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A HISTORY OF NITROUS OXIDE AND OXYGEN ANAESTHESIA

PART IA: THE DISCOVERY OF NITROUS OXIDE AND OF OXYGEN

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"It may be asked: Did Priestley 'discover' nitrous oxide?" (Hartog, 1941).

N.B. Nitrous air is nitric oxide.
Dephlogisticated nitrous air is nitrous oxide.
Phlogisticated air is nitrogen.
Dephlogisticated air is oxygen.
Fixed air is carbon dioxide.
Brimstone is sulphur.
Liver of sulphur is potassium polysulphide.

Priestley's "discovery" of nitrous oxide.

If Priestley did "discover" nitrous oxide, it may be asked: When did he discover it? Various dates between 1772 and 1777 have been suggested (table I).

TABLE I. *Dates quoted by various authors for the discovery or the first preparation of nitrous oxide.*

Before 1766	Robison (1803) cited Partington (1962)
1772	Davy (1812); Roscoe and Schorlemmer (1884) cited Hewitt (1893); Buxton (1914); Flagg (1916); Gardner (1916); Gwathmey (1925); Sykes (1939); Goldman (1941); Lundy (1943); King (1946); Parry-Price (1946); Robinson (1946); Clement (1951); Seward and Bryce-Smith (1957); Wylie and Churchill-Davidson (1960); McKie (1961); Keys (1963); Heironimus (1964); Wood-Smith and Stewart (1964); Faulconer and Keys (1965); Smith (1965) by implication; Lee and Atkinson (1968); Paton and Payne (1968); Davison (1971)
1772–3	Cartwright (1952)
1773	Fülöp-Miller (1938), authority not cited; Marston in foreword to Cartwright (1952)
1774	Dallemagne (1948)
About 1774	Robinson (1922), in posthumous edition of Hewitt's *Anaesthetics and their Administration* in which Hewitt had previously given the alternative dates of 1772 or 1776
1776	Watts (1868) cited Hewitt (1893); Braine (1872); Hadfield (1923); Webster (1924); Dogliotti (1935); Collins (1966)
About 1766	Boyle and Hewer (1923)
1777	Lee (1947); Marston (1949)
Date not specified	Blomfield (1922); Duncum (1947); Collins (1952); Gibbs (1965) but he implied that it was not 1772 when he considered nitrogen rather than nitrous oxide to have been prepared

The date quoted most frequently is 1772. This was the date implied in Part I (Smith, 1965), in which Priestley's vivid description of the diminution of nitrous air by a mixture of iron filings and brimstone made into a paste with water, was quoted as follows:

> The diminution of common air by a mixture of nitrous air, is not so extraordinary as the diminution which nitrous air itself is subject to from a mixture of iron filings and brimstone, made into a paste with water. This mixture, as I have already observed, diminishes common air between one fifth and one fourth . . . but when it is put into a quantity of nitrous air, it diminishes it so much than no more than one fourth of the original quantity be left. The effect of this process is generally perceived in five or six hours, about which time the visible effervescence of the mixture begins; and in a very short time it advances so rapidly, that in about an hour almost the whole effect will have taken place. If it be suffered to stand a day or two longer, the air will still be diminished farther, but only a very little farther, in proportion to the first diminution. The glass jar, in which the air and this mixture have been confined, has generally been so much heated in this process, that I have not been able to touch it.

Following this quotation the statement was made that:

> The remaining air supported combustion and it smelled more like common air than like nitrous air. He named it "dephlogisticated nitrous air". In his own words (Priestley, 1786): "Dephlogisticated nitrous air is the term by which I first distinguished this species of air, because it admitted a candle to burn in it." This is now known as nitrous oxide.

Although it could be argued that this statement is not entirely untrue, it would not have been true in 1772 and it is certainly misleading.

In 1772 Priestley undoubtedly exposed nitrous air to a mixture of iron filings and sulphur, with water, which he found led to a considerable reduction in its volume. He also found that the residual gas "has not the peculiar smell of nitrous air, but smells more like common air in which the same mixture has stood". At that time Priestley evidently appreciated that he had begun the experiment with nitrous air in the container and ended it with a smaller quantity of something which was not nitrous air. He did not, however, record that the end product had any specific properties other than those possessed by common air.

