Experiments on carbonated hydrogenous gas; with a view to determine whether carbon be a simple or a compound substance ... / [William Henry].

To Dr. Babington
with best respects,
from the author

EXPERIMENTS

ON

CARBONATED HYDROGENOUS GAS;

WITH A VIEW

TO DETERMINE WHETHER CARBON BE A SIMPLE OR A COMPOUND SUBSTANCE.

BY

MR. WILLIAM HENRY.

FROM THE

PHILOSOPHICAL TRANSACTIONS.

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EXPERIMENTS, &c.

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THE progress of chemical science depends not only on the acquisition of new facts, but on the accurate establishment, and just valuation, of those we already possess: for its general principles will otherwise be liable to frequent subversions; and the mutability of its doctrines will but ill accord with the unvaried order of nature. Impressed with this conviction, I have been induced to examine a late attempt to withdraw from its rank among the elementary bodies, one of the most interesting objects of chemistry. The inferences respecting the composition of charcoal, deduced by Dr. AUSTIN from his experiments on the heavy inflammable air,* lead to changes so numerous in our explanations of natural phænomena, that they ought not to be admitted without the strictest scrutiny of the reasoning of this philosopher, and an attentive repetition of the experiments themselves. In the former, sources of fallacy may, I think, be easily detected; and in the latter, there is reason to suspect that Dr. AUSTIN has been misled by inattention to some collateral circumstances. Several chemists, however, of distinguished rank have expressed themselves satisfied with the

* Phil. Trans. Vol. LXXX. p. 51.

evidence thus produced in favour of the composition of charcoal; and amongst these it may be sufficient to mention Dr. BEDDOES, who has availed himself of the theory of Dr. AUSTIN, in explaining some appearances that attend the conversion of cast into malleable iron.*

The heavy inflammable air having been proved to consist of a solution of pure charcoal in light inflammable air, is termed, in the new nomenclature, carbonated hydrogenous gas. By repeatedly passing the electric shock through a small quantity of this gas, confined in a bent tube over mercury, Dr. AUSTIN found that it was permanently dilated to more than twice its original volume. An expansion so remarkable could not, as he observes, be occasioned by any other known cause than the evolution of light inflammable air.

When the electrified air was fired with oxygenous gas, it was found that more oxygen was required for its saturation than before the action of the elecric fluid; which proves that, by this process, an actual addition was made of combustible matter.

The light inflammable air disengaged by the electrization, proceeded, without doubt, from the decomposition of some substance within the influence of the electric fluid, and not merely from the expansion of that contained in the carbonated hydrogenous gas: for had the quantity of hydrogen remained unaltered, and its state of dilatation only been changed, there would not, after electrization, have been any increased consumption of oxygen.

The only substances in contact with the glass tube and mercury, in these experiments, besides the hydrogen of the dense

* Phil. Trans. Vol. LXXXI.

inflammable gas, were carbon and water; which last, though probably not a constituent of gases, is, however, copiously diffused through them. If the evolved hydrogen proceeded from the decomposition of the former of these two substances, it is evident that a certain volume of the carbonated hydrogenous gas must yield, after electrization, on combustion with oxygen, less carbonic acid than an equal volume of non-electrified gas; or, in other words, the inflammation of 20 measures of carbonated hydrogen, expanded by electricity from 10, should not afford so much carbonic acid as 10 measures of the unelectrified.

From the fact which has been before stated, respecting the increased consumption of oxygen by the electrified air, it follows, that in determining the quantity of its carbon by combustion, such an addition of oxygen should be made, to that necessary for the saturation of the gas before exposure to the electric shock, as will completely saturate the evolved hydrogen. For if this caution be not observed, we may reasonably suspect that the product of carbonic acid is diminished, only because a part of the heavy inflammable air has escaped combustion. It might, indeed, be supposed, that in consequence of the superior affinity of carbon for oxygen, the whole of the former substance, contained in the dense inflammable gas, would be saturated, and changed into carbonic acid, before the attraction of hydrogen for oxygen could operate in the production of water. But I have found that the residue, after inflaming the carbonated hydrogenous gas with a deficiency of oxygen, and removing the carbonic acid, is not simply hydrogenous but carbonated hydrogenous gas.

