II. *Objections to the Experiments and Observations relating to the Principle of Acidity, the Composition of Water, and Phlogiston, considered; with farther Experiments and Observations on the same Subject. By the Rev.* Joseph Priestley, *LL.D. F. R. S.*

Read November 27, 1788.

HAVING never failed, when the experiments were conducted with due attention, to procure some *acid* whenever I decomposed dephlogisticated and inflammable air in close vessels, I concluded that an acid was the necessary result of the union of those two kinds of air, and not water only; which is an hypothesis that has been maintained by Mr. LAVOISIER and others, and which has been made the basis of an intirely new system of chemistry, to which a new system of terms and characters has been adapted. The *facts* that I alleged were not disputed; but to my *conclusion* it was objected, that the acid I procured might come from the phlogisticated air, which in one of my processes could not be excluded; and that it was reasonable to conclude that this was the case, because Mr. CAVENDISH had procured the same acid, *viz.* the nitrous, by decomposing dephlogisticated and phlogisticated air with the electric spark. In other cases it has been said, that the *fixed air* I procured came from the *plumbago* in the iron from which my inflammable air had been extracted.

With respect to the former of these objections I would observe, that my process is very different from that of Mr.

CAVENDISH;

CAVENDISH; his decompoſition being a very ſlow one by electricity, and mine a very rapid one by *ſimple ignition*, a proceſs by which phlogiſticated air, as I found by actual trial, was not at all affected; the dephlogiſticated and inflammable airs uniting, and leaving the phlogiſticated air (as they probably would any other kind of air with which they might have been mixed) juſt as it was.

I would alſo obſerve, that there is no contradiction whatever between Mr. CAVENDISH's experiment and mine, ſince phlogiſticated air may contain phlogiſton, and by means of electricity this principle may be evolved, and unite with the dephlogiſticated air (or with the acid principle contained in it) as in the proceſs of ſimple ignition the ſame principle is evolved from inflammable air, in order to form the ſame union; in conſequence of which, the water, which was a neceſſary ingredient in the compoſition of both the kinds of air, is precipitated. That in other circumſtances than thoſe in which I made the experiments, the acid wholly eſcaped, and nothing but water was found, may be eaſily accounted for, from the ſmall quantity of the acid principle in proportion to the water, and the extreme volatility of it, owing, I preſume, to its high phlogiſtication when formed in this manner.

In order to aſcertain the effect of the preſence of phlogiſticated air in this proceſs, I now not only repeated the experiment of mixing a given quantity of phlogiſticated air with the two other kinds of air, and found, as before, that it was not affected by the operation; but I made the experiment with atmoſpheric air, inſtead of dephlogiſticated. Since the air of the atmoſphere contains a greater proportion of phlogiſticated air, it might be expected that, if the acid I got before came from the ſmall quantity of phlogiſticated air which I could

not

not possibly exclude, I should certainly get more acid, when, instead of endeavouring to exclude it, I purposely introduced a greater quantity. But the consequence was the production of much less acid than before, the liquor I procured being sometimes not to be distinguished from pure water, except by the greatest attention possible: for though the decomposition was made in the same copper vessel which I used in the former experiments, there was now no sensible tinge of green colour in it.

When I repeated this experiment in a glass vessel, I perceived, as I imagined, the reason of the small produce of acid in these new circumstances: for the vessel was filled with a vapour which was not soon condensed, and being diffused through the phlogisticated air (which is not affected by the process) is drawn away along with it, when the exhausting of the tube is repeated; whereas, when there is little or no air in the vessel besides the two kinds which unite with each other, and are decomposed, the acid vapour, having nothing to attach itself to and support it (by being entangled with it) much sooner attacks the copper, making the deep green liquor which I have described. Sometimes, however, I have procured a liquor which was sensibly green by the decomposition of atmospheric and inflammable air, but by no means of so deep a colour, or so sensibly acid, as when the dephlogisticated air is used.

