

XXIII. *Experiments on the Transmission of the Vapour of Acids through an hot earthen Tube, and further Observations relating to Phlogiston.* By the Rev. Joseph Priestley, LL.D. F. R. S.

Read July 2, 1789.

IN my late experiments on the *phlogistication of spirit of nitre by heat* it appeared, that when pure air was expelled from what is called dephlogisticated spirit of nitre, the remainder was left phlogisticated. This I find abundantly confirmed by repeating the experiments in a different manner, and on a larger scale; and I have applied the same process to other acids and liquors of a different kind. From these it will appear, that oil of vitriol and spirit of nitre, in their most dephlogisticated state, consist of a proper saturation of the acids with phlogiston, so that what we have called the *phlogistication* of them, ought rather to have been called their *super-phlogistication*.

I began with treating a quantity of oil of vitriol as I had done the spirit of nitre, *viz.* exposing it to heat in a glass tube, hermetically sealed, and nearly exhausted; and the result was similar to that of the experiment with the nitrous acid, with respect to the expulsion of air from it, though the phlogistication not appearing by any change of *colour*, I did not in this method ascertain that circumstance. The particulars were as follows.

After the acid had been made to boil some time, a dense white vapour appeared in quick motion at a distance above the acid,

acid, and though, on withdrawing the fire, that vapour disappeared, it instantly re-appeared on renewing the heat. When the tube was cool, I opened it under water, and a quantity of air rushed out, though the acid had been made to boil violently while it was closing, so that there could not have been much air in the tube. This air, which must therefore have been generated in the tube, was a little worse than common air, being of the standard of 1.12 when the latter was 1.04. I repeated the experiment several times, and always with the same result.

That this air should be worse than common air, I cannot well explain. But in my former experiments it appeared that vitriolic acid air injures common air; and that in proportion as pure air is expelled from this acid, the remainder becomes phlogisticated, or charged with vitriolic acid air, clearly appeared in the following experiment.

Making a quantity of oil of vitriol boil in a glass retort, and making the vapour pass through a red-hot earthen tube, glazed inside and out, and filled with pieces of broken tubes, I collected the liquor that distilled over, and found it to be the same thing with water impregnated with vitriolic acid air. The smell of it was exceedingly pungent, and it was evident, that more of this air had escaped than could be retained by that quantity of water. The oil of vitriol used in this process was 1 oz. 9 dw. 18 gr. and the liquor collected was 6 dw. 12 gr. When I collected the air that was produced in this manner, which I did not do at this time, it appeared to be very pure, about the standard of 0.3 with two equal measures of nitrous air.

At another time, expending 1 oz. 11 dw. 18 gr. of oil of vitriol, of the specific gravity of 1856 (that of water being 1000),

1000), I collected 19 dw. 6 gr. of the volatile acid, of the specific gravity of 1340, and 130 oz. measures of dephlogisticated air of the purest kind, *viz.* of the standard of 0.15.

It is easy in this manner to collect a great quantity of dephlogisticated air; but the principal objection to the process is, that after using a few times, the earthen tubes become tender, and too easily break, especially in heating or cooling. It is also difficult to lute the retort containing the acid and the earthen tube. The air produced in this manner is filled with the densest white cloud imaginable.

Going through the same process with spirit of nitre, the result was in all respects similar, but much more striking, the production of both dephlogisticated air and phlogisticated acid vapour being prodigiously quicker, and more abundant. Expending 5 oz. 8 dw. 6 gr. of spirit of nitre, I collected 600 oz. measures of very pure dephlogisticated air, being of the standard of 0.2. I also collected 1 oz. 7 dw. 14 gr. of a greenish acid of nitre, which emitted copious red fumes. All the apparatus beyond the hot tube was filled with the densest red vapour, and the water of the trough in which the air was received was so much impregnated with it, that the smell was very strong; and it spontaneously yielded nitrous air several days, just as water does when impregnated with nitrous vapour. Perceiving the emission of air from the water, after it had stood some time, I filled a jar containing 30 oz. measures with it, and without any heat it yielded two oz. measures of the strongest nitrous air.