Later Priestley (1777), discussing the phenomena attending the diminution of nitrous air by iron filings and brimstone, and also by liver of sulphur, wrote:

> The first remarkable diminution that I observed was occasioned by the fermentation of iron filings with brim-

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stone, made into a paste with water. This process is attended with much heat, the diminution of the air is exceedingly rapid, and whenever I examined the air that remained, it always appeared to be simply phlogisticated air, neither affecting common air, not being affected by nitrous air, and always extinguishing a candle.

This makes it quite clear that in 1772 Priestley was not aware that he had discovered a new air by exposing nitrous air to a paste of iron filings and brimstone. It even casts doubt upon whether he had prepared a new air at the time.

Reporting experiments and observations made in the year 1773, and the beginning of the year 1774 (Priestley, 1774), Priestley described an experiment in which he exposed nitrous air to iron over mercury (without any sulphur) for about two months. He wrote:

. . . a most remarkable and unexpected change was made in the nitrous air; and in pursuing the experiment, it was transformed into a species of air, with properties which, at the time of my first publication on this subject, I should not have hesitated to pronounce impossible, *viz.* air in which a candle burns quite naturally and freely, and which is yet in the highest degree noxious to animals, in so much that they die the moment they are put into it; whereas, in general, animals live with little sensible inconvenience in air in which candles have burned out. Such, however, is nitrous air, after it has been long exposed to a large surface of iron.

It is not less extraordinary, that a still longer continuance of nitrous air in these circumstances (but *how long* depends upon too many, and too minute circumstances to be ascertained with exactness) makes it not only to admit a candle to burn in it, but enables it to burn with an *enlarged flame*, by another flame (extending everywhere to an equal distance from that of the candle, and often plainly distinguishable from it) adhering to it. Sometimes I have perceived the flame of the candle, in these circumstances, to be twice as large as it is naturally, and sometimes not less than five or six times larger; and yet without anything like an *explosion,* such as in the firing of the weakest inflammable air.

There we have Priestley's "discovery" of an air with new and specific properties: his "discovery" of nitrous oxide. The instantaneous death of mice put into this new air can probably be attributed as much to the effects of unchanged nitric oxide as to the effects of nitrous oxide and of anoxia. The crucial experiment was most probably carried out towards the end of 1773 because on the following page he wrote: "Lastly, one quantity of nitrous air, which had been exposed to iron and quicksilver from December 18 to January 20 . . .".

Continuing his account of the discovery of this new air, Priestley made the following observation:

Nor is the farther progress in the transmutation of nitrous air, in these circumstances, less remarkable. For when it has been brought to the state last mentioned, the agitation of it in fresh water almost instantly takes off that peculiar kind of inflammability, so that it extinguishes a candle, retaining its noxious quality . . .

Presumably the explanation of this is that much of the nitrous oxide that he had prepared was dissolved in water. This is most probably why he did not "discover" nitrous oxide in 1772. Confirmation of this point would require critical repetition of his original experiments, using modern methods of gas analysis capable of distinguishing the various oxides of nitrogen.

Priestley's repetition of his experiment of 1772.

Priestley also prepared nitrous oxide by exposing nitrous air to liver of sulphur, and he found that this reaction was quicker than when iron was used. This led him to repeat his previous experiments in which the exposure of nitrous air to a mixture of iron filings and brimstone had produced an air which extinguished a candle. In 1777 he was able to write:

I have since, however, observed that nitrous air diminished by iron filings and brimstone does not really differ from that which is diminished by the other processes; but that this process being made in a large quantity of water, either the superfluous nitrous acid vapour, the superfluous phlogiston, or both, were always absorbed before the experiment was made. This I discovered by repeating the process in the following manner.

Having introduced a pot of iron filings and brimstone into a large jar of nitrous air, I examined the state of the air in all the stages of its diminution, from the time that the fermentation began, till it could be diminished no more by that process. In order to get a small quantity of the air, without moving the jar, or disturbing the apparatus contained in it, I fastened a small phial, or a piece of glass tube, to the end of a stiff wire; and filling it with water, I put it up into the vessel, with its mouth downwards; when, the water running out, it would necessarily be filled with the air of the jar, which I could then with the same ease withdraw, and examine.