The extreme volatility of the acid thus formed (and which accounts for the escape of some part of it in all these processes) is apparent from this circumstance, that if the explosions be made in quick succession (the tube being exhausted immediately after each of them, and filled again as soon as possible) no liquor at all will be collected, the whole of the

 acid

acid vapour, together with the water with which it was combined, being drawn off uncondenſed in every proceſs. I once made twenty ſucceſſive exploſions of this kind, in a copper tube, out of which I found that I drew 37 ounce meaſures of air by the action of the pump, and found not a ſingle drop of liquid, though near an hour was employed in the whole proceſs, and the veſſel was never made more than a little warmer than my hand. This was a degree of heat by no means ſufficient to keep the whole of any quantity of water in a ſtate of vapour; and is a circumſtance that of itſelf ſufficiently proves, that the vapour did not conſiſt of water only.

Indeed, I think it impoſſible for any one to *ſee* this vapour in a tall glaſs veſſel, and eſpecially to obſerve how it falls from one end of it to the other, and the time that is required to its wholly diſappearing, without being ſatisfied that it conſiſts of ſomething elſe than mere water, the vapour of which would be more equally diffuſed. If the appearance to the eye ſhould fail to convince any perſon of this, the ſenſe of *ſmell* would do it: for even in a glaſs veſſel it is very offenſive, though it might not be pronounced to be *acid*. I conjecture, however, that this, and every other ſpecies of *ſmell*, is produced by ſome modification of the acid or alkaline principle. Some may be diſpoſed to aſcribe this ſmell to the *iron* from which the inflammable air was produced; but the ſmell is the ſame, or nearly ſo, when the air is from tin, and would probably be the ſame if it were from any other ſubſtance.

Beſides uſing atmoſpheric air, which contains a greater proportion of phlogiſticated air, I have ſometimes uſed dephlogiſticated air which was not very pure; and in this caſe I have always obſerved, that the liquor I procured had leſs colour, and was leſs ſenſibly acid.

These observations might, I should think, satisfy any reasonable person, that the acid liquor which I procured by the explosion of dephlogisticated and inflammable air in close vessels did not come from the phlogisticated air which could not be excluded, whether it was that which remained in the vessel after exhausting it by the air pump, or that with which the dephlogisticated air was more or less contaminated.

But besides these experiments, in which I procured the green acid liquor by the explosion of dephlogisticated and inflammable air in close vessels, I made another, to which I thought the same objection could not have been made, because no air pump was used in it, and nothing but the purest dephlogisticated air was employed, being separated in the process from *precipitate per se* in contact with the purest inflammable air in a glass vessel which had been previously filled with mercury. Accordingly, the only objection made to *this* experiment was, that the preparation I made use of might be impure, containing something which might yield phlogisticated air. This appeared to me highly improbable, as the precipitate had been made by M. CADET, and for the purpose of philosophical experiments. Besides, if the heat of a burning lens should dislodge phlogisticated air from any unperceived impurity in this preparation, mere *heat* will not decompose this air. Let any person try the effect of a lens on such air, or any substance containing it, and produce an acid if he can.

M. BERTHOLLET, however, thinking that this might be the case, desired that I would send him a specimen of my precipitate *per se*. Accordingly, I sent him all that remained of it; and, in return, he sent me a quantity on the goodness of which I might depend. With this preparation I repeated my former experiment; and, by giving more attention to the

 process,

procefs, found it to be far more decifively conclufive in favour of my opinion than I had imagined. In the former experiment I had attended only to the drop of *water* which was found in the veffel in which the procefs was made; and finding that it turned the juice of turnfole red, I concluded, that it contained nitrous acid: but I now examined the *air* that remained in the veffel, and found that a confiderable proportion of it was fixed air; fo that I am now fatisfied *this* was the acid with which it was impregnated, and not the *nitrous*. Still, however, fome acid is the conftant refult of the union of the two kinds of air, and not water only. A quantity of the fame precipitate *per fe* yielded no fixed air by heat.

Comparing this experiment with that in which iron is ignited in dephlogifticated air, this general conclufion may be drawn, *viz.* that when either inflammable or dephlogifticated air is extracted from any fubftance in contact with the other kind of air, fo that one of them is made to unite with the other in what may be called its *nafcent ftate*, the refult will be *fixed* air; but that if both of them be completely formed before their union, the refult will be *nitrous acid.*

It has been faid, that the fixed air produced in both thefe experiments may come from the *plumbago* in the iron from which the inflammable air is obtained. But fince we afcertain the quantity of plumbago contained in iron by what remains after its folution in acids, it is in the higheft degree improbable, that whatever plumbago there may be in iron, any part of it fhould enter into the inflammable air procured from it. Befides, according to the antiphlogiftic hypothefis, all inflammable air comes from water only.

