

XIX. *Additional Experiments and Observations relating to the Principle of Acidity, the Decomposition of Water, and Phlogiston.* By Joseph Priestley, LL.D. F. R. S. With Letters to him on the Subject, by Dr. Withering, and James Keir, Esq.

Read May 1, 1788.

WHEN I wrote the Paper, which the Society has done me the honour to order to be printed in their Transactions, I had found that the decomposition of dephlogisticated and inflammable air, by means of the electric spark, produced an *acid liquor*, which Dr. WITHERING found to be the *nitrous*; though I should have observed, that he expressed some doubt whether the liquor did not also contain some other acid besides the nitrous.

I have since that time been desirous to ascertain the *quantity of acid* producible from a given quantity of air; and with this view I gave Mr. KEIR as much of the liquor as I had collected from the decomposition of about five hundred ounce measures of dephlogisticated air, and the usual proportion of inflammable air mixed with it. The liquor, he informed me, was 442 grains, of the specific gravity of 1022 (that of water being 1000) and that it contained as much acid as was equivalent to 12.54 grains of concentrated acid of vitriol; which quantity of vitriolic acid is capable of saturating as much vegetable fixed alkali as is contained in 22½ grains of dry nitre,

or about $23\frac{1}{4}$ grains of nitre crytallized in mean temperature. The sediment of the same liquor he also supposed to contain, at least, as much acid as the liquor itself.

That this sediment contains much acid, seems evident from this circumstance, that, when it is first formed, it often emits small bubbles, which rise to the surface of the liquor, and continues to do so a considerable time. This was more particularly the case with the sediment which I had from the tinned iron tubes. These small bubbles, I imagine, consist of nitrous air (formed from the superabundant acid vapour adhering to the metal and the water in the liquor) because when a phial, half filled with this liquor, had stood about a week, the air on the surface of it instantly, and repeatedly, extinguished a piece of lighted wood that was dipped into it.

From the preceding *data*, given me by Mr. KEIR (and making allowance for the indefinite quantity of water contained in the concentrated acid of vitriol) I am inclined to think, that not much more than one-twentieth part of dephlogisticated air is the acidifying principle, and that nineteen parts are water.

This, I would however observe, relates to air fully saturated with water, in consequence of its having been kept in jars standing in water, so that I think it possible that the water in the driest dephlogisticated air may not amount to more than nine-tenths of its weight. But I have not ascertained, by any experiment, how much water any of the kinds of air are capable of holding in a diffused state, without being any necessary part of their constitution.

Though Mr. KEIR found the greatest part of the acid in the liquor with which I furnished him to be the *nitrous*, there were evident signs of its containing a small portion of *marine* acid,

acid, by its making a precipitation with a solution of silver in nitrous acid. But this mixture of marine acid, he observes, is constantly found to accompany the production of nitre in the operations of nature. Whether the different substances from which the dephlogisticated air was extracted made any difference in this case, I cannot tell; but that which I gave Dr. WITHERING was from minium, and that which Mr. KEIR examined was from manganese.

In the notes which I took of the first production of this liquor I termed it *blue*, and Dr. WITHERING also calls it blue, and once a *greenish blue*; but that which I gave Mr. KEIR, and all that I have got since, is a decided and deep *green*, which Mr. KEIR thinks to be owing to the phlogistication of the nitrous acid.

Those philosophers who are unwilling to admit the doctrine of phlogiston, will perhaps say, that, in those experiments in which a calx is revived by means of inflammable air, this air joins the dephlogisticated air that was in the calx; and that, in consequence of this, the metal, being freed from a foreign substance, resumes its proper form and qualities, without having received any addition whatever.

But since it appeared in the preceding experiments, in which inflammable air was procured by means of steam, that the *metal* did not become a *calx*, except in consequence of parting with inflammable air (or rather with something which, when united to water, is inflammable air) it cannot be supposed to recover its metallic form without re-imbibing the same thing that it had lost, which thing may be termed *phlogiston*.

