

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 dephlogificated 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 phlogificated 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 dephlogificated and phlogificated 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 phlogificated air, as I found by actual trial, was not at all affected; the dephlogificated and inflammable airs uniting, and leaving the phlogificated 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 phlogificated air may contain phlogiston, and by means of electricity this principle may be evolved, and unite with the dephlogificated 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 phlogification when formed in this manner.

In order to ascertain the effect of the presence of phlogificated air in this process, I now not only repeated the experiment of mixing a given quantity of phlogificated 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 dephlogificated. Since the air of the atmosphere contains a greater proportion of phlogificated air, it might be expected that, if the acid I got before came from the small quantity of phlogificated air which I could

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 phlogificated 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 dephlogificated 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 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 phlogificated air, I have sometimes used dephlogificated 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, found it to be far more decisively conclusive 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 vessel in which the process was made; and finding that it turned the juice of turnsole red, I concluded, that it contained nitrous acid: but I now examined the *air* that remained in the vessel, and found that a considerable proportion of it was fixed air; so that I am now satisfied *this* was the acid with which it was impregnated, and not the *nitrous*. Still, however, some acid is the constant result of the union of the two kinds of air, and not water only. A quantity of the same precipitate *per se* yielded no fixed air by heat.

Comparing this experiment with that in which iron is ignited in dephlogisticated air, this general conclusion may be drawn, *viz.* that when either inflammable or dephlogisticated air is extracted from any substance in contact with the other kind of air, so that one of them is made to unite with the other in what may be called its *nascent state*, the result will be *fixed* air; but that if both of them be completely formed before their union, the result will be *nitrous acid*.

It has been said, that the fixed air produced in both these experiments may come from the *plumbago* in the iron from which the inflammable air is obtained. But since we ascertain the quantity of plumbago contained in iron by what remains after its solution in acids, it is in the highest degree improbable, that whatever plumbago there may be in iron, any part of it should enter into the inflammable air procured from it. Besides, according to the antiphlogistic hypothesis, all inflammable air comes from water only.

As it cannot be said, that any real fixed air is found in inflammable air from iron (since it is not discoverable 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 $8\frac{1}{2}$ oz. m. of inflammable air was reduced to $2\frac{1}{2}$ oz. m., and of this 0.04 oz. m. at least was fixed air.

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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 have

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 Mess. HASSENERATZ and ADET, subjoined to the new *Nomenclature Chymique*. I shall therefore notice what appears to me to be most important in that publication.

“ One of the articles of the modern doctrine” (of which they say, p. 311. “ that it cost more than twenty years labour, which “ the force of reasoning has obliged many celebrated chemists to “ adopt, and in favour of which much greater numbers are ready “ to decide;” and the evidence for which they say, p. 301. “ is the most complete chemical proof), which seems the “ most solidly established,” p. 298, “ is the formation, the “ decomposition, and recomposition of water; and how is “ it possible,” they add, “ to doubt of it, when we see 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 decomposition, find again these same two principles, “ in the same proportions?”

To this I must say, as I have done, *Experiments*, vol. VI. p. 139. (and when I wrote that, I was myself a believer in the decomposition of water), that I have never been able to find the full weight of the air decomposed in the water produced by the decomposition; and that now I apprehend it will not be denied, that the produce of this decomposition is not mere water, but always some acid.

As to the supposed decomposition of water by means of iron, I have shewn that it is a fallacy; since the iron imbibes nothing but water when it parts with its phlogiston. And I have observed (*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 residuum of the air is purely inflammable, without containing any fixed

air. It is evident, therefore, that the iron had imbibed pure water only. Had the iron imbibed dephlogificated 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 dephlogificated 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 dephlogificated 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.