



PHILOSOPHICAL
TRANSACTIONS.

XI. *Experiments on the Phlogification of Spirit of Nitre.*
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Read March 26, 1789.

AS the colouring of spirit of nitre has some connection with the doctrine of phlogiston, to which I propose to give my best attention, I have lately resumed my experiments on that subject, and beg leave to lay the result of them before the Society.

In my former experiments, vol. IV. p. 2. I found that the colourless acid became smoking, or orange-coloured, and emitted orange-coloured vapours, on being exposed to heat in long glass tubes, hermetically sealed; and I then concluded, that

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this effect was produced by the action of *heat*, evolving, as it were, the phlogiston previously contained in the acid. Afterwards, having found that it was not *heat*, but *light* only, that was capable of giving colour to spirit of nitre, contained in phials with ground stoppers, in the course of several days; and that in this case the effect was produced by the action of *light* upon the *vapour*, which gradually imparted its colour to the liquor on which it was incumbent (see Vol. V. p. 342.), I was led to suspect, that as the glass tubes, in which I had formerly exposed this acid to the action of heat, were only held near to a fire, in the day-light, or candle-light, it might have been this *light*, which, in these circumstances, had, at least in part, contributed to produce the effect.

In order to ascertain whether the light had had any influence in this case, I now put the colourless spirit of nitre into long glass tubes, like those which I had used before, and also sealed them hermetically, as I had done the others; but, instead of exposing them to heat in the open air, from which light could not be excluded, I now shut them up in gun barrels, closed with metal screws, so that it was impossible for any particle of light to have access to them; and I then placed one end of the barrels so near to a fire as was sufficient to make the liquor contained in the tube to boil, which I could easily distinguish by the sound which it yielded. The consequence was, that in a short time the acid became as highly coloured as ever it had been when exposed to heat without the gun barrel. It was evident, therefore, that it had been mere *heat*, and not *light*, which had been the means of giving this colour to the acid, and which has been usually termed *phlogisticating* it.

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When I made the former experiments, I had no suspicion that the *air* contained in the tube had any concern in the result of them; and, in those which I made in the phials in a moderate heat, I found that the acid received its colour when the best *vacuum* that I could make with an air pump was over it,

My friend Mr. KIRWAN, however, having always suspected, that the *air* was a principal agent in the business, I at this time gave particular attention to this circumstance; supposing that, if any part of the common air had been imbibed, it must have been the *phlogificated*, and that it was the phlogiston from this kind of air which had phlogificated the acid. The real result, however, was not so much in favour of this supposition as I had expected; for the principal effect of the process was the emission of dephlogificated air, so that the acid seems to become what we call phlogificated, by parting with this ingredient in its composition.

I put a small quantity of the colourless acid into a long glass tube, which besides the acid would have contained 1.23 ounce measures of common air, but that the vapour of the acid excluded about one-twentieth of the quantity. Having sealed the tube hermetically, I shut it up in a gun barrel, in the manner mentioned above, and exposed it to a boiling heat for several hours, and then opening it under water there came out of it 2.03 ounce measures of air, very turbid and white; and when it was examined, it appeared to be of the standard of 1.02, with two equal measures of nitrous air; when with one measure of the same nitrous air the standard of the common air was 1.07. The quantity of phlogificated air absorbed in this experiment I ascertained by the following computation.

As one measure of common air, and an equal quantity of nitrous air were reduced to 1.07 m. it is evident, that 0.93 m.

had disappeared; but as this was effected by the nitrous air uniting with all the dephlogisticated air contained in the common mass, and as they unite in the proportion of one measure of dephlogisticated air to two measures of nitrous air, one-third of the 0.93 m. *viz.* 0.31 m. will be the quantity of dephlogisticated air that was contained in the one measure of common air on which the experiment was made, the remainder, *viz.* 0.69, having been phlogisticated air. The common air contained in the tube would have been 1.23 oz. m.; but deducting from it one-twentieth in the whole, it will only be 1.17 oz. m. I then say, if one measure of this air contains 0.69 m. of phlogisticated air, 1.17 oz. m. will contain 0.8073 oz. m. of phlogisticated air. This, therefore, was the quantity of phlogisticated air which had been exposed to the action of the acid of nitre in the tube.

