XXIV. *On the Production of nitrous Acid and nitrous Air.* By *the Rev.* Iſaac Milner, *B. D. F. R. S. and Preſident of* Queen's College, Cambridge.

Read July 2, 1789.

1. IT has been known for ſome time, that a relation ſubſiſts between nitrous acid and volatile alkali. The latter has frequently been produced by help of the former; but I do not recollect that, in any inſtance, the volatile alkali has been proved to contribute to the formation of nitrous acid or nitrous air. Some caſes, however, have occurred to me where this evidently happens; and they appear ſo new and extraordinary, that I cannot but think they deſerve the attention of philoſophical chemiſts. The hiſtory of the experiments I allude to is as follows.

2. As ſoon as I had heard of the production of inflammable air by the tranſmiſſion of ſteam through red-hot iron tubes, I had the curioſity to try whether ſome other ſubſtances in the form of air or vapour might not, by a ſimilar proceſs, undergo material alterations. In particular, the nitrous acid ſeemed well to deſerve a trial, both on account of the obſcurity and difficulties attending the theory of its production, and alſo of its important and extenſive uſefulneſs in chemiſtry.

In the relation of my experiments on this head, it will be unneceſſary to mention the exact *quantity* of acid or of air expended or generated, though I noted thoſe quantities pretty accurately

accurately at the time; for the main point I have in view in this deſcription, is to aſcertain the *nature* of the *changes* which took place; and theſe do not depend upon the quantities of aerial fluids, but upon their properties. Beſides, whoever ſhall repeat theſe experiments will find the relative *quantities* to vary very much, according to the manner of operating; and therefore, for the ſake of brevity, I omit to mention them entirely.

3. I began with boiling a little ſtrong nitrous acid in a ſmall retort, the neck of which was cloſely luted to one end of a gun-barrel. The other end of it was immerſed ſometimes in water, and ſometimes in quickſilver, and eighteen or twenty inches of the middle part was ſurrounded with burning charcoal in a proper furnace. In this manner the vapour and fumes of the boiling acid were tranſmitted through the red-hot tube, and the produce received at the end in the uſual manner.

When the acid was made to boil violently, there paſſed over a conſiderable quantity of undecompoſed red nitrous vapour, together with a mixture of nitrous and phlogiſticated airs.

When the proceſs was conducted more moderately, there was leſs nitrous vapour; and in the mixture of airs which was received in the glaſs veſſels, there was a much greater proportion of phlogiſticated air.

4. In order to increaſe the ſurface of the red-hot iron, and effect a more complete decompoſition of the nitrous vapour, the gun-barrel was crammed full of iron filings. The experiments were repeated with great caution, and almoſt the whole of the produce was found to be phlogiſticated air. It is however proper to mention, that, notwithſtanding every poſſible care, ſtill there will generally be in ſome degree an admixture

of nitrous air, and frequently of dephlogiſticated nitrous air. But I am ſatisfied that if the iron tube were ſufficiently long, ſo that a very large portion of it might be heated red-hot, all the air received in this manner from any quantity of nitrous acid ſlowly boiled would be found of that ſpecies called phlogiſticated air.

5. Theſe experiments ſeem altogether analogous to thoſe of Dr. PRIESTLEY, in which nitrous air, by expoſure to iron, is converted firſt into dephlogiſticated nitrous air, and afterwards into phlogiſticated air. The only difference ſeems to be, that in my experiments the effect is brought about ſuddenly; whereas in the method of expoſition to iron much time is required. And farther, in my method of operating, it is very difficult to conduct the proceſs ſo as to inſure the production of that ſingular ſpecies of air called dephlogiſticated nitrous air. If the acid boil very quick, the product is nearly all nitrous vapour and nitrous air. If it boil very ſlow, and a ſufficient quantity of the iron tube be well heated, then the decompoſition is almoſt complete, and little is received but phlogiſticated air. In both caſes, the progreſs of the converſion of nitrous acid to the ſtate of phlogiſticated air ſeems to be the ſame. Firſt, nitrous air is formed, then dephlogiſticated nitrous air, and laſtly phlogiſticated air. This, I ſay, ſeems to me to be the natural order of the converſion, though I do not deny, that in the rapid manner of operating with the red-hot iron tube ſome particles of nitrous acid or vapour may probably be *inſtantly* changed into phlogiſticated air. And even allowing this to be the caſe, the fact may eaſily be explained, by ſuppoſing the ſucceſſive approaches to phlogiſticated air to be made in too ſmall ſpaces of time to be obſerved; nor does it in the leaſt invalidate the general concluſion, that nitrous

air

air is nearer the ſtate of phlogiſticated air than nitrous acid or nitrous vapour; and that dephlogiſticated nitrous air is ſtill nearer. It is very difficult to decide with certainty what the changes are which the particles of the acid undergo in their paſſage through different parts of the hot tube.

