

## **An essay on phlogiston, and the constitution of acids / by Richard Kirwan.**

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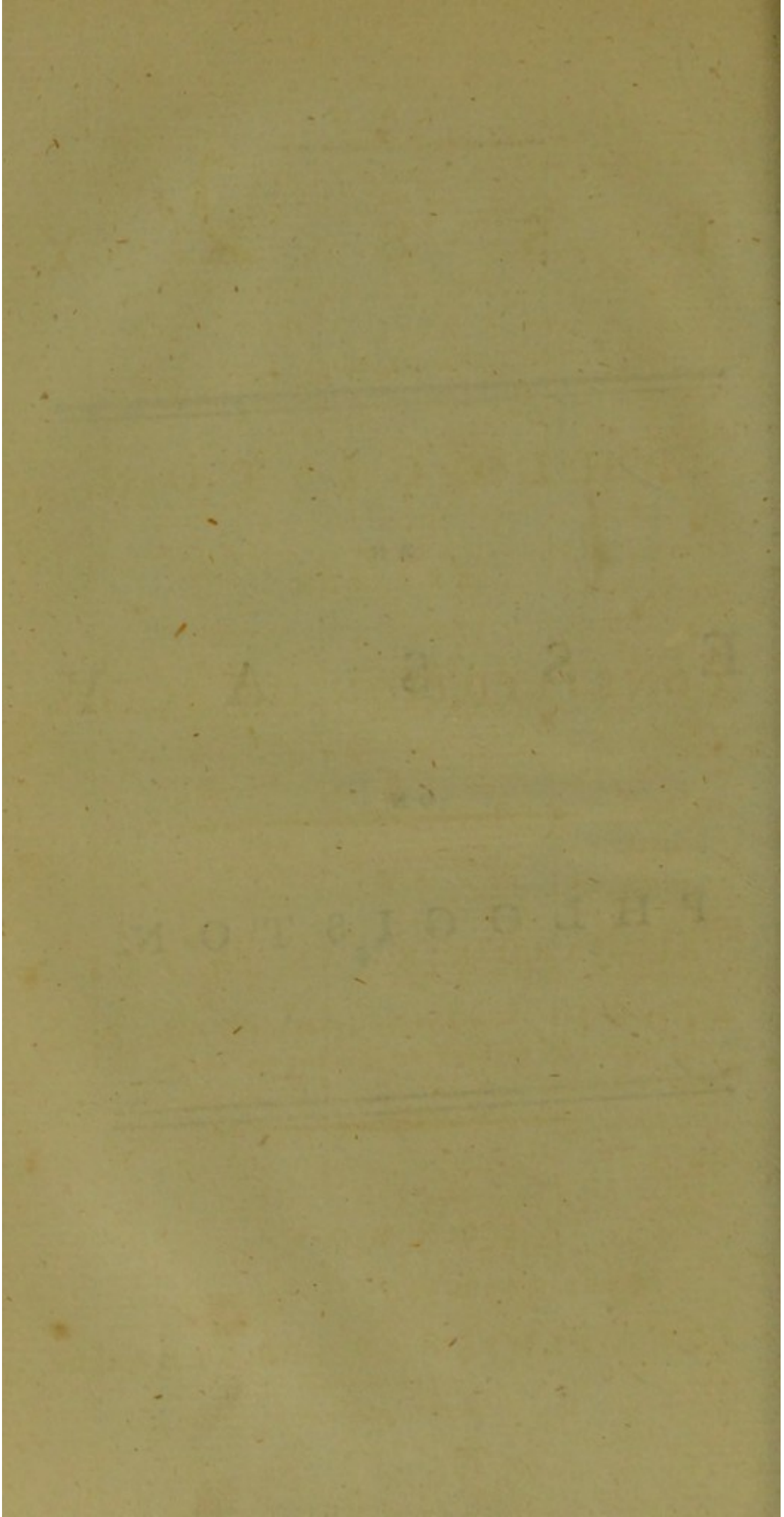
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M E M B E R O F T H E A C A D E M I E S O F S T O C K H O L M, U P S A L, D I J O N,  
D U B L I N, P H I L A D E L P H I A, M A N C H E S T E R, & C.

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L O N D O N

P R I N T E D B Y J. D A V I S,  
F O R P. E L M S L Y, I N T H E S T R A N D.

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M. DCC. LXXXVII.



Y A S S R

P H D O G I S T O

CONSTITUTION OF ACIDS

RICHARD KIRWAN ESQ

LONDON

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FOR A. LINDLEY, 15, ST. MARK'S

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## INTRODUCTION.

**T**HOUGH combustion, together with several of the most striking phenomena of chymistry, and particularly of metallurgy, were known to mankind from the earliest ages, yet it does not appear that any general conclusions were deduced from them, or any theory attempted before the 9th century; in the dark interval between that and the 13th, the qualities of bodies began to be classed both by physicians and alchemists, and, according to the general spirit of the philosophy of those times, attributed to those peculiar substances that seemed to possess them in the most eminent degree. In this distribution of qualities, that of inflammability was assigned to *sulphur*, and in a loose sense, this was erected into one of the five chymical principles; but about the middle of the last century, the Cartesian philosophy then prevailing,

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vailing, vague qualities were every where proscribed, and more exact and precise notions eagerly sought. Beccher, a German metallurgist of great sagacity, and perfectly acquainted with all the chymical facts then extant, which were much more numerous than is commonly believed, perceiving that sulphur, properly so called, did not exist in animal or vegetable substances though inflammable, first asserted, that sulphur was not the principle of inflammability, but that this quality resided in a substance common to sulphur, and to vegetable, animal, and various mineral bodies: this substance he supposed to be of a *dry* nature, and therefore called it an earth, on which, by way of distinction, he bestowed the name of *Phlogiston*.

This doctrine, some years after, was adopted, improved, and extended by the celebrated Stahl, and a theory formed which soon produced a variety of curious and useful discoveries: most chymical phænomena were so happily illustrated and regularly connected by this theory, that since the year 1736, it was universally received all over Europe.

It must be owned, however, that this doctrine rested on the supposition that inflammable bodies contain some substance which uninflammable bodies do not; nor have chymists, until within these few years, been able to afford any proof that this supposition was well founded,

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ed, as they were never able to exhibit this substance singly and by itself, for which inability they accounted by saying, that on quitting one body it always united to another. With this reasoning most chymists acquiesced, and the rather, as they found it impossible to substitute a better theory in its place. Even the weight which many metallic substances were known to gain when they were said to have lost their phlogiston, did not for a long time shake the credit of this favourite hypothesis: it was held by some, that this increase of weight was owing to the accession of igneous particles; by others, that phlogiston was a principle of levity. Rey, in the last century, ascribed it to its true cause, the absorption of air, but on such weak grounds, that he is as little intitled to the honour of a discoverer, as a successful dreamer to that of a prophet: nor can I with justice ascribe this honour to Dr. Hales, though he first extracted air from minium; as he imputed the increase of weight not only to the air, but also to sulphur, which he imagined it absorbed from the fire. Mr. Lavoisier was undoubtedly the first who proved, by direct and exact experiments, that the weight which metals gain by calcination corresponds with that of the air which they absorb; he was also the first who published that the atmosphere consists of two distinct fluids, the one fit for the purposes of respiration and combustion, which he therefore calls *vital* or *pure*



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air; the other unfit for either purpose, and thence called *foul* or mephitic air; and that in the atmosphere the proportion of the first was to that of the last nearly as 1 to 4; he also proved after Dr. Crawford, that pure air (a substance which Dr. Priestley first discovered, and called dephlogisticated air) contained more fire than any other air, and that during combustion, it gave out this fire in the form of heat and light.

On these grounds Mr. Lavoisier reversed the ancient hypothesis; instead of supposing that inflammable bodies contained a peculiar substance which uninflammable bodies do not; he supposes that inflammable bodies are such as have in a certain degree of heat a strong affinity to pure air; and he proved by experiment, that the remains of these bodies after inflammation, and metallic bodies after calcination, contain a substance which they did not contain before; and hence he at first modestly proposed his doubts, whether the supposition of such a substance, as the chymists called phlogiston, were not entirely superfluous: But as the nature of aerial fluids yearly received a fuller illustration from the numerous and ingenious experiments of Dr. Priestley, it was inferred from many of them, as well as from an attentive consideration of various chymical phenomena, that inflammable air, before its extrication from the bodies in which it exists in a concrete state, was the  
very



very substance to which all the characters and properties of the phlogiston of the ancient chymists actually belonged, and consequently that it was no longer to be regarded as a mere hypothetical substance, since it could be exhibited in an aerial form in as great a degree of purity as any other air.

This opinion seems to have met the approbation of the most distinguished philosophers, both at home and abroad \* ; nor can I see what Mr. Lavoisier could reply, before the important discovery of the composition of water made by Mr. Cavendish. This furnished him with a new and unexpected source from which he could derive the inflammable air, extricated in various operations on inflammable and metallic bodies. However, in adopting this explanation, Mr. Lavoisier departs from those laws of philosophic reasoning with the breach of which he before reproached his opponents: that water is a compound substance, has been proved by direct experiment, but that it is decomposed in any chymical operation, is a mere gratuitous supposition ; nor can he say that it is an equal chance whether the inflammable air extricated during the solution

\* Dr. Priestley, Mr. Bewly, Mr. Bergman, Mr. Morveau, De La Metherie, Chaptal, Crell, Wiegleb, Westrumb, Hermstadt, Kaersten, &c.



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of a metal proceeds from the decomposition of water, or from the decomposition of the metal; for the metals that principally afford it, as iron and zinc, are by themselves, and in the total absence of water, perfectly inflammable, and therefore should be deemed to possess the same principle of inflammability as vegetable and animal substances, whose inflammability, without any controversy, is attributed to the presence of inflammable air, whereas water can be inflamed in no circumstances whatsoever.

The substances which Mr. Lavoisier allows to contain the inflammable principle distinct from water, are oils, resins, spirit of wine\*, and volatile alkalis †, and consequently all vegetable and animal substances; even charcoal he allowed at first to be an *unknown modification* of the inflammable principle, though at present he seems to think otherwise; if he allows it to contain the inflammable principle consolidated by unknown means, as ice is a modification of water, we shall hardly dispute it, though in reality, it, together with that, contains also fixed air, as will appear in the sequel.

The controversy is therefore at present confined to a few points, namely, whether the *inflammable principle* be found in what are called

\* Mem. Par. 1781, p. 491, 492.

† 29 Roz. p. 175.



phlogisticated acids, vegetable acids, fixed air, sulphur, phosphorus, fugar, charcoal, and metals.

Limited as this controversy appears to be to a small number of bodies, it is nevertheless of great importance, if an exact arrangement of our ideas, and a distinct and true view of the operations of nature, be of any importance. The bodies above-mentioned are the subject of many, and the instruments of almost all chymical operations: without a knowledge of their composition, and a clear perception of their mode of action, it will be impossible to form even an approximation to a solid theory of this science; the daily accumulation of facts will only increase perplexity and confusion, and if any useful discovery be made, it will be the mere result of chance.

Many strong prejudices, I am well aware, favour the new opinion (which I shall take the liberty of calling the *Antiphlogistic* hypothesis, and its supporters *Antiphlogistians*, not by way of obloquy, but to prevent circumlocution): it has been advanced in an enlightened age and country, it is recommendable by its simplicity, and it owes its origin to a philosopher of great eminence, who was the first that introduced an almost mathematical precision into experimental philosophy; but the old system presents also many strong prejudices in its favour; it originated, it is true, in a less enlightened age, but



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it originated in a country in which chymical knowledge then was, and still is, further advanced than in any other part of Europe. It is to Germany that all modern nations must resort, to improve in mineralogy and metallurgy, as the ancients did to Greece to improve in oratory. By the Germans, as also by the Swedes, the old doctrine has gradually been improved and refined, and their attachment to it is still unshaken. We must not be deluded by a false shew of simplicity; when all is well considered, the ancient doctrine will be found the more uniform of the two; in this, pure air is never said to unite to any substance, but to the principle of inflammability with which it is evidently seen to unite in the deflagration of inflammable air; in the modern, without being an acid, or affording any sign of salinity, the principal prerogative of acid substances, that of uniting to almost all bodies, is assigned to it.

But prejudices of every kind should certainly be laid aside in all scientific inquiries; truth, if it can *evidently* be traced, or if not, the *internal probability* of any principle, should be the only motive of our attachment to it. Now, that doctrine must be accounted the least probable which fails ofteneft in explaining the phænomena, is more arbitrary in its application, and less countenanced by the general rules of philosophic reasoning; that



## I N T R O D U C T I O N. 9

that this is the case of the antiphlogistic hypothesis, I flatter myself will appear after an attentive perusal of the following sections.

SECTION

THE HISTORY OF THE

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S E C T I O N I.  
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**A**S I shall have frequent occasion to calculate the weight of different kinds of air, in the sequel of this treatise, it is proper to premise the means I used to ascertain this weight.

Of Common Air.

Sir George Shuckburgh, by a series of experiments made with a well-constructed barometer, discovered the length of a column of air, equiponderant with  $\frac{1}{15}$  of an inch of mercury,



cury, whose specific gravity was 13,6, at different barometrical heights, and in different temperatures; the weight of  $\frac{1}{16}$  of an inch of mercury of that specific gravity (which may be looked upon as constant, its variation being exceeding small in the usual temperatures of the atmosphere) is 344,32 gr. Pursuing this calculation, it will be found that 100 cubic inches of common air weigh

Bar.	Therm.		Gr.
30	60°	} - -	30,929
	50		31,612
29,5	60	} - -	30,414
	50		31,124
Mean weight - -			31,0197

As the barometer, both here and at Paris, generally stands at or between 29,5 and 30, and the temperature in our apartments is generally between 50 and 60°, I shall consider the mean usual weight of atmospheric air as 31 grains for every 100 cubic inches.

100 cubic inches of water weigh 25318 grains, and as 100 cubic inches of common air weigh 31 grains, it follows that common air is about 816 times lighter in the circumstances above-mentioned than water. I have frequently weighed air in a glass globe containing about 116 cubic inches, and in general found the



results to differ but little from those resulting from Sir George Shuckburgh's calculation, only always somewhat lighter, which I believe denotes an error rather in this method than in the barometrical: when Saussure's hygrometer was above  $90^{\circ}$  the air was *cæteris paribus* lightest.

## Dephlogisticated air.

I procured this air from præcipitate *per se*; its goodness was such, that one measure of it and two of nitrous air left but  $\frac{3}{10}$  of a measure: when 116 cubic inches of common air weighed 35,38 grains, 116 of this dephlogisticated air weighed 39,03 grains, consequently its weight is to that of common air as 1103 to 1000 nearly.

To find the quantity of moisture in this air when produced over water, I filled a large jar, containing 81 cubic inches, with this air, and then raising it out of the water, I laid it on mercury over a faucer of three inches diameter, containing 256,8 grains of oil of vitriol, whose specific gravity was 1,863, and left them together 24 hours; on withdrawing the faucer I found it to have gained 3,47 grains, consequently 100 cubic inches may contain 4,32 of water. The temperature of the room was 58.

To



To try whether the bulk of this air would be greater when obtained over water than when obtained over mercury, I distilled at the same time 240 grains of red precipitate over water, and in another retort of the same size, 240 grains over mercury, and found the quantity of air exactly the same. I could not fill so large a jar as one of the capacity of 81 cubic inches with mercury; but from this experiment, I am induced to think that dephlogisticated air does not in a short time absorb more moisture when received over water than when received over mercury.

#### Inflammable air.

The inflammable air used in this experiment was extracted from clean, newly made filings of soft iron, in the temperature of  $59^{\circ}$ , by vitriolic acid, whose specific gravity was 1,0973, and obtained over mercury; it had scarce any smell, and that which it gave was very different from the usual smell of inflammable air.

The barometer being 29,9, and the thermometer  $60^{\circ}$ , I found the weight of this air to be to that of common air as 84,3 to 1000, consequently nearly 12 times lighter.

I found that the bulk of inflammable air obtained from the same sort and quantity of materials,



materials, with the assistance of heat towards the end, was nearly  $\frac{1}{8}$  greater when it was obtained over water than when obtained over mercury. I have not weighed inflammable air thus obtained over water, but it is well known to be at most but 8 or 9 times lighter than common air.

From 85 cubic inches of inflammable air received over water, I extracted by oil of vitriol, in the manner above mentioned, in 55 hours, 2 grains of water; and though undoubtedly there is an error in all these experiments, yet there can be little doubt but this inflammable air contained  $\frac{1}{2}$  its weight of water; the inflammable air by the subtraction of its water lost its smell, but continued as inflammable as ever, and therefore there is no reason to think it was decomposed, or that water is any way essential to it.

#### Phlogisticated air.

By exposing common air to a mixture of filings of iron and sulphur made into a paste, over mercury, I obtained air so far phlogisticated that it was not in the least diminished by nitrous air; I dried it by frequently introducing dry filtering paper under the jar that contained it, and found its weight to be to that of common air as 985 to 1000, the barometer standing at 30,46, and the thermometer at  
60°:



60°: care must be taken that this air do not stand too long over the martial paste, else inflammable air will be produced.

#### Alkaline air.

I found the weight of alkaline air to that of common air, to be as 600 to 1000, barometer 30, thermometer 61°: its weight probably varies in proportion to the moisture it contains, which must be very considerable.

#### Nitrous air.

As nitrous air would infallibly disorder the metallic apparatus of my globe for weighing airs, I endeavoured to find its weight by comparing the loss of weight of the materials which produced it, viz. 50 gr. of copper, and 580 of nitrous acid, whose specific gravity was 1,1389, with the volume of air produced. With this view I produced over mercury in the temperature of 64, barometer 29,6 in  $8\frac{1}{2}$  hours, 38,74 cubic inches of nitrous air, at the expence of 14 gr. of the materials; therefore 100 cubic inches of this air would weigh 36,1 gr. but 100 cubic inches of common air would weigh but 30,2 gr. therefore the weight of nitrous is to that of common air as 1195 to 1000.

If



If this air had been obtained over water, or in strong heat, its weight would probably have been very different, as it is liable to be mixed with phlogisticated air, nitrous vapour, and a variable quantity of water, nitrous vapour would render it heavier, and phlogisticated air or water probably lighter.

#### Fixed Air.

The barometer being at 29,85, and the thermometer 64°, I found the weight of fixed air extracted from calcareous spar, by marine acid, whose specific gravity was 1,0145, and obtained over mercury, to be to that of common air as 1500 to 1000.

Notwithstanding that this air was obtained in the driest manner possible, and that the globe which contained it appeared perfectly dry, yet when I carried it into a room 27 degrees colder, the inside of the globe was covered with dew, which soon formed visible drops.

#### Vitriolic Acid Air.

I extracted this air in a strong heat from copper, by means of vitriolic acid, whose specific gravity was 1,704, its weight was to that  
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of common air as 2265 to 1000, barometer 30,13, thermometer 60°.

The weight of this air must be somewhat variable, as it contains a variable proportion of water, and also of sulphur.

### Hepatic Air.

That extracted from sulphurated iron, is to common air as 1106 to 1000; but as it contained a little metallic inflammable air, it is probably lighter than that drawn from alkaline or calcareous hepars.

Table of the absolute weight of 100 cubic inches of different kinds of air, and their proportions to common air.

100 Cubic Inches.	Gr,	Proportion to common air,
Common air	31	1000
Dephlogisticated	34	1103
Phlogisticated	30,535	985
Nitrous -	37	1194
Vitriolic -	70,215	2265
Fixed -	46,5	1500
Hepatic -	34,286	1106
Alkaline -	18,16	600
Inflammable	2,613	84,3

By means of the 3d column, the weight of common air being rigorously given, that of any arti-



artificial air in the same temperature, and under the same pressure, may be had pretty nearly; for it must be owned their expansibility in different temperatures has not been as yet accurately determined: in point of compressibility, the difference is inconsiderable. I have set down the weight of dephlogisticated and nitrous air somewhat lower than I found them, for the sake of abridging calculation, and because others have found their weight still lower.

