

XIV. *Remarks on Mr. Cavendish's Experiments on Air. In a Letter from Richard Kirwan, Esq. F. R. S. to Sir Joseph Banks, Bart. P. R. S.*

Read Feb. 5, 1784.

S I R,

HAVING listened with much attention, and derived much useful information from the very curious experiments of Mr. CAVENDISH, read at our last meeting, it is with peculiar regret I feel myself withheld from yielding an intire assent to all he has advanced in his very ingenious paper; and it is with still greater that I find myself obliged, by reason of the opposition of some of his deductions to those I had the honour to lay before the society about two years ago, to expose the reasons of my dissent, through your mediation, before this meeting.

In the paper already mentioned, read in April, 1782, I attributed the diminution of respirable air, observed in common phlogistic processes, to the generation and absorption of fixed air, which is now known to be an acid, and capable of being absorbed by several substances. That fixed air was some how or other produced in phlogistic processes, either by *separation* or *composition*, I took for granted from the numerous experiments of Dr. PRIESTLEY; and among these I selected, as least liable to objection, the Calcination of Metals, the decomposition

tion of nitrous by mixture with respirable air, the phlogistication of respirable air by the electric spark; and, lastly, that effected by amalgamation. In each of these instances Mr. CAVENDISH is of opinion, that the diminution of respirable air is owing to the production of water, which, according to him, is formed by the union of the phlogiston, disengaged in those processes, with the dephlogisticated part of common air; and that fixed air is never produced in phlogistic processes, except some animal or vegetable substance is concerned in the operation, from whose decomposition it may arise. To which of these causes the diminution of respirable air is to be attributed, I shall now endeavour to elucidate.

Of the Calcination of Metals.

I attributed the diminution of air by the calcination of metals, to the conversion of the dephlogisticated part of common air into fixed air, by reason of its union with the phlogiston of the metal, for this plain reason, because I find it acknowledged on all hands, that the calces of all the base metals yield fixed air, when sufficiently heated. Mr. Cavendish allows the fact in general, but ascribes the fixed air found in them to their long exposure to the atmosphere, in which he says fixed air pre-exists; but that it exists in common air in any quantity worth attending to, or is extracted from it in any degree, I take the liberty of denying, grounded on the following facts. First, I have frequently agitated 18 cubic inches of common air in 2 of lime-water, and 2 of common air in 18 of lime-water, but could never perceive the slightest milkiness; and yet the thousandth part of a cubic inch of fixed air would thus be made sensible; for if a cubic inch of it be dissolved in 3 ounces of

water, a few drops of that water let into lime-water will produce a cloud. Mr. FONTANA says, he frequently agitated 1 cubic inch of Tincture of Turnsole in 7 or 800 of common air, without reddening it (23 Roz. p. 188.); and yet, according to Mr. BERGMAN, 1 cubic inch of fixed air is sufficient to redden 50 of Tincture of Turnsole (1 BERGM. II.); from whence I am apt to think, that 700 cubic inches of common air do not even contain $\frac{1}{50}$ th of a cubic inch of fixed air. Dr. WHYTT found that 12 ounces of strong lime-water, being exposed to the open air for 19 days, still retained about 1 grain of lime, (on Lime-water, p. 32.). Now 12 ounces of strong lime-water contain at most 9,5 grains of lime, and 1 grain of lime requires only 0,56 of a cubic inch of fixed air to precipitate it, the thermometer at 55 and the barometer at 29,5, as I have found. Therefore in 19 days this lime-water did not come in contact with more than four cubic inches of fixed air; yet it is certain that a large quantity of fixed air is continually disengaged, and thrown into the atmosphere, by various processes, as putrefaction, combustion, &c. but it seems equally certain that it is either decomposed, or more probably absorbed by various bodies. Mr. FONTANA let loose 20000 cubic inches of fixed air, in a room whose windows and doors were closed, yet in half an hour after he could not discover the least trace of it (ibid.). Though fixed air perpetually oozes from the floor of the *Grotto del Cane*, yet at the distance of four or five feet from the ground none is found; animals may live, lights burn, &c. (Roz. Ibid. Mem. Stockh. 1775.). If distilled water be exposed to the atmosphere, it is never found to absorb fixed air, but rather dephlogisticated air, according to Mr. SCHEELÉ's experiments, which could never happen if the atmosphere contained any sensible proportion of

fixed air; nor has rain-water been ever found to contain any, which it certainly should on the same hypothesis; even Mr. CAVENDISH himself could find no fixed air in the residuum or products of about 1040 ounce measures of common air, which he burnt with inflammable air.

