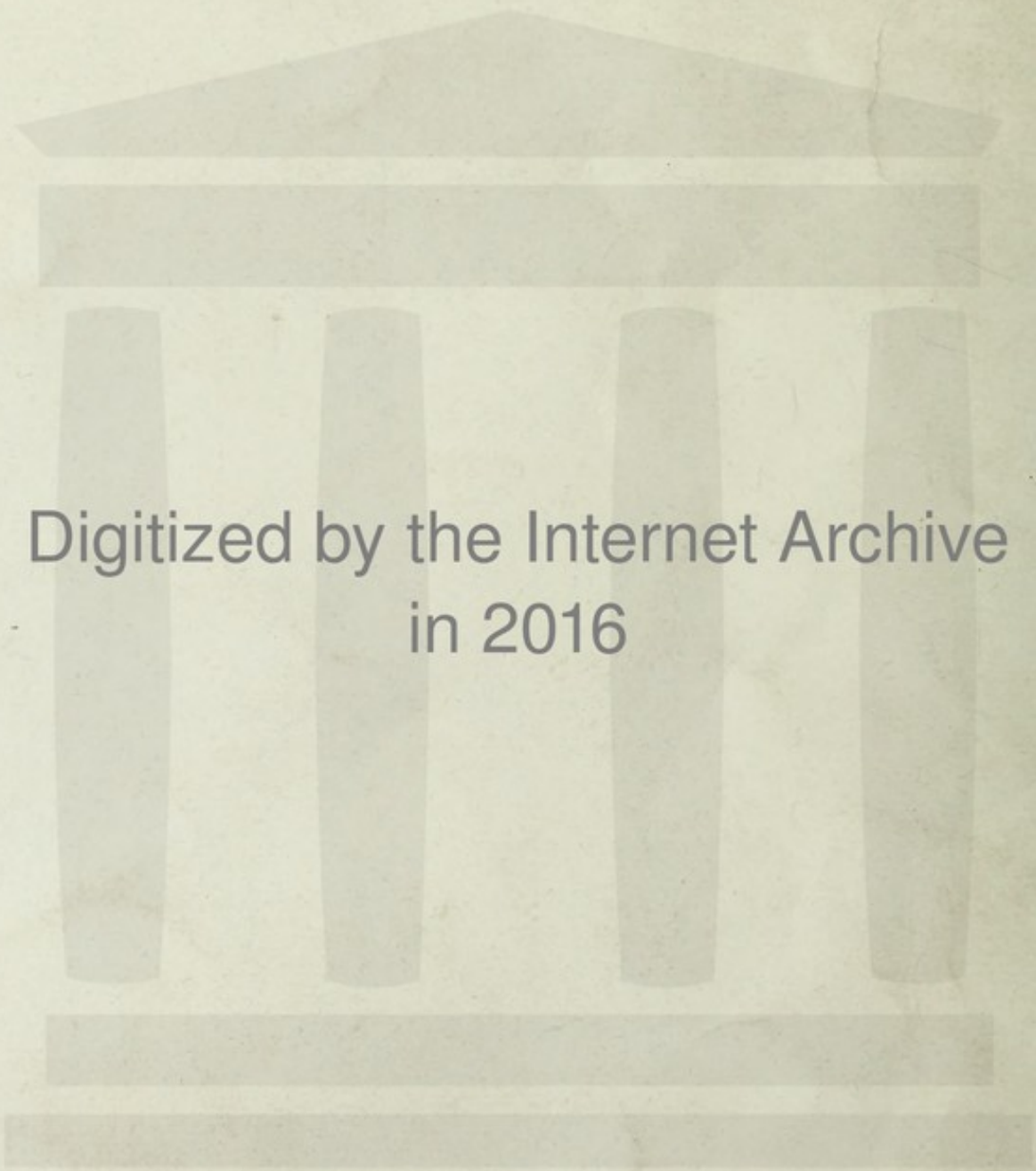
Experiments on the formation of volatile alkali, and on the affinities of the phlogisticated and light inflammable airs / by William Austin.



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EXPERIMENTS

ON THE

FORMATION OF VOLATILE ALKALI,

AND ON THE

AFFINITIES OF THE PHLOGISTICATED AND LIGHT INFLAMMABLE AIRS.

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From the PHILOSOPHICAL TRANSACTIONS.

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EXPERIMENTS, &c.

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IN 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 phlogiſticated air; and after many accurate experiments was fully convinced, that this phlogiſticated air had made a part in the conſtitution of the alkali. This diſcovery induced me to make a variety of ſynthetical experiments on the phlogiſticated 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 phænomena 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.

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 Journals 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 phlogiſticated and light inflammable airs, which have not, I believe, been hitherto taken notice of.

Firſt, I endeavoured to combine the phlogiſticated 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 aëriform 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, in

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

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 aëriform 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 aëriform 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, at the inſtant of its extrication meeting with phlogiſticated air, 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 phlogiſticated part leaves a greater proportion of dephlogiſticated 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. Phlogiſticated 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 phlogiſticated 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 phlogiſticated air in the atmoſphere is only $2\frac{3}{5}$ times that of dephlogiſticated 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 volitile 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 phlogiſticated 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 phlogiſticated and inflammable airs be, in order to form a mixture of this ſpecific gravity?

Let x repreſent the number of grains of phlogiſticated 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 phlogiſticated 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 phlogiſticated 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,

$\frac{x}{,30535}$

$$\frac{x}{,30536} + \frac{9,355 - x}{,02613} = 100;$$

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

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

$$,27922x = 2,05866970$$

$x = 7,372$ the number of grains of phlogiſticated 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 phlogiſticated air is to that of inflammable, as 121 to 32.

According to M. BERTHOLLET's experiments, the quantity of phlogiſticated 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 $\frac{1}{170}$ of calculation; and this difference will be diminiſhed by two-thirds, if we take the ſpecific gravities of the phlogiſticated 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.