

XXIII. *Experiments on the Formation of Volatile Alkali, and on the Affinities of the Phlogificated and light Inflammable Airs.*  
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**I**N the former part of the year 1787, I undertook to examine the elastic fluid produced upon decomposing volatile alkali by the electric stroke, as first suggested by Dr. PRIESTLEY. Some alkaline air being thus decomposed, and all its inflammable part separated by combustion in glass vessels inverted in quicksilver, I observed a considerable remainder of phlogificated air; and after many accurate experiments was fully convinced, that this phlogificated air had made a part in the constitution of the alkali. This discovery induced me to make a variety of synthetical experiments on the phlogificated and light inflammable airs, with the hopes of forming volatile alkali from its simple elements. In this undertaking I also derived much assistance from the ingenious labours of Dr. PRIESTLEY; who, in the course of his experiments, had been repeatedly struck with the smell of volatile alkali from substances not supposed to contain it, and had pointed out some important phenomena attending its production. But having acquired a more perfect knowledge of its constituent parts, I was enabled to produce volatile alkali in a more simple manner, and more demonstrative of its elements, than he had done.

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I was not apprised, when I had these experiments in hand, that the first object of my inquiry, the decomposition of volatile alkali, and analysis of its parts, had been successfully treated by the celebrated M. BERTHOLLET; and that his observations had appeared in ROZIER's Journal some months before. To him therefore I give up that part of the subject; and shall confine myself in the following observations to some experiments on the formation of volatile alkali, and on the affinities of the phlogificated and light inflammable airs, which have not, I believe, been hitherto taken notice of.

First, I endeavoured to combine the phlogificated and light inflammable airs, by mixing them together in various proportions in their elastic state, and adding to them such substances as I thought likely to promote their uniting and forming an alkali. With this view, I threw up to the mixture of these airs, marine acid air, the marine and vitriolic acids, to which I also joined alkaline air. I tried the effect of cold upon these mixtures, by applying to the tubes containing them cloths moistened with ether. I even passed the electric spark repeatedly through them, though with little probability of success. Lastly, I decomposed alkaline air, and tried to reunite the identical parts which formed it by similar additions; but I could not perceive, that in any instance volatile alkali was produced from its two constituent parts mixed together in their simple æriform state.

Yet it is well known, that these two bodies unite very readily, when they are not in an elastic state. An unexpected appearance of volatile alkali had been observed by Dr. PRIESTLEY and Mr. KIRWAN before we were acquainted with its constitution, and by M. HAUSSMAN since this discovery of M. BERTHOLLET. An experiment was exhibited before several Gentlemen at Sir JOSEPH BANKS's House, some years ago,  
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in which the quantity of volatile alkali produced is very remarkable. In this experiment a few ounces of powdered tin are moistened with some moderately strong nitrous acid, and after they have stood together a minute or two, about half an ounce of fixed alkali is mixed with them. A very pungent smell of volatile alkali is immediately perceived. The experiment succeeds equally, if lime be used instead of fixed alkali. Any person, who moistens a drachm, or two of filings of zinc with a solution of cupreous nitre, and, after they begin to act on each other, adds to them a little salt of tartar, will find volatile alkali to be produced. Nitrous acid, or cupreous nitre, mixed with iron filings, sulphur, and a little water, and kept in a close vessel for some hours, yields a smell of volatile alkali; and if a piece of paper, stained with a vegetable blue substance, be thrown into the vessel, it will, in a short time, be turned to a green colour. In each of these experiments the nitrous acid and the water are decomposed. Dephlogisticated air from each of them combines with the metal, and their other constituent parts, the phlogisticated air of the acid, and inflammable air of the water, being disengaged at the same instant, unite and form volatile alkali. Many other similar experiments might be mentioned; but these are abundantly sufficient to prove, that if phlogisticated and light inflammable air be presented to each other at the instant of their separation from solid or liquid substances, and before their particles have receded from each other, they readily combine and generate volatile alkali.