Proceeding in this manner, I found that, in the last stage of the diminution of this air, and not before, a candle burned in it with an enlarged flame. This process, therefore, exactly resembles that with iron only or liver of sulphur, only that in this case the air must be examined very soon, before the water can have had an opportunity to act upon it . . .

The first preparation of nitrous oxide by Joseph Black.

From these later experiments it could be argued that Priestley did prepare nitrous oxide in 1772, but did not know it. If this is admitted as significant evidence for the *"discovery"* of nitrous oxide, however, it may have to be conceded that the credit is due not to Joseph Priestley, but to Joseph Black.

Robison (1803, cited Partington, 1962), publishing Black's *Lectures on the Elements of Chemistry* after his death, added the following note to the account of ammonium nitrate:

In a bundle, marked "old notes, excerpts, &c." I find some experiments on this salt, which deserves some notice. Dr Black seems to aim at the best process for preparing it for medical purposes by sublimation. He was aiming at the same thing with the salt called *acetous ammoniac*, and is surprised that he can prepare the latter very easily, but that the nitrous ammoniac could not be condensed, although its ingredients are not nearly so volatile as those of the other.

In one experiment with a dry nitrous ammoniac, which he had prepared himself by mixing colourless nitrous acid with the purest volatile alkali, the vapours were incoercible *in part*, and what did condense was almost pure water, greatly exceeding in quantity what could be supposed necessary for the crystals of the salt. He was obliged to give passage to the incondensible vapours. He tried whether they were inflammable, by presenting a bit of lighted paper to the hole in the luting. It did not take fire, but it made the paper burn with prodigious violence. He thought, from this circumstance, that it was the nitrous acid: But putting alkaline ley into the receiver, he did not find it condense more readily, nor produce a nitre. Putting lime water into the receiver, he found no precipitation, when he used the pure salt prepared by himself; but employing some gotten in the shop of Mr Hill (which I mention, because it shows the date of the experiment to be previous to 1766), he had a precipitate. He attributes this to impure alkali, containing inflammable matter. He says, that although the incoercible fumes filled the laboratory, the effect on his breathing and sensations was *very far from being unpleasant*. He suspects that the acid suffers some decomposition, and again wonders at the quantity of water obtained. With some particular view, he had mixed with the salt thrice its weight of finely powdered glass. In three succeeding trials, the mixture detonated, and burst the vessels, although the heat was not much above that of boiling water.

These experiments tally in many particulars, with those in the judicious analysis of this salt by Mr Davy of the Royal Institution. Dr Black has had some experience of the wonderful effects of the *gaseous oxyd of azote*, or *nitrous oxyd*, which have given so much amusement of late, and from which mighty medical consequences are expected by some physicians. This subject will come before us some time hence. [See Appendix.]

The significance of the above reference to Mr Hill's shop and to the date 1766, is that Mr Ninian Hill, and Co, surgeon, was proprietor of a "dispensary shop Leeche's land, south side Trongate, No. 54" (Jones' Directory of Glasgow, 1787; personal communication Miss E. G. Jack, 1970), and that Joseph Black moved from Glasgow to Edinburgh in 1766. There is evidence, however, that Black was still in communication with Mr Hill as late as 1768 (Robinson and McKie, 1970), so it is possible that he purchased chemicals from him after 1766.

The following caution has also been given by McKie and Kennedy (1960): ". . . the historical value of the content of the printed *Lectures* is not very great, and statements are to be ascribed to Black only when they can be confirmed by independent evidence from other sources". Unfortunately none of Black's MS. notes used by Robison appear to have survived (Smeaton, W. A., 1970, personal communication), and Black did not publish anything on the subject himself. Manuscript lecture notes made by Thomas Cochrane, when he attended Black's lectures in Chemistry in Edinburgh during the session 1767–68, have survived (edited McKie, 1966). These record:

Ammon Nitros: is the most fusible of the Common Salts; w^{n} the heat is increased is copiously converted into Vapour; the degree of heat Sufficient for its fusion is that of boiling water if exposed to a sudden heat undergoes a deflagration although no inflammable matter be added to it.