Consequently, inflammable air being (in the opinion of those who do not admit the doctrine of phlogiston) the same

thing with the substance from which it was procured, only volatilized, and united to water, it will follow, that any substance imbibing inflammable air must become compounded with that other substance from which the inflammable air was produced; and therefore, all the inferences recited in the former Paper, which tend to establish the doctrine of phlogiston, must be admitted.

It will be asked, what becomes of the dephlogisticated air which is certainly expelled from red precipitate when it is heated in inflammable air, and converted into running mercury, if the inflammable air enters into the calx, in order to its becoming a metal? I answer, that it unites with a part of the inflammable air, and forms nitrous acid; for the water that is collected in this process is strongly acid, as appears by its turning the juice of turnsole red; but the quantity is so small, that it will hardly be possible to ascertain what acid it is. Analogy, however, decides clearly in favour of the nitrous.

It may be supposed, that in this experiment with *red precipitate*, the acid was that which had not been sufficiently expelled from that substance in the process by which it is made. But the result was the very same when I used *precipitate per se*; and on this occasion I used a portion of that which I procured from M. CADET in Paris, of which mention is made in the second Volume of my Experiments, p. 36.

On the other hand, that which is expelled from finery cinder, when it is heated in contact with inflammable air (and thereby becomes *iron*) is *pure water*, without any acid. This I found to be the case even when the inflammable air had been got from iron by oil of vitriol. Does not this prove that the

iron had imbibed what was properly *water*, and not any one constituent part of water only?

That water enters into the constitution of every kind of air I supposed, because it certainly does into that of *inflammable*, *fixed*, and *dephlogisticated* air, and because none of them can be produced except by processes in which water either certainly is, or may be well supposed to be, present. That *nitrous* air also contains water, I have lately found from the iron that is heated in it becoming a proper finery cinder.

At the publication of my last Volume of Experiments, I had found, that iron heated in nitrous air acquired weight, and that what remained of the air was phlogisticated air. Having since that time repeated this experiment, and afterwards heated the iron, which was by this means increased in weight, in inflammable air, the iron lost its additional weight, and water was copiously produced, as in the same process with finery cinder, or, as I sometimes call it, scale of iron.

As nitrous air may be deprived of its water, and become phlogisticated air by heating iron in it, I find that it undergoes the same change by being repeatedly transmitted through hot porous earthen tubes, through which I some time ago discovered that vapour will pass one way, while the air contiguous to the heated tube will pass the other.

I first tried this process with turnings of iron in the tube, by which means the iron was readily converted into finery cinder; but afterwards I found that the same change was produced in the nitrous air by the hot tube only. The two bladders which I made use of in this experiment (and by the alternate pressure of which I made the air contained in them pass through the hot tube) became *red*, just as any bladder does that is filled with nitrous air, and then exposed to the influ-

ence of the atmosphere till it becomes phlogificated air, as may be seen in my former experiments. In this manner I now always treat the bladders in which I make experiments on air. It prevents them from putrefying, and gives them a firmness of texture similar to tanning.

That nitrous air contains water, and that this water can contribute to the formation of fixed air, is evident from the following experiment. I heated five grains of charcoal of copper in eight-ounce measures of nitrous air, till it was increased to ten-ounce measures, and the charcoal had lost one grain. Examining the air, I found about one-fifth of it to be fixed air, and the remainder phlogificated. It seems, therefore, that nitrous air consists of water, and something that may be called the basis of nitrous acid, or that substance which, when united to dephlogificated air, will make nitrous acid; and this seems to be pure phlogiston, since it is found, as the preceding experiments shew, in the purest inflammable air. May we not hence infer, that the nitrous is the simplest of all the acids, and perhaps the basis of all the rest?

It is evident, that more water than enters into the composition of nitrous air is necessary for the change of it into what I have called *dephlogificated nitrous air*, because the contact of iron will not, without water, produce that change in it.

Though fixed air, as I have shewn, contains water as well as nitrous air, it cannot be deprived of it, and be decomposed, by the same means; for I have heated iron in it by a burning lens, and have also made it pass repeatedly through a hot earthen tube containing turnings of iron, without producing any change in it.