In the 2d, 5th, and 6th of Dr. AUSTIN's experiments, in which the quantity of carbon, in the electrified gas, was exa-

mined by deflagrating it with oxygen, the combustion was incomplete, because a sufficiency of oxygen was not employed; and Dr. AUSTIN himself was aware that, in each of them, "a "small quantity of heavy inflammable air might escape unal- "tered." It is observable, also, that the product of carbonic acid, from the electrified gas, increased in proportion as the combustion was more perfect. We may infer, therefore, that if it had been complete, there would have been no deficiency of this acid gas, and consequently no indication of a decomposition of charcoal. A strong objection, however, is applicable to these, as well as to most of Dr. AUSTIN'S experiments, that the residues were not examined with sufficient attention. In one instance we are told, that the remaining gas was inflammable, and in another, that it supported combustion like vital air. I need hardly remark, that a satisfactory analysis cannot be attained of any substance, without the most scrupulous regard not only to the qualities, but to the precise quantities of the products of our operations.

To the 8th and 9th experiments, the objection may be urged with additional weight, which has been brought against the preceding ones, that the quantity of oxygen, instead of being duly increased in the combustion of the electrified gas, was, on the contrary, diminished. Thus, in the 8th experiment, 2,83 measures of carbonated hydrogen were inflamed with 4,58 measures of oxygenous gas; but in the 9th, though the 2,83 measures were dilated to 5,16, and had therefore received a considerable addition of combustible matter, the oxygen employed was only 4,09. To the rest of Dr. AUSTIN'S experiments either one or both of the above objections are applicable.

The first and most important step, therefore, in the repetition

of these experiments, is to determine, whether the carbonated hydrogenous gas really sustains, by the process of electrization, a diminution of its quantity of carbon; because, should this be decided in the negative, we derive from the fact a very useful direction in ascertaining the true source of the evolved hydrogen. The following experiments were therefore made with a view to decide this question, and the error of Dr. AUSTIN, in employing too little oxygen, was carefully avoided.*

Experiment 1. In a bent tube, standing inverted over mercury, 94,5 measures of carbonated hydrogenous gas from acetite of pot-ash, were mixed with 107,5 of oxygen. The total, 202, was reduced by an explosion to 128,5, and was farther contracted by lime water to 54. A solution of hepar sulphuris left only 23 measures.

The diminution by lime water, *viz.* 74,5 measures, makes known to us the quantity of carbonic acid afforded by the combustion of 94,5 measures of carbonated hydrogenous gas: and the residue after the action of hepar sulphuris, *viz.* 23 measures, gives the proportion of azotic gas contained in the carbonated hydrogen; for the oxygenous gaz employed, which was procured

* The apparatus employed in these experiments, was the ingenious contrivance of Mr. CAVENDISH, and is described in the LXXV. Vol. of the Philosophical Transactions. In dilating the gas, I sometimes used a straight tube, furnished with a conductor, in the manner of Dr. PRIESTLEY, (see his Experiments on Air, Vol. I. plate I. fig. 16.). The bulk of the gases introduced, and their volume after the various experiments, were ascertained by a moveable scale, and by afterwards weighing the mercury which filled the tube to the marks on the scale; by which means I was spared the trouble of graduating the syphons. Each grain of mercury indicates one measure of gas; and though the smallness of the quantities submitted to experiment may be objected to, yet this advantage was gained, that the electrified gas could be fired at one explosion, as was done in the 4th, 6th, and 8th experiments. Errors, from variations of temperature and atmospherical pressure, were carefully avoided.

from oxygenated muriate of pot-ash, was so pure, that the small quantity used in this experiment could not contain a measurable portion of azotic gas.

Experiment 2. The same quantity of carbonated hydrogen was expanded by repeated electrical shocks to 188 measures. The addition of hydrogenous gas, therefore, amounted to 93,5. The gas, thus dilated, was fired, at different times, with 392,5 measures of oxygenous gas; and the residue, after these several explosions, was 203 measures. Lime water reduced it to 128,5, and sulphure of pot-ash to 19,5. In this instance, as in the former one, the product of carbonic acid is 74,5 measures.