Similar notes made by George Cayley (1786), nearly twenty years later, record:

Nitros Ammoniac, also called nitrum semi volatile, & some times Nitrum Fulminans. It is the most fusible of ye compound salts; it melts in glass vessels, in a heat not greatly exceeding boiling water, it appears perfectly fluid & transparent like oil, & begins to emit vapours if ye heat is increased, & soon entirely evaporates, but if ye heat is applied more suddenly it takes fire, w^{c} gives a presumption y^{t} ye volatile alkali contains inflammable matters in its composition, & ye other ammoniacs when thrown into melted nitre shows ye same inflammation & there are many other experiments, w^{c} show y^{t} there is some of ye principle of inflammability in ye composition of ye volatile alkali . . .

Cochrane's notes suggest that Black had prepared nitrous oxide by heating ammonium nitrate at least as early as 1767, but Cochrane does not reveal any of the properties of the copious vapour into which the ammonium nitrate was converted. George Cayley tantalizes us with his mention of "many other experiments, w^{c} show y^{t} there is some of ye principle of inflammability in ye composition of ye volatile alkali". Although details of the experiments were withheld, this hint does lend some support to Robison's note quoted above.*

Background to Priestley's "discovery" of nitrous oxide.

If Priestley did "discover" nitrous oxide, it may also be asked: Why did he discover it?

An early reference to Priestley's interest in air is contained in his *History and Present State of Electricity, with Original Experiments (1767)*, in which he wrote:

Having read, and finding by my own experiments, that a candle would not burn in air that had passed through a charcoal fire, or through the lungs of animals, or in any of that air which the chymists call mephitic; I was considering what kind of change it underwent, by passing through the fire, or through the lungs &c., and

* Another set of manuscript notes, dated 1770, and now at the Royal College of Surgeons, Edinburgh, does not throw any further light on the subject.

whether it was not possible to restore it to its original state, by some operation or mixture. For this purpose I gave great intestinal motion to it; I threw a quantity of electric matter from the point of a conductor into it, and performed various other operations upon it, but without any effect.

When Priestley moved from Warrington to Leeds in 1767 he found an abundant supply of carbon dioxide in the brewery adjacent to his temporary home. This was an added stimulus and he began his experiments on different kinds of air which were enthusiastically received when first published in 1772. He then revealed that his interest in nitrous air arose from reading Stephen Hales' *Vegetable Staticks* (1727):

Ever since I first read Dr Hales's most excellent *Statical Essays*, I was particularly struck with that experiment of his, of which an account is given, Vol. I, p. 224, and Vol. II, p. 280, in which common air and air generated from Walton Pyrites, by spirit of nitre, made a turbid red mixture, and in which part of the common air was absorbed; but I never expected to have the satisfaction of seeing this remarkable appearance, supposing it to be peculiar to that particular mineral. Happening to mention this subject to the Hon. Mr Cavendish, when I was in London, in the spring of the year 1772, he said that he did not imagine but that other kinds of pyrites, or the metals might answer as well, and that probably the red appearance of the mixture depended upon the spirit of nitre only. This encouraged me to attend to the subject; and having no pyrites, I began with the solution of the different metals in the spirit of nitre, and catching the air which was generated in the solution, I presently found what I wanted, and a good deal more.

Beginning with the solution of brass, on the 4th of June, 1772, I first found this remarkable species of air, only one effect of which was casually observed by Dr Hales; and he gave little attention to it, and it has been so unnoticed since his time, that, as far as I know, no name has been given to it, I therefore found myself, contrary to my first resolution, under an absolute necessity of giving a name to this kind of air myself. When I first began to speak and write of it to my friends, I happened to distinguish it by the name *nitrous air*, because I had procured it by means of spirit of nitre only; and though I cannot say that I altogether like the term, neither myself nor any of my friends, to whom I have applied for the purpose, have been able to hit upon a better; so that I am obliged, after all, to content myself with it.

Having obtained nitrous air, Priestley investigated its reaction with common air, and he found that:

The diminution of a mixture of this air and common air is not an equal diminution of both kinds, which is all that Dr Hales could observe, but of about one fifth of the common air, and as much of the nitrous air as is necessary to produce that effect; which, as I have found by many trials, is about one half as much as the original quantity of common air. For if one measure of nitrous air be put to two measures of common air, in a few minutes (by which time the effervescence will be over) there will want about one ninth of the original two measures; and if both the kinds of air be very pure, the diminution will still go on slowly, till in a day or two, the whole will be reduced to about one fifth less than the original quantity of common air . . .