In order to find how much of the same kind of air was contained in the tube *after* the process, I examined the result above mentioned in the following manner. Since two measures of nitrous air, and one of this residuum, were reduced to 1.02 m. it is evident, that 1.98 m. had disappeared, and consequently one-third of this quantity, *viz.* 0.66 m. had been dephlogisticated air, and that the remainder of the measure, *viz.* 0.34, had been the proportion of phlogisticated air in one measure of this residuum. If then one measure of this residuum contains 0.34 m. of phlogisticated air, 2.03 oz. m. will contain 0.6902 oz. m. which is less than 0.8073 oz. m. the quantity contained in it before the process; so that a part of the phlogisticated air had been either absorbed or decomposed, its phlogiston having been imbibed by the acid at the same time that it had emitted the dephlogisticated air.

In another process, of the same kind, the glass tube contained 0.92 oz. m. of common air, and the air that came out of it after the process was one ounce measure, of the standard of 1.6 with two measures of nitrous air, and computing as I did before, the phlogificated air in the tube before the process was 0.6072 oz. m., and after the process 0.54 oz. m.

In these computations it is supposed, that the air emitted by the acid was perfectly pure, so that all the phlogificated air that is found after the process is supposed to have been contained in the common air confined in the tube before it was commenced. But I found, that the air emitted by the acid is by no means perfectly pure, so that much of the impurity must be ascribed to this circumstance.

In order to exclude all air from the contact of the acid, I made a quantity of it to boil in the tube, and when the vapour had expelled all the air, I sealed it hermetically, in the manner in which water hammers are made; and then exposing it to heat, found that it acquired as high a colour as when air had been confined along with it; so that it is evident, that *air* is not necessary to this effect. When the tube was opened under water, a quantity of dephlogificated air rushed out, exceedingly white as before; but when I examined it, I found it to be of the standard of only 0.66. When this impurity is considered, it will appear, that when much air is yielded in this process, some phlogificated air may have been imbibed, though, computing in the manner above mentioned, the phlogificated air after the process should be in greater quantity than was contained in the tube before it, as was the case in the following experiment.

In a glass tube which, besides the acid, contained 1.13 oz. m. of common air, I exposed colourless spirit of nitre to heat

till it became of a deep orange colour; and when it was opened under water, there came out of it 2.83 oz. m. of air exceedingly turbid, of the standard of 0.66, with two equal quantities of nitrous air, when that of the common air, with one equal quantity of nitrous air, was 1.07. Computing in the manner above mentioned, there was in the tube before the process 0.7477 oz. m. of phlogificated air, and after the process 0.8792 oz. m. But the dephlogificated air, amounting to 1.7 oz. m. being of the standard of 0.66, will be found to contain 0.374 oz. m. of phlogificated air, which being deducted from 0.8792, there will remain only 0.5052 oz. m. which is considerably less than 0.7477 oz. m.

That the nitrous acid can become coloured, without imbibing any thing from phlogificated air, is evident not only from its becoming so when heated *in vacuo*, as described above, but also, when it was in contact with any other kind of air, as free from phlogificated air as I could make it. But from the manner in which these experiments were necessarily made, it was impossible intirely to exclude phlogificated air, either as part of the atmospheric air, or as contained in the impurities of the air that I made use of; for I first filled the tube with spirit of nitre, then plunging the orifice of it in a vessel of the same, I introduced a quantity of the air which I wished to expose to it. After this, putting my finger upon the orifice, I turned it upside down, and applying to it the closed end of a glass tube, of about the same diameter, I sealed it hermetically with a blow-pipe as expeditiously as I could. This is a necessary imperfection in the experiment; but I know not how to remedy it, if any of the acid is to be left in the tube. However, the phlogificated air introduced in this manner from the atmosphere must have borne a very small proportion to the air in

the tube; and some objection will always remain to the experiment from the impurity of the air made use of.