Taking the specific gravity of the acid before and after this distillation, the former was to the latter as 1471 to 1182. When the weight of the air produced in this experiment, and that of the liquor distilled, is compared with that of the acid

before distillation, it will appear, that there must have been a great loss of acid vapour, which was either retained in the water of the trough, or escaped through it.

I do not see that these experiments can be explained, but on the supposition that the most dephlogisticated oil of vitriol and spirit of nitre are, in a proper sense, saturated with phlogiston; and that when part of the acidifying principle is expelled in the form of the air, the remainder is supersaturated with it.

To try whether the acid, thus supersaturated with phlogiston, was convertible into pure air by this process, I heated the liquor collected after the distillation of the oil of vitriol, that is, water impregnated with vitriolic acid air, and made the vapour pass through the hot tube, but no air came from it; and when collected a second time, it was not at all different from what it had been before. The specific gravity was also the same.

It is evident, however, though this process does not shew it, that the volatile vitriolic acid contains the proper element of dephlogisticated air; since by melting iron in vitriolic acid air, a quantity of fixed air (which is composed of inflammable and dephlogisticated air) is produced. Melting iron in 9 oz. measures of vitriolic acid air, it was reduced to 0.3 oz. measures, and of this 0.17 oz. measures was fixed air. I repeated the experiment with the same result, and putting the residuums together found the air to be inflammable.

But the result was something different when I sent through the hot tube the liquor that I had collected in the process with spirit of nitre. No air, however, was produced at the first, nothing appearing besides a *red vapour* that was wholly absorbed by water, or escaped through it into the atmosphere; but towards the end of the process I collected 10 oz. measures of dephlo-

dephlogisticated air. The quantity of the liquor expended was about 2 oz. measures. It may, however, be presumed, that this small quantity of air came from some of the acid which escaped the action of the fire in the former process. Indeed its coming at the last only may be considered as a proof of this, as all the more volatile acid, which came over first, yielded no air.

I submitted a quantity of *spirit of salt* to both these processes, *viz.* exposing it to a boiling heat in glass tubes, hermetically sealed, and making the vapour pass through a red hot earthen tube, but no air was produced in either case. In the former case, the water rushed into, and completely filled, the tube, when it was opened under water; and in the other process the liquor distilled was precisely of the same specific gravity, and, no doubt, in all other respects, the same as before distillation; but the acid that remained in the retort was of less specific gravity, in consequence of the acid vapour being expelled by the heat in the form of marine acid air, which appeared not to be affected by a red heat.

Though, in the process with spirit of salt, the result be different from that of those with oil of vitriol and spirit of nitre, yet there is an analogy among all these three acids in this respect, *viz.* that the marine and both the volatile acids of vitriol and nitre are made by impregnating water with the acid vapour, so that in its usual state it may be said to be phlogisticated as well as these.

It was evident that the water in the worm-tub was much more heated by the distillation of the spirit of salt than by that of the oil of vitriol, and especially that of the spirit of nitre; so that much of the heat by which it had been raised in vapour must, in the latter case, have been *latent* in the air that was

formed; whereas, in the other case, it was communicated to the water in the worm-tub.

In one of the processes with boiling spirit of salt, in a glass tube, hermetically sealed, I had the same white vapour dancing in the middle of the tube as in the experiment with the oil of vitriol; but this tube burst, and I never had the same appearance again, though I repeated the experiment several times for the sake of it.

The vapour of dephlogificated marine acid, which M. BERTHOLLET discovered, and with which water may be impregnated as with fixed air, being made to pass through the hot earthen tube, became dephlogificated air as in the following experiment.

Having poured a quantity of spirit of salt upon some manganese in a glass retort, I heated it as in the preceding experiments with a proper apparatus both for receiving the distilled liquor, and the air. I found seven-tenths of the air was fixed air, and the remainder very pure dephlogificated. The quantity I could not measure on account of one of the junctures in the apparatus giving way; but I do not imagine that quite so much pure air could be got in this method as from the manganese itself in a direct process. The liquor received in this distillation resembled strong spirit of salt in which manganese had been put.