In the former Paper I said, that manganese of itself gives only the purest dephlogificated air by heat; but I have now
a quantity

a quantity which, after giving pure air with a moderate heat, gives air that is more than half fixed air with a greater degree of heat. It is evident, as I have observed before, that there are very different kinds of manganese.

In these Papers I have supposed, with M. LAVOISIER and others, that the *principle of acidity* is in the dephlogisticated air only; but as the acid is always formed by the union of this air and the inflammable, it may, perhaps, with equal probability be supposed to be in either of them, or to be a compound of them both.

Mr. WATT desires me to mention it as his conjecture, that the nitrous acid is contained in the inflammable air as the acid of vitriol is in sulphur, the phosphoric in phosphorus, &c.; and that the dephlogisticated air does nothing more than develop the acid. Mr. KEIR, who was led to expect that an acid *must* be the result of the union of dephlogisticated and inflammable air, because some acid is always the consequence of its union with other inflammable substances, thinks that both may be necessary ingredients in it. Farther experiments may throw more light on the subject.

TO THE REV. DR. PRIESTLEY.

DEAR SIR,

I at length submit to your consideration the trials which I made upon the liquors you produced, by the firing of *dephlogisticated* and *inflammable air* in close vessels; and if you think

think proper you may transmit them to the Royal Society, by way of Appendix to your own Paper upon that Subject.

§ I.

Dec. 25, 1787. LIQUOR produced by burning, in a close copper vessel, *inflammable air* got from IRON by means of the steam of water, and *dephlogisticated air*, expelled by heat only, from MINIUM.

This liquor was blue, and contained a reddish brown sediment.

Exp. 1. *Terra ponderosa lime water*,

2. *Common lime water*, and

3. *Caustic fixed alkali*, caused a greenish precipitation.

4. *Caustic volatile alkali* produced a beautiful deep blue precipitate, which was wholly re-dissolved by the addition of more volatile alkali.

5. *Phlogisticated alkali* gave a reddish brown precipitate.

6. *Nitre of lead*, no change.

7. *Nitre of silver*, a bluish precipitate.

8. *Litmus*, its colour first turned red, then curdled, and at length nearly destroyed.

9. The *filtering paper*, employed to separate the sediment, was a slow burning touch-paper.

§ II.

Dec. 30. LIQUOR produced, by burning in a close copper vessel, *inflammable air*, obtained as in § I. and *dephlogisticated air*, expelled by heat only, from MANGANESE. This liquor was blue, and contained a reddish-brown sediment.

Exp. 1—9. Similar to those in § I.; and the results being in all points the same, I determined to mix the liquids together,

ther, the quantities being small, and submit them to further examination.

§ III.

- Exp. 1. The united liquids being neutralized by the addition of *caustic vegetable alkali*, a beautiful green precipitate subsided.
2. This *precipitate* dissolved entirely in caustic volatile alkali, changing to a beautiful blue.
 3. The super-natant liquid being slowly evaporated to dryness, the liquor that escaped during this process was nothing but *pure water*.
 4. The imperfectly crystallized residuum (3) effervesced upon the addition of concentrated vitriolic acid, and being submitted to distillation, on the first application of heat, an orange-coloured vapour arose, which was condensed in a receiver previously wetted with pure water.
 5. The distilled liquor (4) had the smell and the taste of *nitrous acid*, which instantly changed the blue of litmus, and that of violet paper to a red; and it acted upon silver.
 6. *Terra ponderosa lime water*, added to it, occasioned no precipitation.
 7. Saturated with vegetable alkali it converted cap paper into touch paper, and formed, upon a slow evaporation, crystals similar to those of nitre.

§ IV.

Jan. 21, 1788. LIQUOR produced by burning *inflammable air*, obtained as before; and *dephlogisticated air* from *mercurius precip. ruber*, in a close tinned iron vessel.

This

This liquor was nearly colourless, but contained a large quantity of a light brown sediment.

