EXPERIMENTS

AND

OBSERVATIONS

RELATING TO

ACETOUS ACID, FIXABLE AIR, DENSE INFLAMMABLE AIR, &c.

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RELATING TO

ACETOUS ACID, FIXABLE AIR, DENSE INFLAMMABLE AIR, OILS, AND FUEL; THE MATTER OF FIRE AND LIGHT, METALLIC REDUCTION, COMBUSTION, FERMENTATION, PUTREFACTION, RESPIRATION,

AND OTHER SUBJECTS OF

CHEMICAL PHILOSOPHY.

BY BRYAN HIGGINS, M.D.

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Under the animating, and FRIENDLY PATRONAGE

Of the MUNIFICENT and MOST NOBLE

HUGH late DUKE of NORTHUMBERLAND

This Volume was commenced and concluded:

To HIM it was to be presented,

The PLEDGE of better Efforts

In his favourite Science:

And NOW

TO HIS EVER HONOURED MEMORY,

It is gratefully and piously inscribed,

BY BRYAN HIGGINS.

THE

PREFACE.

HAVING announced this work to many of my friends in the beginning of the laſt year, when more than a third of it was printed, I think it incumbent on me to relate the circumſtances which have delayed the publication of it to this time.

From the beginning of March to the end of July laſt, all the time that I could ſpare from the daily

 duties

duties of my profeſſion, was fully employed with private pupils in preparing for the enſuing Courſe of Chemiſtry, and in forwarding their reſpective purſuits, and afterwards in the inceſſant buſineſs of the experiments and operations exhibited in that Courſe. During this time it was impoſſible for me to reviſe the proof-ſheets with the requiſite attention, and the printing was neceſſarily ſuſpended.

In the public propoſals for the Courſe, which commenced in April, the following article appeared:--- 3dly. "*That it ſhall exhibit the important advances lately made in the knowledge of air and other elaſtic fluids, of the vegetable acid, phlogiſton, fire, and Light.*"

In

In consequence of this declaration, I introduced in the Course, all that was new in the experiments, or interesting in the doctrines of this volume; and insisted particularly on the circumstances that gave rise to the controversy which was so ably and politely maintained, in the Philosophical Transactions, by Mr. Cavendish and Mr. Kirwan, concerning the principles of fixable air.

By this communication to a very respectable and scientific audience, I deprived the intended work of every advantage of novelty; and having gratified the curiosity of those to whom it was announced, I felt no greater solicitude about the speedy publication of it, than was consistent with my health, and with engage-

engagements which admitted no procraſtination.

During a part of the laſt ſummer, I was totally diſabled by ſickneſs; and for ſix months afterwards, all the time that I could ſpare, was employed in experiments for the perfection of glaſs for optical uſe, which I proſecuted with extraordinary aſſiduity becauſe my venerated patron the late Duke of Northumberland expreſſed ſome wiſhes to this effect, and in enquiries highly intereſting to artiſts who were impatient of delay.

The printing, therefore, was not reſumed until laſt March; ſince which time, ſome unexpected delays were made at the preſs, and lately the publication was deferred on account of the impending lamentable loſs already expreſſed.

Thoſe who conſider that my profeſſion will not permit any ſecluſion from ſociety, or retirement from interruption, and that in the moments occaſionally ſnatched from theſe numerous avocations, the moſt verſatile mind cannot apply to a work of this kind, with all the vigour which it might acquire by deliberation or reſt; will rather wonder at my attempting to publiſh a volume, than at the delay, the numerous uncorrected errors of the preſs and of the author, and that exceſſive brevity, which requires greater attention in the peruſal of many of the following ſections, than readers are uſed to beſtow on temporary publications.

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EXPERIMENTS, &c.

SECTION I.

The Preparation of pure Acetous Acid, and Acetated Vegetable Alkali, or foliated Earth of Tartar.

THE ſalt called foliated Earth of Tartar is generally made in the manufactories from which the ſhops are ſupplied, with pearl-aſh and diſtilled vinegar, and therefore contains ſome marine ſalt, and a portion of the oil of vinegar beyond what is neceſſary to the conſtitution of acetous acid. Theſe extraneous ſubſtances have conſiderable effect in divers operations, and are apt to perplex or miſlead the Experimenter.

 The

The foliated Earth of the Apothecaries' Hall, being prepared for medicinal uſe only, is indeed tolerably free from marine acid, but by reaſon of their obedience to the pharmacopœia, which has adopted none of the recent improvements in Chemiſtry, it is neither ſo white nor ſo free from oil as that of the manufacturers.

