PHILOSOPHICAL

TRANSACTIONS.

XI. *Experiments on the Phlogiſtication of Spirit of Nitre.*

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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

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.

When

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 *phlogiſticated*, and that it was the phlogiſton from this kind of air which had phlogiſticated 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 dephlogiſticated air, ſo that the acid ſeems to become what we call phlogiſticated, 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 phlogiſticated 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

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 phlogiſticated 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 phlogiſticated 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 dephlogiſticated 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 phlogiſticated air may have been imbibed, though, computing in the manner above mentioned, the phlogiſticated 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 phlogiſticated air, and after the proceſs 0.8792 oz. m. But the dephlogiſticated air, amounting to 1.7 oz. m. being of the ſtandard of 0.66, will be found to contain 0.374 oz. m. of phlogiſticated 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 phlogiſticated 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 phlogiſticated air as I could make it. But from the manner in which theſe experiments were neceſſarily made, it was impoſſible intirely to exclude phlogiſticated 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 blowpipe 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 phlogiſticated 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 dephlogiſticated, another phlogiſticated, 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 dephlogiſticated 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 phlogiſticated 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.

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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 phlogiſtion, 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

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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 dephlogiſticated air, and the imbibing of phlogiſticated air at the ſame time, that the former does not conſiſt of dephlogiſticated and phlogiſticated air looſely mixed, but of ſome intimate union of dephlogiſticated air with phlogiſton, though they may be ſeparated by a mixture of nitrous air, and other proceſſes, in the very ſame manner as dephlogiſticated air may be ſeparated from a looſe mixture of phlogiſticated 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 phlogiſticated 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 phlogiſticated air which could not be excluded from the dephlogiſticated 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 phlogiſticated air. Indeed, nothing that we have hitherto known concerning this kind of air could make it probable, that mere *heat*, in contact with dephlogiſticated 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 phlogiſticated air, and reduce it to nitrous acid, the tranſmiſſion of common air (which conſiſts of dephlogiſticated and phlogiſticated 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 dephlogiſticated air by the two proceſſes with nitrous and inflammable air. That nitrous air, when mixed with dephlogiſticated air, has no tendency to produce phlogiſticated 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 phlogiſticated air is well known. If then the firing of dephlogiſticated and inflammable air had a tendency to decompoſe any portion of phlogiſticated air, which ſhould happen to be mixed with them, leſs would remain after the firing of inflammable and impure dephlogiſticated air than after mixing it with nitrous air; for as the impurities of dephlogiſticated air conſiſt of phlogiſticated 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 dephlogiſticated 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.