From what has been ſaid, the moſt common proceſs will probably appear to be, that a particle of the acid in the form of vapour firſt generates nitrous air; that the parts of this are applied to freſh ſurfaces of hot iron, and ſuddenly changed into dephlogiſticated nitrous air; which, laſtly, is applied to ſtill freſh ſurfaces of the tube or fragments of iron, and ſo converted into phlogiſticated air. When theſe ſucceſſive contacts with freſh ſurfaces of hot iron are not ſufficiently numerous or exact, it is not unnatural to conclude, that ſome portion of air may eſcape not perfectly decompoſed.

6. Theſe conſiderations induced me to alter the proceſs a little. Inſtead of boiling the acid in the retort, I put ſome thin pieces of copper into a phial, poured nitrous acid upon them, and forced the nitrous air, as it was generated, to paſs through the red-hot tube. The event anſwered my expectation; the decompoſition was effected in this way eaſier than in the former.

But before I made this experiment, I examined what would be the effect of mere heat upon nitrous air, as I had already learned from the experiments of others, that nitrous acid, forced in the form of ſteam through red-hot tubes of clay or glaſs, underwent the moſt important alterations.

What might be the effect of long continued expoſure to a red heat I cannot ſay; but I was ſoon convinced, that nitrous air might be forced through a red-hot glaſs tube, without ſuffering any material change.

7. Laſtly, I determined to try the effect of the gun-barrel upon dephlogiſticated nitrous air, as from all that I had ſeen it ſeemed reaſonable to expect, that this ſpecies of air would be the eaſieſt reduced to the ſtate of phlogiſticated air. For this purpoſe, I diluted a ſaturated ſolution of copper in the nitrous acid, and put pieces of iron wire into it, and as the neck of the retort which contained the ſolution was luted to one end of the gun-barrel, the dephlogiſticated nitrous air was expoſed in its paſſage to the action of the red-hot tube, and alſo to the ſurfaces of the red-hot iron turnings which it contained. In this caſe, when the proceſs is conducted with proper care, all the air which is received at the other end of the tube will be found phlogiſticated.

8. When the air received at the end of the gun-barrel was in the laſt mentioned ſtate, *viz.* perfectly phlogiſticated, I have frequently obſerved a white fume iſſuing along with the air, and ſometimes aſcending through the water or mercury into the glaſs receivers. Upon examining this white fume, I ſoon perceived by the ſmell that it contained volatile alkali. I was much ſtruck with the obſervation, and immediately recollected Dr. PRIESTLEY's relation of a ſimilar production by expoſing nitrous air to pieces of iron.

9. Moſt of the experiments hitherto related were made in the ſummer of 1786; in general they agree with thoſe of Dr. PRIESTLEY; the changes and productions are much the ſame, and the only new circumſtance is, as was obſerved at art. 5. The ſame effects are brought about *inſtantly* by the action of red-hot iron, which require much time by the method of ſimple expoſure to cold iron.

For which reaſon, though it gave me much pleaſure at the time to ſee ſuch curious tranſmutations brought about in a few minutes,

minutes, yet it ſcarcely appeared worth while to trouble the Royal Society with a detail of the experiments; and I only preſume to do it now, becauſe the conjectures which I then formed have been ſufficiently verified by future experiments.