This process immediately succeeding that in which the glass tube, joining the earthen tube and worm-tub, was left full of black matter by the distillation of the alkaline liquor (which will be mentioned hereafter), the blackness presently vanished, and the tube became transparent as before. On this account, however, it is possible that I might receive less pure air than I should otherwise have done.

Distilled

Distilled vinegar submitted to this process yielded air two-thirds of which was fixed air, and the rest inflammable: expending 2 oz. 19 dw. 0 gr. of the acid, I got 1 oz. 19 dw. 0 gr. of a liquor which had a more pungent smell than it had before distillation. It had also some black matter in it, and some of the same remained at the bottom of the retort when the liquor was evaporated to dryness. The air I received was 90 oz. measures.

Alkaline air is converted into inflammable air in this process as well as by the electric spark, but by no means, I think, in so great a degree. I put 2 oz. 10 dw. 0 gr. of water pretty strongly impregnated with alkaline air into the retort, and heating it, sent the vapour through the hot tube; when I collected 2 oz. 3 dw. 0 gr. of liquor, which had a disagreeable empyreumatic smell, as well as that of a volatile alkali, and it was quite opaque with a *black matter*, which subsided to the bottom of the vessel. Also the tube through which the air and vapour had been conveyed was left quite black, as mentioned above. One of the junctures of the apparatus not having been air-tight, I did not collect all the air, but it came only at the beginning of the process, and before the tube became black, or any liquor was distilled, and it was all strongly inflammable.

I shall now recite a few experiments of a different kind from those that have been mentioned above, and more immediately relating to the doctrine of phlogiston.

It is said, by those who do not admit the doctrine of phlogiston, that the metals are simple substances, which, having a strong affinity to dephlogisticated air, imbibe it when they become calces, without parting with any thing. But that something is really parted with in the calcination (as they will call

it) of iron in dephlogificated air, appears to me to be very evident, as well as in the process with steam.

That fixed air is found in the vessel in which iron is melted in dephlogificated air, I observed before; but I never took much care to ascertain the quantity of it. This I have lately done in many instances, and in all of them find it to be much more considerable than can be accounted for, by supposing it to come from plumbago in the very small quantity of iron that I melted; so that it must necessarily have been formed by the phlogiston from the iron, and the pure air in the vessel, at the same time that the iron became finery cinder by imbibing water from the air; and I have shewn, that by far the greatest part of the weight of this air is water. The experiments were made with a very good burning lens, of sixteen inches diameter, with which Mr. PARKER has generously furnished me; and by means of it I can now make these experiments, which require a great degree of heat, with much more ease and certainty than I could do before.

In $6\frac{1}{2}$ oz. measures of dephlogificated air I melted turnings of malleable iron till there remained only $1\frac{1}{3}$ oz. measure, and of this $\frac{2}{3}$ oz. measure was fixed air. In 6 oz. measures of dephlogificated air, of the standard of 0.2, I melted iron till it was reduced to two-thirds of an ounce-measure, of which one-half was fixed air, and the remainder completely phlogificated. Again, I melted iron in $7\frac{1}{2}$ oz. measures of dephlogificated air, of the same purity with that in the last experiment, when it was reduced to $1\frac{1}{3}$ oz. measure, and of this four-fifths was fixed air, and the remainder phlogificated. In this case I carefully weighed the finery cinder that was formed in the process, and found it to be nine grains, so that the iron that had been melted (being about two-thirds of this weight) had

had been about six grains. I repeated the experiment with the same result.

When the dephlogisticated air is more impure, the quantity of fixed air will always be less in proportion. Thus, having melted iron in seven ounce measures of dephlogisticated air of the standard of 0.65, it was reduced to 1.6 oz. m.; and of this only one-third of an ounce measure was fixed air. This, however, is much more than can come from the plumbago in the iron; but as the production of this fixed air is by many ascribed to this plumbago, it may be worth while to shew by computation that it is impossible that it should have this origin. Both the quantity of plumbago in iron, and the quantity of fixed air in plumbago, are much too small for the purpose.