Having repeatedly observed, that the acid became coloured in consequence of being exposed to heat in contact with any kind of air whatever, I exposed at the same time, and in the same circumstances, three equal quantities of the same colourless spirit of nitre, in three nearly equal tubes, one containing dephlogificated, another phlogificated, and a third inflammable air; that, if there should be any difference in the colouring of the acid in these cases, it might be the more easily perceived. But though I gave all the attention that I could, I did not perceive that there was any difference, except what arose from some of the tubes being placed a little nearer the fire than the rest; and, by changing their places, the colour was at length the very same in them all.

As in these three cases I examined the air before and after the process, in the manner above mentioned, I shall just recite the particulars.

Of the dephlogificated air the tube contained before the process 1.46 oz. m. of the standard of 0.67, and after the process it contained 1.76 oz. m. of the standard of 0.77; a difference owing in part to the mixture of common air, which could not be excluded in the sealing of the tube, and in part to the air emitted from the acid not being pure.

Of the phlogificated air, the tube contained 1.3 oz. m. and after the process 1.95 oz. m. of the standard of 1.38.

Of the inflammable air, the tube contained before the process 1.52 oz. m. and after the process 1.9 oz. m. of the standard of 1.8. They were all measured by a mixture of two equal quantities of nitrous air.

If these results be examined as that of the first experiment, with common air, it will be found that, in all these processes, there was less phlogisticated air, or inflammable air, after the process than before; and this result being thus uniform, I cannot help concluding, that this kind of air is in part decomposed, and purified by this means; so that by this emission of dephlogisticated air which the heat expels from the acid, something, and probably phlogiston, is at the same time imbibed from it; which proves that phlogisticated air is no simple substance, but a compound, and that phlogiston is one constituent part of it; for this acid acquires the same colour, and all the same properties, by adding to it any thing that is supposed to contain phlogiston.

As the spirit of nitre can be rendered smoking, or phlogisticated, by the mere expulsion of dephlogisticated air, it is evident, that it contains two principles in close affinity with each other, and that nothing is necessary to render either of them conspicuous besides the absence of the other.

It is also natural to suppose, that, for the same reason that the *dephlogisticating* principle (as it may be called) is expelled, the *phlogisticating* principle should enter; so that the purification of the air in contact with the acid may be a necessary consequence of the expulsion of the pure air contained in it, the whole tending, as it were, to an equilibrium in this respect. It is therefore by no means difficult to conceive, that phlogiston should be extracted from the contiguous air at the same time that the dephlogisticated air *not pure* (that is, containing a mixture of phlogisticated air) is driven out of it; for the acid always containing phlogiston, whatever air is contained in it, and expelled from it, may necessarily contain phlogiston or phlogisticated air; but the purer air may be emitted, and the less

less pure air be imbibed, till the whole come to be of the same quality. It may, however, perhaps follow from the emission of impure dephlogificated air, and the imbibing of phlogificated air at the same time, that the former does not consist of dephlogificated and phlogificated air loosely mixed, but of some intimate union of dephlogificated air with phlogiston, though they may be separated by a mixture of nitrous air, and other processes, in the very same manner as dephlogificated air may be separated from a loose mixture of phlogificated air.

It is evident from these experiments, that a red heat is not necessary to the conversion of nitrous acid into pure air, though this process, as appeared by my former experiments, produces this effect most quickly and effectually.

I cannot help considering the experiments above recited to be favourable to the doctrine of the phlogiston, and unfavourable to that of the decomposition of water, though not decisively so; for since the red vapour of spirit of nitre unquestionably contains the same principle that has been termed phlogiston, or the principal element in the constitution of inflammable air, and according to the antiphlogistians this is one constituent part of water, they must suppose, that the water in this acid is decomposed by a much more moderate heat than in most other cases. In general, I believe, they have thought a red heat to be necessary for this purpose. It is evident, that the conversion of water into steam by boiling, or by any heat that can be given to it under the strongest pressure, has no tendency whatever to decompose it. But if the mere boiling of water in nitrous acid could produce this effect, I do not see why the same should not be the case when water alone is boiled.