He went on to repeat the experiment over mercury, and noted that there was still a reduction in volume, but not as great as when it was carried out over water.

His next major step was to determine that:

. . . this effervescence and diminution, occasioned by the mixture of nitrous air, is peculiar to common air, or *air fit for respiration*; and as far as I can judge, from a great number of observations, is at least very nearly, if not exactly, in proportion to its fitness for this purpose; so that by this means the goodness of air may be distinguished much more accurately than it can be by putting mice, or any other animals, to breathe in it.

This was a most agreeable discovery to me, as I hope it may be an useful one to the public; especially as, from this time, I had no occasion for so large a stock of mice as I had been used to keep for the purpose of these experiments, using them only in those which required to be very decisive; and in these cases I have seldom failed to know beforehand in what manner they would be affected. . . .

. . . Also the degree of diminution being from nothing at all to more than one third of the whole of the quantity of air, we are by this means, in possession of a prodigiously large *scale*, by which we may distinguish very small degrees of difference in the goodness of air.

Priestley made extensive use of his new test of the goodness of air. Previously he had used mice for his investigation of the power of living plants to restore air which had been injured by the respiration of animals. He used the test, belatedly, when he "discovered" oxygen and its power of supporting respiration. He also applied it to the residual air obtained in the experiment of 1772, in which he exposed nitrous air to a paste of iron filings and brimstone over water. Note his comment, ". . . it always appeared to be simply phlogisticated air, neither affecting common air, *nor being affected by nitrous air*, and always extinguishing a candle".

The idea of exposing common air to iron filings and brimstone also came from his reading of Hales' work. He wrote: "I repeated the experiment and found the diminution greater than I had expected." (The origin of the mixture of iron filings and brimstone made into a paste with water is uncertain. It was used by Lemery as early as 1690 (cited Partington, 1962) to imitate volcanic action, by burying it in the ground.) Having followed Hales' example and tried the effect of the paste of iron filings and brimstone on common air, it is not surprising that he should have tried out its effect on nitrous air.

Priestley's trial of the effect of iron upon nitrous air over mercury, in 1773, was not directly related to his experiment with iron filings and brimstone in 1772. His reasons for carrying out the crucial experiment that led to the "discovery" of nitrous oxide are clearly stated:

As fixed air united to water dissolves iron, I had the curiosity to try whether fixed air alone would do it; and as nitrous air is of an *acid* nature, as well as fixed air, I, at the same time, exposed a large surface of iron to both kinds; first filling two eight ounce phials with nails, and then with quicksilver, and after that displacing the quicksilver in one of the phials by fixed air, and in the other nitrous air; then inverting them, and leaving them with their mouths immersed in basons of quicksilver.

In these circumstances the two phials stood about two months, when no sensible change at all was produced in the fixed air, or in the iron which had been exposed to it, but a most remarkable, and most unexpected change was made in the nitrous air.

Sequel to the "discovery" of nitrous oxide: the "discovery" of oxygen.

Because Priestley had recently "discovered" nitrous oxide he was slow in recognizing that he had "discovered" oxygen. He confused oxygen with nitrous oxide. The story is best told in his own words (Priestley, 1775):

. . . having . . . procured a (burning) lens of twelve inches diameter, and twenty inches focal distance, I proceeded with great alacrity to examine, by the help of it, what kind of air a great variety of substances, natural and factitious, would yield, putting them into vessels . . . which I filled with quicksilver, and kept inverted in a bason of same. . . .

With this apparatus, after a variety of other experiments . . . on the 1st of August, 1774, I endeavoured to extract air from *mercurius calcinatus per se*; and I presently found that, by means of this lens, air was expelled from it very readily. Having got about three or four times as much as the bulk of my materials, I admitted water to it, and found that it was not imbibed by it. But what surprized me more than I can well express, was, that a candle burned in this air with a remarkably vigorous flame, very much like that enlarged flame with which a candle burns in nitrous air, exposed to iron or liver of sulphur; but as I had got nothing like this remarkable appearance from any kind of air besides this particular modification of nitrous air, and I knew no nitrous acid was used in the preparation of mercurius calcinatus, I was utterly at a loss how to account for it.