As it cannot be faid, that any real fixed air is found in inflammable air from iron (fince it is not difcoverable by lime-

 water)

water) it muſt be ſuppoſed, that the elements, or component parts of fixed air are in it; but one of theſe elements is pure air, and the mixture of nitrous air ſhews, that it contains no ſuch thing, though, according to M. LAVOISIER, fixed air contains 72 parts in 100 of pure air.

However, being apprized of this objection to inflammable air from iron, I made uſe of inflammable air from *tin*, and I had the ſame reſult as with that from iron. I alſo calculated the weight of the fixed air which I got in the proceſs, and comparing it with the plumbago which the iron neceſſary to make the inflammable could have contained, I found, that, in all the caſes, it far exceeded the weight of the plumbago; ſo that it was abſolutely impoſſible, that the fixed air which I found ſhould have had this origin. For the greater ſatisfaction, I ſhall recite the particulars of a few experiments of this kind.

In ten ounce meaſures of inflammable air from malleable iron I revived *red precipitate* till there remained only 1.1 oz. meaſure of air, and of this 0.07 oz. m. was fixed air, being completely abſorbed by water. The weight of this air would be 0.063 gr. But, ſince 960 grains of iron will yield 1054 oz. meaſures of inflammable air, the iron employed in procuring all the inflammable air that was uſed in this experiment, *viz.* 8.9 oz. meaſures (without allowing for any that went to the revivification of the mercury) would be 8.1 grains; and ſince M. BERGMAN ſuppoſes, that 100 grains of iron contains 0.12 gr. of plumbago, the quantity of it in this iron would only be 0.01008 gr. which is not quite a ſixth part of the weight of the fixed air.

With the *precipitate per ſe*, ſent me by M. BERTHOLLET, I revived mercury till 8½ oz. m. of inflammable air was reduced to 2½ oz. m., and of this 0.04 oz. m. at leaſt was fixed air. This

This is not quite ſo much in proportion as in the preceding experiment, but abundantly more than the weight of the plumbago.

In 8 oz. m. of inflammable air I revived *minium* (which I found to have exactly the ſame effect in this proceſs as red precipitate, or precipitate *per ſe*), till it was reduced to 1.2 oz. m.; and of this 0.028 oz. m. was fixed air, which would exceed the weight of the plumbago more than three times. In reviving lead from maſſicot (which I prepared by expelling the pure air from minium) I had no fixed air in the reſiduum.

In 7 oz. m. of inflammable air from tin by ſpirit of ſalt, I revived red precipitate till it was reduced to 1.1 oz. m.; and in this the fixed air was ſomething more than in proportion to that in the laſt experiment.

In my laſt volume of Experiments, p. 30. I mentioned ſome inſtances of the revival of red precipitate in inflammable air, without finding any fixed air, though in one I perceived a ſlight appearance of it. To this I can only ſay, that I now always find it, and have, in the preceding caſes, meaſured the quantity of it; ſo that, though I did not find any before, I muſt preſume that I did not uſe the ſame precautions that I did at this time: and it is poſſible, that I might not attend to the effect of admitting a large quantity of water to a ſmall quantity of fixed air, which would preſently abſorb the greateſt part of it. I alſo think I recollect, that I then continued the proceſs as far as I poſſibly could, and conſequently left very little air in the veſſel; whereas I now purpoſely left a good deal, that the admiſſion of water might have leſs effect on the fixed air diffuſed through it.

This alſo may be ſaid in favour of the greater accuracy of my preſent experiments, that they intirely remove a very great difficulty,

difficulty, which I acknowledged, p. 128. in finding different results from seemingly similar circumstances; whereas I now find that both the circumstances and the results are different. Besides, the *positive* evidence of actually finding a substance is always more conclusive than the *negative* one, of not finding it.

I do not know that any objection can be made to the inflammable air from *tin*, as this metal has not been proved to contain plumbago. I wished, however, to repeat this experiment with inflammable air from *sulphur*. But though, when steam is sent over melted sulphur, a small quantity of inflammable air is procured, as I observed in my last volume of experiments; yet, as sulphur cannot part with much phlogiston, except in proportion as it imbibes pure air, to form oil of vitriol, I could not in this manner easily procure enough for my purpose.

