Higgins

Comparative

View

of

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A
COMPARATIVE VIEW
OF THE
PHLOGISTIC AND ANTIPHLOGISTIC
THEORIES.

WITH INDUCTIONS.

A

COMPARATIVE VIEW

OF THE

PHLOGISTIC AND ANTIPHLOGISTIC

THEORIES.

WITH INDUCTIONS.

TO WHICH IS ANNEXED,

AN

ANALYSIS OF THE HUMAN CALCULUS,

WITH OBSERVATIONS ON ITS ORIGIN, &c.

BY WILLIAM HIGGINS,

OF PEMBROKE COLLEGE, OXFORD.

EST QUODAM PRODIRE TENUS, SI NON DATUR ULTRA.

HOR.

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CONTENTS.

INTRODUCTION.

ON comparing the preſent ſtate of chemical knowledge with that which prevailed twelve years ſince, I truſt that every true friend of philoſophy will join me in contemplating with pleaſure the rapid improvements which, even during that ſhort period, have been made in this noble ſcience. And, provided the preſent ardent ſpirit of inquiry continues to diffuſe itſelf, it muſt ſhortly ripen chemiſtry into ſuch perfection, as will contribute more to the

 welfare

welfare and happineſs of mankind in general, than can at preſent be imagined.

He who firſt made glaſs, or extracted a metal from its ore, knew not the value of his diſcovery; nor did he foreſee the benefits that would ariſe to mankind from it. So many chemical facts lately diſcovered, though ſeemingly of ſmall importance, may, hereafter, prove of the greateſt utility. For inſtance, the diſcoveries of the phoſphoric acid in bones, and of the conſtituent principles of volatile alkali, ſeem as yet of no great conſequence; but I venture to predict, that when phyſic is reſcued from its preſent obſcurity, theſe will be equal to any that have hitherto been made. The utility of many facts may depend upon the diſcovery of a ſingle one, which may throw light upon, and connect the whole. Hence, we find the neceſſity of well underſtanding and arranging ſuch facts as we have in our poſſeſſion, and likewiſe of increaſing their number as much as poſſible; but in order to do this with facility and pleaſure, and alſo to profit by them, it is neceſſary that we become perfectly acquainted with the true theory of chemiſtry, for falſe hypotheſes can only tend to confuſe and lead us further aſtray from the paths of truth, which alone ought to be the object and purſuit of true philoſophy.

Nature has but one way of performing her different operations, therefore we may juſtly ſuppoſe that there is but one true mode of accounting for them, and conſequently either the phlogiſtic or antiphlogiſtic theory muſt be falſe.

Des Cartes's vortical fluid appeared very plauſible, and was generally received, until the immortal Newton, by his profound reaſoning, pointed out its inconſiſtency. Des Cartes grounded his hypotheſis upon one phenomenon; the motion of the different planets from weſt to eaſt. In like manner, Becher and Stahl founded their doctrine upon the phenomenon of combuſtion only.

Conſidering the knowledge they had in their days of the conſtituent principles of bodies, their hypotheſis was very ingenious, although, in my opinion, as ill founded as that of Des Cartes. Speculative reaſoning muſt ever fall to the ground when put to the teſt of experiment; ſuch has been the fate of the Carteſian philoſophy.

Although Lavoiſier has not been as yet ſo ſucceſsful as the great opponent of Des Cartes, yet he and his cotemporaries ſeem to promiſe, by their exertions, as ſure and as laſting a theory as the Newtonian: even this has been oppoſed: why then ſhould we be ſurpriſed that the antiphlogiſtic doctrine

ſhould

ſhould meet with its opponents alſo? Notions early imbibed will not be readily exchanged for new ones; the ſlow but ſure hand of time alone can diſpel thoſe clouds which never fail to eclipſe truth at her early appearance.

The preſent controverſy amongſt philoſophers depends upon the following queſtions: 1ſt, Whether water be or be not compoſed of dephlogiſticated and light inflammable air? 2dly, Whether or no the condenſation of dephlogiſticated air, or its union to different bodies, does not depend upon one principle, common to all combuſtible bodies? Or, in other words, whether or no all bodies which burn or calcine, ſuch as ſulphur, phoſphorus, charcoal, oils, metals, phlogiſticated air, &c. contain the matter of light inflammable air as one of their conſtituent principles? One ſhould ſuppoſe if theſe ſubſtances were compoſed of two principles, namely, a peculiar baſis, and the matter of light inflammable air or phlogiſton, that it would be poſſible to reſolve them into theſe principles, more eſpecially when we conſider the great attraction of the matter of light inflammable air to fire; but the maintainers of phlogiſton have not as yet been able to do this: therefore the only ground they have to build their hypotheſis upon is, that theſe bodies unite to dephlogiſticated air; then, according to their philoſophy, dephlogiſticated air has the property of uniting but to one ſubſtance in nature, except fire. If the above ſubſtances were ſimples, or even compounds, but deſtitute of the matter of light inflammable air, or phlogiſton, the antiphlogiſtians cannot do any more than they have done already; for if ſulphur were reſolved into its conſtituent principles, and if theſe were

two

two airs, or more condenſed bodies, different from any other with which we are at preſent acquainted, the phlogiſtians might ſtill ſay that they contained phlogiſton (or the matter of light inflammable air), if they even were the moſt ſimple bodies in nature, provided they had the property of uniting to dephlogiſticated air. Then the antiphlogiſtians, in order to eſtabliſh their doctrine, it ſeems, muſt prove the non-exiſtence of that ſubſtance in bodies, whoſe preſence as one of their conſtituent principles has never yet been proved. On this difficulty the phlogiſtic theory ſeems to reſt.

Hence it appears that this doctrine, which has been generally received throughout Europe, almoſt the laſt half century, ſtill ſtands in need of being ſubſtantiated; and alſo that the joint efforts of the firſt philoſophers of the preſent age cannot fix their favourite doctrine upon a more

firm

firm basis than the celebrated Stahl had done in his obscure days.

Thus seeing upon what principles the phlogistians and antiphlogistians maintained their different doctrines, and the impossibility of persuading us by experiments alone, from what only exists in our imagination, so prone we are to reconcile every phenomenon we see to our manner of thinking, I was obliged to have recourse to a mode of reasoning rather novel in chemistry. I have considered phlogiston as a substance chemically united to bodies in a solid state, and then inquired into the nature of such compounds, and whether the different phenomena in chemistry were consistently explicable on such principles. Again, I have endeavoured to find whether the same phenomena were as explicable by supposing the different bodies which unite to dephlogisticated air to attract it, independent of a common principle or phlogiston; by which means I have been enabled to make a fair comparifon, and to draw, according to my judgment, juft conclufions. If I have appeared more inclined one way than another, it is what the evidence of my fenfes and the love of truth compelled me to. I have not altogether depended upon the affertion of other philofophers, for I have frequently repeated almoft the whole of the different experiments quoted in the following fections; otherwife I fhould not prefume to offer my opinion to the public, knowing how differently we often judge of what is ever fo well defcribed to us, when we fee it. In treating of the acids, I was obliged to have frequent recourfe to the metals; for, in the prefent knowledge of chemiftry, it is impoffible to inquire into the nature and conftitution of the one, without the affiftance of the other. I have alfo been obliged to introduce feveral diagrams, in order to render what I meant to convey

the

the more intelligible; and indeed I thought it the fureft mode of reafoning, and the moft effectual means to come at truth *.

I hope it will appear, that I have not taken pains to felect facts in order to caft the fcale in favour of the antiphlogiftic doctrine; for, as truth was my object, I confidered all facts equally efficacious in bringing her to light; therefore I made ufe of fuch as firft occurred to me, and I thought were confiftent with, and applicable to, the fubject; in fhort, I preferred thofe that have been adduced in favour of the phlogiftic theory; particularly fuch as have been advanced by Mr. Kirwan, in his Effay on Phlogifton, a work which I have frequently alluded to, as being intended to fubvert the antiphlogiftic doctrine.

* The diagrams, placed at the margin, are very frequently to be read at the end of the firft fhort line, as part of the fentence, otherwife the fenfe will appear very obfcure.

Although

Although I adopted the antiphlogiſtic theory four years ago, and although every phenomenon which occurred to me ſince, tended to confirm the truth of that doctrine; yet, when I conſidered the number of able philoſophers, namely, Cavendiſh *, Prieſtley, Kirwan, Black, Higgins, &c. who perſiſted in the old doctrine, I began to waver in my principles, and my deſire to minutely inquire into both doctrines daily increaſed; but knowing how inadequate I was to ſo arduous a taſk, and likewiſe how many there were who might have performed it ſo much better than myſelf, it was ſome time before I could ſummon reſolution enough to begin; but my attachment to the ſcience at length overcame every other conſideration.

If my efforts ſhould, in this enlightened age, be too feeble to do much good, I

* I thought Mr. Cavendiſh had lately adopted the antiphlogiſtic theory, until a good part of this volume had been printed, as appears in the firſt ſection, page the 4th.

hope

hope at leaſt that they will not be productive of evil. I have written with conviction and without prejudice (otherwiſe it would be natural to ſuppoſe, that I would join my countrymen in defence of that doctrine in which I have had my early inſtructions in chemiſtry *).

If I ſhould be ſo unfortunate as to reaſon upon wrong principles, the ſooner I am contradicted the better pleaſed I ſhall be; but if my arguments and inductions be juſt, if I even ſhould meet with cenſure, it cannot laſt long; time, the parent of truth, will operate in my favour.

I fear I ſtand in need of much indulgence in both the ſtyle, and in the many overſights reſpecting the correction of the preſs, a taſk with which I have been totally unacquainted until the printing of theſe ſheets commenced; and indeed I had an occaſion to abſent myſelf part of

* I am indebted to Dr. Higgins for my firſt inſtructions in chemiſtry, who is a phlogiſtian.

the time, and the perſon who officiated for me was wholly ignorant of the ſubject, and equally as ignorant as myſelf with reſpect to the buſineſs of the preſs.

I have annexed an Analyſis of the Human Calculus, which I hope will be acceptable as well to my medical as chemical readers. I was the more induced to publiſh it, as being delivered in to the Royal Society in the year 1787, and read at one of their ſpring meetings in the year 1788.

I have given an exact and true detail of the manner in which I have treated it; in order to give thoſe who were better acquainted with chemiſtry than myſelf an opportunity of pointing out my errors, and to facilitate the labours of leſs experienced chemiſts, who may wiſh to proſecute the ſame ſubject; for, without mutual information, chemiſtry, as well as all other ſciences, could never make any great progreſs.

As

As I have made my calculations according to Mr. Kirwan's table, being, in my opinion, the moſt accurate of any that has as yet appeared, I thought proper to inſert it here, knowing that ſome of my readers will often have an occaſion to refer to it; I have alſo added the heavy inflammable air, as I conſider it a ſubſtance quite different from the light inflammable air.

Mr. Kirwan's 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	985
Nitrous,	37	1194
Vitriolic,	70, 215	2265
Fixed,	46, 5	1500
Hepatic,	34, 286	1106
Alkaline,	18, 16	600
Light Inflammable,	2, 613	84, 3,
Heavy inflammable,	34	1103

COMPARATIVE VIEW, &c.

SECTION I.

Of the Composition and Decomposition of Water.

ALTHOUGH Mr. Lavoisier had shewn the Decomposition of Water, in the year 1781, by a variety of ingenious and accurate experiments, as will appear in the sequel of this work; yet, his hypothesis was not received by any other philosopher; nor was he convinced himself, until the year 1784, when Mr. Cavendish removed all doubts, by uniting light inflammable air and dephlogisticated air, and shewing that the resulting compound was water.

Thus having proved by synthesis what the former philosopher suspected from analysis, the doctrine of Water was universally embraced by all the philosophers in Europe.

It undoubtedly is one of the most interesting discoveries that ever was made in Chemistry. 1. It enables us to account for several very important phenomena, which appeared before very mysterious. 2. It throws light upon vegetation, and the means whereby nature supplies the constant waste of our atmosphere. Lastly, It has thrown great light on the different stages of fermentation, which was not in the least understood before.

Some philosophers have lately suspected that water has never been either composed or decomposed in any of our processes. Mr. Kirwan supposes that water is formed by the union of inflammable air and dephlogisticated air only, when one or both are exposed to a red heat; but that in a lower heat they form fixable air *. Mr. Lavoisier is of opinion, that one hundred parts of water contain eighty-seven of dephlogisticated air, and thirteen of light inflammable air, which is nearly seven to one.

According to Dr. Priestley's estimation of the weight of both airs, it is but five to one.

* Essay on Phlogiston, p. 26.

However, from the variety of circumſtances that may change the real ſpecific gravity of theſe airs, I think we ſhall be nearer to truth if we ſay ſix to one, provided the airs be very pure. Two to one by meaſure appear to be the exact proportion.

Dr. Prieſtley ſuppoſes that the water produced by the condenſation of inflammable air and dephlogiſticated air, is only what was ſuſpended and attached to them in their elaſtic ſtate, and that their reſpective gravitating particles form a different compound, namely, Nitrous Acid. To aſcertain this, he confined his mixture of airs with dry fixed alkali over mercury, in order to abſtract from it as much water as poſſible.

Having thus prepared his mixture of airs, he found, after exploding them, that the product of water fell far ſhort of the weight of both airs; and he obſerved a denſe vapour after every exploſion, which ſoon condenſed, and adhered in a ſolid ſtate to the ſides of the veſſel, which he afterwards found to be the Nitrous Acid*. Though I do not doubt this indefatigable philoſopher's facts, yet, I beg leave to differ from him in his concluſions. I think the facts he adduces are not

* Phil. Tranſ. 1788.

only inſufficient to ground his hypotheſis upon, but do not in the leaſt tend to contradict Mr. Cavendiſh's doctrine of Water and Nitrous Acid. Let us ſuppoſe four ounce meaſures of the mixed airs to produce, by inflammation, in their ordinary ſtate one grain of water, and the ſame bulk of air, by expoſure to lime or alkali, to be deprived of half a grain, and that, after condenſation, the quantity of water produced not to exceed half a grain; are we to conclude from thence that water had not been formed? Beſides, we are to conſider that the ſpecific gravity of air is altered in proportion to the quantity of water abſtracted from it. Therefore, an accurate weight of both airs ſhould be aſcertained after they are deprived of their water, before we conclude that the weight of the water produced falls ſo much ſhort of the weight of the airs employed.

That nitrous acid is often formed I have frequently experienced; but that it ſeparates from the moiſture produced, and, in a ſolid ſtate, is what I could never obſerve nor ſuſpect, conſidering the attraction of nitrous acid for water. I frequently inflamed ſeveral cubic inches of light inflammable and dephlogiſticated air, and never obſerved, by the niceſt teſt, the preſence of an acid, when the airs

worked

worked upon were pure, and when the inflammable air prevailed. But when I reversed the proportion, I always obtained nitrous acid in a single charge. When the dephlogisticated contained one-eighth phlogisticated air, I obtained nitrous acid in great abundance. Hence I infer, if we could procure dephlogisticated air entirely free from phlogisticated, that not a particle of any sort of acid would be produced. If nitrous acid should result from an union of light inflammable and dephlogisticated air, why is not this formed during the slow combustion of a stream of inflammable air in dephlogisticated air? I condensed, as shall be hereafter described, half a gallon of dephlogisticated air by the continual flame of light inflammable air, and I could not detect the smallest vestige of any sort of acid. Then, I ask, what becomes of the airs? they must form some compound; for, from the quantity of fire disengaged, it is evident that a chemical union takes place. The difference in result between this process and that in which we use the electric spark may be easily accounted for. The intense heat produced in the latter process by the general and instantaneous inflammation of both airs, together with that of the electric spark, promotes an union between a portion of the dephlogisticated air and the phlogistic, which is always present in the purest respirable air. Whereas the languid combustion in the former experiment is insufficient to cause such an union. Why is not nitrous acid formed during the combustion of ether or strong spirit of wine, when the quantity of fixable air formed could never employ the whole of the dephlogisticated air expended, as evidently appears by the formation of fixable air by the electric spark? These circumstances, in addition to the many instances we have of the decomposition of water by calcination, fermentation, and vegetation, are sufficient to remove all my doubts respecting its constituent principles. That all elastic fluids hold a considerable quantity of water in solution, is well known to every body; but we are not to infer from thence, that water is a necessary ingredient in them, and that it is chemically united to the real gravitating matter of the different airs, particularly when we can extract the most part of it from them. Therefore, I do not see why we should say with Dr. Priestley, that inflammable air consists of inflammable air and water. We may as well say, that silicious earth (as water is separable from it) is silicious earth and water, or that sulphur is sul-

phur

phur and water, and ſo with all other known ſubſtances.

If the greater part of dephlogiſticated air be water, and if iron be calcined in conſequence of its union to water, as Dr. Prieſtley ſuppoſes, I would aſk, Why is not inflammable air produced during the calcination of iron in dephlogiſticated air, as well as when calcined by the ſteam of water? For the Doctor ſays, "But from the preceding experiments it appears, that by far the greateſt part of the weight of dephlogiſticated air is water; and the ſmall quantity of acid that is in it may well be ſuppoſed to be employed in forming the fixed air, which is always found in the proceſs of calcination." By this it is evident, that the Doctor does not allow the entry of dephlogiſticated air into the calces of iron; and, according to himſelf, there was only the thirteenth of an ounce meaſure found in the reſiduum of ſeven ounce meaſures of dephlogiſticated air abſorbed by iron*. Now ſeven ounce meaſures of dephlogiſticated air are ſufficient to form five, or at leaſt four and a half ounce meaſures of fixable air. Therefore, I would aſk, what becomes of this dephlogiſticated air, or why was not nitrous acid formed?

* Vol. vi. p. 120.

SECTION II.

Of the Composition of Acids.

IT is to Mr. Lavoisier that we are chiefly indebted for our present knowledge of the constituent principles of the different acids; though it is true Dr. Priestley made the first advances towards it. It was by means chiefly of these substances that theoretical chemistry has made so rapid a progress these last ten years: so that we may very well say they have been the keys of philosophical chemistry. Mr. Lavoisier has shewn that dephlogisticated air is one of the constituent principles of all acids, and therefore called it the oxygenous principle, or the principle of acidity.

But yet we find that it is capable of uniting to bodies without possessing this character. Hence it appears doubtful to which of the principles we are to attribute this singular property. The different acid bases are sulphur, phlogisticated air, phosphorus, the matter of charcoal, regulus of arsenic, and the unknown basis of marine acid. Various are the opinions of the phlogistians respecting the nature of the union of dephlogisticated air to the above bafes, though they all agree that they contain phlogifton. Some of thefe gentlemen fuppofe that the different bafes are faturated with phlogifton, which uniting to dephlogifticated air, forms water, at the fame time that another portion of dephlogifticated air combines with the bafis, and conftitutes the acid. Others fuppofe that thefe bafes contain all the principles of their refpective acids faturated, or as if it were enveloped by phlogifton; and that the air only feparates this phlogifton by its fuperior attraction, whereby the occult acid is liberated.

Mr. Kirwan fuppofes that the dephlogifticated air unites to phlogifton, and forms fixable air, which, by combining with the bafis, conftitutes the acid. Thus he thinks that fixable air is the principle of acidity, and enters into the conftitution of all acids. I fhall endeavour to point out, in the following pages, the neceffity of this laft philofopher's doctrine towards the fupport of the phlogiftic theory, and likewife his grounds for adopting fuch an hypothefis. Undoubtedly the doctrine of fixable air will enable phlogifton to ftand its ground much longer than it otherwife would; for, it may be adopted where the other phlogiftic doctrines are found infufficient; and again, in their turn, thefe

may

may be introduced to explain ſuch phenomena as are inexplicable in the former doctrine. Thus, by the mutual aſſiſtance of theſe different hypotheſes, the phlogiſtians, by ſhifting their ground, may remain for ſome time in the field.

The antiphlogiſtians are of opinion, that ſulphur, phoſphorus, &c. are, according to our preſent knowledge of chemiſtry, ſimple bodies, which, when united to dephlogiſticated air, conſtitute their reſpective acids. Thus the antiphlogiſtians conſider all acids to conſiſt of two principles only; one peculiar to each.

Mr. Lavoiſier's Table of the affinities of the Oxygenous Principle. Mem. Par. 1782, p. 535.

Baſes.	*Reſulting Compounds.*
Baſis of marine acid.	Dephlogiſticated marine acid.
Reg. of man.	
Charcoal.	Fixed air.
Zinc.	Calx of zinc.
Iron.	Calx of iron.
Sulphur.	
Inflammable principle.	Water.
Nickle.	Calx of nickle.
Lead.	Calx of lead.
Tin.	Calx of tin.

Phoſ-

Phoſphorus.	Phoſphorous 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.
Smoaking marine acid.	
Nitrous acid.	
Black calx of manganeſe.	

Mr. Kirwan objects to the foregoing table, 1. Becauſe he ſuppoſes charcoal, according to its precedency, ſhould decompoſe water, in a boiling heat at leaſt, conſidering that iron, which is placed lower, will produce inflammable air under the ſame circumſtances. But the nature of charcoal ſhould be firſt conſidered. Though its aggregate attraction appears weaker than that of iron, from its facility of pulverization; yet when reduced into powder, or ſmall molicules, its ultimate particles may cohere with greater force. The frangibility of charcoal is in a great meaſure owing to the number of minute cavities which interfect its texture, from the expulſion of the ſucculent part of the wood. Independent of the aggregate attraction, which certainly counteracts chemical union more than we are aware of, I think the ultimate particles of charcoal are ſurrounded with ſome repelling fluid, which defends them from the action of air and water; and the ſame may be ſaid with reſpect to ſpirit of wine, ether, and oil: for they all have greater affinity to dephlogiſticated air than phoſphorus, which combines with it in the common temperature of the atmoſphere. This, whether it be the electric fluid, common fire, or ſome other fluid, with which we are not acquainted, deſerves attention. Nitrous air will ruſh into union with dephlogiſticated air in any temperature, and yet ſugar will not, though it deprives it of its dephlogiſticated air. Pure calcareous earth, perfectly dried, will not attract marine acid air; and yet water, to which it has leſs affinity, will condenſe it, and enable it to unite to this. Light inflammable air and dephlogiſticated air will not combine in their ordinary ſtate but by the help of fire, either the electric, or a common ſpark; yet they will unite very readily when one or both are partially condenſed. Thus nitrous air, which, as ſhall hereafter appear, is compoſed of dephlogiſticated air and phlogiſtic only, will condenſe hepatic gas. Hepatic gas, as I ſhall endeavour to ſhew in the ſequel, is light inflammable air in its full extent, holding ſulphur in ſolution. The ſulphur is precipitated, and the reſiduum is dephlogiſticated nitrous air. Here a portion of the dephlogiſticated air of the nitrous combines with the inflammable air of the hepatic gas, and forms water. It cannot be ſaid that this takes place in conſequence of a double affinity. Phlogiſticated air is with difficulty united to dephlogiſticated air, though it attracts it with greater force than nitrous air. Iron moiſtened with water, and confined by mercury, will yield inflammable air. Iron, treated in the ſame manner, and confined with dephlogiſticated air, will produce no inflammable air: but the air will be diminiſhed. Iron will yield no inflammable air if it be confined in very dry dephlogiſticated air, neither will the air be diminiſhed, nor will the iron tarniſh in any length of time. Hence it appears, that iron has no effect on air in a common temperature, but that it is the water which is decompoſed, and that the dephlogiſticated air and inflammable air unite at the very inſtant of its liberation, and re-compoſe water. Theſe are difficult to be accounted for. All

that

that we can ſay of them is, that a certain degree of condenſation facilitates their union; but this conveys no idea of the true cauſe. It may be ſaid, that water condenſes marine air in conſequence of its capacity for fire. But why phoſphorus, and not oils, or ſugar? or, why nitrous air, and not phlogiſticated, unite to dephlogiſticated, in a common temperature? Or, again, why iron takes the oxygenous principle from water in preference to that in its aërial ſtate, when the light inflammable air diſengaged condenſes it, is, in my opinion, very little underſtood.

It is true, all this may be juſtly attributed to fire, which, from its attraction to bodies, counteracts their chemical union to one another: but, from the following conſiderations, I think ſome other power muſt interfere. It is generally allowed, and juſtly, that nitrous air conſiſts of dephlogiſticated air and phlogiſtic in the proportion of two of the former to one of the latter. The ſuppoſition of its containing phlogiſton, I hope, will hereafter appear to be erroneous; therefore every ultimate particle of phlogiſticated air muſt be united to two of dephlogiſticated air; and theſe molicules combined with fire conſtitute nitrous air. Now if every of theſe molicules were ſurrounded with an atmoſphere of fire equal

equal in ſize only to thoſe of dephlogiſticated air, 100 cubic inches of nitrous air ſhould weigh 98,535 grains; whereas, according to Kirwan, they weigh but 37 grains. Hence, we may juſtly conclude, that the gravitating particles of nitrous air are thrice the diſtance from each other that the ultimate particles of dephlogiſticated are in the ſame temperature, and of courſe their atmoſpheres of fire muſt be in ſize proportionable; or elſe ſome other repelling fluid muſt interpoſe. The ſize of the repelling atmoſpheres of nitrous air thus conſidered, and likewiſe the weaker attraction of the molicules of this air to dephlogiſticated air than that of the ultimate particles of phlogiſtic in their ſimple ſtate. It is ſurpriſing to me, with how much more facility the former unites to dephlogiſticated air than the latter. The decompoſition of nitrous air, by the light inflammable air of the hepatic gas, is equally extraordinary, conſidering, as I ſaid before, that the inflammable air is not in a condenſed ſtate; and, therefore, combined with its natural portion of fire. Do atmoſpheres of equal denſity favour the union of their reſpective gravitating particles? Or, do a denſe and a rare atmoſphere, by eaſily blending, promote their chemical union, by ſuffering them to ap-

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proach nearer? Or does the electric fluid interfere?

From the foregoing confiderations, it feems to me that the attractive forces of bodies are not to be eftimated by the facility of compounding, but rather by the difficulty of decompounding thefe again. Therefore, I beg leave to differ with Mr. Kirwan in his objections (page 24) to Mr. Lavoifier's Table of Affinities, until he adduces more fubftantial reafoning.

I think fulphur fhould be placed before light inflammable air, and manganefe before charcoal, for reafons which will hereafter appear. Therefore, without making any alteration in Mr. Lavoifier's Table, I took the liberty of having thefe placed between both columns. In order to be the more explicit, I fhall ufe the term aggregate attraction alone, in explaining that power which folid or lefs condenfed bodies have of counteracting chemical union. Though, as I have obferved above, I fufpect fome other force to co-operate with this: but I fhall not prefume to defcribe to others what I do not well underftand myfelf. Thus, let us fuppofe charcoal to attract dephlogifticated air with the force of ten, and contrary powers, which I fhall call the

the aggregate attraction, to resist this with the force of eleven. Let us likewise suppose iron to attract dephlogisticated air with the force of seven, and its aggregate attraction to counteract this with the force of six and seven-eighths. It would require greater heat to unite the two former than the two latter, though they have by far the greater affinity to one another. But when once the scale is cast in favour of the former, the rapidity of their union ought to be greater than that of the latter; which is really the case.

SECTION III.

On the Vitriolic Acid.

MR. Kirwan is of opinion, that ſulphur conſiſts of a baſis, or a radical principle, which, when ſaturated with phlogiſton, conſtitutes ſulphur, but with fixed air vitriolic acid; and when combined partly with the one and partly with the other, volatile ſulphureous acid *.

Let us for a moment allow ſulphur to be what Mr. Kirwan ſuppoſes, that is, a certain baſis ſaturated with phlogiſton, and which, when expoſed to dephlogiſticated air, with due application of heat will unite to it, exhibit the phenomenon of combuſtion, and produce vitriolic acid. I aſk Mr. Kirwan, What takes place in this proceſs? He of courſe will ſay, that the dephlogiſticated air unites to the phlogiſton of the ſulphur, and forms fixable air, which re-unites to the radical baſis, and conſtitutes the acid.

According to Mr. Kirwan himſelf, water ought to reſult from an union of dephlogiſticated air and phlogiſton during the combuſ-

* Eſſay on Phlogiſton, p. 28.

tion

tion of ſulphur, conſidering that this cannot take place but in a red heat; therefore it appears to me, that his doctrine is a little contradicted in this proceſs.

Other phlogiſtians, on the contrary, will ſay, that a portion of the dephlogiſticated air unites to the phlogiſton of the ſulphur, and forms water, while another part unites to the baſis of ſulphur, and conſtitutes the vitriolic acid. I muſt confeſs, in this one circumſtance, this laſt hypotheſis appears to me to be the moſt rational and moſt flattering mode of ſupporting this imaginary theory.

Mr. Kirwan muſt acknowledge, that light inflammable air and dephlogiſticated air conſtitute water; and, in his opinion, light inflammable air is pure phlogiſton combined with fire, but when united to metals, the baſis of ſulphur, &c. that it is in a concrete ſtate. Fixed air has never been known to reſult from an union of dephlogiſticated air and light inflammable air in its pure ſtate. I condenſed upwards of one hundred cubic inches of dephlogiſticated air by the combuſtion of light inflammable air in a jar inverted over lime water. The inflammable air was produced from iron entirely free from ruſt, and the vitriolic acid uſed was highly concentrated, and afterwards diluted with three times its bulk of water. The inflammation of both airs took place during the extrication of the inflammable air, which paſſed through a copper tube ſeven inches long, with a bulb in the middle, which contained a ſmall quantity of ſoap lees, both to retain any fixable air that may be ſeparated from the iron, and likewiſe any vitriolic acid that may be mechanically forced up. The combuſtion was carried on at the extremity of this tube in a continual flame, and water trickled down the ſides of the jar during the whole proceſs; but not a particle of fixable air could I detect. I repeated the ſame experiment over diſtilled water, which I carefully boiled in order to expel any fixable air it may contain, and could not detect the ſmalleſt veſtige of any acid. When theſe airs are combined by the electric ſpark, no fixable air is produced. During the deflagration of zinc in dephlogiſticated air, no fixable air is produced, provided they be both pure. All philoſophers agree that fixable air is an acid; then I aſk, What are its conſtituent principles? Mr. Kirwan will no doubt ſay, Dephlogiſticated air and phlogiſton. Again, I aſk, what the conſtituent parts of water are? He will ſay, as above, Dephlogiſticated air and phlogiſton. That is to ſay, they are the ſame things, but differently modified.

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Let us confider how widely different thefe two fubftances are in their properties, and we fhall find that no modification could make this vaft difference.

Fixed air will unite to different bodies, and change their phyfical and chemical qualities; even it will unite to water, according to Mr. Kirwan, its fecond felf, and make a vaft alteration in its properties. Allowing then, as I faid before (and which is but a temporary indulgence), fulphur to be what the phlogiftians fuppofe, a certain bafis and phlogifton, where are the materials for fixed air? for, from what has been obferved, it cannot be fuppofed that phlogifton, either in its aerial or denfe ftate, will form fixable air. What anfwer can Mr. Kirwan make to this, though I allow him phlogifton? In my opinion, he muft give up his fixed air, and fay, with other phlogiftians, that vitriolic acid is formed by an union of dephlogifticated air to the bafis of fulphur, and that the phlogifton flies off; or adopt a more modern, and indeed the ftrongeft argument in favour of phlogifton, the formation of water. I expofed near fixty grains or more of highly concentrated vitriolic acid and light inflammable air to heat fufficient to convert the whole into volatile fulphureous acid: the procefs was carried on with a gradual heat, to prevent the diftillation of the acid until decompofed. The refiduum contained volatile vitriolic acid and light inflammable air, but not a particle of fixable air. If fixable air were one of the conftituent principles of vitriolic acid, and if this again were compofed of light inflammable air, or phlogifton, and dephlogifticated air; whether the inflammable air united to the bafis of the fulphur, or whether it deprived the original phlogifton of the fulphur of its dephlogifticated air, fixable air ought to be produced: for the above procefs has been, according to Mr. Kirwan, very favourable to the formation of fixable air*. When ftrong vitriolic acid was reduced to the fame ftate by iron filings, fixable air was produced in very fmall proportion; which fhews, that the fixable air did not refult from an union of dephlogifticated air and light inflammable air, but muft come from plumbago, or from fome other impurity in the iron. If very pure alum be heated to ignition, it will yield dephlogifticated air and volatile fulphureous acid, but no fixable air. Mr. Kirwan will undoubtedly explain it thus, *viz.* That the bafis of the fulphur de-

* Effay on Phlogifton, p. 26.

prives

prives the fixed air of its phlogiston, and that its dephlogisticated air is disengaged, at the same time that the volatile sulphureous acid retains a sufficient quantity of fixable air and phlogiston to keep it in an intermediate state.

Here then the basis of sulphur seems to have greater affinity to phlogiston, than dephlogisticated air has, or than it has to both dephlogisticated air and phlogiston united; which even the phlogistians themselves will not allow. If it should be urged, that this decomposition is in consequence of the attraction of the different fluids for fire, light inflammable air should be produced; or, according to Mr. Kirwan, the fixable air should be converted into water, considering the degree of heat necessary for the process, and the basis of sulphur disengaged in its simple state.

Water could not be decomposed in this process. For, admitting the most plausible phlogistic hypothesis, that of the union of dephlogisticated air to the basis of sulphur, while another part forms water, by combining with its phlogiston, a double decomposition must take place, *viz.* the basis of the sulphur must give up its dephlogisticated air in consequence only of the mediation of fire; the water then muſt be decompoſed in conſequence of the attraction of the baſis of ſulphur for phlogiſton being ſuperior to that of dephlogiſticated air. Is it likely that the baſis of ſulphur ſhould give up its dephlogiſticated air ſo readily, at the ſame time that it unites to a ſubſtance of equal volatility, and to which it has leſs attraction? The dephlogiſticated air of the water alone muſt be ſufficient to prevent ſuch an union. Sulphur gives up its phlogiſton (if uniting to dephlogiſticated air be ſuch) in any degree of heat above ignition. Its phlogiſton will even take a portion of their dephlogiſticated air from metallic calces, notwithſtanding two contrary powers, according to the phlogiſtic doctrine, oppoſe the union: for, if ſulphur were a compound of phlogiſton and a certain baſis, how could its phlogiſton take dephlogiſticated air from the phlogiſton of the metal? Is not here phlogiſton to oppoſe phlogiſton?

The phlogiſtians conſider metallic ſubſtances to be compoſed of certain baſes and phlogiſton; allowing this, and likewiſe vitriolic acid, to be compoſed of three principles, phlogiſton, the baſis of ſulphur, and dephlogiſticated air; and the phlogiſton and dephlogiſticated air to be in the form of fixable air intimately united to the baſis of ſulphur;

and likewife the metallic bafis to attract its phlogifton with great force, as indeed it muft, when the ftrongeft heat cannot part them, notwithftanding the volatility of phlogifton. In this cafe, how can metals decompofe vitriolic acid? for it cannot be fuppofed that the dephlogifticated air already united to phlogifton will quit it, to unite to the phlogifton of the metal: even the attraction of the bafis of fulphur for both tends to render this improbable, as does likewife the attraction that muft fubfift on the other fide between phlogifton and its metallic bafis. It may be faid, that the fixable air of the vitriolic acid unites to the metallic bafis, at the fame time that its phlogifton either paffes off in an aerial ftate, or unites to the bafis of the fulphur. If fo, the metallic bafis muft have greater attraction to phlogifton and dephlogifticated air jointly, than to phlogifton alone; therefore, it muft part with its phlogifton to unite to fixable air. If this fhould be the cafe, phlogifton in an aeriform ftate, or light inflammable air, could not deprive the metallic bafis of its fixable air, even in the ftrongeft heat; nor could it take dephlogifticated air from the metallic bafis and its phlogifton; though it is true fire may weaken their union, and thereby enable the dephlogifticated air to quit the phlogifton

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of the metal, to unite to the disengaged phlogiston. Is it likely that this should take place, especially when it appears that phlogiston and dephlogisticated air united will expel phlogiston from metals? Is it reasonable to suppose, that phlogiston will take dephlogisticated air from phlogiston, when the advantage and disadvantage of heat must be the same to both?

Let us now consider the other phlogistic hypothesis, that of the formation of water by the union of phlogiston and dephlogisticated air, while another portion of dephlogisticated air unites to the basis of sulphur, and forms vitriolic acid. Diluted vitriolic acid will calcine iron in any temperature, and light inflammable air is produced, which, in the opinion of the phlogistians, is the phlogiston of the metal combined with fire. What does the metallic basis unite with in preference to its phlogiston? If it only unites to that portion of dephlogisticated air attached to the basis of sulphur, then this basis might be obtained in its purity. Besides, if only dephlogisticated air united to the metals during solution, inflammable air would not be produced; for this is never obtained during calcination in dephlogisticated air. The basis of sulphur and its dephlogisticated air very likely unite to the metallic bafis, and expel its phlogifton. But then, if this were the cafe, pure alkali, or calcareous earth, would precipitate the bafis of iron in its pure ftate ; a circumftance which has never yet taken place ; for the precipitate is heavier than the iron, and it contains dephlogifticated air enough to faturate or condenfe the inflammable air extricated during the folution. Whence comes this dephlogifticated air? Not from the vitriolic acid ; for it is not decompofed, as evidently appears from Mr. Lavoifier's experiment, who found that a folution of vitriol of iron required as much alkali to faturate it, as the fame quantity of acid in its fimple ftate. I have repeated this experiment, and found it to be fo. Hence, I think the phlogiftians muft have recourfe to water to enable them to attempt an explanation of the folution and calcination of metals in the vitriolic acid ; and, in my opinion, they will then approach nearer to truth than before. Does the water itfelf unite to the metallic bafis, and expel its phlogifton? The phlogiftians muft fay it does, or allow the decompofition of water, which they are unwilling to do. If water alone were the chief agent in the calcination, as Mr. Kirwan himfelf obferves, obſerves*, it would calcine iron with as much facility in its purity, as when mixed with vitriolic acid. Here, then, the metal is deprived of its phlogiſton, and its baſis united to dephlogiſticated air: the acid is not decompoſed, and the phlogiſtians will not allow the decompoſition of water; and from what has been ſaid above, the union of water itſelf is inadmiſſible; therefore, they muſt allow water to be decompoſed. Does the dephlogiſticated air of the water unite to the phlogiſton of the metal, and let go its own phlogiſton? Dephlogiſticated air, as already obſerved, can hardly be ſuppoſed to quit one principle to unite to another of the ſame ſort, which muſt be already intimately united to the metallic baſis. Let us add to this, the attraction that muſt ſubſiſt between the principles of water.

The phlogiſtians, if they even muſt allow the decompoſition of water, may ſtill have recourſe to one more mode of argument in ſupport of their almoſt wrecked hypotheſis; which appears to be but a plauſible evaſion of truth, and which is, that the metallic baſis and its phlogiſton attract dephlogiſticated air jointly, with greater force than either ſeparately; and in conſequence thereof, that the phlogiſton of the water muſt yield its dephlogiſticated

* Eſſay on Phlogiſton, p. 99.

air to a ſuperior force. Indeed, if this were the truth, we could not well account for the reduction of metallic calces by inflammable air in the ſtrongeſt heat, when we ſuppoſe phlogiſton to oppoſe phlogiſton, and likewiſe when we conſider the attraction of the metallic baſis for both; which muſt be very conſiderable, when almoſt all the metallic calces will not yield either in the ſtrongeſt heat, notwithſtanding their volatility and attraction for fire. It is true, fire may weaken the union of phlogiſton and dephlogiſticated air to the metallic baſis, but not ſo materially as to enable phlogiſton to expel them both. In ſhort, the phlogiſtic theory, taken in the moſt partial point of view, preſents to me ſuch numberleſs inconſiſtencies, that I ſhould imagine its obſcurity alone has prevented its fall long before this time.

Water will not apparently act upon iron in the common temperature of the atmoſphere; but, diluted vitriolic acid will rapidly diſſolve it, and inflammable air will be produced. This evidently ſhews, that the acid takes an active part in the calcination; and, from what has been already ſaid, it ſtill is found to contain all its principles. Whence, then, does the iron receive its dephlogiſticated air? or, let the phlogiſtians explain, in their

their doctrine, how the acid acts in this process. If highly concentrated vitriolic acid be used, very little inflammable air is obtained, but chiefly volatile sulphureous acid; and if heat be used for a considerable time, sulphur will be formed.

Let the phlogistians account, in their doctrine, for so material a difference in these two processes from the mere presence of water. I think they have remaining but one method of accounting for the latter; which is, that the basis of sulphur gives up its dephlogisticated air to the iron, at the same time that the iron yields its phlogiston to the basis of sulphur.