From half an ounce of the purest plumbago, I first got, in a coated glass retort, 13 ounce-measures of air, of which only three ounce measures were fixed air, the rest being inflammable; then putting it into an earthen tube, I kept it some hours in as great a heat as I could produce, and got 22 oz. m. more; and of this also only three were fixed, and the rest inflammable, and the last portion was wholly so.

But instead of supposing the fixed air that I got to be that which was expelled from the plumbago in the iron, I will suppose that even the whole of this plumbago afforded only one of the elements of the fixed air, *viz.* phlogiston, or that which the French chemists call *carbone*; and that this principle, by its union with the dephlogisticated air in the vessel, forms the fixed air, yet on this most unfavourable and improbable supposition the quantity will be found to be insufficient.

If 100 gr. of iron contain, according to M. BERGMAN, 0.12 gr. of plumbago, 7 gr. (which is the most that in any of the preceding processes I converted into finery cinder) would

contain only 0.0084 gr. of plumbago; and if we suppose with Mr. KIRWAN, that an hundred cubic inches of fixed air contains 8.14 gr. of phlogiston, the fixed air produced in one of the above-mentioned processes (*viz.* four-fifths of an ounce-measure) would contain .032 gr. of phlogiston, which is above three times more than the plumbago in the iron could furnish. It is evident, therefore, that the quantity of fixed air that I found must have been formed by phlogiston from the iron uniting with the dephlogisticated air in the vessel.

If, as I have inferred, from burning charcoal of copper in dephlogisticated air (see Experiment, Vol. VI. p. 272.) fixed air consists of 3.45 parts of dephlogisticated air and 1.5 of phlogiston, it will be found, that four-fifths of an ounce measure of fixed air will contain 0.21 gr. of phlogiston, which is much more than on the supposition of Mr. KIRWAN.

Another argument against the antiphlogistic doctrine may be drawn from an experiment which I made upon Prussian blue; if the small quantity of fixed air, that may be expelled from it by heat, be compared with the much greater quantity which is produced when heated in dephlogisticated air.

Prussian blue is generally said to be a calx of iron super-saturated with phlogiston, though of late it has been said by some that it has acquired something that is of the nature of an *acid*. From my experiments upon it, with a burning lens in dephlogisticated air, I should infer, that the former hypothesis is true, except that the substance contains some fixed air, which is no doubt an acid; for much of the dephlogisticated air disappears, just as in the preceding similar process with iron.

I threw the focus of the burning lens upon 2 dw. 5 gr. of Prussian blue in a vessel of dephlogisticated air, of the standard of 0.53, till all the colour was discharged. Being then weighed,

weighed, it was 1 dw. 2 gr. In this process $7\frac{1}{4}$ oz. of fixed air had been produced, and what remained of the air was of the standard of 0.94. Heating the brown powder to which the Prussian blue was reduced in this experiment in inflammable air, it imbibed $8\frac{1}{2}$ oz. m. of it, and became of a black colour; but it was neither attracted by the magnet, nor was it soluble in oil of vitriol and water, as I had expected it would have been.

Again, I heated Prussian blue in dephlogisticated air, of the standard of 0.2, without producing any sensible increase of its bulk, when I found three ounce measures of it to be fixed air, and the standard of the residuum, with two measures of nitrous air, was 1.35. The substance had lost eleven grains, the greatest part of which was evidently water.

To determine what quantity of fixed air Prussian blue would yield by mere heat, I put half an ounce of it into an earthen tube, and got from it 56 oz. m. of air, of which 16 oz. m. were fixed air, in the proportion of one-third in the first portion, and one-fourth in the last. The remainder was inflammable. There remained 5 dw. 20 gr. of a black powder, with a very little of it (probably the surface) brown.

Comparing these experiments, it will appear, that the fixed air procured by means of Prussian blue and dephlogisticated air must have been formed by phlogiston from the Prussian blue and the dephlogisticated air in the vessel: for if 240 gr. of this substance yield 16 oz. measures of fixed air, ten grains of it (which is more than was used in the experiment) would have yielded only 0.6 oz. m. Nor is it possible to account for the disappearing of so much dephlogisticated air, but upon the supposition of its being employed in forming this fixed air.