The mean weight of common air by Mr. Lavoisier's calculation, differs very little from that which I assign to it, that is to say, only by 7 Troy grains, in a 1000 English cubic inches, his calculation exceeding mine by so much; but with respect to other airs, the difference between us is greater, as may be seen by the following table.

100 French cubic inches by my calculation.	French Gr.		By Mr. Lavoisier.
Common air	45,69	-	46,81
Dephlogisticated	50	-	47,317
Fixed air	68,74	-	69,50
Nitrous	54,53	-	40,

The weight of each of these airs being so different from that on which I grounded my former calculation of the proportion of their ingredients, I have been obliged to re-calculate the whole. To inflammable air, I still assign



the same weight as before, as it has not the great levity I found it to have, except it be made with particular care, so that I consider it in the usual state as only ten times lighter than common air; I also consider these airs as united with their usual proportion of water, and not as perfectly pure. In such circumstances

100 cubic inches of	Gr.	Gr.
Nitrous air contain 6,7 of phlogiston and		30 of nitrous basis
Fixed air - 8,14		38,36 dephlog. air

100 Gr. of			
Nitrous air +	18	-	82 nitrous basis
Fixed air -	17	-	83 dephlog. air



S E C T. II.

*Of the Composition of Acids, and General Principles of the New Theory.*

WITH respect to the nature and internal composition of acids, it must be owned that the theory of chymistry has been much advanced by the deductions and reasonings of Mr. Lavoisier : that a certain quantity of pure air disappeared during the combustion of sulphur and phosphorus, and on uniting pure air with nitrous air, was first discovered by Dr. Priestley ; but the connection and relation of this air to the resulting acids, was first attended to by Mr. Lavoisier. I have shewn in different papers, in the Philosophical Transactions, that this air always unites to the phlogistic principle, and is converted into fixed air, but I neglected tracing it any farther ; I am now of opinion that it becomes an essential constituent part of acids.

All acids consist of two principles, one peculiar to each, which, in the opinion of the antiphlogistians, has not as yet been decomposed, and consequently must be looked upon, relatively to the present state of our knowledge, as a *simple* substance ; and the other, *pure air* in a concrete state, that is, deprived of the



greater part of its specific heat, and condensed into a smaller volume; the first they call the acid *basis*, the last, the *oxygenous* principle; thus the vitriolic acid, according to them, consists of *sulphur* as its basis, and pure air, in a concrete state, as its *acidifying* or *oxygenous* principle.

This doctrine of the composition of acids has been admitted by some of the ablest defenders of phlogiston, and particularly by that distinguished philosophic chymist Mr. de Morveau, with this single modification, that the bases of acids contain phlogiston, which they lose on uniting to pure air; yet it seems to me very difficult to conceive how pure air can unite to phlogiston, a substance to which it has the greatest affinity, without forming a new compound, endowed with very different properties from those which it possessed before such union; it seems, therefore, more reasonable to conclude, either that it forms water, as Mr. Cavendish thinks, or fixed air, as I shall endeavour to prove in the following sections. It must be allowed, that the constant extraction of fixed air from the vegetable acids, and the impossibility of procuring pure air from them, forms a strong presumption in favour of this last opinion.



Table of the affinities of the oxygenous principle, according to Mr. Lavoisier, Mem. Par. 1782, p. 535.

Bases.	Resulting Compounds.
Basis of the marine acid	Dephlog. marine acid
Charcoal - -	Fixed air
Zinc - -	Calx of zinc
Iron - -	Calx of iron
Inflammable principle	Water
Regulus of manganese	Calx of manganese
Cobalt - -	Calx of cobalt
Nickel - -	Calx of nickel
Lead - -	Calx of lead
Tin - -	Calx of tin
Phosphorus - -	Phosphoric acid
Copper - -	Calx of copper
Bismuth - -	Calx of bismuth
Regulus of antimony	Calx of antimony
Mercury - -	Calx of mercury
Silver - -	Calx of silver
Regulus of arsenic -	Calx of arsenic
Sugar - -	Acid of sugar
Sulphur - -	Acid of vitriol
Nitrous air - -	Acid of nitre
Principle of heat -	Dephlogificated air
Gold - -	Calx of gold
Smoking marine acid	
Nitrous acid	
Black calx of manganese	



This table is liable to numerous objections, which I shall have occasion to mention in the sequel; I shall here mention only a few which apply generally to the whole table.

1st. Of the first 19 substances which have the greatest affinity to the oxygenous principle, not one unites to it in the common temperature of the atmosphere; and yet nothing prevents this union but the affinity of the principle of heat with the oxygenous principle, which affinity is laid down in this table as weaker than that of any of the nineteen substances that precede it.

2dly. The only substance which unites to the oxygenous principle in every temperature, and constantly expels the principle of heat, is nitrous air, which yet, in this table, is set down as having almost the weakest affinity with the oxygenous principle.

3dly. No proof is given that pure air, while pure air and uncombined with any other substance, unites to any thing except inflammable air; nor has it been produced from any substance except the calces of the perfect metals, mercury and lead, unless they were previously combined with some acid.



Of the Composition and Decomposition of  
Water.

The experiments of Mr. Cavendish, and of Mr. Monge, appear to me to leave no room to doubt that when very pure dephlogisticated air and inflammable are inflamed, the product is mere water; for when these airs are employed in the proper proportion, only  $\frac{1}{30}$  of the mixture of both airs retains its aerial form\*; now it is impossible to suppose that all the water obtained pre-existed in these airs, that is, that 49 parts in 50 were water.

According to Mr. Lavoisier, 100 parts of water by weight, contain about 87 of dephlogisticated air, and 13 of inflammable air, that is, nearly in the proportion of 7 to 1; and supposing the weight of these airs to be such as given in the first section, 100 troy gr. of water will contain 254,4 cubic inches of dephlogisticated air, and 497 of inflammable air, that is nearly as 1 to 2; however, this calculation is somewhat precarious, as it is grounded chiefly on the experiment of Mr. Monge, the most accurate of those made in France; and his inflammable air was certainly saturated with water, its specific gravity being

\* Philosophical Transf. 1784, p, 134.



not quite seven times below that of common air\*.

The only circumstance in which water has clearly been proved to result from the union of inflammable and dephlogisticated air, is that in which one or both were exposed to a red heat, but it cannot fairly be inferred that water results from their union in any lower heat; on the contrary, it appears that another compound of both, viz. fixed air, is then formed; thus mercury and sulphur in a low heat form æthiops, and in a greater cinnabar; yet it is certain that in low heats, both these airs may remain long together without forming any union, and when they do unite, it is because one of them has not its whole quantity of specific fire; but in high degrees of heat, their *specific* becomes *sensible* heat, as Mr. Watt has discovered †. How great an impediment specific heat is to the union of bodies, when the compound that should result from such union must contain much less of it than either of the ingredients, I have elsewhere shewn by the example of fixed air and quicklime, and oil of vitriol and water ‡.

Another principle assumed by the patrons of the new theory, and which indeed is the corner stone of their whole system, is the *decom-*

\* Mem. Par. 1783, p. 79.

† Philosophical Transf. 1784, p. 335.

‡ Philosophical Transf. 1784, p. 168.



*position* of water, but of which the maintainers of the old doctrine have as yet received no satisfactory proof; according to Mr. Lavoisier's table, water should be decomposed by charcoal at least in a boiling heat, which is full sufficient to communicate as much specific heat to the inflammable part of water as is necessary to its aerial form: yet water has not yet been decomposed in that manner; whereas water and iron will produce inflammable air in the temperature of the atmosphere, though iron has in his system less affinity to the oxygenous principle than charcoal has to that principle, an evident sign that it is not from the water, but from the iron, that the inflammable air proceeds.



## S E C T. III.

## Of the Vitriolic Acid.

ACCORDING to the new theory, this acid considered abstractedly from the water which it always contains, consists of sulphur (which is considered as a simple substance), united to a large proportion of the oxygenous principle. In my opinion, it consists of a *basis* or radical principle, which, when saturated with phlogiston, constitutes *sulphur*; when saturated with fixed air, becomes common *fixed vitriolic acid*; and when combined partly with the one and partly with the other, becomes *volatile vitriolic acid*: so that vitriolic acid is nothing else but common vitriolic acid holding sulphur in solution. This view of the volatile acid I owe to Mr. Berthollet, and it seems to be the only improvement made in its theory since the days of Stahl.

That sulphur during its conversion into vitriolic acid, unites to air of some sort or other, is evident from the quantity of air which it absorbs in whatever way that conversion is brought about. Thus, first, during combustion in respirable air, I have shewn that 100 gr. of sulphur absorb 420 cubic inches of pure air,  
or



or about 143 gr. but the proportion of this pure air actually united with a given quantity of sulphur, is not easily determined, because it is vitriolic air that is constantly formed, and this air essentially contains some portion of sulphur in solution, which portion is variable. Secondly, Pyrites, during their decomposition, absorb a considerable proportion of pure air, as Mr. Lavoisier has observed, so also does liver of sulphur exposed to the atmosphere, for after some time it is converted into tartar vitriolate.

But whether the pure air thus absorbed remains pure air, or is converted into fixed air or water, is not agreed upon: that it is converted into fixed air seems to me most probable from the following facts:

1st. I took 60 gr. of red precipitate, and 12 of flowers of sulphur, and having well mixed them, I distilled them with a gentle heat from a glass retort, whose capacity with that of its adopter was 6,18 cubic inches, and received the air over mercury:  $1\frac{1}{2}$  cubic inch first passed, which was nothing else but part of the air of the vessels; after this a slight inflammation took place in the retort, accompanied with a rapid production of air and white fumes, and part of the mass sublimed into the neck of the retort. The quantity of air now obtained, added to that had before inflammation, amounted to  $6\frac{1}{2}$  cubic inches, then changing the receiver by a greater heat, and without any inflammation,

10 cubic



10 cubic inches of air passed clear and colourless. Of the  $16\frac{1}{2}$  cubic inches thus produced, I found 14 to be vitriolic air, being absorbed by the solution of marine baroselenite; one continued unabsobered until lime water was added; the remainder was worse than common air.

From this experiment, I infer that the air that united to the sulphur was fixed air, for if it had been pure air, the combustion must have continued during the whole time of their union. It is to no purpose to say that this combustion was prevented by the presence of the vitriolic air, for if this air could prevent the combustion (that is, the expulsion of heat and light from the pure air), it should also prevent the union of the pure air and sulphur, just as it does when sulphur is burned in pure air; but since an union took place without the expulsion of heat and light, it is evident that the air which entered into this union was not pure air, and by the same reasoning, it follows that water was not produced; the first inflammation arose from the common air of the vessel. The diminution by lime water shews also that some uncombined fixed air remained. In this experiment the sulphur was decomposed, its phlogiston uniting to the mercury, and its basis to the fixed air contained in the mercurial calx: some part remained undecomposed, and contributed to the formation of the vitriolic air.



2dly. I have already mentioned, in my Treatise on Hepatic Air, that 6 cubic inches of vitriolic air, and 5 of hepatic air, left a residuum of fixed air, which must have been contained in the vitriolic air.

3dly. Doctor Priestley constantly obtained a residuum of fixed air from the distillations of the vitriols of iron, copper, or Mercury. 3 Priestley, 216, 227. Mr. Lavoisier observed, that the dephlogisticated air obtained from vitriol of mercury precipitates lime water. Mem. Par. 1777, p. 327. If sulphur be burned in a large quantity of dephlogisticated air, some fixed air is always found in the residuum. 6 Pr. 267.

4thly. If the vapour of oil of vitriol be made to pass through a red hot earthen tube, a quantity of fixed air will be obtained. 1 Chy. Annals 1785, p. 523.

5thly. If sulphur be digested in oil of turpentine, and then slowly distilled for 10 or 12 days, it will be converted into vitriolic acid, according to Homberg. Mem. Par. 1703. Here it appears that the sulphur is first dephlogisticated, and then unites to the fixed air of the oil: it evidently can receive no pure air from it. It must be remembered, that if this experiment be not cautiously conducted, it is very dangerous.

These facts leave no reasonable doubt, but that fixed air is produced by the combustion of sulphur, and becomes a constituent part of  
the



the vitriolic acid. The following tends to prove that sulphur contains phlogiston, which may also be easily inferred from the foregoing.

1st. Doctor Priestley converted oil of vitriol into sulphur, by evaporating it to dryness under a receiver filled with inflammable air. 6 Pr. 22 : but as this experiment may be explained otherwise, I lay no great stress upon it, though it is perfectly satisfactory to those who do not receive the antiphlogistic theory.

2d. The same excellent philosopher, by means of a burning glass, melted some iron in vitriolic air ; sulphur was immediately formed, part of which united to the iron and rendered it brittle, and part sublimed : the residuary air was partly fixed and partly inflammable air \*. Here the vitriolic air was converted into sulphur by the inflammable air of the iron, and the fixed air found was that which was expelled from the vitriolic air in the instant of its conversion into sulphur ; so that this curious experiment demonstrates both points of my theory. I am sensible the antiphlogistians will reply, that the inflammable air proceeds from the decomposition of the water contained in the vitriolic air, and the fixed air from the plumbago of the iron ; but not to anticipate what I shall hereafter urge against the decomposition of water, I shall only say, that it is not possible to ascribe the fixed air to the de-

\* 6 Pr. 116.



composition of the plumbago; for Doctor Priestley's burning glass cannot melt above 20 grains of iron, and according to Mr. Bergman 100 gr. of iron contain but 0,12 of a gr. of plumbago, and consequently the whole 20 gr. contain but 0,24 of a gr. and of this only  $\frac{1}{3}$  is fixed air, a quantity almost imperceptible.

3d. If the most dephlogisticated calx of iron, and on that account perfectly insoluble in dephlogisticated nitrous acid, be made into a paste with sulphur and water, and slightly heated, it will become soluble in the nitrous acid, having taken phlogiston from the sulphur.\* It cannot be said that sulphur took part of the oxygenous principle from the iron; for by Mr. Lavoisier's table, iron has far a greater affinity to that principle than sulphur has.

4th. If sulphur be inclosed in a heated earthen tube, and the vapour of water made to pass through it, the sulphur will be decomposed, and inflammable air obtained.† It cannot be said that the water was decomposed; for, by Mr. Lavoisier's table, the oxygenous principle has a stronger affinity to the inflammable than to sulphur.

5th. It is allowed by the antiphlogistians, that volatile alkalis contain phlogiston; now, if vitriolic ammoniac be sublimed, part of it will be decomposed, and the acid becomes sulphureous.‡

\* Stahl, 300 Observ. p. 352.

† Mem. Par. 1783, p. 736.

‡ 6 Pr. 150.



6th. Mr. Westrumb threw about a drachm of calcined magnesia into an ounce of concentrated black vitriolic acid; in an instant both heated, and a bright flame appeared; but with dephlogisticated vitriolic acid, or strong nitrous acid, this did not happen.\* Here the vitriolic acid having a strong affinity to the magnesia, and its phlogiston a strong affinity to the common air, a separation and double union rapidly ensued, and hence the flame. But as the dephlogisticated vitriolic acid contained no phlogiston, flame could not be produced.

7th. If sulphur be digested in the nitrous acid, it is gradually decomposed; the nitrous acid becomes phlogisticated, and is in great measure converted into nitrous air, while the greater part of the sulphur is converted into vitriolic acid.† Now, nitrous acid cannot be converted into nitrous air, without the addition of phlogiston, as will be seen in the next section.

The vitriolic acid impregnated with nitrous air, has less affinity to water, and may subsist in a dry state.‡

\* Chy. Annals, 1784, p. 432.      † Chaptal. p.  
and Cornette Mem. Par. 1779, p. 484.    ‡ 4 Pr. p. 26.



## S E C T IV.

*Of the Nitrous Acid.*

**T**HE important discovery of the substances which contribute to the artificial production of the nitrous acid, made by Mr. Cavendish, and of those which nature employs, made by Mr. Thouvenel, together with the numerous and ingenious experiments contained in Dr. Priestley's last publication, have at last dissipated most of the obscurity attending its operations, and the nature of its modifications. Nor have the labours of the antiphlogistians been useless; both Mr. Lavoisier and Berthollet, by carefully distinguishing the component parts, particularly of nitrous air, have thrown great light on the subject, though by neglecting one essential part, namely, the phlogiston, they have obliged me to differ from them in some particulars. By these helps I am enabled to give a new, and to me at least a more satisfactory theory of this singular acid than has yet appeared; and at the same time, to shew the weakness of the antiphlogistic doctrine.

Mr. Cavendish has shewn, that the nitrous acid may be formed by taking the electric spark in a mixture of 3 measures of phlogisti-



cated air, and 7 of dephlogisticated air, or in weight, 1 part of the former, and about 2,6 of the latter.

According to Mr. Lavoisier, nitrous acid consists of nitrous air, as its *basis*, united to the oxygenous principle. And 100 grains of *dry nitrous acid* consists of 64 grains of *nitrous air*, united to 36 grains of *pure air* deprived of its specific fire—that is, by measure, according to my calculation, 173 cubic inches of *nitrous air*, and 105 of *pure air*.

But *nitrous air* itself, as he well remarked, is a compound; 100 grains of it, according to him, contain 32 of phlogisticated, and 68 of *pure air*. And, consequently, 64 grains of it contain 20,5 of phlogisticated air, and 43,5 of *pure air*.\* Hence, according to him, 100 grains of dry nitrous acid contain  $79\frac{1}{2}$  *pure air*, and  $20\frac{1}{2}$  phlogisticated air.

This proportion of *pure air* and *phlogisticated air* differs, as we see, very considerably from that of Mr. Cavendish; but, as Mr. Lavoisier well remarks, the nitrous acid is not always in the same condition, the *red* sort differing very considerably from the *pale and colourless*; the former contains more nitrous air, which may be separated from it by mere heat, and, therefore, must contain more phlogisticated air than the latter; and in fact, the nitrous acid produced by Mr. Cavendish was of the red sort, or that

\* 11 Mem. Scav. Etrang. p. 629.

which



which we call highly phlogisticated, and, consequently, must have contained more phlogisticated air than the pale or colourless. In my opinion 100 gr. of pure, dry, *colourless*, nitrous acid contain 38,17 gr. of *fixed air* as its acidifying principle, 57,06 of *nitrous basis*, and 4,77 of phlogiston united to the nitrous basis. —As to the *nitrous basis*,  $\frac{1}{3}$  of its weight is phlogisticated air, and  $\frac{2}{3}$  dephlogisticated or pure air, both in a concrete state. It has an affinity both to fixed air, and to phlogiston.

Nitrous basis saturated with phlogiston constitutes *nitrous air*: 100 gr. of this basis take up nearly 22 of phlogiston. The proofs of this theory will presently be seen.

Hence the constituent principles of nitrous acid are fixed air, dephlogisticated air, phlogisticated air, and inflammable air, all in their concrete state.

*Red, yellow, green, and blue* nitrous acids, when those colours are intense, owe their origin to the absorption of nitrous air, and, consequently, the proportion of their principles are variable, though all have the dephlogisticated acid for their ground. Thus Dr. Priestley having exposed strong pale yellow nitrous acid, whose specific gravity could not be less than 1,400 to nitrous air, found that 100 gr. of this acid absorbed in 2 days 247 cubic inches of nitrous air; now 100 gr. of this spirit of nitre must have contained, by my calculation, about 21 gr. of dry acid, and these 21 gr. took up 91,39 gr. of nitrous air. When about 20 cubic inches of nitrous air were absorbed (that



is, about 7 gr.), the acid became of an *orange* colour; when 50 cubic inches were absorbed (about 18 gr.) it became *green*; and when nearly the whole was absorbed, it evaporated in the form of nitrous vapour, carrying off part of the water with it.\*

Hence we see that *nitrous vapour* consists of nitrous acid, united to 3 or 4 times its weight of nitrous air, and a little water. This vapour is always of a *red* colour. We see also that the nitrous acid is phlogisticated by absorbing nitrous air. This red vapour must carefully be distinguished from another colourless invisible vapour, which Dr. Priestley often mentions, and which is nothing else but the nitrous acid itself disengaged from water.