For theſe reaſons I never employ the foliated Earth of the ſhops, except for producing a large quantity of Acetous Acid, which by the following treatment I obtain in the pureſt and moſt concentrated ſtate.

To a convenient quantity of oil of vitriol in a glaſs retort, an equal weight of the foliated Earth of Tartar, is to be gradually introduced in ſmall pieces, and at ſuch intervals, that the heat excited ſhall never exceed 100 degrees of Farenheit. If in theſe intervals the mouth of the retort be looſely ſtopped, little or none of the acetous vapour eſcapes; for it condenſes in the upper part and neck of the retort, and if this laſt be duly placed, returns into the charge.

When

When about one-third of the foliated Earth is introduced, the vitriolic acid concretes with it in cooling, and both occupy the bottom of the retort; then the remainder may be introduced at once, without causing any heat or commotion. Thus the salt covers the vitriolic acid, and intercepts any portion of it which might otherwise arise when the charge is heated.

A smaller quantity of vitriolic acid may serve; but as an excess of it is necessary for the total decomposition, and this quantity renders the charge more fusible, I prefer it as promoting equable mixture in a moderate heat, and preventing that decomposition of acetous salt which it undergoes by heat alone, without affording any acid from the portions which escape the action of the vitriolic acid.

The Retort is then to be set in a sand heat, and luted to a long neck, terminating in a tubulated receiver, which delivers its contents through the tube into a bottle, that may be removed at pleasure, in order to keep the ſucceſſive products apart. No luting ought to be uſed where the tube enters the bottle; becauſe the dilated air of the veſſels, or the elaſtic fluids expelled, will force the luting, if the egreſs elſewhere be prevented, and becauſe there is never any ſenſible loſs of a condenſible vapour, whilſt the receiver is cool, and the only paſſage is between the contiguous ſurfaces which the tube and bottle preſent to each other.

The diſtillation is to be carried on very ſlowly at firſt, leſt the ſalt laſt added, by ſuddenly falling into the liquefied vitriolic maſs beneath, ſhould excite ſo much heat and intumeſcence as to endanger the veſſels, or emit the acetous vapour quicker than the long neck and recipient can condenſe it.

When as much acetous acid as amounts to half the weight of the acetous ſalt is diſtilled, the bottle is to be removed; and what follows, until a white ſulphureous vapour ſhews itſelf in the long neck, is to be received in another. This laſt portion of acetous acid is weak, and ſlightly impregnated

nated with volatile vitriolic acid, from which it cannot eaſily be freed. It is therefore to be kept apart.

The former portion is eaſily purified from the marine acid which riſes along with it, in conſequence of the decompoſition of the marine ſalt contained in the acetous ſalt, by diſtilling it from a twelfth part of freſh Ter. Foliata. In this caſe there is an encreaſe of the quantity of acetous acid proportionate to the quantity of marine acid abſorbed by the alkali of the foliated earth, and expended in decompoſing it: and the acetous acid is obtained in a ſtate of purity and high concentration, becauſe this acid is more volatile than water, and the undecompoſed part of the acetous ſalt retains the water until the chief part of the acid is diſtilled. I generally reſerve the firſt half of this acet. acid for accurate experiments, diſtinguiſhing it by the name of Purified Acetous Acid, and ſometimes, where my notes are literally tranſcribed, it is called my Acetous Acid; the other half ſerves for any purpoſe in which the purity but not the ſtrength or ſpecific gravity of the acid is regarded.

To prepare Terra Foliata Tartari of a purer kind, and which, after the example of the celebrated Bergman, I ſhall call by the more unexceptionable name of Acetated Vegetable Alkali, I ſaturate a ſolution of purified alkali of Tartar, with my purified acetous acid, and evaporate the neutral liquor until it is capable of forming a dry white ſalt, when cold; in which it never fails, if the evaporation be very ſlowly conducted towards the end, in a heat not exceeding 212 degrees; and if it be cooled very ſlowly.

In the preparation of this ſalt, the following particulars are to be noticed:

In four ounces Troy, or 1920 grains of ſalt of Tartar, freed from earthy matter, there are 1344 grains of mere alkali, and 576 of fixable air and water.

To this alkali an equal weight of water is added, in order to keep the intended neutral ſalt in ſolution, without which the point of ſaturation cannot be aſcertained. The ſtrongeſt and pureſt acetous acid, whoſe ſpecific gravity is 1,068, is then poured in, in ſmall portions, at diſtant intervals, to prevent waſte by the intumeſcence and rapid emiſſion of the fixable air of the alkali, until it is ſaturated: the ſaturation is not effected until 1900 grains of the acid are expended.