In order to supply the sulphur with pure air, I mixed with it a quantity of *turbith mineral*; but this made it yield vitriolic acid air, though in great abundance, there not being, I imagine, *water* enough to form inflammable air: for when iron is dissolved in concentrated acid of vitriol, vitriolic acid air is produced; but in diluted vitriolic acid, the produce is inflammable air. With a view to supply these materials with water, I sent steam over them; but it did not combine with the air, which was still only vitriolic acid air.

Since, however, vitriolic acid air unquestionably contains the same principle which forms the inflammability of inflammable air, this experiment proves, that sulphur is not that simple substance which the antiphlogistians suppose it to be; but that it contains phlogiston. Had it been nothing more than a substance which had a strong affinity to pure air, it would

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have united with the pure air from the turbith mineral, and have made vitriolic acid; but no vitriolic acid air would have been produced.

That vitriolic acid air contains the ſame inflammable principle with inflammable air is evident from the quantity of vitriolic acid air which I produced by reviving copper from blue vitriol in inflammable air. See my Experiments, vol. VI. p. 15. Mr. KIRWAN alſo produced this air from ſulphur and red precipitate. See his Treatiſe on Phlogiſton, p. 29.

When I uſed a ſmall quantity of ſulphur in proportion to the turbith mineral, the firſt produce was vitriolic acid air, and afterwards dephlogiſticated air, from the turbith mineral alone, the effect of the ſulphur having been exhauſted.

According to the antiphlogiſtic theory, *phoſphorus*, as well as ſulphur, is a ſimple ſubſtance; and when it is ignited imbibes pure air, and thereby becomes the phoſphoric acid, without parting with any thing. But I find, that after the accenſion of it in dephlogiſticated air, there is a conſiderable quantity of fixed air in the reſiduum; and this fixed air could only be formed by the union of the dephlogiſticated air in the veſſel with the phlogiſton contained in the phoſphorus. Mr. KIRWAN had a ſimilar reſult from phoſphorus confined in atmoſpheric air. As it is not pretended, that there is any plumbago in phoſphorus, this experiment is not liable to the objection that has been made to thoſe in which inflammable air from iron was made uſe of.

It will be expected, that in this reply to the objections that have been made to my experiments eſtabliſhing the doctrine of phlogiſton, I ſhould conſider what has been alledged by Meſſ. LAVOISIER, BERTHOLLET, and DE FOURCROY, in favour of their new ſyſtem, in their *Report* on the ſubject of the new chemical

chemical characters invented by Meff. HASSENFRATZ and ADET, fubjoined to the new *Nomenclature Chymique*. I fhall therefore notice what appears to me to be moft important in that publication.

" One of the articles of the modern doctrine" (of which they fay, p. 311. " that it coft more than twenty years labour, which " the force of reafoning has obliged many celebrated chemifts to " adopt, and in favour of which much greater numbers are ready " to decide;" and the evidence for which they fay, p. 301. " is the moft complete chemical proof), which feems the " moft folidly eftablifhed," p. 298, " is the formation, the " decompofition, and recompofition of water; and how is " it poffible," they add, " to doubt of it, when we fee that, " in burning together 15 grains of inflammable air and 85 of " pure air, we get exactly 100 grains of water; and when we " can, by decompofition, find again thefe fame two principles, " in the fame proportions?"

To this I muft fay, as I have done, Experiments, Vol. VI. p. 139. (and when I wrote that, I was myfelf a believer in the decompofition of water), that I have never been able to find the full weight of the air decompofed in the water produced by the decompofition; and that now I apprehend it will not be denied, that the produce of this decompofition is not mere water, but always fome acid.

As to the fuppofed decompofition of water by means of iron, I have fhewn that it is a fallacy; fince the iron imbibes nothing but water when it parts with its phlogifton. And I have obferved (Experiments, vol. VI. p. 83.), that when this finery cinder is reconverted into iron by inflammable air, nothing but water is expelled from it; and that the refiduum of the air is purely inflammable, without containing any fixed

air.

air. It is evident, therefore, that the iron had imbibed pure water only. Had the iron imbibed dephlogiſticated air from the water, and not water itſelf, there ſeems to be no reaſon why fixed air ſhould not be found in this, as well as in the exactly ſimilar proceſs with minium and precipitate *per ſe.* Alſo, it can never be ſuppoſed, that the addition which iron gains, of one-third of its weight, is from air contained in ſteam, if it could be proved to contain any; becauſe, if there be a ſufficient quantity of iron, the whole of the water will be imbibed; ſo that, on this hypotheſis, water muſt be nothing but dephlogiſticated air condenſed.