*Nitrous air* is seldom perfectly pure; it is subject to two contaminations, one from nitrous vapour, and the other from phlogisticated air, whose origin I shall here explain: When a metal or any phlogisticated substance is dissolved in the nitrous acid, this substance attracts the acidifying principle of the nitrous acid, and its phlogiston is attracted by the nitrous basis; and thus by a double affinity the nitrous acid is in part decomposed, and nitrous air formed. Part of this nitrous air escapes out of the solution, but a part of it unites to the undecomposed acid, particularly if this acid were dephlogisticated, and with it forms nitrous vapour; of this nitrous vapour part unites to the metallic salt or calx, and part flies

\* 3. Pr. 123.



off mixed with the nitrous air, which it contaminates: from the union of the nitrous air with the undecomposed acid and metallic calx, proceed the various colours which strike the beholder during the solution of mercury in strong nitrous acid. Again, when iron, and particularly zinc, tin, or regulus of antimony, are rapidly dissolved in nitrous acid, as these substances give out their phlogiston very copiously, or at least very readily, not only the acidifying principle, or fixed air, unites to them; but the nitrous basis itself, by reason of the heat generated, and the sudden eruption of phlogiston, is decomposed, its pure air uniting to the phlogiston, and forming fixed air, while the phlogisticated air flies off, mixes with and contaminates the nitrous air.

The *nitrous basis*, free from the acidifying principle and adventitious phlogiston, forms that species of air which Dr. Priestley calls *dephlogisticated nitrous air*, and to which I have given the name of *deacidified nitrous air*: both appellations considered in a proper view, are equally just; for when it is so pure as to admit a candle to burn with an enlarged flame, it is equally free from the small portion of phlogiston which usually adheres to it, and from nitrous vapour. The dephlogisticated air it contains is so strongly combined with the phlogisticated air, that they cannot be separated but in a red heat, or by a double affinity: And hence, though it admits a candle to burn more or less perfectly, as it is more or less pure, yet an



animal cannot live in it. A sure sign that it generally contains a small portion of phlogiston, is its reddening with dephlogisticated air; but it will not decompose nitrous air, because its pure air is already united to phlogisticated air. It may appear extraordinary that this air, which (since it is a part of the nitrous acid) is formed by the electric spark, should also be decomposed in a red heat; but it should be remembered, that during its formation, the pure air meets with no phlogiston but that contained in the phlogisticated air, which is incapable of inflammation; but when the flame of a candle is presented to it, it meets with uncombined phlogiston, with which in that heat it can readily unite.

Having explained these modifications of the nitrous acid in a general way (for a detail of particulars would be much too prolix); it now remains for me to prove the presence of phlogiston in phlogisticated air and in nitrous air, and also the existence of fixed air in nitrous acid; in doing which it will appear that dephlogisticated air and nitrous air should not be looked upon as its constituent principles: after which I shall examine the most remarkable experiments that have been made with this acid.

With respect to *phlogisticated air*, it must be owned we have no direct proof that it contains phlogiston, as no inflammable air has as yet been extracted from it, nor is it the general result of phlogistic processes; but since the ni-  
trous



trous acid formed of this air and dephlogisticated air, was found strongly phlogisticated, and since the phlogisticated nitrous acid is constituted such, by its union with nitrous air, it is evident that phlogisticated air must contain phlogiston, if nitrous air contains any.

That *nitrous air* contains phlogiston, appears by the following experiments :

1st. The nitrous acid dephlogisticates *sulphur*, and in so doing, is converted in great measure into nitrous air ; now it has been already proved that sulphur contains phlogiston : it also dephlogisticates phosphorus, sugar, and metals, in which the presence of that principle will hereafter be shewn.

2d. If the electric spark be taken in nitrous air, it will be reduced to  $\frac{1}{3}$  of its bulk, and the residuum is mere phlogisticated air,\* and a little acid is deposited. Now the antiphlogistians own that nitrous air contains both pure air and phlogisticated air ; since, therefore, this pure air disappears, is it not evident that it was converted into water ? and since the formation of water requires the presence of inflammable air, does it not follow that the nitrous air contained this also ? and will not then the phlogisticated air remain single and alone ? As to the acid deposited, it evidently proceeds from the nitrous vapour almost always dispersed through nitrous air.

\* 6 Pr. 430, and 312 Van Marum, 27 Roz. 150.



Analogous to this, is the following experiment made by Dr. Priestley: If a few grains of iron be melted in nitrous air, the iron increases in weight, and nothing but phlogisticated air remains.\* Here the nitrous air is in the same manner decomposed, the phlogiston of the iron and its own uniting to the pure air, form water, which, uniting to the iron, increases its weight, and only the phlogisticated air remains.

3d. Dr. Priestley having thrown the focus of a burning glass on nitrated lead, in a receiver filled with inflammable air, found the inflammable air to disappear; the lead in great measure revived, and  $\frac{2}{3}$  of the receiver filled with nitrous air; in this case, therefore, the inflammable air was taken up partly by the metal which it revived, and partly by the decomposed nitrous acid, whose basis is converted into nitrous air. The antiphlogistians will, probably, reply, that the acid was decomposed, the inflammable air uniting to its oxygenous principle, and forming water, while the nitrous air was barely let loose, and not formed. This answer supposes that nitrous air is a constituent principle of the nitrous acid, which we shall presently prove to be false, and is indeed inconsistent with their own principles, for it would follow from thence that the nitrous acid should be decomposed, and nitrous air produced by boiling charcoal in this acid; since, by the antiphlogistic table,

\* 6 Pr. 304.



charcoal has far a greater affinity to the oxygenous principle than nitrous air has. Yet Mr. Lichtenstein has lately shewn that charcoal rather retains than sets loose nitrous air.\*

The following experiments shew that nitrous air is not a constituent principle of the nitrous acid; but that fixed air is, which is the 3d. point that remained to be proved.

1st. There is not a doubt, but that pure nitrous acid enters intire, and without decomposition into fixed alkalis, and forms nitre. Now if nitre be distilled in a good earthen retort, it will be wholly decomposed, and so also will the acid itself, except a few drops which pass in the beginning of the distillation;† and nothing but dephlogisticated air more or less pure (and, consequently, intermixed with phlogisticated air), and a slight proportion of fixed air, will be found: these, therefore, are its true constituent parts, when disengaged from substances that cannot communicate phlogiston to it in any remarkable quantity, such as alkalis and earths; but if it be separated from substances that contain phlogiston, such as metals, it will then indeed be resolved into nitrous air, and dephlogisticated air more or less pure, the phlogiston of the fixed air being detained by the metal. These facts being of great consequence towards understanding the composition of this acid, require to be more fully stated.

\* Chy. Annal. 1786. p. 217.

† Mem. Par. 1781. p. 23.



Mr. Berthollet, who seems to have made this experiment with most exactness, from 472,5 grs. troy, of nitre, obtained 701,22 English cubic inches of air, that is, at the rate of 714 from a troy ounce of nitre.\* This air is far from being of the purest kind, since the standard of the greater part of it is 0,95, by Dr. Priestley's test, whereas that of the best is 0,03, therefore it contains phlogisticated air. And both Dr. Priestley, Mr. Berthollet, and Mr. Succow, observed that the portion of air which first passes, contains fixed air, rendering lime-water turbid.† Mr. Succow observed it also in the last portion of this air. Here, then, we have the three constituent parts of nitrous acid, with scarce any nitrous air, which the antiphlogistians suppose to be one of its constituent parts, and to make  $\frac{2}{3}$  of the bulk of the acid, when exhibited in an aerial form.

However, a small quantity of nitrous vapour is generally diffused through the air thus obtained, because the acid, as well as the alkali, of which nitre is formed, are both somewhat phlogisticated; the alkali being common potash, which is more or less in a saponaceous state, or mixed with coal, and the acid as being generally extracted from calcareous earths, mixed with animal substances. In the begin-

\* Mem. Par. 1781. p. 23.

† 4 Pr. 252. Mem. Par. *ibid.* 1 Chym. Annal. 1785. p. 104.



ning of the distillation, part of the acid passes undecomposed, by favour of the water of chryftallization.

It may be said with great appearance of truth, that the proportion of fixed air, thus obtained, is too small to deserve to be ranked among the constituent parts of the nitrous acid. Before I answer this objection, it will be proper to determine in what proportion it should be contained in this acid; this proportion, as we have already seen, is variable, the phlogisticated acid containing least, and the dephlogisticated most; but, in general, we may rate it at  $\frac{1}{3}$  of the acid, as existing in nitre. When the nitre is exposed to a red heat, the union of the constituent parts of the acid is gradually broken; that part of the acid which is at the surface of the alkali, being in contact with the water, which is the most volatile ingredient, is not so strongly acted upon by heat, but passes undecomposed. The residuary nitrous acid becoming now more and more concentrated, decomposes its own fixed air, and thereby becomes more and more phlogisticated.\* This phlogistication continues to the last, the retained part always dephlogisticating that which escapes, until it is

\* Of this phlogistication of the nitrous acid, by re-action on itself, we have a full proof, in the red colour which it assumes when heated in glass tubes, hermetically sealed.  
3 Pr. 187.

itself



itself at last forced out ; and hence the last portion is the most impure, and even contains nitrous air.

That fixed air may be decomposed in this manner, appears from fundry other experiments ; for instance, that in which Dr. Priestley obtained dephlogisticated air from acetous selenite, 6 Pr. 292, and also, that in which both he and Mr. Laffone obtained air nearly of the goodness of common air, from limestone, after the greater part of the fixed air had passed. 6 Pr. 227.

To make this matter still more intelligible, it must be observed, that if nitre be heated ever so long, yet if we examine it at any period before its total decomposition, no part of the acid will be found phlogisticated, but that near the surface, which, in the instant of its extrication, is dephlogisticated by the portion of the acid next under it, which then becomes phlogisticated, and is in the same manner decomposed in its turn, by the next inferior stratum ; and this process continues until the whole is decomposed. This I have found, by pouring nitrous acid on melted nitre, which never expelled any more than a small portion of nitrous vapour ; hence, Mr. Berthollet imagined that Mr. Bergman was deceived, in asserting that phlogisticated nitre might be decomposed by the acetous acid ; for, in effect, it can decompose but a small part of it, as only a small part of any portion of melted nitre is really



really phlogisticated; even dephlogisticated air from red precipitate, contains a portion of fixed air, as Dr. Priestley, Mr. Lavoisier, and Mr. Monge have observed.\*

2d. Mr. Berthollet distilled 472,5 grs. of nitre with  $\frac{1}{2}$  that weight of filings of iron, and obtained 453,37 English cubic inches of air, nearly of the same goodness as common air, that is, containing a mixture of pure, and phlogisticated air, and not a particle of nitrous air; but the alkaline mass that remained, contained fixed air.† It were absurd to attribute this fixed air to the plumbago of the iron, of which Mr. Bergman says, *ferrum ductile fere nihil plumbaginis fovet.*‡ But it may, in this case, come either from the decomposition of the nitrous acid, or from the union of the phlogiston of the iron, with the dephlogisticated air of the nitre, but most probably from both. When equal weights of nitre and filings of iron were used, still there was not a particle of nitrous air; because, in effect, the iron was not attacked by the undecomposed nitrous acid, but there was a greater mixture of phlogisticated air, because the nitre was, by reason of the presence of iron, decomposed by a more moderate heat, and the alkali, for the same reason, contained still more fixed air than in the former case.

\* 2. Pr. 217. Mem. Par. An. 1782. p. 495, and 1783. p. 85.

† Mem. Par. 1781. p. 234.

§ 3 Bergm. 49.



The same experiment succeeded in the same manner with Mr. Achard;\* he found fixed air not only in the alkalized nitre, but also in the air that escaped, having probably used a greater heat, by which more fixed air was produced than the alkali could retain in that heat. Mr. Berthollet found a mixture of 120 grs. of nitre, and 60 of zinc, to produce so much fixed air, during detonation, as to precipitate 3 or 4 quarts of lime-water; he also found a mixture of nitre and copper to produce fixed air, though they scarcely detonated, as copper difficultly parts with its phlogiston. Mr. Cavallo found a mixture of 3 parts nitre, 1 of sulphur, and 1 of copper, to afford fixed air, and phlogisticated air; the fixed air was  $\frac{1}{10}$  of the whole.† Hence I think it evidently follows, that fixed air is a constituent part of the nitrous acid; yet I have often thrown nitre on red hot filings of iron, and always found the alkali caustic, the reason of which may be, either that water, and not fixed air, is produced in a red heat, or that the dry alkali could not retain the fixed air in so high a heat.

Sixty grs. of nitre, and 3 of charcoal, distilled, produce fixed air and phlogisticated air; 60 grs. of nitre and 6 of charcoal, slightly detonated, and produced also fixed air, and

\* Chy. Annal. 1784. p. 493.

† Cavallo on Air, p. 815.



more of phlogisticated air, but no nitrous air ;\* here the fixed air is partly an educt, and partly a product. The quantity of phlogisticated air is greater, when more charcoal is used, because the nitrous acid is decomposed in a more moderate heat, and the phlogisticated air it contains is not decomposed ; for I do not esteem it a product of the operation. But as the nitrous acid is decomposed before it unites with the charcoal, no nitrous air can be formed.

But the result is very different, when nitre is distilled with a small proportion of sulphur : † here nitrous air is the principal product, and a small portion of dephlogisticated air, which, being immediately converted into nitrous acid, by contact with a small portion of the nitrous air, cannot be had separate, but subsists in a state of vapour, in the remainder of the nitrous air. The reason why nitrous air is produced in this case is (as will be shewn more fully further on), that part of the sulphur being inflamed in the beginning, and converted into vitriolic acid, this acid reacts on the nitre, and expels its acid without decomposition ; but the expelled acid meeting the uninflamed sulphur, is immediately decomposed by it, and robbed of its fixed air, at the same time that it robs the basis of the sulphur of its phlogiston, and is thereby converted into nitrous air. The vitriolic

\* Mem. Par. 1781. p. 231. † Ibid.



acid, thus formed of the fixed air of the nitrous acid, and of the basis of the sulphur, expels more nitrous acid, which is decomposed in the same manner, until the nitre is converted into tartar vitriolate: towards the end, a small part of the nitre is decomposed by heat alone, and hence the dephlogisticated air arises.

If mercury, &c. be dissolved in nitrous acid, and the solution distilled to dryness, nitrous air will be produced in the beginning, and at the last dephlogisticated air. The nitrous air is here formed of the union of the phlogiston of the metal with the nitrous basis, while the fixed air unites to the metallic calx: at the end the fixed air is decomposed, its dephlogisticated part set loose, while its phlogiston revives the metal, as will presently be seen more at large.

3. If spirit of nitre be made to boil, and its vapour received through a red hot earthen tube, it will be converted into dephlogisticated air, in which a portion both of phlogisticated and fixed air is found, as Dr. Priestley has discovered: the water through which this air passes will contain also fixed air.

Here then are several ways of decomposing the nitrous acid, and in one only it is resolved into nitrous and dephlogisticated air, and in this way it may, at least, be strongly suspected to receive an addition of another principle; why then should these be regarded



as its constituent principle? and as in the two simplest methods of decomposition, in which the reaction of no foreign substance can be suspected, it appears in the form of dephlogisticated, phlogisticated, and fixed air (the former always containing a mixture of the two last), why should not these be accounted its true constituent parts?

4. This theory is further confirmed by reflecting on the manner in which nitrous acid is generated by nature. Mr. Thouvenel\* found that this acid is constantly produced when chalk is exposed to a mixture of putrid air and common air, or putrid air and dephlogisticated air; but if the putrid air be passed through lime-water, it is never generated, and that it is rarely produced by exposure of quicklime, or fixed alkalis, to these airs. Does not this experiment imply that fixed air is an essential ingredient in this production? The reason that alkalis, though aerated, are not so proper, is, that they do not combine with phlogisticated air, as calcareous earths do. Mr. Cavendish, indeed, produced nitrous acid, without any apparent mixture of fixed air; but the atom of fixed air, necessary for the formation of the small quantity of nitrous acid he produced (about  $\frac{1}{3}$  of a grain), might well be contained in the phlogisticated air he used, or perhaps formed in the operation;

\* 11 Sçav. Etrang. p. 126. 128.



for it is impossible to deny all credit to those who asserted that lime-water was precipitated by taking the electric spark in common air, though it did not succeed with him, either from his using an instrument of different power from that used by others, or air phlogisticated by a different process.

5. Having dissolved, or rather calcined, 371 gr. of clean iron filings in 1451 gr. of red nitrous acid, whose specific gravity was 1,456, which I slightly diluted, and let the nitrous air escape, I distilled the solution with a gradual heat until the retort was perfectly red hot, and received the air over mercury, having an apparatus for receiving the acid liquor apart. After some common and nitrous air had passed, I obtained air somewhat worse than common, in 4 portions, each portion containing fixed air; the next day adding more water, I obtained still more fixed air as long as any liquor remained.

6. Dr. Priestley having distilled a quantity of iron filings, converted into perfect rust by long exposure to nitrous air, obtained from them a large quantity of air, the far greater part of which was fixed air, mixed with a little phlogisticated air, and at last pure air. 6 Pr. 319. The fixed air here proceeded for the most part from the decomposition of the nitrous air, its dephlogisticated part taking phlogiston from the iron.

I shall



I shall now examine the explanation of these phænomena given by other philosophers, and particularly by the antiphlogistians.

My ingenious friend Mr. Watt, and also Mr. Cavendish,\* are of opinion, that the whole quantity of dephlogisticated air, produced from the distillation of nitre, arises from the dephlogistication of the water it contains, it being decomposed by the nitrous acid which then becomes phlogisticated. This opinion is exposed to insurmountable difficulties; for in the first place, nitre affords dephlogisticated air at the rate of 146,125 cubic inches for every hundred grains of nitre; and supposing 100 cubic inches of dephlogisticated air to weigh but 32 gr. which is the lowest computation, and may be allowed on account of the mixture of phlogisticated air, 146,125 cubic inches should weigh 46,77 gr. but then dephlogisticated air is only one of the constituent parts of water; for it contains 13 per cent. of inflammable air, that is to say, 87 gr. of dephlogisticated air: to form 100 gr. of water requires an addition of 13 gr. of inflammable air, consequently 46,77 gr. of dephlogisticated air require nearly 7 of inflammable air, and would then form 53,77 gr. of water, which exceeds half the weight of the nitre, as Mr. Watt candidly owns, which quantity of water is certainly inadmissible; for it

\* Phil. Trans. 1784, p. 144 and 337.



evidently contains at least  $\frac{1}{2}$  its weight of alkali, and then no room would be left for the acid; besides, the phlogisticated air cannot be derived from the water, and it makes up about  $\frac{1}{8}$  of the whole, so that of necessity the acid must be decomposed: besides, no satisfactory account is given of what becomes of the acid. Mr. Watt found that the water over which the air proceeding from the decomposition of 960 gr. of nitre, had been received, contained only the acid belonging to 120 gr. of nitre, and even this small quantity he inferred only from my experiments; but my experiments are totally inapplicable in this case, for I used only the dephlogisticated nitrous acid, and alkalis are saturable by a much smaller quantity of phlogisticated than of dephlogisticated acids, as is evident in the case of the dephlogisticated marine acid, as Stahl long ago observed; for he says that the volatile acid of sulphur saturates 10 times as much alkali as the fixed.\* Mr. Bergman and also Scheele observed, that melted nitre is still neutral, though it is phlogisticated; therefore it is air, and not water, which it wants; accordingly Dr. Priestley found it to injure common air, by attracting its dephlogisticated part: but if it be kept some time in fusion, it loses its acid, and becomes alkaline, and the air it recovers must surely

\* See his *Treatise on Salts*, p. 160 of the French edition.



be deemed rather to recompose the acid than to form water, of whose formation in the temperature of the atmosphere we have no sort of proof. On the contrary, the impossibility of accounting for the loss of acid in this case, is an evident proof of the fallacy of that hypothesis.

