XVII. Experiments on muriatic acid gas, with observations on its chemical constitution, and on some other subjects of chemical theory

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To cite this article: John Murray M.D. F.R.S. E. (1818) XVII. Experiments on muriatic acid gas, with observations on its chemical constitution, and on some other subjects of chemical theory , Philosophical Magazine Series 1, 52:244, 107-112, DOI: [10.1080/14786441808652015](https://doi.org/10.1080/14786441808652015)

To link to this article: <http://dx.doi.org/10.1080/14786441808652015>

Published online: 23 Jul 2009.

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lysis of hydrochloric acid ; or it might be derived from the combined water of muriatic acid, of which the oxygen became fixed in the muriate of tin. When chlorine also at high heats was made to act on earths or common metallic oxides, the evolved oxygen could be referred with equal probability either to the solid or to the gas.

And though we ignite by the strongest Voltaic power, charcoal or other combustibles in chlorine, still we shall not be able to convert it into muriatic acid gas, for want of the essential constituent water ; no more than we can, without the same water, obtain oil of vitriol. Present water to chlorine, then light alone will separate its oxygen, and leave muriatic acid. Such, indeed, is the affinity existing between the muriatic acid basis and water, that those muriates which of themselves resist decomposition at a red heat, when exposed at that temperature to the vapour of water, are speedily resolved into gaseous muriatic acid, and their peculiar bases.

By restoring the theory of Lavoisier and Berthollet, we get rid of those mysterious and almost incomprehensible transformations which a drop of water has been lately conceived to produce on some of the muriates. Dried sea-salt, for example, when viewed as a compound of chlorine and sodium, is no sooner moistened, than a portion of water resolves itself into oxygen and hydrogen ; whence result soda and hydrochloric acid, and a solution of muriate of soda. Expel the drop of water, we have a chloride of sodium once more ; and we may repeat this invisible change for an indefinite number of times by the addition or subtraction of a little moisture. Thus we must consider dry salt and moist salt to be bodies widely and essentially different, the former containing neither alkali nor acid, while the latter contains both. This supposition, which the chloridic theory compels us to make, must surely be reckoned somewhat violent.

XVII. *Experiments on Muriatic Acid Gas, with Observations on its Chemical Constitution, and on some other Subjects of Chemical Theory.* By JOHN MURRAY, M.D. F.R.S. E. Fellow of the Royal College of Physicians of Edinburgh.*

SOME years ago I proposed, as decisive of the question which has been the subject of controversy on the nature of oxymuriatic and muriatic acids, the experiment of procuring water from muriate of ammonia, formed by the combination of dry ammo-

* From the Transactions of the Royal Society of Edinburgh.

niacal and muriatic acid gases. Muriatic acid gas being the sole product of the mutual action of oxymuriatic gas and hydrogen, it follows, that if oxymuriatic gas contain oxygen, muriatic acid gas must contain combined water; while, if the former be a simple body, the latter must be the real acid, free from water. When muriatic acid gas is submitted to the action of substances which combine with acids, water is obtained; but though the most simple and direct conclusion from this is, that the water is deposited from the muriatic acid gas, the result may be accounted for, on the opposite doctrine, by the supposition that it is water formed by the combination of the hydrogen of the acid with the oxygen of the base. Ammonia, however, containing no oxygen, if water is obtained from its combination with muriatic acid gas, we obtain a result which cannot be accounted for on this hypothesis, but must be regarded as a proof of the presence of water in the acid gas. And this, again, affords a proof equally conclusive of the existence of oxygen in oxymuriatic gas.

The results of the experiment which I had brought forward were involved in much controversial discussion: and a brief recapitulation of the objections that were urged to it is necessary, as an introduction to the experiments I have now to submit, and to the consideration of the present state of the question.

The original experiment was performed by combining thirty cubic inches of muriatic acid gas with the same volume of ammoniacal gas carefully dried. The salt formed was exposed in a small retort with a receiver adapted to it, to a moderate heat gradually raised. Moisture speedily condensed in the neck of the retort, which increased and collected into small globules*.

This result was admitted by those who defended the new doctrine, when the experiment was performed in the manner I have described,—water being obtained, it was allowed, “in no inconsiderable quantity.” But, to obviate the conclusion, it was asserted, that this is water which has been absorbed by the salt from the atmosphere. This was affirmed by Sir Humphry Davy, who stated that the salt absorbs water in this manner to a very considerable extent; that it is only from the salt in this state that water can be procured; and that when it is formed from the combination of the gases in a close vessel, and heated without exposure to the air, not the slightest trace of water appears, even when the experiment is performed on a large scale.