If this were the case, the same circumstance should take place in diluted vitriolic acid: besides, if the metal should exchange phlogiston for dephlogisticated air only, turbith mineral could not be reduced by the mere expulsion of it, provided phlogiston be a necessary principle in the constitution of metals. I think these facts tend strongly to prove the delusion of the phlogistic theory; for let us trace it which way we will, though it may flatter us in a few circumstances, it will lead us into a wilderness, where we lose sight of that concatenation of nature which

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the adverſe doctrine enables us to inveſtigate without interruption.

What is the ſtrongeſt proof of the exiſtence of phlogiſton in bodies? Inflammation when expoſed to heat in atmoſpheric air. Is not the fire given out by the condenſed air? Does dephlogiſticated air unite to any ſubſtance but to that which contains phlogiſton? According to the phlogiſtic theory, it does not. Is it inconſiſtent with the natural courſe of things, to ſuppoſe, that there are bodies which do not contain a particle of light inflammable air, and whoſe attraction for dephlogiſticated air may be ſuch as to combine with it (under favourable circumſtances) ſo as to diſengage its fire, denſe enough to exhibit the phenomenon of combuſtion?

If the condenſation of dephlogiſticated air by the different bodies which yield flame and light were occaſioned by the ſame principle common to them all, too great inertneſs would prevail between thoſe bodies which contain dephlogiſticated air, and thoſe that are ſuppoſed to contain phlogiſton; for phlogiſton muſt counteract phlogiſton, and thereby preſerve a neutrality ſufficient to reſiſt numberleſs operations, as well conducted on the large ſcale of nature as in our elaboratories.

Though we have not hitherto been able to decompoſe pure calcareous, argillaceous, ſiliceous, barytic and magneſian earths, or fixed vegetable and mineral alkalies, yet we ſuſpect them to be compounds. Indeed, the very circumſtance attending the increaſe of calcareous earth in the animal kingdom, is a ſtrong inſtance of its being a compound, as likewiſe is that of fixed vegetable and mineral alkalies in the vegetable kingdom: but until we reſolve theſe into their conſtituent principles, we muſt conſider them as ſimple ſubſtances, and not attribute their different properties to one common principle. I think I may preſume to ſay, that ſulphur, phoſphorus, phlogiſticated air, and metals, are as ſimple bodies as the earths, and that we know as little of their origin or conſtituent principles.

The latter will unite to dephlogiſticated air, but ſome with more facility than others, and preſent during the union nearly the ſame phenomena. But are we to infer from thence, that the ſame principle is common to them all, when the reſulting compounds are quite different? The former (two excepted) will unite to acids, and preſent like pheno-

mena;

mena; and may we not infer from this, with as great probability of truth, that the ſame principle which promotes a chemical union between the acid and any of theſe, is common to all, and which we may call the alkalinate principle? Is not this laſt as rational an hypotheſis as that of the principle of inflammability? There are as ſtrong grounds for the one as for the other.

If ſteam be paſſed over fuſed ſulphur, light inflammable air will be obtained, as Dr. Prieſtley has obſerved. From whence does this air come? The phlogiſtians will undoubtedly ſay that it is diſengaged from the ſulphur. If ſo, the baſis of ſulphur attracts water with greater force than it does phlogiſton; but will water and the baſis of ſulphur form vitriolic acid? By no means; though volatile ſulphureous acid is formed in this proceſs, which actually requires dephlogiſticated air for its conſtitution; a clear proof that water muſt be decompoſed. I ſhould like to know how the phlogiſtians can account for this decompoſition. Let us ſuppoſe ſulphur to be a compound of a certain baſis and phlogiſton, and water to be compoſed of dephlogiſticated air and phlogiſton: would the dephlogiſticated air of the water quit its own phlogiſton, to unite to the phlogiſton of the ſulphur? Unleſs ſome other power co-operated, and what can this be? The baſis of ſulphur unites to dephlogiſticated air, and forms a compound in itſelf. Therefore it cannot be ſuppoſed that it could give any aſſiſtance to its phlogiſton, which unites to the ſame principle, and forms a ſeparate compound: on the contrary, we ſhould expect that their mutual attraction to one another ſhould prevent the decompoſition of water. Let us ſuppoſe dephlogiſticated air to attract light inflammable air with the force of 4, and the baſis of ſulphur to attract phlogiſton or concrete inflammable air with the force of 3, and its aggregate attraction to be equal to one more, which muſt be nearly the proportion, conſidering that ſulphur will not unite to dephlogiſticated air in the common temperature of the atmoſphere, but requires fire to remove its aggregate attraction. In this caſe water muſt be decompoſed in conſequence of the attraction of the baſis of ſulphur alone for dephlogiſticated air, which muſt be more than equal to the contrary powers already mentioned (making an allowance for the attraction of aggregation), that is, it muſt exceed 7 to ſubdue them. The ſame ſtatemen, may be obſerved with reſpect to the calcination of metals by water, if we suppose these to contain phlogiston.

A good many more facts might be urged on this subject; but in my opinion enough has been adduced to convince an impartial reader, that all the phenomena above recited are only explicable by entirely leaving out phlogiston, and supposing sulphur to be a simple substance, whose ultimate particles attract dephlogisticated air with forces inherent in themselves, independent of phlogiston or concrete inflammable air, as an alkali does an acid, or gold and tin mercury; and likewise supposing the combustion of sulphur to be as simple a process as that of light inflammable air; that is, that there is no dephlogistication or formation of water during the union of the oxygenous principle to sulphur, as containing not a particle of light inflammable air in its constitution. I have often combined sulphur rendered perfectly dry, and dephlogisticated air likewise, deprived of its water by fused marine selenite in large proportion over mercury, and could never observe that water was produced. Indeed it may be said, that the volatile sulphurous acid, which is always the result of this process, may re-dissolve it; but this is not very likely, when a ſmall portion of water will deprive it of its elaſticity.

According to Mr. Kirwan, 100 grains of ſulphur require 143 grains of dephlogiſticated air to convert them into volatile vitriolic acid; but they require much more in order to become perfect vitriolic acid. Highly concentrated vitriolic acid contains 2 parts of dephlogiſticated air, and 1 of ſulphur, excluſive of water.

One hundred and forty-three grains of dephlogiſticated air contain 41 of water, for lime will abſtract 26 grains from it, and the remainder cannot be ſeparated from it in its aerial ſtate; therefore 100 grains of ſulphur, making an allowance for water, require 100 or 102 of the real gravitating matter of dephlogiſticated air to form volatile vitriolic acid; and as volatile vitriolic acid is very little ſhort of double the ſpecific gravity of dephlogiſticated air, we may conclude, that the ultimate particles of ſulphur and dephlogiſticated air, contain equal quantities of ſolid matter; for dephlogiſticated air ſuffers no conſiderable contraction by uniting to ſulphur in the proportion merely neceſſary for the formation of volatile vitriolic acid. Hence we may conclude, that, in volatile vitriolic acid, a ſingle ultimate particle of ſulphur

phur is intimately united only to a ſingle particle of dephlogiſticated air; and that, in perfect vitriolic acid, every ſingle particle of ſulphur is united to 2 of dephlogiſticated air, being the quantity neceſſary to ſaturation.

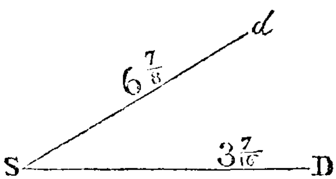
As 2 cubic inches of light inflammable air require but 1 of dephlogiſticated air to condenſe them, we muſt ſuppoſe that they contain equal number of diviſions, and that the difference of their ſpecific gravity depends chiefly on the ſize of their ultimate particles; or we muſt ſuppoſe that the ultimate particles of light inflammable air require 2 or 3, or more, of dephlogiſticated air to ſaturate them. If this latter were the caſe, we might produce water in an intermediate ſtate, as well as the vitriolic or the nitrous acid, which appears to be impoſſible; for in whatever proportion we mix our airs, or under whatſoever circumſtance we combine them, the reſult is invariably the ſame. This likewiſe may be obſerved with reſpect to the decompoſition of water. Hence we may juſtly conclude, that water is compoſed of molicules formed by the union of a ſingle particle of dephlogiſticated air to an ultimate particle of light inflammable air, and that they are incapable of uniting to a third particle of either of their conſtituent principles. The above notions of water and vitriolic acid being ſtrictly kept in view, let us now proceed to enquire into the nature of ſulphur and vitriolic acid, and their various effects on different bodies in the antiphlogiſtic doctrine.

It has been already obſerved, that metals attract dephlogiſticated air with greater force than ſulphur, and that ſulphur attracts it with greater force than light inflammable air. It has likewiſe been obſerved, that vitriolic acid and water, mixed in a certain proportion, will calcine metals with greater facility than concentrated vitriolic acid, and that water will have very little effect on metals in a common temperature. Theſe facts, though they may appear contradictory in themſelves when ſlightly conſidered, may be accounted for on the following principles, and are, in my opinion, inexplicable by any other means whatever.

Let us ſuppoſe iron or zinc to attract dephlogiſticated air with the force of 7, ſulphur to attract it with the force of $6\frac{7}{5}$, and light inflammable air with the force of $6\frac{5}{8}$. Let us again ſuppoſe theſe to be the utmoſt forces that can ſubſiſt between particle and particle. That is to ſay, in water dephlogiſticated

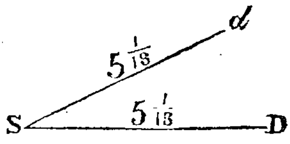
giſticated air is retained with the above force, and likewiſe in volatile vitriolic acid, with the force already mentioned. It is unneceſſary to introduce here the aggregate attraction which frequently preſerves a neutrality between bodies, as, for inſtance, between water and zinc, or water and iron. Stating the attractive forces in the above proportion, which I am led to believe is juſt, from facts already obſerved, we ſhould imagine that iron or zinc would calcine in water with greater facility than in vitriolic acid; and if ſome other circumſtance did not interfere, it muſt be the caſe. This the following will in ſome degree illuſtrate.

Let S be a particle of ſulphur, *d* a particle of dephlogiſticated air, which it attracts with the force of $6\frac{7}{8}$, and let the compound be volatile ſulphureous acid; here the tie between S and *d* is greater by $\frac{2}{8}$, than that between the conſtituent principles of water, which is but $6\frac{5}{8}$. As the attraction of bodies is mutual, let us ſuppoſe S to poſſeſs one-half of this force, which is $3\frac{7}{16}$, and



this to be its utmoſt exertion, and likewiſe *d* to poſſeſs the other half, which is $3\frac{7}{16}$ more, which will unite them with the above-mentioned force. Let us ſuppoſe another particle of dephlogiſticated air D to have a tendency to unite to S, with the force of $3\frac{7}{16}$, in order to form perfect vitriolic acid: to receive D, S muſt relax its attraction for *d* one-half. That is, the force of $3\frac{7}{16}$ will be divided and directed in two different points, which will reduce the attachment of dephlogiſticated air and ſulphur in perfect vitriolic acid to $5\frac{1}{18}$.

In order to more perfectly underſtand this, let S be ſulphur, *d* D two different particles of dephlogiſticated air united to it, with the different forces annexed to them. If D were taken away, S and *d* would attract one another with the



force of $6\frac{7}{8}$, and when again reſtored would reduce this force to $5\frac{1}{18}$, and ſo alternately. This ſeems to be a general law. Mild, fixed, vegetable alkali will part with a portion of its fixable air in a moderate degree of heat, but requires a very intenſe heat to expel the whole. In like manner vitriolated tartar will conſolidate a portion of water during its cryſtallization; in this ſtate it will melt in a degree of heat below ignition, and part with its water of fusion, and consolidate in the same degree of heat. If the mass be ignited, it will again fuse, and continue parting with water for some time; and when the whole is expelled, though the fire be on the increase, it will again consolidate, and require a much stronger heat to fuse it over again. Here we see that, in proportion as the alkali is deprived of a part of its fixed air, its power of retaining the remainder is redoubled, and that of the vitriolated tartar for water; for in the first fusion it parts with a portion of its water very readily, but during the second fusion it parts with the remainder with difficulty. Here we find, notwithstanding the volatility of water, the force of attraction subsisting between it and the salt retains it until it is red hot; and how great these powers must be, when we consider the mechanical force necessary to keep water in a condensed state, when simply exposed to the same degree of heat! I shall forbear mentioning several other circumstances of the like nature: let it suffice to say, that this explains the necessity of raising the fire towards the end of all chemical processes.

The true state of water and vitriolic acid being considered, when these fluids are mixed in different proportion, and then iron or zinc introduced, what are we to expect will take place? Undoubtedly the following decompositions. The iron will attack the dephlogisticated air of the vitriolic acid with the force of 7, which resists but with the force of $5\frac{1}{18}$, in preference to the dephlogisticated air of the water, which resists with the force of $6\frac{5}{8}$. We are not to suppose that the metal will attract *d*, in preference to D, but that it will influence them both equally alike; more especially when it presents surfaces enough. The sulphur being thus despoiled of its dephlogisticated air, but still preserving its extreme division, exerts the force of $6\frac{7}{8}$ on the dephlogisticated air of the water, which it readily gains as meeting but with the resistance of $6\frac{5}{8}$, while the inflammable air is disengaged. The phlogistians may object to this by saying, that sulphur will not decompose water in the temperature of the above process. I will join them in this opinion; but be it recollected that fused sulphur, as already observed, will decompose water when brought in contact with it in the state of steam; and what promotes a decomposition here, but the interposition of fire between the ultimate particles of the sulphur, whereby its aggregate attraction is removed? But, if this

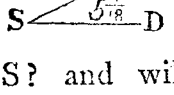
this does not interfere in a low temperature, which is the cafe after the decompofition of vitriolic acid by metals, the decompofition of water will take place the eafier; for, though fire removes the chief obftacle to the decompofition, it interferes a little itfelf. The ultimate particles of fulphur, when deprived of their dephlogifticated air, cannot recover more of this from the water, than is neceffary to the formation of volatile vitriolic acid, fee $S \underline{\quad 6\frac{7}{8} \quad} d$, which being re-attracted by the calcined metal, acts as a folvent.

If concentrated vitriolic acid be ufed, the application of heat is neceffary, and very little inflammable air is produced; but chiefly volatile vitriolic acid. The ufe of fire here is to remove the aggregate influence of the vitriolic acid, as well as to weaken that of the iron; both which circumftances favour the new union, or, as properly fpeaking, facilitate the decompofition. When water is mixed with the vitriolic acid, it interpofes itfelf between its fluggifh particles, which puts them beyond the fphere of their mutual influence; and thereby, though it is attracted by the vitriolic acid, anfwers the fame purpofe that fire

fire does; ſo that the ſolution goes on rapidly without the application of heat.

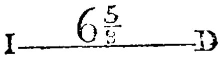
The volatile vitriolic acid diſengaged, and the ſmall quantity of inflammable air produced, when concentrated vitriolic acid is uſed, may, I think, be very ſatisfactorily accounted for in the following manner.

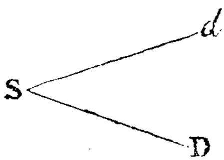
The firſt effort of the metal wholly deprives the particles of vitriolic acid in contact with it of their dephlogiſticated air, and they inſtantly exert the force of $6\frac{7}{8}$ on the dephlogiſticated air of the neighbouring indecompoſed vitriolic acid, which can only reſiſt with the force of $5\frac{1}{18}$: they will not take D and *d* from S, but D or *d*, whichever happens to be moſt contiguous to them; therefore two portions of volatile vitriolic acid are formed. In order to render this the more intelligible, let S be an ultimate particle of ſulphur, recently deprived of its dephlogiſticated air, and ſtill poſſeſſed of the power of $6\frac{7}{8}$ to recover this again; and let



be a particle of vitriolic acid in the vicinity of S: will not S take D or *d* from S? and will not the volatile compounds S —$6\frac{7}{8}$— *d* S —$6\frac{7}{8}$— D be formed? The latter will paſs off in an elaſtic ſtate, while the former, S —$6\frac{7}{8}$— *d*, being nigher the metallic

metallic calx, is attracted by it. As the moſt concentrated vitriolic acid contains a portion of water, part of this likewiſe is decompoſed; hence ariſes the inflammable air. Let A be a particle of water, I and D its conſtituent principles; I inflammable air, and D dephlogiſticated air, combined with the force of $6\frac{5}{8}$; if A ſhould be interpoſed between S, and would not S the rather deprive I of D, than wait the approach of the vitriolic molicule which is beyond its reach? particularly when the above-mentioned force of S is conſtantly rivetted or levelled, if I may uſe the expreſſion, towards dephlogiſticated air, in whatever compound, or in whatever ſtate it meets with it, unleſs ſome other power counteracts it; and what can this be, but the union of the ultimate particles of ſulphur to ſome other ſubſtance which attracts them more forcibly, or their own attachment to one another ſo as to form an aggregate? neither of which circumſtances interferes here. In addition to the above explanation of the interference of the ſmall quantity of aqueous particles in concentrated vitriolic acid, I need only ſay, that when this



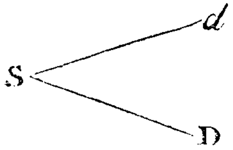


this acid is ſo diluted as to afford only inflammable air, the particles of water, by ſurrounding theſe of the acid, or by the intermixture of their more numerous ſurfaces, are expoſed to the influence of the ſulphur, the inſtant it is deprived of its dephlogiſticated air by the metal, and thereby prevent the formation of the volatile ſulphureous acid, marked S——D, while S——*d*, which is neceſſary to ſolution, is conſtantly forming by the decompoſition of water. Thus the water, though it is decompoſed itſelf, defends the vitriolic acid, whereby we obtain inflammable air in ſuch abundance.

From what has been ſaid reſpecting the ſolution of metals in diluted vitriolic acid, we find that $\frac{1}{3}$ more dephlogiſticated air ſhould be contained in the metallic ſolution, than is neceſſary to the formation of perfect vitriolic acid. That is, it contains that portion which the ſulphur takes from the water, in addition to the quantity originally contained in the vitriolic acid; which the following circumſtances tend to corroborate.

Fixed vegetable alkali will decompoſe a ſolution of vitriol of iron, and form vitriolated tartar, at the ſame time that the iron is diſengaged of a dirty bluiſh colour, combined only with about $\frac{1}{3}$ the portion of dephlo-

dephlogiſticated air neceſſary for its thorough calcination. It could not receive this dephlogiſticated air from the vitriolic acid, for this is united to the alkali in its perfect ſtate. See



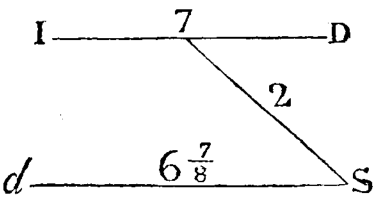
otherwiſe we ſhould have a compound reſulting from an union of the alkali to S——*d*, which is called the ſulphurous ſalt of Stahl.

If a ſaturated ſolution of martial vitriol be expoſed to dephlogiſticated air, a yellowiſh calx is depoſited, and in time nearly the entire of the iron is brought to this ſtate. I frequently examined different calces of this ſort well waſhed with hot water, and found that ſome contained vitriolic acid, and that others did not. If the ſolution be expoſed to the air for a conſiderable time, it acquires an acid taſte by the liberation of a portion of the vitriolic acid. Fixable air will likewiſe decompoſe this martial ſolution, as ſhall hereafter appear. Perfect vitriolic acid will have no effect on the perfect calx of iron, but volatile ſulphurous acid will partially diſſolve it.

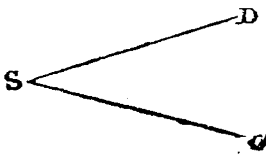
Theſe facts ſeem to correſpond, and I think may be thus accounted for. Let I be iron; D dephlogiſticated air united with the force of 7; let us ſuppoſe D to be the

quantity

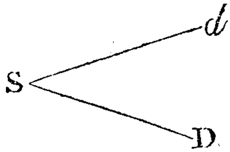
quantity neceſſary to ſaturate I, ſo as to form a perfect calx; let S be ſulphur, *d* dephlogiſticated air attached with the force of $6\frac{7}{8}$. Let us ſuppoſe S to have a tendency to unite to more dephlogiſticated air; and let us likewiſe ſuppoſe, which is well known to be the caſe, a ſmall attraction to exiſt between S and I. Let us ſtate the whole ſum of theſe forces between S, D, and I, to be 2; which power, though it will not ſeparate I from D, or *d* from *S*, yet is ſufficient to combine I——D to S——*d* when in contact, and when no other power is to counteract it.



If the vitriolic ſolution above conſidered be expoſed to dephlogiſticated air, the following decompoſition will take place, *viz.* another particle of dephlogiſticated air will unite to S, which will counteract the attraction of I——D for S——*d*; therefore the ſeparate compounds I———D and will be formed. For the attraction of *d* for S, which I have already ſtated to be $3\frac{1}{16}$, is ſufficient



ficient to ſubdue the power of 2, which united I——D and S——*d*. In order to prove this more fully, let the calx of iron I——D and perfect vitriolic acid be mixed; they will not unite; for I being ſaturated with D, can have no



effect on *d* D; and S in like manner being ſaturated with *d* D, can have no effect on D. We are to conſider the particles of dephlogiſticated air D D *d* to have no ſenſible attraction for one another; and likewiſe the attraction of *d* D to S to be ſuch as to more than counteract the attraction of S to I. For though S may be deprived of *d* D by a force not much ſuperior to $5\frac{1}{18}$, yet it would require more than the force of $10\frac{1}{36}$, to ſeparate S from *d* D, provided the latter were not influenced. Hence ariſe ſeveral very important phenomena in chemiſtry, which arrangement forbids me to introduce here; and which, from their being little conſidered, gave birth to the phlogiſtic theory.

I introduced ſome iron nails, free from ruſt, into ſtrong volatile vitriolic acid; when it ſtood for a few minutes, it acquired a milky appearance, and the ſolution went on without ebullition or extrication of air. On ſtanding for a few hours, the ſolution acquired a darkiſh colour, and a black powder was precipitated. This powder, when collected and waſhed, put on red hot iron, burned partly like ſulphur, and partly like charcoal duſt, and the incombuſtible reſiduum was of a purpliſh colour. The filtered ſolution was perfectly neutralized, and free from the leaſt ſulphurous pungency. Its taſte was ſtrongly chalybeat, but not ſo diſagreeable as that of the ſolution of iron in the perfect vitriolic acid, or in any of the mineral acids.

Nitrous acid dropped into the ſolution inſtantly produced a cloudineſs, which immediately diſappeared without ebullition, though volatile ſulphureous acid was diſengaged in its utmoſt degree of pungency. The vitriolic, marine, and acetous acids decompoſed this ſolution, but cauſed no turbidneſs, nor was any inflammable air produced *.

In order to know whether the ſulphur

* I would beg leave to recommend a trial of this preparation of iron in diſorders that require the uſe of chalybeates; but as this preſumption is rather founded on theory, I ſhall not take the liberty of ſaying any thing particular in its favour, until experience enables me to urge it with confidence.

was

was difengaged from the volatile fulphureous acid or the iron, I poured marine acid on the fame nails, when light inflammable air and hepatic air were copioufly produced, and likewife fulphur was depofited in its crude ftate. When I ufed vitriolic or the nitrous acid, no fulphur was produced. I tried different nails, and likewife iron filings, with the fame refult. Thefe facts convinced me, that the fulphur was feparated from the iron; but that all forts of iron contain fulphur is what I cannot pretend to know, as I have not tried fteel or varieties enough of malleable iron. However I have ftrong reafon to fufpect, that fulphur has more to do in the different properties of iron than we are aware of. That iron fhould contain fulphur, notwithftanding the different proceffes it muft neceffarily undergo before it acquires malleability, confidering the volatility of fulphur, points out the force of their attraction to one another; and the feparation of this again by volatile fulphureous acid, fhews likewife the greater attraction of iron to fulphur and dephlogifticated air jointly. That volatile fulphureous acid fhould diffolve iron without the extrication of inflammable air or phlogifton, is a very ftrong inftance of the fallacy

 of

of the phlogiſtic doctrine *. If volatile vitriolic acid were a compound of phlogiſton, a certain baſis and dephlogiſticated air, a greater quantity of inflammable air ſhould have been diſengaged during the ſolution of iron in this acid than when the perfect vitriolic acid is uſed. Let us even ſuppoſe volatile ſulphureous acid to be compoſed of the baſis of ſulphur, phlogiſton and dephlogiſticated air, which is the opinion of all the phlogiſtians, though they differ with reſpect to the modification of theſe three principles; and, likewiſe, iron to be compoſed of a certain baſis and phlogiſton: I would aſk the phlogiſtians what becomes of the phlogiſton of the iron during its ſolution? They cannot ſay it is diſengaged in an aeri-form ſtate, for there is hardly any inflammable air produced. Therefore, all they can ſay is, that the phlogiſton of the metal, and that of the volatile vitriolic acid, are preſent in the ſolution; but this contradicts their own principle, viz. that metals muſt loſe their phlogiſton, in order to

* A ſmall quantity of inflammable air is produced, but it is ſo trifling, comparatively to what ſhould be produced from the quantity of iron diſſolved, that it is hardly worth noticing, and, in my opinion, proceeds from a portion of perfect vitriolic acid, which is generally inſeparable from the volatile acid.

become ſoluble in acids. What principle is there in volatile ſulphureous acid that can attract the phlogiſton of the iron? The dephlogiſticated air cannot unite to it, as being already united with phlogiſton according to Mr. Kirwan. The baſis of ſulphur can have no influence over it, being united to phlogiſton and dephlogiſticated air; or, if even the baſis of ſulphur were to unite to the phlogiſton of the metal, it muſt have formed ſulphur, which is in itſelf inſoluble, and incapable of holding metals in ſolution. Beſides, if the quantity of phlogiſton they imagine be preſent in the ſolution, nitrous air ought to have been produced on the addition of nitrous acid, or inflammable air on the addition of the marine acid; neither of which had been procured, though they diſplaced the volatile vitriolic acid, and united to the iron. A ſolution of nitrated iron thus prepared, and completely freed from volatile ſulphureous acid, will yield a more perfect calx than vitriolated iron, when both are precipitated by pure fixed vegetable alkali. The nitre thus obtained will yield leſs dephlogiſticated air, and more phlogiſticated air, than the ſame quantity of common nitre, but in what proportion I cannot ſay. I am induced to ſuppoſe, that the difference of purity is in proportion to the quantity of dephlogiſticated air united to the precipitate. I am ſorry I have not an opportunity at preſent to aſcertain this, by a more accurate repetition of the experiment.

The ſolution of a metal in an acid without the production of inflammable air, and the decompoſition of this again by nitrous acid without the production of nitrous air, is very well worthy of attention; more eſpecially when we conſider that nitrous acid is always partly decompoſed during its union to metals in the common way. Surely theſe differences cannot ariſe from phlogiſton; for if ſuch a thing exiſted in metals, it would be as prevalent in the ſolution, when we know it did not make its eſcape, and likewiſe when it is evident that there can be nothing to envelope or protect it, as when the metal is introduced in its ſimple ſtate into diluted nitrous acid. When I treat of nitrous acid, I ſhall have an opportunity of reſuming the latter part of this ſubject; and, as I have ſaid ſufficient to anſwer my preſent purpoſe, I will poſtpone it until then.

The ſolution of iron in volatile vitriolic acid is quite clear, but when expoſed to the air it acquires a brown colour in a very little time; indeed, the ſurface of the liquor changes colour in a few minutes. I expoſed part of this ſolution to fixable air confined by mercury, and the ſame change took place: fixable air and dephlogiſticated air mixed, affected this ſolution in a ſhorter time than either ſeparately. From the effects of fixable air as well on this ſolution as on other preparations of iron, I am induced to ſuppoſe, that the brown colour of ruſt and of other calces of iron, is occaſioned chiefly by fixable air.

I precipitated ſome iron from a common ſolution of martial vitriol, and waſhed it well. I put a part of this into perfect vitriolic acid, and another portion into the volatile vitriolic acid; they ſeemed very quieſcent, and no ſolution appeared to take place. I cloſed both up very tight in two vials, and laid them by for two or three days, when almoſt all the iron was taken up. I filtered both ſolutions, and into the vol. vit. ſolution gradually dropped aerated volatile alkali, which threw down a bluiſh precipitate. Aerated volatile alkali, dropped into the other ſolution, diſengaged a brown precipitate, which was inſtantly re-diſſolved. I continued dropping in the alkali until the ſolution was ſaturated, when an orange-coloured precipitate was obtained; very little fixable air was produced, until the ſolution was nearly ſaturated. I think we may attribute the re-diſſolution of the precipitate to fixable air: for the ſolution having a ſuperabundance of vitriolic acid in it, the aerial acid was more copiouſly liberated than if it had been a ſaturated ſolution; ſo that the diſengaged calx was ſo much the better ſupplied with this ſolvent. Mild, fixed, vegetable alkali precipitated the iron from the vol. ſulp. acid of a darkiſh blue colour; it likewiſe precipitated the above ſolution of perfect vitriolic acid of the ſame colour. Why was not the iron precipitated by the volatile alkali from both ſolutions of the ſame colour? Or why did not the mild fixed alkali precipitate as perfect a calx from the latter ſolution as the volatile alkali did? Or why did not the aerial acid diſſolve the precipitate from the volatile acid, ſo well as it did that from the perfect acid? And laſtly, why was not inflammable air diſengaged during the ſolution of the iron in the above acids? If the precipitate of iron from the vitriolic acid by fixed alkali be dried or expoſed to air for ſome time, the vitriolic acid will only take up a ſmall portion of it, for the moſt calcined part is left behind.

Hence

Hence we find, that a precipitate procured from a ſolution of iron in perfect vitriolic acid, diſſolves as well in diluted vitriolic acid, as in the volatile vitriolic acid, without the production of inflammable air, though it is but $\frac{1}{3}$ calcined, or in other words, dephlogiſticated. Why is not at leaſt one-half the quantity of inflammable air, or phlogiſton, diſengaged here, that is ſeparated during the ſolution of ſimple iron in vitriolic acid? I think this is not conſiſtently explicable in the phlogiſtic doctrine; at the ſame time that it is not only explicable in the antiphlogiſtic theory, but likewiſe tends to prove the non-exiſtence of phlogiſton in iron, and to corroborate what has been already advanced relating to the ſolution of metals in vitriolic acid.

It has been already obſerved, that fixed vegetable alkali precipitates iron from the vitriolic acid, and that perfect vitriolated tartar is obtained, though the iron is found to be partly calcined. Therefore it appeared, that the water furniſhed the dephlogiſticated air, and that the iron contained only that portion which it received from the water. It has likewiſe been obſerved, that this portion of dephlogiſticated air, in addition to that contained in perfect

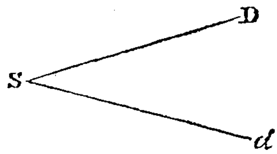
vitriolic

vitriolic acid, is the greateſt quantity that can be retained in the ſolution of iron, and that more dephlogiſticated air will decompoſe it. But it has been ſhewn, that volatile ſulphureous acid will diſſolve iron without the extrication of inflammable air, and that the ſolution contains but $\frac{1}{3}$ the portion of dephlogiſticated air contained in the ſolution of iron in perfect vitriolic acid. This ſhews, though a ſmall quantity of dephlogiſticated air will promote the union and ſolubility of iron and ſulphur, that more will do it better; but that a larger quantity will ſeparate them. Then, if this calx of iron contains only that portion of dephlogiſticated air taken from the water, and if this, in addition to the quantity contained in perfect vitriolic acid, be the *quantum ſufficit* for holding iron in ſolution; no wonder that the union ſhould take place without the production of inflammable air, if this be diſengaged by the decompoſition of water; but if diſengaged from the iron, it is as remarkable we ſhould not obtain it. If a larger quantity of dephlogiſticated air were united to the above calx, it would then be, as already explained, inſoluble in perfect vitriolic acid, on the ſame principle that a ſolution

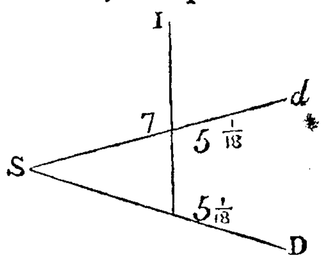
lution of martial vitriol is decompofed when expofed to air.

It may appear extraordinary that inflammable air is not produced during the folution of iron in volatile vitriolic acid, at the fame time that it is fo copioufly difengaged during its folution in perfect vitriolic acid. This, I confefs, puzzled me for fome time before I could account for it. I think it is demonftrable in the following manner:

Let I be iron



vitriolic acid: let us fuppofe I to attract dephlogifticated air with the force of 7, and S, from its divided attachment, to retain its dephlogifticated air with the force of $5\frac{1}{18}$, as ufual; and let us likewife fuppofe iron, from the clofenefs of its texture, to prefent a greater number of ultimate particles to a given furface than the vitriolic acid, particularly than the dilute vitriolic acid from the interpofition of water.



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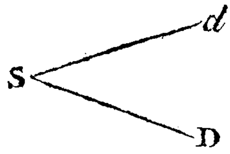
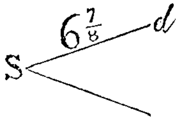
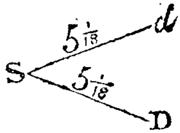
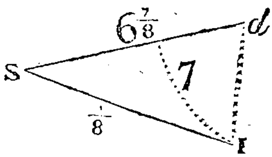


be brought within one another's influence under theſe circumſtances, and I will take *d* D from S; or S, in conſequence of its attraction for I, which is but very ſmall, comparatively to the oppoſite powers, will be forced along with D *d*. This latter is not likely to take place; for the force of 7, exerted at once by a number of the martial particles on D *d*, ſuddenly ſnatches them as it were from S, which cannot move with the ſame pace towards I; becauſe, being in contact with water, it exerts its whole force on that compound. Therefore it is the violence and ſuddenneſs of the pull from the metal, and the velocity of the motion of D *d* towards it, that leaves S ſo circumſtanced as to be able to decompoſe water in the manner already deſcribed.

The contrary takes place during the ſolution of iron in volatile ſulphureous acid; for though the iron attracts the dephlogiſticated air of the volatile vitriolic acid with the force of 7, it meets with the reſiſtance

ſiſtance of $6\frac{7}{8}$ 

as before deſcribed; ſo that that ſuperiority of force does not prevail here, as when perfect vitriolic acid is uſed. See 

Indeed, if there were a greater inequality of force between S and I for *d*, S, from its attraction to *d*, and its tendency to I, would move with *d* towards I, and form the compound of S———*d*———I, already deſcribed. Let S attract *d* with the force of $6\frac{7}{8}$: let I attract *d* with the force of 7, and let I attract S with the force of $\frac{1}{8}$ only; the attachment of S to *d*, and likewiſe its tendency to I, make up the force of 7. Therefore the force of 7, 

ſubſiſting between I and *d*, will influence S and *d* equally the ſame; ſo that S and *d* will move with equal pace to unite to I. Hence no decompoſition takes place, and of courſe no inflammable air is produced. Theſe two important

important facts do not only throw mutual light upon one another, but likewise upon several abstruse phenomena in chemistry.

Sulphur, in its simple state, will unite to mostly all the substances that vitriolic acid will. It unites to all the earths (the siliceous excepted), to the alkalies, to the metals (a few excepted), and likewise to the oils. The union of sulphur to the first class of these does not throw much light on its nature, as we are as yet unacquainted with their constituent principles.

The union of sulphur and volatile alkali admits of much more speculation than the former substances. It is now very well known, from the experiments of Mr. Berthollet and Doctor Austin, that volatile alkali is composed of phlogisticated air and light inflammable air. Sulphur will not chemically unite to inflammable air so as to consolidate it; though, as I shall hereafter be obliged to observe, it enables sulphur to combine with fire, and acquire an elastic state, whereby they are both held in solution, as sugar or Glauber salt is in water. Therefore, if sulphur be a compound of a certain basis and phlogiston, this basis must be fully saturated with phlogiston. It is not certain that volatile alkali will unite to

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any more light inflammable air than it is known to contain in its ordinary ſtate, ſo that we muſt conſider this likewiſe to be ſaturated with light inflammable air or phlogiſton. Then, how can theſe ſubſtances unite, when their baſes are already attached and ſaturated with that to which they have greater affinity, than they have to one another? Should not the ſame inertion prevail here, as when the perfect calx of iron is mixed with the perfect vitriolic acid; or when Glauber's ſalt is mixed with vitriolated tartar; or when ſelenite and baroſelenite; or vitriol of zinc and vitriol of iron are mixed? Do not like theſe, ſubſtances of the ſame kind, and which have no ſenſible influence on one another, interfere between volatile alkali and ſulphur? The ſame may be obſerved with reſpect to the union of ſulphur to metals and oils.

The effects of oils on vitriolic acid correſpond with the foregoing explanations. A ſmall quantity of oil, or any other vegetable or animal ſubſtance that attracts dephlogiſticated air, or, in other words, that is combuſtible, will partly decompoſe vitriolic acid, and diſcolour a large quantity. Vitriolic acid thus coloured, expoſed to a ſtrong heat, will emit volatile vitriolic acid

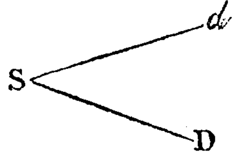
in

in great abundance, and likewiſe fixable air, until it acquires its former tranſparency. Vitriolic acid, poured in ſmall proportion on a large quantity of oil, will turn it to a darkiſh brown colour. This expoſed to heat will yield fixable air and volatile vitriolic acid, with a ſmall quantity of phlogiſticated and heavy inflammable air; and, if the charge be urged with a tolerable ſtrong heat, a ſmall quantity of ſulphur may be produced. Hence we may infer, that the acid is only deprived of a portion of its dephlogiſticated air. Animal and vegetable inflammable bodies have certainly ſtronger affinity to dephlogiſticated air than iron has, though they will not readily unite under any circumſtance below the temperature of ignition. Oils, animal or vegetable, provided they be free from volatile alkali, will not mix or unite with water in a common temperature, but when diffuſed with it by agitation will aſſume a globular figure, and inſtantly ſeparate from it again on ſtanding: here the repulſive force between oil and water is evident. If oil and water be boiled under the common preſſure of the atmoſphere, no decompoſition will take place; but if water be gradually dropped into boiling hot oil, inflammable air will be produced,

duced, as has been firſt obſerved by Mr. Lavoiſier. The joint action of air and water can have no great effect on theſe, and if any at all, it muſt be in a great length of time. Suet and butter are not decompoſed by water alone; for I can affirm, that I have been preſent when a ſmall tub of butter had been taken from under ground at leaſt three feet deep, and which, from the ſituation of the ſoil and the decay of the wood, muſt have lain there for upwards of fifty years. It was ſurrounded with water, for it lay in a marſhy ſoil. It had a diſagreeable taſte, and a ſpongy white appearance, but did not ſeem much changed in its chemical properties. From theſe, and ſimilar facts too tedious to mention, we ſee the difficulty of uniting oils, butter, tallow, and charcoal to dephlogiſticated air in a common temperature. In my opinion, as I have heretofore conjectured, theſe are protected from the action of air and water by ſome repelling fluid that ſurrounds their ultimate particles, independent of common fire, and which they are deſtitute of while enveloped in their reſpective kingdoms. For all animal and vegetable organic bodies which contain theſe, are readily decompoſed by expoſure to air and water, or to water alone.

Conſidering theſe circumſtances, it cannot be ſuppoſed that water ſhould be decompoſed, and inflammable air diſengaged during the commixture of diluted vitriolic acid and oils. This reluctance oils have to unite to dephlogiſticated air in a low temperature, in addition to their attraction for ſulphur, oppoſes that ſudden decompoſition of vitriolic acid, or rapid ſeparation of dephlogiſticated air from the ſulphur, by which, as in the inſtance of the ſolution of iron in diluted vitriolic acid, it is enabled to decompoſe the water.

When vitriolic acid, whether diluted or not, is mixed with oil, an ultimate particle of vitriolic acid influences with a certain force an ultimate particle of oil, while the latter attracts the vitriolic with the ſame force. The oil will not take D *d* from S:



but from the joint attraction

traction of S——D——*d* to oil, they will approach with equal pace, and combine. Thus this mixture more than mechanically, but not quite chemically united, may be resolved into the different fluids mentioned above. The particle of oil will retain D or *d*, and form fixable air; at the same time that S will retain *d* or D with its full force, and form volatile vitriolic acid.

Volatile vitriolic acid is not so readily decomposed by oils as perfect vitriolic acid, from the retention of its dephlogisticated air with so much the greater force. Therefore volatile vitriolic acid has not the property of charing oils as common vitriolic acid has, but it mixes with them, and forms a whitish or a saponaceous-like substance.