It is true, Dr. PRIESTLEY supposed common air to contain $\frac{1}{5}$ of its bulk of fixed air; but he drew this conclusion not from any direct experiment, but from the quantity of fixed air produced by breathing, which he at that time believed to have been barely precipitated, and not generated, an opinion which he has found reason to alter from his own experiments. I think I may therefore conclude, that the quantity of fixed air contained in the atmosphere is absolutely inappreciable.

Secondly, supposing the atmosphere to contain a very small proportion of fixed air, yet I do not think it can be inferred that metals, during their calcination, extract any, because I find that lime exposed to red heat ever so long extracts none, though it is formed by a calcination in open air, which lasts at least as long as that of any metal; neither does precipitate *per se* attract any, though its calcination lasts several months; nor does this proceed from the want of affinity, for if a saturated solution of mercury in any of the acids be precipitated by a mild vegetable alkali, very little effervescence is perceived, and the precipitate weighs much more than the quantity of mercury employed, and that this increase of weight arises in part from the fixed air absorbed will presently be seen.

Since then metals may be calcined in close vessels, since they then absorb one fourth part of the common air to which they are exposed, since all metallic calces (except those of mercury, which I shall presently mention) yield fixed air, since common

air contains scarce any fixed air; is it not apparent that the fixed air thus found was generated by the very act of calcination, by the union of the phlogiston of the metal with the dephlogisticated part of the common air, since after the operation the metal is deprived of its phlogiston, and the air of its dephlogisticated part?

But Mr. CAVENDISH objects, that no one has extracted fixed air from metals calcined in close vessels. To which I answer, that this further proof is difficult, and no way necessary; it is difficult, because the operation can easily be performed only on small quantities; it is unnecessary, because it differs from the operation in open air only by the quantities of the materials employed; in every other respect it is exactly the same. Since Mr. CAVENDISH suspects the results are different, it is incumbent on him to shew that difference; but until then, according to Sir ISAAC NEWTON's second rule, *to natural effects of the same kind the same causes are to be assigned, as far as it may be done*, that is, until experience points out some other cause.

It may further be urged, that precipitate *per se* yields only dephlogisticated air, that minium also yields a large proportion of it. This difficulty I have formerly answered by asserting, that these calces are in fact united only to fixed air, and that they yield dephlogisticated air, merely because the fixed air is decomposed by the total or partial revivification of the metallic substances; this I think may be demonstrated by the following experiments. Let sublimate corrosive singly be treated in any manner, it will not yield dephlogisticated air (4 Pr. 240.); but let a solution of sublimate corrosive be precipitated by a mild fixed alkali, this precipitate washed, dried, and distilled in a pneumatic apparatus, will yield dephlogisticated air, and the

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mercury will be revived ; but, if the solution of sublimate corrosive be precipitated by lime-water, it seems no air will be produced. Here then we see, 1st, that the calx of mercury unites with fixed air ; and, 2dly, that this fixed air is, during the revivification of the mercury, converted into dephlogisticated air. Again : let one ounce of red precipitate, which, according to Mr. CAVENDISH, contains no nitrous acid, be distilled with two ounces of filings of iron ; this quantity of precipitate, which, if distilled by itself, would yield 60 ounce measures of dephlogisticated air, will, when distilled with this proportion of filings of iron, yield 40 ounce measures of fixed air, as Dr. PRIESTLEY has shewn in his last paper : whichever way this is explained, some or other of my opinions are confirmed ; for either the mercurial calx is already combined with fixed air (which I believe to be the case), and this air passes undecomposed, because the mercury extracts phlogiston from the iron ; or it contains dephlogisticated air, which is converted into fixed air by its union with the phlogiston of the iron.

If precipitate *per se* be digested in marine acid, the mercury will be revived (3 BERGM. 415.). Now this calx does not dephlogisticate the marine acid ; for this acid, when dephlogisticated, dissolves mercury ; how then does it revive it, if not by expelling the fixed air contained in it, which in the moment of its expulsion is decomposed, leaving its phlogiston to the mercury, which is thereby revived ?

Again : if litharge be heated in a gun-barrel, it will afford more fixed and less dephlogisticated air than if heated in glass or earthen vessels. Does not this happen, because the calx of lead, receiving some phlogiston from the metal, does not dephlogisticate so great a proportion of the fixed air as it otherwise would ?