The conjectures were as follow:

10. Almoſt immediately upon ſeeing the volatile alkali produced by means of nitrous acid and metals, I conceived the poſſibility of inverting the order of the proceſs, and of producing nitrous acid or nitrous air by the decompoſition of volatile alkali. I knew of no experiments wherein this had been done, or any thing like it; yet as volatile alkali was beyond all diſpute produced in the method juſt deſcribed, and as the iron turnings and inſide of the gun-barrel were left after the operation in a ſtate of calcination, it ſeemed not unnatural to ſuppoſe, that by forcing volatile alkali through the red-hot calces of ſome of the metals, nitrous acid or nitrous air might be produced. Some of my friends, to whom I mentioned the idea, conſidered it as a random conjecture. However, I made a memorandum of it as a thing that deſerved to be tried, though in fact I neglected for near two years actually to make the trial. It was ſome time in the month of March, 1788, that the calx of manganeſe on account of its very great infuſibility, and its yielding abundance of dephlogiſticated air, occurred to me as a very proper ſubſtance for the purpoſe. I immediately crammed a gun-barrel full of powdered manganeſe; and to one end of the tube I applied a ſmall retort, containing the cauſtic volatile alkali. As ſoon as the manganeſe was heated red-hot, a lighted candle was placed under the retort, and the vapour of the boiling volatile alkali forced through the gun-barrel. Symptoms of nitrous fumes and of nitrous air ſoon diſcovered themſelves,

and

and by a little perſeverance I was enabled to collect conſiderable quantities of air, which on trial proved highly nitrous. I have ſince frequently repeated this experiment, and have always in ſome degree ſucceeded. Much depends on the *kind* of manganeſe employed, much on the heat of the furnace, and much on the patience of the operator; as theſe are varied, there will be great variations of the products. A minute detail of all the particulars of my experiments ſeems unneceſſary; but it may be proper to give a general account of the principal facts, and of the methods which were uſed to avoid erroneous concluſions.

11. In general I made uſe of clean gun-barrels with which no previous experiments had been made. The manganeſe was uſed in rough powder; for when it is too finely powdered, the tube is choaked, and the air cannot paſs.

In ſome experiments I applied the vapour of the volatile alkali directly to the hot manganeſe. In others I ſuffered the manganeſe to remain a conſiderable time in a red heat before I made the volatile alkali, contained in the retort at the end of the tube, to boil; and by this means I informed myſelf of the nature of the airs which the manganeſe yielded *per ſe*.

In neither caſe could I ever perceive the leaſt appearance of nitrous acid or nitrous air till the volatile alkali was uſed. Manganeſe, *per ſe*, gives airs of different kinds (but chiefly fixed and dephlogiſticated airs) as ſoon as ever it is ſubjected to a conſiderable heat; but nothing nitrous comes from it, either on the firſt application of heat, or after it has been continued a long time; and I examined this point with great diligence. But ſoon after the volatile alkali begins to be applied, the jars in which the air is received will frequently turn

ſlightly

ſlightly red, and this redneſs will increaſe on admitting atmoſpherical air.

The cauſtic alkali ſhould be ſtrong, and as far as I have obſerved the longer the proceſs is continued, the ſtronger will be the nitrous air produced. At leaſt this evidently appeared to be the caſe in ſeveral inſtances, where the operation was continued for a long time.

In moſt inſtances, on the very commencement of this proceſs, a ſmall jar of the air thus collected diſcovers by the *ſmell* a nitrous impregnation. But it ſometimes happens, that ſeveral jars of air may be collected, and the admiſſion of atmoſpherical air to them will not produce a ſenſibly red colour.

Here, however, there exiſts a cauſe of deception againſt which the operator ought to be on his guard, leſt he ſhould conclude that no nitrous air is formed, when in reality there is a conſiderable quantity. The volatile alkali, notwithſtanding every precaution, will frequently paſs over in great quantities undecompoſed. If the receivers are filled with water, a great part of this will indeed be preſently abſorbed; but ſtill ſome portions of it will mix with the nitrous air formed by the proceſs. Upon admitting the atmoſpherical air, the nitrous air is decompoſed, and the red nitrous fumes inſtantly combine with the volatile alkali. The receivers are preſently filled with white clouds of nitrous ammoniac; and in this manner a wrong concluſion may eaſily be drawn, from the want of the orange colour of the nitrous fumes. A conſiderable quantity of nitrous air may have been formed, and yet no orange colour appear, owing to this circumſtance; and therefore it is eaſy to underſtand how a ſmall quantity of nitrous air may be moſt effectually diſguiſed by the ſame cauſe.