What has been said above, might be very well illustrated by minutely describing the various phenomena attending the different stages of that beautiful process of making vitriolic ether.

Here the vitriolic acid retains the oleaginous and aqueous part of the spirit of wine, while the most volatile part passes over in

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the ſtate of ether, the nature of which cannot be diſcuſſed here. Ether of my own making, and which I carefully rectified from deliquiated fixed vegetable alkali, expoſed to ſpontaneous evaporation, in the temperature of 37 or 40° of Fahrenheit's thermometer, left a ſmall reſiduum of oil, water, and vitriolic acid. The quantity of vitriolic acid was ſo ſmall, that I could only detect it by acetated barytes. However, it ſhews that vitriolic acid enters into the conſtitution of vitriolic ether. A portion of the ſame ether left no reſiduum in the temperature of 60°. A ſolution of terra ponderoſa ſhewed no appearance of vitriolic acid in this ether. It appears to me, that ether is to light inflammable air, what the groſſer oils are to the heavy which is favourable to the explanation of fermentation, &c.

Charcoal or oils will wholly decompoſe vitriolic acid when combined with fixed alkalies, and expoſed to heat. Two circumſtances favour this decompoſition: 1ſt, The attraction of the inflammable matter for D *d*. 2dly, That of S for the alkalies. Liver of ſulphur expoſed to the atmoſphere,

atmoſphere, or to dephlogiſticated air in cloſe veſſels, will attract the latter, and form vitriolated tartar; though ſulphur alone will have no effect on dephlogiſticated air, nor will alkalies in their ſimple ſtate unite to it. On reflection, theſe circumſtances appear very ſingular; but if we conſider that the ſulphur is united to the alkali in its extreme diviſion, and that its attraction to dephlogiſticated air is ſtronger than its attachment to the alkali, and likewiſe that the attraction of alkalies for vitriolic acid is greater than their attraction to ſulphur, we may eaſily account for all this. The ſulphureous ſalt of Stahl expoſed to air, will unite to the dephlogiſticated part, and form a perfect vitriolic ſalt; though volatile vitriolic acid in its ſimple ſtate will not readily unite to dephlogiſticated air. Theſe facts clearly demonſtrate, why alkalies take vitriolic acid in its perfect ſtate from iron, at the ſame time that it is thrown down in a ſemi-calcined ſtate; for, as I have before endeavoured to ſhew, the iron takes D *d* from S, by its ſuperior attraction to dephlogiſticated air, at the ſame time that S takes *d* from the water;

 there-

therefore S——*d* holds I < D / *d*

or the calx of iron in ſolution; from which circumſtance we might imagine, that S——*d*, or the volatile vitriolic acid, ſhould unite to the alkali, and form the ſulphureous ſalt of Stahl, and that the iron ſhould be precipitated in a more calciform ſtate, that is, united with D——*d*, or double the quantity of dephlogiſticated air which the precipitate generally contains. But finding that S——*d*, or volatile vitriolic acid united to alkalies or earths, attracts dephlogiſticated air with greater force than when in its ſimple ſtate, we can eaſily explain why the contrary takes place.

Sulphur partly acquires an aeriform ſtate, when diſengaged from the different hepars by acids. Liver of ſulphur in its dry ſtate is quite inodorous; but when moiſtened with water, it emits a ſtrong hepatic ſmell, as Mr. Gengembre has obſerved. From this effect of water on liver of ſulphur it is evident, that it promotes the diſunion and volatilization of a portion of the ſulphur; but on what principle is not well underſtood. If this ſhould take place in conſequence of a decompoſition of water, vitriolic acid ought to be formed, and of courſe vitriolated tartar; but it has not been found, to my knowledge, that liver of ſulphur, either earthy or alkaline, has ever been vitriolated by the decompoſition of water alone, but always requires the acceſs of air*. However, as the hepatic ſmell, or emiſſion of the gas, is moſt predominant when only a ſmall quantity of moiſture is uſed, and on its firſt application, it may be ſaid, that the dry hepatic compound has only then the power of decompoſing water, and that the continuance of the ſmell is occaſioned by a portion of the gas remaining in the compound from the difficulty of its expulſion. Iron filings will unite to ſulphur in a moderate degree of

* Since the above was written, Dr. Auſtin informed me, that liver of ſulphur will not afford an hepatic odour when wetted in cloſe veſſels, and confined in mercury. It ſeems he has made ſeveral experiments on liver of ſulphur, which he has given to the Royal Society.

heat, and form a black brittle mafs, which on the addition of an acid will yield hepatic air in the utmoft purity, and in great abundance, though it will not produce an hepatic fmell when moiftened with water, as calcar. pond. or alkaline livers of fulphur will. This fhews the greater attraction of alkalies and fulphur jointly to dephlogifticated air than that of iron and fulphur, and likewife tends to prove what has been already faid on the precipitation of iron by alkalies.

Dr. Auftin has paffed the electric fpark repeatedly in hepatic air, and by that means precipitated all the fulphur without changing its dimenfions. The refiduary air was incondenfible by water, and when wafhed had no hepatic fmell. On burning this with dephlogifticated air, it appeared to be light inflammable air. This fhews the conftituent principles of hepatic gas, better than any other experiment that has hitherto been made on the fubject. That fulphur is fufpended in its natural ftate in light inflammable air, may be inferred from the above experiment; but whether in its extreme divifion is difficult to determine; or whether it be chemically united to the inflammable air, or combined independently with its own atmoſpheres of fire, and mechanically mixed with this, cannot be ſatisfactorily proved. In my opinion it is mere ſolution, ſuch as takes place between the neutral ſalts and water, or the alkalies and water, or ſugar and water, &c. Though the facility whereby this is decompoſed favours the above hypotheſis, yet there are circumſtances that are apparently againſt it; ſuch as their united condenſation in water, and their joint expulſion from it again. Upon what principle this attraction exiſts between bodies, has not yet been explained, or the difference between this and a chemical union ever defined. It appears to me that ſolution, that power whereby water diſſolves aerial acid, alkaline air, vitriolic acid air; and that power whereby light inflammable air diſſolves ſulphur and phoſphorus; and likewiſe that power whereby all the aeriform fluids diſſolve water in their elaſtic ſtate; and laſtly, whereby water diſſolves the neutral ſalts, &c. without changing their properties, is occaſioned by a ſort of intermediate attraction, not differing from

chemical

chemical attraction but in its degree of force, and not at all different from that power whereby the heavenly bodies influence one another.

Dr. Austin fused sulphur in light inflammable air, in phlogisticated air, and in heavy inflammable air. The two former airs were not in the least altered; but the latter afforded one-third its original bulk of hepatic gas. It is remarkable, that the bulk of the air was not in the least altered in this process; and likewise that the residuary air, when the hepatic air was separated from it by water, should not appear in the least changed; for by inflaming it with a due proportion of dephlogisticated air, it yielded the usual quantities of fixed and phlogisticated air. The sulphur acquired a coally appearance in this operation; which induces me to suppose that it must have precipitated something from the air, the loss of which enabled the inflammable air to take sulphur in exchange.

The same philosopher passed the electric spark repeatedly in heavy inflammable air, until it increased nearly one-half in bulk; this he inflamed with dephlogisticated air over mercury by the electric ſpark. He likewiſe inflamed the ſame quantity of heavy inflammable air, not treated by the electric ſpark. By ſeveral repetitions of the above experiments, and from an accurate compariſon of their reſpective reſiduums, he found that there was leſs fixable air, and a larger quantity of phlogiſticated air in the former than in the latter; from which he concluded that heavy inflammable air is phlogiſticated and light inflammable air, and that fixable air is compoſed of theſe two and dephlogiſticated air. He likewiſe concluded, and juſtly, from the increaſe of bulk, and the ſmall quantity of the heavy inflammable air that was decompoſed, that if the entire were decompoſed it would increaſe ten times its bulk. The converſion of heavy inflammable air into hepatic air without increaſe of bulk, and without any change in the reſiduary air, does not favour the above hypotheſis: 1ſt, Becauſe, as has appeared, and as ſhall be hereafter confirmed, light inflammable air is held in hepatic gas at its full extent. 2dly, Becauſe the decompoſed air ſhould increaſe ten times in bulk.

3dly, Be-

3dly, Becaufe no increafe of phlogifticated air was found in the refiduary air.

However, the Doctor fuppofes that volatile alkali is formed, whereby a portion of the inflammable air and the entire of the phlogifticated air remain united. Volatile alkali contains not much more by meafure than four of inflammable to one of phlogifticated air; therefore the decompofed air fhould ftill increafe fix times its bulk. Befides, as this experiment was performed in dry mercury, the volatile alkali itfelf fhould remain in an elaftic ftate.

As the Doctor intends to favour the public with thefe experiments, I fhall not prefume to fay much on the fubject. That heavy inflammable air contains light inflammable air, is certain from the formation of hepatic gas, as well as from its expanfion by the electric fpark; but I cannot avoid entertaining a doubt, whether the real matter of inflammable air with which dephlogifticated air forms fixable air, and which does not in the leaft differ from the ultimate particles of charcoal, be compofed of light inflammable air and phlogifticated air. Indeed, confidering that thefe are the

conftituent

conſtituent principles of volatile alkali, it appears rather improbable.

It ſeemed to me, for I was preſent, that ſomething was precipitated from the air by the electric ſpark; for the lower part of the glaſs tube appeared black, while the ſides ſeemed lined with a greyiſh ſubſtance. It likewiſe appeared to me, after the air acquired the expanſion already mentioned, that a contraction took place by continuing the electric ſpark. This at leaſt I can ſay with truth, that one hundred ſparks at one time contracted it nearly one meaſure in eight or nine; but how much more it would diminiſh by continuing the operation, I cannot tell. I am almoſt perſuaded to think, that the matter of charcoal in its extreme diviſion, held in ſolution in light inflammable air and water, and combined with fire, conſtitutes the heavy inflammable air, on the ſame principle that ſulphur and light inflammable air conſtitute hepatic gas; with this difference only, that the former gravitate more towards each other, which cauſes a greater condenſation of the light inflammable air in the heavy than in hepatic gas, and of courſe a greater difficulty of decompoſing it. Such likewiſe is the nature of phoſphoric air, as has been obſerved by Mr. Gengembre, who I find, although I have not ſeen his analyſis, has paid vaſt attention to this ſubject. Fire, it is true, is the firſt ſolvent in nature; next to this comes water; and next to this again light inflammable air, whether in its aerial or condenſed ſtate, ſuch as in ethers and ſpirits. To this property of light inflammable air, I attribute partly the ſpirituous fermentation, and chiefly the reſult. From theſe, and other ſimilar circumſtances, my doubts ariſe reſpecting the conſtituent principles of the heavy inflammable air, although experience convinces me that it contains a ſmall quantity of phlogiſticated air. Thus far I have ventured to treſpaſs upon the patience of my reader, thinking that the heavy inflammable air may tend to caſt light on the nature of hepatic gas, and *vice verſâ*.

I mixed equal parts of hepatic air produced from iron filings and ſulphur, and dephlogiſticated air obtained from nitre. Seven meaſures of the former were abſorbed

ſorbed by water all to a ſmall bubble, and the latter contained only one-tenth of phlogiſticated air. Nine meaſures of this mixture were reduced by the electric ſpark to $2\frac{1}{2}$; the nitrated ſolution of terra ponderoſa condenſed theſe to one-twelfth of a meaſure or leſs; and the ſolution did not appear in the leaſt turbid, nor did any cloudineſs take place on the addition of lime water. The reſiduum left unabſorbed was too ſmall to be examined; but the portion condenſed by the ſolution ſeemed by the ſmell to be volatile vitriolic acid. In order to be convinced of this, I inflamed another charge of the ſame airs, and transferred the reſiduum into a clean jar, which the ſulphur depoſited on the ſides of the inflaming jar obliged me to do. To this I added an equal bulk of hepatic air, which inſtantly rendered it turbid, and reduced it to one-third, or a little more.

This aſſured me that the reſiduum was volatile ſulphureous acid, and likewiſe that volatile ſulphureous acid will not decompoſe nitrated terra ponderoſa.

This experiment not only proves the conſtituent principles of hepatic gas, but

abſolutely

abſolutely proves what I have advanced reſpecting the proportion of the principles of volatile vitriolic acid. It has been ſhewn by Dr. Auſtin, that the ſolution of ſulphur in light inflammable air, neither contracts nor expands it; therefore the above charge contained $4\frac{1}{2}$ meaſures of light inflammable air, independent of the ſuſpended ſulphur. Theſe $4\frac{1}{2}$ ounce meaſures of light inflammable air, require at leaſt $2\frac{1}{4}$ of dephlogiſticated air to condenſe them. $2\frac{1}{4}$ meaſures more were expended in the experiment, two of which muſt be contained in the volatile vitriolic acid; and as the moſt part of the phlogiſticated air diſappeared, we may juſtly conclude, that the remainder of the dephlogiſticated air, which is but one-fourth of a meaſure, was expended in the formation of nitrous acid. Hence we may conclude, that the two meaſures of volatile vitriolic acid contained two meaſures of dephlogiſticated air; and as the ſpecific gravity of volatile vitriolic acid, excluding the inflammable air, is the mathematical main of the two fluids, we muſt ſuppoſe that only the ſulphur of two meaſures

meaſures united to dephlogiſticated air, and that the ſulphur of 2½ meaſures was precipitated. Hence likewiſe we may infer, that the molicules of volatile vitriolic acid are ſurrounded with as large atmoſpheres of fire as the particles of dephlogiſticated air, or at leaſt that they are as far aſunder; and that the number of the ultimate particles of ſulphur in hepatic gas, are to thoſe of the inflammable air as nine to five.

SECTION IV.

Of Nitrous Acid.

NO ſubject in chemiſtry, until the deciſive experiment of Mr. Cavendiſh, favoured the phlogiſtic doctrine more than the nitrous acid, from the variety of its modifications.

The large quantity of dephlogiſticated air contained in this acid, and condenſed by ſo ſmall a portion of phlogiſticated air, is very well worthy the attention of ſpeculative men, at the ſame time that it enables us to account for the eaſy decompoſition (more eſpecially in part) of this acid; whereby it aſſumes the different appearances obſervable from the ſtate of dephlogiſticated nitrous air, down to the moſt perfect ſtate of colourleſs nitrous acid. It is not an eaſy matter to aſcertain exactly the greateſt quantity of dephlogiſticated air, that a given quantity of nitrous acid may contain. I always found nitre to vary in its product of of phlogifticated and dephlogifticated air, and likewife in their proportion to one another. The pureft nitre will yield, about the middle of the procefs, dephlogifticated air fo pure as to contain but about one-thirteenth only of phlogifticated air. In the beginning, and nearly at the latter end of the procefs, air will be produced about twice better than common air. I mixed the different products of a quantity of pure nitre, and found by expofure to liver of fulphur that one-fixth was left unabforbed. This was the utmoft degree of purity in which I obtained dephlogifticated air from nitre.

According to Mr. Lavoifier, 100 grains of nitrous acid contain 79½ of dephlogifticated air, and 20½ of phlogifticated air, which is not quite four to one. But his experiments contradict this; for whatever mode he adopted to decompofe nitrous acid, it appeared that the proportion of dephlogifticated air was nearly as five, to one of phlogifticated air.

Mr. Cavendifh has proved, that nitrous acid may be formed by taking the electric fpark in a mixture of three parts of phlogisticated air, and seven of dephlogisticated air, which is but $\frac{1}{7}$ more of dephlogisticated air than nitrous air contains. This may apparently contradict Mr. Lavoisier's as well as my own estimation of the proportion of the constituent principles of nitrous acid when in its perfect state.

The red nitrous vapour contains three parts of nitrous air and one of dephlogisticated air, or one of phlogisticated and three of dephlogisticated air; but nitrous vapour may be formed with a less proportion of dephlogisticated air, and which, though it may not be so condensible as a more perfect nitrous vapour, yet will, when in contact with pure alkali, unite to it and form nitre, as was the case in the experiment of Mr. Cavendish.

The common straw-coloured nitrous acid contains more dephlogisticated air than the red nitrous acid or vapour; the proportion appears to be four to one; but the colourless contains about five of dephlogisticated to one of phlogisticated air.

Having once a charge of nitre and vitriolic acid in a green glass retort, I placed it in a sand-pot to distil; but the pot being small,

ſmall, the edge came too near the retort, about a quarter of an inch or more above the charge, which before the proceſs commenced, and when it acquired more than the heat of boiling water, cracked it all round in that direction. Being thus ſituated I was obliged to withdraw the fire, and, before the charge got cold, to ladle it into an earthen pan. I again introduced it into a freſh retort, and obtained from it nitrous acid nearly as colourleſs as water. As the vitriolic acid was not very perfect, I attributed the goodneſs of the nitrous acid to the purity of the nitre. Therefore I procured more of the ſame nitre in order to lay in a ſtock of nitrous acid; but to my ſurpriſe, though I uſed purer vitriolic acid than in the former proceſs, my product of nitrous acid was of an high ſtraw colour. Some months after, having an occaſion for more nitrous acid, and recollecting the above circumſtance, I mixed the vitriolic acid and nitre in due proportion, and expoſed them in an earthen pan ſet in ſand to nearly the heat of boiling water for half an hour or more, continually expoſing freſh ſurfaces to the air. When the charge was quite cold I introduced it into a retort, and diſtilled as colourleſs nitrous acid as the former. As the charge emitted no nitrous air during digeſtion, it muſt have attracted dephlogiſticated air.

I would recommend this manner of treatment, to obtain nitrous acid in the utmoſt degree of perfection.

Before I proceed any farther on this ſubject, I think proper to mention the phlogiſtians' opinion of this acid, particularly Mr. Kirwan's, who has adopted a new phlogiſtic hypotheſis reſpecting the modification of the conſtituent principles of the nitrous acid, and of all other acids.

This philoſopher ſuppoſes, that 100 grains of nitrous acid in its pure colourleſs ſtate, 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; and that the nitrous baſis contains $\frac{1}{3}$ of its weight of phlogiſticated air, and $\frac{2}{3}$ dephlogiſticated air, both in a concrete ſtate, and that it has an affinity both to fixed air and phlogiſton. Mr. Kirwan moreover ſuppoſes, that nitrous baſis ſaturated with phlogiſton, conſtitutes nitrous

air,

air, and that 100 gr. of this baſis take up nearly 22 of phlogiſton. By this he means, that the principles of nitrous acid are fixed air, dephlogiſticated air, phlogiſticated air, and inflammable air, all in their concrete ſtate.

According to this ſtatement of nitrous acid, 100 grains of it in its pure dry ſtate, provided the fixable air be decompoſed, ſhould yield about 60, .25 of dephlogiſticated air, 15, .75 of heavy inflammable air, 19, .02 gr. of phlogiſticated air, and 4, .77 gr. of light inflammable air*. But if the fixable air ſhould acquire an aeriform ſtate, and ſo paſs over in decompoſing nitrous acid by heat, we ſhould obtain the following proportion, viz. 38, .17 gr. of fixable air, 38, .04 of dephlogiſticated, 19, .02 of phlogiſticated air, and 4, .77 of light inflammable air, which in its aeriform ſtate ſhould occupy nearly the ſpace of 200 cubic inches under the common preſſure and temperature of the atmoſphere; or if it ſhould during the proceſs be condenſed into water, 100 cubic

* The variation and increaſe of weight which the preſence of water muſt neceſſarily produce in all aerial bodies are not here conſidered.

inches of dephlogisticated air must contribute to it: if this were the case, dephlogisticated air could never be obtained during the decomposition of nitrous acid.

I calcined 4 ounces of purified fixed vegetable alkali, to avoid any matter that may afford the inflammable principle of fixable air. On this I poured, diluted with distilled water, $\frac{1}{4}$ more of the pure nitrous acid, obtained in the manner above described, than was sufficient to saturate it. Having digested it for half an hour in a matrass, I charged it into a coated glass retort, and exposed it to a gentle heat, until all the water and superabundant acid were expelled. I then gradually raised the fire until the decomposition of the acid commenced. The first measure rendered lime water turbid, but the contraction was hardly measurable.

Measure 2 ditto.
3 ditto.
4 ditto.
5 ditto.
6 ditto.
7 less turbid.
8 ditto.
9 ditto

Measure

Meaſure 10 hardly rendered lime water turbid.

16 no appearance of fixable air, and continued ſo until the charge diſſolved the retort. The quantity of fixable air obtained here could not amount to more than a cubic inch, and I make no doubt but this is an ample allowance for it, though 400 meaſures were obtained before the retort failed. As I made this experiment only with a view to aſcertain the preſence of fixable air, I attended to nothing elſe.

If fixable air be a neceſſary principle in nitrous acid, what became of it in the above proceſs? If it had been decompoſed, we ſhould have obtained inflammable air, either light or heavy, neither of which was obtained. I frequently had an opportunity of examining the reſiduary alkali after the nitrous acid had been wholly expelled, and never could obtain from it either nitrous or fixable air, though there is generally an ebullition on the addition of an acid, occaſioned by the generation of heat. I aſk, what becomes of the 4, .77 grains of pure phlogiſton, or the matter of light inflammable air, contained, as Mr. Kirwan ſuppoſes,

poses, in every hundred grains of pure dry nitrous acid? As has been observed above, no inflammable air had been produced; and to suppose phlogisticated air to contain light inflammable air, is an hypothesis founded upon such weak grounds, that the phlogistians cannot produce one single instance to prove it. Even Mr. Kirwan himself, who is so strong an advocate for phlogiston, seems to doubt its presence in phlogisticated air; for he says, * "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 acid formed of this air, and dephlogisticated air, was found strongly phlogisticated, and since the phlogisticated nitrous acid is constituted such by its union to nitrous air, it is evident that phlogisticated air must contain phlogiston, if nitrous air contains any." Besides, according to Mr. Kirwan, the phlogisticated air in the nitrous acid contains its own proper phlogiston, together with the 4, .77 gr. of pure

* Essay on Phlogiston, p. 40.

phlo-

phlogiſton; ſo that it cannot be ſaid they were expended in forming phlogiſticated air. Therefore the only way left to account for them is, that they united to a portion of dephlogiſticated air, and formed water. 4, .77 gr. of light inflammable air require about 34 grains, or 100 cubic inches of dephlogiſticated air to condenſe them into water, and there are but 4 gr. more of dephlogiſticated air left, according to Mr. Kirwan himſelf. If this were to take place, we ſhould obtain the following products from every 100 gr. of pure dry nitrous acid, viz. phlogiſticated air 19, .02 gr. fixed air 38, .17 gr. water reſulting from the phlogiſton, and dephlogiſticated air 38, .77 gr. dephlogiſticated air 4 gr. How far this proportion correſponds with the products of the different airs obtained from nitre, I leave my chemical reader to judge.

Mr. Cavendiſh repeated his proceſs for making nitrous acid on a tolerable large ſcale laſt ſpring *. Dr. B———y, another gentleman, and myſelf, have had the pleaſure of ſeeing it. The tube which confined the airs and ſoap-lees was accidentally

* Anno 1788.

raiſed out of the mercury the day before, which gave me an opportunity not only of ſeeing but of taſting the nitre, which was in ſmall cryſtals on the ſurface of the mercury. It does not appear that Mr. Cavendiſh uſed fixed air in the above proceſs. But Mr. Kirwan attempts to obviate this by ſaying, that a ſufficiency of fixable air may be ſuſpended in the fluids worked upon. This could not be the caſe; for as Mr. Cavendiſh uſed ſoap-lees, he muſt neceſſarily paſs his airs in it, ſo that no fixable air could be ſuſpended. It may be ſaid, that the ſoap-lees itſelf was not entirely free from fixable air. Even allowing this, it could have no ſhare in the formation of the nitrous acid, as it muſt be formed by the union of the dephlogiſticated and phlogiſticated air, before they can unite to the alkali.

I mixed three parts of light inflammable air, and two of dephlogiſticated air, which ſtood ſeparately over lime 24 hours. The dephlogiſticated air contained $\frac{2}{10}$ of phlogiſticated air. I inflamed 7 meaſures, or about 2 cubic inches of this, which left a reſiduum of $\frac{1}{4}$ of the charge, which meaſured $\frac{1}{4}$ of an inch. I added another charge to this reſiduum, and after inflammation it increaſed to half an inch. I inflamed a third charge, expecting a proportionable increaſe of reſiduum; but here I was deceived; for it contracted to $\frac{1}{4}$ of an inch, being only the reſiduum of one charge. I continued the operation with nearly the like ſucceſs, until the reſiduum got too large. I fired 12 charges in all, and the quantity of condenſed liquor was by eſtimation about 4 gr. The ſurface of the mercury and braſs conductors were much corroded. I let up a quarter of an ounce of diſtilled water, with about 2 drops of cauſtic fixed alkali, and left the whole to ſtand for a few hours. I then filtered the liquor, and evaporated it to dryneſs. I collected the ſalt, which weighed $1\frac{1}{2}$ gr. it ſeemed not to be ſaturated, for it attracted moiſture ſtrongly; but ignited upon paper, it detonated like nitre. Thus it appears that nitrous acid had been formed in the above proceſs, though I am certain that neither the inflammable air, nor the dephlogiſticated air, contained an atom of fixable air. It cannot be urged that the dephlogiſticated and in-

flammable

flammable air by their union furniſhed fixable air; for I hope I have already ſhewn that they conſtitute no ſuch thing.

When I uſed very pure dephlogiſticated air, no ſenſible portion of nitrous acid was produced, unleſs the dephlogiſticated air predominated, and then there was very little procured. Hence we may conclude, that nitrous acid was formed in the above proceſs, in conſequence merely of the preſence of phlogiſticated air. When the above proportions were reverſed, that is, when the inflammable air predominated, though the dephlogiſticated air contained a large quantity of phlogiſticated air, little or no nitrous acid was formed, which ſhews the ſuperior attraction of light inflammable air to dephlogiſticated air. Thus we find, provided the proportion be adjuſted, that two proceſſes may be carried on at once, viz. the formation of nitrous acid and water. I am confident, if we could get entirely rid of the phlogiſticated air, that water may be produced in the above proceſs in whatever proportion we mix our airs, without a particle of nitrous acid.

These

Theſe facts muſt be ſufficient to convince an unprejudiced perſon, that fixable air is not one of the conſtituent principles of nitrous acid, and that phlogiſticated air is abſolutely neceſſary to its conſtitution, and that the gravitating matter of light inflammable air, as ſome philoſophers are pleaſed to ſuppoſe, is not one of the conſtituent parts of nitrous acid.

The formation of nitrous acid, without the preſence of fixable air, or the materials to compoſe it, and the reſolution of this again into its conſtituent principles, without the production of fixable air, muſt carry with them the utmoſt conviction. It may be ſaid, that fixable air was produced during the decompoſition of the above charge of nitre; but can it be ſuppoſed that 1, or even 8 cubic inches of fixable air, could render ſo highly acid as well as cauſtic, the quantity of nitrous acid that will ſaturate four ounces of fixed alkali? Beſides, the fixable air obtained, was expelled at the commencement of the proceſs; and before $\frac{1}{100}$ part of the acid could be decompoſed, a true ſign that it was rather an extra production proceeding from ſome impurity in the nitre, than one of the conſtituent principles of the nitrous acid; for if fixable air were one of the conſtituent parts of this acid, we ſhould obtain it equally copious at every period of the proceſs, particularly when its extrication depends upon the decompoſition of the acid, and likewiſe when we know that the alkali, after the decompoſition of the nitre, contains no fixable air. Indeed the alkali, from its attraction to fixable air, if the nitrous acid could furniſh this, ſhould be obtained in a mild ſtate; on the ſame principle that the alkali of foliated tartar is, after its decompoſition. For though foliated tartar requires a ſtrong heat towards the end of the proceſs to completely decompoſe the acid, yet the alkali is always obtained in a mild ſtate. Hence the reaſon why we obtain leſs fixable air in the beginning, than towards the latter end of the proceſs.

Conſidering the univerſality of fixable air from putrefaction, combuſtion, and reſpiration, proceſſes which muſt neceſſarily be carried on wherever mankind exiſts; and likewiſe conſidering, that all animal

and

and vegetable ſubſtances contain more or leſs of this in a combined ſtate, and that they are chiefly compoſed of one of its conſtituent principles, and that nitrous acid contains the other principle, it is not to be wondered at, that we ſhould obtain more or leſs fixable air in all proceſſes wherein nitre is uſed. Indeed, it is impoſſible for the moſt accurate experimentaliſt to guard againſt impregnations that may be productive of fixable air, 1ſt, Becauſe the atmoſphere is not only impregnated with aerial acid already formed, but is likewiſe loaded with moats that may adhere to our materials. 2dly, Our breath whilſt we are preparing our charge, and inſenſible perſpiration in addition to theſe, may all contribute to the generation of aerial acid.

I charged ſome ounces of common ſaltpetre, procured at the druggiſt's, into a coated glaſs retort. This I placed in a reverberating furnace; and when the air of the veſſels was expelled, I examined the firſt meaſure, which rendered lime water turbid; but the contraction was ſcarcely meaſurable. The meaſure I uſed contained about 8 cubic inches, and the proportion of fixable air was as follows:

Meaſures.			Fixable Air.
2	—	—	$\frac{1}{30}$
4	—	—	ditto.
6	—	—	ditto.
7	—	—	$\frac{1}{27}$
9	—	—	$\frac{1}{20}$
12	—	—	$\frac{1}{16}$
14	—	—	$\frac{1}{16}$
18	—	—	$\frac{1}{12}$
19	—	—	ditto.
26	—	—	$\frac{1}{23}$
30	—	—	$\frac{1}{26}$

40 ſcarcely meaſurable.

50 by conjecture, ſcarcely ſenſible.

60 no appearance of fixable air, and continued ſo during the whole proceſs. The greater quantity of fixable air procured here than in the former proceſs, proves that its production muſt be occaſioned by the impurity of the nitre.

All ſpongy bodies, or the moſt compact ſubſtances when reduced to powder, will, though they may not have any chemical attraction to it, condenſe a ſmall quantity of fixable air by capillary attraction. Even nitrous

nitrous acid will condenſe a ſmall quantity of fixable air, though it will not enter into chemical union with it.

I deflagrated 2 ounces of pure nitre, prepared as above deſcribed, with about 7 dwts. of freſh made filings of zinc; and when the maſs cooled, diluted vitriolic acid did not diſengage a particle of fixable air from it. The ſame quantity of iron filings and nitre, after deflagration, yielded a ſmall quantity of fixable air. If the fixable air proceeded from a decompoſition of the acid in this laſt experiment, why was not the ſame quantity of fixable air produced when zinc filings were uſed? Or, if the fixable air was produced in conſequence of an union of the dephlogiſticated air of the nitrous acid and the phlogiſton of the iron, why did not a ſimilar union take place when zinc filings were uſed? for, if the one contains phlogiſton, the other muſt. If the difference ſhould be attributed to the greater quantity of phlogiſton in iron than in zinc, I would anſwer, that this could make no difference, when there is a ſufficiency in both to decompoſe the whole of the nitre. Beſides, as I have obſerved before, light inflammable air and dephlogiſticated air have never been known to form fixable air. I would likewiſe aſk, what becomes of the phlogiſton of the metal during deflagration? for, according to Mr. Kirwan, the dephlogiſticated air of nitrous acid is already attached to phlogiſton.

If nitrous acid were compoſed of the principles Mr. Kirwan ſuppoſes; and likewiſe, if metals were compoſed of a certain baſis and phlogiſton, nitre would never be decompoſed by metallic ſubſtances. The phlogiſton of the metal being oppoſed by the phlogiſton of the nitrous acid, can have nothing to do in the decompoſition; and as the union of all the ingredients nitre is compoſed of, is diſſolved when the dephlogiſticated air is withdrawn from them, the metallic baſis alone muſt overcome the following forces to unite to the dephlogiſticated air, viz. 1ſt, The force whereby the nitrous acid and the alkali attract each other. 2dly, The force whereby the phlogiſticated air attracts dephlogiſticated air. 3dly, The force whereby nitrous baſis attracts fixable air; and laſtly, the attraction of their pure phlogiſton to all

theſe;

theſe; let us add to theſe forces, the attraction of the metallic baſis on the other ſide to its own phlogiſton. Therefore, if the metallic baſis ſhould attract dephlogiſticated air ſo forcibly as to overcome all theſe collectively, can it be ſuppoſed that it would yield it again to phlogiſton, or that it would exchange it for phlogiſton? Undoubtedly not; though an allowance be made for the agency of fire in this circumſtance.

If we conſider nitrous acid to be compoſed of what in my opinion it really is, namely, dephlogiſticated air and phlogiſticated air, and metals to be compoſed of two principles, viz. earth and phlogiſton, we may account for the decompoſition of nitre upon a very rational principle; viz. the joint attraction of phlogiſton and its metallic baſis for dephlogiſticated air. But we cannot account for the revivification of metallic calces again by inflammable air, upon this principle, conſidering that the phlogiſton or light inflammable air of the metal muſt reſiſt it, and likewiſe that the attraction of the metallic basis itself to dephlogisticated air adds to this resistance.

It is true, it may be justly observed, that intense heat may weaken the union of the dephlogisticated air, the metallic basis, and its phlogiston, and thereby enable uncombined phlogiston, or light inflammable air, to unite to the former, or, what is the same in effect, to the metallic basis, and disengage its own phlogiston and dephlogisticated air in the state of water.

If we admit this mode of reasoning, it proves, that the metallic basis has greater attraction to inflammable air or phlogiston, than to dephlogisticated air alone, or than to dephlogisticated air and phlogiston jointly.

This, considered abstractedly, appears certainly very plausible; but, if we take a more extensive view of the subject, we shall find, that it will not correspond with other connected facts. For if iron had stronger affinity to phlogiston, or light inflammable air, than it has to water, or to dephlogisticated air simply, light inflammable air could not be produced from iron filings and water in a boiling heat, whether it comes from the water or metal; or much lefs could this be produced by paffing fteam over the furface of red-hot or fufed iron, particularly over the latter, as in this ftate it feems to retain its phlogifton with greateft force, if affuming a metallic ftate be fuch. Do not all the calcinable metals in the dry way, mercury excepted, unite to dephlogifticated air in the ftrongeft degree of heat that our furnaces can produce? And will not inflammable air reduce thefe again to their metallic ftate in the fame degree of heat? Therefore dephlogifticated air cannot be retained in metallic calces by the double force of the metallic bafis and inflammable air, or its condenfed phlogifton. If, as I believe I have already obferved, the union of dephlogifticated air depended on the metallic phlogifton alone, inflammable air, by the affiftance of heat, would decompofe it. But, then, would this take dephlogifticated air from water? Indeed, I might as well have afked, if vitriolic acid would take fixed vegetable alkali from vitriolic acid? For furely phlogifton cannot take dephlogifticated air from phlogifton, more efpecially when it is already attached to the metallic bafis.

These circumstances strictly considered, it appears to me, that in order to connectedly and consistently account for the decomposition of the different bodies into whose composition dephlogisticated air enters by metallic substances, sulphur and phosphorus, phlogiston must be left out.

If we consider metals as simple bodies, and of course destitute of the gravitating matter of light inflammable air; and likewise nitrous acid as a substance composed of phlogisticated and dephlogisticated air only, we may be able to account for the decomposition of nitre and nitrous acid, by the different metals, &c.

It has been observed, that metals have greater attraction to dephlogisticated air than sulphur, and sulphur than light inflammable air. Light inflammable air has greater attraction to dephlogisticated air than phlogisticated air has. Let us, in order to be the more explicit, suppose these different bodies to attract dephlogisticated air with the following forces:

Metals	—	—	7,
Sulphur	—	—	6,$\frac{7}{8}$
Light inflam.		—	6,$\frac{5}{8}$
Phlog. air	—	—	3,

Let

Let us likewiſe ſuppoſe fixed alkali to attract nitrous acid with the force of 4, which in addition to 3 enables the nitre to retain its dephlogiſticated air with the force of 7. Hence filings of iron or zinc, though they will decompoſe the nitrous acid itſelf, will not decompoſe nitre in powder, or in ſolution, in a common temperature. The conſtituent principles of nitre attached with the above force, will recede from each other when expoſed to heat by the interpoſition of fire, whereby their union or mutual influence is weakened; and this diminution of the force of their attraction, is in a duplicate ratio to the ſquares of their diſtances. Metallic ſubſtances, having their ultimate particles likewiſe removed from each other when expoſed to heat, by which their aggregate influence is diminiſhed, attract dephlogiſticated air with the greater force.

Theſe circumſtances enable us to account for what takes place when we project nitre and zinc, or iron, or charcoal, and ſulphur, into a red-hot crucible.

That famous philoſopher, and accurate experimentaliſt, Mr. Lavoiſier, having mix-

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ed and reduced into a moſt ſubtile powder 708,6 grains of nitre, and 93,52 of charcoal, preſſed them into a copper tube, and after ignition introduced the tube, with its aperture turned down, under a jar of water, where the whole of the charcoal was conſumed, and the nitre decompoſed. The products were as follow:

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

Mr. Lavoiſier was juſtly led to conclude from this experiment, that nitrous acid was compoſed of dephlogiſticated and phlogiſticated air, and that the latter was in the proportion of $\frac{1}{5}$ of the whole of the acid; and likewiſe, that fixable air was compoſed of the matter of charcoal and dephlogiſticated air.

The accuracy wherewith this experiment was performed, and the inferences drawn from it (particularly at a time when the conſtituent principles of nitrous acid were unknown),

unknown), ſhew the excellency of this great philoſopher. There were 6,49 gr. miſſing, which muſt certainly be water. Indeed, conſidering the quantity of water in nitre, and likewiſe that the airs were produced in water, the loſs of weight was very inconſiderable. In my opinion, 100 gr. of pure nitre contain, of

Cauſtic alkali	—	57 grains.
Dephlogiſticated air	-	27
Phlogiſticated air	—	,6
Water —	—	10
	Total	100

From this ſtatement I am induced to think, that the 329,33 of fixable air produced in the above proceſs, contained the following proportion of its conſtituent principles, and water:

		Gr.
Dephlogiſticated air	—	191,
Charcoal —	—	89,52
Water —	—	48,81
	Total	329,33

59,8 of phlogiſticated air contain, beſides its real gravitating matter, 18 grains of water. The quantity of water held in ſo- lution

lution in both airs 66,81, in addition to 6,49, which was the loſs of weight, accounts for the water of the nitre and charcoal. The following is the proportion of the different ingredients contained in the whole charge:

		Gr.
Dephlogiſticated air	—	191,
Charcoal	— —	89,52
Water	— —	73,30
Phlogiſticated air	—	41,8
Cauſtic alkali	—	406,5
	Total	802,12

In decompoſing nitre *per ſe*, when the proper apparatus was uſed for collecting the different products, I always obtained water ſlightly acidulated; but, as this is produced in the beginning of the proceſs, I think, if the quantity of water contained in nitre were retained until the whole was decompoſed, the different fluids would diſſolve the entire of it, or rather more, if they could be properly ſupplied with it. Therefore fixable air holds leſs water in ſolution, than the quantity of dephlogiſticated air contained in it would in its ſimple ſtate.

ſtate. There is no poſſibility of aſcertaining the exact quantity of water 93,52 grains of charcoal would hold in ſolution; for, during its converſion into an aerial ſtate, a portion of the water is generally decompoſed, more eſpecially if too much be uſed, whereby we obtain fixable air and light, and heavy inflammable air, in various proportion. Hence we cannot actually prove the greateſt weight 93,52 grains of charcoal would acquire, on its aſſuming an aerial ſtate. The pureſt heavy inflammable air is that which is obtained from foliated tartar, and 5 parts of this require about 7 of dephlogiſticated air to condenſe them into fixable air; from which I infer, that 93,52 grains of charcoal, in order to arrive at the above pr portion, muſt hold much more water in ſolution in its elaſtic ſtate, than 191 grains of the matter of dephlogiſticated air, for there is very little difference in the ſpecific gravity of theſe two airs.

Mr. Kirwan ſuppoſes, that the whole of the fixable air produced in the above proceſs, does not reſult from the union of charcoal and dephlogiſticated air; but that the nitre itſelf yields 91, 86 grains of fixable air, as one of the conſtitu-

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ent principles of the nitrous acid; and according to him, 708, 6 gr. of nitre contain but 92 gr. of dephlogisticated air, besides the portion combined in the fixable air. 11,43 gr. of pure phlogiston, or the matter of light inflammable air, besides phlogisticated air, are intimately united to the above portion of dephlogisticated air, which at least are sufficient to convert 430 cubic inches, or nearly 146 grains, or, to make an ample allowance for water, 80 grains of the pure solid gravitating matter of dephlogisticated air, into water.