Exp. 1. 2. 3. 4. 5. 8. 9. Similar to those of § I. and II. except the different colour of the precipitates, and that made by the phlogificated alkali being a fine blue.

10. The liquor saturated with vegetable alkali being slowly evaporated to dryness, and the precipitate mixed with the brown sediment being put into a retort, some concentrated vitriolic acid was added, and heat was applied. A *very* faint smell of nitrous acid arose, but no visible red vapour; nor did any thing distil into the receiver until the heat was very considerable.

11. The liquor then distilled was evidently acid; but this acid was wholly precipitated by terra ponderosa lime water.

§ V.

Feb. 19. Having now received a larger quantity of the *liquor* and sediment, produced as § I. *viz.* 329 grains of the bluish green liquor, and 12 grains of the reddish brown sediment, I proceeded to repeat the experiments, but the results corresponding with the former ones, I need only mention, that the liquor changed litmus red, and coagulated it; that with phlogificated alkali it gave a brownish red, and with caustic vegetable alkali a blue precipitate; that after saturation with the vegetable alkali, both the dried salt and the sediment being submitted to distillation with the addition of concentrated vitriolic acid, an orange-coloured vapour instantly arose, and the peculiar smell of nitrous acid was strongly perceived. The distilled liquor,

liquor, besides having the taste of nitrous acid, dissolved silver; and when neutralized by vegetable alkali and slowly evaporated, afforded well-formed crystals of common nitre.

These, Sir, are all the trials I have made with the liquors produced in your experiments. They pretty clearly prove the acid generated to be the same, whether the dephlogisticated air was procured from red precipitate of mercury, from minium, or from manganese, and that this acid is the *nitrous acid*. It is not quite so clear why the liquor and sediment in § IV. gave no stronger marks of the presence of nitrous acid; but it is evident, that the acid had united itself to the iron, if not to the tin, of the vessel employed: and I find, that when nitrous acid is fully saturated with iron by being boiled with it, and fixed alkali is added, this mixture submitted to distillation, with the addition of concentrated vitriolic acid, yields no red vapours, and very little smell of nitrous acid.

I remain, &c.

W. WITHERING.

Birmingham,
February 22, 1788.

TO THE REV. DR. PRIESTLEY.

DEAR SIR,

I HAVE examined the green liquor which I received from you, with a view to determine the two points you wished prin-

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cipally to know, namely, the *quantity* and the *kind* of the
contained acid.

The quantity of the green liquor was 442 grains, and its specific gravity was to that of water as 1022 to 1000. When the green liquor was poured out of the phial, there remained at the bottom 72 grains of a brown powder, which upon examination was found to be a calx of copper, soluble in acids, but not in water.

The colour of the liquor shewed that it was a solution of copper. However, it gave no cupreous precipitation to polished steel, till a few drops of acid had been added. This circumstance seemed to shew the perfect saturation of the acid of the green liquor with the copper; and this complete saturation was further evinced by the very small alteration of colour which litmus suffered on being mixed with this liquor. This test did indeed seem to acquire a little tendency to redness, but the effect was so minute as not to deserve consideration, and might probably be owing to some slight phlogification, as it is called, of the acid contained, rather than to its superabundance.

Upon evaporating the green liquor by exposure to air, without the application of heat, no crystals were formed, but a dry green powder, insoluble in water, but soluble in acids. You had before acquainted me with this fact. As solutions of copper in the nitrous acid are known to yield deliquescent crystals, and as no crystallization happened in this instance, although the acid was evidently nitrous, I was desirous of discovering the cause of this difference between this liquor and common solutions of copper in the nitrous acid. Upon making some trials with this view, I found that there were three periods or stages to be distinguished in the combination of copper with the nitrous acid. The first period is when the acid is super-
abundant,

abundant, and deliquescent crystals formed. The second period is when the acid has been completely saturated, or perhaps supersaturated, by repeated and alternate evaporation to dryness, and re-dissolution in water, and then no crystals but a green powder is formed. The third period is when, by a further evaporation of acid and increase of heat, the green powder is changed into a brown or black calx. The complete saturation of the green liquor seems then to be the cause of the formation of the green powder on evaporation, instead of deliquescent crystals; and the production of the brown calx may be supposed to be either the result of a calcination of a part of the solution of copper which may have taken place in consequence of the great heat excited by the inflammation of the two airs; or to have been formed by the action of the heated dephlogisticated air on the copper.