By Mr. Lavoisier's analysis\* 100 gr. of nitre contain 57 of caustic alkali; by Mr. Bergman's, 49; by Mr. Wenzel's, 52; by Mr. Wiegleb's,  $46\frac{1}{2}$ ; by mine 63; the mean of all which is  $53\frac{1}{2}$ , which leaves 46,5, for acid and water, which is very nearly the weight of the air expelled. The different quantity of acid assigned by different persons to nitre, is, in part, owing to its degree of phlogistication in nitre †. I believe at present that 100 gr. of nitre contain 34 of acid, and about 12 of water, including the water in the acid, and that of chrySTALLIZATION.

The antiphlogistians have as yet given no explanation of the decomposition of nitre by heat.

The detonation of nitre with charcoal was well executed, and the different aerial products well discriminated, though in my opinion not so well explained by Mr. Lavoisier. ‡

\* 11 *Scav. Etrang.* 627. † For of the dephlogisticated acid, as it becomes phlogisticated in uniting to the alkali, less is required. ‡ 11 *Mem. Scav. Etrang.* p. 626. Here, as in most other places, the French weights and measures are converted into English.



Having reduced to a subtil powder, and well mixed together, 708,6 gr. of nitre and 93,52 of charcoal, he pressed them into a copper tube; and after inflammation, plunged the tube, with its aperture turned down, under a jar of water, where it remained until the whole of the charcoal was consumed, and the nitre decomposed. The products were as follows:

Materials.	Gr.	Products.	Cub. Inches.	Weight, Gr.
Nitre	708,6	Fixed air	- 708,25	- 329,33
Charcoal	93,52	Phlog. air	- 195,56	- 59,8
	<hr/>	Caustic alkali	- -	<hr/> 406,5
	802,12	Total of the products	-	795,63
		Loss	- -	6,49

Mr. Lavoisier thinks that the whole of the air of the nitre, except the 59,8 cubic inches of phlogificated air, united to the charcoal, and with it formed the fixed air; and yet we find a deficiency of 6,49 gr. which does not appear in his account, because he estimated the weight of the fixed air too high. I shall not at present examine whether charcoal in specie unites to pure air, and forms fixed air, as that matter will be amply discussed in another section.

In my theory this experiment may be explained as follows: In the first place 708,6 gr. of nitre contains 240,9 gr. of real acid; of this 59,8 gr. (allowing some water contained



tained in this air) are phlogificated air; the remainder 181,1 gr. are dephlogificated air, or, which is the same in effect, pure air mixed with fixed air. This air, if totally pure, would take from the charcoal 37 gr. of phlogiston, and then form 218,1 gr. of fixed air, to which adding the fixed air in the charcoal itself, we have 274,62 gr. of fixed air, and adding to this  $\frac{1}{3}$  of its weight of water, we shall have 329,62 gr. of fixed air. The particulars may be seen in the following detail.

	Gr.
Total weight of the air expelled from nitre	- 240,9
Subtract for phlogificated air	- 59,8
	-----
Dephlogificated air from nitre	- 181,1
Add to this inflammable air from the charcoal	37
	-----
Fixed air formed	- 218,1
Residuum of the charcoal, being fixed air $93,52 - 37 = 56,52$	
Total fixed air $= 218,1 + 56,52 = 274,62$	
Add $\frac{1}{3}$ of its weight of water $= 55$	
	-----
Total weight of fixed air	329,62
Weight of phlogificated air	- 59,8
Caustic alkali	- 406,5
	-----
	795,92

This experiment, though not altogether exact, as the quantity of water in different airs has not as yet been exactly determined, has great merit. Mr. Lavoisier has judiciously inferred from it that nitrous acid contains about  $\frac{1}{3}$  of its weight of phlogificated air, even



even before Mr. Cavendish's discovery. It must also be allowed to be a complete proof of the formation of fixed air from dephlogisticated and inflammable air, by all those that believe charcoal to be a compound; for the whole of the fixed air here found could not by any possibility exist in the charcoal, it being more than triple its weight. We may also infer from it, that phlogisticated air may be decomposed and burnt during the distillation of nitre *per se*, for the resulting air never contains  $\frac{1}{5}$  of phlogisticated air.

The detonation of nitre with sulphur, has also been well observed by Mr. Berthollet. He found that if nitre and sulphur be well mixed in the proportion of 2 of the former to 1 of the latter, there is always a detonation; but if the proportion of sulphur be to that of nitre, as 1 to 4, the nitre is decomposed without detonation, and nitrous air is produced. Thus he found that 30 gr. of sulphur distilled with 120 of nitre, produced 108,8 cubic inches of nitrous air, that is 40,27 gr. and the nitre was totally decomposed. This experiment is thus explained in my principles:

100 gr. of nitre contain about 46 of acid, comprehending the water which always accompanies it, and which cannot be separated; therefore 120 gr. of nitre contain 55 of acid.

$\frac{2}{5}$  of the nitrous acid in nitre is nitrous basis. Now the  $\frac{2}{5}$  of 55 is 36,6, therefore in this case we have 36,6 of nitrous basis.



But nitrous air consists of nitrous basis united to 0,18 of its weight of phlogiston. Now 0,18 of 36,6 is 6,6, then  $36,6 + 6,6 = 43,2$ , then 43,2 should be the quantity of nitrous air.

Again,  $\frac{1}{3}$  of the nitrous acid in nitre is fixed air; therefore, 55 gr. of this acid should contain 18 of fixed air, which it imparts to the sulphur at the same time that it robs it of 6,6 gr. of phlogiston; but 18 gr. of fixed air are far too little to convert 23,34 gr. of sulphur, or rather of dephlogisticated sulphur into fixed vitriolic acid: it converts it therefore into vitriolic air, and saturates the alkaline basis of the nitre.

In this case, therefore, there not being more phlogiston than is necessary for the conversion of the acids into nitrous air and vitriolic air, a gradual production of these airs ensue in the manner explained, p. 49.

But if a greater proportion of sulphur be used, then the nitrous basis itself is decomposed, meeting with a larger proportion of phlogiston, and hence scarce any nitrous air is found, but only phlogisticated, dephlogisticated, and vitriolic air; and as a larger quantity of air is suddenly let loose in a confined situation, a slight detonation necessarily ensues.

This experiment shews that nitrous air does not consist of nitrous acid, to which phlogiston is superadded, as Mr. Cavendish and I myself



myself formerly thought. According to Mr. Cavendish, 87,5 gr. of nitre contain the acid of 98,53 cubic inches of nitrous air, and consequently 120 should contain the acid of 134 cubic inches of nitrous air: yet in this experiment, though the nitre was totally decomposed, only 108,8 cubic inches of nitrous air are produced. It is evident, therefore, that the nitrous acid loses one of its constituent parts when it acquires the phlogiston that converts it into nitrous air, and acquires that same constituent part, when, by the addition of pure air, nitrous air is converted into nitrous acid, therefore the phlogiston and pure air are not merely converted into water.

Before I enter on an explanation of Mr. Lavoisier's experiments on the decomposition of the nitrous acid by mercury, it will be necessary to explain some particulars relative to the formation of nitrous acid, from nitrous air and dephlogisticated air.

When 1 measure of what is generally called very pure dephlogisticated air, is carefully mixed with 2 measures of good nitrous air, they unite so perfectly, that only 0,27 of a measure remains: 1 measure of dephlogisticated air, therefore, takes up 1,73 of nitrous air, but most commonly only 1,7. Yet in one case Dr. Priestley found both airs so pure, and mixed them so skilfully, that only ,03 of a measure remained; therefore, we may well suppose, that if both airs were perfectly pure  
and



and properly mixed, *nothing* would remain unabsorbed, and consequently that 200 cubic inches of nitrous air would absorb 100 cubic inches of dephlogisticated air: however they unite, they always unite in this proportion, and the acid, thus formed, has all the pure air it is capable of taking up, and is what is called dephlogisticated nitrous acid.

Hence 200 cubic inches of nitrous air require for their thorough saturation 100 cubic inches of dephlogisticated air; and since the weight of that quantity of the former is 74 gr. and of the latter 34, the weight of the resulting acid is 108 gr. And as 112,8 cubic inches of dephlogisticated air take 8,14 gr. of phlogiston\*, 100 cubic inches of it should take 7,216 of phlogiston.

Now 100 cubic inches of dephlogisticated air = 34 gr. to which adding 7,216 of phlogiston, we have 41,216 of fixed air in 108 of dephlogisticated nitrous acid: and if 108 of such acid contain 41,216, 100 gr. of this acid will contain 38,16 of fixed air. But it is seldom that given quantities of nitrous air and dephlogisticated air unite so completely; for as soon as any part of the nitrous acid is formed by the union of the two airs, some part of the nitrous air unites to the newly formed acid, and some part of the dephlogisticated air remains unfa-

\* See p. 20. and Phil. Trans. these 112,8 enter into 100 cubic inches of fixed air.

turated :



turated: hence if the two airs do not immediately come into full and perfect contact, the diminution is not so great as it should be, in proportion to the purity of both airs. Hence the acid thus formed is more or less phlogisticated according to the quantity of unfaturated nitrous air combined with it, and this is a great source of uncertainty in eudiometrical experiments.

From what has been said, we may see that even dephlogisticated nitrous acid contains some phlogiston, independent of that which is contained in the fixed air and phlogisticated air, which are its constituent parts: for 200 cubic inches of nitrous air contain 13,4 of phlogiston, and 100 cubic inches of dephlogisticated air deprives these of only 7,216 gr. of this phlogiston; therefore 6,184 still remain in 108 gr. of this acid, and consequently 100 gr. of the acid retain 5,72 of phlogiston, still united to the nitrous basis. By acid I always mean the dry acid, or at least that which contains no more water than the air of which it was formed.

I now proceed to the celebrated experiment of Mr. Lavoisier, which first gave rise to the antiphlogistic theory, and on which it is still chiefly founded.

To 945 gr. of nitrous acid, whose specific gravity was 1,316, Mr. Lavoisier added 1104 gr. of mercury.\* Nitrous air was produced

\* Mem. Par. 1776, p. 673.



to the amount of 273,234 cubic inches; heat being applied, and the mercurial salt distilled to dryness, when it became red, dephlogisticated air appeared, and continued until almost the whole of the mercury was revived: it amounted to 287,742 cubic inches.

Hence Mr. Lavoisier concluded, 1st. That the nitrous acid was totally decomposed, since it was resolved into 2 species of air, by the reunion of which it might again be recomposed, and consequently that the weight of these two airs gives the weight of *real* acid contained in 945 gr. of spirit of nitre, whose specific gravity is 1,316: 2dly. That since the mercury was recovered without any loss or alteration, there is no reason to suppose that it lost any thing during its solution in the acid, but that it was reduced to a calx merely by its union with pure air, since in proportion as this pure air was expelled, it recovered its metallic form.

To justify the *first conclusion*, three points should have been proved; 1st. That during the distillation no part of the nitrous acid had escaped into the water over which the airs were distilled: 2dly. That the nitrous air produced during the solution, was not produced at the expence of some constituent part of the mercury, especially as this was the point contested: 3dly. That by the reunion of the two airs, the same quantity of acid might be reproduced, which might easily be shewn by  
its



its again dissolving the same weight of mercury; and if this were done, the first point would be sufficiently clear.

Each of these points is so far from being proved, that it is clearly contradicted by experiment. To say nothing of my own experiments, nor of those of Mr. Watt,\* Mr. Lavoisier himself found that a part of the acid always passes undecomposed during the distillation of a solution of mercury: † 2dly. Nitrous air does contain one of the constituent parts of mercury, since the nitrous acid never affords nitrous air, but when it is distilled from a substance that contains the same constituent part that is attributed to mercury, namely, the inflammable principle. Thus nitrous acid treated with spirit of wine, oils, or resins, which the antiphlogistians allow to contain inflammable air, affords nitrous air, accompanied with other sorts of air produced from those substances; ‡ but distilled from alkalis, or earths, it yields none: 3dly. Not only the quantity of acid really decomposed, cannot be restored by the union of the two airs obtained, but there is a large excess of one of them, which cannot be accounted for in the antiphlogistic hypothesis; for the nitrous air obtained amounted to 273,234 cubic inches, or 101,09 gr. and the dephlogisticated

\* Phil. Transf. 1784, p. 339. † Mem. Par. 1782, p. 495. ‡ 2 Pr. 126, &c.



air, to 287,742 cubic inches, or 97,83 gr. and the sum of the weights of both airs arising from the decomposed acid was 198,92 gr. Now if we mix both these airs together, they will unite, according to Mr. Lavoisier (and this is the most favourable supposition), in the proportion of 69 of nitrous to 40 cubic inches of dephlogisticated air.\* Then as 69 : 40 :: 273,234 : 143,8 : therefore 144 cubic inches, at most, of dephlogisticated air will be taken up, the weight of which is 48,96, or 49 gr. consequently the quantity of *restored acid* is almost  $101,09 + 49 = 150,09$  gr. though the weight of both airs be 198,92 gr.

$$\begin{array}{r} 198,92 \\ \text{---} 150,09 \\ \hline \end{array}$$

Deficit 48,83, that is, above  $\frac{1}{4}$  of the whole.

Again, if from the whole quantity of dephlogisticated air produced (that is 287,74 cubic inches) we subtract the quantity which enters into union with the nitrous air, we shall find an excess of 143,742 cubic inches, which is about  $\frac{1}{2}$  of the whole. This half must, according to Mr. Lavoisier himself, have existed in the nitrous acid, united to something else, which is now missing. I ask to what? nor do I see what can be reasonably

\* Mem. Par. 1782, p. 488.



answered: the nitrous acid has therefore lost something, which this new hypothesis does not account for.

It is true, Mr. Lavoisier makes two attempts to obviate this objection. In the Memoirs of the Academy for 1776, he says this spirit of nitre was extracted by means of clay, and that such acid always contains an excess of pure air; but can a principle actually combined with the nitrous acid, and which so far from weakening, strengthens and increases its acid properties, be called an excess? His second attempt is to be found in the Memoirs of 1782: here he asserts, contrary to all experience, that nitrous acid consists of equal parts by weight, of nitrous air and pure air, and by so doing, gives up the seeming advantage he had, by recomposing the nitrous acid from both airs, for equal weights of both can by no art be brought to unite.

To ground the *second conclusion*, Mr. Lavoisier should shew that mercury, during its revivification, took nothing from the substance to which it was united while a calx, of which substance the pure air might have been a component part: this cannot be shewn by stating the equality of weight of the calx, with that of the mercury and air together; for supposing the mercurial calx to have weighed 100 gr. the revived calx 90, and the air produced 10 gr. we should then have  $100 = 90 + 10$ , and in this way Mr. Lavoisier would  
have



have the matter understood: but the same equality will be found, if we suppose the mercurial part of the calx, before its revivification, to weigh 89 gr. and the aerial part to weigh 11 gr. and that during the revivification, the calx attracts 1 gr. from the aerial part, for then the products will be equally  $90 \times 10$ . It is true negatives in general need not be proved; but here there is a strong presumption that the aerial part has really lost something during its production, since it is incapable of forming a part of the same acid with which it was before combined; not, as happens in other cases, by reason of its specific heat, since a part of it will enter into such combination, but for want of some other ingredient, which is lost, and given up to the metal; and we may rather say there is a defect of nitrous air, than an excess of pure air.

The most reasonable account of the above experiment seems to me to be the following.

945 gr. of spirit of nitre, whose specific gravity is 1,316, contain by my table 219 gr. of real acid.

The weight of the acid actually combined with the mercury during the solution, must agree with that of the airs obtained; for though the phlogiston of the nitrous air was taken from the metal, and therefore foreign to the acid; yet as the metal was at last revived, it must have taken from the acid as much phlogiston,



as it gave to it: the weight of both the airs obtained amounts to 198,92 gr. therefore only about 200 gr. of the acid were decomposed, and 19 gr. must have passed over during the distillation, as Mr. Watt also found; and, in fact, I found that 22 gr. of real acid dissolve with the assistance of heat 100 gr. of mercury, and consequently in this case, only 900 gr. of mercury were dissolved, and 104 remained undissolved, which might well escape notice.\*

The nitrous air we have already seen to amount to 101,09 gr. and the dephlogisticated to 97,83; this quantity of nitrous air contains 18,18 gr. of phlogiston, and consequently 82,91 gr. of nitrous basis.

Let us now examine the proportion and quantity of the constituent parts of the 200 gr. of acid that were decomposed. I say 200, to avoid fractions, as 198,92 approaches very nearly to that quantity.

This acid, according to Mr. Lavoisier's expression, contained an excess of pure air, that is, it was what we called dephlogisticated nitrous acid; 100 gr. of such acid we have already seen to contain 38 gr. of fixed air, and 62 of nitrous basis, therefore the 200 gr. here decomposed, contained 76 gr. of fixed air, and 124 of nitrous basis; of these 124 gr. of nitrous basis, 82,91 united immediately to part of the phlogiston of the metal, namely, to 18,18 gr. of

\* Mr. Scheele also observed that some mercury in its metallic state always remains in the nitrous solution of mercury. P. 222 of the French edition of his works.



t, and formed with it 101,09 gr. of nitrous air, which were caught in the receiver. The remainder of the nitrous basis, that is, 41,09 gr. remained in the solution, and were decomposed towards the middle of the operation. To understand this decomposition, it is necessary to recollect that metallic substances, in uniting to nitrous acid, unite to it principally through their affinity to the acidifying principle, namely, to fixed air, and take up the basis chiefly by reason of the union of this basis to the acidifying principle. During the middle period of this experiment, the metal being heated gives out more phlogiston than can be taken up by the undecomposed nitrous basis. This surplus is taken up by the pure air contained in the nitrous basis, which pure air is thereby converted into fixed air, and unites to the metallic calx; the phlogisticated air is therefore set loose.

As the nitrous basis consists of pure air, and phlogisticated air in the proportion of 2 to 1, the 41,09 gr. of nitrous basis which remained in the solution, contained 27,42 of pure air, and 13,67 gr. of phlogisticated air; the pure air was converted into fixed air, by the phlogiston of the metal, and the phlogisticated air mixed partly with the nitrous air that escaped, and partly with the fixed air that remained with the metal; and when this was decomposed during the revivification of the metal, a small part of the phlogisticated air was also decom-



posed: in this manner, all the phænomena are exactly accounted for.

Thus we have, 1st. —	—	101,09 gr. of nit. air.	
2d. Pure air contained in	}	76 gr. of fixed air	63,08
Pure air in the nitrous		basis	27,42
		—	
		90,50	
3d. Mixture of phlogif. air,	}	and pure air, from the decom-	7,33
position of part of it		97,83	97,83 dephlogif. air.
		—	—
Total weight of air		198,92 grains.	

Further, the mercury lost 18,18 gr. of phlogiston, carried off in the nitrous air; but this quantity was restored to it by the decomposition of the 76 gr. of fixed air, originally contained in the nitrous acid, which contained 12,92 gr. of phlogiston, and by the absorption of that quantity of phlogiston, which 200 gr. of this sort of acid holds, which we have seen to amount to 11,44 gr. so that there is an excess of 6,2 gr. which compensate for the phlogistication of the 19 gr. of undecomposed acid, which were phlogisticated at the expense of the metal, and passed over into the receiver as already mentioned.

But it may be said, that according to my table of the absolute weight of phlogiston in metals, 100 gr. of mercury contain 4,56 gr. of phlogiston, and, consequently, 900 gr. should contain 41,04, and therefore much more should be restored to it, than was here set forth. To which I answer, that part of it was employed  
in



in the conversion of 27,42 gr. of pure air in the decomposed nitrous basis, into fixed air, and part united to the compound of acid and calx, which, as Scheele remarked, takes up more phlogiston than either singly, and in the end the whole was resorbed by the metal.

Here it will be proper to observe, that the same decomposition of the nitrous basis, which happens during the solution of mercury with heat, takes place in a much greater degree during the solution of zinc, tin, iron, and regulus of antimony.