In this case, also, though I did not give sufficient attention to the circumstance at that time, the flame of the candle, besides, being larger, burned with more splendor and heat than in that species of nitrous air; and a piece of red hot wood sparkled in it, exactly like paper dipped in solution of nitre, and it consumed very fast; an experiment which I had never thought of trying with nitrous air.

At the same time that I made the above mentioned experiment, I extracted a quantity of air, with the very same property from the common *red precipitate*, which being produced by a solution of mercury in spirit of nitre, made me conclude that this peculiar property, being similar to that of the modification of nitrous air above mentioned, depended upon something being communicated to it by the nitrous acid; and the *mercurius calcinatus* is produced by exposing mercury to a certain degree of heat, where common air has access to it, I likewise concluded that this substance had collected something of nitre, in that state of heat, from the atmosphere.

. . . I entertained some suspicion that the mercurius calcinatus, on which I had made my experiments, being bought at a common apothecary's, might, in fact, be nothing more than red precipitate; though, had I been any thing of a practical chymist, I could not have entertained any such suspicion. However, mentioning this suspicion to Mr Warltire, he furnished me with some that he had kept for a specimen of the preparation, and which, he told me, he could warrant to be genuine. This being treated in the same manner as the former, only by a longer continuance of heat, I extracted much more air from it than from the other.

This experiment might have satisfied any moderate sceptic: but, however, being at Paris in the October following, and knowing that there were several very eminent chymists in that place, I did not omit the opportunity, by means of my friend Mr Magellan, to get an ounce of mercurius calcinatus prepared by Mr Cadet, of the genuineness of which there could not possibly be any suspicion; and at the same time, I frequently mentioned my surprize at the kind of air which I had got from this preparation to Mr Lavoisier, Mr le Roy, and several other philosophers, who honoured me with their notice in that city; and who, I dare say, cannot fail to recollect the circumstance.

At the same time, I had no suspicion that the air which I had got from the mercurius calcinatus was even wholesome, so far was I from knowing what it was that I had really found; taking it for granted, that it was nothing more than such kind of air as I had brought nitrous air to by the processes above mentioned; and in this air I have observed that a candle would burn sometimes quite naturally, and sometimes with a beautiful enlarged flame, and yet remain perfectly noxious.

At the same time that I had got the air above mentioned from mercurius calcinatus and the red precipitate, I had got the same kind from *red lead* or *minium*. In this process, that part of the minium on which the focus of the lens had fallen, turned yellow. One third of the air, in this experiment, was readily absorbed by water, but, in the remainder a candle burned very strongly, and with a crackling noise.

That fixed air is contained in red lead I had observed before; for I had expelled it by the heat of a candle, and found it to be very pure. See Vol. I, p. 192. I imagine it requires more heat than I used to expel any of the other kind of air.

This experiment with *red lead* confirmed me in my suspicion, that *mercurius calcinatus* must get the property of yielding this kind of air from the atmosphere, the process by which that preparation, and this of red lead is made, being similar. As I never make the least secret of any thing that I observe, I mentioned this experiment also, as well as those with the mercurius calcinatus, and the red precipitate, to all my philosophical acquaintance at Paris, and elsewhere; having no idea at that time, to what these remarkable facts would lead.

Presently after my return from abroad, I went to work upon the *mercurius calcinatus*, which I procured from Mr Cadet; and, with a very moderate degree of heat, I got from about one fourth of an ounce of it, an ounce measure of air, which I observed to be not readily imbibed, either by the substance itself from which it had been expelled . . . or by water, in which I suffered this to stand a considerable time before I made any experiment upon it.

In this air, as I had expected, a candle burned with a vivid flame; but what I observed new at this time (Nov. 19), and which surprized me no less than the fact I had discovered before, was, that, whereas a few moments agitation in water will deprive the modified nitrous air of its property of admitting a candle to burn in it; yet, after more than ten times as much agitation as would be sufficient to produce this alteration in the nitrous air, no sensible change was produced in this. A candle still burned in it with a strong flame; and it did not, in the least, diminish common air, which I have observed that nitrous air, in this state, in some measure, does.