In order to find the quantity of acid that was contained in the green liquor, I added, by slow degrees, to 100 grains of this liquor, a solution of mild fixed alkali, till no more precipitation took place, taking great care to cease adding alkali as soon as the copper ceased to precipitate, to prevent a re-dissolution of the precipitated metal. Upon examining how much of this alkaline solution was required to saturate a given quantity of oil of vitriol of the common specific gravity, *viz.* to water as 1844 to 1000, I found that the 100 grains of green liquor required for its precipitation as much alkali as would saturate 2,837 grains of the above-mentioned acid of vitriol. And as the whole quantity of green liquor was 442 grains, its precipitation would require as much alkali as would be capable of saturating 12,54 grains of the concentrated vitriolic acid.

This quantity of vitriolic acid is capable of saturating as much vegetable fixed alkali, as is contained in $22\frac{1}{2}$ grains of dry

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nitre, or about $23\frac{1}{4}$ grains of nitre crystallized in mean temperature*.

The difficulty of finding even an approximation of the quantity of acid, or of air expended in forming the brown calx, must be very great; and this circumstance shews the disadvantage of using metallic vessels, although in other respects more commodious for your large experiments than those of glass. I think it is probable, that the quantity of acid expended in this manner is as much or more than the quantity retained in the solution; but I am sorry I am not able to give you any grounds for a true determination. However, the experiment which I made with the calx was as follows. I dissolved it in vitriolic acid, and having saturated with alkali the superfluous acid, I precipitated the solution by a fixed alkali of known strength, and I found that the quantity of alkali requisite for this precipitation was as much as would saturate ten grains of the oil of vitriol before mentioned. This quantity of vitriolic acid is so much less than I should expect, that I regret I have not an opportunity of repeating the experiment.

The next point to be determined is the *species* of acid that is contained in the green liquor. The acid produced in your former experiments of burning inflammable and dephlogistified airs was determined to be the nitrous; and every trial which I have made of this green liquor has convinced me, that the same acid is contained in it also. Upon adding to this liquor some vitriolic acid and distilled water, I obtained by

* I say the *mean temperature*, because the proportion of water retained by salts varies very considerably, according to the temperature in which they are crystallized; the warmer the weather, the less water being retained. The consideration of this fact ought to enter into the estimates of the proportions of the component parts of salts.

distillation a colourless acid liquor, which from the smell, the properties of dissolving silver very readily, and of giving a de-flagrating quality to paper soaked in this liquor when saturated with alkali, evidently manifested the presence of the nitrous acid. But besides the nitrous, which is undoubtedly the acid in greatest abundance, I think I may venture to affirm the existence also of the marine acid.

Upon adding to the green liquor a solution of silver in which the acid was superabundant, the mixture became turbid; and when it was boiled, the minute particles collected and fell to the bottom in form of white flocks, which, on exposure to light, became dark coloured, and were re-dissolved by volatile alkali; all which appearances are indications of a luna cornea. Although these appearances left no doubt in my mind of the existence of a marine acid, I am nevertheless much obliged to our ingenious philosophical friend Mr. JOHNSON for reminding us, that Mr. CAVENDISH had also observed, in the acid produced in his experiment of passing the electric spark through a mixture of dephlogisticated and phlogisticated airs, a precipitation upon adding a solution of silver; from which, however, that most accurate philosopher would not infer the presence of marine acid, having discovered that the precipitation might be produced by the nitrous acid itself, when that acid is much phlogisticated. The acid of the green liquor is in some degree phlogisticated, as appears both from the smell which I perceived on adding the solution of silver, which, as I have mentioned, contained a superabundant acid, and from the green colour of the liquor; for I have never been able to make any but blue or greenish-blue saturated solutions from copper and nitrous acid, although they sometimes appear green from a superabundant quantity of yellow acid, or from the yellow fumes.