Further: there is no substance which yields dephlogisticated air, but yields also fixed air, even precipitate *per se* not excepted; (3 PRIEST. 16.) and what is remarkable, they all yield fixed air first, and dephlogisticated air only towards the end of the process. Does not this happen because metallic calces attract phlogiston so much more strongly, as they are more heated? Thus many calciform iron ores become magnetic by calcination, though they were not so before; so also do all the calces of iron when exposed to the focus of a burning glass (5 Dict. Chy. 179). Thus mercury cannot be calcined but in a heat inferior to that in which it boils; thus minium cannot be formed but in a moderate heat, and if heated still more it returns to the state of massicot, in which it was before it became minium, and much of it is reduced. So if a solution of luna cornea in volatile alkali be triturated with mercury, the silver will be revived, and the marine acid unite to the mercury, which shews this acid has a stronger attraction to Mercury than to silver; yet if sublimate corrosive and silver be distilled in a strong heat, the mercury will be revived, and the marine acid unite to the silver, which shews that the attraction of mercury to phlogiston increases with the heat applied.

Before I conclude this head, I will mention another experiment, which I think decisive in favour of my opinion of the composition of fixed air. If filings of zinc be digested in a caustic fixed alkali in a gentle heat, the zinc will be dissolved with effervescence, and the alkali will be rendered in great measure mild. But if, instead of filings of zinc, flowers of zinc be used, and treated in the same manner, there will be no solution, and the alkali will remain caustic. In the first case the effervescence arises from the production of inflammable air, which

which phlogisticates the common air contiguous to it, and produces fixed air, which is immediately absorbed by the alkali, and renders it mild. In the second case, no inflammable air is produced, the common air is not phlogisticated, and consequently the alkali remains caustic*. This experiment also proves that metallic calces attract fixed air more strongly than alkalies attract it; for the calces of zinc are known to contain fixed air, and yet alkalies digested with them remain caustic; and this accounts for the slight turbidity of lime-water when metals are calcined over it; for as soon as the phlogiston is disengaged from the metal, and before it has absorbed the whole quantity of fire requisite to throw it into the form of inflammable air, it meets with the dephlogisticated part of the common air on the surface of the metal, and there forms fixed air, which is instantly absorbed by the calx with which it is in contact, so that it is not to be wondered that it does not unite to the lime from which it is distant.

*Of the Decomposition of Nitrous Air by mixture with
Common Air.*

AS soon as I had heard Mr. CAVENDISH's paper read, I set about trying whether lime would be precipitated from lime-water during the process, an experiment I had never made before with common air, taking it for granted that it was so, from the repeated experiments of Dr. PRIESTLEY, and indeed of all others who had treated this subject †: and, in effect,

* See Mr. LASSONE's Experiments on zinc. Mem. Par. 1777. p. 7 & 8.

† See 1 Pr. 114. 189. 2 Pr. 218. Font. Recherches Physf. p. 77. 1 Chy. Dij. 324.

when I made the experiment with nitrous air prepared and confined by the water of my tub, I found lime-water admitted to it instantly precipitated. But after I had read Mr. CAVENDISH's paper, which he had the politeness to permit me, and had, according to his direction, received the nitrous air over lime-water, I did not then perceive the least milkiness after admitting common air. After 12 hours I indeed perceived a whitish dust, on the bottom of the glass vessel in which I made the experiment, which I cannot assure to be calcareous; and, on breathing into the lime-water, an evident milkiness ensued; so that I little doubt but the precipitation I observed in the first experiment arose from the decomposition of the aerial selenite contained in the water of the tub. And it is very possible that the precipitation of lime, which I perceived some years ago on mixing dephlogisticated air and nitrous air, might have arisen from the same cause, or from fixed air pre-contained in the dephlogisticated, as this last had not been washed in lime-water. Yet I do not think the failure of this experiment at all conclusive against the supposed production of fixed air on this occasion, because the quantity of fixed air is so small, that it may well be supposed to unite to the nitrous selenite formed in the lime-water. It is well known that a small quantity of fixed air is capable of uniting to all neutral salts: thus Dr. PRIESTLEY has extracted it from tartar vitriolate and alum, (2 PR. 115, 116.) and gypsum, (2 PR. 80.); and Dr. MAC BRIDE found it in nitre and common salt, though in small quantity. But to try whether nitrous selenite would attract any, I made a solution of chalk in nitrous acid, which, when saturate, weighed 381,25 grains; but, being exposed to the air for a few hours, it weighed 382,25. I afterwards took a very dilute nitrous acid, in which an acid taste was barely perceptible, and impregnated it with a very small proportion

portion of fixed air, and then let fall a few drops of it into lime-water; not the smallest cloud was perceived, and yet when I breathed into it afterwards it became milky in a few seconds; so that this experiment is perfectly analogous to that in which nitrous and common air were mixed.