Priestley then found that even two days of contact with water did not rob this air of its property of allowing a candle to burn. He continued:

These facts fully convinced me, that there must be a very material difference between the constitution of the air from mercurius calcinatus, and that of phlogisticated nitrous air, notwithstanding their resemblance in some particulars.* But though I did not doubt that the air from *mercurius calcinatus* was fit for respiration, after being agitated in water, as with every other kind of air without exception, on which I had tried the experiment, had been, I still did not suspect that it was respirable in the first instance; so far was I from having any idea of this air being, what it really was, much superior, in this respect, to the air of the atmosphere.

In this ignorance of the real nature of this kind of air, I continued from this time (November) to the 1st of March following; . . . But in the course of this month, I not only ascertained the nature of this kind of air, though very gradually, but was led by it to the complete discovery of the air we breathe.

Till this 1st March, 1775, I had so little suspicion of the air from mercurius calcinatus, &c. being wholesome, that I have not even thought of applying it to the test of nitrous air; but thinking (as my reader must imagine I frequently must have done) on the candle burning in it after long agitation in water, it occurred to me at last to make the experiment; and putting one measure of nitrous air to two measures of this air, I found, not only that it was diminished, but that it was diminished quite as much as common air, and that the redness of the mixture was likewise equal to that of a similar mixture of nitrous and common air.

After this I had no doubt but that the air from mercurius calcinatus was fit for respiration, and that it had all the other properties of genuine common air. But I did not take notice of what I might have observed, if I had not been so fully possessed by the notion of there being no air better than common air, that the redness was really deeper, and the diminution something greater than common air would have admitted.

. . . the next day I was more surprised than ever I had been before, with finding that, after the above mentioned mixture of nitrous air and the air from the mercurius calcinatus, had stood all night, . . . a candle burned in it, and even better than in common air.

I cannot, at this distance of time, recollect what it was that I had in view in making this experiment; but I know I had no expectation of the real issue of it. . . . If, however, I had not happened, for some other purpose, to have had a lighted candle before me, I should probably never have made the trial; and the whole train of my future experiments relating to this kind of air might have been prevented. . . .

On the 8th of this month I procured a mouse, and put it into a glass vessel, containing two ounce-measures of the air from mercurius calcinatus. Had it been common air, a full grown mouse, as this was, would have lived in it about a quarter of an hour. In this air, however, my mouse lived a full half hour; and although it was taken out seemingly dead,† it appeared to have been only exceedingly chilled; for, upon being held to the fire, it presently revived, and appeared not to have received any harm from the experiment.

By this I was confirmed in my conclusion, that the air extracted from mercurius calcinatus, &c. was, *at least, as good as* common air: but I did not certainly conclude that it was any *better*; because, though one mouse would live only a quarter of an hour in a given quantity of air, I knew that it was not impossible but that another mouse might have lived in it half an hour; so little accuracy is there in this method of ascertaining the goodness of air. . . .

This experiment with the mouse, when I had reflected upon it for some time, gave me so much suspicion that the air into which I had put it was better than common air, that I was induced, the day after, to apply the test of nitrous air to a small part of that very quantity of air which the mouse had breathed so long; so that had it been common air, I was satisfied it must have been very nearly, if not altogether, as noxious as possible, so as not to be affected by nitrous air; when, to my surprise again, I found that though it had been breathed for long, it was still better than common air. . . . Thinking of this extraordinary fact upon my pillow, the next morning I put another measure of nitrous air to the same mixture, and, to my utter astonishment, found that it was farther diminished to almost one half of its original quantity. I then put a third measure to it; but this did not diminish it any farther, but, however, left it one measure less than it was even after the mouse had been taken out of it.

Priestley then tried the effect of the air on another mouse which lived for about three-quarters of an hour, but was unable to revive it afterwards, and he again suspected that the mouse had succumbed to cold. He continued:

Being now fully satisfied of the superior goodness of this kind of air, I proceeded to measure that degree of purity, with as much accuracy as I could, by the test of nitrous air. . . . I conclude that it was between four and five times as good as common air.

