocks are passed through a mixture of carbonated hydrogen and muriatic acid gases, the water held in solution by these gases, is decomposed by the carbon of the compound inflammable gas; and carbonic acid and hydrogenous gases are the result.

6. When all the water of the two gases has been decomposed, no effect ensues from continuing the electrization; or, if the water of each gas has been previously destroyed, by electrifying them separately, no further effect ensues from electrifying them conjointly.

7. Since therefore carbon, though placed under the most favourable circumstances for abstracting from the muriatic acid, and combining with, its oxygen, evinces no such tendency, it may be inferred, that if the muriatic acid be an oxygenated substance, its radical has a stronger affinity for oxygen than charcoal possesses.

Though the first impressions excited in my mind by the total failure of the above experiments, in accomplishing one of the greatest objects of modern chemistry, have induced me for some time to withhold them from the society, I am satisfied by reflection, that this communication is not without expediency. The means employed in attempting the analysis of the muriatic acid,

were such as, after mature deliberation, appeared to me most to promise success; and the experiments were attended with a degree of labour, which can only be estimated by those who have been engaged in similar pursuits; not one third of those which were really made having been described, in the foregoing account of them. It may spare therefore to others, a fruitless application of time and trouble, to be made acquainted with what I have done; and the collateral facts, which have presented themselves in the inquiry, are perhaps not without curiosity or value.

From the result of these experiments, I apprehend, all hope must be relinquished, of effecting the decomposition of the muriatic acid, in the way of single elective affinity. They furnish also a strong probability, that the basis of the muriatic acid is some unknown body; for, no combustible substance with which we are acquainted, can retain oxygen, when submitted, in contact with charcoal, to the action of electricity, or of a high temperature. The analysis of this acid must, in future, be attempted with the aid of complicated affinities. Thus, in the masterly experiment of Mr. TENNANT, phosphorus, which attracts oxygen less strongly than charcoal, by the intermediation of lime decomposes the carbonic acid. Yet, led by the analogy of this fact, its discoverer found that a similar artifice did not succeed in decomposing the muriatic acid. "As vital "air," he observes, "is attracted by a compound of phosphorus "and calcareous earth, more powerfully than by charcoal, I was "desirous of trying their efficacy upon those acids which may "from analogy be supposed to contain vital air, but which are "not affected by the application of charcoal. With this intention, "I made phosphorus pass through a compound of marine acid

"and calcareous earth, and also of fluor acid and calcareous "earth, but without producing in either of them any alteration. "Since the strong attraction which these acids have for calca- "reous earth tends to prevent their decomposition, it might be "thought, that in this manner they were not more disposed to "part with vital air than by the attraction of charcoal: but "this, however, does not appear to be the fact. I have found, "that phosphorus cannot be obtained by passing marine acid "through a compound of bones and charcoal when red-hot. "The attraction, therefore, of phosphorus and lime for vital "air, exceeds the attraction of charcoal, by a greater force than "that arising from the attraction of marine acid for lime."*

By means similar to those employed in attempting the analysis of the muriatic acid, I tried to effect that of the fluoric acid. When electrified alone, in a glass tube coated internally with wax, it sustained a diminution of bulk, and there remained a portion of hydrogenous gas. But, neither in this mode, nor by submitting it, mixed with carbonated hydrogenous gas, to the action of electricity, was any progress made towards its analysis. These experiments, however, render it probable, that the fluoric acid, like the muriatic, is susceptible of still farther oxygenation, in which state it becomes capable of acting on mercury. The carbonic acid, on the contrary, appears not to admit of different degrees of oxygenation. When the electric shock has been repeatedly passed through a portion of this acid gas, its bulk is enlarged, and a permanent gas is produced, which is evidently

* Phil. Trans. Vol. LXXXI. p. 184.

a mixture of oxygenous and hydrogenous gases; for, when an electrical spark is passed through the gas that remains after the absorption of the carbonic acid by caustic alkali, it immediately explodes. These results even take place on electrifying carbonic acid from marble, previously calcined in a low red heat, to expel its water, and then distilled in an earthen retort.*

* Messieurs LANDRIANI and VAN MARUM (*Annales de Chimie*, Tom. II. p. 270.) obtained only hydrogenous gas, by electrifying the carbonic acid gas. But the conductor of their apparatus was an iron one; which metal would combine with the oxygen of the water, and prevent it from appearing in a gaseous state. In my experiments, the conductors were of platina.

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