I think it will also be more difficult to explain the purification of the incumbent atmospherical air on the antiphlogistic

than on the phlogistic hypothesis, whatever be the constitution of phlogificated air.

As, in the experiments above mentioned, *heat* without *light* gives colour to the nitrous acid, and the reflection or refraction of light is always attended with heat, it may perhaps be *heat* universally that is the means of imparting this colour, though the mode of its operation be at present unknown. And in these experiments, as well as the former, it is the *vapour* that first receives the colour, and imparts it to the liquid when it is sufficiently cold to receive it.

The rushing out of a quantity of turbid white air from a transparent tube, quite cold, is a striking phænomenon in these experiments. It may be worth while to examine of what it is that this remarkable cloudiness of the air consists. There is the same appearance, as I have more than once observed, in the rapid production of any kind of air, which is perfectly transparent as it passes along the glass tube through which it is transmitted, till it comes into contact with the water in which it is received.

P. S. Not to multiply my communications on the subject of *phlogiston* unnecessarily, I would beg leave to observe, at the close of this article (in reply to what has been objected to my former experiments, as being liable to exception from the phlogificated air which could not be excluded from the dephlogificated air when it was decomposed by means of inflammable air) that I have found the process I made use of to have no tendency whatever to decompose phlogificated air. Indeed, nothing that we have hitherto known concerning this kind of air could make it probable, that mere *heat*, in contact with dephlogificated or inflammable air, *could* have this effect. And

it is of no consequence whatever to say, that any particular substance, imagined to be decomposed, is *present* in a process, unless it can be shewn that, in that process, there are agents capable of decomposing it. If mere *heat* (which is all that my process requires) would decompose phlogificated air, and reduce it to nitrous acid, the transmission of common air (which consists of dephlogificated and phlogificated air) through a red hot tube would have this effect, which it is well known not to have.

But what I have asserted above is a conclusion which I have drawn from comparing the decomposition of dephlogificated air by the two processes with nitrous and inflammable air. That nitrous air, when mixed with dephlogificated air, has no tendency to produce phlogificated air, is evident from the almost total evanescence of both of them, when they are very pure, and mixed in due proportions; and that nitrous air has no effect on phlogificated air is well known. If then the firing of dephlogificated and inflammable air had a tendency to decompose any portion of phlogificated air, which should happen to be mixed with them, less would remain after the firing of inflammable and impure dephlogificated air than after mixing it with nitrous air; for as the impurities of dephlogificated air consist of phlogificated air, those would disappear in a greater proportion in the former process than in the latter. But by many careful trials I find, that I can reduce any kind of dephlogificated air no farther by a mixture of inflammable air than I can by nitrous air. When the proportions are well managed, the diminution is as nearly as possible the same in both the cases.

I must observe, however, that it requires more nitrous air than inflammable air (from iron by steam) to produce this effect

in the proportion of about 10 to 9 ; so that nitrous air does not contain quite so much phlogiston as an equal bulk of inflammable air, as I had before thought to be the case.

In this Paper it will be observed, that I make the diminution of common air by nitrous air to be considerably less than I have usually done before. This has been the consequence of giving the two kinds of air a little agitation at the instant of mixing, which will generally make the diminution less by two tenths of a measure. But I have found, that when these mixtures of air, with and without agitation, have been kept some time, they approach to an equality of bulk.

At the same time I have observed, what I think not a little extraordinary, that agitation prevents the greatest diminution of dephlogisticated and nitrous air. I have found it to be 2.5 without agitation, and 6. with it.

The less diminution of the mixture of nitrous and common air is probably owing to the presence of so much phlogisticated air, which impedes the meeting of the nitrous air with the dephlogisticated air in the mixture ; because I find the same to be the case when I mix the same proportion of inflammable air with dephlogisticated air ; and when dephlogisticated air is agitated with nitrous air, the *water* may impede their union, as the phlogisticated air did before.

There is, therefore, no source of the *nitrous acid* which I find on the decomposition of dephlogisticated and inflammable air, besides the union of those two kinds of air, which therefore do not make *mere water*, as the antiphlogistians suppose.