His researches into what he later called dephlogisticated air did not end there, but the rest of the tale is not directly relevant to this article.

Conclusion.

Present evidence suggests, therefore, that Joseph Black prepared nitrous oxide by heating ammonium nitrate at least as early as 1767, and possibly as early as 1766. Although he never published this experiment he promulgated it in his lectures. There is also inconclusive evidence that he was aware of its property of supporting combustion. In 1772 Joseph Priestley, by exposing nitric oxide to a paste of iron filings and sulphur over water, would have

* Misprint for dephlogisticated nitrous air in Priestley's original work.

†A case of "suspended animation" due to the accumulation of carbon dioxide. Priestley had previously rendered animals comatose by holding them over the vats of fermenting liquor in the brewery next door to his home, and found that they recovered in common air.

prepared nitrous oxide, but he was quite unaware of this at the time, presumably because the nitrous oxide was lost into solution before he was able to observe its properties. He did not pursue the experiment at that time. Later, following a completely different line of thought, he prepared nitrous oxide by exposing nitric oxide to iron over mercury, and on this occasion he observed that it permitted a candle to burn with an enlarged flame. The date of this experiment is almost certainly 1773, probably towards the end of the year. On August 1, 1774, Priestley heated mercuric oxide and obtained a gas which supported combustion, as if, it seemed to him, it was nitrous oxide. This puzzled him and he pursued the matter. It was not until November 19 that he found that the gas supported combustion even after agitation with water and from this time he recognized that it could not be nitrous oxide. On March 1, 1775, he applied his test of "goodness" and found that it was as "good" as common air. On March 8 he found that a mouse could live in this gas for more than twice the time it would have done in common air, and testing the "goodness" of the gas that the mouse had breathed he then concluded that it must be "better" than common air. This he confirmed by trying its effect on another mouse and by very careful and repeated tests of its "goodness", and he concluded that it was four to five times as "good" as common air.

APPENDIX

Despite Robison's conviction that the "vapour" produced by Black was nitrous oxide—which was not contradicted by Partington (1963)—ammonium nitrate can sublime as a white cloud on heating just above its melting point. This could have been the "vapour" referred to, in which case it would have had a slightly ammoniacal smell (Dr T. A. Austin, 1972, personal communication). On raising the temperature further, however, nitrous oxide would have been formed. That the temperature was raised is evident from the following extract from another set of notes taken during Black's lectures by N. Dimsdale, in 1767 (MS. 3534 pp. 4–6, National Library of Scotland).

> "Ammon: Nitrosum. . . . The same heat requisite to its Fusion, converts it into a stinking Vapour. If it be exposed to a Degree approaching red Heat, it is liable to undergo a sort of Inflammation; . . ."

The description of the vapour as "stinking" does not accord with Robison's version of Black's own notes, which refers to the effect on the breathing and sensations as being "very far from unpleasant". One can only guess the origin of the stink. There may have been impurities or higher oxides of nitrogen, or someone may have found the smell of subliming ammonium nitrate to be objectionable.

Some time after 1775 Priestley (1777) produced nitrous oxide using nitric acid and zinc, but repeat experiments did not always produce the same results and nitric oxide was always present. He had tried adding zinc to nitric acid as early as 1772 when he was experimenting with different methods of making nitric oxide. In one of these experiments he would have produced oxygen. Having obtained all the gas that he was able to at room temperature, he then boiled the solution in a sand-heat until all the fluid part was evaporated and there remained a brown fixed substance. A part of this he threw into a small red-hot crucible which he immediately covered with a receiver, standing in water. He wrote:

> "I observed that very dense red fumes rose from it, and filled the receiver. This redness lasted about as long as that which is occasioned by a mixture of nitrous and common air; the air is also considerably diminished with the receiver . . .
>
> "It is remarkable, however, that though the air *within the receiver was diminished* about one-fifth by this process, it was itself affected with a mixture of nitrous air, as common air is, and a candle burned in it very well . . ."

The latter observations indicate that he had obtained more than sufficient oxygen to react with both the nitric oxide which was also evolved, and with the nitric oxide which he then added. Presumably his brown residue was a nitrate. Priestley does not appear to have appreciated the significance of this finding.

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