There is, I acknowledge, a great difficulty in explaining the experiment of iron firſt imbibing water, and parting with phlogiſton, and again parting with its water, and imbibing phlogiſton, in circumſtances of heat ſo nearly ſimilar as thoſe which I have deſcribed. It ſeems as if the affinity of iron to water and to phlogiſton was each, in their turns, ſtronger than the other. To this I can only ſay, that the whole doctrine of affinities, as far as it is true, is founded on facts; and theſe are clearly ſuch as I have repreſented; and that a difference of circumſtances, which is not apparent at preſent, may become ſo when we ſhall have given ſufficient attention to them.

In order to ſatisfy myſelf whether any thing beſides *water* was expelled from finery cinder by heat, I went through ſimilar proceſſes with this ſubſtance and *maſſicot*, from which all air had been previouſly expelled; and after reviving both of them in inflammable air, I found the reſults, in all reſpects, the very ſame. The reſiduums of the inflammable air were equally free from fixed air; and when they were fired with equal quantities of dephlogiſticated air, the diminutions of bulk

bulk were very nearly the same, less than when the original inflammable air was used, because all the impurities in the whole quantity were retained in a small residuum, the metals having imbibed nothing but pure phlogiston. Also the inflammable air had been long confined by water, in consequence of which it is always altered more or less. The particulars of the processes were as follows:

The finery cinder was revived in 7 oz. m. of inflammable air, which was thereby reduced to $1\frac{1}{4}$ oz. m.; and an oz. m. of this residuum being fired together with an equal quantity of dephlogisticated air, not very pure, the diminution of both was to 28 divisions of a tube, of which 30 was one oz. m. when with equal quantities of the same dephlogisticated and the original inflammable air the diminution was to 18.

The massicot was reduced in 8 oz. m. of inflammable air till it was reduced to $1\frac{1}{4}$ oz. m.; and after the process with the dephlogisticated air, the diminution was to 29, when with the original inflammable air it was to $17\frac{1}{2}$.

In both the residuums, after the explosion, there was a slight appearance of *fixed air*, though none could be perceived before the explosion; but in both cases it was so slight that it could not have been perceived by the diminution of its bulk. But since both fixed air and nitrous acid are produced from the same materials in different circumstances, it cannot be thought extraordinary if, in some cases, both should be produced at the same time.

M. Lavoisier and his associates farther observe, p. 300. with respect to my experiments, that "when a calx is revived "in inflammable air, more water is found in the vessel than the "weight of inflammable air that disappears, so that it could "not have been contained in that air." They only refer to my experiments in general; but as they ſpeak of the water produced as appearing both on the inſide of the veſſel, and on the ſurface of the mercury, it can be no other than the experiment of the revival of iron from finery cinder; and the water that is found in this proceſs was never ſuppoſed to come from the little that is contained in the inflammable air, but the much greater quantity contained in the cinder.

Before I conclude this Paper, I ſhall juſt mention a few circumſtances attending the many exploſions I have made of inflammable and dephlogiſticated air in the long metallic and glaſs veſſels I have made uſe of, as they were pretty remarkable. The exploſions were made by a ſmall electric ſpark at one end of the veſſel, and the greateſt force of the exploſion was always at the other end. No tinned iron veſſel could bear many of them before they ſwelled out at that end, and at length burſt; and even the flat end of the copper veſſel, which was not leſs than one-tenth of an inch thick, was in time made quite convex, and the cylindrical part next to it was made very ſenſibly wider than any other part of the tube. This muſt have been effected by mere *force*, and not by *heat*; for the hotteſt part of the tube, after every exploſion, was never there, but always about the middle, though ſomething nearer to that end than the other, and in the glaſs veſſel the denſe cloud was always formed at that end.

The probability is, that the air where the electric ſpark is made taking fire firſt, the inflammation does not extend itſelf ſo rapidly but that the air at the oppoſite end is firſt condenſed, in conſequence of the inflammation and expanſion of the air at the other end, ſo that the air is there fired in a condenſed ſtate; and hence its greater force.