Thus, according to Mr. Kirwan, the quantities of combustible matter and dephlogisticated air contained in the above charge, exclusive of what was already combined in the form of fixable air, were in the following proportion, viz.

Charcoal — —	93,52 gr.
The gravitating matter of light inflammable air -	11,43 gr.
Dephlogisticated air —	92, gr.

Is this quantity of dephlogisticated air sufficient to saturate 11,43 gr. of light inflammable air, and consume 93,52 grains of charcoal? Undoubtedly not; and yet the

the whole of the charcoal was expended, and no inflammable air was produced. In my opinion, it needs no great ſhare of ſagacity to ſee into the fallacy of this doctrine. The above portion of combuſtible materials would require at leaſt 261 gr. of the pure gravitating matter of dephlogiſticated air, free from water, to conſume or burn them; a quantity far exceeding the whole of the acid.

I fuſed a quantity of nitre in a ſmall earthen tubulated retort, whoſe neck was elongated with a glaſs tube which immerged in water, and introduced into it 10,33 gr. of red-hot charcoal, which was expoſed to a ſtrong heat for half an hour. It was a whole piece, and the weight was aſcertained as ſoon as it was taken out of the fire. When it got in contact with the fuſed nitre, a rapid deflagration enſued, attended with a copious extrication of fixable air. When I obtained about 40 cubic inches of air the deflagration ceaſed, and the charcoal was about $\frac{2}{5}$ conſumed. The fixable air was very pure, containing but 7 cubic inches of phlogiſticated air. The difficulty of ſeparating the alkali from the reſiduary charcoal

charcoal without waſte, and the impoſſibility of conſuming the entire of a quantity of charcoal, as it muſt be uſed whole in this experiment, render it impracticable to exactly aſcertain the quantity of fixable air a given quantity of charcoal would yield; for, as ſoon as the nitre next the charcoal is decompoſed, the proceſs ceaſes. In order to obviate this inconveniency as much as poſſible, I introduced a long and flat piece of charcoal weighing 10 grains, into a freſh charge of nitre; and as ſoon as the deflagration commenced, I kept the charge in continual agitation; which, with the large ſurface the charcoal itſelf expoſed, enabled me to nearly conſume the whole. The quantity of charcoal left could not exceed 2 grains. I obtained 80 cubic inches of air, 67 of which were fixed air, and the remainder phlogiſticated air. Theſe proportions induce me to ſuppoſe, that either the charcoal Mr. Lavoiſier uſed contained phlogiſticated air, or that I uſed purer nitre than he did; or, which is very likely, that the nitre was only partially decompoſed in the above experiment, whereby phlogiſticated air had been retained.

As the charcoal ufed in this experiment contained neither water, phlogifticated, nor fixable air, being expofed to a ftrong heat for a confiderable time, (unlefs we admit that phlogifticated air is one of the conftituent principles of charcoal), 67 cubic inches of fixable air, or 31 gr. contain 8 gr. of charcoal, and the remaining 23 gr. are furnifhed by the dephlogifticated air and water.

That the real matter of charcoal enters into combination with dephlogifticated air, is hardly to be doubted, however fixable air is generated, whether by the combuftion of oils, fpirit of wine, refpiration, &c. or by uniting heavy inflammable air and dephlogifticated by the electric fpark. Sulphur will decompofe nitre with various refults and phenomena, according to the proportion ufed; if two parts of nitre and one of fulphur be mixed, the nitre is decompofed with detonation, and volatile vitriolic acid, dephlogifticated air, and phlogifticated air, are produced; as Mr Berthollet has obferved. The fame philofopher found that one part of fulphur and four of nitre will not detonate, though the nitre is decomposed, and nitrous air produced. He distilled 120 grains of nitre, and 30 gr. of sulphur, and obtained 108,8 cubic inches of nitrous air, at the same time that the whole of the nitre was decomposed. This experiment is explained in the following manner, by Mr. Kirwan*.

According to this philosopher, 120 gr. of nitre, contain 55 of acid, comprehending the water which is inseparable from it. Of these $\frac{2}{3}$ or 36,6 gr. are nitrous basis, which require 6,6 gr. of phlogiston to convert them into nitrous air; the remainder of the 55 gr. of acid is fixable air: the following are his proportions, viz.

Nitrous basis	36,6
Fixable air	18
	54,6

There are 2-10ths of a gr. unaccounted for. Mr. Kirwan having stated the principles of nitrous acid in the above proportion, supposes it to be decomposed by a double elective attraction, viz. the nitrous basis attracts the phlogiston of the sulphur, which he computes to be 6,6 gr. at the

* Essay on Phlogiston, p. 58-9.

same

ſame time that the dephlogiſticated baſis of the ſulphur unites to its fixable air; and as 18 gr. of fixable air, are too little to convert the dephlogiſticated ſulphur (as he is pleaſed to call it) into fixed vitriolic acid, they convert it into vitriolic air, which unites to the alkaline baſis of the nitre. This is certainly a very ingenious mode of reaſoning; but, in my opinion, it is not diſplayed in the cauſe of truth.

Mr. Kirwan, in the laſt ſtatement of nitrous acid, left out the 2,73 gr. of pure phlogiſton, which, according to himſelf, 55 grains of pure dry nitrous acid ſhould contain, and which is united to the nitrous baſis*.

Therefore, counting this with the 6,6 gr. of phlogiſton, which the baſis takes from the ſulphur, the 36,6 gr. of nitrous baſis muſt be united to 9,43 grains of phlogiſton, which ſhould increaſe the weight of nitrous air proportionably; ſo that, inſtead of 43,2, we ſhould obtain 46,03 grains of nitrous air.

Thus we find, according to Mr Kirwan himſelf, that 100 gr. of nitrous baſis muſt unite to 29,37 gr. of phlogiſton,

* Eſſay on Phlogiſton, p. 34.

though he ſays that 100 gr. of this, will take up but 22 of phlogiſton. I think 2,73 grains of the matter of light inflammable air, in 55 gr. cannot be ſo very trifling as to be over looked in a compound of which dephlogiſticated air conſtitutes the major part, more eſpecially when we conſider the quantity of dephlogiſticated air which 2,73 of light inflammable air is capable of converting into water.

I think it is needleſs to ſay much more on the hypotheſis of fixable air; it would be troubling my reader, and pointing out what, I flatter myſelf, he muſt be already convinced of. In my opinion, phlogiſton muſt be entirely left out, in order to explain the different phenomena that attend the two laſt experiments. In the firſt of theſe experiments, Mr Berthollet uſed two parts of nitre, and one of ſulphur: the nitre was decompoſed, and the ſulphur (to make uſe of the language of others) was dephlogiſticated. Phlogiſticated, and dephlogiſticated air, were produced, but no nitrous air. When the ſame philoſopher uſed four of nitre, to one of ſulphur, vitriolic air, and nitrous air, were produced, and the ſulphur was likewiſe dephlogiſticated; or (to make uſe of a more unexceptionable expreſſion) vitriolated. In both experiments, it ſeems, the ſulphur loſt its phlogiſton.

It appears extraordinary to me, if phlogiſton ſhould be one of the conſtituent principles, both of the nitrous acid and ſulphur, that we did not the rather obtain nitrous air, or, if not nitrous air, phlogiſton, or light inflammable air, when a greater quantity of ſulphur was uſed, than a leſſer. Mr. Kirwan attempts to account for this by ſaying, that the nitrous baſis itſelf is decompoſed when it meets with too much phlogiſton.

If the nitrous baſis were capable of uniting only to a limited quantity of phlogiſton, and that a greater portion was diſengaged in the proceſs, the ſurplus ſhould undoubtedly paſs over in the ſtate of inflammable air. Let us even, allow, for a ſhort time, the nitrous baſis to be decompoſed, when we uſe one of ſulphur, and two of nitre; and let our quantities be 120 of nitre, and 60 of ſulphur. According to Mr. Kirwan, 120 gr. of nitre contain 36,6 gr. of nitrous basis, and 24,4 gr. of this is dephlogisticated air. 60 gr. of sulphur must part with 13,2 gr. of phlogiston, in order to become volatile vitriolic acid; which in addition to 2,73, make 15,93 gr. of phlogiston: therefore, the charge contained, besides the quantity contained in the volatile vitriolic acid, and fixable air, which we have nothing to do with at present, 15,93 gr. of phlogiston, and only 24,4 gr. of dephlogisticated air. It contained moreover, 18 gr. of phlogisticated air. The phlogisticated air is obtained in this process; but the 15,93 gr. of phlogiston seem to be totally lost, for no inflammable air is produced. The only rational mode of accounting for this lost phlogiston is, that it united to the dephlogisticated air of the nitrous basis, and formed water. Is it possible for 24,4 gr. of dephlogisticated air to condense, or either to convert into water or fixable air 15,93 gr. of the pure solid matter of light inflammable air? Besides, dephlogisticated air is obtained in this process; the quantity I cannot determine, although I have repeated the experiment. If we even leave out the fixable air supposed to be contained in the nitrous acid, and admit its weight of dephlogiſticated air, which, with the dephlogiſticated air of the nitrous baſis, would amount to 42,4 gr. we ſhould ſtill find the quantity neceſſary to condenſe the phlogiſton, ſhort by 68 gr. at leaſt. It cannot be ſaid that this is converted into fixable air, from facts already adduced; beſides, the ſulphur is not more acidified here, than when nitrous air is produced; which could not be the caſe if fixable air were formed, and if this were the acidifying principle of the vitriolic acid. It is true, there is double the quantity of ſulphur here, that is uſed when we obtain nitrous air; but let it be conſidered, that 48 gr. of the ſolid matter of fixable air ſhould reſult from the above quantity of phlogiſton, or the matter of charcoal, which is the conſtituent principle of fixable air.

Theſe are my reaſons for objecting, as well to Mr. Kirwan's doctrine, as to that of the phlogiſtians at large. In my opinion, the decompoſition of nitre by ſulphur may be accounted for more rationally in the following manner.

Although I do not think ſulphur contains phlogiſton, or the ſolid matter of light inflammable air, I by no means ſuppoſe it to be a ſimple body, but to be, relatively to our knowledge of chemiſtry, as ſimple as the earths, or the two fixed alkalies; all of which I make no doubt will be analyzed at ſome future period, when the ſcience of chemiſtry will be more cultivated than at preſent, by men of genius, fortune, and leiſure.

Hence, I conceive the ultimate particles of ſulphur to unite in ſpecie to theſe of dephlogiſticated air, as phlogiſticated air does during the formation of nitrous acid, without loſing any thing but fire, which is always diſengaged when a chemical combination takes place.

Of the conſtituent parts of the nitrous acid I have given my opinion, as deduced from facts. I have likewiſe ſuppoſed dephlogiſticated air to be retained in nitre, with the force of 7, and ſulphur to attract it with the force of $6\frac{7}{8}$. I do not mean to intimate that theſe are their abſolute forces; but, nearly the proportion they bear to one another. Thus, ſulphur will not decom-

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pofe nitre, until expofed to heat fufficient to alter thefe forces. Nitre and fulphur mixed and comminuted, and put on hot iron, will not detonate, nor will the nitre be decompofed, though the fulphur will be burned out with a languid phofphore-fcent-like flame. Gunpowder alfo will not detonate, though the fulphur may be burned out with the fame phenomenon, as may be feen by putting a little on a hot cinder, foon after it lofes ignition. But, when nitre and fulphur are expofed to that degree of heat, which will fo relax the chemical tie of the conftituent principles of nitre, as to caft the fcale in favour of the fulphur, it will then rapidly unite to the dephlogifticated air of the nitre, and prefent the phenomena of combuftion and detonation.

Thus, two parts of nitre and one of fulphur will detonate when expofed to fufficient heat, at the fame time that the nitrous acid is wholly decompofed. Sulphur will not unite to more dephlogifticated air, in the degree of heat neceffary to conduct this procefs, than is fufficient to convert it into volatile vitriolic acid; or if it even

did,

did, its attraction is not ſtrong enough to take it from the nitre; as has been ſhewn in the third ſection of this work. Therefore we obtain, from the above proportion, volatile vitriolic acid, dephlogiſticated air, and phlogiſticated air; there is likewiſe ſome ſulphur ſublimed in the beginning of the proceſs. When one part of ſulphur, and four of nitre are uſed, the products are different; for then, the quantity of ſulphur being very ſmall, it preſents but a few ſurfaces when mixed with the nitre, ſo that it can only take the portion of dephlogiſticated air from the nitre which is over and above the quantity contained in nitrous air; thus the nitrous air, being deprived of its dephlogiſticated air, is readily expelled from the alkali. The reaſon no deflagration takes place is, the particles of ſulphur being but few, and interpoſed by the nitre, the quantity of fire diſengaged by the more intimate union of dephlogiſticated air to the ſulphur, is inſenſibly diſſipated; that is, it is not liberated in a ſufficient degree of accumulation, to preſent the phenomena of light and combuſtion. The reverſe takes place when a

greater

greater quantity of ſulphur is uſed: then the particles of ſulphur being more numerous, and of courſe, cloſer to one another, fire is diſengaged in a more concentrated ſtate; at the ſame time that the whole, nearly, of the dephlogiſticated air of the nitre is taken up. In order to deprive the nitre of the whole of its dephlogiſticated air, it is neceſſary to uſe more ſulphur than can unite to the dephlogiſticated air. 1ſt, Becauſe an ultimate particle of ſulphur can only take an ultimate particle of dephlogiſticated air from the nitre, whereby it forms volatile vitriolic acid. 2d, As every ultimate molecule of nitre contains, moſt commonly, four ultimate particles of dephlogiſticated air, and one of phlogiſticated air, which being enveloped thus in aggregates by alkali and water, are partly defended from the action of the ſulphur.

Therefore, as the former cannot be ſo ultimately divided as the latter; if only that quantity of ſulphur be mixed with the nitre, which will expoſe but ſurfaces enough to deprive the molecules of nitre of one half of their dephlogiſticated air, nitrous air is produced; but if, on the contrary,

trary, a ſufficiency be uſed to deprive the molecules of nitre of $\frac{3}{4}$ of their dephlogiſticated air, we obtain phlogiſticated, dephlogiſticated, and vitriolic air.

If four parts of nitre, two of ſulphur, and three of charcoal, be mixed and well powdered, they will burn rapidly, and emit a volatile vitriolic, and an hepatic ſmell. The entire of the ſulphur is not here converted into volatile vitriolic acid. The charcoal having greater attraction to dephlogiſticated air, unites to the moſt part of it, while a portion of the ſulphur unites to the alkali of the nitre. Hence ariſes the hepatic ſmell during the inflammation of gunpowder.

Charcoal detonates with nitre in various proportions, but will not diſengage nitrous air in any proportion whatever. If nitrous air were produced, in conſequence of a certain portion of phlogiſton, as Mr Kirwan ſuppoſes, a leſs quantity of charcoal than is ſufficient to decompoſe a quantity of nitre, ſhould diſengage it, if charcoal contains phlogiſton. I think this may be explained on the ſame principle with the deflagration of ſulphur and nitre. Charcoal and nitre diſtilled

diſtilled in various proportion, will afford phlogiſticated and fixable air, but not a particle of nitrous air is produced. I would aſk the phlogiſtians, why nitrous air is not procured here, when we obtain it from ſulphur and nitre under the ſame circumſtances?

Charcoal not only unites to a larger quantity of dephlogiſticated air, than ſulphur does, in order to become volatile vitriolic acid, but likewiſe attracts the portion neceſſary to its converſion into aerial acid with greater force. Thus charcoal mixed with nitre in a very ſmall proportion will detonate, and fixable and phlogiſticated air is produced. Every ſingle molecule of charcoal (for we cannot reduce it into its ultimate particles by attrition) is capable of deſpoiling a ſingle molecule of nitre of the whole of its dephlogiſticated air; and this decompoſition is ſo rapid, that the molecule of charcoal directs its whole attraction to the molecule of nitre, which firſt influences it; otherwiſe we ſhould expect that the charcoal would take a portion of dephlogiſticated air from different ni-

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trous molecules at the ſame time, and thereby diſengage nitrous air.

Metals decompoſe nitre, and preſent the ſame phenomena which charcoal does, but with a different reſult; for they produce little or no fixable air: and even the ſmall quantity obtained from ſome metals, particularly from iron, is ſo liable to vary, that its preſence appears to be accidental. Nitrous air is not produced during the decompoſition of nitre by iron filings. Mr Berthollet diſtilled 472,5 gr. of nitre, with 236,23 of iron filings, and obtained 453,37 cubic inches of air, of nearly the ſame ſtandard with atmoſpheric air*. In ſhort, all the imperfect metals will detonate with nitre, without producing a particle of nitrous air. As this is explicable on the ſame principle with charcoal and nitre, I ſhall not trouble my reader with it; but only obſerve, that if nitrous air were compoſed of nitrous baſis and phlogiſton, we could not but adjuſt the proportion of the nitre and metal favourable to the production of it, provided the metals contained phlogiſton.

* 2 pr. 217 mem. par. An. 1782, p. 495; and 1783, p. 85.

The regulus of arſenic put on red-hot iron, will burn with a flame. This does not indicate its greater attraction than other metals to dephlogiſticated air, but the weaker adheſion of its ultimate parts to one another. The white calx of arſenic, although it is capable of uniting to more air, will not preſent the ſame phenomenon.

The regulus of arſenic will detonate rapidly with nitre. Equal parts of the white calx of arſenic and nitre, projected into a crucible hot enough to fuſe them inſtantly, will not detonate. Two of nitre and one of the calx will not detonate. Three parts of nitre and one of arſenic exhibit a few brilliant ſparks here and there; as do likewiſe two of arſenic and one of nitre, provided the crucible be very hot: but it ſeems to me to proceed from a few reguline particles, accidentally interſperſed in the calx; otherwiſe the deflagration muſt have been more general. Nitrous air is produced from either of theſe proportions, but in a larger quantity when two of nitre and one of arſenic are uſed. Hence, we find that the regulus of arſenic *per ſe* will unite to dephlogiſticated air, and preſent the phenomenon of com-

combuſtion, and that the calx will not; and likewiſe that the regulus will detonate with nitre, and that the calx will not; and laſtly, that nitrous air is produced by the calx, and none by the regulus. Let us view theſe facts narrowly, and comparatively, and we ſhall find that they tend much to corroborate the foregoing explanation of deflagration, and the production of nitrous air.

That the regulus of arſenic combines with a certain portion of dephlogiſticated air, and that on this union depends its calciform ſtate, is unqueſtionable; and likewiſe that the calx of arſenic will unite to more air, is beyond a doubt, as ſhall preſently appear. Thus then, the regulus of arſenic, having greater attraction to dephlogiſticated air, and being likewiſe capable of uniting to a larger quantity than the calx, as being already nearly ſaturated with it, wholly decompoſes the nitre; and as a great number of the particles of dephlogiſticated air unite with ſuch rapidity and accumulation, in a given time, the phenomenon of combuſtion is produced.

When we take the calx, the reſult and appear-

appearances are different from the former; becaufe, being already combined with dephlogifticated air, it can only unite to a fmall portion of it, and this it even attracts with lefs force than the quantity neceffary to its calcination. Thus, it can take only a portion of its dephlogifticated air from the nitre; whereby, as has been already explained, we obtain nitrous air, at the fame time that no deflagration takes place.

The phlogiftians would explain the above facts by faying, that the different phenomena proceeded from phlogifton. Does the calx of arfenic contain phlogifton, uncombined to dephlogifticatedair? If it does, all the metallic calces contain phlogifton. Can any reafon be affigned for fuppofing the calx of arfenic to contain phlogifton, but its property of uniting to more dephlogifticated air? Or, is the production of nitrous air a fure fign that the bodies that difengage it, lofe their phlogifton? If fo, the following facts are quite repugnant to it. The white calx of arfenic expofed to heat, in a crucible, will decompofe nitrous acid, and difengage nitrous air very copioufly. Thus, if nitrous acid in fmall tities be poured on it, from time to time, when every preceding portion takes due effect, the arsenic is acidified. In conducting this process, the fire should be gradually increased, in proportion as the arsenic draws near a saturation with dephlogisticated air; for the violent ebullition that takes place, particularly in the beginning, swells the charge, and puffs it over. The fumes should likewise be guarded against. Marine acid, mixed with the nitrous acid in small proportion, expedites this process. If the acid of arsenic, thus prepared, be exposed to a stronger heat than is necessary to its formation, it yields dephlogisticated air, and the arsenic is reduced to the state of a calx, and no fixable air is produced.

If the nitrous air were composed of nitrous basis, and the vast quantity of phlogiston which the phlogistians suppose, the calx of arsenic must be deprived of a large portion of phlogiston in the above process; and if the presence of this phlogiston were necessary to the reduction of the acid into a calx again, how is it supplied? In my opinion, this is inexplicable in the phlogistic doctrine, unless we admit the hypothesis

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of fixable air; the fallacy of which, I flatter myself, my reader is already aware of. Mr. Kirwan would explain the above process by saying, that the fixable air of the nitrous acid unites to the calx, at the same time that its phlogiston unites to the dephlogisticated basis of the nitrous acid, and forms nitrous air; and that a stronger heat decomposes the fixable air, whereby its phlogiston remains attached to the calx, at the same time that its dephlogisticated air is expelled in an aerial state. As this mode of reasoning appears plausible enough for equivocation, it may be adopted in this one circumstance. But what correspondence does it bear to other connected facts? A concatenation of facts, which regularly correspond with each other, will always bring truth to light; although a number of facts ever so well understood or arranged, are seldom without a few, which may separately admit of a quibble, for those who wish to confound truth with falsehood, either out of a spirit of obstinacy, prejudice, or a desire of displaying their ingenuity. Hence arise so many theological controversies, as well as difference of opinion in

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philoſophy. But happily for mankind, the moſt ingenious projects, which the moſt fertile imagination can produce to ſuppreſs truth, generally appear, ſooner or later, as ſo many evidences in her favour.

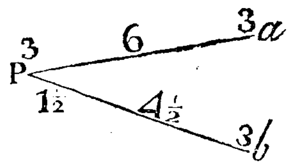
Having treated of the decompoſition of nitre, I am now to inquire into the nature of nitrous acid in its ſimple ſtate. In order to well underſtand the variety of changes which this acid is capable of undergoing by the mediation of different ſubſtances, it will be neceſſary, firſt, to be acquainted with the force by which its conſtituent principles are united.

In my opinion, the pureſt nitrous acid contains 5 of dephlogiſticated to 1 of phlogiſticated air. Nitrous air, according to Kirwan, contains 2 of dephlogiſticated to 1 of phlogiſticated air. According to Lavoiſier, 100 gr. of nitrous air contain 32 gr. of phlogiſticated air, and 68 of dephlogiſticated air. I am myſelf of the former philoſopher's opinion: I likewiſe am of opinion, that every primary particle of phlogiſticated air is united to two of dephlogiſticated air, and that theſe molecules

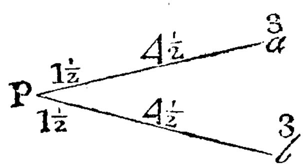
lecules are ſurrounded with one common atmoſphere of fire.

To render this more explicable, let us ſuppoſe P to be an ultimate particle of phlogiſticated air, which attracts dephlogiſticated air with the force of 3; let *a* be a particle of dephlogiſticated air, whoſe attraction to P we will ſuppoſe to be 3 more, by which they unite with the force of 6: the nature of this compound will be hereafter explained.

Let us conſider this to be the utmoſt force that can ſubſiſt between dephlogiſticated and phlogiſticated air.



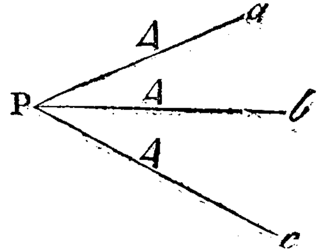
Let us ſuppoſe another particle of dephlogiſticated air *b* to unite to P, they will not unite with the force of 6, but with the force of 4½; that is, the whole power of P, which is but 3, will be equally divided and directed in two points towards *a* and *b*; ſo that P and *a b* will unite with the forces annexed to them;



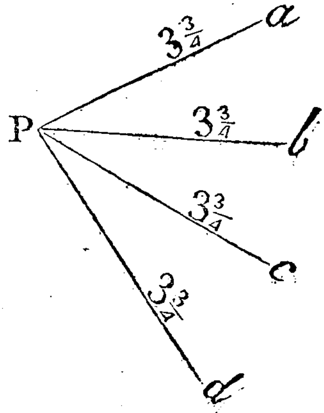
for the attraction of *a* and *b* to P meeting with no interruption, will

 ſuffer

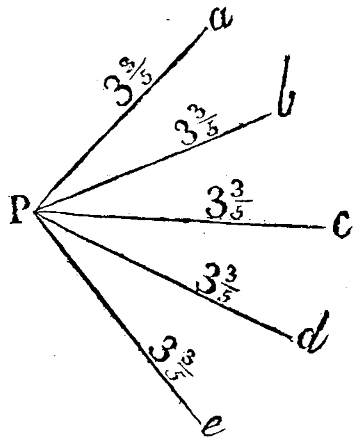
ſuffer no diminution. This I conſider to be the true ſtate of nitrous air. Let us now ſuppoſe another particle of dephlogiſticated air *c* to unite to P, it will combine only with the force of 4, whereby *a b c* and P will gravitate toward one another. Such is the ſtate of the red nitrous vapour, or the red nitrous acid.



Let us again ſuppoſe a fourth particle of dephlogiſticated air *d* to combine with P, it will unite only with the force of $3\frac{3}{4}$. This I think is the ſtate of the pale or ſtraw-coloured nitrous acid.



Laſtly, let us ſuppoſe a fifth particle of dephlogiſticated air *e*, to unite to P, it will combine with the force of $3\frac{3}{5}$, ſo that *a b c d* and *e* will each gravitate towards P as their common centre of gravity.



This is the moſt perfect ſtate of colourleſs nitrous acid; and in my opinion no more dephlogiſticated air can unite to the phlogiſticated air, as having its whole force of attraction expended on the particles of dephlogiſticated air, *a b c d e*. This illuſtrates the nature of ſaturation. Thence we find that dephlogiſticated air is retained with leſs force in the perfect or colourleſs nitrous acid, than in the ſtraw-coloured, or in the red, or in nitrous air. This explains the eaſy ſeparation of dephlogiſticated air from perfect nitrous acid, when expoſed to the ſun, or even to an artificial light or heat, at the ſame time that the nitrous acid is coloured*. If we expoſe nitrous acid in any other ſtate to the ſun, we do not obtain a particle of dephlogiſticated air, but moſt frequently red nitrous vapour.

If the red nitrous acid be expoſed to the air, it emits red nitrous vapour, and acquires a pale colour; becauſe nitrous vapour cannot take dephlogiſticated air from the pale, as the pale retains it with as great force as the red vapour attracts it. Nitrous air will deprive either the ſtraw-coloured or colourleſs nitrous acid of a portion of their dephlogiſticated air. The former, as Dr. Prieſtley firſt obſerved, acquires an orange colour, on combining with a portion of it; but, on uniting to more nitrous air, becomes green; and laſtly, when ſaturated with it, acquires a red colour, and aſſumes the ſtate of vapour. Nitrous air will not deprive the red nitrous acid of any portion of its dephlogiſticated air, on the ſame principle that the red nitrous acid

* Dr. Prieſtley found that dephlogiſticated air was produced from nitrous acid, by paſſing the electric ſpark in a ſmall quantity of common air confined in it. Vol. VII. p. 339.

will not decompoſe the pale nitrous acid, or the pale, the colourleſs.

Hence we find that nitrous air, though it cannot take dephlogiſticated air from the red nitrous acid, will take it from the pale; and likewiſe, although the red nitrous acid will not take dephlogiſticated air from the pale, that it will take it from the colourleſs.

If the colourleſs nitrous acid be mixed with water, it will preſerve its tranſparency; but the red nitrous acid treated in the ſame manner, will acquire a blueiſh green colour. Water in this caſe condenſes nitrous vapour ſo much, from its attraction to it, that it has the ſame effect as if a portion of it had been expelled.

Having premiſed thus much on the different ſtages of nitrous acid, I ſhall now proceed to the decompoſition of it again, and endeavour to explain it in as few words as perſpicuity will allow me.

If a metal be introduced into the red, pale, or colourleſs nitrous acid, it will be calcined, and nitrous air will be extricated; that is, it will deprive the nitrous air of that portion of dephlogiſticated air neceſſary to its condenſation, or to the formation of nitrous acid. The metal deprives the particles of acid in contact with it, of the whole of their dephlogiſticated air. The force of 7, with which we have ſuppoſed metals to attract dephlogiſticated air, being ſo much ſuperior to $3\frac{3}{5}$ if we make uſe of the colourleſs, or to $3\frac{1}{4}$ if we uſe the pale, together with the number of ultimate ſurfaces a metal muſt preſent, deprives the phlogiſticated air (of the nitrous acid) of its dephlogiſticated air, with ſuch quickneſs, that it is at once left deſtitute of both fire and dephlogiſticated air; but before it has time to collect an atmoſphere of fire, which would prevent a ſecond union, it exerts the force of 3 on its neighbouring particle of acid, which as yet did not reach the metallic influence, and thereby recovers that portion of dephlogiſticated air neceſſary to the formation of nitrous air. This again, in paſſing in the acid, if it be the pale or colourleſs, will recover air ſufficient to form nitrous vapour, or red nitrous acid. Thus it is, when firſt a metal is introduced into the pale or colourleſs nitrous acid, though a ſolution takes place, that little or

no

no nitrous air is produced, until the acid is coloured. As the metal, after it is calcined, requires red nitrous acid to hold it in ſolution (for perfect nitrous acid will not do, as ſhall hereafter appear), the nitrous acid, which the phlogiſticated air deprives of a portion of dephlogiſticated air, unites to it.

The foregoing explanation may appear, at firſt ſight, more ſpeculative than real. But does not the decompoſition of nitre by metallic filings, whether theſe be deflagrated in a red-hot crucible, or diſtilled by a more gentle and gradual heat in a retort, tend to confirm it? Is not the acid completely decompoſed here, whatever proportion of the materials be uſed? In this latter caſe, the metallic ſurface deprives the nitrous molecules, in contact with it, of the whole of their dephlogiſticated air; by which the phlogiſticated air, as having no ſenſible attraction to the alkali, is diſengaged in its ſimple ſtate, if uniting to fire be ſuch; for its attraction to dephlogiſticated air is not ſtrong enough to recover any portion of it from the joint force of phlogiſticated air and alkali.

I in-

I introduced ſome iron filings, recently prepared, into a mixture of about 16 parts of water, and 1 of pale nitrous acid: when they ſtood ſome time, phlogiſticated air was produced, but not a particle of nitrous air. It may be proper to acquaint my reader, that I gueſſed the above proportion; but as a variety of proportions will anſwer, the experiment cannot fail of ſucceſs. Here the few particles of the nitrous acid which come in contact with the metal, are wholly deprived of their dephlogiſticated air; and as the phlogiſticated air is at too great a diſtance from the molicules of nitrous acid, and as its attraction is too weak to decompoſe water, it inſtantly collects atmoſpheres of fire, which defend it, in its paſſage through the ſolution, from the action of the dephlogiſticated air of the ſuſpended acid.

When firſt I made this experiment, I obtained inflammable air, which puzzled me very much; but recollecting that I purchaſed the acid at a common chemiſt's, I immediately ſuſpected what I afterwards found to be true; for, on dropping the ſolution of ſilver in ſome of this acid, an im-

mediate

mediate cloudineſs ſucceeded: therefore I was obliged to have recourſe to this method of purifying it.

In order to ſeparate the whole of the marine acid from the nitrous acid, without an impregnation of nitrated ſilver, I would recommend both time and patience. A ſingle drop only of the ſolution of ſilver ſhould be uſed at a time, and the cloudineſs of each drop ſhould ſubſide before another is added.

This experiment not only confirms the foregoing explanation of the decompoſition of nitre and nitrous acid by metals, but likewiſe tends ſtrongly to confute the phlogiſtic theory. Here the metal is calcined, and there is neither inflammable nor nitrous air produced. Let us add to this an experiment already deſcribed, viz. the ſolution of iron in volatile vitriolic acid, without the production of inflammable air; and the decompoſition of this again by nitrous acid, without the extrication of nitrous air or phlogiſticated air, though the metal is calcined. Let the phlogiſtians explain theſe two laſt experiments on rational principles in their doctrine, and then I have done; unleſs

unleſs they ſuppoſe that phlogiſticated air itſelf is a compound of phlogiſton and ſomething elſe; and they might as well ſay, that the concrete matter of light inflammable air, or of dephlogiſticated air, is a compound: beſides, there is no phlogiſticated air produced by decompoſing a ſolution of iron in volatile vitriolic acid, by the nitrous acid. This experiment may be accounted for in the antiphlogiſtic doctrine, in the following manner:

The volatile vitriolic acid, as has been already ſhewn, diſſolves the iron, by which it is reduced into its primary particles, and diſperſed through the ſolution. Nitrous acid dropped into this, mixes likewiſe in the ſolution; and from the quantity of water which muſt neceſſarily be preſent in volatile vitriolic acid, and in nitrous acid, the ultimate molicules of both ſubſtances are removed from one another; whereby only a ſingle primary particle of iron can meet only a ſingle molicule of nitrous acid, which can ſupply it with both dephlogiſticated air of calcination and acid of ſolution; and thus no nitrous air is produced.

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The multiplicity of ultimate surfaces, which are as if it were concentrated, or crowded into so small a compass in metals, from the nature of their texture, is the chief cause of the decomposition of nitrous acid during their solution in it; particularly when the pale or colourless nitrous acid is used.

Mr. Lavoisier, to whom we are chiefly indebted for reducing this useful science into a rational system, and expelling that gloom which had overwhelmed it for all ages past, took 945 gr. of nitrous acid, whose specific gravity was 1,316, and to this he added 1104 gr. of mercury *. The whole of the mercury was dissolved, and he obtained 273,234 cubic inches of nitrous air. He afterward exposed the mercurial salt to a red heat, and obtained from it 287,742 cubic inches of dephlogisticated air, at the same time that the mercury was revived.

Mr. Lavoisier justly drew the following conclusions from the above experiment: 1st, That the weight of the airs produced

* Mem. Par. 1776, p. 670.

gave the weight of the real acid contained in 945 grains of ſpirit of nitre, whoſe ſpecific gravity was 1,316. 2d, That nitrous air was a conſtituent principle in nitrous acid; and that its production merely depended upon a portion of dephlogiſticated air being withdrawn from it, as it formed nitrous acid again on the reſtoration of its dephlogiſticated air. Laſtly, That the mercury loſes nothing; but that its calcination depended ſolely upon its union to dephlogiſticated air, as it had been revived by the mere expulſion of it again.

Mr. Kirwan objects to theſe concluſions *, 1ſt, Becauſe the whole of the acid could not be decompoſed, as a portion muſt have neceſſarily paſſed over during the diſtillation of the mercurial ſolution. 2dly, Becauſe it had not been proved by Mr. Lavoiſier, that the nitrous air was not produced at the expence of one of the conſtituent principles of the mercury. 3dly, As the ſame quantity of nitrous acid had not been produced by the re-union of both airs, and as there had been an exceſs of one of them.

* Eſſay on Phlogiſton, p. 63.

I do not ſee the force of the firſt of theſe objections; for what does it avail whether the acid was in part, or wholly decompoſed? The only inference that can be drawn from it, is, that the ſpirit of nitre uſed contained more real acid than Mr. Lavoiſier or Mr. Kirwan himſelf ſuppoſed; or, that the airs contained more water than they imagined, or ſomething elſe which did not exiſt in the ſpirit of nitre, and which of courſe the metal muſt impart. But Mr. Kirwan allows, that the airs do not acquire any additional weight from the mercury; for he ſays *, "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."

Mr. Kirwan's ſecond objection is certainly the only loop-hole left for the phlogiſtic theory, and for that reaſon requires

* Eſſay on Phlogiſton, page 67.

the ſtricteſt ſcrutiny. He ſuppoſes, as I have already obſerved, and as I ſhall mention here in a few words, that the mercury gives up its phlogiſton to the nitrous baſis, by which it is converted into nitrous air, at the ſame time that the fixable air of the nitrous acid unites to the metallic baſis and forms a calx. He likewiſe diſpoſes of another portion of phlogiſton, by ſaying, that it decompoſes part of the nitrous baſis, and forms fixable air by uniting to its dephlogiſticated air. The remainder of the phlogiſton, as he ſuppoſes, combines both with 19 grains of phlogiſticated acid that come over uncombined, and with the compound of acid and calx. After thus diſtributing the quantity of phlogiſton contained in the metal (and indeed he might have contrived to diſpoſe of as much again in the ſame manner), he ſuppoſes that the fixable air is decompoſed during the revival of the mercury; and that its phlogiſton unites to the metallic baſis, at the ſame time that its dephlogiſticated air is expelled in its ſimple aerial ſtate. But, as the quantity of phlogiſton in the fixable air is not equal to the quantity the mercury gives out in order

to

to become calcined, and of courſe inſufficient to revive the metallic baſis, he contrives to have this deficiency ſupplied by that portion combined with the acid and calx. This is Mr. Kirwan's opinion, and I muſt confeſs I do not ſee how he can juſtify it. Therefore, convinced that his method of ſupporting this hypotheſis carries with it no ſort of conviction, to avoid prolixity, I ſhall not enter into a detail of it, but refer my reader to the author's own words *.

Mr. Kirwan's calculating the quantity of phlogiſton contained in the ingredients uſed in the above experiment, does not in the leaſt tend to prove the preſence of the ſmalleſt quantity of phlogiſton, or the matter of light inflammable air. It is a very eaſy matter to make numbers agree with what never exiſted but in imagination.

The hypotheſis of fixable air being demonſtrably erroneous, the phlogiſtic doctrine appears very defective in the above experiment. The phlogiſtians muſt actually acknowledge, that either the metal or the nitrous air contains no phlogiſton.

* Eſſay on Phlogiſton, pages 67-8-9.

If nitrous air were composed of nitrous basis, saturated with phlogiston, how comes it to pass that metals are calcined in it?

Dr. Priestley fused some iron in nitrous air; it calcined and increased in weight, and nothing but phlogisticated air remained *. Mr. Kirwan explains this experiment by saying, that the dephlogisticated air of the nitrous air unites to both the phlogiston of the metal and to that contained in the nitrous air itself, and forms water, which unites to the metallic basis. Here he supposes a calx to be formed by the union of water to the metal, and in other circumstances by the union of fixable air. Is this consistent? 122 gr. of nitrous air, according to Mr. Kirwan, contain 22 gr. of phlogiston, 66,36 gr. of dephlogisticated air; or, to make a good allowance for it, let us say 68 gr. and the remainder is phlogisticated air. By this, the proportion the dephlogisticated bears to the inflammable air, is nearly as 3 to 1.

According to Mr. Lavoisier, the proportion of dephlogisticated air in water, is to the inflammable air as 7 to 1; and indeed,

* vi. Pr. 304.

agreeable to all experience, it is at leaſt 6 to 1.

Therefore, laying aſide the phlogiſton of the metal, after the condenſation of the dephlogiſticated air into water, we ſhould have a large reſiduum of inflammable air in the above experiment. Beſides, if metals be ſaturated with phlogiſton in their perfect ſtate, they muſt either part with it on uniting to water, or elſe, by the joint attraction of it, and the metallic baſis, unite with dephlogiſticated air ſimply, and leave the whole of the phlogiſton of the nitrous air behind.

The ſame excellent philoſopher reduced nitrous air, by taking the electric ſpark in it to $\frac{1}{3}$ of its bulk; nitrous acid was produced, and the reſiduum was phlogiſticated air. At another time he reduced nitrous air to $\frac{1}{4}$ of its original bulk by the electric ſpark, and the reſiduum contained $\frac{1}{4}$ of nitrous air *. He likewiſe, in one experiment, reduced one and a half meaſure to 0,4 of a meaſure, by electric exploſions taken in a veſſel of mercury, with water on the ſurface of it. The water was acid to the taſte, and his iron conductor was partly diſſolved.

* Vol. vi. p. 312.