Mr. Watt, and a few others, suspect that the dephlogisticated air, in this and all other cases where the nitrous acid seems to be decomposed, arises entirely from the dephlogistication of water, whose phlogiston, they say, is taken up by the nitrous acid, or by the metal; but surely the mixture of phlogisticated air, which is always found with the dephlogisticated air, cannot be derived from the water. Besides, the same quantity of acid and water cannot be recovered by the union of both airs, as it should were this theory exact, for some dephlogisticated air always remains, that cannot be combined; and that the acid is decomposed is evident, for the half of it cannot be recovered.

Independently of metallic substances which give a tinge to nitrous acid, its colour depends, as has been already said, on the proportion of nitrous air combined with it. Hence, if a bottle  $\frac{1}{2}$  full of colourless nitrous acid, be ex-



posed to the light, it becomes of a greenish yellow, and dephlogisticated air is produced; for *light* has the property of increasing the capacity of the dephlogisticated part of fixed air for containing fire, and, consequently, of diminishing its union with phlogiston; the phlogiston then unites to a part of the nitrous basis, and becomes nitrous air, which combines with the nitrous acid, and tinges it. When the bottle is full, the dephlogisticated air cannot be separated, and, consequently, no decomposition can take place.

If nitrous air be mixed with its own weight of hepatic air, the hepatic air attracts the nitrous vapour generally diffused through the nitrous air, and this vapour drags with it the phlogiston of the nitrous air. By these attractions the capacities are changed, and the quantity of fire necessary to the fluid state escapes; consequently, both the sulphur, the nitrous vapour, and much of the phlogiston are precipitated. Hence the water with which this precipitate is washed, precipitates the nitrous solution of silver white,\* which Mr. Cavendish discovered to be a character of the phlogisticated nitrous acid. The nitrous basis is then left almost perfectly pure and dephlogisticated; and as it contains double the portion of dephlogisticated air that it does of phlogisticated, it admits a candle to burn naturally,

\* This is mentioned in my Dissertation on Hepatic Air.



or even better than in common air, according as it is more or less perfectly deacidified and dephlogisticated; the deacidification, and consequent dephlogistication, is brought about in the same manner by exposure to iron or liver of sulphur,



## S E C T. V.

*Of the Marine Acid.*

C O M M O N marine acid appears to me to consist of a peculiar basis united to phlogiston, and a certain proportion of fixed air, to both of which the basis seems to have a strong affinity.

If the marine basis be deprived of its phlogiston, its affinity to fixed air becomes much stronger; it unites to so large a portion of it, that the affinities of the resulting acid, to bodies that contain little or no phlogiston, become nearly as weak as those of fixed air itself, equally condensed: but with respect to bodies that contain a considerable proportion of phlogiston, its affinities are much stronger, as its basis attracts the phlogiston, while those bodies attract its excess of fixed air. The acid resulting from the union of the dephlogisticated basis, with an excess of fixed air, is called the *dephlogisticated marine acid*.

Before the discoveries of Mr. Berthollet, the properties of this acid seemed to me to furnish strong proofs of the falsehood of the antiphlogistic theory; but they appear in quite a different light since the publication of the experiments



nature of this excellent liquor, in its nature that, I must own, they have been so far as afford any plausible ground for the hypothesis.

According to the supposition, then, the common marine acid consists of a portion of the united or a small portion of pure air, or oxygenous principle, and the dephlogogenated marine acid follows from it, only by excluding an excess of this principle.

If the common marine acid be distilled over the black salt of magnesia, or nitrous, it becomes dephlogogenated, as the numerous Experiments just discovered; but then it seems to be a considerable portion of the air contained in these salts, as appears by the experiments of Messrs. Berthollet and Lavoisier. According to Mr. Lavoisier's table, the basis of the marine acid has a stronger affinity to the oxygenous principle than any metallic salt, or the basis of any acid, has to that principle; why then does it not become dephlogogenated by distillation over the salts of iron or over the stibic acid? and why does it not convert the acid into sulphur? is it not because these salts cannot dephlogogenate it?

The dephlogogenated marine acid unites to water almost as diffusibly as fixed air, because being over saturated with that air, it participates in a great degree of its properties.

This acid does not expel fixed air from



aerated fixed alkalis or earths, until it is heated, and then dephlogisticated air separates from it, and it becomes in all respects common marine acid. For as it contains an excess of fixed air, it acts nearly as an acid of the same nature; but when heat is applied, its basis dephlogisticates its own fixed air, which then becomes dephlogisticated air, at the same time that the acid becomes *common marine acid*, and acts as such. Heat alone would not dephlogisticate this acid, because of its volatility; its affinity to alkalis detains it, and helps its decomposition. But the dephlogisticated marine acid unites and effervesces with volatile alkalis, whether aerated or caustic, because these alkalis are composed of inflammable air, and phlogisticated air; the marine basis seizes the inflammable, and sets loose the phlogisticated air.

It destroys vegetable colours, by depriving the colouring matter of its phlogiston, and saturating it with fixed air. And hence the colour is not restored by the addition of an alkali, as the alkalis cannot restore the phlogiston.

All metallic substances are soluble in the dephlogisticated acid, without affording inflammable air; because the phlogiston separated from them, is absorbed by the marine basis, and the compound of acid and calx.

If a solution of mercury in the nitrous acid be dropped into common marine acid, it forms a white precipitate, which is phlogisticated,  
since



since it affords red vapours, when re-dissolved in the nitrous acid. But if the nitrous solution of mercury be dropped into dephlogisticated marine acid, it forms sublimate corrosive, which does not give red vapours when the nitrous acid is poured on it. The reason is, because in the first case, the quantity of nitrous acid is too small to dephlogisticate the marine which expels it; but in the second case, the marine is already dephlogisticated. This is the test Mr. Berthollet uses for distinguishing the dephlogisticated marine acid.

The experiments which chiefly induce the antiphlogistians to maintain the presence of pure air in the dephlogisticated marine acid, are the following:

1st. Because this acid is procured by distilling it from manganese, and the manganese, if distilled by itself, before the acid is distilled from it, affords dephlogisticated air; but after the acid is distilled from it, it gives none.

But this experiment proves no more, but that the manganese contains some air which is dephlogisticated during calcination, and that this air is fixed air, appears from the following considerations. The black calx of manganese almost always gives out fixed air at first, before any dephlogisticated air appears, whence it is natural to think that the dephlogisticated air proceeds from the dephlogistication of the fixed. And hence if it be distilled with filings of iron, or in a gun barrel, it scarce gives out any



any other than fixed air;\* if at any time it gives out dephlogisticated air, with little or no mixture of fixed air, this is owing to a very perfect dephlogistication of the calx, and to its containing very little moisture; thus Dr. Priestley having passed the steam of boiling water through manganese heated in an earthen tube, obtained a very large quantity of fixed air, and scarce any other†; though, on repeating this experiment with manganese well freed from calcareous earth, I obtained a large proportion of dephlogisticated air; but I believe much depends on the degree of heat to which the tube is subjected. But having distilled manganese, which yielded of itself some fixed air, with common spirit of salt, I obtained dephlogisticated marine acid, and not a particle of fixed air, which shews that this last combined with the dephlogisticated basis, and formed the dephlogisticated acid. Mr. Hermstadt, a German chymist of the highest reputation, having dissolved the black calx in common marine acid, and precipitated it with an aerated fixed alkali, obtained, as usual, a white precipitate, which, when heated, afforded a great part of the fixed air it had absorbed from the alkali; but when heated to such a degree as to be of a brown red colour, and consequently dephlogisticated, it converted common spirit of salt into a dephlogisticated acid, which could pro-

\* 4 Pr. 239. † Hermst. Phys. Chym. Versuche, p. 277.

† 6 Pr. 354. † Hermst. 173.



ceed only from some fixed air, yet unexpelled. Yet if sal ammoniac be distilled with the black calx of manganese, it will be expelled in a caustic state; for the fixed air unites to the dephlogisticated marine basis in preference to the volatile alkali.

If equal quantities of inflammable air and dephlogisticated marine air be mixed, a dense white cloud immediately appears,  $\frac{1}{2}$  of the bulk of both airs is soon absorbed, and is found to be common marine acid. The residuum is said to detonate like a mixture of inflammable and dephlogisticated air.\* As this experiment seemed to be of great importance, I repeated it; and having mixed 6 cubic inches of inflammable air with 6 of dephlogisticated marine air over water, I observed a dense white cloud immediately formed, attended with a diminution of 1 cubic inch; but in  $\frac{1}{4}$  an hour 7 cubic inches were absorbed: into the residuum, I put a bit of phosphorus stuck on an iron wire, and endeavoured in vain to fire it by approaching a red hot iron on the outside. It shone and even smoked and sublimed, but no detonation took place, so that clearly the residuum was not a mixture of inflammable and dephlogisticated air: the detonation observed by Mr. Pelletier, must rather have proceeded from the union of the inflammable and dephlogisticated marine air.

\* 26 Roz. 453.



For greater certainty I again mixed equal quantities of both airs, and after more than  $\frac{1}{2}$  disappeared, I fired the residuum in a narrow-mouthed bottle, and found it to give 4 successive explosions, which evidently proves it was mere inflammable air, and not a mixture of inflammable and dephlogisticated air. This experiment establishes, beyond all doubt, that inflammable air unites to dephlogisticated marine air, and converts it into common marine acid. To try whether the dephlogisticated marine air were united to fixed air, I mixed 6 cubic inches of inflammable air once more, with 6 of marine air, over lime-water; in about 10 minutes after the greater part of the diminution had taken place, a white cloud appeared on the surface of the lime-water, and by agitation it became still more turbid: as it was possible that the manganese might be mixed with calcareous earth, I extracted from another portion of it, some dephlogisticated marine air, and received it on lime-water, but it was wholly absorbed, without forming the least cloud, though there was lime enough; for on adding aerated water, a cloud appeared. This experiment therefore fully confirms my opinion, and subverts that of the antiphlogistians. Even if the manganese had contained calcareous earth, this would not affect my theory, for I have obtained dephlogisticated marine acid from chalk, and Mr. Gallish obtained it from magnesia; for the  
fixed



fixed air unites to the acid as soon as it parts with its phlogiston.

If nitrous air be mixed with dephlogisticated marine air over water, both immediately become visible and are absorbed.\* Here a double decomposition takes place, by virtue of which, the common marine acid, and the nitrous acid, are regenerated: the marine air dephlogisticates the nitrous air, and at the same time gives to the nitrous basis its acidifying principle.

If sulphur be exposed to the action of the concentrated dephlogisticated marine acid, it is decomposed, and the marine acid becomes common spirit of salt.† This shews that sulphur contains the same principle as inflammable air, which, as we have just seen, restores the dephlogisticated acid to its common state. Phosphorus also is decomposed with the assistance of heat.

If dephlogisticated marine acid be exposed to the solar light, it emits dephlogisticated air, and becomes common marine acid;‡ the fixed air being decomposed, as already seen, p. 72.

Mr. Berthollet and Morveau tried in vain to combine dephlogisticated air directly with the common marine acid. † Encyclop. p. 254.

\* 26 Roz. 393. per Pelletier. † 1 Nouvelle Encyclop. 252. Chy. Beytr. 1 Band. 3 Stuck.

‡ 29 Roz. 82.



## S E C T. VI.

*Of Aqua Regia.*

**I**F the common marine acid be mixed with an equal bulk of strong colourless nitrous acid, the marine will deacidify in great measure the nitrous, while the nitrous dephlogisticates the marine; that is to say, the marine will take up a great part of the fixed air of the nitrous acid, while the nitrous will take up the phlogiston of the marine. Hence part of the nitrous acid is converted into nitrous air, which immediately unites to the undecomposed part of the nitrous acid, and forms phlogisticated nitrous acid, and hence the red colour of the liquor.

If the nitrous acid be in small proportion, it will be wholly decomposed; for the marine basis, and the phlogiston of that part which is converted into nitrous air, both solicit the pure air in the nitrous basis, which, when disengaged, is converted into fixed air, and unites to the marine basis, and the phlogisticated air is set loose.\*

\* See the curious Experiments of Mr. Pelletier, 26 Roz. 393.



Thence if the marine acid be made to imbibe nitrous vapour, a very strong aqua regia will be produced, as Dr. Priestley has discovered; for nitrous vapour contains a large proportion of nitrous basis, as already shewn, and very little water, and this basis being decomposed affords a larger quantity of fixed air to the marine basis, than triple the bulk of aqueous nitrous acid.

Shortly after the mixture of the nitrous and marine acids, an air arises which is immediately absorbed by water, 26 Roz. 323; because it is a mixture of dephlogisticated marine air and of nitrous air, and these decompose each other, and form nitrous and common marine acids.

When aqua regia is made with a certain proportion of sal ammoniac, the volatile alkali is destroyed; for when the marine acid is dephlogisticated, it reacts upon and decomposes the volatile alkali.

But as water in the common temperature of the atmosphere, can retain but a very inconsiderable quantity of dephlogisticated marine acid, it seems very difficult to explain why in aqua regia so considerable a quantity of that acid remains. This appears to me to be occasioned by its affinity to the undecomposed nitrous acid; to see if that were the case, I mixed the nitrous and marine acids in different proportions, and examined whether the specific gravity of the mixture were greater



than the mean that should result, and I always found it less; but as during the union of the two acids, and while weighing, a great quantity of air escapes, no conclusion can be drawn from these experiments.

The antiphlogistic explanation of these phenomena appears to me perplexed and difficult to understand. According to Mr. Berthollet,\* though nitrous air attracts the oxygenous principle more strongly than marine acid attracts it, “yet by a double affinity on the one hand the nitrous air combines with the marine acid, and nitrous acid of the aqua regia, and on the other, the vital air of part of the nitrous acid combines with part of the marine acid.” With respect to the affinity of nitrous air to marine acid, it can scarce be allowed; for, according to the experiments of Dr. Priestley, the marine acid scarcely absorbs any in a *short* time, and not above  $\frac{1}{4}$  of its bulk even in 2 months, † whereas aqua regia is made in  $\frac{1}{2}$  an hour; and upon the whole, this explanation says no more than that the two acids unite, since the marine acid unites to both principles of the nitrous acid, viz. the nitrous air and vital air; yet that something more happens is evident even by the smell, for this is the same as that of marine acid digested with manganese.

\* 1 Encyclop. 259. † 3 Pr. 129.



S E C T. VII.

*Of the Phosphoric Acid.*

**F**ROM various experiments, and particularly those of Mr. Lavoisier, which appear to have been made with great accuracy, it appears that the phosphoric acid consists of a peculiar basis united to 2,265 of its weight of the acidifying principle, that is, fixed air; or in other words, 100 gr. of dry phosphoric acid contain about 69 of fixed air, and 31 of its peculiar basis: 100 gr. of the phosphoric basis take up 226,5 of fixed air, or 32,9 of phlogiston, when it becomes phosphorus; and 100 gr. of phosphorus contain 75,24 of basis and 24,76 of phlogiston.

The antiphlogistians think that the phosphoric acid consists of phosphorus itself united to the oxygenous principle, and that phosphorus does not contain phlogiston.

Mr. Morveau made an experiment that evidently proves the dephlogistication of this substance during its acidification, and that pure air becomes fixed air before it unites to it: Having left a piece of phosphorus in a large glass vessel well stopped for 3 or 4 days, ex-



posed to a temperature of 70 or 72°, and afterwards opened it in lime-water, the lime-water entered and became turbid, and being filtered, left a precipitate which effervesced with the nitrous acid, and consequently the precipitation did not arise from the union of the lime with the phosphoric acid. 1 Encyclop. p. 220.

Mr. Lavoisier having *gradually* introduced a quantity of phosphorus into nitrous acid, whose specific gravity was 1,299 heated to 133°, observed a large quantity of nitrous air to be produced, and the phosphorus almost wholly converted into phosphoric acid, and increased in weight above the double.\* As I have already shewn that nitrous air contains a large quantity of phlogiston, and that it does not pre-exist in nitrous acid, I must consider that produced on this occasion, as a proof that phosphorus contains phlogiston, and that it took fixed air from the nitrous acid; but the surplus weight which the phosphoric substance possessed after the operation, cannot be entirely derived from the nitrous acid, as much common air must have been admitted during the gradual introduction of the phosphorus.

The celebrated Mr. Sage has shewn that phosphorus precipitates copper, silver, and other metals from their diluted solutions in their metallic form, and that at the same time

\* Mem. Par. 1780, p. 350.



it is converted into an acid.\* This is a full proof that phosphorus contains phlogiston, if metals contain any, when in their metallic form. If the phosphoric acid be distilled with zinc, it will be converted into phosphorus, 1 Margr. 146; so it will if distilled with tin, which contradicts Mr. Lavoisier's table of affinities.

The basis of the phosphoric acid, as Mr. Morveau well remarks, is the only one which can be procured free, both from phlogiston and the acidifying principle; it is what is called (though improperly, since it is not soluble in water) the glacial phosphoric acid.

\* 18 Roz. 263.



## S E C T. VIII.

*Of the Saccharine Acid.*

**V**EGETABLE substances in general are resolvable into water, fixed, inflammable, and phlogisticated airs; in the number, proportion, and degree of condensation of each of these, the sole difference betwixt them lies; and if we suppose each of them to be capable of only 10 degrees of condensation, we shall have 40 principles, exclusive perhaps of fixed alkalis, whose composition is not yet known: the combinations of which these are capable, are fully sufficient to furnish all the varieties that can be supposed to exist. Every combination of two or more of these, and also every degree of condensation, seems to have properties peculiar to it; but as we are in a great degree ignorant of the manner of combining or condensing these principles, we are as yet unable to recompose even unorganized vegetable substances.

*Sugar* is a compound of fixed air with a much larger proportion of inflammable air and some water, all condensed to a degree of which we are ignorant, but retaining upon  
the



the whole much more specific heat than either oil or charcoal; this last indeed seems to exclude water from its composition. Mr. Morveau conjectures, with great probability, that sugar has for its basis a fine æthereal oil, to which a large proportion of condensed inflammable air is superadded.

The *acid of sugar* consists then of this peculiar basis, stripped of its superadded phlogiston, and united to a large proportion of fixed air in a condensed state: the saccharine acid therefore does not pre-exist in sugar, but is formed by the operation that exhibits it; and thus it differs from neutral salts, soaps, and phlogisticated mineral acids.

This acid derives the greater part of its acidifiable principle from the nitrous acid, which, as well as the sugar itself, is decomposed during the operation that produces the acid of sugar: the nitrous basis takes up the phlogiston of the sugar, while the fixed air of the nitrous acid combines with the saccharine basis.

In explaining many of the phænomena of the mineral acids, the antiphlogistic theory appears to great advantage from its seeming simplicity; but in explaining those of the analysis and production of the vegetable acids, this advantage is entirely lost, and its insufficiency becomes very apparent.

Mr. Lavoisier distilled 236,25 gr. of sugar, with 945 gr. of nitrous acid, whose specific gravity



gravity was 1,316, diluted, with 945 gr. of water, in an apparatus for receiving airs, and an intermediate bottle for receiving the liquor that might pass over during distillation. The total amount of the materials was therefore 2126,25 gr. and when the operation was over, the amount was

	Grains.	
Nit. air 229,71 cubic inches	= 85	which contain 15 of
Fixed air 108,81	= 50,6	phlogiston, and
Inflam. air 30,22	= 1	6,7 of nitrous
Liquor and salt in the retort	1316	basis.
Weight gained by the in- termediate bottle	} 599	
<hr style="width: 10%; margin: 0 auto;"/>		
Total 2051,6		

Original Weight 2126,25 gr.

Deduct 2051,6

---

  
Loss 74,65

This loss is so considerable, that it were superfluous to enter into an account of the quantity of nitrous acid decomposed,\* and so much the more as the decomposition of the nitrous acid is not contested. But he takes for granted what cannot be allowed, that the nitrous air pre-existed in the nitrous acid, and even that this acid contained an equal bulk of

\* Mem. Par. 1778, p. 541. There seems to be a contradiction in Mr. Lavoisier's account, for he says, the intermediate bottle gained 1 oz. 2 gros and 12 gr. and a few lines after, that only 3 gros and 56 gr. had passed into it.

nitrous



nitrous and pure air, which has been already shewn to be impossible.