12. Theſe obſervations are made principally for the ſake of thoſe who may wiſh to repeat theſe experiments. The main point to be eſtabliſhed, is the actual formation of nitrous air by this method. And this truth I conſider as proved beyond all controverſy; for by continuing the proceſs patiently, and applying repeatedly freſh portions of ſtrong volatile alkali to the ſame manganeſe, kept conſtantly hot in the gun-barrel, I have often collected large jars of air, which was proved to be highly nitrous by mixture with atmoſpherical or with dephlogiſticated air.

13. It is not eaſy to ſay, whether in this proceſs dephlogiſticated nitrous air, or even nitrous acid itſelf, be not ſometimes immediately formed by the action of the volatile alkali on the manganeſe. Traces of the former, in ſome inſtances, ſeem to diſcover themſelves; but I do not ſpeak decidedly on this head. As to the latter, it is very certain, that fumes of the nitrous acid often circulate in the jars that receive the air. But poſſibly theſe fumes may ariſe from the decompoſition of nitrous air, by means of the ſuperfluous dephlogiſticated air of the manganeſe.

14. The ſteam of boiling water was applied to red hot manganeſe in a ſimilar way; not the leaſt nitrous appearance; but the fixed and dephlogiſticated airs were generated much more plentifully than when the manganeſe was urged by mere heat. When theſe airs had been collected in large quantities, the volatile alkali was applied as before to the reſiduum of the manganeſe, and nitrous air ſoon appeared.

15. As manganeſe is known to produce a very extraordinary change upon ſpirit of ſalt in a moderate heat, it ſeemed not improbable, that a ſtill greater change might take place by working in this method. Accordingly I forced the vapour of

boiling ſpirit of ſalt to paſs through red-hot manganeſe. This experiment did not anſwer my expectation; the product was a mixture of fixed and inflammable air. But it deſerves to be noticed, that even in this caſe, after the effect of the ſpirit of ſalt had been tried for a long time, a production of nitrous air upon the application of volatile alkali to the ſame manganeſe ſoon took place.

16. As there are many other ſubſtances beſides the calx of manganeſe, which are known, *per ſe*, to afford dephlogiſticated air, or a mixture of this with fixed air, it was natural to conclude from analogy, that ſuch ſubſtances upon the application of volatile alkali would not fail to afford nitrous air.

It is beſt, however, in theſe matters to truſt as little as poſſible to conjectures, and to bring every opinion to the teſt of experiment. Manganeſe is ſo ſingular a ſubſtance, that it is perhaps hardly ſafe, from what happens in making trials with it, to infer in any inſtance of another calx of a metal a ſimilarity of effect. Red lead, however, is known to agree in ſuch a variety of chemical effects with manganeſe, that I find it difficult to perſuade myſelf that the volatile alkali properly applied to it would not yield nitrous acid or nitrous air; yet I have hitherto in vain attempted to bring this about. The red lead, indeed, melts during the proceſs, flows into the cooler parts of the tube, and often choaks the paſſage of the air; but in ſome trials a great deal of air has been collected before that happened, and without any ſymptom of a nitrous mixture. It ſeems difficult to explain the reaſon of the failure; perhaps with a better adapted apparatus, and more perſeverance, either the production in queſtion may be obtained, or the cauſe of the failure diſcovered.

17. With calcined green vitriol I had much better ſucceſs. The ſalt was calcined to whiteneſs, and put into a gun-barrel; and, after ſeveral trials of forcing the volatile alkali through the hot tube, I procured by the operation ſome ounces of ſtrong nitrous air.

So extraordinary an effect would no doubt have proved highly grateful to the ancient chemiſts, and have been by them denominated a tranſmutation.

In the courſe of my enquiries, I conſidered this experiment as important, becauſe it proved, that the ſame combinations might take place when ſubſtances were made uſe of different from manganeſe.

18. As calcined green vitriol, *per ſe*, in a ſtrong heat yields dephlogiſticated air, I had now no doubt but that any ſubſtance which had this property might, by ſimilar treatment, be made to afford nitrous air.

