AN ESSAY ON PHLOGISTON, AND THE CONSTITUTION OF ACIDS.

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INTRODUCTION.

THOUGH 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 alchymiſts, 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 pre-

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,

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*

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.

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.

phlo-

phlogiſticated acids, vegetable acids, fixed air, ſulphur, phoſphorus, ſugar, 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

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 ſcientifical 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 oftenеſt in explaining the phænomena, is more arbitrary in its application, and leſs countenanced by the general rules of philoſophic reaſoning; that

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

SECTION

SECTION I.

OF THE

WEIGHT

OF

DIFFERENT SORTS OF AIR.

AS 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 $\frac{1}{10}$ of an inch of mercury,

cury, whoſe ſpecific gravity was 13,6, at different barometrical heights, and in different temperatures; the weight of $\frac{1}{10}$ 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° 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 $\frac{3}{100}$ 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 ſaucer 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°, 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°, 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 8½ 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

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,

SECT.

SECT. 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 -	Dephlogiſticated 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 $\frac{1}{50}$ 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 Tranſ. 1784, p, 134.

not

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 Tranſ. 1784, p. 335.
‡ Philoſophical Tranſ. 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.

SECT.

SECT. 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: 1½ 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 6½ 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 16½ cubic inches thus produced, I found 14 to be vitriolic air, being abſorbed by the ſolution of marine baroſelenite; one continued unabſorbed 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

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

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 024 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. † 6 Pr. 150.
‡ Mem. Par. 1783, p. 736.

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. and Cornette Mem. Par. 1779, p. 484. † Chaptal. p. ‖ 4 Pr. p. 26.

SECT.

SECT IV.

Of the Nitrous Acid.

THE 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 79½ pure air, and 20½ 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

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 nitrous

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

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.

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.

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

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 ſundry 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. Laſſone 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.

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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

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

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

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, 46½; by mine 63; the mean of all which is 53½, 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 Sçav. Etrang. 627. † For of the dephlogiſticated acid, as it becomes phlogiſticated in uniting to the alkali, leſs is required. ‡ 11 Mem. Sçav. 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
		Cauſtic alkali - -		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 phlogiſticated 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 phlogiſticated air; the remainder 181,1 gr. are dephlogiſticated 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 $\frac{1}{5}$ 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 phlogiſticated air -	59,8
Dephlogiſticated 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 $\frac{1}{5}$ of its weight of water = 55	
Total weight of fixed air	329,62
Weight of phlogiſticated 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 $\frac{1}{5}$ of its weight of phlogiſticated 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. $\frac{2}{3}$ of the nitrous acid in nitre is nitrous baſis. Now the $\frac{2}{3}$ 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 unſa-

* 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 unſaturated 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

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. Tranſ. 1784, p. 339. † Mem. Par. 1782, p. 495. ‡ 2 Pr. 126, &c.

air,

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.

198,92
— 150,09

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 + 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.

it,

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 phlogiſ. air, and pure air, from the decompoſition of part of it	7,33 / 97,83	97,83 dephlogiſ. 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 expence 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

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.

SECT.

SECT. V.

Of the Marine Acid.

COMMON 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

ments of this excellent chymiſt, in ſo much that, I muſt own, they alone ſeem to me to afford any plauſible ground for that hypotheſis.

According to the antiphlogiſtians, then, the common marine acid conſiſts of a peculiar baſis united to a ſmall proportion of pure air, or oxygenous principle, and the dephlogiſticated marine acid differs from it, only by containing an exceſs of this principle.

If the common marine acid be diſtilled over the black calx of manganeſe, or minium, it becomes dephlogiſticated, as the immortal Scheele has firſt diſcovered; but then it unites to a conſiderable proportion of the air contained in thoſe calces, as appears by the experiments of Meſſrs. Berthollet and Pelletier.* According to Mr. Lavoiſier's table, the baſis of the marine acid has a ſtronger affinity to the oxygenous principle than any metallic calx, or the baſis of any acid, has to that principle; why then does it not become dephlogiſticated by diſtillation over the calces of iron or over the vitriolic acid? and why does it not convert this acid into ſulphur? is it not becauſe theſe ſubſtances cannot dephlogiſticate it?

The dephlogiſticated marine acid unites to water almoſt as difficultly 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

* 26 Roz. 322, and 389.

aerated

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. 1 Hermſt. Phyſ. Chym. Verſuche, p. 277.
† 6 Pr. 354. 1 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

For greater certainty I again mixed equal quantities of both airs, and after more than ½ 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. 1 Encyclop. p. 254.

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

‡ 29 Roz. 82.

SECT. VI.

Of Aqua Regia.

IF 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

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 phænomena 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.

SECT.

SECT. VII.

Of the Phoſphoric Acid.

FROM 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 preexiſt 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

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.

SECT. VIII.

Of the Saccharine Acid.

VEGETABLE 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 baſis.
Liquor and ſalt in the retort		1316	
Weight gained by the intermediate bottle		599	
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, 1ſt. 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 $\frac{2}{7}$ of the quantity of ſugar employed;† Mr. Sage only $\frac{10}{16}$:‡ 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.

SECT.

SECT. IX.

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

TO 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,

cination, 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. Tranſ. 1782. p. 195.

added

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 ſynonimous. "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, developes 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°, 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 $\frac{1}{4}$ 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

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. Sauſſare'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.

com-

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

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, $\frac{1}{5}$ 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 ½ 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. Maſſicot, 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 phænomena.

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

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 flower 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 ½ 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 $\frac{1}{24}$, 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.

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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 that 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.

ph-

phlogiſton and fixed air, muſt alſo 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

* 6 Pr. 97. 172.

of

of metallic calces with charcoal, by aſſuming that the charcoal does nothing more than attract the oxygenous principle from them by its ſuperior affinity; yet the acid of ſugar, which they allow to contain the inflammable principle, and contains no charcoal, and is even irreducible to charcoal, will alſo, I doubt not, reduce metallic calces, in a ſtrong heat.

To the arguments already adduced to prove that metallic calces are reduced by union with inflammable air, I ſhall add one more that appears to me unanſwerable. If to a ſolution of mercury in the Pruſſian acid, ſome filings of iron be added, and a ſmall quantity of vitriolic acid, this acid will immediately diſengage inflammable air from the iron, and this air uniting to the mercurial calx, will expel the Pruſſian acid and revive the mercury, as Mr. Scheele has diſcovered.* This experiment I repeated. Now let it be conſidered, that the Pruſſian acid does not contain dephlogiſticated air, but is a compound of fixed air, inflammable air, and volatile alkali, intimately combined together, and ſuffers no decompoſition or alteration by being expelled from the mercury, therefore the inflammable air does not affect it, but barely expels it by its ſuperior affinity to the mercurial calx, which at the ſame time it reduces.

* Scheele, p. 162, French tranſlation.

SECT.

SECT. X.

Of the Diſſolution of Metals.

THE 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

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 phænomena 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.

SECT. XI.

Of the Precipitation of Metals by each other.

TO 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

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, 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 an 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, withou

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 phænomena of that kind.

SECT. XII.

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

IRON 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

Crude iron, they ſay, contains a quantity of[f] 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,

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. Rinm. § 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 1 Newm. p. 272.

light

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

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, Rinm. § 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.

SECT.

SECT. XIII.

Concluſion.

THE 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 further 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.

FINIS.

ERRATA.

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.