The reverse of this I was able to demonstrate by further experimental investigations. It was shown, that the salt absorbs no moisture from the air in the common state of dryness and

* Nicholson's Journal, vol. xxxi. p. 126.

temperature in which the experiment is performed: when weighed immediately on its formation, in an exhausted vessel, it gains no weight from exposure, but remains the same after a number of hours; and when exposed to the air in the freest manner, it remains, after many days, perfectly dry. It was further shown, that when the other circumstances of the experiment are the same, it yields no larger portion of water when it has been exposed to the air, than it does without this previous exposure. And, lastly, it was proved, that when the salt has been formed, and is heated without the air having been admitted, water is obtained from it. This last result was even at length admitted by those who had advanced the opposite assertion, in an experiment performed with a view to determine the fact. The quantity of water was indeed less than what is procured in the other mode; but this was obviously owing to the circumstances of the experiment being unfavourable to its expulsion,—more particularly to the difficulty of applying a regulated temperature to a thin crust of salt, so as to separate the water without volatilizing the salt itself,—and to the effect arising from the whole internal surface of a large vessel being encrusted with the salt; so that, if the heat is locally applied, the aqueous vapour expelled from one part is in a great measure condensed and absorbed at another; or, if the heat is applied equally, is retained in the elastic form, and, as it is cooled, is equally condensed. Accordingly, when the experiment was repeated, obviating these sources of error as far as possible, the water obtained was in larger quantity. And as no fallacy belongs to the conducting the experiment in the more favourable mode in which it was first performed, (the assertion of the absorption of water from the air being altogether unfounded,) the quantity procured in that mode is to be regarded as the real result*.

The argument was maintained, that the water might be derived from hygrometric vapour in the gases submitted to experiment. This it was easy to refute. Dr. Henry had shown that ammonia after exposure to potash, and muriatic acid after exposure to muriate of lime, retain no trace of vapour whatever. And these precautions had been very carefully observed. The assertion was brought forward, too, only to account for the minute quantity of water obtained in that mode of conducting the experiment which affords the least favourable result; and, were it even admitted to all the extent to which it can be supposed to exist, is inadequate to account for the larger quantity obtained in the other.

* Nicholson's Journal, vol. xxxii. p. 186 &c.; vol. xxxiv. p. 271.

That

That the entire quantity of water contained in the muriatic acid gas is not to be looked for, is evident from the nature of the ammoniacal salt, particularly its volatility, whence the due degree of heat to effect the separation of the water cannot be applied. If the other muriates yield the greater part of their water, only when raised nearly to a red heat, (which is the case,) it is not to be supposed that muriate of ammonia shall do so at a temperature so much lower, as that which it can sustain without volatilization. What is to be expected, is a certain portion of water, greater as the arrangements employed are better adapted to obviate the peculiar difficulty attending the experiment. There is a production of water in every form of it; and there exists no just argument whence it can be inferred, that the quantity is less than what ought to be obtained. On the opposite doctrine, none whatever should appear.

To effect the more perfect separation of the water from the muriate of ammonia, I had performed the additional experiment of passing the salt formed from the combination of the two gases in vapour through ignited charcoal, on the principle that by the interposition of the charcoal the transmission of the vapour would be impeded, and it would be exposed to a more extensive surface, at which a high temperature would operate, while some effect might also be obtained from the affinities exerted by the carbonaceous matter. To remove any ambiguity from the effect of the charcoal, it was previously exposed in an iron tube to a very intense heat, until all production of elastic fluid had ceased; and removed, while still warm, into a tube of Wedgwood's porcelain, containing the muriate of ammonia, which was then placed across a furnace so as to be raised to a red heat. As soon as the vapour of the salt passed through the ignited charcoal, gas was disengaged, which was conveyed by a curved glass tube adapted to the porcelain one, and received in a jar over quicksilver. Moisture was at the same time pretty copiously deposited, condensing both in the glass tube in globules, and being brought in vapour with the gas, which it rendered opaque, and condensing on the surface of the quicksilver within the jars. The elastic fluid consisted of carburetted hydrogen and carbonic acid, products evidently of the decomposition by the ignited charcoal of a portion of the liberated water. In this experiment, then, the result was still more satisfactory than in the other. That no ambiguity arose from any effect of the charcoal in affording water, is evident from this,—that the water appeared at the moment the salt began to pass in vapour, and at a temperature far below that at which the charcoal had ceased to afford any gas. In another variation of the experiment,

ment, muriate of ammonia was passed in vapour through an ignited porcelain tube alone. Water was obtained in larger quantity than when the salt had been exposed to a heat short of its volatilization; and even the salt which had yielded water by that operation, afforded an additional quantity in this mode,—a proof of the more perfect separation of the water by the effect of a higher temperature*.