Mr. Kirwan explains these experiments, by supposing, that the dephlogisticated air unites to the phlogiston of the nitrous air, and forms water; and that the nitrous acid produced was originally formed and suspended in the air. From what I have already said, it appears, if nitrous air contained phlogiston, we should have a residuum of inflammable air in these experiments, as not containing dephlogisticated air enough (according to Mr. Kirwan's own calculations), at least by $\frac{4}{7}$, to convert the whole of the phlogiston into water. July 1787 I repeated the above experiment (with a view different to the present); and, after passing the nitrous air in caustic volatile alkali, reduced it by repeatedly taking the electric spark in it to about $\frac{1}{4}$ of its bulk, nitrous acid was produced, and the residuum was pure phlogisticated air. Having narrowly attended to this experiment, I was at that time induced to suppose, but am now fully convinced, that nitrous acid is formed here in consequence of a decomposition of part of the nitrous air, whereby the remainder is furnished with dephlogisticated air, and so forms nitrous acid, at the same time that

gisticated

the phlogiſticated air of that portion of dephlogiſticated air that forms the new compound, remains ſingle and alone. Whenever Dr. Prieſtley diminiſhed nitrous air by fuſing iron in it, no acid (as he obſerves) was formed. He likewiſe found, that minium could not be reduced by the heat of his burning lens in nitrous air *. If the quantity of phlogiſton, which Mr. Kirwan ſuppoſes, exiſted in nitrous air, metallic calces ſhould be revived in it; but, on the contrary, metals are calcined in it. This muſt be very unfavourable to Mr. Kirwan's doctrine; for the ſuppoſition that nitrous air retains, as one of its conſtituent principles, the phlogiſton of the metal, is the whole ſupport of his theory; as, by this, he is enabled to ſay, that the fixable air is decompoſed by giving up its phlogiſton to the metal, whereby we obtain dephlogiſticated air in its ſimple aerial ſtate. But if the metal ſhould not loſe its phlogiſton, fixable air cannot by any means be ſuppoſed to be decompoſed; and of courſe, if it were one of the conſtituent parts of

* Vol. VI. p. 11.

nitrous acid, it ſhould be obtained from the calx in its natural ſtate. Indeed, if we compare the quantity of fire diſengaged, during the union of dephlogiſticated air and light inflammable air, or the heavy inflammable air, or even the ſolid matter of charcoal, ſulphur, and phoſphorus, to that developed during the rapid combination of nitrous air and dephlogiſticated air, we ſhall not heſitate a moment to ſay, that it unites in this latter to a ſubſtance quite different from either of the former ſubſtances, and that the compound is of a different nature. Dr. Prieſtley found, that nitrous air, confined above a year in contact with iron ſtanding in water, was reduced, and that the reſiduum was phlogiſticated air *. I have expoſed nitrous air to iron filings and water for three months; it was diminiſhed nearly $\frac{2}{3}$, and extinguiſhed a candle.

It is very well known, that iron expoſed to water alone will produce inflammable air; then if nitrous air were compoſed of light inflammable air, dephlogiſticated air and phlogiſticated air, we ſhould obtain

* Vol. ii. p. 177.

pure

pure phlogiſton, or light inflammable air, in the above experiment.

Is it not contrary to all laws, ſo far as experience has enabled us to judge, to ſuppoſe that iron, if it were ſaturated with phlogiſton, ſhould give it out in contact with water, which is compoſed of dephlogiſticated air and light inflammable air, at the ſame time that, expoſed under the ſame circumſtances to an aerial compound of light inflammable air, dephlogiſticated and phlogiſticated air, it ſhould abſorb an additional quantity of phlogiſton? This likewiſe appears the more extraordinary, when we find that iron, and other metals, unite in the dry way to a ſufficiency of dephlogiſticated air to ſaturate them; which ſhews, if they attract it in conſequence of phlogiſton, that they contain phlogiſton enough of their own, without the aſſiſtance of foreign phlogiſton. Hence I ſhould ſuppoſe, that iron could not influence the phlogiſton of nitrous air; or if it ſhould attract it and dephlogiſticated air jointly, that it muſt part with its own phlogiſton.

This circumſtance alone of metals withdrawing dephlogiſticated air from nitrous air,

air, and leaving only phlogisticated air behind, proves that either the metal or the nitrous air contains no phlogiston; and indeed, in addition to other adduced facts, it convinces me, that neither contains a particle of the matter of light inflammable air.

It is now very well known, that hepatic air is composed of light inflammable air and sulphur. If equal parts of hepatic air and nitrous air be mixed, they will contract to more than $\frac{3}{4}$ of their bulk. Sulphur will be precipitated, and the residuum is dephlogisticated nitrous air; which, as shall hereafter appear, contains no such thing as phlogiston. Is it reasonable to suppose, that hepatic gas should take light inflammable air, or phlogiston, from the nitrous air, when it is already saturated with what they call phlogiston? Dr. Priestley likewise reduced nitrous air to more than one half, by exposing Homberg's pyrophorus to it, which had taken fire in it, and the residuum was dephlogisticated nitrous air, and no acid was produced. These facts tend strongly to prove, that nitrous air does not contain the matter of light inflammable air.

Mr.

Mr. Kirwan's third and laſt objection does not appear to me to be of ſuch moment as the former. It is true, as this philoſopher obſerves, there had been an exceſs of dephlogiſticated air produced: I mean by exceſs, a greater quantity than the nitrous air obtained could condenſe in the ordinary way of mixing them.

The quantity of nitrous air obtained was 273,234 cubic inches, or 101,09 gr. and the dephlogiſticated air amounted to 287,743 cubic inches, or 97,83 gr. The above quantity of pure nitrous air contains 91,78 cubic inches of phlogiſticated air, and 182,156 cubic inches of dephlogiſticated air, which, in addition to the quantity expelled from the calx, make 469,898 cubic inches of dephlogiſticated air; which, ſubtracting 14,512 cubic inches from them, make five of dephlogiſticated air to one of phlogiſticated air, being the exact proportion of perfect nitrous acid.

By theſe calculations I find, if Mr. Lavoiſier uſed perfect nitrous acid, that the exceſs of dephlogiſticated air is not ſo great as Mr. Kirwan imagines. Before we attempt to judge of the exceſs of dephlogiſticated air, in the above experiment, the quantity of phlogiſticated air mixed with both the airs ſhould have been firſt aſcertained, by which we might eſtimate the quantity of nitrous air this would form.

Mr. Kirwan ſeems to make no allowance for this, though he acknowledges that phlogiſticated air is diſengaged, which partly mixes with the nitrous air, and partly unites to the fixable air combined with the calx; which, he ſays, is partly decompoſed during the decompoſition of the fixable air by the revivification of the mercury *. I do not underſtand what he means by the decompoſition of phlogiſticated air, for it has not, to our knowledge, been as yet decompoſed. Mr. Kirwan likewiſe mentions, that during the decompoſition of nitre *(per ſe)* a portion of the phlogiſticated air is decompoſed and burned, without any farther information on the ſubject. If he can decompoſe this, he certainly will do more than I at preſent ſuſpect.

Taking the foregoing circumſtances into conſideration, by what I can infer from Mr.

* Eſſay on Phlogiſton, p. 69.

Lavoiſier's

Lavoiſier's experiment, together with my own obſervations on the ſame ſubject, I think both the combined and uncombined phlogiſticated air muſt be to the dephlogiſticated as one to four, which is the portion of the pale nitrous acid. Can this be called an exceſs? Nitrous air is allowed to contain one of phlogiſticated to two of dephlogiſticated air: pure nitrous air will readily unite with half its bulk of dephlogiſticated air, and form the orange coloured nitrous acid. Every 54 gr. of this acid contain, including the water which the airs hold in ſolution, 41,665 gr. of dephlogiſticated air, and 12,335 gr. of phlogiſticated air. Therefore it contains 5 grains in 24 more than the red nitrous vapour does. Theſe proportions differ widely from thoſe of the perfect nitrous acid, which ſhews, though nitrous air will not readily unite to more air in the ordinary way than the proportion mentioned above, that it will in time condenſe a larger quantity. Analogous to this is the formation of vitriolic acid; for ſulphur will not combine during its combuſtion with much more dephlogiſticated air than is ſufficient to convert it into volatile vitriolic acid, but in time, by help of water, heat,

heat, and expoſure to air, it abſorbs a ſufficient quantity to form perfect vitriolic acid.

Red nitrous acid expoſed to dephlogiſticated air, will gradually abſorb it, and in time, if ſupplied with a ſufficient quantity of it, will become colourleſs. I repeated this experiment to my ſatisfaction in the year 1786. I do not claim the originality of it; it is to Dr. Prieſtley we are indebted, as well for this, as for his many other valuable experiments. The ſame philoſopher found, that fuming ſpirit of nitre, which is not the moſt perfect, phlogiſticates, as he is pleaſed to call it, common air*. He likewiſe obſerves, that the colourleſs nitrous vapour will not affect dephlogiſticated air, or vitiate common air †. I expoſed dephlogiſticated air to the perfect nitrous acid for three weeks, and it was not in the leaſt changed. I found, that the red nitrous vapour will diminiſh common air, but not ſo readily as the red nitrous acid. Though the perfect nitrous vapour will not diminiſh dephlogiſticated air, yet it has the reverſe effect, for it will readily contract nitrous air. This ſhews that it is fully

* Vol. II. p. 165. † Vol. II. p. 165.

ſaturated with dephlogiſticated air, and is in the ſtate already deſcribed. Dr. Prieſtley found, that melted nitre abſorbs dephlogiſticated air *. A ſolution of nitre, which had been melted, likewiſe abſorbed dephlogiſticated air. I have ſhewn, that nitre and vitriolic acid, heated together, abſorb dephlogiſticated air, whereby we obtain the moſt perfect nitrous acid. Hence it is evident we are not raſhly to conclude, that, becauſe dephlogiſticated and nitrous air will only unite in certain proportion, the compound will not take in more dephlogiſticated air under more favourable circumſtances. Theſe are my reaſons for differing from Mr. Kirwan, in his objections to Mr. Lavoiſier's concluſions reſpecting the decompoſition of nitrous acid by mercury.

As moſtly all animal and vegetable ſubſtances, which have an affinity to pure air, decompoſe nitrous acid on the ſame principle with the metals, I ſhall paſs them over in ſilence, except the two following. Charcoal does not decompoſe nitrous acid, even by help of digeſtion; the acid may

* Vol. II. p. 165.

be

be expelled from it in whitifh fumes. It is extraordinary, if nitrous air be produced in confequence of phlogifton, that it is not obtained in the above procefs; for the bafis of nitrous air will take phlogifton from the metals, and the metals will take it from charcoal; which proves, that metals, if they do contain phlogifton, hold it with greater force than charcoal. In fhort, almoft the whole of charcoal is phlogifton, if fuch we may call a fubftance which will wholly unite to dephlogifticated air, or, in other words, burn.

It is true it may be faid, that the attraction of the metallic bafis to the fixable air of the nitrous acid, enables the nitrous bafis, by virtue of a double affinity, to combine with its phlogifton during the folution; and that there is nothing in charcoal to attract the fixable air. In anfwer to this, I would obferve, that the production of nitrous air by oils and fpirits of wine and turpentine, contradicts fuch an hypothefis; for they contain nothing to attract fixable air, and they even produce uncombined fixable air, which ftrongly proves, if nitrous air contains phlogifton, that it can expel fixable

able air from its basis, in consequence of its superior affinity to it.

I have already shewn the difficulty of uniting charcoal to dephlogisticated air, notwithstanding their strong affinity to each other; and that this proceeds from the aggregate attraction of charcoal. I have likewise observed the necessity of applying heat sufficient to overcome this attraction, in order to combine charcoal with dephlogisticated air; and I think this is the most reasonable mode of accounting for the above experiment.

The carbonaceous matter is held in chemical solution, in oils and spirit of wine, by light inflammable air, water, and a small quantity of fixable air; therefore two substances contribute to the decomposition of nitrous acid in oils and spirit of wine, by which we obtain fixable air, phlogisticated air, and nitrous air, at the same time that water is likewise formed.

Mr. Proust found, that strong nitrous acid will set fire to charcoal, if it be rendered very dry *. He likewise remarked, that charcoal exposed a few hours to the

* Tourn. de Medicine, 1778.

air, after calcination, was unfit for the experiment. Charcoal, as Mr. Prouſt well obſerves, attracts moiſture very forcibly. Therefore the firſt effect of the charcoal on the nitrous acid, is to withdraw a portion of its water from it, by which it is rendered highly concentrated, at the ſame time that the condenſation of the water heats the charcoal in a ſmall degree, but ſufficiently to volatilize a nitrous vapour; which as ſoon as it reaches that portion of dry charcoal next the humid part, is condenſed by it, and generates heat enough to promote the decompoſition of the nitrous acid. Hence we find, why the experiment will not ſucceed if the acid be poured on the ſurface of the charcoal.

The effect of nitrous acid on blood is very ſingular; and though it has not much to do with what we are upon at preſent, yet, hoping that any fact relating to ſo intereſting a ſubject may be acceptable to my reader, I ſhall give as brief an account of it as I can.

Two parts of blood procured freſh at the butcher's, one of ſtrong nitrous acid, and about $\frac{1}{5}$ of the whole of water, were digeſted

gested in the heat nearly of boiling water (fresh portions of water being occasionally added), until the whole of the acid was expelled, when it acquired nearly the colour, and exactly the taste, of bile. When mixed with a large quantity of water, it acquired a fine yellow colour; and, on standing, deposited a substance of a brighter yellow, though the supernatant liquor still retained a yellow colour, and bitter taste, but not so intensely as when the precipitate was suspended in it.

The different stages of this process were well worthy of observation. No nitrous air was produced, and the acid was expelled in the state of a white vapour. I tasted the liquor at different periods of the process, and was highly pleased at the gradual progress of the bitterness in proportion as the acidity vanished. About the middle of the process the solution first tasted acid, but was quickly succeeded by a bitter sensation. It appears to me that the nitrous acid took dephlogisticated air from the blood; for though I used the red nitrous acid, it was expelled in a perfect state. At this time I had not leisure to make any farther inquiries into this ſubject, being buſy in aſſiſting at a public courſe of chemiſtry, at Oxford; nor have I had ſince an opportunity of enjoying the pleaſure I then promiſed myſelf in ſo intereſting an inveſtigation.

I think a ſeries of experiments made on this ſubject, could not fail of being productive of ſome benefit to mankind. For how can chemiſtry be better applied than in thoſe inveſtigations, which may tend to throw light on the different diſorders incident to man?

Dr. Prieſtley has diſcovered a ſpecies of nitrous air which ſupports combuſtion, deſtroys animal life, and is condenſible in water. This he has called dephlogiſticated nitrous air. I conſider dephlogiſticated nitrous air to be the laſt ſtage of nitrous acid, and to be leſs underſtood than the four preceding. I expoſed four equal quantities of nitrous air in different tubes, to a nearly equal proportion of iron and water. In three weeks the air was diminiſhed $\frac{1}{6}$, and the reſiduum extinguiſhed a candle, and reduced common air. In three weeks more it was reduced about $\frac{1}{4}$, and the reſiduum ſuffered a candle to burn in it faintly. When it ſtood a fort-

fortnight longer, the diminution was nearly ⅓ of its bulk, and a candle burned in the reſiduum with an enlarged flame. I let the other tube ſtand until the air contracted to more than ⅓ of its original bulk; the reſiduum was phlogiſticated air, and had the ſmell of volatile alkali. From the progreſs of theſe experiments, I did not heſitate to conclude, but that which is called dephlogiſticated nitrous air, is common nitrous air, deprived only of a portion of its dephlogiſticated air. Dr. Prieſtley found that nitrous air, which ſtood in contact with iron and water for four months, extinguiſhed a candle *. He likewiſe found that a candle burned with an enlarged flame in nitrous air which had been in contact with iron, over mercury, about ſix months. The ſame philoſopher found that nitrous air expoſed to liver of ſulphur for a day was diminiſhed ⅓ of its bulk; a candle burned in the remainder with an enlarged flame, and it was not in the leaſt diminiſhed by nitrous air †. I have frequently obſerved that nitrous air, when reduced to

* Vol. II. p. 177. † Vol. II. p. 178.

$\frac{2}{3}$ of its bulk, always admitted a candle to burn in it with an enlarged flame; but that in proportion as it got below this ſtandard, it ſupported flame ſo much the worſe, until it was reduced nearly to $\frac{1}{5}$, when it extinguiſhed a candle.

Theſe facts leave no room to doubt, but that dephlogiſticated nitrous air contains leſs dephlogiſticated air than the common nitrous air.

Dr. Prieſtley found that clean ſmall needles expoſed to nitrous air, confined in dry mercury, did not in the leaſt diminiſh it, though they had ſtood ſix or eight months in the ſame ſtate. But when he introduced a few drops of water, the air was diminiſhed in a few days, and continued ſo to do until $\frac{1}{3}$ diſappeared, and the reſiduum was dephlogiſticated nitrous air *. He likewiſe found that a quantity of nitrous air which had been expoſed nine months to iron filings, over mercury, was diminiſhed $\frac{1}{4}$, and a candle burned in the remainder, better than in common air, though a mouſe died in it. Theſe two experiments ſhew

* Vol. VI. p. 316.

that

that moiſture promotes the decompoſition of nitrous air. For, 1ſt, when the materials were perfectly dry, no ſenſible change took place in the nitrous air. 2dly, When water was added, the abſorption took place very ſoon. 3dly, When leſs moiſture was uſed, the decompoſition went on very ſlow. Hence it appears that the water is decompoſed, and that its dephlogiſticated air unites to the metal, at the ſame time that the dephlogiſticated air of the nitrous air combines with the inflammable air, at the very inſtant of its liberation, and regenerates water. I have already rather conjectured on what principle this laſt union takes place.

It is very well known that iron, when expoſed to a very dry atmoſphere, does not ruſt; and likewiſe that iron confined in water will yield inflammable air, though it will produce no inflammable air when advantageouſly expoſed both to water and dephlogiſticated air. Thus iron filings and ſulphur wetted with water, and expoſed to dephlogiſticated air, will yield little or no inflammable air, until the whole of the dephlogiſticated part is nearly abſorbed, and then inflammable air is produced in abundance. Dr. Prieſtley reſolved dephlogiſticated nitrous air into its conſtituent principles, viz. phlogiſticated and dephlogiſticated airs, by heating bits of dry crucibles in it *. He likewiſe rendered this air wholly immiſcible with water, by paſſing the electric ſpark in it, and it was of the ſtandard of 1,45. I repeated this experiment with a view to the preſence of fixable air, and inflammable air, but I could not detect a particle of either. It is evident from the correſpondence of theſe facts, that nitrous air and the dephlogiſticated nitrous air are compoſed only of two principles, namely, phlogiſticated and dephlogiſticated air, and that they only differ in the proportion of theſe; and likewiſe that neither contains a particle of light inflammable air, or fixable air.

It is the opinion moſt generally received from the formation of volatile alkali, during the diminution of nitrous air, by iron and water, that the property of dephlogiſticated nitrous air proceeds from a condenſation of a portion of its phlogiſti-

* Vol. VI. p. 332.

cated air. I was inclined to this myſelf; but when I conſidered the greater number of ſurfaces which the dephlogiſticated air muſt expoſe to the iron, than the phlogiſticated, being in the proportion of two to one; together with the greater affinity of dephlogiſticated air to inflammable air than the phlogiſticated, I began to be in ſuſpenſe. It is true, a portion of phlogiſticated air is condenſed, but the quantity is trifling in compariſon to that of the dephlogiſticated air; for generally $\frac{1}{3}$ of the bulk of a quantity of nitrous air is left unabſorbed, which is nearly the whole of its phlogiſticated air. There is no volatile alkali formed during the combuſtion of Homberg's pyrophorus in nitrous air, for it contains nothing to condenſe phlogiſticated air, and yet the reſiduary air after the combuſtion is dephlogiſticated nitrous air. The ſame may be obſerved with reſpect to the contraction of nitrous air, by liver of ſulphur: it can neither withdraw phlogiſticated air nor light inflammable air from it, and yet there is a reſiduum of dephlogiſticated nitrous air obtained, when the air is diminiſhed $\frac{1}{3}$. The

progreſs

progreſs of this laſt experiment may atteſt the truth of what I ſay.

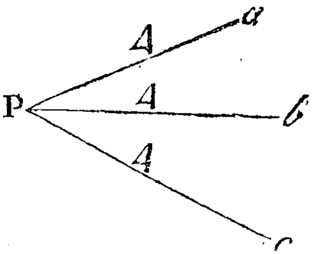
Indeed the method of procuring dephlogiſticated nitrous air, by the ſolution of metals in nitrous acid, favours the foregoing notions; for we can never obtain dephlogiſticated nitrous air from nitrous acid, until it is nearly ſaturated with a metal; and then by introducing more of the ſame metal, or a different metal, we obtain dephlogiſticated nitrous air.

In order to underſtand this, we muſt firſt conſider, that the nitrous acid which holds the metallic calx in ſolution, is in the ſtate of red nitrous acid; or rather more imperfect. Therefore, though the metal deprives the acid of ſolution in contact with it, of the whole of its dephlogiſticated air, yet the particles of phlogiſticated air recover a portion of it again from their neighbouring particles of acid, on principles which I have already endeavoured to explain.

To render this the more perſpicuous, let us ſuppoſe the acid of ſolution to be

P *a*

P *a b c*. Let *a b c* be its portion of dephlogiſticated air, combined with the annexed forces; if a metal be introdu-

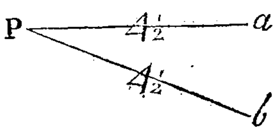


ced into ſuch ſolution, it will deprive P of *a b c*; then P being in contact with another particle of acid of ſolution, will inſtantly deprive it of either *a* or *b* or *c*. I ſhould ſuppoſe, from what has already been ſaid on this ſubject, that it would be ſuperfluous to explain here, why P cannot unite to *a b* or *b c*. I have ſhewn above, that the conſtituent principles of the new compound P—6—*a*, or dephlogiſticated nitrous air, are united with the force of 6.

It may at firſt ſight appear, that a metal introduced into the red nitrous acid in its ſimple ſtate, ſhould on this principle produce dephlogiſticated nitrous air. But be it conſidered, that though a particle of phlogiſticated air can only take one particle of dephlogiſticated air from a ſingle molecule of acid; yet that another molecule in its vicinity will ſupply it with another particle of dephlogiſticated air, by which perfect

perfect nitrous air is formed. This cannot take place in the metallic ſolution; for when once P is ſupplied with *a*, its power of attracting more dephlogiſticated air is ſo diminiſhed as to be equipoiſed, even by the weak attachment of the acid of ſolution to its ſuſpended metal.

Having thus endeavoured to explain the nature of perfect and imperfect nitrous airs, for ſuch I ſhall for the future take the liberty of calling them; we can readily account to a degree of certainty, why theſe do not affect each other when mixed. Let *p*—6—*a* be imperfect nitrous air, and P—*a*—*b* perfect nitrous air;



if theſe be mixed, P—*a* cannot take *a* or *b* from P, for P retains them both with as great force as P—*a* can attract either. Why this ſpecies of air is more ſoluble in water than the perfect nitrous air, is what I cannot account for, unleſs it be from the ſmallneſs of its atmoſpheres of fire, which admit the molecule of air to come within the gravitating influence of the water. It is rather remarkable, that

the

the imperfect nitrous air should favour combustion, when the perfect nitrous air, though it contains more dephlogisticated air, has the reverse effect. It is likewise very singular, that the perfect will unite to more dephlogisticated air in a common temperature, and that the imperfect will not, though it has greater attraction to dephlogisticated air than the former.

That the red nitrous vapour, which contains much more dephlogisticated air, with less force than the two former, should not favour combustion, is still more singular. Again, why Homberg's pyrophorus, as has been observed by Dr. Priestley, will burn in perfect nitrous air, and not in the imperfect, is difficult to be accounted for; unless it proceeds from a better supply of moisture by the one, than by the other.

As these facts cannot be satisfactorily accounted for, I think it better to suspend my opinion, than to attempt plausible explanations, which are generally more productive of evil than good, and only serve as so many allurements to decoy us out of the right path.

If we consider that neither light nor

heavy inflammable air, nor dephlogisticated air, will unite to phlogisticated air, notwithstanding their attraction to it, without the aid of fire, either the electric or a common spark; and compare this to the easy union of dephlogisticated air and nitrous air, though the latter attracts dephlogisticated air with less force than the three former; we cannot help attributing it to something that surrounds their gravitating particles, and this we must suppose to be partly fire, as it is disengaged during their condensation. But why fire should not exert this power when nitrous air and dephlogisticated air are brought in contact, is very extraordinary; more especially when we know, as I have already demonstrated, that their atmospheres of fire must be nearly thrice deeper than those of phlogisticated air; and likewise when we have every reason to suppose that nitrous air contains nearly the quantity of fire which the dephlogisticated and phlogisticated airs contained in their simple state. It is true, fire is not developed during the union of these last two fluids, which may favour their combination. But how do their

their extenſive atmoſpheres ſo blend as to bring their gravitating particles within each other's influence?

The condenſation of dephlogiſticated air, by perfect nitrous air, without the ſecluſion of fire, is certainly a very ſtriking fact *.

That nitrous acid contains nearly as much fire as its conſtituent principles contained before their union, can hardly be doubted; and that it parts with very little of this by its union to an alkali, is alſo as true as it is ſingular. Here then nitre contains, in a ſolid ſtate, fire ſufficient to give elaſticity to at leaſt 100 times its bulk of dephlogiſticated air.

Hence ariſe the deflagration of nitre and charcoal in cloſe veſſels, and the quantity of fire diſengaged, though fixable air is produced at the ſame time.

Theſe facts convince us, that fire unites chemically to bodies, and of courſe muſt gravitate towards them. Can we therefore doubt but that fire is a ſubſtance, and not a quality, as ſome philoſophers are pleaſed to ſuppoſe?

* There is heat generated, but not more than ſhould be expected from the re-action of the new formed acid upon the ſuſpended water.

Although the conſtituent principles of nitrous acid are known, and though they have been united by art, yet we do not well know how nature performs this operation.

Some philoſophers, but Mr. Thouvenel in particular, have found that putrefaction favours the production of nitrous acid. All animal ſubſtances, during their decay, give out a vaſt quantity of phlogiſticated air; therefore, if dephlogiſticated air be preſent, it will unite to the phlogiſticated air in its naſcent ſtate, and before it unites with fire. However, I have had an opportunity of obſerving, that nitrous acid may be copiouſly generated, where no putrid proceſſes are carried on. The chemical elaboratory at Oxford is near ſix feet lower than the ſurface of the earth. The walls are conſtructed with common lime ſtone, and arched over with the ſame; the floor is alſo paved with ſtone. It is a large room, and very lofty. There are ſeparate rooms for the chemical preparations, ſo that nothing is kept in the elaboratory, but the neceſſary implements for conducting experiments. There is an area adjoining it on a level with the floor, which, though not very large, is

ſufficient

ſufficient to admit a free circulation of air. The aſhes and ſweepings of the elaboratory are depoſited in it. There is a good ſink in the centre of this area, ſo that no ſtagnated water can lodge there. The p——y, which is ſeldom frequented, is over ground, and unconnected with the elaboratory. Notwithſtanding all this, the walls of the room afford freſh crops of nitre every three or four months.

Dr. Wall, who paid particular attention to this circumſtance, and who told me it contained fixed vegetable alkali, requeſted I would analyze it, and let him know what proportion of it a quantity would yield. Accordingly I did, and found that two ounces of it contained ſix drachms of nitrated fixed vegetable alkali, and three of calcareous nitre. The nitre firſt appears in ſmall whitiſh filaments, as fine as cob-web, which, when they get a little larger, drop off, ſo that they never acquire growth ſufficient to diſtinguiſh their figure to a naked eye. On finding that they contained fixed vegetable alkali, I concluded that it proceeded from minute vegetation; but in this I was miſtaken; for I found that they were ſoluble in water, and that they detonated with charcoal at every ſtage of their growth. Having ſwept this ſaline efflореſcence from the wall, I dug deep into it, but could not obtain nitre from it. When a part had been white-waſhed, it yielded nitre, but not ſo abundantly as a neighbouring ſpot which had not been treated in the ſame manner. Hence it is evident, that nitrous acid may be formed without the aſſiſtance of putreſcent proceſſes, in a ſtill damp air, where there is a ſubſtance to attract it when half formed, whereby it is in time brought to perfection. The above facts moreover prove, that fixed vegetable alkali is a compound. Thus we find that chemiſtry is ſtill in its infancy, and that there is a great deal to be done in order to bring it to perfection.

SECTION V.

Of the Marine Acid.

THE basis of marine acid has not as yet been discovered; but that dephlogisticated air is one of the constituent principles of this acid is very evident, if it enters into the constitution of the nitrous or vitriolic acid.

Charcoal, sulphur, *light* inflammable air, or phosphorus, cannot take its dephlogisticated air from the marine basis, whether the acid be combined, or in its simple state.

Lead will take the acid from the fixed alkalies without decomposing it, as will likewise iron when exposed to a damp air for a considerable time, as the celebrated Scheel has observed. I mixed common salt and manganese in various proportions, and exposed them in a reverberating furnace in a well closed crucible for three hours, to heat nearly sufficient to melt cast iron. I treated manganese, salt, and charcoal, in the ſame manner, but with no effect. I mixed clay, ſalt, and charcoal, and ſalt and clay alone, with very little ſucceſs. I treated calcined bones, ſalt, and charcoal, and calcined bones and ſalt, and likewiſe lime and ſalt, in like manner, without effecting any apparent change in the ſalt.

I have been informed by a Mr. Robertſon, an apothecary in Biſhopſgate-ſtreet, who has made ſeveral attempts to decompoſe common ſalt, that he partially alkalized it, by expoſing it and clay to a fierce heat; but, ſoon after it got into contact with air, that it became neutral again. It is certain, that ſalt loſes a portion of its dephlogiſticated air very readily, as may be ſeen by its property of accelerating combuſtion when thrown on the fire. If common ſalt and litharge be fuſed, it is in part decompoſed; the acid ſuffers no decompoſition, but unites to the lead; whereby it acquires, when the ſaline matter is waſhed away, a yellow colour. It is evident from theſe facts, that the baſis of marine acid is a combuſtible body, and quite different from light inflammable air, charcoal, or any known inflammable ſubſtance; and that it attracts dephlogiſticated

phlogiſticated air with greater force than any ſubſtance hitherto diſcovered. Though charcoal will decompoſe all other acids (except a few), when united to bodies which will fix them until they acquire a ſufficient degree of heat, yet it has no effect on marine acid. In my opinion, metals decompoſe marine acid during their ſolution in it, though iron will condenſe marine air without decompoſing it.

Mr. Kirwan is of opinion, that the marine acid conſiſts of a particular baſis united to phlogiſton, and a certain proportion of fixable air; and that when the marine baſis is deprived of its pholgiſton, its affinity to fixed air becomes much ſtronger, whereby it unites to a large portion of it *. Though I have attentively peruſed Mr. Kirwan's Fifth Section on Phlogiſton, wherein he treats of marine acid, I muſt confeſs I could not make out on what grounds he founded this hypotheſis. However, before I preſume to offer my opinion deciſively upon it, I ſhall minutely inquire into it. Therefore, let us firſt ſuppoſe iron to be

* Eſſay on Phlogiſton, p. 74.

 compoſed

composed of a certain basis, and phlogiston, intimately combined. Let us also suppose marine acid to consist of a peculiar basis, and phlogiston, intimately united to fixable air, and that this basis attracts fixable air with greater force than it does phlogiston. This granted, when these are brought in contact, what is likely to take place, according to well known chemical laws? for, in matters of ambiguity, we are justified in reasoning from analogy, more especially when it is an established fact, that the decomposition and composition of all bodies, whether they prevail by virtue of a single or double affinity, are regulated by the same power, though variously modified. The acid most undoubtedly cannot be decomposed, as the attraction of its basis to fixable air on the one side, together with the attraction of the metallic basis for its own phlogiston on the other side, are sufficient to prevent it; for, as the inflammable matter or phlogiston of the metal is expelled in its aëriform state, a double affinity does not prevail in the operation, laying aside the agency of fire, which does not much interfere with the present ſubject.

Hence it appears that the acid, without ſuffering a decompoſition, unites to the metallic baſis, and expels its phlogiſton; which is Mr. Kirwan's opinion. In this caſe, pure fixed alkali, or lime, ſhould precipitate the metallic baſis in its purity, and thereby enable us to obtain that ſubſtance, which occaſions ſuch a conteſt amongſt philoſophers.

I ſaturated half an ounce of marine acid with clean iron nails, firſt having aſcertained the quantity of pure fixed alkali neceſſary to ſaturate ſo much acid in its ſimple ſtate, and found that the ſolution required the ſame quantity of alkali to precipitate the whole of the iron; nor did I find any difference in both ſalts, when evaporated to dryneſs. Therefore the acid was not in the leaſt decompoſed, though the metal was calcined, and its phlogiſton diſengaged. Whence did it receive its dephlogiſticated air; or, according to Mr. Kirwan, its fixable air? The phlogiſtians have but one mode of anſwering this, which is, that the metallic baſis unites to water. If metallic ſubſtances were calcined, as Mr. Kirwan himſelf obſerves, and as I had an occaſion to mention in treating of vitriolic acid, in conſequence of water alone, it ſhould not remain ſo inert when metals are introduced into it, in a common temperature, when iron is calcined by marine acid in the ſame temperature very rapidly.

If metallic calces, precipitated by pure alkali from the different acids, owed their additional weight and colour to an union with water; a given weight of iron, calcined in the different acids, ſhould be precipitated by the ſame pure fixed alkali of the ſame weight and colour. I obſerved that the precipitates of 20 gr. of iron from the vitriolic, the marine, and the nitrous acid, dried and treated exactly in the ſame manner, varied in their weights; that from the nitrous being the heavieſt, and the marine precipitate next to it again: they likewiſe differed in colour, which ſhews their different degrees of calcination. To make this experiment accurately, the precipitates ſhould be well waſhed with hot diſtilled water, and by no means expoſed to the

the air while they are drying; for they change colour in a few minutes by abſorbing both fixable and dephlogiſticated air from the atmoſphere. The precipitate of iron attracts fixable air in ſmall proportions, with as great avidity as the alkalies, and I ſuſpect with as great force as pure lime; but this fixable air may be expelled again from it by a ſtrong heat, without being decompoſed. Hence I am induced to ſuppoſe, that fixable air is never decompoſed during the reduction of mercury by heat. Why are the precipitates from the different acids of unequal degrees of calcination, if water be the calcining ſubſtance, if the acids do not impart ſomething to them, more eſpecially when they are equally well ſupplied with water? That the acids take an active part in the ſolution of metals, cannot be denied; for it is very well known that water will not diſſolve them, and that it will not even in any length of time ruſt gold, ſilver, platina, or mercury; though they are ſoluble in different acids. Then I aſk, How the marine acid acts, when iron is introduced into it? Whether the acid or water divides it into its ultimate particles,

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and expels its phlogiſton; or whether they do this jointly; or whether the acid, by its ſolvent power, only diſſolves what the water calcines and deprives of phlogiſton, by which it may enable the water to attack freſh ſurfaces?

This laſt is certainly the moſt plauſible phlogiſtic hypotheſis in favour of the doctrine of water; although it may with equal plauſibility be ſaid, that the marine acid alone unites to the metallic baſis, diſſolves it, and expels its phlogiſton; and when the acid is withdrawn from it by lime or alkalies being in its extreme diviſion, that it inſtantly ruſhes into union with water, and forms a calx. Allowing the phlogiſtians all this, which is the moſt that can be urged in their favour; there is one circumſtance which, I think, if ſtrictly inquired into, will be found ſufficient to overthrow it; namely, the precipitation of metals by each other in their metallic ſtate.

In order to know the full force of what I am going to obſerve, it will be neceſſary, firſt, to conſider, that if calcination depends upon the union of water, and the expulſion of phlogiſton, the metallic baſis muſt have greater attraction to water than it has to phlogiston; as evidently appears from the calcination of metals by steam. Therefore, on this principle, a metal could never precipitate another metal in its metallic state, from a very dilute solution of marine acid, or of any other acid. For if water, agreeably to the first phlogistic hypothesis, should calcine the metal, while the marine acid dissolved it, how could iron, though it unites to the acid, precipitate copper in its metallic state? Considering that it is surrounded with uncombined water, is it likely that it would influence the water attached to the metallic basis in any degree?

Then all that can be said with the smallest appearance of plausibility is, that the disengaged phlogiston of the precipitating metal expels its water, and unites to the basis. This I think needs no contradiction. The second and last hypothesis that I considered most favourable to the phlogistic doctrine, is that of the water uniting to the metallic basis, the instant the alkali deprives it of its acid of solution. In this case, all the phenomena may be accounted for thus, viz. that the precipitating metal takes the acid from the precipitated, at the ſame time that it imparts phlogiſton to it, whereby it is reduced. This moſt undoubtedly, loſing ſight of all analogical reaſoning, ſeems very plauſible, and may appear, to ſuperficial inquirers into this ſubject, very ſatisfactory. I muſt own I ſhould be thoroughly convinced of the truth of it myſelf, were it not for the following conſiderations: 1ſt, The eaſy expulſion of inflammable air from metals by water; which ſhews, if this comes from the metals, the greater affinity of their baſes to water than to phlogiſton. 2dly, The ultimate diviſion of the precipitated metal, which favours calcination. 3dly, The preſence of ſuch an abundance of water, which they conſider to be the calcining ſubſtance.

Thus far I have impartially inquired, on the phlogiſtic principle, into the nature of marine acid by its effects, as we cannot obtain its conſtituent parts ſeparately; and though I am not much pleaſed with it yet, I leave my reader to judge for himſelf.

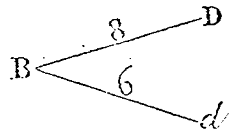
Let us now trace the ſame ſubject ſo far in the antiphlogiſtic doctrine, and without prejudice compare them to each other.

But

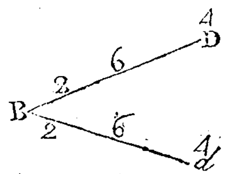
But before we proceed on this, I would have my reader not to loſe ſight of the following facts, which have already been particulariſed: 1ſt, The ſeparation of the marine acid from the metallic ſolution in its perfect ſtate. 2dly, The precipitation of the metal in a calciform ſtate. 3dly, The active part acids take in the calcination of metals. 4thly, The inconſiſtency of ſuppoſing that the calces of metals are compoſed of water and a metallic baſis. 5thly, The ſeparation of inflammable air, during the ſolution of metals. And laſtly, the precipitation of one metal by another in its metallic ſtate.

It appears to me, and indeed I have no other rational mode of accounting for it, that the acid is firſt decompoſed, and that its baſis inſtantly decompoſes the water, and liberates inflammable air; although I think the marine baſis has greater attraction for dephlogiſticated air than the metals have. It likewiſe ſeems to me, that marine acid is compoſed of two principles only, viz. an unknown inflammable baſis, and dephlogiſticated air, intimately combined. It may appear rather ſtrange at firſt ſight, that metals

tals ſhould deprive this baſis of its dephlogiſticated air, notwithſtanding their weaker attraction to it. However, I think this may be very well accounted for on the following principles: Let B be the baſis of marine acid, D dephlogiſticated air; and let theſe attract each other with the force of 8; and let this be the utmoſt ſum of their joint forces. Let B be poſſeſſed of one half of this force, and D of the other half. In this ſtate, metals which I have ſuppoſed to attract dephlogiſticated air with only the force of 7, could not deprive B of D. Let B, in order to form common marine acid, be united to



another particle of dephlogiſticated air *d*. They will only unite with the force of 6; that is, the whole force of B will be divided between D and *d*, on principles which I have already explained, in treating of the vitriolic and nitrous acid. Therefore B will retain its dephlogiſticated air with only the



force of 6; for B can only gravitate with the force of 2 towards D, although D gravitates

vitates with the force of 4 towards B, and ſo with *d* and B. If iron, whoſe attraction for dephlogiſticated air is 7, were brought in contact with the above compound in the preſence of water, whoſe conſtituent principles are united with the force of $6\frac{5}{8}$, would it not deprive B of both D and *d*, and would not B inſtantly re-act on the water, and take from it half the quantity of dephlogiſticated air which it before gave up to the metal, and then unite to the calx? Dry marine acid air will unite to iron, without producing inflammable air; which ſhews that it muſt come from the water. It is true, it may be ſaid, that the union of marine air to iron, without any ſeparation of its principles, is unfavourable to the hypotheſis of the decompoſition of marine acid, when in contact with water. But be it conſidered, although the force of 7 overcomes the attraction of B to dephlogiſticated air, that the force of $\frac{1}{1000}$ is ſufficient to move it with its dephlogiſticated air towards the iron, when there is nothing elſe to influence it; and we may ſuppoſe that the iron itſelf muſt attract it with greater force than this. When water is preſent,

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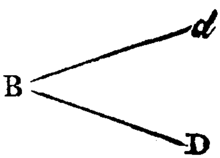
the cafe is different: for, when the iron influences the dephlogifticated air of the marine bafis with fo fuperior a force as $3\frac{1}{2}$ to 2; B, or the marine bafis, being in contact with water, which retains its dephlogifticated air with the force of $6\frac{5}{8}$, or, laying afide reciprocal attraction, with only the force of $3\frac{5}{16}$, yields its own dephlogifticated air to the iron, and directs the whole force of its attraction, which is 4, towards the dephlogifticated air of the water; by which it is decompofed, and inflammable is produced. The marine bafis being thus furnifhed with half the quantity of dephlogifticaed air which is neceffary to the formation of common marine acid, unites to the calx, and diffolves it. To render this the more intelligible, let I—*d* be a molecule of water,



a molecule of marine acid, and I a furface of iron; let us fuppofe thefe to be influenced with the different forces expreffed by the numbers annexed to them; is it not reafonable to fuppofe, as foon as I, or iron, fhould influence *d* D, that B would re-act

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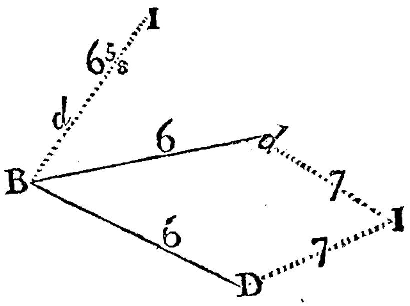
on *d*, or the dephlogiſticated air of the water, and diſengage I, or inflammable air.