However, he infers from this experiment that sugar is a *sort* of charcoal, which uniting with the oxygenous principle of the nitrous acid, decomposes that acid, sets loose the nitrous air, and forms the saccharine acid; but towards the end of the operation, the saccharine acid itself is, as he thinks, decomposed, and hence the origin of the fixed air, which is nothing else but the oxygenous principle united to charcoal.

On this I remark, 1<sup>st</sup>. That according to this theory, the acid of sugar and fixed air should be one and the same thing, since both are composed of the oxygenous principle united to charcoal. Mr. Lavoisier may reply, that the acid of sugar, besides charcoal, and the oxygenous principle, contains also inflammable air; but then he must own that sugar contained a larger proportion of inflammable air, than was given out during the formation of the acid of sugar, and cannot deny that part of this inflammable air united with the nitrous basis, and formed nitrous air. He may perhaps also say, that this charcoal is different from common charcoal; but if so, how came it to make fixed air like common charcoal? Besides, if it were a different sort of charcoal, the acid of sugar should, in his system, be decomposed by common charcoal and sugar regenerated; for, according to his table, charcoal has a much stronger affinity to the oxygenous



genous principle than sugar has to that principle. Nay, sugar should be regenerated by various metallic substances, which, by his table, stand before it in the order of attraction to the oxygenous principle.

2d. If the acid of sugar consisted of sugar itself united to the oxygenous principle, this acid should weigh more than the sugar itself of which it is formed, notwithstanding that some fixed air and inflammable air escape from it. For in Mr. Lavoisier's experiment, the quantity of sugar employed was 236,25 gr. the quantity of oxygenous principle taken up was 83 gr. so that if there had been no loss, the whole quantity of saccharine acid should have been 319,25 gr. and if we deduct the loss of 50 gr. of fixed air, and 1 gr. of inflammable air, we still have 268,25 gr. that is, 32 gr. more than the weight of the sugar. But this increase of weight is contrary to the experience of all who have examined the matter with any accuracy. Mr. Bergman from 3 parts of sugar obtained but 1 of saccharine acid\*; Mr. Chaptal, from  $\frac{1}{3}$  to  $\frac{2}{3}$  of the quantity of sugar employed;† Mr. Sage only  $\frac{1}{6}$ ‡ and yet if we consider the proportion and strength of the acid employed by Mr. Lavoisier, we shall find it very improbable that even the whole of the sugar he employed was converted into saccharine acid.

\* 1 Bergman, 253.

† Chaptal, 61.

‡ Mem. Par. 1777, p. 437.

3d. If



3d. If the saccharine acid consisted of sugar undecomposed, and barely united to the oxygenous principle, then it should be formed by treating sugar with the black calx of manganese, or with dephlogisticated marine acid; for both these substances contain abundance of the oxygenous principle, and easily give it out: yet after various trials, neither Mr. Scheele nor Mr. Morveau were able to form a particle of the saccharine acid; by means of either of these substances. Let it not be thought that this arises from want of affinity in the oxygenous principle to sugar, for by Mr. Lavoisier's table, it has a stronger affinity to sugar than to either of these substances, and passes from them to sulphur (to which, by that table, it has a weaker affinity), as Mr. Morveau has shewn. The only reason then, why sugar cannot be converted into an acid by these substances, is, because neither of them can strip it, and carry off that quantity of phlogiston which it must lose before it can become an acid.

Lastly, If the acid of sugar be distilled, it is wholly converted into water, fixed and inflammable air, and not a particle either of coal or dephlogisticated air is found in it. It is not therefore reasonable to look on either of them as its constituent principles; but as fixed air alone can be extracted from all vegetable acids, it seems to be the true acidifiable principle.



## S E C T. IX.

*Of the Calcination and Reduction of Metals, and  
the Formation of Fixed Air.*

**T**O calcine a metal is to deprive it of its metallic splendor, or reduce it to a brittle, less coherent and pulverent form: malleable metals thereby lose their malleability, and mercury its liquidity. To reduce a metal is to restore to it the metallic lustre, and the degree of coherence and malleability that are peculiar to it.

Metallic calces are *heavier* than the metal of which they are formed, and hence are evidently united to some new substance; but they are specifically *lighter* than before calcination, and hence this new substance is lighter than that to which they were united before calcination, if they were united to any.

The different substances, by whose means in different degrees of heat, different metallic substances may be calcined, are respirable air, water, acids, alkalis, mercury, with the assistance of respirable air, and various other metallic substances in different circumstances.

According to the new theory, metallic substances lose no peculiar substance during calcination,



ination, but barely take in, and unite to the oxygenous principle, that is, pure air deprived of the greater part of its specific heat.

Those who admit the existence of the inflammable principle in metals, are mostly agreed, that during calcination it is separated from them; but with regard to the new substance which metals take in, few of the present adherers to the old system have as yet declared their sentiments. I shall forbear entering on a discussion of antiquated opinions long ago exploded, and also of that of Mr. Scheele, which has scarcely been embraced by any body, and has been sufficiently refuted by Mr. Lavoisier, and the experiments of Dr. Fordyce.

Mr. Cavendish inclines to think that the imperfect metals lose their principle of inflammability or phlogiston, during calcination, and take in water in its stead. But with respect to the calces of mercury (and of the perfect metals) he thinks it ridiculous to decide, whether the mercury, and not the water, or the water, and not the mercury, have lost the principle of inflammability.

Hence, in the antiphlogistic system, to reduce a calcined metal, is barely to deprive it of the oxygenous principle; and in that of Mr. Cavendish, it is in most cases barely requisite to decompose the water to which the calx is united; the inflammable principle of the water uniting to the metal and the pure air, its other ingredient being set loose.



In my opinion, metallic substances by calcination lose their phlogiston, which is nothing else but pure inflammable air in a concrete state, and at the same time unite most commonly to fixed air, formed during the operation; but sometimes some of them unite to water and other substances, by whose means they are calcined. The calces of the perfect metals may therefore be reduced by the decomposition of their fixed air, and those of the imperfect, and semi-metals, partly by the decomposition of their fixed air, and partly by its expulsion, and that of the other foreign bodies they had absorbed, and their simultaneous reunion to the inflammable principle.

To substantiate this opinion, it is necessary to prove, that phlogiston, or inflammable air in a concrete form, exists in metallic bodies endowed with their metallic splendor and peculiar coherence. This, I flatter myself, I have sufficiently performed on another occasion.\* I have there shewn, 1st. That many metals, during their solution in acids, produce inflammable air; yet that the same metals placed in the solution of other metals in the same acids, though they are dissolved, yield no inflammable air; but at the same time, and in the same proportion, the metal before dissolved and calcined, is restored to its metallic lustre; from whence I inferred, that the substance which the

\* Phil. Transf. 1782. p. 195.



added metal would, if alone, give out in the form of inflammable air, is, on this occasion, imbibed and absorbed by that which is restored to its metallic lustre.

2dly. That metallic calces are reduced to metals, by merely heating them in inflammable air, which they visibly absorb. 3dly. That inflammable air has been expelled from them *in vacuo*, by mere heat, at least with the assistance of moisture. And 4thly. That imperfect metallic substances are never restored to their perfect metallic state, but by substances that contain the inflammable principle. I shall, therefore, now do little more than reply to the objections that have been made to the general conclusion, and to my theory of fixed air, by whose decomposition the calces of mercury are revived.

In the first place, the antiphlogistians contend that the inflammable air produced during the solution of metals, proceeds from the decomposition of water. "For" (says that eminent mathematician and philosopher, Mr. De la Place, who first suggested this improvement on the antiphlogistic system) "by the action of acids the metal is calcined, that is, united to vital air." These expressions are not yet allowed to be synonymous. "That no part of the vitriolic acid is altered by iron, appears by Mr. Lavoisier's experiments, who found it to saturate the same quantity of alkali as before." This, if admitted, only proves that



the inflammable air does not proceed from the acid. "If the inflammable air originated from the metal, we should obtain it likewise by means of the nitrous acid." By no means; the nitrous acid is evidently decomposed, the inflammable air unites to its basis, and forms nitrous air. "If it formed nitrous air, it should appear on uniting nitrous air with pure air." No, it unites to the pure air, and forms fixed air. "Moreover the action of nitrous acid on mercury, develops nitrous air, yet it does not appear that the mercury imparts inflammable air, since the resulting calx of mercury is revived without the addition of inflammable air." This revivification has been explained at large, at the end of the fourth section. That it is due to inflammable air will again be seen in the ninth.

And in effect, if we consider the decomposition of water in this case, in a chymical point of view, it cannot but appear exceeding improbable; every decomposition arises either from a single or a double affinity; therefore, if during the dissolution of iron in the dilute vitriolic acid, water is decomposed, this must happen either by virtue of a single or of a double affinity; yet neither can be said to take place: Not a double affinity, since the inflammable air escapes without uniting to the acid; not a single affinity, since there is no proof that any such affinity exists in this case, and if it did exist, water should as easily be decomposed by iron without an acid, as when



an acid is present, or rather more easily, since the affinity of water to the acid must diminish its tendency, or that of any of its component parts, to unite to any other substance, and on that account we find a variety of solutions precipitated by the vitriolic acid, merely because it attracts the water necessary to hold them in solution.\* I would be glad to know what part the acid acts here; in the new theory it seems to be quite idle, and contributes nothing to the solution. Why does not its oxygenous principle unite to the inflammable air of the water, at the same time that the oxygenous principle of the water unites to the metal? since, by the table of Mr. Lavoisier, this principle has a greater affinity to inflammable air, than to sulphur. How comes it that volatile vitriolic acid disengages inflammable air from iron? since its own oxygenous principle is sufficiently developed, and sufficiently copious to unite to iron, without having recourse to that of water. How does fixed air expel inflammable air from iron? Do all acids help the decomposition of water, and yet remain inert?

Besides, though iron and zinc are the only metals which by Mr. Lavoisier's table have a greater affinity to the oxygenous principle, than inflammable air has to that principle; yet inflammable air is also set loose during the solution of other metals, which by that table

\* As tartar vitriolate, alum, &c. See 1 Mem. Scav. Etrang. p. 105, and Vogel, § 769.



have a weaker affinity to the oxygenous principle than inflammable air has to it. Thus inflammable air is produced by the solution of manganese in the dilute vitriolic acid,\* and by the solution of tin in the marine acid; by this table also vitriolic acid and charcoal should decompose water, in the same circumstances in which vitriolic acid and iron decompose it, which yet is not pretended.

I am very sensible that all general reasonings should give way to *facts*; but surely, when adduced against *mere inference and conjecture*, they must have their due weight.

To destroy this supposition still more effectually, I made the following experiment: Having heated some pounds of mercury to  $212^{\circ}$ , and kept it in that heat for 6 hours, often stirring it to dissipate all moisture, I amalgamated one pound of it by frequent agitation with 360 gr. of filings of zinc, which had been previously heated nearly to redness, in a dry glass bottle, and poured the whole, with about 40 gr. more of zinc strewed over its surface, into a coated glass retort made as dry as possible, and which with its adopter contained about 20 cubic inches. I then distilled the whole with a gentle heat, and received the air in 5 portions over mercury: the first and second portions, each about 5 cubic inches, were common air; the third, nearly 5 cubic inches, was in-

\* 2 Bergm. 210.

flammable



flammable air, and detonated with common air; the 4th, also about 5 cubic inches, made 4 successive explosions, after which a considerable absorption took place, and the mercury began to distil over; a fifth portion of air passed slowly,  $\frac{1}{2}$  of which was fixed air, and the other  $\frac{1}{2}$  slightly reddened with nitrous air.—In this experiment, the fairest I could devise, moisture was avoided as much as possible, and none could be present, but that included in the air necessarily absorbed during the amalgamation: the inflammable air seems then to have proceeded from the zinc, which, like all other imperfect metals, is in some measure calcined during its union with mercury, and thrown into an aerial form by the heat applied, when there was but little common air in the retort: this air had a very peculiar smell.

It is true that vitriol of iron, when distilled, gives at last dephlogisticated air; but this air evidently proceeds from the decomposition of part of the acid, and not from that of the water; for its production is always preceded by a large quantity of vitriolic air,\* arising from the absorption of part of the fixed air of that acid, by the metallic calx.

To prove the decomposition of water, Mr. Lavoisier made the following experiments: 1st. He let up a mixture of water and filings

\* 4 Priestley, 216. 220.



of iron, into a tube filled with mercury, and in a few days obtained a small quantity of inflammable air. 2dly. Having passed the steam of boiling water through a red hot iron tube, he obtained a large quantity of inflammable air; the inner surface of the tube was calcined, and had the appearance of what is called the *specular*, or *tessular iron ore*, of great hardness, scarcely magnetic, and affording no air with acids.\* The iron increased in weight from 25 to 30 per cent.

These experiments seem to me to prove nothing more than that water unites to iron, and expels inflammable air from it, which is further confirmed by the following considerations: If a little water be thrown on a large heap of filings of iron, a considerable heat is soon produced,† which appears to proceed from the condensation of the water while uniting to the iron; the heat given out, exceeding that absorbed by the inflammable air, whose weight is exceeding small. In Mr. Lavoisier's hypothesis, it is only the oxygenous principle of the water, which is absorbed by the iron; and as this is already exceedingly condensed in water, it does not appear to me likely to give out much heat. 2dly. This calx is very different from that formed by the absorption of air, such as rust; for fixed air may be extracted from this, and even dephlogisticated

\* Mem. Par. 1781. p. 271, 272, and 487. † 3 Bergm. 94.

air;



air; but no air of any sort can be extracted from iron calcined by water.

Dr. Priestley has also made many curious experiments on this subject, which deserve particular attention, as their results are incompatible with the new theory, and set the absorption of water *in specie*, beyond contradiction. By the help of a burning glass he heated a bit of iron in dephlogisticated air, extracted from precipitate *per se*, and presently perceived the air to be diminished, and visibly absorbed by the iron, which was converted into a slag, and gained a weight very nearly corresponding to that of the air which was absorbed; but when he afterwards heated this slag in inflammable air, the inflammable air also disappeared, a considerable quantity of water was produced, the iron recovered its metallic state, and lost a weight nearly equal to that of the water it had given out.\* In the first experiment the phlogiston of the iron united to the dephlogisticated air, and formed water, which the iron absorbed, became a slag, and must thereby have gained the weight of the dephlogisticated air. In the second experiment the water was expelled, and converted into vapour, while the inflammable air was absorbed, and the iron thereby restored to its original state and weight. In the antiphlogistic hypothesis it must be said,

\* 6 Pr. 73—85.



that in the first experiment the pure air united to the iron, and formed a slag; but in the second, the dephlogisticated air quitted the iron, united to the inflammable air, and formed water: but this contradicts Mr. Lavoisier's table, where pure air is represented as having a stronger affinity to iron than to inflammable air; nor can heat be said to be the cause of the expulsion of pure air from iron, and its reunion to inflammable air, since this expulsion takes place in the very circumstance in which water is said to be decomposed by the avulsion of the oxygenous principle from inflammable air, and the union of the oxygenous principle to iron: if it be replied that we also assert that water is expelled from iron by inflammable air, in the very circumstance in which we before asserted that inflammable air was expelled from it by water, I shall answer that the circumstances are not the same; when water expels inflammable air from iron, the water contains much more specific heat than either iron or its phlogiston, and the phlogiston has room to escape in the form of inflammable air; but when inflammable air expels water from iron, the inflammable air is confined, and having an equal affinity to iron, and more specific heat than the condensed water, and pressing upon the iron with considerable force by reason of its heat and confinement, it gives out its heat to the water, which is immediately converted into vapour,  
and



and condensed on the sides of the glass. In the antiphlogistic hypothesis this reason will not apply, because according to it, the oxygenous principle has a strong affinity to iron, and the inflammable air none at all; so that there is no substance at all that tends to expel the former, and the communication of specific heat to the oxygenous principle, should rather impede than promote its union with the inflammable, since this heat must be given out before that union can take place.

If the above mentioned slag (that is, iron calcined by the steam of water) be mixed with charcoal perfectly dried, and out of which all loose inflammable air has been expelled, and then distilled in an earthen retort well baked and glazed on the outside, fixed and inflammable air will be produced, and the iron reduced to its metallic form.\* Here I ask from whence the inflammable air proceeded? The antiphlogistians cannot say it proceeds from the charcoal, for they deny it to contain any; nor can they have recourse to the decomposition of water; for, according to them, the slag contains the oxygenous principle singly, and not water: this decisive argument is urged against them by Dr. Priestley.

The next set of experiments, which Mr. Lavoisier adduces in proof of the decomposition of water, are those which he made on char-

\* 6 Priest. 109.



coal, which I shall examine in conjunction with those of Dr. Priestley, on the same subject.

Mr. Lavoisier placed 248,62 gr. troy of charcoal, out of which all adventitious air and moisture had been expelled, in an iron tube lined with copper (water having no action on copper); and having passed through it the steam of boiling water, to the amount of 1122 gr. the result was that 6644 cubic inches of inflammable air were produced, whose weight he estimates at 550 gr. : by introducing a caustic alkali, he found  $\frac{1}{4}$  of the bulk of this air to consist of fixed air, and there remained 5 gr. of ashes: as the weight of this product was more than double that of the charcoal employed, he infers that the water must have been decomposed; its inflammable principle forming the inflammable air, and its oxygenous principle uniting to the charcoal, forming the fixed air.\*

On this experiment I remark, 1st. That Mr. Lavoisier supposes that the inflammable air and fixed air here produced, were free from water, a supposition, which neither Mr. Saussure's experiments, nor my own, can allow; and if we suppose that above  $\frac{1}{2}$  of the weight of these airs was water, a supposition fully justified by my experiments, there will be no necessity for inferring that water was de-

\* Mem. Par. 1781, p. 280.



composed, but only the charcoal, which was resolved in great measure into its constituent principles, inflammable air and fixed air; and even this resolution is not quite perfect, the inflammable air being still combined with a quantity of fixed air, as appeared by its weight, and its burning with a blue flame.

2dly. I observe that the iron tube was not so completely coated, as to prevent the iron from being calcined;\* some part therefore of the inflammable air must have been derived from the iron; therefore no calculation founded on this experiment can be conclusive.

3dly. The weight of the fixed air (supposing it to make  $\frac{1}{4}$  of the whole volume of the air obtained) must have exceeded that of the whole; for the whole is said to have weighed but 550 gr. but the fixed air amounting to  $\frac{6644}{4} = 1661$  cubic inches, should weigh 772 gr. estimating 100 cubic inches at 46,5 grains.

Dr. Priestley in making similar experiments found considerable variations in the results.† When he passed no more water than was sufficient for the production of the air, he never found any uncombined fixed air; but the whole was inflammable air. When a greater quantity of water was used, the uncombined fixed air constituted from  $\frac{1}{12}$  to  $\frac{1}{3}$  of the whole:

\* Mem. Par. 1781, p. 280. † 6 Pr. 95.



the inflammable air was more than  $\frac{1}{2}$  lighter than common air, 100 cubic inches of it weighing 14 grains.

In the experiment he most depended upon, he found that 94 gr. of charcoal, from which all uncombined air had previously been expelled by heat, afforded, by the help of 240 gr. of water, 294 gr. of air, or 1591 cubic inches,  $\frac{1}{3}$  of which by bulk, was fixed air. However, as this weight was not deduced from a direct experiment, no great stress can be laid upon it, as the Doctor himself allows: it must be remembered that charcoal perfectly stripped of its adventitious air, rapidly re-attracts it, and therefore cannot be exactly weighed, and after being weighed, still continues to attract more of it: and if to this cause of inaccuracy we add the weight of the air of the vessels, and of the water absorbed, we may well account for the great excess of weight of the air obtained, over that of the charcoal.