fumes during the solution. By adding a solution of melted nitre to the blue solutions of copper either in the nitrous or vitriolic acids, the phlogificated acid of the melted nitre immediately communicates a green colour. The marine acid tends more than the other acids to give a green colour; but I am inclined to impute the colour of your liquor principally to the phlogification of the acid, because upon adding a very small portion of vitriolic, marine, or nitrous acid, the colour was immediately changed to a light blue. The solution of silver, being purposely acid, always produced this change of colour, and I therefore considered, that the phlogificated acid was expelled in the operation, and could not affect the precipitation.

Experiments have taught me, that an exceedingly slight degree of that quality which is called the phlogification of nitre, is sufficient to produce an alteration in the colour of solutions of copper, and that the colour will be changed when the degree of phlogification is incapable of producing any precipitation of silver. Not only a solution of melted nitre will always change the colour of cupreous solutions, but even crystals of nitre, when mixed with the nitrous acid, and the mixture boiled to dryness upon copper, and re-dissolved in water, will give a green solution. If crystals of nitre be dissolved in a colourless solution of silver in nitrous acid, and this mixture added to a solution of copper in the same acid, the blue colour of the latter will be changed to a green, although neither the nitre nor solution of silver will separately have this effect, neither will nitre dissolved in a dilute nitrous acid. I do not know what degree of phlogification may be required to precipitate silver, but I suppose it to be very great; at least it is certain, that the degree of phlogification capable of giving a
green

green colour to solutions of copper is insufficient to precipitate silver. Mr. CAVENDISH, when he relates the fact of the precipitation of silver, speaks only of nitre, *much* phlogisticated, possessing this property.

To obviate any suspicion of the precipitation of silver being owing to the phlogistication of the acid, I added to some of the green liquor about an equal quantity of colourless nitrous acid and some distilled water, and I kept this mixture boiling half an hour, in order to disengage and expel any phlogisticated acid which it might contain. To the liquor, which remained perfectly pellucid, I added a solution of silver, upon which the precipitation immediately took place with all its usual circumstances, and in as great a degree as before.

If, upon examining the acids which you or others may hereafter obtain by the inflammation of airs, a mixture of marine acid be constantly found to accompany the production of the nitrous, the fact will be only analogous to all the other known productions of nitrous acid; in all which, either in the natural formation of nitre as in Spain and India, or in the nitre beds and walls made by art, a very large proportion of marine salts is constantly observed to accompany the nitre.

I shall conclude my letter with mentioning a fact, which I observed in making some experiments to find the cause of the formation of the green powder above-mentioned, and which, though not relative to the present subject, may be thought not unworthy of communication. It is the *decomposition of common salt and separation of its alkali by copper*. As I conceived the opinion that the formation of this green powder by evaporation of this green liquor was owing to the perfect saturation of the acid, among other modes of obtaining a perfectly saturated solution of copper, I sprinkled upon plates of copper strong solutions

of common salt and of sal ammoniac. In a few days the sal ammoniac was found to have converted the copper into a dry green calx; but the common salt acted more slowly upon the copper, and continued moist during several weeks. At length, however, at the end of two months, a dry green calx was formed, and I observed, that round the edges of the calx where it joined to the surface of the copper not acted upon, and where the liquor had last stood before it was dried, an efflorescence had formed of mild mineral alkali, which seems to have been separated from its acid by the action of the copper on the acid, and perhaps aided by the affinity of the alkali itself to fixed air.

The sal ammoniac also had probably been decomposed by the copper, but the volatility of its alkaline basis, when disengaged, had prevented its appearance.

Wishing you may long continue to add to the numerous and splendid list of discoveries with which you have already enriched natural philosophy,

I am, &c.

JAMES KEIR,

March 26, 1788.