Finding, from the first experiment and other similar ones, that the carbonated hydrogenous gas, which was the subject of them, contained a very large admixture of azotic gas, I again submitted to distillation a quantity of the acetite of pot-ash, with every precaution to prevent the adulteration of the product with atmospherical air. Such an adulteration, I have observed, impedes considerably the dilatation of the gas, and for a time even entirely prevents it. This explains the failure, which some experienced chemists have met with, in their attempts to expand the carbonated hydrogenous gas by electricity. Gas which is thus vitiated becomes, however, capable of expansion, after exposure to the sulphure of pot-ash.

Experiment 3. Carbonated hydrogen 340 measures were exploded with the proper proportion of oxygenous gas. The carbonic acid produced amounted to 380 measures, and the residue of azotic gas was 20 measures.

Experiment 4. The same quantity, when expanded to 690, gave on combustion 380 measures of carbonic acid, and 19,8 of azotic gas.

Experiment 5. Three hundred and fifteen measures of carbonated hydrogen yielded 359 measures of carbonic acid, and 18,5 measures of azote.

Experiment 6. The same quantity, after expansion to 600, afforded the same products of carbonic acid and azotic gases.

Experiments 7 and 8. As much carbonic acid was obtained by the combustion of 408 measures of carbonated hydrogenous gas, expanded from 200, as from 200 measures of the non-electric fired gas; and the residues of azotic gas were the same in both cases.

It is unnecessary to state the particulars of several other experiments, similar to those above related, which were attended with the same results. They sufficiently prove that the action of the electric spark, when passed through carbonated hydrogenous gas, is not exerted in the decomposition of carbon; for the same quantity of this substance is found after as before electrization. Even granting that charcoal is a compound, the constituents of which are held together by a very forcible affinity, it does not appear likely that the agency of the electric shock, which seems, in this instance, analogous to that of caloric, should effect its decomposition under the circumstances of these experiments. For it is a known property of charcoal to decompose water, when aided by a high temperature; and its union with oxygen is a much more probable event, when this body is present, than a separation into its constituent principles. As an argument, also, that water is the source of the light inflammable air in this process, it may be observed, that the dilatation in Dr. AUSTIN'S experiments could never be carried much farther than twice the

original bulk of the gas.* This fact evidently implies that the expansion ceased only in consequence of the entire destruction of the matter, whose decomposition afforded the light inflammable air, and this substance could not be carbon, because Dr. AUSTIN admits that a large portion, and I have shewn that the whole of it, still remains unaltered.

If the dilatation of the carbonated hydrogenous gas arose from the decomposition of water, the effect should cease when this fluid is previously abstracted. To ascertain whether this consequence would really follow, I exposed a portion of the gas, for several days before electrization, to dry caustic alkali. On attempting its expansion, I found that it could not be carried beyond one-sixth the original bulk of the gas. By 160 very strong explosions it attained this small degree of dilatation, but 80 more produced not the least effect; though the former number would have been amply sufficient to have dilated the gas, in its ordinary state, to more than twice its original volume. A drop or two of water being admitted to this portion of gas, the expansion went on as usual; and I may here observe, that when a little water gained admission into the tube along with the gas, in any experiment, which often happened before I had acquired sufficient expertness in transferring the air from water to mercury, the dilatation went on with remarkable rapidity.

* "After the inflammable air has been expanded to about double its original bulk," says Dr. AUSTIN, "I do not find that it increases further by continuing the shocks. "Conceiving that the progress of the decomposition was impeded by the mixture of the "other airs with the heavy inflammable, I passed the spark through a mixture of the "heavy inflammable air and light inflammable; but the expansion succeeded nearly as "well as when the heavy inflammable was electrified alone." Phil. Trans. Vol. LXXX. p. 52.

Carbonic acid gas, according to the discovery of M. MONGE,* undergoes, when submitted to the electric shock, a change similar to that effected on the carbonated hydrogen; and the expansion has been shewn, by Messrs. LANDRIANI and VAN MARUM,† to be owing to the same cause, *viz.* the extrication of light inflammable air. The added gas, M. MONGE ably contends, cannot proceed from any other source than the water held in solution by all aeriform bodies, the oxygen of which he supposes to combine with the mercury. That the decomponent of the water, however, in the experiments which I have described, is not a metallic body, will appear highly probable when we reflect that there is present in them a combustible substance, *viz.* charcoal, which attracts oxygen much more strongly than metals; and the following experiments evince that the mercury, by which the air was confined, had no share in producing the phænomena.

