

XV. *Answer to Mr. Kirwan's Remarks upon the Experiments on Air.* By Henry Cavendish, Esq. F. R. S. and S. A.

Read March 4, 1784.

**I**N a paper lately read before this Society, containing many experiments on air, I gave my reasons for supposing that the diminution which respirable air suffers by phlogistication, is not owing either to the generation or separation of fixed air from it; but without any arguments of a personal nature, or which related to any one person who espouses the contrary doctrine more than to another. This being contrary to the opinion maintained by Mr. KIRWAN, he has written a paper in answer to it, which was read on the fifth of February. As I do not like troubling the Society with controversy, I shall take no notice of the arguments used by him, but shall leave them for the reader to form his own judgement of; much less will I endeavour to point out any inconsistencies or false reasonings, should any such have crept into it; but as there are two or three experiments mentioned there, which may perhaps be considered as disagreeing with my opinion, I beg leave to say a few words concerning them.

Mr. DE LASSONE found that filings of zinc, digested in a caustic fixed alkali, were partially dissolved with a small effervescence, and that the alkali was rendered in some mea-

ture mild. This mildness of the alkali Mr. KIRWAN accounts for by supposing, that the inflammable air, which is separated during the solution, and causes the effervescence, unites to the atmospheric air contiguous to it, and thereby generates fixed air, which is absorbed by the alkali. But, in reality, the only circumstance from which Mr. DE LASSONE judged the alkali to become mild, was its making some effervescence when saturated with acids; and this effervescence is more likely to have proceeded from the expulsion of inflammable air than of fixed air, as it seems likely, that the zinc might be more completely deprived of its phlogiston by the acid than by the alkali.

In the abovementioned paper I say, Dr. PRIESTLEY observed, that quicksilver fouled by the addition of lead or tin, deposits a powder by agitation and exposure to the air, which consists in great measure of the calx of the imperfect metal. He found too some powder of this kind to contain fixed air; but it must be observed, that the powder used in this experiment was not prepared on purpose, but was procured from quicksilver fouled by having been used in various experiments, and may therefore have contained other impurities besides the metallic calces. On this Mr. KIRWAN remarks, that Dr. PRIESTLEY did not at first prepare this powder on purpose, but he afterwards did so prepare it (4 PR. p. 148. and 149.), and obtained a powder exactly of the same sort. It was natural to suppose from this remark, that Dr. PRIESTLEY must have obtained fixed air from the powder prepared on purpose, and that I had overlooked the passage; but, on turning to the pages referred to, I was surprised to find that it was otherwise, and that Dr. PRIESTLEY not so much as hints that he procured fixed air from the powder thus prepared.

With regard to the calcination of metals it may be proper to remark, that this operation is usually performed over the fire, by methods in which they are exposed to the fumes of the burning fuel, and which are so replete with fixed air, that it is not extraordinary, that the metallic calx should, in a short time, absorb a considerable quantity of it; and in particular red lead, which is the calx on which most experiments have been made, is always so prepared. There is another kind of calcination, however, called rusting, which is performed in the open air; but this is so slow an operation, that the rust may easily imbibe a sufficient quantity of fixed air, notwithstanding the small quantity of it usually contained in the atmosphere.

Mr. KIRWAN allows that lime-water is not rendered cloudy by the mixture of nitrous and common air; but contends that this does not prove that fixed air is not generated by the union, as he thinks it may be absorbed by the nitrous selenite produced by the union of the nitrous acid with the lime. This induced me to try how small a quantity of fixed air would be perceived in this experiment. I accordingly repeated it in the same manner as described in my paper, except that I purposely added a little fixed air to the common air, and found that when this addition was  $\frac{1}{73}$ th of the bulk, or  $\frac{1}{30}$ th of the weight of the common air, the effect on the lime-water was such as could not possibly have been overlooked in my experiments. But as those who suppose fixed air to be generated by the mixture of nitrous and common air, may object to this manner of trying the experiment, and say, that the quantity of fixed air absorbed by the lime-water was really more than  $\frac{1}{73}$ th of the bulk of the common air, being equal to that quantity over  
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and above the air generated by the mixture, I made another experiment in a different manner; namely, I filled a bottle with lime-water, previously mixed with as much nitrous acid as is contained in an equal bulk of nitrous air, and having inverted it into a vessel of the same, let up into it, in the same manner as in the above-mentioned experiments, a mixture of common air with  $\frac{1}{75}$ th of its bulk of fixed air, until it was half full. The event was the same as before; namely, the cloudiness produced in the lime-water was such that I could not possibly have overlooked. It must be observed, that in this experiment no fixed air could be generated, and a still greater proportion of the lime-water was turned into nitrous selenite than in the above-mentioned experiments; so that we may safely conclude, that if any fixed air is generated by the mixture of common and nitrous air, it must be less than  $\frac{1}{75}$ th of the bulk of the common air.

As for the nitrous selenite, it seems not to make the effect of the fixed air at all less sensible, as I found by filling two bottles with common air mixed with  $\frac{1}{400}$ th of its bulk of fixed air, and pouring into each of them equal quantities of diluted lime-water; one of these portions of lime-water being previously diluted with an equal quantity of distilled water, and the other with the same quantity of a diluted solution of nitrous selenite, containing about  $\frac{1}{400}$ th of its weight of calcareous earth; when I could not perceive that the latter portion of lime-water was rendered at all less cloudy than the former. Though the nitrous selenite, however, does not make the effect of the fixed air less sensible, yet the dilution of the lime-water, in consequence of some of the lime being absorbed by the acid, does; but, I believe, not in any remarkable degree.