That these two substances do not combine in their elastic state, seems to be owing principally to the inflammable air. When these two airs combine, it seems necessary that they part with a certain quantity of that fire to which they owe their elasticity; and that, unless their attraction to each

other exceed their attraction to fire, they will not unite. Even when they are combined in the form of volatile alkali, if heat be applied, they immediately recede from each other, and the alkali is decomposed. When they are not in an æriform state their attraction to each other is greater, on account of the proximity of their parts; it is then superior to their attraction to fire, and therefore they combine; but when their particles have receded from each other, as in the æriform state, their attraction to each other is so diminished by the distance of their parts, that their attraction to fire, which is uniform, prevails, and keeps them in a separate state. The specific gravity of inflammable air being eleven times less than that of phlogisticated air, the distance of its particles must be greater than the distance of the particles of phlogisticated air in the proportion of  $\sqrt[3]{11}$  to 1, if the elementary particles of the two airs be of equal magnitude; and its effect, on this account, in diminishing attraction must be greater than that of phlogisticated air, in the proportion of, or more probably as the squares of, those numbers.

Whether it be admitted, that fire thus combines with other substances, and is separated from them by their mutual attractions, according to the general law, is not further material to the present enquiry, than as it accounts for a circumstance which seems to be established by the following experiments; namely, that the combination of the phlogisticated and inflammable airs, and the formation of volatile alkali, depends chiefly, if not altogether, on the approximation of the parts of inflammable air, when phlogisticated air is presented to them.

Into a cylindrical glass tube, filled with, and inverted in, quicksilver, I introduced some phlogisticated air, and afterwards some iron filings moistened with distilled water. By this

this arrangement light inflammable air, which is given out from water in contact with iron filings, meeting with phlogisticated air at the instant of its extrication, combines with it, and forms volatile alkali. In order to detect the minute quantities of volatile alkali, which were thus generated, I fixed to the inside of the glass tube a small piece of paper, stained with the rind of the blue raddish. The vegetable blue was in twenty-four hours changed to a green colour. As an additional proof of the production of volatile alkali, I kept in the same tube some paper, which had been dipped in a solution of cupreous nitre, expecting to see its colour converted from green to blue, by the alkali which was to be produced. The green paper became gradually paler, and in a few days the blue colour appeared. This experiment affords a very satisfactory demonstration of the formation of volatile alkali. Water and iron filings mixed together yield inflammable air; but if this be given out in contact with phlogisticated air, volatile alkali is produced. In these circumstances a double attraction takes place: one part of the water is attracted by the iron; the other is attracted by the phlogisticated air; and the water seems by these compound affinities to be much more rapidly decomposed, than when iron and water are mixed by themselves.

Volatile alkali is formed in a very few hours, if nitrous air be used instead of the phlogisticated, all other circumstances remaining as in the former experiment. When I have made use of nitrous air not well freed from its acid, by which the vegetable blue colour has been turned red, a sufficient quantity of alkali has been generated in twenty-four hours to change it to a green. If iron filings and water be exposed to nitrous air for a considerable time, the nitrous air is so altered that a candle burns in it with increased brightness, as was observed by

Dr.

Dr. PRIESTLEY. This change is accounted for by the formation of the alkali, which depriving the nitrous air of its phlogificated part leaves a greater proportion of dephlogificated air.

This experiment also succeeds in atmospheric air, though a longer time is necessary to produce a sensible alteration in the colours employed as tests of the alkali; but the change is very evident in a day or two. Hence we may conclude, that whenever iron rusts in contact with water in the open air, or in the earth, volatile alkali is formed. Phlogificated air is present in all parts of the terraqueous globe, and operations are constantly going on, by which inflammable air is separated from water, and perhaps from other bodies. Thus we may account for the frequent appearance of volatile alkali in the earth, particularly where inflammable matters abound, among coals and volcanic productions, as also in animal and vegetable substances.

When iron, water, and sulphur act upon each other in atmospheric air, volatile alkali is produced. The eudiometer recommended by SCHEELE is, for this reason, incorrect. Some phlogificated air disappears, and volatile alkali is formed. This method therefore seems to have misled that great chemist in his analysis of the atmosphere, and induced him to suppose, that the quantity of phlogificated air in the atmosphere is only  $2\frac{2}{3}$  times that of dephlogificated air.

There is a combination of light inflammable air with sulphur forming hepatic air. It has been observed by the celebrated Mr. KIRWAN, that if nitrous air be mixed with hepatic air volatile alkali will be formed. I have often repeated this experiment, and marked the formation of the volatile alkali by the change of the vegetable blue to a green colour. In hepatic  
air

air the parts of inflammable air are brought nearer to each other than they are in their simple aëriform state\*, and therefore the phlogisticated air of the nitrous air combines with them, and generates volatile alkali.