Experiment 9. A portion of carbonated hydrogenous gas was introduced into a glass tube closed at one end, into which a piece of gold wire was inserted that projected both within and without the cavity of the tube. The open end of the tube was then closed by a stopper perforated also with gold wire, so that electric shocks could be passed through the confined air, without the contact of any metal that has the power of decomposing water. On opening the tube with its mouth downwards, under water, a quantity of air immediately rushed out.

Experiment 10. The dilatation of the gas was found to proceed very rapidly when standing over water, and exposed to the action of the electric fluid, conveyed by gold conductors.

We have only, therefore, in the two preceding experiments,

* 29 *Journal de Physique*, 277. † 2 *Annales de Chimie*, 273.

one substance in contact with the gas which is capable of decomposing water, *viz.* charcoal. The union of this body with the oxygen of the water would be rendered palpable by the formation of carbonic acid; but Dr. AUSTIN did not observe that any precipitation was occasioned in lime water, by agitating it with the electrified gas. On passing up syrup of violets to the electrified air, with the expectation of its indicating the volatile alkali, as in the experiments of Dr. AUSTIN, no change of colour took place, though the test was of unexceptionable purity. On examining, however, whether any alteration of bulk had been produced in the air by the contact of this liquid, it appeared that of 709 measures, 100 had been absorbed. Suspecting that the absorption was owing to the presence of carbonic acid, I introduced some lime water to a volume of the expanded gas amounting to 556 measures, when they were immediately reduced to 512. The contraction would probably have been still more remarkable if the gas had been farther expanded before the admission of the liquid. The change in the lime water was very trifling; but my friend Mr. RUPP, who witnessed this as well as several of the other experiments, and who is much conversant in the observation of chemical facts, was satisfied that, after a while, he saw small flocculi of a precipitate on the surface of the mercury. This contraction of bulk cannot be ascribed to any other cause than the absorption of carbonic acid; for besides the fact that the colour of syrup of violets and of turmeric, which I also tried, were not affected by exposure to the electrified gas, I have this objection to the absorbed gas being ammoniac, that no diminution either of bulk or transparency occurred on the admixture of muriatic acid gas with the electrified air; whereas ammoniac would

have been exhibited under the form of a neutral salt. When water was passed up to this mixture of the two gases, there was an absorption not only of the muriatic gas, but of something more.

Conceiving that the demolition of charcoal, by the action of the electric fluid, was sufficiently proved by his experiments, Dr. AUSTIN assigns the evolved hydrogen as one of its constituents, and the other he concludes to be azote. This inference, however, rests almost entirely upon estimates, in which material errors may be discovered. Some of these it may be well to point out, for the satisfaction of such as have acquiesced in Dr. AUSTIN's opinion.

The carbonated hydrogenous gas submitted to Dr. AUSTIN's experiments clearly appears, from his own account, to have been largely adulterated with azotic gas. One source of its impurity he has disclosed, by informing us that the gas "had "been very long exposed to water;"* for Dr. HIGGINS has somewhere shewn that the heavy inflammable air, after standing long over water, leaves a larger residue of azote, on combustion, than when recently prepared.† It is probable also, that the proportion of azote derived from the water, would increase with the time of its exposure; and thus a fertile source of error is suggested, which appears wholly to have escaped Dr. AUSTIN's attention. In repeating his experiments, I was careful that comparative ones, on two equal quantities of the

* 80 Phil. Trans. 54.

† Similar facts respecting the deterioration of other gases, by standing over water, may be seen in Dr. PRIESTLEY's Experiments on Air, Vol. I. p. 59, 158. I found that oxygenous gas, from oxygenated muriate of pot-ash, acquired, by exposure a few weeks to water, .125 its bulk of azotic gas.

electrified and unelectrified gas, should be made without the intervention of any time that could vary the proportion of azote in either of the gases.