By all these results, then, I consider the existence of water in muriate of ammonia, and of course in muriatic acid gas, as demonstrated.

Dr. Ure has lately laid before the Society the result of another mode of conducting the experiment,—that of subliming the muriate of ammonia over some of the metals at the temperature of ignition. Water is thus stated to be obtained in considerable quantity, with a production of hydrogen gas.

No objection appeared to Dr. Ure's experiment, except, perhaps, that the salt operated on was not that formed by the direct combination of its constituent gases, but the common sal ammoniac, in which water might be supposed to exist, either as an essential or an adventitious ingredient, as it is abundantly supplied to it in the processes by which it is formed. I had found, indeed, in some of my former experiments †, that sal ammoniac yields no water when exposed to a heat sufficient to sublime it, but affords it only when exposed to a red heat by transmission of its vapour through an ignited tube;—that, therefore, (owing no doubt to its previous sublimation,) it contains apparently even less water than the salt formed by the combination of the two gases. Still, objections entitled to less consideration than this one, had been maintained in the course of this controversy. I therefore thought it right to repeat the experiment, with the necessary precaution to obviate it, and to observe the actual result.

Thirty grains of muriate of ammonia, formed from the combination of muriatic acid and ammoniacal gases, were put into a glass tube with a slight curvature. Two hundred grains of clean and dry iron filings were placed over it. The tube was put in a case of iron with sand, and placed across a small furnace, so that the middle part, where the iron filings were, was at a red heat, the extremity terminating in the mercurial trough. The salt, from the heat reaching the closed extremity of the tube, soon passed in vapour through the ignited iron. Gas issued from the extremity, and moisture appeared in the cold part of the tube. A large quantity of gas was collected, which had the odour quite strong of muriatic acid, and was in part condensed.

* Nicholson's Journal, vol. xxxi. p. 128.

† Id. vol. xxxiv. p. 274.
 condensed

densed by water; the residue burned with the flame of hydrogen. The tube, for several inches, was studded with globules of water, and was bedimmed with vapour further. I did not prosecute the experiment, so as to ascertain the weight of water produced, as I had other experiments in view, which I conceived might afford more conclusive results. But it proves the point it was designed to establish, that water is obtained from the salt formed by the combination of the gases, as well as from the common sal ammoniac.

My attention having been thus recalled to the subject, I have again executed the experiment in its original and simplest form,—that of obtaining water from the salt by heat alone; and to this I was led more particularly, as it had occurred to me, that a more perfect abstraction of its water might be effected, by conducting the experiment in an apparatus somewhat on the principle of the instrument invented by Dr. Wollaston, which he named the *Cryophorus*. In a retort of the capacity of seven cubic inches, fitted with a stop-cock, and exhausted, sixty cubic inches of ammoniacal gas were combined with the requisite quantity of muriatic acid gas, each previously carefully dried,—the former by exposure to potash, the latter by exposure to muriate of lime. The stop-cock was then detached from the retort; the excess of ammoniacal gas was removed by a caoutchouc bottle, and replaced by atmospheric air; the salt was pushed down from the neck; and it was connected with another similar retort, the joining of the two being secured by cement. This last retort was also fitted with a stop-cock adapted to a tubulature at its curvature; and heat being applied to it, a little of the included air was allowed to escape. It was then placed in a mixture of muriate of lime and ice, while the other, containing the muriate of ammonia, was placed in warm oil. The heat of this was raised to 420° of Fahrenheit: moisture condensed at the upper part of the neck, when the heat had been raised to 220°, and continued for some time to increase. It then diminished, from the continued application of the heat, carrying it forward into the cold retort; and at the end of the experiment a considerable part of the body of this was encrusted with a thin film of ice. This result, therefore, coincides entirely with what had been before obtained*.

* The other papers in this controversy by Dr. Ure and Dr. Murray, will be given in a subsequent number.