From all these experiments it follows, that whether phlogisticated air be in a state of purity, or mixed with dephlogisticated air, as in the atmosphere, or combined with it as in nitrous air, it will in either case unite with the gravitating matter of light inflammable air, provided this substance be presented to it in a state of condensation; but if the circumstances be reversed, the same combination does not take place. No union is formed between inflammable air and the phlogisticated part of nitrous air, even though marine acid be added, which, by its attraction to dephlogisticated air, would contribute to decompose the nitrous air, and by its attraction to volatile alkali would tend to unite its constituent parts: or if to light inflammable air we add nitrous air and iron filings, no combination ensues; though it has been often observed, that volatile alkali is readily generated, when nitrous air is presented to the inflammable at the instant of its extrication from water and iron.

The proportions of the phlogisticated and inflammable airs in volatile alkali, as discovered by calculation, approach very near

\* Since these experiments were made, I have found that this is not the case. The electric spark decomposes hepatic air, and leaves a quantity of inflammable air equal in bulk to the hepatic air very nearly. However, as the inflammable air leaves the sulphur upon the application of the electrical spark, it should seem, that the proper matter of inflammable air is more disposed to combine with fire than with sulphur; which may be the reason why hepatic air is decomposed by nitrous air, while pure inflammable air is not affected by it.

to the result of M. BERTHOLLET's experiments. If we take the specific gravities of these airs, given in Mr. KIRWAN's late publication,

100 cubic inches contain 18,16 grains of alkaline air.

— — — 30,535 — of phlogificated air.

— — — 2,613 — of inflammable air.

According to M. BERTHOLLET alkaline air is expanded upon decomposition from 1,7 to 3,3. Its specific gravity after decomposition must therefore be lessened in the same proportion; and 100 cubic inches will be found to contain only 9,355 grains of alkaline air thus expanded. In what proportion must the phlogificated and inflammable airs be, in order to form a mixture of this specific gravity?

Let  $x$  represent the number of grains of phlogificated air in 100 cubic inches of the mixture: then  $9,355 - x$  will express the number of grains of inflammable air. As the weight of one cubic inch is to a cubic inch, so will the weight of either air in the mixture be to the cubic inches of that air in the mixture; and therefore  $\frac{30,535}{100}$  the weight of a cubic inch of phlogificated air, or which is the same, ,30535 shall be to 1, as  $x$  is to  $\frac{x}{,30535}$  which must be the number of cubic inches of phlogificated air in 100 cubic inches of the mixture; and the weight of a cubic inch of inflammable air, that is,  $\frac{2,613}{100}$ , or ,02613 : 1 ::  $9,355 - x$  :  $\frac{9,355 - x}{,02613}$  the cubic inches of inflammable air in 100 cubic inches of the mixture. Thus we have an expression for the cubic inches of each air; these two quantities taken together are equal to 100 cubic inches by supposition. We have then,



$$\frac{x}{,30535} + \frac{9,355-x}{,02613} = 100;$$

$$x + \frac{2,85654925 - ,30535x}{,02613} = 30,535;$$

$$,02613x + 2,85654925 - ,30535x = ,79787955;$$

$$,27922x = 2,05866970$$

$x = 7,373$  the number of grains of

phlogificated air in 100 cubic inches, or in 9,355 grains of the mixture; and  $9,355 - 7,373 = 1,982$ , the grains of inflammable air.

Now  $7,373 : 1,982 :: 121 : 32$ ; the quantity of phlogificated air is to that of inflammable, as 121 to 32.

According to M. BERTHOLLET's experiments, the quantity of phlogificated is to that of inflammable air, as 121 : 29. This is not very wide of calculation. If we consider the great difficulty of obtaining these specific gravities with exactness, we must be pleased to find so near a concurrence, and place more confidence in experiments on the specific gravities and combinations of aëriform bodies, than has generally been given them. M. BERTHOLLET's experiments come within  $\frac{1}{10}$  of calculation; and this difference will be diminished by two-thirds, if we take the specific gravities of the phlogificated and inflammable airs in the proportion of 11 to 1, as he has done, instead of Mr. KIRWAN's proportion, which I have followed in this calculation.