On evaporating the neutral ſaline liquor, it continually exhales acetous acid, even when the heat does not amount to 200 degrees. When a dry froth forms on it to the depth of a quarter of an inch, or when a drop taken up on a glaſs rod ſets quickly, and when cold feels dry and pulverable, the evaporation is to be diſcontinued; for a further continuance or augmentation of heat will decompoſe the ſaline matter, and blacken it. At this period, it is the required ſalt in a ſtate of fuſion, which on cooling gradually concretes into a ſnow white dry pulverable maſs, ſimilar to Ter. Foliata in the cryſtaline luminated and ſilvery appearance which it preſents when broken into pieces; and being equally deliqueſcent, it ought to be guarded from the air.

The dry ſalt now weighs 2672 grains; 1344 grains of which being mere alkali, the remaining 1328 grains are acetous acid and water; and the waſte of acetous acid during the evaporation amounts to about 572 grains.

Thus it appears, that even vegetable alkali does not retain as much acetous acid, in the form of a dry ſalt, as is neceſſary to neutralize it in water.

SECT. II.

Phlogiſton is a conſtituent Principle of Acetous Acid.

THE pureſt concentrated acetous acid is inflammable, but not in a high degree; for by reaſon of its volatility, and of the water inſeparable from it in this form, it eludes in a great meaſure the ignition neceſſary for its combuſtion. But when it is detained by lime, magneſia, metallic ſubſtances, or alkaline ſalts which previous to their combination with this acid were perfectly incombuſtible, and is ſufficiently heated in contact with air, it gives deciſive evidence of its combuſtibility, and ſhews that Phlogiſton is a conſtituent principle of this acid.

This appears in the moſt ſtriking manner, in the following experiment:

I ſaturated fixed vegetable alkali, which had been well calcined, and was perfectly incombuſtible,

incombuſtible, with pure acetous acid, and by evaporation prepared the dry acetated vegetable alkaline ſalt already deſcribed. Having then taken the weight of a red-hot ſhallow earthen diſh, after it had been kept two hours in this heat, I placed it in a reddened muffle, and threw on it in ſucceſſive portions eight ounces Troy = 3840 grains of the ſalt, to which air was freely admitted, during the whole time.

The ſalt firſt melted like wax, with a ſlight hiſſing, until ſome moiſture was expelled; ſoon after it was compleatly fuſed, it catched fire, and burned with a denſe bright durable flame of great volume, and which afforded no viſible ſoot.

After the flame had ceaſed, that is to ſay, after the emiſſion of combuſtible vapour or elaſtic fluid from the ſalt had ſlackened conſiderably, a black alkaline coal remained, which was ſtill ſlowly and weakly combuſtible, and ſoon became white on the ſurface expoſed to the air. After half an

hour's

hour's red heat, this ſalt weighed 2544 grains.

When it was cooled, the whiteneſs was found to have extended but very little into the maſs, which was black every where, except in the ſurface expoſed to the air.

It taſted and diſſolved in water like mild fixed vegetable alkali; but the ſolution was turbid, and blackened by a light coaly powder; which ſeparated by filtration, and waſhed repeatedly with diſtilled water, in which it was not at all ſoluble, weighed when dry, 30 grains. It reſembled fine tinder, catched fire freely from a ſpark, and burned without flame like tinder, until it was reduced to grey aſhes, which by ſlight calcination became incombuſtible, and were found to be mild fixed vegetable alkali weighing four grains.

The liquor from which this tinder was filtrated, was not found to contain any thing worth notice, except fixed vegetable alkali, combined with fixable air.

Hence

Hence it was inferred, that Phlogifton is a conftituent part of acetous acid, and that after a great part of the Phlogiftic matter of this acid is expelled from the fixed vegetable alkaline bafis of the acetous falt by a red heat, and is expended in the luminous flame and aerial products, a confiderable portion of the like matter is obftinately retained in the alkali, wherever the free accefs of air is interrupted; and that the portion of alkali which remains fully impregnated with this matter, forms with it a black coaly fubftance, which is infoluble in water, and freely combuftible, but without exhibiting any flame; and which confifts of about one part of mere vegetable alkali, combined intimately with fourteen or more of pure or compounded Phlogiftic matter of acetous acid.