I make no doubt but a good mathematician (for I acknowledge my own deficiency) would demonſtrate this to a degree of certainty. However, although I am convinced of the truth of it myſelf, I would have my philoſophical reader to ſtrictly inquire into it before he either approves or diſapproves of it.

The reſt of the antiphlogiſtians differ from me with reſpect to the manner in which water is decompoſed; for they ſuppoſe (if I miſtake not) that the marine or vitriolic acid firſt unites to the metal, and that the compound decompoſes the water, from the joint attraction of its conſtituent principles to dephlogiſticated air. If this were true, water, when brought in contact with iron united to marine air, would yield inflammable air, which is not the caſe; or iron would yield inflammable air with greater rapidity in volatile vitriolic acid, than in perfect vitriolic acid; or marine acid would produce inflammable air during the decompofition of a folution of iron in volatile vitriolic acid.

I fhall not trouble my reader with any more demonftrations on this fubject, but only obferve, that when metals are calcined by the mediation of acids and water, there is lefs inflammable air produced, by one half, as Dr. Prieftley obferves, than when they are calcined by fteam *. This is not only explicable on the foregoing principles, but alfo tends ftrongly to corroborate them; and, if narrowly infpected, will be found very unfavourable to the phlogiftic theory. If the calcination of metals depended folely upon their union to dephlogifticated air, it muft be fupplied by water, when fteam is brought in contact with them; and as every particle of light inflammable air is united but to a fingle ultimate particle of dephlogifticated air, inflammable air muft be difengaged in proportion to the quantity of dephlogifticated air which unites to the metal; or, in other words, according to the degree of calcination it acquires.

* Vol. VI. p. 102.

But

But this is not the caſe when metals are calcined in the marine or in the vitriolic acid; for though the baſes of theſe acids impart two or more portions of dephlogiſticated air to the metal, they can recover but one half of it from the water, as has been fully demonſtrated. Therefore, when acids are uſed, only one half of the quantity of inflammable air ſhould be produced, that is extricated when ſteam is the calcining menſtruum; which could not be the caſe, if light inflammable air were one of the conſtituent principles of the metal.

It is true, it may be ſaid, that the metallic precipitate from the above acids correſponds in its degree of calcination with the quantity of inflammable air or phlogiſton diſengaged, and for that reaſon retained phlogiſton in ſolution. But I have already ſhewn, in treating of the vitriolic acid, that the precipitant, whether it be an alkali or an earth, enables the baſis of the acid, in quitting the metal, to take from it, its full portion of dephlogiſticated air, by which the precipitate contains but the portion taken from the water. When the nitrous acid is uſed, which contains more dephlogiſticated air lefs intimately combined than the marine or vitriolic acid does, the precipitate is found united with more dephlogifticated air; and the nitre obtained by precipitating a neutral folution of nitrated iron by fixed alkali, is far from being fo perfect as what may be produced by combining thefe previous to the above treatment. When iron is introduced into a neutral folution of marine copper, the latter is precipitated in its metallic ftate, and no inflammable air is produced. This fact, feparately confidered, appears very favourable to the phlogiftic theory. Iron attracts dephlogifticated air with greater force than copper does, although iron alone will not reduce the mere calx of copper diffufed in water; but, aided by the bafis of marine acid, it will wholly deprive it of its dephlogifticated air. The marine acid, having greater affinity to iron than to copper, quits the latter to unite to the former; and, affifted by the iron itfelf, it forces with it the dephlogifticated air feparated from the water. Thus, by their joint forces, they accomplifh what the iron alone could not; and as this quantity of dephlogifticated air is fufficient for the folution

lution of the iron, no decompoſition of water takes place, and of courſe no inflammable air is produced. In ſhort, the dephlogiſticated air of the marine acid itſelf, together with the ſmall portion ſeparated from the water during the ſolution of the copper (for but little inflammable air is produced), move jointly to unite to the iron, and affect it as dephlogiſticated marine acid would, which is known to diſſolve metals without generating inflammable air.

Having, as fairly as lay in my power, inquired into the nature of marine acid on the antiphlogiſtic and the different phlogiſtic principles, ſo far as it is affected by metals, I ſhall now proceed to its other principal properties.

When common marine acid is diſtilled over red lead or manganeſe, it undergoes a very great change, as the celebrated Scheel has diſcovered, in taſte, ſmell, volatility, &c. : diſtilled or mixed with nitrous acid, it acquires partly the ſame properties. I doubt whether arterial blood would not effect the ſame change in it. Marine acid thus treated is ſaid to loſe phlogiſton, or the matter of light inflammable air: hence it has got the name of dephlogiſticated marine acid.

Some phlogiſtians attribute this change in marine acid to a loſs of its phlogiſton, and an union to dephlogiſticated air; others, to an union of dephlogiſticated air to its phlogiſton: but Mr. Kirwan imagines, that it exchanges its phlogiſton for fixable air, in order to become what is called dephlogiſticated marine acid. Thus the phlogiſtians themſelves differ in opinion; a clear proof of the inconſiſtency of their doctrine.

The antiphlogiſtians, on the contrary, are of opinion, that the baſis of marine acid, from its great attraction to dephlogiſticated air, is capable of uniting to a greater portion of it than it is found combined with in its ordinary ſtate, provided it be preſented to it under favourable circumſtances.

* Mr. Kirwan affirms, that he has obtained dephlogiſticated marine acid from chalk. Chalk has no ſenſible attraction to inflammable air; therefore the marine baſis muſt

* Eſſay on Phlogiſton, page 80.

attract fixable air with greater force than it does phlogiston, for a double affinity does not prevail here. According to Mr. Kirwan, common marine acid must part with phlogiston in order to unite to fixable air; for he supposes, that the marine basis cannot retain both when in the state of dephlogisticated marine acid: then I ask, whether Mr. Kirwan obtained inflammable air in this experiment, or what became of the phlogiston of the marine acid? However, Mr. Kirwan has been more successful than I have been; for I attempted in vain to prepare dephlogisticated marine acid by means of chalk: in short, it had the contrary effect, for it decomposed dephlogisticated marine acid obtained from manganese.

I saturated a quantity of pure volatile alkali with dephlogisticated marine acid carefully prepared; phlogisticated air was produced, but not a particle of fixable air, and the resulting salt was found to be common sal ammoniac. Volatile alkali is composed of light inflammable air and phlogisticated air; therefore it must be partly decomposed, by which phlogisticated air is obtained; and the inflammable air must unite to something elſe, which attracts it more forcibly than the phlogiſticated air. I aſk, to what? Not to the marine baſis, for it appears to have already parted with phlogiſton to unite to fixable air; therefore it muſt have greater attraction to it than it has to phlogiſton.

Beſides, the attraction of the phlogiſticated air to light inflammable air, renders ſuch an union very improbable. Or, allowing that the gravitating matter of the light inflammable air united to the marine baſis, it muſt then let go its fixable air in order to become common marine acid; for it cannot hold both, according to Mr. Kirwan himſelf. Then I aſk, what becomes of its fixable air? for I diſtilled the ſalt to dryneſs, and could not obtain it. It cannot be ſaid, that it has been decompoſed by the inflammable air of the alkali; for it would be inconſiſtent to ſuppoſe, that phlogiſton ſhould influence dephlogiſticated air already ſaturated with phlogiſton, and united to another ſubſtance.

Equal parts of dephlogiſticated marine air and light inflammable air mixed over water, will form, according to Mr. Kirwan *, a denſe white cloud; more than one

* Eſſay on Phlogiſton, page 80.

half

half is abſorbed, and is found to be common marine acid, and the reſiduary air is pure inflammable air. Mr. Kirwan conſiders this experiment as very favourable to his hypotheſis, and ſufficient to ſubvert that of the antiphlogiſtians. In my opinion, if it be narrowly inquired into, it will be found more unfavourable to the former than to the latter doctrine. Therefore, allowing dephlogiſticated marine air to be convertible into common marine acid by the mere admixture of light inflammable air: how does the inflammable air act in this caſe? Does it unite to the baſis of marine acid? If ſo, fixable air (if it were one of the conſtituent principles of the dephlogiſticated marine acid) ſhould be diſengaged; but Mr. Kirwan himſelf has ſhewn, that not a particle of fixable air is produced. Then all that can be ſaid in favour of the doctrine of fixable air is, that it is decompoſed. I ſhould like to know how ſuch a decompoſition can take place; for, in order to this, the marine acid baſis muſt exert a certain force on the phlogiſton of the fixable air on the one ſide, while the light inflammable air pulls at its dephlogiſticated air on the other, and ſo, by their contrary powers, force the conſtituent principles of fixable air aſunder. Is this conformable to the laws of nature, ſo far as they govern chemical attraction? May not we as well ſay, that a rope which ſuſpends a weight ſhould firſt break in the ſtrongeſt part? Is it not more reaſonable to ſuppoſe, that the marine baſis would the rather unite to the diſengaged phlogiſton, than ſtruggle for that which is already intimately combined? Even allowing ſuch a decompoſition, fixable air ſhould be regenerated; for, according to Mr. Kirwan himſelf, water has never been formed but in a red heat *.

The black calx of manganeſe, free from calcareous earth and iron, will not yield a particle of fixable air by expoſure to heat. The acids, even thoſe that will diſſolve it, do not expel a particle of fixable air from it. I fuſed manganeſe and borax into a vitreſcent maſs, and yet no fixable air was produced, and little or no dephlogiſticated air; but this I do not wonder at, as dephlogiſticated air enters into the conſtitution of

* Eſſay on Phlogiſton, p. 26.

glaſs. If ſal ammoniac and manganeſe be diſtilled, the ſal ammoniac is decompoſed, and the volatile alkali is obtained in a cauſtic ſtate; and the acid is dephlogiſticated, as Mr. Kirwan obſerves. Hence he infers, that the fixable air of the manganeſe unites to the marine acid; but he ſhould firſt prove that the manganeſe contains fixable air. I have diſtilled cauſtic volatile alkali and manganeſe, and yet the alkali was ſtill cauſtic. Cauſtic fixed alkali boiled over manganeſe received no fixed air from it. Lime and manganeſe treated in the ſame manner did not ſhew the ſmalleſt veſtige of fixable air; and the manganeſe thus treated, afforded the uſual quantity of dephlogiſticated air. Theſe circumſtances induce me to believe that manganeſe, when free from calcareous earth, does not contain fixable air in any conſiderable proportion; and that dephlogiſticated marine acid does not contain a particle of fixable air, as one of its conſtituent principles. In my opinion, the phlogiſtians muſt have recourſe to ſome other mode of accounting for the formation of dephlogiſticated marine acid, beſides that of fixable air; and

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what can this be? They cannot attribute it to the mere ſeparation of phlogiſton from the marine acid; for it is evident that dephlogiſticated air unites to it, during its diſtillation with manganeſe, when we can expel it from the acid again by uniting it to fixed alkali, and when the ſalt is found to be the ſame as if the alkali had been combined with common marine acid. Beſides, the manganeſe, after the diſtillation of marine acid, will yield no dephlogiſticated air, although previous to this proceſs it affords it in abundance. Hence it appears, that the phlogiſtians muſt allow the preſence of dephlogiſticated air in the dephlogiſticated marine acid; and to ſupport the doctrine of phlogiſton, they can only ſay, that the manganeſe unites to it at the ſame time that it imparts dephlogiſticated air to the marine acid. If the marine acid parts with phlogiſton to unite to dephlogiſticated air, how does it recover this again on uniting to fixed vegetable alkali, when its dephlogiſticated air is expelled? for it is converted into common marine acid, and, according to the phlogiſtians, the preſence of phlogiſton is indiſpenſably neceſſary to this ſtate. Let us now inquire into the nature of dephlogisticated marine acid, and aqua regia, in the antiphlogistic doctrine.

I have already described the nature of marine acid with respect to the attraction of its basis for dephlogisticated air, and the intimacy of their union when in the state of common marine acid. No wonder then that it should unite to more dephlogisticated air, when it meets with it condensed and united with less force than its basis attracts it. A moderate degree of heat will expel dephlogisticated air from red lead and manganese; but the fiercest heat we can produce will not expel the whole of their dephlogisticated air from them. Hence we may infer, that the marine basis may with very little resistance deprive these of a portion of their air, and thereby assume the character of dephlogisticated marine acid. The calces of iron, tin, copper, antimony, &c. will not part with dephlogisticated air in the most intense heat; which shews that they retain it with greater force than the former calces, and of course will not give it up to the marine basis so readily.

I have endeavoured to shew, that dephlogisticated air is retained with less force in the

the nitrous acid than in the vitriolic acid; and in the vitriolic, than in the marine acid. I would now obſerve that, though the marine baſis, when united to its natural portion of dephlogiſticated air, cannot take this from the vitriolic acid, it will deprive the nitrous acid of a portion of its dephlogiſticated air, as holding it with ſo inferior a force.

Thus, when marine acid is mixed with the nitrous acid, nitrous air is ſometimes produced, according to the proportion uſed. If theſe two acids be mixed in the proportions of two of the nitrous to three of the marine, provided the acids be ſtrong and complete, and the mixture be kept in a cool place, nitrous air will firſt be diſengaged, attended with heat; but on ſtanding for ſome time, and when it gets cool, the nitrous air ceaſes coming over, and ſmall bubbles of air are generated in different parts of the mixture, which are abſorbed almoſt as ſoon as they get birth. Theſe ſometimes make their firſt appearance at the bottom of the liquor, and are carried upwards in ſlender ſtreams, gradually diminiſhing in their progreſs, until they can-

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be no longer traced, and attended with a hiſſing noiſe, occaſioned by the abſorption. I endeavoured in vain to obtain ſome of this air. This beautiful appearance does not always take place. A ſimilar phenomenon may be obſerved in preparing nitrous ether in Dr. Black's method.

Thus we find that the marine acid will take dephlogiſticated air from the nitrous, with as much facility as from the calx of manganeſe, and that it affects this acid as the metals do, by withdrawing dephlogiſticated air from it, and not, as the phlogiſtians imagine, by imparting phlogiſton to it; for I flatter myſelf I have already ſhewn that nitrous air contains no ſuch thing.

It is very well known that fixable air will not affect nitrous air in the leaſt, and that they cannot be combined by any means whatever. It is likewiſe very obvious, that nitrous air will not form nitrous acid without the preſence of dephlogiſticated air. Yet Mr. Pellitier formed nitrous and common marine acid, by mixing dephlogiſticated marine air and nitrous air, 26 Roz. 393. This is not only a convincing proof

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of the entry of dephlogiſticated air, in its ſimple ſtate, into the conſtitution of dephlogiſticated marine acid, but likewiſe points out the weakneſs of the phlogiſtic theory. For, if nitrous air were diſengaged during the action of the marine on the nitrous acid, in conſequence of the marine imparting phlogiſton to it, and withdrawing from it either dephlogiſticated air or fixable air; is it likely that they would decompoſe each other again, eſpecially when they are in an aërial ſtate, and guarded by fire? Indeed, the phlogiſtians may urge a ſimilar objection againſt the antiphlogiſtic doctrine, by ſaying that, if the marine acid deprived the nitrous air of its dephlogiſticated air, in order to become dephlogiſticated marine acid, nitrous air could not deprive it of this again. All this is very fair, and would be difficult to get over, were it not for our minute inquiry into the nature and internal ſtructure of the acids; and likewiſe the force with which their conſtituent principles unite, and the manner in which this force muſt be influenced, according to the proportion of dephlogiſticated air united to their baſes.

I have already ſuppoſed, that the imperfect or dephlogiſticated nitrous air is united to its dephlogiſticated air with the force of 6; the perfect or common nitrous air with the force of $4\frac{1}{2}$; the red nitrous vapour, or perfect red nitrous acid, with the force of 4; the pale with the force of $3\frac{3}{4}$; and the colourleſs or perfect nitrous acid with the force of $3\frac{3}{5}$. But I would obſerve that theſe are often mixed, ſo that it is a difficult matter to obtain them ſeparately, particularly the red and pale, for the colourleſs cannot exiſt in contact with the red. I have likewiſe ſuppoſed that the marine baſis, though it attracts dephlogiſticated air with the force of 8, is only attached in its common ſtate to its dephlogiſticated air with the force of 6; and that it has a tendency to unite to more dephlogiſticated air when it meets with it combined with a force inferior to its own attraction to it.

From this ſtatement of the force of union of the conſtituent principles of common marine acid, and its tendency to unite to more dephlogiſticated air, we may ſuppoſe that its baſis attracts the quantity neceſſary to its dephlogiſticated ſtate with the force of 4.

Thus ſtating the comparative attraction of both acids to dephlogiſticated air, rather than their abſolute forces, which I think are impoſſible to be aſcertained, we ſhall be the better able to account for the following facts. Mr. Pellitier has obſerved, if the nitrous acid be added in ſmall proportion to the marine acid, that it is wholly decompoſed, and that its phlogiſticated air is diſengaged, notwithſtanding phlogiſticated air attracts the quantity of dephlogiſticated air neceſſary to the formation of perfect nitrous air, with greater force than the marine acid.

This I think is only explicable on the following principles: When a ſmall portion of nitrous acid is diffuſed in a large quantity of marine, the latter expoſes ſurfaces enough to at once ſeparate the whole of its dephlogiſticated air from the phlogiſticated. For the force of 4 is ſufficient to overcome, if the perfect nitrous acid be uſed, the force of $3\frac{3}{5}$, or if the pale $3\frac{3}{4}$; but if the red nitrous acid be uſed in its purity, it will not be decompoſed, for it retains its dephlogiſticated air with as great force as the marine acid attracts it; therefore they will partially unite without a decompofition.

I have already obferved the nature of the above decompofition of nitrous acid, in treating of the effects of metals on it when highly diluted.

When a larger quantity of nitrous acid is mixed with the marine acid, nitrous air is produced; for, as a molecule of the marine can only deprive a fingle molecule of nitrous acid at moft but of two ultimate particles of dephlogifticated air, there are not a fufficient number of the former in contact with the latter to effect a total decompofition; and as it cannot take place but by a number of uniform pulls from different quarters at once, while the nitrous molecule is perfect, the nitrous air, retaining its fmall portion of dephlogifticated air with greater force than when united to a larger quantity, paffes off unmolefted in its aerial ftate in the marine acid.

Thus it is that nitrous air is difengaged by the marine acid, though the nitrous air will take its dephlogifticated air from dephlogifticated marine air.

I think the dephlogisticated marine air retains its dephlogisticated air with nearly as great force as the nitrous air attracts it; for when the airs are perfectly dry, and mixed over mercury, no decomposition seems to take place until water is introduced. Hence I infer, that water assists in the decomposition from its attraction to marine acid. If a small quantity of marine acid be mixed with a large portion of perfect nitrous acid, no nitrous air is produced, and no change appears in the acid. If more be added, the acid changes colour; but if a larger quantity be added, nitrous air is produced, but no phlogisticated air. This confirms the above demonstration of the total decomposition of nitrous acid; for we find a correspondence in reversing the proportion of the acids.

If marine ammoniac be mixed with the nitrous acid in the temperature of 70° or 80°, a violent action takes place, and a large quantity of nitrous air is extricated, mixed with a small portion of dephlogisticated marine air and phlogisticated air. Here the marine ammoniac is decomposed; for the nitrous acid, from its superior attraction

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volatile alkali, takes it from the marine acid. The marine acid in its turn takes dephlogisticated air from the remainder of the nitrous acid, and forms aqua regia, or dephlogisticated marine acid; a portion of this dephlogisticated marine acid re-acts on the newly formed nitrous ammoniac, withdraws from it its inflammable air, and converts it into water, by supplying it with dephlogisticated air, at the same time that its phlogisticated air is disengaged. This accounts for the greater production of nitrous air when we use marine ammoniac, than when the quantity of marine acid which it contains is used. If the regulus of antimony in fine powder be exposed to the airs disengaged during the action of nitrous acid on marine ammoniac, it is instantly calcined, and sparks of fire are emitted. This beautiful appearance will not take place, if the regulus be exposed to the dephlogisticated marine air alone; so that it requires the presence of nitrous air. This is very unfavourable to the phlogistic doctrine; for, if the nitrous air be already saturated with phlogiston, how can it contribute to the rapid calcination of the

 antimony?

antimony? Or, if it ſhould take place in conſequence of the attraction of the marine acid to phlogiſton, the metal muſt retain it with leſs force than the nitrous air. But if this ſhould depend on the attraction of the metallic baſis for fixable air, at the ſame time that the dephlogiſticated baſis attracts its phlogiſton, and ſo by a double affinity promote the calcination or decompoſition, it ſhould take place in pure dephlogiſticated marine air. It cannot be attributed to water; for ſteam in its rareſt ſtate cannot produce it, nor will ſteam and nitrous air afford this phenomenon.

It appears to me, that it can only take place at the very inſtant that the dephlogiſticated marine air unites to red nitrous vapour, which is formed by an union of atmoſpheric air to the nitrous air, extricated with the dephlogiſticated marine air; for both acids attached and deſtitute of water, which would imperceptibly carry off the fire diſengaged by the rapid union of dephlogiſticated air to the metal, favour calcination more when thus partially condenſed, than either would ſeparately in an

aerial

aerial ſtate, being then too intimately united to fire.

The marine acid will condenſe red nitrous vapour in conſequence of its dephlogiſticated air; and provided the proportion be adjuſted, little or no nitrous air will be produced. In like manner, red nitrous vapour, or red nitrous acid, from its attraction to dephlogiſticated air, will unite to dephlogiſticated marine acid, and not a particle of nitrous air will be produced: here the attraction of both acids to dephlogiſtilocated air is nearly equal; therefore they unite without a ſeparation of either of their principles. Hence ariſes the difference between what is called aqua regia, and dephlogiſticated marine acid; for when marine acid is even combined with a ſufficiency of dephlogiſticated air to form dephlogiſticated marine acid, it will influence the nitrous vapour ſo as to render it impoſſible to ſeparate them, from their nearly equal degree of volatility. Although the heat generated by the admixture of the marine and perfect nitrous acid, ſhews the more intimate union of the dephlogiſticated air of the nitrous acid to the marine; yet the volatility of the compound, or the little force with which its molecules gravitate towards each other, accounts for the ſpecific gravity of aqua regia.

Dr. Prieſtley diminiſhed common air by paſſing the electric ſpark in it, in contact with marine acid; and though he continued the operation ſome time after the contraction took place, the reſiduum neither increaſed nor diminiſhed*. Dephlogiſticated marine acid expoſed to the ſolar light will yield dephlogiſticated air, 29 Roz. 82. Theſe two facts, not to adduce any more, are ſufficient to confirm the antiphlogiſtic doctrine. When Dr. Prieſtley took the electric ſpark in common air, in contact with dephlogiſticated marine acid, it was diminiſhed to one half; but I ſuſpect, as ſome of the phlogiſticated air diſappeared, that nitrous acid had been formed.

Thus finding that this change in marine acid depends upon its union to dephlogiſticated air ſimply, we can eaſily account for the calcination of metals in this acid, without the extrication of inflammable air; for though the metal takes this de-

* Vol. VI. p. 340.

phlogiſticated air from the marine acid, it cannot recover it again from the water; therefore it re-acts on the metallic calx, and diſſolves it. From the attraction of common marine acid to dephlogiſticated air, it will diſſolve the calces even of thoſe metals which it has no power over when in their metallic ſtate, without producing inflammable air. We can explain on the ſame principle, why dephlogiſticated marine acid will not diſſolve metallic calces; for the marine baſis and the metals being ſaturated with dephlogiſticated air, cannot influence each other until either loſes a portion of its air, by which this neutrality or equilibrium is deſtroyed. The effect of perfect or pale nitrous acid on manganeſe and other metallic calces confirms this; for, as the immortal Scheel has long ſince obſerved, this acid muſt be deprived of a portion of its dephlogiſticated air, before it can diſſolve them; and this is done by the addition of any ſubſtance which attracts dephlogiſticated air, ſuch as ſugar, ſpirit of wine, &c.

The converſion of ſulphur into vitriolic acid by dephlogiſticated marine acid, is rather

ther againſt the phlogiſtic theory, when we conſider that this again, when combined with clay, and expoſed to heat, will yield dephlogiſticated air. This I mention, becauſe Mr. Kirwan urges it againſt the antiphlogiſtians. Bergman ſays, that ſulphur is not vitriolated in dephlogiſticated marine acid; but, not having repeated the experiment, I muſt reſt in ſuſpenſe. Several other facts might be adduced in favour of the antiphlogiſtic doctrine, but in my opinion it is unneceſſary to ſay any more. Indeed I think every ſingle fact in chemiſtry is in its favour, even thoſe that have been urged in oppoſition to it. Therefore it appeared unneceſſary to ſelect from the general ſtock of facts, which induced me to adopt ſuch truths as firſt occurred to me in my demonſtrations.

SECTION VI.

Of the Calcination of Metals Via Sicca.

ALL the metals, except gold, platina, and ſilver, are calcined by the joint action of air and fire. That is to ſay, they are deprived of their metallic brilliancy, aſſume an earthy appearance, and acquire an additional weight.

Philoſophers vary in opinion reſpecting the nature of the calcination of metals. The antiphlogiſtians ſuppoſe that metals are ſimple bodies, which unite to dephlogiſticated air, and form calces; and that the mere expulſion of it is ſufficient to reduce them again to their metallic ſplendour; and likewiſe when charcoal is uſed to reduce the refractory calces, that it imparts nothing to the metal; but that, by its ſuperior attraction to dephlogiſticated air, it ſeparates this from it, by which it is revived.

The phlogiſtians, on the contrary, are of opinion, that metals are compoſed of two principles,

principles, viz. metallic bases, and phlogiston (or light inflammable air), in a solid state. Although all the phlogistians allow that dephlogisticated air unites to some of the metals during calcination, yet they do not agree with respect to the nature of the union. Some phlogistians suppose that the dephlogisticated air unites to the phlogiston of the metal, and forms water, which combines with the metallic basis, and constitutes the calx. Others are of opinion, that fixable air is sometimes formed. Dr. Priestley thinks that metals, during their calcination in dephlogisticated air, unite to the water suspended in it, at the same time that the gravitating matter, or acidifying principle of the dephlogisticated air, unites to its phlogiston, and forms an acid.

These are the latest received opinions in the phlogistic doctrine respecting the calcination of metals. That metals give out nothing, but take in dephlogisticated air during calcination, appears from Dr. Priestley's and Mr. Lavoisier's experiments; but that this absorption depends on inflammable air (or phlogiston) has not been proved, and, in my opinion, there have been very little grounds for ſuch an hypotheſis.

Allowing metals to be what the phlogiſtians ſuppoſe, is it likely that phlogiſton, which muſt be the ſame wherever it is, or however combined, ſhould at one time form fixable air, and at another time water; or, according to Dr. Prieſtley, nitrous acid? The former doctrine is certainly an excellent improvement on the phlogiſtic theory; for, without it, this could not ſtand its ground much longer. But although this hypotheſis of fixable air may at firſt ſeem plauſible in calcination in the dry way, yet that advantage is totally loſt when acids are uſed. Fixable air is formed during the calcination of mercury *per ſe*, according to Mr. Kirwan; ſo that mercurius calcinatus is a compound of a metallic baſis and fixable air, as are likewiſe all the mercurial calces. The phlogiſtians may perſiſt in this hypotheſis, for, in my opinion, it appears very favourable to them. 1ſt, Becauſe it is very well known that fixable air is compoſed of dephlogiſticated air and heavy inflammable air, and therefore can be ſuppoſed to impart phlogiſton during its decompoſition.

composition. 2dly, Because a vast quantity of nitrous air is produced during the calcination of mercury in the nitrous acid, which they suppose to be the phlogiston of the metal and nitrous basis intimately combined. 3dly, Because this last supposition of nitrous air could not be admitted but on the doctrine of fixable air, as the nitrated calx is reduced without addition; which, according to the phlogistians, would be impossible, as the nitrous air carried off its own phlogiston, unless it was united with something which could impart phlogiston to it. Hence we find that, laying aside the presence of fixable air, phlogiston must be subverted. As the phlogiston of the mercury is carried off in the nitrous air, according to the phlogistians, and of course no phlogiston left to form fixable air, which is necessary to the calciform state of the mercury, Mr. Kirwan has been pleased to say, that fixable air is one of the constituent principles of nitrous acid itself, and that it unites to the mercurial basis ready formed. I have already given my reasons for refusing my assent to this; and it has appeared that phlogiston, or light inflammable air, does not enter

enter into the conſtitution of nitrous air; therefore it is evident, that the doctrine of fixable air is as deluſive as any other phlogiſtic doctrine. Mercury, as that great philoſopher Mr. Lavoiſier has firſt obſerved, unites to a certain portion of dephlogiſticated air during its calcination *per ſe*, and the additional weight of the calx correſponds with the weight of the air abſorbed. By the mere application of heat the air is expelled again, and the mercury is revived. Laying aſide all prejudices, this moſt undoubtedly is a ſtrong argument in favour of the antiphlogiſtic doctrine, and is, to me, together with the facts already adduced, a convincing proof of the truth of it. Mr. Kirwan would explain this proceſs in the following manner, viz. That the phlogiſton of the metal unites to the dephlogiſticated air, and forms fixable air, which, re-uniting to the metallic baſis, conſtitutes the calx; but when a greater degree of heat is applied than was neceſſary to the calcination, that this fixable air is decompoſed, by which its dephlogiſticated air is diſengaged, at the ſame time that its phlogiſton re-unites to the metallic baſis. Even loſing ſight of

what

what has been already adduced on the ſubject, it appears to me, that this mode of reaſoning, if ſtrictly ſcrutinized, will be found to carry with it ſelf-contradiction. For, in the firſt place, it ſhews that phlogiſton, or the matter of light inflammable air, has greater affinity to dephlogiſticated air than it has to the metallic baſis. In the ſecond place, during the revivification, this evidently appears not to be the caſe. If mercurius calcinatus were compoſed of three principles, viz. a metallic baſis, phlogiſton, and dephlogiſticated air; and if the two latter were intimately combined from their ſuperior attraction in the ſtate of fixable air, and attached to the metallic baſis, is it likely that any degree of heat, but particularly that ſufficient to revive mercury, would ſeparate the conſtituent principles of the fixable air; more eſpecially when they attract each other with greater force than the metallic baſis does either? This ſtill appears the more improbable, when we conſider the volatility of fixable air and of its conſtituent principles. Is it not the property of fire to promote the elective attraction of bodies, or elſe to reſolve compounds

pounds into their conſtituent principles? And is not this eſtabliſhed law wholly perverted, if we ſuppoſe mercury to contain phlogiſton (or the gravitating matter of light inflammable air)?

Indeed, there are ſome circumſtances in which bodies will decompoſe others of ſuperior attraction, when expoſed to heat; as, for inſtance, phoſphoric acid will decompoſe vitriolated tartar; but this proceeds from the extreme fixity of the alkali and phoſphoric acid, and the volatility of vitriolic acid; a circumſtance which does not interfere in the reduction or calcination of mercury.

If mercury were a ſimple body, whoſe ultimate particles attract dephlogiſticated air, but which, from their own influence on each other, cannot unite to it until this is counteracted by heat, we could account for the calcination of mercury, and the decompoſition of the calx again when expoſed to a ſtronger heat, on the ſame principle that copper and zinc, or gold and mercury, or tin and mercury, unite in a low heat, and ſeparate again in a higher degree.

If the calces of mercury contained fixable air, they would yield it during their re-

 duction

duction in light inflammable air; which is not the case, as appears from Dr. Prieſtley's experiments. This philoſopher heated red precipitate of mercury in contact with light inflammable air, in cloſe veſſels, until eight ounce meaſures were abſorbed, and no fixable air was produced, but a ſmall portion of water*.

Mr. Kirwan would ſay, that the fixable air is here decompoſed, or rather condenſed into water; which hypotheſis is founded upon no experiment whatever. For I am perſuaded that no chemiſt can convert all the principles of fixable air into water, or into any other fluid.

If fixable air was decompoſed during the reduction of mercurial calces, the ſame ſhould take place during the revivification of white lead in light inflammable air, which, we know, contains fixable air in great abundance; but this does not appear to be the caſe. If fixed air be convertible into water by intenſe heat, as Mr. Kirwan ſuppoſes, fixed vegetable alkali, or barites, ſhould not yield it after they have been expoſed to a ſtrong heat for ſome time; or the

* Vol. VI, p. 129.

electric

electric ſpark would condenſe it into water, which Dr. Prieſtley has ſhewn does not happen; though, as he has obſerved, a partial decompoſition had taken place. I frequently mixed an aſcertained quantity of fixable air with a charge of light inflammable and dephlogiſticated air; and though I inflamed them by paſſing a ſtrong electric ſpark in them, I found no ſenſible change in the fixable air. From theſe and many other ſimilar circumſtances I am led to believe, if the calces of mercury contained fixable air, that we ſhould obtain it when we ſupply the metallic baſis with pure phlogiſton.

It is ſurpriſing to me, if metals be compoſed of ſo volatile a ſubſtance as light inflammable air and fixed baſes, that we cannot ſeparate them in the moſt intenſe heat. Surely all the metallic baſes are not the ſame. Therefore we ſhould ſuppoſe that there might be one or more amongſt them all, that would be ſo little tenacious of their phlogiſton as to yield, if not the whole, a portion of it when urged with a fierce heat. Yet the phlogiſtians themſelves could never obtain from metals what they ſo earneſtly contend for, without the presence of water. Indeed, Dr. Priestley acknowledges that metals will not give a particle of air without water. As to a metallic basis, they have not yet been able to produce it. Therefore it is obvious, that the contention or difference between the phlogistians and antiphlogistians is this: the former are led away by imagination, and the latter confine themselves to the evidence of their senses. I charged four drachms of iron filings, which I carefully prepared, into a small glass retort; and though I applied heat sufficient to melt the glass, I obtained little more than one cubic inch of inflammable air; and this was produced in the beginning of the process; so that it must have proceeded from moisture. I exposed lead, tin, zinc, bismuth, cobalt, copper, and regulus of antimony, to heat sufficient to melt cast iron, in a well closed deep crucible; and although I sublimed and dissipated all of them (copper excepted), I could not effect the smallest change in their constitution; for what sublimed and adhered to the upper part of the crucibles, possessed its natural brilliancy and specific gravity. Mr. Kirwan supposes that

fixable

fixable air is only formed during calcination in a low heat, but that water is formed in a higher degree. If it were fo, red lead would not yield dephlogifticated air; for the phlogiftians will not allow the decompofition of water. Mr. Kirwan attempts to obviate this by faying, that red lead is prepared in a low degree of heat, but that litharge, which requires a higher, will afford none. However, I converted litharge into red lead in a degree of heat not much fhort of that which will convert red lead into litharge; and it gave dephlogifticated air in fmall quantities; and by the addition of oil of vitriol I obtained dephlogifticated air from it in abundance, but not a particle of fixable air. Part of the fame red lead, expofed to the atmofphere for a few weeks, yielded fixable air both with and without vitriolic acid; which induces me to think that fixable air is not a neceffary ingredient in red lead, but that it abforbs it after it is formed.

The truth is, minium contains more dephlogifticated air than litharge does; and, in its tranfition from the former to the latter, it parts with it, as Dr. Prieftley has fhewn.

And as litharge contains leſs of dephlogiſticated air than minium, it is the more tenacious of it, and will not give it up until ſomething elſe is preſented to it which has greater affinity to the air than the lead has. Dr. Higgins has ſhewn, that 7581,5 gr. of litharge, when completely reduced, will yield 6835,2 gr. of pure lead, and that 7680 gr. of red lead will yield but the ſame quantity; whence he juſtly inferred, that 6835,2 gr. of lead require, in order to become minium, 98,5 gr. more of air than is neceſſary to its converſion into litharge. To confirm this, he converted the above quantity of minium into litharge, and obtained during the proceſs 98,5 gr. of air, 24 of which he found to be fixable air, and 74,5 dephlogiſticated mixed with phlogiſticated air *. This does not correſpond with Mr. Kirwan's account of a ſimilar proceſs; for he found that minium, during its tranſition to litharge, abſorbed air †.

The expulſion of fixable air from minium and other metallic calces, which Mr. Kirwan ſeems to lay great ſtreſs upon, does

* Exp. and Obſ. on Acet. Acid, &c. p. 210.

† Eſſay on Phlogiſton, p. 111.

not in my opinion favour his hypothesis in the least; for, if the dephlogisticated air absorbed, formed fixable air by an union to the phlogiston of the metal, considering that some metals are revived again without the addition of foreign phlogiston; it should seem that metals never suffer any part of their natural portion of phlogiston to be carried off: and, indeed, if metals contain what they call phlogiston, it must be so; for I found that red precipitate, or turbith mineral, recently prepared, afforded no fixable air, although Dr. Priestley discovered a trifling portion of it in dephlogisticated air obtained from mercurius calcinatus. But much depends upon the time they are kept; for they absorb fixable air from the atmosphere, like all other spongy or porous substances. Hence I think, that the fixable air obtained as well during the calcination of metals, as afterwards from their calces, depends upon some impregnation in the materials, and does not in the least tend to prove the existence of phlogiston in metals. Iron quickly calcined by fire, or in the nitrous acid, will not yield a particle of fixable air, though rust of iron will afford it in

 abundance.

abundance. Mr. Kirwan may object to the former procefs, by faying, that water is formed during the calcination; but this cannot be faid when the calx is prepared by nitrous acid. Therefore, if the calcination in the nitrous acid depended upon an union to fixable air, why fhould not this afford fixable air as well as the ruft of iron, when both appear equally well calcined?

Dr. Prieftley calcined iron fhavings over mercury in dephlogifticated air, by means of a burning lens, and found fome fixed air in the refiduum, but it was not more than the 13th of a meafure, after the abforption of 7 ounce meafures of dephlogifticated air. The fame philofopher reduced a quantity of the calx of iron, carefully prepared, by means of fpirit of nitre in light inflammable air; but it does not appear that he obtained fixable air*. He likewife reduced 17 gr. of lead in alkaline air: the refiduum was phlogifticated air, and it did not contain a particle of fixable air. Dr. Prieftley reduced 150 ounce meafures of light inflammable air to 10 ounce meafures, by re-

* Vol. VI. p. 16.

ducing in it the calx of lead over mercury, and the refiduum contained no fixable air *.

If the fixable air generated during the calcination of the iron, in the above experiment, proceeded from its phlogifton and dephlogifticated air, why was not fixable air formed during the reduction of the calces, whereas they were expofed only to the fame degree of heat?

In my opinion, metals contain fomething not at all neceffary to their conftitution, which forms fixable air with dephlogifticated air. The phlogiftians muft all allow, if metals contain phlogifton or inflammable air, that it is of the explofive kind; for no other is obtained during their calcination in the humid way, whatever menftruum is ufed. Then why does not this form fixable air with the dephlogifticated air during the revival of the calx of mercury in it, if a fubftance of the fame fort be united to it in the ftate of fixable air in the calx? The phlogiftians will fay, that the heat neceffary to the reduction is too great for the formation of fixable air. But then, if fo, why will inflammable air from foliated tartar, or from charcoal, which

* Vol. VI. p. 9.

are known not to contain a particle of ready formed fixable air, generate this under the same circumstance? Or why will it form fixable air in the most intense degree of heat? I ask, if there ever has been an instance of the formation of fixable air by an union of light inflammable air and dephlogisticated air? It appears to me a matter of impossibility. Therefore, how can we suppose that the fixable air produced when we use iron filings and red precipitate, results from an union of both these airs?