But in this ſuppoſition I was entirely miſtaken. The volatile alkali was applied to ſome calcined alum at the moment when it was yielding in a ſtrong heat plenty of dephlogiſticated air. The product was an aſtoniſhing quantity of inflammable air, mixed with hepatic air and actual ſulphur. The reſiduum of the alum had a ſtrong hepatic ſmell, and contained particles of perfectly formed ſulphur.

Moſt of theſe experiments, if not all, were repeated in earthen tubes inſtead of gun-barrels, and with the ſame ſucceſs.

19. It now only remains, that I ſhould briefly propoſe what occurs to me as the probable theory and explanation of the facts related.

The ingredients which enter into the compoſition of nitrous acid ſeem to be the two principles or elements of the atmoſphere,

ſphere, *viz.* phlogiſticated and dephlogiſticated air. That this is the caſe, there ſeems little reaſon to doubt. Both the compoſition and decompoſition of nitrous acid renders the ſuppoſition probable. For,

1. Nitrous air and dephlogiſticated air by mixture produce nitrous acid; and nitrous acid, by mere heat, is converted into a mixture of phlogiſticated and dephlogiſticated airs.

2. Nitrous air, by the methods already related, is changed into phlogiſticated air, and theſe methods ſeem to conſiſt in abſtracting from the nitrous air a quantity of dephlogiſticated air.

3. When nitrous acid and nitre are produced in a natural way, the proceſs is not well underſtood; but the preſence of the atmoſphere is known to be neceſſary.

4. Mr. CAVENDISH's experiment is deciſive on this point. The union of the two airs in queſtion is effected by means of the electrical ſpark, and nitrous acid is the product.

In the next place we are to conſider, that volatile alkali contains phlogiſticated air; for,

1. Volatile alkali, by mere heat, or by the electrical ſpark, is changed into a mixture of phlogiſticated and inflammable air; and,

2. The reſiduum of volatile alkaline air, after the calces of lead have been revived in it, is phlogiſticated air.

Therefore, when volatile alkali, in the form of fume or air, is applied to red-hot manganeſe, or calcined green vitriol (ſubſtances which are then yielding dephlogiſticated air), with theſe facts in view, it ſeems not difficult to conceive, that one of the ingredients of the alkali, *viz.* phlogiſticated air, ſhould combine with dephlogiſticated air, and form nitrous acid or nitrous air. If nitrous acid be formed, it will indeed in that

heat, as has been obſerved, be inſtantly decompoſed; but if the effect of the union be nitrous air, that will ſuſtain the heat without decompoſition. How it happens, that nitrous air ſhould be formed, and not nitrous acid, or what the reaſon is, that nitrous air can ſuſtain a red heat without decompoſition, when nitrous acid cannot, I am unable to ſay; and it is better to acknowledge our ignorance than advance groundleſs conjectures. So much, I think, may be pronounced as certain, *viz.* that nitrous air contains leſs dephlogiſticated air than nitrous acid; becauſe it requires the addition of dephlogiſticated air to become nitrous acid.

And, laſtly, if I miſtake not, the experiment with the calcined alum proves, that, in order to produce nitrous air, it is not ſufficient merely to apply volatile alkaline air to a ſubſtance which is actually yielding dephlogiſticated air.

Perhaps the preſence of another ſubſtance is required, which has a ſtrong attraction for phlogiſton. Perhaps, in the experiments with the calces of manganeſe and of iron, the inflammable principle of the volatile alkali combines with the calces of the metals, and the phlogiſticated air, the other component part, unites with the dephlogiſticated air; and if ſo, it ſeems not improbable to ſuppoſe, that when alum is made uſe of, the inflammable principle of the volatile alkali having little or no attraction for clay, the baſis of the alum, ſhould combine with its acid and form ſulphur. If this reaſoning be true, then it follows, that the vitriolic acid has a ſtronger affinity to the inflammable principle than it has to phlogiſticated air; and the proceſs with the green vitriol and manganeſe is to be explained by the operation of a double affinity: the inflammable principle of the volatile alkali joins with the calx of iron, the baſis

baſis of the vitriol, or with the manganeſe, and the phlogiſticated air with the dephlogiſticated air produced by the acid in the red heat.

Thoſe who chuſe to reject the doctrine of phlogiſton muſt make the neceſſary alteration in theſe expreſſions; but the reaſoning will be much the ſame.