But if nitrous air and common air be mixed over dry mercury, the result is intirely adverse to the opinion of Mr. CAVENDISH, and favourable to mine; for in this case the common air is not at all diminished until water is admitted to it, and the mixture agitated a few minutes, and then the diminution is nearly the same as if the mixture were made over water. Thus when I mixed two cubic inches of common air with one of nitrous air, they occupied the space of two inches and one-eighth, and the surface of the mercury was immediately calcined; which shews that the inch of nitrous air was decomposed, and produced nitrous acid; but the common air was undiminished; and the one eighth of an inch over and above the two inches of common air, proceeded from an addition of new nitrous air, formed by the corrosion of the surface of the mercury. That the common air should remain undiminished is easily explained in my system, because fixed air is formed, which, on this occasion, must remain unabsorbed, at least for a long time, as there is nothing at hand that can immediately receive it; and hence, if water be admitted soon after the mixture of both airs, the diminution will be nearly the same as if the mixture had been originally made over water, though not exactly the same; because the nitrous air, produced by the union of the newly formed nitrous acid with the mercury, is not entirely absovable by water. But, in Mr. CAVENDISH'S hypothesis, the common air should be diminished just as much as if the mixture were made over water; for, according to him,

this diminution arises from the conversion of the dephlogistified part of the common air into water, which water should immediately unite to the nitrous salt of mercury, and leave the common air lessened in its bulk by a portion commensurate to that converted into water, or, if he will not allow the water to have immediately united to the mercurial salt, at least by the difference of the bulk of the water produced, and that of an equal weight of the common air converted into it: but neither happens; for the common air is not at all diminished; not can he explain, consistently with his system, why the admission of water should immediately produce a diminution in the common air, as, according to him, it contains nothing that can be absorbed. Dr. PRIESTLEY has remarked, that if a mixture of both airs be suffered to stand several hours, even the admission of water will produce no diminution. This is owing to two causes; 1st, because a large quantity of nitrous air is produced, by the continued action of the concentrated nitrous acid newly formed; and, 2dly, because the fixed air, on whose absorption the diminution depends, is absorbed by the mercurial salt, as may be inferred from the experiment in LAVOISIER, p. 248.

Of the Diminution of Common Air by the Electric Spark.

Of all the instances of the artificial production of fixed air, by the union of phlogiston with the dephlogistified part of common air, there is none perhaps so convincing, as that exhibited by taking the electric spark through common air, over a solution of litmus, or lime-water; for the common air is diminished one fourth, the litmus reddened, and the lime-water precipitated. Mr. CAVENDISH indeed attributes the redness of
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the litmus to fixed air; but he thinks it proceeds from a decomposition of some part of the vegetable juice, as all vegetable juices contain fixed air. Yet that such a decomposition does not take place, I think may be inferred from the following reasons: first, if the electric spark be taken through phlogistified or inflammable air confined by litmus, no redness is produced, the air not being in the least diminished; and, 2dly, if the litmus were decomposed, inflammable air should be produced as well as fixed air; and then there should be an addition of bulk instead of a diminution; but what sets the origin of the fixed air from the phlogistification of the common air beyond all doubt is, that if lime-water be used instead of litmus, the diminution is the same, and the lime is precipitated. Here Mr. CAVENDISH says, the fixed air proceeds either from *some dirt in the tube*; a supposition, which, being neither necessary nor probable, is not admissible; or else *from some combustible matter in the lime*; but lime contains no combustible matter, except perhaps phlogiston, which cannot produce fixed air but by uniting to the common air, according to my supposition; but it is much more probable, that the diminution does not arise from any phlogiston in the lime, as it is exactly the same whether lime-water be used or not; and the lime does not appear to be in the least altered, and in fact contains scarce any phlogiston.

Of the diminution of Common Air, by the Amalgamation of Mercury and Lead.