These are all the experiments hitherto adduced to prove the decomposition of water; and we have seen that when well considered they have no such tendency, but only prove the power that steam has of decomposing both charcoal and iron, and of uniting in great plenty with the air produced from the former, and when no more water is used than is barely necessary, the air produced seems to be nothing else but charcoal itself in an aerial form, united to a quantity of water: but the follow-



following experiments shew that charcoal is composed of inflammable and fixed air.

1st. Mr. Scheele distilled caustic fixed alkali with charcoal, and obtained inflammable air, at the same time that the alkali became effervescent.

2dly. I heated about  $\frac{1}{2}$  an ounce of dry powdered charcoal to redness, in a small loosely covered crucible, which it nearly filled, for several hours; the cover had a hole, through which the air produced might issue. I found it to yield inflammable air, which burned with a blue flame during the whole time, which I tried, by firing it from time to time with a lighted paper: it is impossible to ascribe this continual flow of inflammable air to any foreign quantity of it which the charcoal might contain.

The second proof which I alleged in favour of the existence of phlogiston in metals, was deduced from the reduction of their calces to a metallic state, when heated in inflammable air, and the concomitant absorption of that air: to elude this proof, Mr. Lavoisier replied, that metallic calces, when heated, give out pure air, and that this air meeting the inflammable air, formed water. As most of these calces were heated to redness in Dr. Priestley's experiments, I allow water to have been formed by part of the inflammable air, while another part united to the calces, and therefore this experiment is not now as conclusive as it was



was when I alleged it, the composition of water being then unknown; but the experiment of Mr. Pelletier still supports the conclusion, as there is no reason to think that water can be formed by the union of inflammable and pure air in the temperature of the atmosphere.

That metallic calces are immediately united to pure air, is admitted by many, who yet are of opinion that metals contain phlogiston: yet this admission seems to me inconsistent with the latter opinion; for they allow that metals during their calcination give out phlogiston, and that they are incapable of calcination in any other than pure air; this air therefore meets the phlogiston, and must, with it, form either fixed air or water, one or both of which are absorbed by the calx, and augments its weight.

Calcination *by fire*, is performed in a low heat below redness, or in a red heat. Maficot, minium, precipitate *per se*, and rust, are formed in low heats, and consequently contain fixed air, and some water which they imbibe after calcination; but litharge, flowers of zinc, iron scales, which Dr. Priestley calls finery cinder, being formed in a red heat, absorb the water formed during their calcination, and some fixed air also: the metallic substances that absorb fixed air, will (according to the affinity of the metal to phlogiston) decompose either the whole, or the greater part  
of



of that air, when they are heated to a higher degree than that at which they absorbed it; and in an exceeding high degree of heat, as that to which calces of iron are exposed, in the focus of a burning glass, it may possibly happen that even the water they contain may be decomposed. This theory appears to me deducible from the following phenomena.

1st. Massicot, and the grey calx of lead when moistened and heated, give out no other but fixed air, as Dr. Priestley assures us. When dry, I found them rather to absorb air by undergoing a further calcination.

2dly. Minium also gives out a large portion of fixed air, about  $\frac{1}{4}$  of its whole aerial contents, as Mr. Lavoisier owns; and to this air it seems to owe its colour, which it loses the instant it is deprived of it, and regains when it recovers it, as Mr. Abich has shewn. It does not derive it from either flame or smoke; for by Mr. Abich's experiments, that which is formed without contact of either, is much redder, and more perfect, than that formed in a reverberatory furnace.\*

It has been said that minium, newly made, affords no air at all: to try this, I made some ounces of it, and in fact neither by distilling it with or without water, could any air be obtained; on the contrary, it absorbed air, and was converted into litharge and glass, and passed

\* 1 Chym. Annal. 1784, p. 400, and 407.

through



through the retort; but we must not infer from thence that it contains no air, for having mixed 120 gr. of the same minium with 18 of sulphur, I obtained 14 cubic inches of vitriolic air. The former experiment therefore proves no more, than that no air can be expelled from any substance until it has absorbed some moisture, of which we have a clear proof in the case of native aerated baroselenite, which will sooner vitrify than yield any air, though acids expel fixed air from it very readily.

3dly. Rust is well known to yield no other than fixed air, and precipitate *per se* yields some traces of it\*.

Thence if marine acid be digested with minium, or precipitate *per se*, it becomes dephlogisticated, as it takes up fixed air and parts with a portion of its own phlogiston to these calces: but if it be distilled over calces that contain chiefly water, as the calces of zinc, antimony, litharge, or iron, it does not become dephlogisticated, or only in a very slight degree†, which shews the great difference between these calces and the former.

It is impossible to suppose, that metallic calces formed in the dry way, should give out any more than a small quantity of fixed air undecomposed, if we allow that the affinity of metallic substances to phlogiston increases when they are exposed to a very strong heat;

\* 2 Pr. 217. 3 Pr. 16. and post p. † 1 Hermst. 176.



and this we have strong reason to believe, since scarce any of them is reducible by contact with phlogistic substances, but in a strong heat, and the most perfect calces of iron are in some measure revived in the focus of a powerful lens.

The only proof therefore which can be expected that calces formed in the dry way in a low heat, contain no other but fixed air, is, that the quantity of this air should be greater, when the calces can take phlogiston from some other substances, or at least have their decomposed fixed air recomposed by the phlogiston of some other substance, and of this we have some instances.

1st. Mr. Hermstadt has shewn, that the black calx of manganese gives abundance of fixed air when distilled with certain proportions of iron or zinc.\*

2d. From 1 ounce of red precipitate, and 1 of filings of iron, Dr. Priestley obtained 38 cubic inches of fixed air, of which not above 5 remained unabsorbed by water; and the result was equally conclusive when he used brass or zinc instead of iron, or turpeth mineral instead of red precipitate. † Mr. Scheele and Mr. Cavendish also obtained a considerable quantity of fixed air by this method. ‡

\* Hermstadt, 277. † 6 Pr. 253.

‡ 1 Chym. Annal. 1785, p. 154.



My success in repeating this experiment was somewhat different; from a mixture of 300 gr. of iron newly filed, and 240 of red precipitate, I obtained no air at all; on the contrary, there was a considerable absorption. Thinking that water might be necessary, I repeated this experiment, using precipitate *per se* instead of red precipitate, and varying the proportion. From 240 gr. of this and 120 of newly-made filings of iron, distilled in a very small coated glass retort, and sprinkled over with water, I got 4,5 cubic inches of fixed air, and 36 of a mixture of dephlogisticated air and inflammable air: the iron after the operation weighed 144 grains.

Mr. de la Metherie, from equal parts of filings of iron and red precipitate obtained only the air of the vessels; and from 2 ounces of red precipitate and 1 drachm of filings of iron, he obtained a small quantity of fixed air, the greater part being dephlogisticated.\* I believe much to depend on the size of the retort and the purity of the filings: when the retort is large, there is air enough to calcine the filings to some degree before the precipitate is decomposed; if small, the fixed air unites to the iron in proportion as it is formed. In my last experiment it appears that water unites to iron more readily than fixed air does, and that mercury decomposes its own air more

\* 27 Roz. 146.



readily than it takes up inflammable air, as being more intimately united to it, and as it is already condensed.

240 gr. of *lead*, and 240 of red precipitate, afforded me no air; the lead was calcined for the most part.

400 gr. of *tin*, and 460 of red precipitate, inflamed in the retort and burst it.

240 gr. of *bismuth*, and the same quantity of red precipitate, distilled with a very low heat, afforded only five cubic inches of air, of which two were fixed air. The same mixture distilled with a rapid heat, afforded 19 cubic inches of air, of which one was fixed air, the remainder somewhat better than common air: the bismuth was converted into litharge.

240 gr. of *zinc*, and the same weight of red precipitate, being treated in the same manner, the zinc sublimed, stopped the neck of the retort, inflamed and broke it. The same mixture, in a larger retort, and slower heat, produced no air. 60 gr. of the residuum, mixed with 240 of red precipitate, inflamed and burst the retort.

200 gr. of copper, and 240 of red precipitate, gave no air, though the mercury distilled over.

Hence it appears, that in some cases, particularly when water is used, a quantity of fixed air passes undecomposed, but that in general mercury decomposes its own fixed air, and the



dephlogisticated air produced, unites to the nascent inflammable air of the metals with which it comes in contact, and is absorbed by them.

Calces formed in the moist way by water, or amalgamation, afford much clearer proofs of the principles of fixed air, and that this air or water are the only substances that metals take up in calcination.

On the 22d of June, 1785, I put 3 ounces of filings of *lead*, and  $\frac{1}{2}$  an ounce of distilled water, into a glass bottle, whose capacity was 433 cubic inches, and closed it with a glass stopper; in a few days the surface of the lead became white. I agitated it from time to time; after a few weeks, I with much difficulty opened the bottle to let in more air, and on the 5th of September I withdrew the contents, of which the greater part was calcined, and separating this part from the rest, by the help of a large quantity of distilled water, I evaporated it to the consistence and colour of starch, but somewhat bluer, and then distilling 472 gr. of it, obtained 24 cubic inches of fixed air, with scarce any residuum: what remained in the retort was converted into litharge.

A quantity of filings of *iron*, treated in the same manner, afforded no air at all.— From *zinc* calcined in this manner, I obtained some fixed air, but by accident the greater part of it was lost.

N. B The



N. B. The water in which zinc had been calcined, became sapid, and with aerated fixed alkali, afforded a precipitate; but Prussian alkali produced no change in it.

Again, having made an amalgama of some pounds of mercury, and 300 gr. of zinc, by shaking them in a large bottle with some distilled water, and leaving  $\frac{1}{4}$  of the bottle empty, I separated 857 gr. of a whitish-grey calx, and by distillation procured from it 15 cubic inches of fixed air. When this ceased to be produced, and an absorption began to take place, I admitted more common air, but after some time the zinc inflamed, which shews that some part of it remained uncalcined.

From a black powder, obtained from a similar treatment of 480 gr. of lead filings, and some pounds of mercury, I obtained 8 cubic inches of fixed air, and 6 of air somewhat better than common air. The lead in the retort was partly in the state of massicot, partly minium, and the greater part litharge. Dr. Priestley, who first made this experiment, repeated it several times with the most scrupulous attention, and constantly obtained a large portion of fixed air, and at the end some dephlogisticated air.\*

These experiments induce me to believe, not only that fixed air is formed during the calcination of metals, and absorbed by them,

\* 6 Pr. 256.



but also that its constituent principles are dephlogisticated air and phlogiston. As an analytical confirmation of this opinion, I shall mention the two following experiments.

1st. Mr. Hermstadt having exhausted a quantity of manganese of all its pure air, by a strong and long-continued heat, he placed it in an earthen tube, and heating this tube to redness, he passed through it 150 cubic inches of fixed air 8 times, at last it became so pure, that it admitted a candle to burn in it, and many white spots appeared in the manganese.\*

2dly. Mr. Monge having taken the electric spark in fixed air, found, 1st. That the air by this operation increased in bulk  $\frac{1}{4}$ , and its volume continued to increase even after the electric spark ceased to be taken in it. 2dly. That the iron conductor was calcined; but this circumstance need not be considered, as the principal effect was the same when a conductor of platina, which could not be calcined, was used. 3dly. That on exposing the air after the operation, to caustic fixed alkali, 3 parts out of 5 were absorbed, but the residuum was inflammable air.† This experiment he explains thus: 1st. All fixed air contains water, and this water increases its bulk. 2dly. The mercury being heated by the electric spark, decomposes the water and sets loose the inflam-

\* 1 Hermst, 280.

† 29 Roz. 277.



mable air. 3dly. The fixed air dissolves a portion of mercury and water, but when the operation is over, it deposits it and dissolves more mercury, and the mercury thus dissolved increases its bulk. This explanation appears to me very unsatisfactory; for in the first place, if the inflammable air and increase of bulk arose from the decomposition of water by mercury, then inflammable air should equally be produced by taking the electric spark in phlogisticated or dephlogisticated airs, for these also contain water; and yet Mr. Cavendish could not produce the least alteration by taking the electric spark in them. 2dly. The dimensions of inflammable air were not altered by taking the electric spark in it, as appears by the experiments of Dr. Priestley and Mr. Van Marum;\* yet this air contains more water than any other. 3dly. There is no sort of proof that mercury is soluble in fixed air, any more than in phlogisticated, dephlogisticated or inflammable air, whose dimensions remain unaltered; and if fixed air could dissolve any, and increase in bulk, it should surely dissolve more while hot than after the operation, when it becomes cold. 4thly. If fixed air could dissolve mercury, it does not follow that the bulk of this air should be increased, but rather diminished, as Mr. Berthollet found that of inflammable air to be by dissolving plumbago. 5thly. That mer-

\* 4 Pr. 367. 27 Roz. 151.



cury should decompose water, is contrary to Mr. Lavoisier's table of affinities, according to which, the inflammable principle has a stronger affinity to the oxygenous than mercury has; and let it not be said, that this is only true in low heats, for in low heats neither of them unite to the oxygenous principle, and in very high heats the mercury rather expels than absorbs that principle. 6thly. It is highly improbable, if not incredible, that the surface of the mercury should be so heated as to incline to calcination, while the remainder of its mass is cold.

It seems therefore much more probable, that fixed air itself is decomposed in this experiment, and water formed; but as fixed air contains more phlogiston than water does, part of the phlogiston is let loose and the bulk thereby increased: the water mixing with the mercury forms the black powder, as Dr. Priestley often observed. The increase of bulk after the operation may arise from the re-union of several small bubbles of air, dispersed through the mercury during the commotion attending the electric spark.

The Antiphlogistians are of opinion, that fixed air arises from the union of dephlogisticated air with charcoal. An obvious, and in my opinion an insurmountable objection to this opinion, arises from its formation in many cases where charcoal cannot be supposed to be present; as in the calcination of metals, in  
respira-



respiration, in vegetation, &c. charcoal is no farther concerned than as it contains inflammable air.

Mr. Lavoisier placed a certain quantity of charcoal in a box, with a bit of tinder and phosphorus; this box he introduced under a jar filled with dephlogisticated air, and standing on mercury, and then fired it by means of a red-hot iron: the operation being over, he found the charcoal to have lost 17,2 gr.\* but that 67,1787 gr. of fixed air were produced, and that of the original quantity of dephlogisticated air, namely, 95,745 gr. only 34,075 gr. remained: but on comparing the weight of the charcoal consumed, and that of the original quantity of dephlogisticated air, with that of the fixed air produced, and that of the unconsumed dephlogisticated air, he found a difference of about 11 gr. which he ascribes to the formation of water, from the union of some aqueous inflammable air remaining in the coal, with part of the dephlogisticated air.†

This experiment proves no more than that fixed air is formed of the union of dephlogisticated air with one of the constituent parts of charcoal, namely, the phlogiston or inflammable air, which I have constantly contended for, and which all chymists, who admit phlogiston, and that charcoal is a compound of

\* French weight and measures are here given.

† Mem. Par. 1781, p. 448.



phlogiston and fixed air, must all allow; for here the weight of the fixed air produced, is more than triple that of the charcoal employed.

That fixed air is formed, not by the union of dephlogisticated air with charcoal in the aggregate, but with the inflammable air it contains, appears from the experiments of Dr. Priestley; for having driven the steam of water through charcoal in a red hot earthen tube, he obtained a large quantity of inflammable air, together with some uncombined fixed air, as already mentioned: but after separating this fixed air, taking the electric spark in a mixture of this inflammable, with an equal bulk of dephlogisticated air, he produced a bulk of fixed air superior in weight to the inflammable air employed;\* so that here, either fixed air is formed, or fixed air is pre-contained in this inflammable air and set loose, while the real inflammable part is converted into water, and causes the increase of weight, which I am inclined to think is what really happens, and confirms the opinion I advanced in p. 106; but if this fixed air pre-exists, then charcoal contains fixed air, whose weight may be increased to the double by the mere production of water, which destroys Mr. Lavoisier's inferences.

The antiphlogistians explain the reduction



1850

1850

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## S E C T. X.

*Of the Dissolution of Metals.*

**T**HE general opinion of chymists, since the beginning of this century, has always been, that the solution of metals proceeds from their affinity to the menstruums that dissolve them; yet, as they have also a strong affinity to phlogiston, and must be deprived of part of it before they can be dissolved, I found it necessary to explain this matter more circumstantially in a paper contained in the Philosophical Transactions of the year 1784; but being at that time unacquainted with the constitution of the mineral acids (a more intimate acquaintance with which I acknowledge to have derived from attention to the writings of Mr. Lavoisier, and Berthollet), I neglected mentioning, that the nitrous acid is always partially decomposed in the act of dissolving metals; that its fixed air and part of the undecomposed acid unites to the metal, while another part of the decomposed acid, namely, its basis, uniting with the phlogiston of the metal, forms nitrous air, part of which flies off and part is retained: the vitriolic acid, on the contrary, is sometimes partially decom-



decomposed, and sometimes not, according to its proportion of water. If it be concentrated and heated, its fixed air, and part of its undecomposed acid, will unite to the metallic body, while its basis will unite to the phlogiston of the metal, and form sulphur; or it will only be partially decomposed, its basis retaining part of its fixed air, and partly uniting to the phlogiston of the metal, and thus forming vitriolic air, which generally holds sulphur in solution, part of this air will escape and part will be retained. But if the vitriolic acid be dilute, it will not unite to the phlogiston, nor consequently be decomposed, but will expel the phlogiston in the form of inflammable air, and unite to the metal. The arsenical and phosphoric acids are also capable of phlogistication, but not the marine acid, nor the vegetable acids, as far as I can recollect.

The antiphlogistians think that metals are soluble in acids, merely by their affinity to the oxygenous principle,\* with which, during solution, they become saturated: consequently all acids are decomposed in dissolving metals, or at least promote the decomposition of water, a supposition which I have already shewn to be destitute of foundation.

If metals become soluble by saturation with the oxygenous principle, I would ask,

\* Mem. Par. 1782, p. 492.



1st. Why calces, saturated with the oxygenous principle, are not soluble in water, nor even in vitriolic acid?

2dly. Why the calces of iron, tin, and regulus of antimony, saturated with the oxygenous principle, are insoluble in the nitrous acid, whereas, when unsaturated, they are soluble in that acid? whereas the calces of lead, silver, and mercury, when saturated are soluble in that acid. Do not these differences indicate another affinity besides that of the oxygenous principle?

3dly. Why the calces of iron are more easily dissolved by the marine than by the nitrous acid even when unsaturated?

4thly. Why most calces are more easily solved by the vegetable acids, than their respective metals?

5thly. Why a solution of iron in dilute vitriolic acid is decomposed by exposure to the air? and why an excess of acid re-dissolves the calx, or prevents its precipitation?

6thly. Why a solution of zinc in the dilute vitriolic acid is not so easily decomposed by exposure to the air?

7thly. Why a solution of iron in the marine acid is not easily decomposed by exposure to the air?

8thly. Why regulus of antimony totally decomposes the nitrous acid, while copper, which has a greater affinity to the oxygenous principle, does not decompose it totally?

9thly. How



9thly. How comes it to pass, that calces of gold are soluble in the nitrous acid, and calces of iron insoluble? Do not all these phenomena prove, that another affinity intervenes, besides that of metals, to the oxygenous principle?

10thly. Whence do copper, lead, and zinc, dissolved in caustic fixed alkali, and copper in caustic volatile alkali, derive the oxygenous principle?

11thly. Since zinc and iron are soluble in the concentrated vitriolic acid, only by the assistance of heat, and in the dilute acid, without heat, the antiphlogistians must say, that zinc and iron take away the oxygenous principle from sulphur, only by the assistance of heat, but are able to take it from the inflammable principle without the assistance of heat; yet by their own doctrine, the oxygenous principle has a far greater affinity to the inflammable principle than to sulphur. How is this consistent?

SECT.