Dr. Priestley obtained 40 ounce measures of fixable air from one ounce of red precipitate and two ounces of iron filings *. From 300 grains of iron newly filed, and 240 of red precipitate, Mr. Kirwan obtained no air; but, on the contrary, there was an absorption. When he used precipitate *per se*, instead of red precipitate, and varied the proportion, and sprinkled the ingredients with water, he got 4,5 cubic inches of fixable air, and 36 of a mixture of dephlogisticated and inflammable air. Mr. De la Metherie obtained no air from equal

* Vol. VI. p. 27.

parts

parts of red precipitate and iron filings; and from two ounces of red precipitate, and one drachm of iron filings, he obtained a very ſmall quantity of fixable air*. Equal parts of lead and red precipitate gave no air at all to Mr. Kirwan, though the lead was nearly calcined. 240 gr. of biſmuth, and the ſame quantity of red precipitate, diſtilled with a low heat, afforded Mr. Kirwan two ounces of fixable air. The ſame mixture, urged with a ſtrong heat, gave but one cubic inch of fixable air, and the biſmuth was calcined. Equal parts of red precipitate and zinc did not produce any air; nor did 200 gr. of copper, and 240 of red precipitate, though the mercury was revived †.

One ounce of red precipitate, and one ounce and a half of iron filings newly made, diſtilled in a ſmall coated glaſs retort, afforded but ſix ounce meaſures of fixable air, and about one ounce meaſure of phlogiſticated air, though the mercury was nearly revived, and the iron a good deal calcined. I ſuſpect that the iron was impure, for the air had the ſmell of volatile vitriolic acid

* 27. Roz. 146.

† Eſſay on Phlogiſton, p. 114, 115.

towards the end of the procefs; and as I was obliged to receive the airs in water, a fmall portion might have been abforbed. However, thefe experiments differ widely from Dr. Prieftley's, and clearly prove, that fixable air is not a neceffary production in them; but that it depends upon chance, and the prefence of fome foreign fubftance which we are not aware of.

Dr. Prieftley partially calcined lead in mercury by repeated agitation, with free accefs of air; and after feparating the fluid mercury from a black powder thus obtained, it afforded fome fixable air. From fix ounces of this black powder he obtained four and a half ounce meafures of air, one and a half of which was fixable air *. 10 ounces of the fame powder gave 23 ounce meafures of air; 8 or 9 ounces of which were fixable air. 4 ounces of this black powder, and 2 ounces of iron filings, gave only 4 ounce meafures of fixable air †. 20 ounces of this, and one of iron filings, afforded but 4 or 5 ounce meafures of fixed air ‡. 2 ounces of this black powder, moiftened and dried again, gave very little fixed air §. Al-

* Vol. VI. page 258.
† Ib. p. 261.
‡ Ib. p. 262.
§ Ib. p. 265.

though 4 ounces, treated in the ſame manner, afforded 120 ounce meaſures of air, 12 meaſures of which were fixed air.

Thus we find how theſe experiments vary in their reſults; which ſhews that the fixable air proceeds partly from ſome impurities in the materials, but chiefly from abſorption of fixable air from the atmoſphere. I diſtilled ſome mercury with iron filings, in order to obtain it pure, and introduced ſix ounces of it, and ſome lead filings, into a five ounce phial with a ground ſtopple, and tied a bladder half full of dephlogiſticated air, which I previouſly waſhed in lime liquor, to the neck of it. The bladder being flaccid, I could take out the glaſs ſtopple at pleaſure, and let in dephlogiſticated air when I thought neceſſary. Having by repeated concuſſions produced ſome of this black powder, though the air in the bladder did not ſeem much diminiſhed, I diſcontinued the proceſs, fearing that the wet bladder might be a ſource of fixable air. When I ſeparated the running mercury from it, it weighed near half an ounce, which I quickly introduced into a ſmall coated glaſs retort, and obtained

 from

from it one ounce meaſure of air, which, although it rendered lime-water a little turbid, was not ſenſibly diminiſhed, and a candle burned in it ſomewhat better than in common air.

Having enumerated thoſe experiments which the phlogiſtians adduce as the chief ſupport of their doctrine, I think, they do not in the leaſt help to prove the exiſtence of phlogiſton in metals. Let us review them all, and carefully compare their different products of fixable air, and we ſhall be convinced that it cannot reſult from any neceſſary principle in metals; for, if ſo, the products ſhould be invariably the ſame under the ſame circumſtances.

Beſides, I think, the reduction of one metal by another, in the dry way, rather proves that they contain no ſuch thing as the matter of light inflammable air, or phlogiſton. For, let us ſuppoſe the dephlogiſticated air to be united to the phlogiſton of the metal, in the ſtate either of fixable air or water, and theſe to be attached to the metallic baſis with any force; is it likely that the phlogiſton of another metal, which is intimately combined with its own baſis, ſhould diſturb this

this union in the leaſt? The phlogiſtians may ſay, that the baſis of the reviving metal (we will take, for inſtance, copper) attracts the fixable air or water of the calx at the ſame time that the baſis of the calx attracts its phlogiſton; and ſo, by a double affinity, effect a decompoſition. But I would obſerve, if ſuch a decompoſition ſhould take place, in conſequence of the influence of their different metallic baſes, that it muſt be impoſſible for us to obtain either water or fixable air, as a product reſulting from any of the conſtituent principles of the metal, in the degree of heat neceſſary to reduce red precipitate. Becauſe, if the iron, or copper, or zinc, or biſmuth, all of which will reduce a mercurial calx, ſhould exchange their phlogiſton for the fixable air or water of the calx, they muſt undoubtedly retain this with at leaſt as much force as they do their phlogiſton; and it is well known that no heat will expel this from them.

SECTION VII.

Of the Calcination of Metals by Steam, and the Decompoſition of Water.

MR. Lavoiſier has ſhewn us, that ſteam, when brought in contact with red hot iron, calcines it, at the ſame time that inflammable air is abundantly produced; from which he inferred, that the water is decompoſed. He likewiſe found that the water is decompoſed by iron without the aſſiſtance of heat; for he obtained inflammable air by confining iron filings and water over mercury. Dr. Prieſtley, who has made a vaſt number of very accurate experiments on the ſame ſubject, has found that 294 gr. added to the weight of a quantity of iron, made it to yield 1000 ounce meaſures of inflammable air, which he eſtimates would weigh 60 gr. and which is nearly 5 to 1 *. But this eſtimation, ac-

* Vol. VI. p. 121.

cording

cording to Lavoisier and Kirwan, is too high. Dr. Priestley likewise found, that the addition of 12 ounce measures of dephlogisticated air added 6 gr. to the weight of the iron which had been fused in it. Therefore, the dephlogisticated air absorbed, carries with it into the calx the quantity of water it holds in solution. Whether a quantity of dephlogisticated air, when as much water as possible is abstracted from it, would calcine the same weight of iron, or any other metal, that it would in its ordinary state, is very well worth ascertaining. As this cannot be done without the assistance of a lens, it is not in my power, at present, to make the experiment. The same philosopher observes, that, making an allowance for the small quantity of dephlogisticated air expended in the formation of fixable air during calcination, which did not exceed the 13th of an ounce measure in 7 ounce measures of dephlogisticated air, the quantity of water produced by the reduction of the iron in light inflammable air, nearly corresponded with the weight of both airs. He moreover observes, that the loss of weight in the iron, after its reduction, was equal to that of ſuch a quantity of dephlogiſticated air as would have been one half of the bulk of the inflammable air that diſappeared in the proceſs *. A mixture of 1 part of dephlogiſticated air and 2 of light inflammable air, provided the airs be pure, will, by paſſing the electric ſpark in it, form water, as Mr. Cavendiſh has ſhewn; which proportion very well agrees with the above eſtimation of Dr. Prieſtley. All theſe facts ſtrongly concur in favour of the decompoſition of water. I charged half an ounce of charcoal into a ſmall tubulated retort; the orifice was very ſmall, and well fitted with a ſtopple, though, from its conical figure, it was readily taken out at pleaſure. Having then expoſed the charcoal to a ſtrong heat until nothing came over but pure inflammable air, and this very ſlowly, I took out the ſtopple, and poured in nearly half a thimble full of water, and inſtantly cloſed it again; when 3 or 4 ounce meaſures of air guſhed from the retort with violence, and then ceaſed giving out any more until freſh water was

* Vol. VI. p. 121.

introduced.

introduced. Thus I obtained 10 or 12 cubic inches of air, of which one-fifth was fixable air, and the remainder inflammable, intermediate, I thought, between the light and heavy.

It is very well known that charcoal is wholly convertible into inflammable air, and that this inflammable air cannot, by any means whatever, form fixable air without the presence of dephlogisticated air *. Therefore water must have been decomposed in the above experiment, by which the matter of charcoal was supplied with dephlogisticated air. Dr. Priestley converted the whole of a quantity of charcoal into inflammable air, without the slightest appearance of fixable air †.

* It may be supposed that the atmospheric air, by pressing into the retort, contributed to the formation of the fixable air; but if so, fixable air would have been produced by merely taking out the stopple, which was not the case: besides, atmospheric air could not rush in during the short time the stopple had been out, considering that the charcoal yielded inflammable air, and that the pressure of the water up the neck of the retort must more than counterbalance the external pressure of the atmosphere.

† Vol. VI. p. 245.

Mr. Lavoiſier, having carefully calcined a quantity of charcoal, in order to expel any water or fixable air it might contain, introduced 248,62 gr. troy of it into an iron tube lined with copper, and having paſſed through it 1122 gr. of water, in the ſtate of ſteam, obtained 6644 cubic inches of air, whoſe weight he eſtimated at 550 gr. one-fourth of the bulk of which he found, by introducing cauſtic alkali, to be fixed air; and there remained 5 grains of aſhes in the tube. As the weight of the airs produced was more than double that of the charcoal, he inferred that the water muſt have been decompoſed; its oxygenous principle uniting to a portion of the charcoal, and forming fixable air, while the remainder acquired an aerial ſtate, and mixed with the inflammable air of the water. That water had been decompoſed in this experiment is evident; elſe, whence came the fixable air? for, from Mr. Lavoiſier's previous treatment of the charcoal, it could not contain any.

Mr. Kirwan does not allow the decompoſition of water in the above experiment. He ſuppoſes that the fixable air came from the

the charcoal, being one of its conſtituent principles, and that the inflammable air is its other conſtituent principle, and that the additional weight proceeded from the ſolution of water in both airs.

Mr. Kirwan's firſt ſuppoſition is abſolutely contradicted by Dr. Prieſtley's experiments *, where he has ſhewn that charcoal does not contain an atom of fixable air. Therefore, to ſay any more on the ſubject would be ſuperfluous. That water is held in ſolution in all airs, is what we do not diſpute, but not in that quantity which the phlogiſtians imagine. A ſmall quantity of moiſture is undoubtedly neceſſary to the converſion of charcoal into pure inflammable air: if a little more be uſed, fixable air is produced in very ſmall quantities; but if a larger portion of water be uſed, the quantity of fixable air is ſtill greater. The extremes Dr. Prieſtley obſerved in the proportion of fixed to the inflammable air has been from one-twelfth to one-fifth of the whole. Why the ſmall quantity of water neceſſary to the aerial ſtate of charcoal ſhould not be decompoſed, is difficult to be ac-

* Vol. VI. p. 345.

counted for, eſpecially when a larger quantity is readily decompoſed. I expoſed ſome wort to dephlogiſticated air until it began to ferment, yet the air was not in the leaſt diminiſhed, though the liquor acquired an acid taſte. The ſame change took place in the liquor when I prevented all communications with dephlogiſticated air.

Theſe facts narrowly inquired into, will remove all doubts reſpecting the decompoſition of water. If it were not decompoſed, we could not account for ſeveral facts relating as well to the calcination, as the reduction of metals. Let us even ſuppoſe the inflammable air to come from the metal in conſequence of a ſuperior attraction of its baſis to water; is it likely that this would diſlodge the water again in any degree of heat, eſpecially when the inflammable air is combined with fire? It may be ſaid, that intenſe heat diſſolves the union of the water and the metallic baſis. But ſhould not, as already obſerved, the ſame cauſe prevent the union of the inflammable air to the metallic baſis, if it even were as fixed as water, and uncombined with fire, unleſs we ſuppoſe phlogiſton to have greater attraction

attraction to the metallic basis than water has? Then, water could never expel inflammable air from the metal.

To account for the calcination of metals by steam, &c. and for the reduction of these again to their metallic splendour in inflammable air, we must, in my opinion, have recourse to a mode of reasoning quite different from the preceding; and consider metals to be simple bodies, whose ultimate particles attract dephlogisticated air with greater force than light inflammable air. The phlogistians may say, that light inflammable air in this case could not decompose metallic calces; but this is foreign to that which I urged last against them. For, metals being fixed bodies, and dephlogisticated air having strong attraction to fire; when calces are exposed to heat, the force of union between them is much weakened, as is evident by the reduction of gold, silver, and mercury by heat alone, having less attraction to dephlogisticated air than the other metals.

To render this more intelligible, let us suppose dephlogisticated air to be attached to the metal in a common temperature, with the force of 7, and the attraction of light inflammable air to dephlogiſticated air to be any degree below this, we will ſay the force of 6. Let us now ſuppoſe this compound or calx to be expoſed to intenſe heat, though not ſtrong enough to decompoſe it, yet ſufficient to reduce its force of union to its dephlogiſticated air to $5\frac{1}{2}$. If inflammable air were brought in contact with the calx in this ſtate, is it not reaſonable to ſuppoſe that it would deprive it of its dephlogiſticated air? But then I aſk the phlogiſtians, whether the inflammable air could unite to the metal under theſe circumſtances?

I think this alone, ſtrictly conſidered, would go a great way towards overthrowing the phlogiſtic theory.

SECTION VIII.

Of the Reduction of Metallic Calces by means of Charcoal, and the Formation of Fixed Air.

DR. Prieftley has obferved, that fixable air muft have been actually formed during the union of heavy inflammable air and dephlogifticated air, as he often found that the fixable air produced, exceeded the weight of the inflammable air.

Dr. Higgins has fhewn (and I think I am authorized to particularize it, for I had an active fhare in all the experiments fet down in his laft publication), that 3,15 gr. of the pureft dephlogifticated air, and 1,1 gr. of inflammable air from foliated tartar, afford, when inflamed by the electric fpark, 2,85 gr. of fixable air. As the weight of the fixable air fell fhort of that of the two airs employed, by 1,4 gr. and as there had been a quantity of moifture precipitated, Dr. Higgins fuppofes that a part of the de-phlogifticated phlogisticated air unites to phlogiston, and forms water, while the remainder, which he estimates to be two thirds of the whole, unites to the acid matter of acetous acid, as he is pleased to call it, and forms the fixable air. When he used inflammable air from charcoal, the result was the same. These experiments clearly shew, that fixable air is composed of the matter of charcoal and dephlogisticated air. I have my doubts respecting the water produced in the above experiment: in my opinion, the most part of it is precipitated from both airs on their contracting an union, as the compound cannot hold in solution as much water as its constituent principles in their simple aerial state; although heavy inflammable air from foliated tartar contains light inflammable air, as appears from Dr. Austin's experiments. But this I consider to be as foreign to the gravitating matter of charcoal, as the matter of sulphur is to the inflammable air, which holds it in solution in the state of hepatic gas. For both will burn, or, in other words, will unite to dephlogisticated air, and form separate compounds. I think, neglecting to discrimi-

nate

nate between the light and heavy inflammable airs, has been the chief caufe of all the errors and confufion that at prefent prevail in the fcience of chemiftry.

Dr. Higgins introduced fome pieces of well burned charcoal into a deep crucible, and covered them over an inch deep with powdered charcoal. Having luted on a cover, he expofed them for two hours to heat fufficient to melt filver; he then placed the crucible in fuch a manner, that the powder might remain red hot for fome time after the pieces next the bottom had cooled. This he had done in order, as the charcoal muft imbibe fomething on cooling, both to fupply it with inflammable air, and to prevent a communication with the external air, which the charcoal would have otherwife imbibed.

One hundred and twenty grains of this charcoal quickly powdered were well mixed with 7680 gr. of litharge, which had been previoufly fufed to feparate any uncalcined lead which it may contain. This mixture was charged into a coated retort juft large enough to contain it, fo that the common air muft have been nearly fecluded. Being then

then placed in a reverberating furnace, and heat duly applied, it yielded by eſtimation, after cooling to the mean temperature of the atmoſphere, 384 gr. of fixable air, at the rate of ,57 gr. to a cubic inch, 8,704 of phlogiſticated air, and 0,911 gr. of dephlogiſticated air, beſides 49 gr. of water. On breaking the retort, 3888 gr. of revived lead were found, beſides ſome vitrified litharge; but not an atom of charcoal was left, nor was there a particle of inflammable air produced*. Now let my reader conſider the weight that 3888 gr. of lead acquire by its converſion to litharge, and the quantity of inflammable air that 120 gr. of charcoal will afford (which, according to Dr. Prieſtley, is about 360 ounce meaſures), and he will find, making an allowance for the phlogiſticated air, that theſe nearly correſpond with the proportion of heavy inflammable air and dephogiſticated air neceſſary to the formation of fixable air by the electric ſpark. Hence we may conclude, that not a particle of charcoal entered into the conſtitution of the

* Exp. and Obſ. on Acet. Acid, Sect. XIX. p. 274-276.

revived lead, but muſt have been wholly converted into fixable air. Mr. Kirwan cannot ſay, that this quantity of fixable air exiſted ready formed in the charcoal, when it is more than two thirds the weight of the charcoal; nor can he attribute this weight to water. Then I aſk the phlogiſtians, whence came the dephlogiſticated air which formed this fixable air? If they can anſwer this without contradicting themſelves, it is more than I at preſent foreſee. For, in the firſt place, if they ſhould ſay that the metallic calx affords fixable air, or that its fixable air is decompoſed, by which the charcoal is furniſhed with dephlogiſticated air, they contradict their own aſſertion; for they do not allow the refractory calces to contain any ſuch thing, but, on the contrary, they ſuppoſe theſe to be combined with water. In the ſecond place, if they ſhould ſay that the dephlogiſticated air is ſupplied by the water of the calx, it is contradictory to their own principles, for they do not allow the decompoſition of water.

SECTION IX.

Of the Solubility of Metals.

METALS in their ſimple ſtate are inſoluble in water; but when combined with acids they are ſoluble. Iron and ſulphur fuſed form an inſoluble maſs; iron and dephlogiſticated air form likewiſe an inſoluble compound; but iron, dephlogiſticated air, and ſulphur will form a very ſoluble compound. Phlogiſticated air in its ſimple ſtate has no ſenſible affinity to metals; yet, when combined with dephlogiſticated air, it will unite to them and render them ſoluble. The affinity of the marine baſis to metals is not known; but that they have greater attraction to the dephlogiſticated air attached to it than they have to the baſis itſelf, has been already demonſtrated. That the attraction of the marine baſis to metals is increaſed by their previous union

union to dephlogiſticated air, may be inferred from its property of diſſolving the calces of thoſe metals which will not yield to it in their ſimple ſtate. That common marine acid has an attraction to dephlogiſticated air, is very well known; and it has been above obſerved, that, when fully ſaturated with this, it will not affect metallic calces, though it will diſſolve thoſe metals which the common marine acid will not touch. Oils will not diſſolve metals in their ſimple ſtate, provided the oils be pure, except iron and copper, which are deſtructible wherever they meet moiſture and fixable air, both of which are generally preſent in oils. But the oils will unite to the calces, and conſtitute ſoluble ſaponaceous compounds. As oils have an attraction to dephlogiſticated air, though they cannot unite to it in a common temperature, nor take it from the metals but by the aſſiſtance of a ſtrong heat; it may ſo far influence them as to promote their union to metallic calces. It is clear from theſe facts, although dephlogiſticated air alone will not render metals ſoluble in water, that it is through its media-

tion,

tion, or influence, that a third body will unite, and form a ſoluble compound. But which of the three ſubſtances has this ſolvent power moſt inherent in it, is what we cannot pretend to explain; nor is it neceſſary towards the eſtabliſhment of the antiphlogiſtic theory to know this. It is ſufficient for us to prove, that dephlogiſticated air is indiſpenſably neceſſary for the ſolution of metals in every menſtruum, except a few which I ſhall preſently obſerve. The foregoing principles will account for Mr. Kirwan's firſt four queries, Section 10. I muſt confeſs I do not ſee the force of thoſe eleven queries of his, nor can I find how they oppoſe the antiphlogiſtic theory in the leaſt.

The moſt rational of his queries are explicable in this doctrine; and of theſe the moſt difficult to be accounted for is the ſolubility of ſome calces in the nitrous acid, while others are inſoluble in it. But we may attribute this in a great meaſure to their property of uniting to more dephlogiſticated air when in ſolution, than they can retain in their dry, pure, calciform ſtate. Thus the calces of lead are ſoluble in all the acids

acids. The calces of gold, mercury, and ſilver are likewiſe ſoluble in the nitrous acid on the ſame principle. The calces of iron, tin, biſmuth, cobalt, zinc, antimony, &c. when perfectly calcined, contain more dephlogiſticated air, together with the quantity which enters into the conſtitution of perfect nitrous acid, than is neceſſary for ſolution; therefore either muſt loſe a portion of their air before they can unite. I do not diſpute but the baſes of the different acids have, independent of their dephlogiſticated air, different degrees of attraction to the different metals. I have ſhewn this to be the caſe in treating of the vitriolic and marine acid.

Mr. Kirwan's 10th query is not eaſily accounted for: before we can attempt this, we muſt be acquainted with the conſtituent principles of fixed alkali. I doubt whether he can give even a plauſible explanation of it himſelf, in his own doctrine. The diſſolution of copper in volatile alkali, likewiſe, cannot be accounted for in any theory until we know more of chemiſtry. I at one time ſuppoſed that it proceeded from the abſorption of dephlogiſticated air from the

 atmoſphere;

atmosphere; but I found this not to be the case by experiment. Indeed Mr. Kirwan might as well have asked why liver of sulphur, or mercury, dissolves gold. Mr. Kirwan's last and 11th query has been amply accounted for in describing the effect of metals on vitriolic acid.

SECTION X.

Of the Precipitation of Metals by each other.

THAT ſome metals attract dephlogiſticated air with greater force than others, is now an eſtabliſhed fact. Gold, platina, and ſilver will not unite with it in the ſtrongeſt heat of our furnaces. Mercury, likewiſe, will not unite to dephlogiſticated air until heated ſeveral hundred degrees above that which is neceſſary for its fuſion only. The reſt of the metals will abſorb dephlogiſticated air by mere fuſion, but ſome with greater rapidity than others; as for inſtance, zinc, biſmuth, and arſenic will preſent the phenomenon of combuſtion, when ſufficiently heated in atmoſpheric air. Again we find, that thoſe metals which combine with dephlogiſticated air with moſt difficulty, will yield it with the greateſt facility. Mercury, gold, ſilver, and platina are reſtored to their metallic brilliancy by mere heat; while all the other calces require the addition of ſomething which has greater affinity to dephlogiſticated air than their reſpective metals, before they can be reduced to their ſimple ſtate.

The ſame order takes place in the precipitation of metals by each other in their metallic ſtate. Gold is precipitated in its ſemi-metallic ſtate by ſilver, and ſilver by mercury, and mercury by copper; and all three yield to the reſt of the metals. The ſame law holds good with reſpect to moſt of the refractory metals. They precipitate each other according to their different affinities to dephlogiſticated air; although there are a few exceptions; but theſe, I fancy, proceed chiefly from the attachment of the acid baſis to the different metals. Thus iron will not precipitate lead from marine acid; and regulus of arſenic precipitates mercury with difficulty from the vitriolic acid. Marine acid will take ſilver from the nitrous; and as we cannot attribute this to dephlogiſticated air alone (both acids having this in their conſtitution), it is evident, that the

the acid bafes are differently influenced by the different metals. Indeed, if they had not different forces of attraction as well to the metals as to the alkalies and earths, we could not very well account for the expulfion of one acid by another from thefe different fubftances, more efpecially when the acids are in their perfect ftate; although we may attribute this very frequently to the agency of fire. Hence we may conclude, though the acid bafis difturbs the affinity of the oxygenous principle to metals in a few inftances, that we are not from thence to pronounce the invalidity of the antiphlogiftic theory.

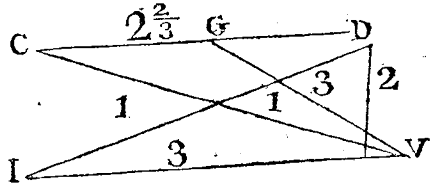
I have already fhewn, in treating of marine acid, that the bafis of this acid contributes much to the reduction of the precipitated metal, otherwife the precipitating metal could never deprive it of the whole of its dephlogifticated air; and the fame may be faid of the other acid bafes.

In a neutral mixture of vitriolated copper, the calx is held in folution by volatile vitriolic acid, which is lefs intimately attached to the copper than its dephlogifticated air.

Iron will precipitate the copper from this ſolution in its ſimple metallic ſtate.

In order to illuſtrate this decompoſition, I think it neceſſary to have recourſe to the following method:

Let C be copper, D dephlogiſticated air, which (let us ſuppoſe) attract each other with the force of $2\frac{2}{3}$, (to avoid perplexity, reciprocal attraction is not conſidered) and let this be the calx of copper. Let V, or volatile vitriolic acid, be attached to this compound with the force of 3, and let us ſuppoſe 2 of this force to proceed from the dephlogiſticated air attached to the copper, and the remainder, which is but 1, to be in conſequence of the influence of the copper itſelf on the ſulphur and dephlogiſticated air of the volatile vitriolic acid; therefore let G be the centre of gravity of V. Let us ſuppoſe this to be



the ſtate of a neutral ſolution of copper in the vitriolic acid. Here the copper attracts V and D with only the force of $3\frac{2}{3}$, and C and D attract V with the force of 3. Let us us again ſuppoſe I to be iron, which attracts V, or volatile vitriolic acid, with the force of 3, it cannot take it from C and D, which hold it with the force of 3; but it ſo counteracts the attachment of D and V to C, that it is reduced to $\frac{2}{3}$. Let us now ſuppoſe I, from its attraction to dephlogiſticated air, to influence D with the force of 1: in this caſe C will be deprived of D and V, for the force of $3\frac{2}{3}$ muſt readily obey the power of 4. This, in my opinion, is what takes place in all metallic precipitations. If the precipitant cannot take up the whole of the dephlogiſticated air of the precipitated, it is thrown down in a ſemi-reduced ſtate. Thus lead and ſilver will precipitate gold of a dirty purple colour, while copper and iron throw it down in its brilliant metallic ſtate. If the iron united firſt to the volatile vitriolic acid, the reſulting compound would not deprive the calx of its dephlogiſticated air. For the calx of copper, diffuſed in a ſolution of iron in volatile vitriolic acid (although no inflammable air had been diſengaged), was not in the leaſt reduced. Hence we may infer, that the whole force of the iron, in order to throw down the copper in its pure ſtate, muſt be exerted at once towards V and D; by which, with the aſſiſtance of V, V and D move jointly to unite to I, or iron.

If tin be introduced into a neutral ſolution of tin in the nitrous acid, it is calcined, a calx is thrown down, and dephlogiſticated or imperfect nitrous air is produced. Dephlogiſticated nitrous air, according to the phlogiſtians, contains no phlogiſton; then I aſk, what becomes of the phlogiſton of the newly calcined metal? If tin contained phlogiſton, either inflammable air or nitrous air would be produced, or a portion of the diſſolved tin would be precipitated in its metallic ſtate; neither of which will take place, if the experiment be well conducted. Hence I ſhould ſuppoſe, that metals do not precipitate each other in their metallic ſtate, in conſequence of a double affinity proceeding from the matter of light inflammable air (or phlogiſton), and likewiſe that metals part with no ſuch thing during their calcination in acids.

Metallic calces do not precipitate each other, as the celebrated Bergman has ſhewn, but are rather ſoluble even in neutral ſolu-

tions

tions of different metals. Hence he inferred, that the ſame acid takes up the different metallic calces without diſtinction, provided they have loſt a certain portion of their phlogiſton; but, to ſpeak in the language of the preſent time, provided they are not united to too much dephlogiſticated air. To aſcertain the different degrees of calcination the different metals require to render them equally ſoluble in the ſame acid, is a difficult taſk; for, as the above excellent chemiſt obſerved, a very ſmall quantity of dephlogiſticated air, over and above a certain portion, will render ſome metals quite inſoluble; and the ſame may be obſerved on the contrary extreme.

Hence apparent exceptions ariſe to this law; for the ſame acid will take up the ſome calces, although it will not affect others. Thus the acetous acid readily diſſolves the calx of mercury, but ſcarcely takes up any of the calx of biſmuth. However, as the ſame acid does not make that diſtinction between the calces that it does between their reſpective metals, it is evident that dephlogiſticated air is the chief cauſe of metallic ſolution; although this cannot take place

when

when the attraction of the acid basis to the metal itself, and to the dephlogisticated air attached to it, is destroyed. For, when the metal is fully saturated with dephlogisticated air, it cannot influence the acid basis to which it must have much less affinity; nor can the dephlogisticated air of the calx influence the acid basis, being already saturated with dephlogisticated air; and the metal, having all its force of attraction to dephlogisticated air expended on the quantity already attached to it, cannot influence the dephlogisticated air of the acid basis in the least: therefore, when perfect calces and perfect acids are mixed, they do not affect each other, except in a few instances, which have been already observed.

Mr. Lavoisier, who first attributed the precipitation of metals in their metallic state by each other, to the superior attraction of the precipitant to dephlogisticated air, deduces the proportion of the oxygenous principle necessary to the solution of different metals, from the quantity of one metal necessary to the precipitation of a given quantity of another metal, by the following

lowing analogy, which, as I cannot at present refer to the author, I ſhall give in Mr. Kirwan's words: "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 grains of mercury are neceſſary "for the precipitation of 100 gr. of ſilver "from the nitrous acid, it is evident that "135 gr. of mercury require for their ſolution the ſame quantity of the oxygenous "principle as 100 grains of ſilver; and "therefore that the quantity neceſſary to "diſſolve 100 gr. of mercury, is to that "neceſſary to diſſolve 100 gr. of ſilver, as "100 to 135. 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 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.

	Metals.	Oxygenous Principle. Grains.	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	
	Nickel,	14,721	
	Reg. of Ant.	13,746	22, 383
	Tin,	14	23, 555
	Regulus of Arſenic	11,739 / 24,743	
	Silver,	10,800	
	Biſmuth,	9,622	
	Mercury,	8,000	
	Lead,	4,470	14, 190

Mr. Kirwan objects to this part of the antiphlogiſtic doctrine *, 1ſt, Becauſe a ſolution of gold in aqua regia is precipitable in its metallic ſtate, by a freſh made ſolution of vitriol of iron, but not of copper or any

* Eſſay on Phlogiſton, p. 131.

other

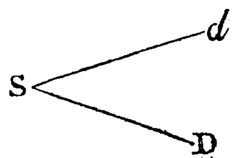
other metal. The precipitate of gold obtained in the above manner, is generally combined with more or leſs dephlogiſticated air; and conſidering that 100 gr. of iron freſh diſſolved can take 10 grains of dephlogiſticated air from 100 grains of gold, that a precipitation ſhould take place is not to be wondered at, eſpecially when gold is rendered inſoluble on loſing a ſmall portion of the dephlogiſticated air neceſſary for its ſolution. Beſides, the iron does not precipitate an equal quantity of gold, which muſt make a vaſt difference. Mr. Kirwan thinks this manner of accounting for it inſufficient; 1ſt, Becauſe a ſolution of vitriol of copper takes up only 15,85 parts of the oxygenous principle, and yet is capable, by precipitation, of taking up 36 gr. and although it has greater attraction to the oxygenous principle than gold has (according to Mr. Lavoiſier), it does not precipitate a particle of gold. 2dly, Becauſe platina is not precipitable by a ſolution of vitriol of iron, which, in the antiphlogiſtic doctrine, muſt retain its dephlogiſticated air with very little force, when it cannot take it from nitrous

nitrous air, as its inſolubility in the nitrous acid indicates.

To the firſt of theſe objections I would make anſwer, that the attraction of copper to dephlogiſticated air is not near ſo ſtrong as that of iron; and its ſtronger attachment to the acid of ſolution reduces this ſtill lower, ſo as to bring both ſolutions to an equilibrium. To the ſecond cauſe I would ſay, that platina, by being ſoluble in various proportions of dephlogiſticated air, may afford the martial ſolution a portion of it, and ſtill remain in ſolution.

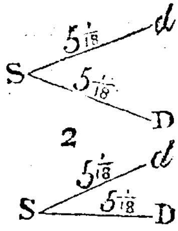
As copper is precipitated by iron, and likewiſe as copper is inſoluble in diluted vitriolic acid, Mr. Kirwan ſuppoſes that the diſſolution of copper in a diluted ſolution of vitriol of iron, by expoſure to air or in a boiling heat, is difficult to be accounted for in the antiphlogiſtic theory; and on this he grounds his ſecond objection. In my opinion, it is very unfavourable to the phlogiſtic doctrine; becauſe the copper is diſſolved, and no inflammable air produced, and yet the iron is thrown down in a calciform ſtate.

Mr. Kirwan grounds his third objection, page 132, on the following fact: "Iron," he ſays, "is diſſolved by the concentrated "vitriolic acid only by the aſſiſtance of "heat; yet, if to a ſolution of ſilver or "mercury, in that concentrated acid, a piece "of iron be inſerted, the ſilver or mercury "will immediately be precipitated in their "metallic form, and the iron diſſolved. "This ſeems inexplicable in the new "theory; for ſince iron cannot without the "aſſiſtance of heat deprive ſulphur of its "oxygenous principle, how does it happen "that, without that aſſiſtance, it deprives "ſilver or mercury of that principle, though "they have a ſtronger attraction to it than "ſulphur has?" This, certainly, is a very fair query, and deſerves attention. Therefore, I ſhall give my opinion of it in as clear a manner as I can.



Let the two diagrams, be molecules of concentrated vitriolic acid; which let us ſuppoſe influence each other with the force of 2, which in addition to $5\frac{1}{18}$ makes $7\frac{1}{18}$.

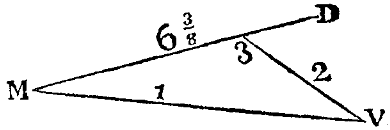
Now,



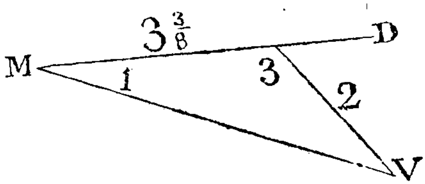
Now, if iron be introduced into this acid, it will not be diſſolved in it; for the force of 7, with which we have already ſuppoſed iron to attract dephlogiſticated air, being inferior to $7\frac{1}{18}$, a perfect neutrality prevails until the force of 2, which we may call the aggregate influence, is diminiſhed; and this is done by fire or water. Again, let us ſuppoſe mercury to attract dephlogiſticated air with the force of $6\frac{3}{8}$; in this ſtate concentrated vitriolic acid will not influence it, until its aggregate attraction is wholly removed by fire, and then it will readily diſſolve it. Let us now ſuppoſe the mercury in a ſtate of ſolution, to be influenced by its dephlogiſticated air and volatile vitriolic acid, which is the acid of ſolution, with the following forces. Let M be mercury, D the quantity of dephlogiſticated air neceſſary for ſolution; let us ſuppoſe theſe, if there had not been any thing elſe preſent to influence either, to attract each other with the force of $6\frac{3}{8}$,

and

and let us ſup-poſe this to be the utmoſt ſum of their reci-



procal attractions. Let us likewiſe ſuppoſe V, or volatile vitriolic acid, to be attached to M——D, or the calx of mercury, with the force of 3; let 1 of this proceed from the mercury itſelf, and the other 2 from the dephlogiſticated air attached to it, which muſt reduce the attraction of M for D to $3\frac{3}{8}$; which, in addition to the force of 1, that prevails in conſequence of the attachment of M and V, makes $4\frac{3}{8}$: thus, V and D are attached to M with the force of $4\frac{3}{8}$. Now, if iron were introduced into ſuch a mixture, is



it not to be expected that it would with the force of 7 readily overcome the above force, and precipitate the ſilver or mercury, even in the preſence of concentrated vitriolic acid, which is always inſeparable from theſe ſolutions, and which, from its weak attachment to the mercurial ſalt, may oppoſe the decompoſition a little? Mr. Kirwan's fourth query, page 133, is very much in favour of the antiphlogiſtic doctrine: for, as I had an occaſion to obſerve above, the precipitation of one metal by another in its calciform ſtate, without the production of inflammable air, at the ſame time that the precipitant is held in ſolution, tends ſtrongly to prove the non-exiſtence of the matter of light inflammable air in metals; beſides, it is very explicable in the antiphlogiſtic doctrine. I have already endeavoured to ſhew upon what principle the acid baſes retain their dephlogiſticated air with leſs force, when fully ſaturated with it, than when united to a ſmall portion; and I have ſhewn, in treating of nitrous acid, that the attachment of its baſis to dephlogiſticated air is in exact proportion to the quantity united to it. The ſame law holds good in all other combinations, and is explicable on the ſame principles. Almoſt all bodies will unite with the different ſubſtances to which they have an affinity, in various proportions, until they arrive at the point of ſaturation, which limits their power of chemical attraction.

There

There are a few exceptions to the above law; for, the principles of water will only unite in one proportion, ſo that we can never obtain it in an intermediate ſtate. The cauſe of this I have already attempted to demonſtrate. I have my doubts whether the ſame may not be ſaid of the aerial acid. Thus, metals will unite with dephlogiſticated air in various proportions, until ſaturated. If 100 grains of a metal are capable of uniting to 15 gr. of dephlogiſticated air only, they will attract and retain 5 gr. of dephlogiſticated air with greater force than they will 10 gr. and 10 gr. with greater force than 15 gr.

Let us ſuppoſe every 100 gr. of tin, when in perfect ſolution, to be united to 15 gr. of dephlogiſticated air with the force of 5½. Let iron attract dephlogiſticated air with the force of 7, and let us ſuppoſe this force to be reduced to 6, by the acceſſion of 7½ gr. of dephlogiſticated air, and the attraction of the tin to its dephlogiſticated air to be increaſed by loſing 7½ of dephlogiſticated air: in this caſe, iron cannot precipitate tin in its metallic ſtate, although it may have greater attraction to dephlogiſticated air than the tin has. Hence it is evident, that a metal, in order to precipitate another in its metallic ſtate, muſt not only unite to dephlogiſticated air in greater quantities, and attract it more forcibly, but that this ſuperiority of force muſt be very great indeed.

Mr. Kirwan's fifth, ſixth, and ſeventh queries have been explained, pages 260—1. One ounce of the nitrated calx of mercury, two ounces of Pruſſian blue, and twenty-four of water, boiled for a few minutes with conſtant agitation, acquire a cineritious yellow colour. The mercury unites to the tinging acid of the Pruſſian blue, and forms a ſoluble ſalt. If to the filtered ſolution a ſmall quantity of iron filings and vitriolic acid be added, the whole maſs turns black, and the mercury is reduced*. As iron filings and vitriolic acid produce inflammable air, and as the Pruſſian acid is diſengaged and the mercury revived, Mr. Kirwan ſuppoſes, that a portion of the inflammable air unites to the mercury, revives it, and expels from it the Pruſſian acid.

* Scheel, p. 162, French tranſlation.

This

This being urged againſt the antiphlogiſtians by Mr. Kirwan, as unanſwerable in their doctrine *, I ſhall endeavour to inquire into it minutely.

In the firſt place we are to conſider, that the Pruſſian acid, being united to the calx in its perfect ſtate, cannot take any thing from it during its ſeparation; therefore the reduction muſt ſolely depend upon the attraction of the mercury to inflammable air. 2dly, Be it remembered, that Mr. Kirwan conſiders the calx of mercury as a compound of fixable air and the baſis of mercury. Now, I ſhould like to know how the inflammable air can act in this caſe; for it has two powers to encounter. Firſt, The attachment of the aerial acid to the metallic baſis. 2dly, The attraction of the Pruſſian acid to both, beſides its own attraction for fire, which is very conſiderable. I muſt confeſs, as the decompoſition depends upon a ſingle elective attraction, I cannot conceive how the inflammable air can expel both acids. If the inflammable air diſengaged by the acid and iron filings, ſhould

* Eſſay on Phlogiſton, p. 123.

 unite

unite to the metallic basis, its own proper phlogiston would be disengaged, united to dephlogisticated air in the state of fixable air; for it cannot be said that there is heat sufficient to form water. Then what becomes of the fixable air? for I repeated the experiment with the utmost caution, and could not obtain a particle of fixable air. It cannot be said, that the inflammable air united to the dephlogisticated air of the calx, and formed water, if we suppose it to be already attached to the matter of light inflammable air in the calx; for bodies of the same sort cannot disturb each other's affinity to different substances so materially, as to cause a decomposition.