I attributed this diminution to the phlogistification of the common air by the process of amalgamation, and the consequent production and absorption of fixed air. On this Mr. CA-

VENDISH observes, " that mercury, fouled by the addition of
 " lead or tin, deposits a powder which consists in great measure
 " of the calx of the metal : he found also, that some powder of
 " this sort contained fixed air ; but it is not clear that this air
 " was produced by the phlogification of the air in which the
 " mercury was shaken, as the powder was not prepared on
 " purpose, but was formed from mercury fouled by having
 " been used for various purposes, and may therefore contain
 " other impurities, besides the metallic calx." On this I re-
 mark, that Dr. PRIESTLEY did not indeed at first prepare this
 powder on purpose ; but he afterwards did so prepare it (4 PRIEST.
 p. 148, 149.) and obtained a powder exactly of the same sort ; and
 it is certain that the fixed air found in it proceeded from the
 common air, both because metallic calces, not formed by amal-
 gamation, will not unite with mercury, as is well known ; and
 because this calx cannot be formed by agitation of the mercury
 and lead, in phlogificated, inflammable, or any other air which
 is not respirable ; and the fixed air cannot proceed from any
 impurity, as mercury will not unite in its running form to any
 other but metallic substances, which it always partially dephlo-
 gificates, like other menstruums (3 Chy. Dijon, 425.).

Of the Diminution of Respirable Air by Combustion.

Though I have no doubt but the diminution of respirable air,
 by the combustion of sulphur and phosphorus, proceeds also in
 great measure from the production and absorption of fixed air,
 yet I avoided mentioning this operation, as the presence of a
 stronger acid renders the presence of a weaker impossible to be
 proved, more especially, as both these acids precipitate lime
 from lime-water ; but the great increase of weight which the

phosphoric acid gains is a strong additional inducement to think that it absorbs fixed air. During the combustion of vegetable substances, I think it highly probable that fixed air is formed, both from my own experiments on the combustion of wax candles, and that mentioned in the first volume of Dr. PRIESTLEY'S Observations, p. 136; but when inflammable air from metals and dephlogisticated air are fired, as a great diminution takes place, and yet no fixed air is found, I am nearly convinced, by Mr. CAVENDISH'S experiments, that water is really produced; nor am I surprized that, in this instance, the union of phlogiston and dephlogisticated air should form a compound very different from that which it forms in other instances of phlogistication, but should rather be led to expect it *a priori*; for in this case the phlogiston is in its most rarefied known state, and unites to dephlogisticated air, the substance to which it has the greatest affinity, in circumstances the most favourable to the closest and most intimate union; for both, in the act of inflammation, are rarefied to the highest degree; both give out their specific fire, the great obstacle to their union, it being by the inflammation converted into *sensible* heat (a circumstance which, in my opinion, constitutes the very essence of flame); the resulting compound having then lost the greatest part of its specific fire, is necessarily reduced, according to Dr. BLACK'S theory, into a denser state, which the present experiment shews to be water; whereas, in common cases of combustion, the phlogiston being denser and less divided, unites less intimately with the dephlogisticated part of common air, consequently expels less of its specific fire, and therefore forms less dense compounds, *viz.* fixed and phlogisticated airs; and so much the more, as a great part intirely escapes combustion; but it seems
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probable that in very strong and bright inflammations, the union is more perfect, and water formed.

Water being then the result of the closest and most intimate union of dephlogificated air and phlogiston, it seems to me very improbable, that it is ever decomposed by the affinity of any acid to phlogiston, as all the experiments hitherto made seem to prove, that phlogiston has a stronger affinity to dephlogificated air than to any other substance, except hot metallic calces; and these, in my opinion, are incapable of forming any union with water, except as far as they are saline, but they never can be reduced by it. So also water is incapable of uniting with any more phlogiston, as sulphur is, both being already saturated.

Mr. CAVENDISH is inclined to think, that pure inflammable air is not pure phlogiston, because it does not immediately unite with dephlogificated air, when both airs are simply mixed with each other; this reason seems to me of no moment, because I see several other substances, that have the strongest affinity to each other, refuse to unite suddenly, or even at all, through the very same cause that dephlogificated and inflammable airs refuse to unite; *viz.* on account of the specific fire which they contain, and must lose, before such union can take place: thus fixed air will never unite to dry lime, though they be kept ever so long together; thus, if water be poured on the strongest oil of vitriol, they will remain several weeks in contact, without uniting, as I myself have experienced; and yet, in both cases, the specific fire need be expelled only from one of the substances, and not from both: but after a long time they will unite; so also will inflammable and dephlogificated air, as Dr. PRIESTLEY has discovered since his last publication.

That phlogificated air should consist of supersaturated nitrous air, I think improbable, as it retains its phlogiston much more strongly than nitrous air, which, according to the general laws of affinities, it should not, if it contained an excess of phlogiston; and as Dr. PRIESTLEY and Mr. FONTANA repeatedly assure us, they have converted it into common air, by washing it in water, in contact with the atmosphere. I am, &c.

London,
Jan. 29, 1784.

R. KIRWAN.