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There is an experiment mentioned by Mr. KIRWAN which, though it cannot be considered as an argument in favour of the generation of fixed air, as he only supposes, without any proof, that fixed air is produced in it, does yet deserve to be taken notice of as a curious experiment. It is, that, if nitrous and common air be mixed over dry quicksilver, the common air is not at all diminished, that is, the bulk of the mixture will be not less than that of the common air employed, until water is admitted, and the mixture agitated for a few minutes. The reason of this in all probability is, that part of the phlogisticated nitrous acid, into which the nitrous air is converted, remains in the state of vapour until condensed by the addition of water. A proof that this is the real case is, that, in this manner of performing the experiment, the red fumes produced on mixing the airs remain visible for some hours, but immediately disappear on the addition of water and agitation.

The most material experiment alledged by Mr. KIRWAN is one of Dr. PRIESTLEY's, in which he obtained fixed air from a mixture of red precipitate and iron filings. This at first seems really a strong argument in favour of the generation of fixed air; for though plumbago, which is known to consist chiefly of that substance, has lately been found to be contained in iron, yet one would not have expected it to be decomposed by the red precipitate, especially when the quantity of pure iron in the filings was much more than sufficient to supply the precipitate with phlogiston. The following experiment, however, shews that it was really decomposed; and that the fixed air obtained was not generated, but only separated by means of this decomposition.

500 grains of red precipitate mixed with 1000 of iron filings yielded, by the assistance of heat, 7800 grain measures of fixed  
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air, besides 2400 of a mixture of dephlogificated and inflammable air, but chiefly the latter. The same quantity of iron filings, taken from the same parcel, was then dissolved in diluted oil of vitriol, so as to leave only the plumbago and other impurities. These mixed with 500 grains of the same red precipitate, and treated as before, yielded 9200 grain measures of fixed air, and 4200 of dephlogificated air, of an indifferent quality, but without any sensible mixture of inflammable air. It appears, therefore, that less fixed air was produced when the red precipitate was mixed with the iron filings in substance, than when mixed only with the plumbago and other impurities; which shews, that its production was not owing to the iron itself, which seems to contain no fixed air, but to the plumbago, which contains a great deal. The reason, in all probability, why less fixed air was produced in the first case than the latter is, that in the former more of the plumbago escaped being decomposed by the red precipitate than in the other. It must be observed, however, that the filings used in this experiment were mixed with about  $\frac{1}{13}$ th of their weight of brass, which was not discovered till they were dissolved in the acid, and which makes the experiment less decisive than it would otherwise be. The quantity of fixed air obtained is also much greater than, according to Mr. BERGMAN'S experiment, could be yielded by the plumbago usually contained in 1000 grains of iron; so that though the experiment seems to shew that the fixed air was only produced by the decomposition of the impurities in the filings, yet it certainly ought to be repeated in a more accurate manner.

Before I conclude this paper, it may be proper to sum up the state of the argument on this subject. There are five methods of phlogification considered by me in my paper on air; namely,

namely, first, the calcination of metals, either by themselves or when amalgamated with quicksilver; secondly, the burning of sulphur or phosphorus; thirdly, the mixture of nitrous air; fourthly, the explosion of inflammable air; and, fifthly, the electric spark; and Mr. KIRWAN has not pointed out any other which he considers as unexceptionable. Now the last of these I by no means consider as unexceptionable, as it seems much most likely, that the phlogistication of the air in that experiment is owing to the burning or calcination of some substance contained in the apparatus\*. It is true, that I have no proof of it; but there is so much probability in the opinion, that till it is proved to be erroneous, no conclusion can be drawn from such experiments in favour of the generation of fixed air. As to the first method, or the calcination of metals, there is not the least proof that any fixed air is generated, though we certainly have no direct proof of the contrary; nor did I in my paper insinuate that we had. The same thing may be said of the burning of sulphur and phosphorus. As to the mixture of nitrous air, and the combustion of inflammable air, it is proved, that if any fixed air is generated, it is so small as to elude the nicest test we have. It is certain too, that if it had been so much as  $\frac{1}{70}$ th of the bulk of the common air employed, it would have been perceived in the first of these methods, and would have been sensible in the second though still less. So that out of the five methods enumerated, it has been shewn, that in two no sensible quantity is generated, and not the least proof has been assigned that any is in two of the

\* In the experiment with the litmus I attribute the fixed air to the burning of the litmus, not decomposition, as Mr. KIRWAN represents it, which is a sufficient reason why no fixed air should be found when the experiment is tried with air in which bodies will not burn.

others; and as to the last, good reasons have been assigned for thinking it inconclusive; and therefore the conclusion drawn by me in the above-mentioned paper seems sufficiently justified; namely, that though it is not impossible that fixed air may be generated in some chemical processes, yet it seems certain, that it is not the general effect of phlogisticating air, and that the diminution of common air by phlogistication is by no means owing to the generation or separation of fixed air from it.