To the 9th experiment, in which the quantity of azote seems to have been increased by electrization, I must repeat the objection, that a sufficiency of oxygenous gas was not used in the combustion. In the 8th experiment, 2,83 of the unelectrified air were fired with 4,17 oxygenous gas, and only 0,15 of the latter remained above what was sufficient for saturation; but in the 9th, though the 2,83 measures were expanded to 5,16, the quantity of oxygen employed was 0,08 less than in the former experiment; and it may therefore be presumed that a small quantity of inflammable air might escape unaltered, and might add apparently to the product of azote. In the 8th experiment also, the portion of oxygenous gas that was more than sufficient to saturate the carbonated hydrogen, would probably combine, in part, with the remaining azote, as in the experiments of Dr. HIGGINS* and Dr. PRIESTLEY.† But in the 9th, the quantity of oxygenous gas was hardly sufficient to saturate both kinds of inflammable air after electrization, and could not therefore diminish the azotic gas. When the proportion of oxygen is duly increased, and the inflammation of the electrified air is performed in small portions, there is no augmentation, but on the contrary a decrease of the quantity of the azote, as will appear on comparing the 1st and 2d of the experiments which I have related.

Two circumstances were observed, in the experiments of Dr. AUSTIN, which have not been noticed in the preceding account

* Experiments and Observations on acetous Acid, &c. p. 295.

† 79 Phil. Trans. 7.

of the repetition of them, *viz.* the appearance of a deposit from the carbonated hydrogenous gas during its electrization, and the formation of ammoniac by the same process. In some experiments, which I made on the first portion of gas, both these facts were sufficiently apparent; but neither of them occurred on electrifying the gas which was afterwards procured. Suspecting that the cessation of them arose from the superior purity of the latter portion from azotic gas, I passed the electric shock through a mixture of carbonated hydrogen with about one-fourth its bulk of azote, and thus again produced the precipitate, which would have been of a white colour, if it had not been obscured by minute globules of mercury, that were driven upwards by the force of the explosion. An infusion of violets was tinged green when admitted to the electrified gas; but the change of colour did not occur instantly, as happens from the absorption of ammoniacal gas; and required for its production that the liquid should be brought extensively into contact with the inner surface of the tube. From this effect on a blue vegetable colour, we may infer that the precipitate was an alkaline substance, and probably the carbonate of ammoniac; but the quantity was much too minute to be the subject of more decisive experiment.

I shall conclude this memoir, with a brief summary of the facts that are established by the preceding experiments.* Those included under the first head are deducible from the experiments of Dr. AUSTIN.

* Since this paper was written I have extended the inquiry to phosphorated hydrogenous gas, which expands equally with the carbonated hydrogen; loses its property of inflaming when brought into contact with oxygenous gas; and affords evident traces of a production of phosphorous or phosphoric acid.

1. Carbonated hydrogenous gas, in its ordinary state, is permanently dilated by the electric shock to more than twice its original volume; and as light inflammable air is the only substance we are acquainted with, that is capable of occasioning so great an expansion, and of exhibiting the phænomena that appear on firing the electrified gas with oxygen, we may ascribe the dilatation to the production of hydrogenous gas.

2. The hydrogenous gas evolved by this process does not arise from the decomposition of charcoal; because the same quantity of that substance is contained in the gas after, as before electrization.

3. The hydrogenous gas proceeds from decomposed water; because when this fluid is abstracted as far as possible from the carbonated hydrogenous gas, before submitting it to the action of electricity, the dilatation cannot be extended beyond one-sixth its usual amount.

4. The decomponent of the water is not a metallic substance, because carbonated hydrogenous gas is expanded when in contact only with a glass tube and gold, a metal which has no power of separating water into its formative principles.

5. The oxygen of the water (when the electric fluid is passed through carbonated hydrogenous gas, that holds this substance in solution), combines with the carbon, and forms carbonic acid. This production of carbonic acid, therefore, adds to the dilatation occasioned by the evolution of hydrogenous gas.

6. There is not, by the action of the electric matter on carbonated hydrogenous gas, any generation of azotic gas.

7. Carbon, it appears, therefore, from the united evidence of these facts, is still to be considered as an elementary body; that is, as a body with the composition of which we are unacquainted, but which may nevertheless yield to the labours of some future and more successful analyst.