## S E C T. XI.

*Of the Precipitation of Metals by each other.*

**T**O explain the precipitation of metals dissolved in acids, by other metals, Mr. Lavoisier thinks it sufficient that the oxygenous principle should have a greater affinity to the *precipitant* than to the *precipitated* metal; thus, in his system, copper precipitates mercury, because copper has a greater affinity to the oxygenous principle, than mercury has to that principle.\*

As to the proportion of the oxygenous principle necessary to the solution of different metals, he deduces it from the quantity of one metal necessary to the precipitation of a given quantity of another metal by this analogy: *As the quantity of the PRECIPITANT is to that of the PRECIPITATED metal, so is the quantity of the oxygenous principle necessary for the solution of the precipitated, to that necessary for the solution of the precipitant.* Thus, since 135 gr. of mercury are necessary for the precipitation of 100 gr. of silver from the nitrous acid, it is evi-

\* Mem. Par, 1782, p. 512.



dent that 135 gr. of mercury require for their solution the same quantity of the oxygenous principle as 100 gr. of silver, and therefore that the quantity necessary to dissolve 100 gr. of mercury, is to that necessary for the solution of 100 gr. of silver, as 100 to 135. Now by his own experiments, 8 gr. of the oxygenous principle are necessary to dissolve 100 gr. of mercury, therefore 10,8 are necessary for the solution of 100 gr. of silver. The proportion of the *precipitants* to the *precipitated*, he finds, in all cases, by Mr. Bergman's experiments: his general formula may be expressed thus:

Let the weight of the precipitant be P, that of the precipitated p, that of the oxygenous principle necessary for the solution of the precipitant O, and that necessary for the solution of the precipitated o; then, as P. p :: o. O.

By these means he found the absolute quantity of the oxygenous principle necessary for the solution by precipitation of 100 gr. of the different metals, to be as expressed in the second column of the annexed table, and that necessary for solution only, as in the third column.



Metals.	Oxygenous principle.	
	Gr.	For solution merely
100 gr. of Platina	81,690	
Gold	43,612	
Iron	27 } 37 }	
Copper	36,000	15,85
Cobalt	29,190	
Manganese	21,176	
Zinc	19,637	
Nikel	14,721	
Reg. of ant.	13,746	22,383
Tin	14	23,555
Reg. of ars.	{ 11,739 24,743	
Silver	10,800	
Bismuth	9,622	
Mercury	8,000	
Lead	4,470	14,190

But the phænomena of precipitation are much more complicated; I have already endeavoured to explain many of them on a former occasion, of which I shall select a few, and would wish to know how they may be explained on the principles of the new theory.

1st. A solution of gold in aqua regia is precipitable in its metallic form, by a fresh made solution of vitriol of iron; but not by a solution of vitriol of copper, or of any other metal. The antiphlogistians will probably re-  
ply,



ply, that gold, during its solution, takes up 43 parts *per cent.* of the oxygenous principle and iron, though capable of taking 37, yet when newly dissolved, takes only 27; and as it has a far greater affinity to the oxygenous principle than gold has, it takes from the solution of this latter, the difference between 27 and 37. And hence, to deprive the gold totally of the oxygenous principle, and reduce it to its metallic form, the vitriol should be in 10 or 12 times a larger quantity than the gold.

But this answer is insufficient. For, 1st. Copper by solution in acids takes up only 15,85 parts of the oxygenous principle, and yet is capable, by precipitation, of taking up 36; it has also, by Mr. Lavoisier's table, p. 23, far a greater affinity to that principle than gold has, and yet the solution of copper will not precipitate a particle of gold. 2d. Platina takes up a still larger quantity of the oxygenous principle, and as it is insoluble in the nitrous acid, it must be deemed, in the antiphlogistic doctrine, to have less affinity to that principle than nitrous air has, and consequently its affinity must be very small, and yet vitriol of iron in no quantity will precipitate an atom of it. The same reasoning applies to the solutions of other metals, which have less affinity to the oxygenous principle than iron has, and which contain a smaller quantity of it than a fresh made solution of iron can take up, none of which are



precipitated by it in a metallic form, or at all, if the affinity of the vitriolic acid does not intervene.

Again, why iron precipitates copper from the vitriolic acid, may be explained in the antiphlogistic hypothesis, since iron is said to have a greater affinity to the oxygenous principle than copper has, and also to take up more of it. But why copper, which is insoluble in the dilute vitriolic acid, should become soluble in a dilute solution of vitriol of iron exposed to the air, or in a boiling heat, seems to me difficult to conceive in the new hypothesis, for the iron should not only retain the oxygenous principle, with which it is far from being saturated, but also take up that which comes from the atmosphere. Whence then does the copper attract that necessary for its solution? or if the iron divides with the copper, why does it cease to be soluble? or if not, why does it cease to be soluble when saturated with the principle of solubility?

3d. Iron is dissolved by the concentrated vitriolic acid, only by the assistance of heat; yet if to a solution of silver or mercury in that concentrated acid, a piece of iron be inserted, the silver or mercury will immediately be precipitated in their metallic form, and the iron dissolved. This seems inexplicable in the new theory, for since iron cannot, without the assistance of heat, deprive sulphur of its oxygenous principle, how does it happen, that,  
without



without that assistance, it deprives silver or mercury of that principle, though they have a stronger attraction to it than sulphur has?

4th. Why can neither zinc, iron, or mercury precipitate tin in its metallic form, though they are said to have a stronger affinity to the oxygenous principle, and to take up more of it than tin does?

5th. Why is regulus of antimony scarcely able to precipitate mercury from the vitriolic acid, though it has a greater affinity to the oxygenous principle, and takes up more of it than mercury does? On the contrary, the nitrous salt of mercury is easily precipitated by it.

6th. Why does not iron precipitate lead in its metallic form from the nitrous acid, since lead takes so small a quantity of the oxygenous principle?

7th. Why does not iron precipitate lead from the marine acid, in any form?

These are but a few of the many difficulties in which the antiphlogistic hypothesis is involved. They are sufficient to shew that its simplicity, though seducing in some cases, becomes insufficiency in many others. I pass over many other embarrassing objections arising from the precipitation of metals by different acids, as the antiphlogistians have not even attempted to explain any phenomena of that kind.



## S E C T. XII.

*Of the Properties of Iron in its different States,  
and its Conversion into Steel.*

**I**RON ores, perfectly exhausted of their iron by fusion through charcoal in high furnaces, produce what is called *crude iron*, because it is not malleable; being cast in moulds, it is called *cast iron* or *pig iron*.

The colour and properties of crude iron differ according to the proportion of the charcoal it was melted with.

If iron ores be melted with no more charcoal than is barely necessary for their fusion, the crude iron will be *white*; but *grey*, if a larger proportion of coal be used, and if a still larger *black*. The white sort is the hardest, specifically heaviest, most brittle, and imperfectly metallized; the grey more flexible, the black the softest, but very brittle.

*Malleable, or bar iron* differs from crude iron in softness, flexibility, and malleability, and from steel, in being incapable of acquiring the same degree of hardness or elasticity by tempering: it contains less plumbago than either crude iron or steel; but when treated with acids, it  
gives



gives out more inflammable air than either of them.

*Steel* is capable of more malleability, hardness, and elasticity than malleable iron, gives out more inflammable air than crude iron, and contains less plumbago than crude, but more than malleable iron. The proportion of inflammable air by measure, in these 3 sorts of iron, were found to be different both by Mr. Bergman, and Mr. Vandermond, Berthollet, and Monge, who repeated many of Mr. Bergman's experiments,

C. Iron. Steel. Bar Iron.

According to Bergman, 100 gr. contain of inflam. air.	} 40	48	50 measures
According to the French Academicians	} 54	74	76
The absolute quantity of plumbago in 100 gr. according to Bergman.	} 2,2	0,5	0,12 gr.

Malleable iron is convertible into steel, by cementation with various substances, and particularly with charcoal, in a welding heat, and by this process it gains some weight. Hence it is plain that plumbago is a factitious substance, since it is formed in iron during cementation; but its production, and the properties of iron in its different states, are accounted for by the antiphlogistians on principles very different from those of Mr. Bergman, and will form the subject of the following discussion.



According to Mr. Bergman,\* malleable iron giving out more inflammable air than steel, must contain more phlogiston than is necessary to its metallic state; in cementation the iron attracts the fixed air of the charcoal, which, meeting with the superfluous phlogiston, combines with it, and forms plumbago, which, like charcoal, is a compound of inflammable air and fixed air, but differs from it in this; that in plumbago both airs are more condensed, at least it forms a more compact body, and is specifically heavier. Hence, 1st. Steel is heavier than the iron of which it was formed, having acquired fixed air. 2d. Steel gives out less inflammable air than the same weight of iron, as the superfluous phlogiston which it contained while iron, now enters into the composition of its plumbago, which is indecomposable by acids.

The French Academicians, on the contrary, think † that bar iron, during cementation, absorbs charcoal *in specie*, and that this charcoal saturated with iron, of which it takes  $\frac{1}{10}$  of its weight, becomes *plumbago*. Hence they derive the increase of weight in steel, and explain why it gives less inflammable air than bar iron does. They also think that the inflammable air produced by steel, is contracted in its dimensions by holding some plumbago in solution.

\* 3 Bergm. 54.

† 29 Roz. 217.



Crude iron, they say, contains a quantity of dephlogisticated air; bar iron less, and steel none: if by containing a quantity of dephlogisticated air, they meant no more than that crude iron generally contains some parts not thoroughly metallized, bar iron fewer, and steel none; it should not be denied, and certainly this is all they can prove: with regard to the condensation of inflammable air by holding plumbago (a valuable discovery made by Mr. Berthollet), I must perfectly agree to it, as I found inflammable air extracted from black crude iron, almost as heavy as common air. But with respect to the introduction of so dense a substance as charcoal into a bar of iron an inch thick, it seems to me very improbable; and that such a supposition is useless and insufficient, will, I flatter myself, appear from a review of some facts relative to iron in its 3 states.

Facts relative to crude Iron.

*Grey* crude iron, melted without any addition, in a crucible, whether open or covered, is converted into steel. 3 Bergm. 45. This fact is equally well explained in either system, the plumbago being decomposed by the unmetallized part of the crude iron, which thereby becomes metallized, and only so much of it remaining, as is necessary to the state of steel, or, according to the new theory, the charcoal being converted into fixed air by the dephlogisticated air of the unmetallized part.

If



If grey crude iron be exposed without any addition, to a cementing, that is, a strong white heat for a few days, its surface will be found covered with scales, underneath the surface it will be found *soft iron*, still deeper *steel*, and in the center *crude iron*. Rinm. § 265. 1. Here the progressive destruction of the plumbago is well marked, in proportion to the facility with which its decomposed airs can escape, and the states of the iron agree with that proportion. But the antiphlogistic hypothesis, which supposes pure air in crude iron and soft iron, cannot explain how it comes to pass, that the steel, which, in this case, lies between both, should contain none. And in fact, there is no sort of proof that soft iron always and necessarily contains unmetallized parts.

Crude iron, cemented with charcoal, becomes more brittle. Rinm. § 265, and 266. This is conformable to both systems: but so it will also if cemented with plumbago. Rinm. 265. 21. This contradicts the antiphlogistic hypothesis, for by this hypothesis the plumbago is already saturated with iron, and therefore should attract it no longer\*.

The only proof which the French Academicians give, that crude iron contains pure air,

\* Mr. Bergman, it is true, was of opinion that crude iron was not altered by cementation with plumbago. 3 Bergm. 47. But the only reason he gives is, that it had lost weight; the piece itself was lost before it could be further examined: why it had lost weight is easily accounted for, as it must have lost fixed air.



is, that having placed two pieces of crude iron in immediate contact with each other in a crucible, and surrounded them with charcoal, after a few hours exposure to heat, they increased in weight; but the surfaces in contact with each other were calcined. But this experiment proves no more, than that crude iron is not perfectly metallized, but contains some particles in a calcined state, and that the internal parts give out fixed air or water, which calcines the surfaces not in contact with the charcoal.

Facts relative to malleable Iron.

IF malleable iron be surrounded with charcoal in a covered crucible, and exposed to a welding heat for 8 or 10 hours, it will be converted into steel, as is well known; but if the experiment be made in a glass vessel hermetically sealed, this conversion will not take place in any length of time or degree of heat. *Newm.* § 267, N. 7. This is inexplicable in the antiphlogistic theory, for the charcoal should equally be absorbed, whether the vessel be hermetically closed or not. But in Mr. Bergman's it is easily explained, for the charcoal cannot be decomposed, unless the inflammable air be at liberty to assume an aerial form; just as vitriol of iron will remain in contact with an aerated alkali, without expelling the fixed air, or any union of the acid and alkali, when both are dissolved in a vessel well closed,\* and as

\* See Lewis on *Newm.* p. 272.



light will not separate pure air from nitrous acid in a vessel perfectly full and closed.

If a bar of soft iron be put into a crucible well covered and luted, without any addition, and kept in a welding heat for 11 days, it will be converted into steel, its surface covered with plumbago, and it will weigh about 1 per cent more than before. Rinm. § 73. xviii. Here it is plain the charcoal could not penetrate through the crucible, but fixed air easily can, as it is well known that crucibles in a white heat are pervious to air. The plumbago then clearly owes its origin to this air, as Mr. Bergman explains it.

Mr. Rinman also cemented bar iron with *chalk*, and after keeping them 11 days in a welding heat, he found the iron converted into steel, and covered with plumbago. It is true, he says, the effect was the same, when, instead of chalk, he used quick-lime; but it is probable the lime he used on this occasion was not well burned, for, at another time, when he used, as he expressly says, lime perfectly burned, though it had been exposed to the air half a year, so far from converting the iron into steel, it rendered it perfectly soft. When iron was cemented with chalk for 3 hours only, it had no effect upon it, as it could not give out its air in so short a time; on the contrary, the iron lost part of its weight. § 73. ix. Here also we see plumbago formed without charcoal.

Bar iron cemented with the black calx of  
man-



manganese, was not calcined as it should be, according to the antiphlogistic theory, but on the contrary, converted into steel. Rinm. § 73. xvii. The result was the same when it was cemented with flowers of zinc, and the zinc was reduced to its metallic form. Ibid. iii. Which last circumstance contradicts Mr. Lavoisier's table: plumbago appears in both cases to have been formed without charcoal.

Malleable iron cannot be melted in furnaces without addition; but if it be surrounded with charcoal, it first becomes steel, then crude iron, and at last melts: this crude iron surely contains no unmetallized parts.

#### Facts relative to Steel.

THE French Academicians say, that if crude iron be long kept in fusion in a covered crucible, it will at last be reduced to the state of malleable iron; but steel in the same circumstances will remain unaltered. Hence they infer that crude iron contains some principle which destroys the charcoal, namely, pure air, but that steel contains none.\* Yet Rinman expressly says that steel also, by long continued fusion, will become malleable iron, § 266; and in their own experiment crude iron must pass through the state of steel before it arrives at that of malleable iron.

If steel be cemented with quick-lime, it will be converted into malleable iron, because

\* 29 Roz. 217.



by the affinity of quick-lime to fixed air, the plumbago is more easily decomposed; but by cementation with calx of zinc, it is not altered, *Rinn.* § 73; because steel contains no superfluous phlogiston. According to the antiphlogistic theory, the pure air of the calces should destroy the plumbago.

Thence we see that the new theory explains no incident or property of iron which is not as well explained without it; on the contrary, Mr. Bergman's theory elucidates facts, which the new theory leaves in obscurity.

To the proofs which Mr. Scheele has given that plumbago consists of inflammable air and fixed air in a concrete state, I shall add one more resulting from Mr. Pelletier's experiments.\* If plumbago be distilled with dry caustic alkali in a pneumatic apparatus, it will yield inflammable air, and the alkali will become aerated.

\* 27 *Roz.* 352.



## S E C T. XIII.

*Conclusion.*

**T**HE patrons of the new theory agree, that metallic inflammable air, uniting to pure air in a read heat, produces water.

2dly. That spirit of wine, during its inflammation, produces both fixed air and water. Mr. Lavoisier even found that the quantity of water left after the combustion of spirit of wine was so great as to exceed the original weight of the spirit, which shews it must have contained a large quantity of phlogiston.

3dly. That oils and resins also contain inflammable air, and consequently during combustion produce both water and fixed air.

4th. That both inflammable air and pure air give out fire during their inflammation.

But sulphur, phosphorus, zinc and regulus of antimony, to mention no other, also inflame, in common air, as does iron in dephlogisticated air; therefore, according to the rule which requires that *to natural effects of the same kind, the same cause should be assigned*, we are led to conclude, that the flame in this case  
also



also proceeds from the union of inflammable air and pure air, unless it should be proved that those substances contained no inflammable air, which has not yet been done: all that the antiphlogistians say, amounts to no more, than that inflammable air is not necessary, since dephlogisticated air gives out fire enough, a reason sufficiently refuted by the inflammation of spirit of wine and oils.

Again, volatile alkalis confessedly contain inflammable air, and though they hardly detonate with melted nitre on account of their volatility, yet sal ammoniac, and particularly vitriolic ammoniac, being more fixed, readily makes nitre detonate; but substances which confessedly contain no phlogiston, or hardly any, as stones, glass, metallic calces, &c. will not make nitre detonate. Hence we are authorized to conclude that other substances which make nitre detonate, contain phlogiston, unless the contrary be shewn; now sulphur, charcoal, and most of the imperfect metals detonate with nitre, and hence we have a second reason deduced from analogy to conclude that they contain phlogiston.

Further, if nitrous ammoniac be projected into a red hot crucible, nitrous air is produced; if nitrous acid be digested with spirit of wine, nitrous air is also produced; therefore, in other cases where we see nitrous air produced, we are authorized to think that phlogiston is present; now sulphur, phosphorus, and metals  
treated



treated with nitrous acid afford also nitrous air, we have then a farther reason to conclude they contain phlogiston.

Therefore when we see inflammable air proceed from the solution of metals, or by passing the steam of water through them, or through sulphur, it is much more reasonable to infer that it proceeds from the metals and sulphur than from the decomposition of water, of which we have not a single undoubted instance.

To the proofs I have heretofore given that inflammable air and phlogiston are the same substance, just as ice and the vapour of water are called the same substance, no objection of any weight has since been made. Some have thought I should have included the matter of heat or elementary fire in the definition of inflammable air, but as fire is contained in all corporeal substances, to mention it is perfectly needless, except where bodies differ from each other in the quantity of it they contain, and in this respect I expressly mentioned its difference with phlogiston to consist. Others attending to the quantity of water contained in inflammable air, have supposed it to be an essential ingredient in the composition of this air, and have called it *phlogisticated water*; but they may as well suppose water to be an essential ingredient in common air or fixed air, and call this last *acidulated water*; for inflammable air, equally as other airs, may



be deprived of its water without any limitation, and yet preserve all its properties unaltered, which shews the presence of water to be no way essential to it. Lastly, others have thought that it essentially requires an acid or an alkali, or some saline substance for its basis, as if there were any more repugnance in the nature of things that phlogiston should exist in an aerial state without any basis, than marine air, or alkaline air, or dephlogisticated air, &c. when it is evident that an aerial state requires no more than a certain proportion of latent heat; but the production of inflammable air from iron by means of distilled water without any acid or salt, has effectually done away every suspicion of this sort.

F I N I S.



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## E R R A T A.

- Page 51, line 1, for *principle* read *principles*.  
58, — 3 from the bottom, after acid add  $\frac{2}{3}$   
67, — 8, take out the multiplication sign  $\times$ , and  
add the sign of addition  $+$   
88, — 7, read 10 *different degrees*.  
95, — 2 from bottom, dele *and*; add after metal a  
comma.  
116, — 20, dele the comma.  
131, — 19, read solution of *vitriol of copper*.  
137, — 1, *of* to be joined.



TABLE

1. The first part of the work	1
2. The second part of the work	10
3. The third part of the work	20
4. The fourth part of the work	30
5. The fifth part of the work	40
6. The sixth part of the work	50
7. The seventh part of the work	60
8. The eighth part of the work	70
9. The ninth part of the work	80
10. The tenth part of the work	90







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