Let us now inquire into the above process in the antiphlogistic doctrine. I have already shewn, that bodies which have less attraction to dephlogisticated air than sulphur has, may wholly decompose the vitriolic acid, from the nature of its constitution. Thus mercury will calcine in concentrated vitriolic acid by the assistance of heat only, and volatile sulphureous acid is disengaged. The rationale of the production of this acid has been given before. As water has no effect on mercury, it is evident that light inflammable air attracts dephlogisticated air with greater force than mercury does.

If sulphur and the calx of mercury be distilled, volatile vitriolic acid is formed, and the mercury is partly revived; and if a large portion of sulphur be used, cinnabar is formed. Hence it appears, that sulphur has greater attraction to dephlogisticated air than mercury has. These facts kept in view, we can readily account for the reduction of mercury, when vitriolic acid and iron are introduced into the solution of the mercurial calx in the Prussian acid. Iron, as I have already endeavoured to explain, during its dissolution in vitriolic acid, totally deprives the sulphur of its dephlogisticated air; the sulphur again, while in its ultimate division, and before it is influenced by fire, or by the aggregate attraction, recovers this from the water, by which inflammable air is produced. If the calx of mercury reduced into its ultimate division, in which state it must be when held in solution, were in contact with vitriolic acid thus decomposed, is it not reasonable to suppose, that it would yield its dephlogiſticated air to the ſulphur, more eſpecially when it retains it with leſs force than water does? But as water is preſent, a portion of it is likewiſe decompoſed, by which we obtain inflammable air. Whether the inflammable air itſelf, at the inſtant that it is deprived of its dephlogiſticated air, may not contribute to the reduction of the mercury, by uniting to its dephlogiſticated air, and reproducing water, is what I cannot pretend to determine; although, from the attraction of the matter of light inflammable air to fire, together with the interference of the Pruſſian acid, I am rather inclined to ſuppoſe it does not. The mercury being thus deprived of its dephlogiſticated air by the ſuperior attraction of ſulphur to that principle, rejects the Pruſſian acid, as having no ſenſible attraction to it in its metallic ſtate.

N O T E.

FINDING that Mr. Bertholette, in his notes to the French verſion of Mr. Kirwan's Eſſay on Phlogiſton (which I had not ſeen until my ſection on marine acid had been printed, which is now ſome months ſince, the preſs has been ſo very tedious), affirms, that dephlogiſticated marine air is not decompoſed by inflammable air, as Mr. Kirwan has aſſerted, I made the following experiment:

I poured ſome colourleſs nitrous acid highly diluted upon a quantity of manganeſe, in order to ſeparate any calcareous earth it might contain (the perfect acid having no effect on the pure calx of manganeſe), and triturated them for ſome time; then filtered the ſolution, and waſhed the calx repeatedly with hot diſtilled water, until the whole of the nitrous acid was waſhed away. Having introduced it into a retort, I poured ſome pure marine acid upon it; and, when it had worked ſome time, received ſome of the air in hot diſtilled water: equal parts of this and inflammable air produced from vitriolic acid, which ſtood in lime liquor for two days, were mixed over lime water; the marine air was gradually abſorbed, no precipitation took place, and the inflammable air did not ſeem diminiſhed. I repeated the experiment with the ſame reſult. In haſtily peruſing the page in which Mr. Kirwan mentions his experiment on inflammable and dephlogiſticated marine air over lime water, I ſuppoſed, he meant, that no fixable air had been produced during the union of both airs: this was my chiefeſt motive to repeat the above experiment, the reſult of which tends to corroborate my arguments on that ſubject.

An Analyſis of the Human Calculus, with Obſervations on its Origin, &c.

INTO a ſmall earthen retort well coated, I introduced one ounce and three quarters (Troy weight), or 840 grains of dry and well powdered calculus, which, on being broke, appeared to be laminated with a ſmall nucleus, which was likewiſe minutely laminated. It was compoſed of coats or layers ſomewhat like an onion; the outward cruſt appeared very porous, but increaſed in firmneſs of texture towards the centre. The retort thus charged was placed in a ſide furnace, with a conical glaſs tube, and an air apparatus adjoined to it. The firſt impreſſion of fire after the air of the veſſels was expelled, occaſioned a ſlow emiſſion of an elaſtic fluid, the firſt meaſure of which appeared to conſiſt of equal parts of phlogiſticated and fixed air.

The 2d meaſure $\frac{2}{3}$ fixable, $\frac{1}{3}$ phlogiſticated.
3d $\frac{2}{3}$ ditto, $\frac{1}{3}$ ditto.
4th $\frac{7}{8}$ ditto, $\frac{1}{8}$ inflammable.
5th, 6th, and 7th meaſures ſame as the laſt.

laſt. Here the elaſtic fluids began to come over very faſt, attended with an urinous ſmell. The 8th meaſure conſiſted of $\frac{2}{3}$ fixable, $\frac{1}{3}$ inflammable, with an alkaline ſmell, 9th meaſure $\frac{2}{3}$ fixable, $\frac{1}{3}$ inflammable, and burned with a greeniſh flame. The elaſtic fluids now iſſued ſo rapidly, it was impoſſible to keep an exact account of the number of meaſures; and as I was obliged to work in mercury, the meaſure which I uſed was ſmall, containing but five cubic inches; therefore I only examined the elaſtic fluids at different periods of the proceſs. About the fourteenth meaſure by conjecture, a very pungent alkaline, urinous and ſuffocating ſmell was very ſenſible, not only on the ſurface of the mercury, but throughout the elaboratory. The ſixteenth meaſure was rapidly attracted by lime water to $\frac{1}{2}$, and the lime water was not rendered ſo turbid as it ought to have been, if all the air abſorbed had been fixable air: on continuing the agitation the contraction ſtill went on, though much ſlower than at firſt, until the air was reduced to $\frac{1}{4}$, which was inflammable; the laſt portion, that was ſlowly abſorbed, precipitated the lime very faſt. After loſing about five meaſures, the next was rapidly contracted in common pump water partially impregnated with fixable air, until reduced to $\frac{2}{3}$, and here ſeemed ſtationary, though frequently agitated; but on removing it to lime water, it was contracted $\frac{1}{6}$, rendering the lime water turbid. From theſe facts it appears, that fixed and alkaline airs iſſued at the ſame time; but why they did not unite in their paſſage, or when received into the meaſure, is a myſtery to me; probably the ſmall quantity of inflammable air interfered. From the beginning of the 10th meaſure, a black charry and greaſy matter began to line the conical tube and the air veſſel; and may not the alkaline air diſſolve this partially, though not in ſuch proportion as to render it ſolid, yet at the ſame time to weaken its attraction for fixable air? Were they to ſtand for ſome time, I do not doubt but mild volatile alkali would have been formed; but this circumſtance did not occur to me during the proceſs. The laſt proportions continued for four meaſures, and then the alkaline air increaſed to $\frac{3}{4}$, and the remainder was inflammable. It is remarkable, that this proportion

proportion of alkaline and inflammable airs ſhould burn as well as if the whole had been inflammable. At this period more than two thirds of the proceſs were over, and the proportion of alkaline air decreaſed, while that of the inflammable air increaſed, until towards the end, when the laſt nine meaſures were all inflammable, and the operation ceaſed, though the retort was urged with a white heat.

On breaking the retort when cold, I found a black powder on the bottom, which weighed 95 grains; this I digeſted in ten ounces of diſtilled water for one hour, and then filtered and evaporated it to two ounces, when a yellowiſh powder was depoſited; and on letting the whole ſtand for one night, no cryſtals were formed. I filtered the liquor to ſeparate the powder, and evaporated the filtered ſolution to one ounce, during which time it continued to depoſit more of the ſame powder; this again I paſſed through the ſame filter I uſed laſt, in order to have it all upon one filter, and when the liquor was all through, I waſhed the powder with diſtilled water, which I added to the reſt of the ſolution. This being evaporated to eight

eight pennyweights, or half an ounce, began to deposit a very white powder, and to emit a subacid astringent vapour, not unlike vitriolic acid. The white precipitate when collected, washed, and dried, weighed one grain: it had a shining appearance, and felt very soft, not unlike mica in powder: exposed to a white heat for ten minutes, it acquired no change, but looked rather whiter. It dissolved in distilled water; caustic volatile alkali caused no precipitation; mineral alkali, and the acid of sugar, rendered the solution turbid, and likewise nitrated terra ponderosa: hence I inferred that this powder was selenite. After separating the selenite, I evaporated the remaining part of the solution to dryness, with a gentle heat, during which time it emitted subacid vapours. The powder weighed eleven grains, was of a dirty yellow colour, and had an aluminous taste. To this powder I added as much distilled water as was nearly sufficient to dissolve it; and then put it by for three weeks, being interrupted by some other business. At the expiration of this time, small transparent, and seemingly cubical crystals appeared on the ſide of the veſſel, above the ſurface of the ſolution; and theſe likewiſe had an aluminous taſte. I diſſolved the whole in diſtilled water, and filtered the ſolution: acid of ſugar had no effect on it at leaſt for five minutes; cauſtic volatile alkali occaſioned an immediate cloudineſs; and the ſolution when filtered, though the cauſtic alkali predominated, was rendered turbid by a ſolution of mineral alkali; nitrated terra ponderoſa threw down a copious precipitate, and Pruſſian alkali detected a ſmall portion of iron. This aluminous ſolution, as I may now venture to call it, left on the filter a yellow ſubſtance, which when waſhed and dried weighed half a grain; it diſſolved in nitrous acid without effervefcence; acid of ſugar cauſed no precipitation, but cauſtic volatile alkali threw down a precipitate, which diſſolved in diſtilled water. This ſolution was rendered turbid by the acid of ſugar, and muriated terra ponderoſa; but cauſtic volatile alkali, or lime water, had no effect on it. The ſolution of ſelenite in either of the mineral acids, and its precipitation undecompoſed by cauſtic volatile alkali, ſhould always be guarded againſt by every experimentaliſt.

The

The yellow powder firſt depoſited during evaporation from the ſolution (page 286) weighed two grains and a half, and, expoſed to a tolerably ſtrong heat, acquired a deep orange colour. I digeſted it with two ounces of diſtilled water in a ſand heat for half an hour, and then filtered the ſolution, which did not contain any thing but ſelenite. A yellow powder was left on the filter, which weighed ¾ of a grain; it ſeemed to be iron, and ſuch I found it, for marine acid readily diſſolved it; phlogiſticated alkali precipitated Pruſſian blue, and tincture of galls turned the ſolution black; muriated terra ponderoſa ſeemed to detect a vitriolic impregnation; but, on examining the marine acid, it contained a ſmall veſtige of vitriolic acid, though not ſo much as appeared to be preſent in this martial ſolution. Indeed the acid vapour riſing from the ſolution of alum, during the depoſition of this iron and ſelenite, renders it probable that it may be partially combined with vitriolic acid, in ſuch a proportion as not to render it ſoluble in water, and in ſuch a ſtate as to be diſengaged by marine acid. Thus ſeparating all that was ſoluble in diſtilled water from the charry ſubſtance left in the earthen retort, I dried and weighed the remainder, and found the loſs of weight by this treatment to be fifteen grains. I calcined the remaining eighty grains in an open crucible expoſed to a ſtrong red heat; it was difficult of calcination, and took three quarters of an hour to be reduced to a bright grey powder; it firſt burned with a flame, and afterwards calcined with very vivid ſparks at every freſh ſurface expoſed to the air; when thoroughly calcined and cold, it weighed twenty-one grains, having loſt fifty-nine grains during calcination. I plunged it into ſix ounces of hot diſtilled water, and when it ſtood half an hour filtered it: the ſolution taſted like lime water, turned ſyrup of violets green, and diluted vitriolic acid had no effect on it; but aerated volatile alkali, and acid of ſugar, rendered it turbid. The remaining part of this powder left on the filter, when well dried, weighed ſixteen grains; therefore, five grains of lime ſeem to have been taken up by the diſtilled water; theſe ſixteen grains diſſolved in nitrous acid, firſt, with a little efferveſcence, and when this ceaſed the ſolution went on very ſlow, until the

whole

whole was taken up: acid of ſugar cauſed no precipitation in this ſolution, but cauſtic volatile alkali precipitated the whole; about one grain of Pruſſian blue was thrown down by the phlogiſticated alkali, or perhaps more, for I could not ſeparate it from the filter. I digeſted the precipitate, when well waſhed and freed from the volatile alkali, in diſtilled vinegar, which took up with effervefcence one grain and a half, which was precipitated by cauſtic volatile alkali. I waſhed what was inſoluble in the vinegar, and digeſted it in diſtilled water for half an hour, then filtered the ſolution: cauſtic volatile alkali had no effect on this ſolution; but acid of ſugar and nitrated terra ponderoſa cauſed an immediate cloudineſs. Seven grains and a half of the powder, which was inſoluble in diſtilled water and acetous acid, were readily taken up by diluted vitriolic acid, and precipitated by cauſtic volatile alkali: ſo the ſixteen grains laſt treated, ſeem to contain of clay ſeven grains and a half; of ſelenite ſix grains; of magneſia one and a half; and of iron one grain. The proportions of the different ingredients are as follow, viz.

Iron - - - - - - -	$2\frac{1}{9}$	Grains
Selenite - - - - - -	11	Ditto
Clay - - - - - - -	$7\frac{1}{2}$	Ditto
Alum - - - - - - -	8	Ditto
Pure calcareous Earth -	5	Ditto
Aerated Magnesia - - -	$1\frac{1}{2}$	Ditto
Charry combustible Substance	59	Ditto
Total	$94\frac{1}{9}$	Grains

I found a darkish yellow saline sublimate adhering to the neck of the retort, of a lamellar spongy texture, except the inner part next the retort, which was more compact, and coloured: this being carefully collected, weighed 425 grains, and readily dissolved in half a pint of hot distilled water. I filtered the solution, and separated a coally substance, which when washed and dried weighed ten grains, and, when exposed to a red heat, burnt with a greenish flame, and emitted white fumes, in smell not unlike vitriolic ammoniac: the residuum after calcination weighed half a grain, and was of a whitish colour; it seemed insoluble in distilled water, but nitrous acid dissolved it with effervescence; acid of sugar caused a very little precipitation,

tion, which did not take place until it ſtood ſome time; but cauſtic volatile alkali inſtantly threw down a precipitate, which was taken up, when waſhed, by acetous acid: The quantity was too ſmall to be examined more accurately, but it ſeemed to poſſeſs the properties of magneſia. The ſaline ſolution had the colour of ſmall beer, and, when evaporated to two ounces, did not depoſit any thing, nor on cooling yielded any cryſtals. The black matter which lined the conical tube and air veſſel, weighed twenty-eight grains; indeed it adhered ſo faſt to the glaſs, it was impoſſible to collect the whole from the broken fragments, ſo that a few grains may be loſt. I diſſolved it in diſtilled water, and ſeparated four grains of a black coal from it, which did not differ in the leaſt from that obtained from the former ſublimate: this ſolution likewiſe evaporated to one ounce, and, after ſtanding one night, did not ſhew the ſmalleſt appearance of a depoſition, or a cryſtallization. I mixed both ſolutions together, and evaporated them to one ounce; which, when cold, acquired the conſiſtence and colour of treacle; ſo that I was now aſſured this was not a cryſtallizable ſalt, and that a ſufficient knowledge of it could not be acquired by this treatment. I charged it into a ſmall tubulated glaſs retort, with ſix ounces of diſtilled water, in order to waſh it down; and then placed it in a ſand bath, and diſtilled over three ounces of water, which ſeemed to be impregnated with nothing but a ſmall quantity of the ſolution, which adhered to the neck of the retort, and which gave it a light ſtraw colour: this being removed, I applied a clean receiver; and when about half an ounce more of the liquor came over, the diſtillation was attended with an alkaline ſmell, merely ſenſible, until an ounce and a half of the liquor paſſed over; and then it got ſo very pungent, though the diſtillation was carried on very ſlow, and the veſſel kept cool, that I was convinced of its being in a cauſtic ſtate; but a ſmall quantity of mild volatile alkali adhered to the lower part of the neck of the retort, part of which was waſhed down by the diſtillation, ſo that it was in vain for me to attempt to aſcertain the proportions which the mild and cauſtic

alkali

alkali bore one to another. The volatile alkaline ſolution in the receiver, had the colour and ſmell of ſpirits of hartſhorn, but more empyreumatic, and like ſpirits of hartſhorn, when expoſed to the air for ſome time, acquired a deeper colour, in conſequence of part of the alkali eſcaping, and the reſt attracting fixable air, which rendered it incapable of keeping the charry matter in ſolution, which it had before diſſolved. When all the liquor had paſſed over, and nothing appeared in the retort but a ſmall black maſs, I raiſed the fire; and, according as the heat increaſed, this black ſubſtance acquired a white colour, with a kind of arrangement on the ſurface, which was occaſioned by the heat applied to the bottom of the retort being only ſufficient to raiſe the ſalt to the top of the charge; but when the ſand got nearly red hot, white fumes began to appear, which condenſed on the upper part of the retort, and a little way down the neck. The proceſs laſted until the charge was nearly red hot, when the white fumes ceaſed, and nothing elſe paſſed over. On breaking the retort the following day, I collected the ſublimate, which weighed ſeventy-two grains, and a black porous brittle ſubſtance was found on the bottom of the retort, which weighed twelve grains; and which, when expoſed to a ſtrong red heat, emitted white fumes, with a ſlight alkaline ſmell: by this proceſs it was reduced, with very little appearance of combuſtion, to a grey powder, which weighed three grains: this I cannot give any account of, as it has met with an accident; but I could venture to ſay, that four grains of the black powder were the ſame as the ſublimate, and that the remaining five grains conſiſted of volatile alkali, and a charry combuſtible ſubſtance.

Having the ſublimate now, as I thought, tolerably pure, and wiſhing to know its nature and properties (as I ſuſpected it to be a combination of volatile alkali and ſome acid), I took five grains of well burnt and powdered quicklime, and with it mixed five grains of the ſublimate, but without the leaſt ſmell of volatile alkali; and thrown upon a red hot iron, it emitted white fumes: the ſame proportion of vegetable alkali and ſublimate had the like effect. I made two equal diviſions of the remaining

maining part of the ſublimate, which was ſixty-two grains; the one I mixed with two ounces of diſtilled water; it readily diffuſed through it, being in fine powder; and on the other poured ſixty grains of vitriolic acid, diluted with half an ounce of diſtilled water: having thus mixed them in two large beer glaſſes, I was obliged to ſet them by for ſix weeks, being interrupted by other chemical experiments; and at the expiration of that time, neither ſeemed to be much acted upon. I poured the vitriolic mixture into a ſmall matraſs, and boiled it on ſand for half an hour, with two ounces of diſtilled water, when the whole was taken up: the ſolution looked clear, and depoſited nothing on ſtanding; mild mineral alkali had no effect on it; but mild vegetable alkali threw down a copious precipitate in white floculi, which was rediſſolved by cauſtic alkali, lime water, and partially by mild mineral alkali. Phlogiſticated alkali, acid of ſugar, and acid of tartar, had no effect on this ſolution. The other portion of ſublimate, which I mixed with water, was very little diſſolved, and in pouring it into a matrafs, fmall round lumps which appeared on the bottom of the glafs, drew my attention; they were fix or feven in number, fome weighing more than one grain, and the fmalleft about half a grain. They were very hard and compact, with a very fmooth furface, and in figure refembling the nucleus found in this calculus. I charged the whole into a matrafs, with three ounces of water, and boiled it on fand for three quarters of an hour, when about one half was taken up; the folution filtered very clear while hot, but on cooling it got turbid, and in time depofited white floculi, which were redif-folved by cauftic volatile alkali and lime water: it turned fyrup of violets green; but this may be occafioned by its retaining volatile alkali, though it had not the fmall-eft appearance of fuch impregnation. I have often obferved, that, fometimes, the pureft fixed vegetable alkali contains vola-tile alkali, notwithftanding the many ope-rations and different degrees of heat it muft undergo before it arrives at that degree of purity in which we find it fold at the fhops, under the name of ſalt of tartar*. I filtered the ſolution, to ſeparate what it depoſited on cooling: mineral alkali had no effect on it; but mild vegetable alkali cauſed a cloudineſs, which was rediſſolved by mineral alkali and lime water. Pruſſian alkali had no effect on this ſolution; the acids of arſenic, of tartar, of ſugar, and of borax, had likewiſe no effect on it; and alſo the three mineral acids. I was obliged to diſcontinue my experiments on this ſublimate here, having no more of it, and no calculus to obtain it from.

I introduced five pennyweights, or 120 grains, of the ſame calculus into a ſmall tubulated retort, and on this poured half an ounce of ſtrong nitrous acid, which acted upon it with efferveſcence. I collected ſome of the air extricated during ſolution, and found it to be fixable, with a ſmall quantity of nitrous air. When the efferveſcence ceaſed, I added a quarter of an ounce more

* I have obſerved that fixed alkali, when firſt moiſtened with water, very frequently produced volatile alkali; and as the conſtituent principles of volatile alkali were not well known when this paper had been written, I ſuppoſed it to be ready formed in the fixed alkali.

of nitrous acid, and digested it in hot sand for one hour, during which time it emitted nitrous vapour and nitrous air; but the latter in very small proportion. When the solution was perfected, I poured it into a small matrass, with the addition of one ounce of distilled water, and boiled it gently, until the superabundant nitrous acid was nearly expelled. The solution was of a deep yellow colour, and appeared turbid; but, on adding five ounces more of water, and digesting it a quarter of an hour longer, it acquired the colour and transparency of what is called dephlogisticated nitrous acid. On cooling it got a little turbid, and in a few days deposited a darkish yellow powder. I filtered the solution to separate this powder, which, when washed and dried, weighed a little more than a quarter of a grain: pure nitrous acid had no effect on it, but marine acid readily dissolved it; in short, it had all the properties of calx of iron. Being again interrupted, I was obliged to lay the solution by for some time; and wishing to know what effect a long exposure to the heat of the sun would have on it, I placed it in a window, in one of the upper rooms of the elaboratory at Oxford, where the sun had full power over it four hours every day. A little moiſture ſeemed to exhale from it daily, the weather being hot, and the matraſs, which had a ſhort wide neck, being only covered with a piece of bibulous paper to keep out the duſt. Thus ſituated, in the courſe of a week a few very ſmall cryſtals appeared to float on the ſurface, which in time ſunk to the bottom, where they adhered together, ſo as to form a hard concretion, ſtill retaining a cryſtalline appearance, but being ſo ſmall and confuſed, it was impoſſible to diſtinguiſh their figure: this depoſition continued for near a month, and then ſeemed to ceaſe. I filtered the ſolution to ſeparate the ſalt; and, to expedite the proceſs, as I thought, evaporated half an ounce of the liquor away, and then ſet it by in the uſual place for a fortnight longer; but no more of theſe cryſtals appeared. I digeſted the ſalt, which, when waſhed and dried, weighed three grains, in four ounces of diſtilled water for two hours, and no part ſeemed to be taken up. I decanted off three ounces of the water, and added to the remainder ſix drops of vitriolic acid, which, by help of digeſtion, ſeemed to diſſolve it ſlowly; but on the addition

addition of half an ounce more of diſtilled water, the whole was readily taken up. Acid of ſugar had no effect on the ſolution, but lime water rendered it turbid. I precipitated the whole with cauſtic volatile alkali, and filtered the ſolution, which likewiſe threw down the lime from lime water. I waſhed the precipitate, and poured diſtilled vinegar upon it, which did not take it up: marine acid diſſolved it; phlogiſticated alkali had no effect on the ſolution; and the acid of ſugar cauſed very little turbidneſs on ſtanding three or four hours. Theſe appearances induced me to ſuppoſe, that this ſalt was phoſphorated clay. The ſolution being now free from iron and phoſphorated clay, had a ſub-acid taſte, and looked clearer, but ſtill retained a yellow caſt: acid of ſugar had no effect on it; but nitrated terra ponderoſa threw down a copious precipitate; as did likewiſe the cauſtic volatile alkali. Mild fixed vegetable alkali (which at firſt ſurpriſed me much) cauſed no precipitation; but, when I conſidered the ſolvent power of fixable air on calcareous earth and magneſia, which earths I knew were held in ſolution in ſmall proportions, and the quantity of fixable air diſengaged by the uncombined and combined acids, I could readily account for the above phenomenon. I charged two-thirds of this ſolution into a ſmall glaſs retort, and diſtilled over two ounces of liquor, which ſeemed taſteleſs; but had a very agreeable ſmell, not unlike roſe water. When all the liquor paſſed over, white fumes appeared in the retort, which were ſoon ſucceeded by a ſlow emiſſion of an elaſtic fluid. I collected ſome of this fluid, and found that a candle immerſed in it burned with an enlarged flame. Nitrous air did not diminiſh it in the leaſt; it ſeemed to be that ſpecies of air that nitrous ammoniac is convertible into: no more than thirteen or fourteen cubic inches of this air were obtained; and as ſoon as it ceaſed to come over, I obſerved ſome ſalt in irregular cryſtals in the lower part of the neck of the retort. On increaſing the heat, a white ſalt began to ſublime, and adhere to the upper part of the retort. I continued the operation until the bottom of the retort was obſcurely red hot, and then raiſed it in the ſand. The following day, when I broke the retort, the quantity of ſublimate was ſo trifling, I could collect but very little from

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the broken glaſs: however, there was ſuffici-ent to convince me, that it was the ſame with what I obtained in my former analyſis. The ſalt mentioned above, which cryſtalliſed in the neck of the retort, was nitrous ammoniac; it inflamed and detonated *per ſe*, &c. A grey powder was left on the bottom of the retort, which hot diſtilled water partly diſſolved; muriated terra ponderoſa, acid of ſugar, and vegetable alkali rendered this ſolution turbid, but cauſtic volatile alkali had no effect on it. The remaining part of the powder which the diſtilled water left behind, was readily diſſolved with effervеſcence by marine acid, and precipitated by cauſtic volatile alkali: that part taken up by the diſtilled water ſeems to be ſelenite, and that diſſolved by the marine acid to be magneſia.

This laſt mode of treating the calculus, was partly to correct my former analyſis, but chiefly in conſequence of Dr. Beddoe's very judiciouſly ſuſpecting, that it contained ſomething which might be decompoſed by the ſtrong heat I firſt uſed (how far this conjecture was right is very evident); therefore I only attended to the proportions of that which evaded my former analyſis.

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The phoſphoric acid muſt have been united to volatile alkali in the calculus, previous to its treatment with the nitrous acid, notwithſtanding its ſuperior attraction to calcareous earth: the preſence of alum ſhews how enveloped with an oleaginous matter the volatile alkali and pure calcareous earth muſt have been; therefore it appears, that the calculus was compoſed of the following different compounds blended together, viz. ſelenite, alum, microcoſmic ſalt, mild-volatile alkali, lime, and cauſtic volatile alkali combined with oil, ſo as to form a ſaponaceous maſs, calx of iron, magneſia combined with aerial acid, clay enveloped by a ſaponaceous and oily matter, and the ſublimate already deſcribed. Conſidering this to be the true ſtate of the calculus in the bladder, the ſmall proportions of clay, ſelenite, magneſia, and iron, which are the moſt inſoluble of the ingredients, the great ſolubility of microcoſmic ſalt, and alum, and the miſcibility of lime, volatile alkali, and oil in water, tend to ſhew, that the ſublimate is the cementing ingredient: indeed, its inſolubility in water, and property of forming nuclei out of the body, as above obſerved, leave no room to doubt it. The proportion of the other ingredients, and very likely their presence, depend upon chance, volatile alkali and oil excepted; therefore this sublimate should be the object of our investigation. May not strict researches into the nature of this singular substance throw new light on the original cause of other disorders, as well as that of the calculus, particularly the gout, which hitherto has baffled the skill of our physicians? The effect of mild mineral alkali on the sublimate, is worthy the attention of those who may have an opportunity of trying its efficacy. Mild mineral alkali may be taken in large doses, and continued for a length of time with impunity to the most delicate constitutions, only observing a few circumstances; but this alkali in a caustic state must very often be attended with mischievous consequences. Besides, if we consider that it must enter the mass of blood before any part can reach the bladder, and the small portion of the dose taken secreted with the urine; and, lastly, the action of caustic alkali upon animal substances, we shall be at a loss to know on what principle caustic alkalies have been recommended in preference to the mild. Soap itself might as well be prescribed at once; for soon after caustic alkali is taken, it must be in a saponaceous state. Fixed vegetable alkali should be avoided, and the preference given to the other two alkalies. As it is evident that alkalies have no real action on the stone in the bladder, though their efficacy has been experienced in alleviating the disease when timely administered, their mode of action is only explicable in the following manner: They either prevent the generation of the sublimate in the system, or else keep it in solution in the mass of fluids; and being in the utmost degree of divisibility, its ultimate particles are capable of passing through the most minute emunctories, by which it is carried off by other secretions as well as by the urinary. Thus the urine not being saturated with this matter, acts as a solvent on the stone; and as the most soluble parts are first washed away, it in time falls into fragments of irregular surfaces, which, by their friction, irritate and inflame the bladder, as has been observed by several practitioners.

Allowing that the ſublimate is the cementing ſubſtance in the calculus, and judging from the effects of alkalies upon it, their *modus operandi* in the conſtitution, it remains now to inquire into the origin of the calculus. The immortal Scheele has found this ſublimate in the urine of different perſons, and hence inferred, that it was a common ſecretion; but it ſtill remains to be aſcertained, whether there be a greater quantity of it procured from the urine of patients who have the misfortune to labour under this diſorder, than in that of thoſe who never felt its pangs. If this latter ſhould not be the caſe, another path lies open for our reſearches, which promiſes moſt ſucceſs. May not a deficiency of volatile alkali in the conſtitution, be the cauſe of concretions in the bladder, kidneys, &c. or, which muſt have the ſame effect, too great a proportion of acid, which, uniting with the alkali, may take up that portion which would have kept the ſublimate in ſolution, until conveyed out of the ſyſtem by the urinary and other ſecretions; and may not this be the phoſphoric acid? If this latter ſhould be the caſe, an increaſe of micro-

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cofmic falt muft be found in the urine; but if the former, a decreafe of the volatile alkali, and no increafe of the neutral falt. The fmall quantity of phofphoric acid found in the calculus, proceeds from the folubility of microcofmic falt. Do not volatile alkali and phofphoric acid conftitute a great part of the human frame? and is there not a procefs continually carried on to generate thefe in the fyftem *? and is not this procefs liable

* It is nearly three years fince I firft had an opportunity of making fome obfervations on volatile alkali, which confirmed my opinion of its conftant generation in the human fyftem, to fupply its continual wafte; and likewife enabled me to form a faint idea of its conftituent parts. As others have publifhed fome experiments and obfervations, made fubfequent to mine, I find it neceffary to be more minute in the following recital, than I otherwife would wifh. About the latter end of March 1785, I found that nitrous acid poured on tin filings, and immediately mixed with fixed vegetable alkali, generated volatile alkali in great abundance: fo fingular a fact did not fail of deeply impreffing my mind, though at the time I could not account for it. I mentioned this to Dr. Higgins (for the obfervation was made in his elaboratory), but he took little or no notice of it. Thus, unable to awake his attention to fo fingular a fact, and having no opportunity of making experiments of my own, I was obliged to lay afide all thoughts of it.

liable to be retarded or checked by intemperance, &c. which may vary their quantities and proportions? and may not a due proportion of these be necessary to a vigorous and sound constitution? If so, no wonder that an

About a fortnight after, I mentioned the circumstance to Dr. Brocklesby. He told me he was going to meet some philosophical gentlemen at Sir Joseph Banks's, and desired I would generate some alkali for him to exhibit before them: accordingly I did, and had the pleasure of accompanying him thither.

The December following, I chanced to get acquainted with my late worthy friend, Dr. Caulett, to whom I mentioned the fact already related, respecting volatile alkali, and likewise its copious generation from Prussian blue, fixed vegetable alkali, and water. Pleased with what I told him, we agreed to procure the necessary apparatus for making a set of experiments on the subject. At present it is needless to give a detail of our different experiments; though at that time, when volatile alkali was less known, they might have been of some importance: therefore I shall only give an account of the following, which drew our particular attention. Into a glass cylinder made for the purpose, we charged three parts of alkaline air, and to this added one part of dephlogisticated air; we passed the electrical spark repeatedly in it, without apparently effecting the smallest change. When it had received about a hundred strong shocks, a small quantity of moisture appeared on the sides of the glass, and the brass conductors seemed an increaſe or deficiency in either or both of theſe, ſhould be productive of ſeveral diſorders. I make not the ſmalleſt doubt but a ſeries of accurate experiments, made by a ſacacious obſerver on the latter part of this

ſeemed to be corroded: when we had paſſed ſixty more ſhocks in it, the quantity of moiſture ſeemed to increaſe, and acquire a greeniſh colour, though at this time the column of air ſuffered no increaſe or diminution. On examining the air, it burned with a languid greeniſh flame, from which we inferred that the dephlogiſticated air was totally condenſed; it ſtill retained an alkaline ſmell, and the alkaline part was not readily abſorbed by water. This and another phenomenon obſerved in the firſt part of this paper, reſpecting alkaline and fixable airs iſſuing at the ſame time, without forming an union, induce me to ſuppoſe, that volatile alkali, like other ſubſtances, may be found in an intermediate ſtate, and in proportion as it is deprived of one of its conſtituent parts, that it attracts fire ſo much the ſtronger, which counteracts its attraction to other bodies. Thus nitrous air is a compound of phlogiſticated and dephlogiſticated airs, requiring a larger proportion of dephlogiſticated air to condenſe and render it combinable with alkalies. I often obſerved, that fixable air obtained from different ſubſtances, was not under the ſame circumſtances always condenſed with equal facility*: hence muſt ariſe the impoſſibility

* Since the above has been written, I have been induced to ſuppoſe that fixable air is never found in an intermediate ſtate, as obſerved in the beginning of this volume.

this ſubject, would be attended with uſeful diſcoveries. If God will grant me health and opportunity, I ſhall perſevere in this taſk, and wiſh that others would do the ſame; for the importance and extent of the ſubject

ſibility of aſcertaining the ſpecific gravity of the compound elaſtic fluids. From Mr. Cavendiſh's famous diſcovery of the conſtituent parts of water, we could readily account for the loſs of the dephlogiſticated air in this experiment; but the quantity of water produced was more than we could expect from this: therefore water muſt have been precipitated from the decompoſed alkali; for volatile alkali, from its great attraction for water, muſt keep ſome in ſolution, even in its aeriform ſtate. From the above circumſtances, it might be expected that a contraction of the column of air ſhould take place; but be it conſidered, that the union took place gradually, in proportion as the alkali was decompoſed; and that in this caſe the expanſion muſt equal the condenſation. Being obliged to ſet out for Oxford, our experiments were ſuſpended, and, alas! never to be reſumed. If a young man of uncommon ſagacity, perſeverance and induſtry, and whoſe philoſophical mind was ſtrongly bent towards new inveſtigations, promiſed to extend ſcience, the premature death of the late Dr. Caulett muſt be a ſevere loſs to ſociety, as well as a grievous one to thoſe who had the pleaſure of his acquaintance. During the ſpring of the year 1786, I often had an opportunity of mentioning different facts to Dr. Auſtin, relating to volatile alkali, who at that time was too much engaged to pay attention to the ſubject. In the latter end of June ſubject point out to me, that we ſhall all find work enough, and that our labours will not be in vain, provided they be attended with diligence.

The above Analyſis is an exact copy of what has been read before the Royal Society. I am ſorry I have not had an opportunity of proſecuting the ſubject as I would wiſh, as I promiſed two years ſince, when this paper was written. I have made ſome

1787, I received a letter from him at Oxford (for he then lived in London), requeſting my exact mode of obtaining volatile alkali, as he was engaged in that ſubject. I mentioned the purport of his letter to Dr. Beddoes, our preſent lecturer in chemiſtry at Oxford, who had readily ſeen into the importance of what I told him, and candidly ſaid, it ought to have been made public a long time ago. On my arriving in London the following Auguſt, Dr. Auſtin gave me an account of a ſet of experiments which he had made, and which actually proved, that volatile alkali conſiſts of light inflammable and phlogiſticated airs, not knowing at that time what Meſſ. Hauſman and Bertholet had done. Without depreciating the merit of theſe two gentlemen, Dr. Auſtin has an equal claim to the diſcovery, laying aſide priority; as his experiments are as deciſive as theirs. Dr. Prieſtley made the firſt ſtep towards our knowledge of volatile alkali. See his Sixth Volume on Air.

experiments, but they are not numerous enough, or of sufficient importance, to afford a satisfactory conclusion; for, in order to this, it would require at least 500 experiments. But I hope shortly to have it in my power, to offer the public something on this subject. That the urinary sublimate is present in tubercles found in the lungs of persons who die of pulmonary consumptions, and likewise in what are vulgarly called chalk stones, is what I have experienced; but in what proportion, or whether in quantities sufficient to cause the concretion, is what I cannot say, for I have had but a few grains of each to examine; nor could I procure any more, notwithstanding a diligent inquiry amongst my friends. I have every reason to suspect, that consumptions and scorbutic complaints very frequently arise from a superabundance of this sublimate in the system; and that it is chiefly the cause of the gout and rheumatism, and solely the cause of the stone in the bladder. I make no doubt but these disorders generally proceed from obstructions; and it is probable that either a precipitation of this sublimate in the system, or else

elſe a deficiency of ſome other ſecretion, which would hold it in ſolution until conveyed out of the body, may be the chief cauſe of thoſe obſtructions; and likewiſe, that different degrees of precipitation may produce different ſymptoms and different diſorders.

That mineral or volatile alkali and bark have been uſeful in the above diſorders, has been affirmed by experienced phyſicians; and I know an inſtance myſelf of mineral alkali and nitrous ammoniac being ſerviceable in a pulmonary complaint of ſome ſtanding.

With reſpect to the ſtone, when it acquires a certain magnitude, it is abſurd to attempt to diſſolve it in the bladder, it waſtes ſo very ſlowly, and during this time the patient muſt ſuffer vaſt pain, particularly when the ſtone acquires a rugged ſurface; therefore cutting for it at once is much preferable.

Mineral alkali taken in the beginning of the complaint, and before the ſtone accumulates, will no doubt check its progreſs, and may in time change that diſpoſition in the habit. Patients who are cut for the ſtone

ſtone ſhould, I think, take mineral alkali for ſome time when the wound is healed, but not before, for fear of bringing on a mortification. Theſe are my opinions, or rather queries, reſpecting the effects of the above ſalt or ſublimate found in the urine, calculus, &c. on the human conſtitution; and my ſole motive for laying them before the public, is to promote an inquiry into ſo intereſting a ſubject.

I flatter myſelf, that at leaſt an attentive peruſal of the above experiments may point out the ignorance of thoſe empirics who have too long impoſed upon the public with their pretended lithontriptics, and likewiſe that it may tend in future to check ſuch proceedings.

THE END.

E R R A T A.

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2, 12 from top, after laſtly, *inſert* a full point

3, 17, *dele* mixture of

11, 25, *read* molecules, and ſo elſewhere

15, 16, *dele* full point, and *inſert* a ſemicolon

15, three laſt lines, *read* Or do a denſe and a rare atmoſphere promote their chemical union, by eaſily blending and ſuffering them to approach nearer ?

16, 7, *for* theſe *read* them

16, 8, *for* with *read* from

20, 16, *for* may *read* might

44, 13, *for* indecompoſed *read* undecompoſed

46, 20, *dele* that is

59, 24, *for* dilute *read* diluted

83, 7, *dele* only

114, 16, *dele* 2-10ths and *inſert* $\frac{4}{10}$

129, 14, *dele* comma

129, 15, *for* to *read* with

144, 10 from bottom, for loſes *read* loſt

154, 11, *dele* full point, and *inſert* a ſemicolon

169, ult. *inſert* $\frac{1}{5}$

188, 5 from bottom, *inſert* a comma after *it*

207, 2 from bottom, *dele* comma, and *inſert* a full point.

226, 3 from bottom, *for* barites *read* barytes