To try whether the acetous acid derives its combuftibility, and its capacity to form a combuftible fubftance or tinder with alkalies and indeed with all other bodies with which it is combinable, from fome volatile oily matter which is expelled along with

with it, in the decompoſition of the acetated ſalt, and which may not be an eſſential ingredient of this acid; I have combined the pureſt part of it with alkali again, and detached it by different mineral acids, and repeated the combinations of it with alkalies, lime, and magneſia, and the decompoſitions whereby it was ſeparable from them, five or ſix times; but ſtill found that any ſalt made with it, and particularly the foliated ſalt, was ſtill as combuſtible as that prepared in the manner deſcribed in the Firſt Section.

Wherefore I conclude, without awaiting the further proofs which follow, that acetous acid cannot exiſt, poſſeſſing the form and characters by which we diſtinguiſh it from others, without a conſiderable quantity of Phlogiſton, and that Phlogiſton is a neceſſary principle in the compoſition of this acid.

SECT. III.

Analyſis of Acetated Vegetable Alkali by Fire, and Inductions relative to Acetous Acid, Fixable Air, Inflammable Air, Phlogiſton, and Fire.

THE apparatus employed in the following experiment conſiſts of a tubulated receiver, whoſe neck is 12 or 18 inches in length, and duly tapered to receive the neck of the retort, to which I generally cement it with a paſte made of liquid glue and freſh powdered lime, which ſoon acquires a ſtony hardneſs, adheres perfectly, is impervious to elaſtic fluids, and is eaſily removed after being ſteeped for ſome hours in marine acid. By the length of the neck the body of the receiver is kept at a ſufficient diſtance from the hot walls of the furnace; and by its tube it enters the mouth of a ſeparating funnel to which it is accurately ground. The tube is made in the receiver in the part which is loweſt, when it is ſet for diſtillation, and by this means all that is condenſed runs immediately into the ſeparating funnel, which is provided with a glaſs cock at the pointed extremity, by the uſe of which, the ſucceſſive or different products of the diſtillation may be drawn off into bottles which fit the extremity of the ſeparating funnel, without ſuffering any elaſtic fluid to eſcape that way, or any external air to communicate with the contents of the veſſels.

In the upper hemiſphere of the ſeparating funnel, an aperture ſtrengthened with a neck of glaſs is provided, into which one extremity of a bent glaſs tube is well fitted by grinding, ſo as to be perfectly air tight, whilſt the other extremity, by the due flexure of the tube, enters a trough of water or mercury, through which it may freely deliver any elaſtic fluid into the veſſels intended for the menſuration of it.

Thus the mixture of elaſtic fluid and condenſible vapour which iſſues from the charge of the retort, is forced to paſs firſt through the long narrow and cool neck of the receiver, to circulate in the ſpacious body of it, to paſs again through its narrow tube, to circulate again in the ſeparating funnel; and finally, after depoſiting all that can be condenſed under theſe advantageous circumſtances, the incondenſible part paſſes off through the narrow bore of the bent tube.

Into a ſtrong crown glaſs retort, well coated with clay, I introduced 16 ounces Troy=7680 grains of my acet. veg. alkali, conſiſting of 3862.994 of pure alkali, and 3817.006 of acetous acid and water; and knowing by former experiments that it is impoſſible to heat this ſalt to any conſiderable degree, without boiling it over into the neck of the retort, unleſs the fire be applied in ſuch a manner as to make the upper part of the veſſel hotter than the bottom, I placed the retort on the ſand-bed of a reverberatory furnace, with the uncoated extremity of its neck projecting a few inches through the door: and having adjuſted the apparatus lately deſcribed, to the

the uncoated part of the neck, I ſecured the juncture with glue lute.

The furnace was then gradually heated, and the heat uniformly encreaſed during ſix hours.

The quantity of common air in the retort and condenſing veſſels was 346.5 cubic inches; and the veſſels which were ready for meaſuring the incondenſible product of this charge contained nine cubic inches each.

On the firſt impreſſion of the fire, the air in the retort being dilated, a portion of it iſſued, which at the temperature of 52 of Farenheit, and under the mean preſſure of the atmoſphere, meaſured 36 cubic inches, and was not different from common atmoſpheric air. Now water began to ſhew itſelf in the recipient, and was afterwards collected to the quantity of 120 grains, when about 63 cubic inches more of common air had iſſued. The water was not in the leaſt degree acid or coloured, but ſmelled and taſted like the oil hereafter deſcribed. The laſt portions of the 63 cubic inches of air, were fit for combuſtion, but in this reſpect not quite ſo good as common air, and ſmelled like the water. At this period, the emiſſion of air was ſuddenly followed by a preſſure of the external air into the veſſels, which would have forced the water, in which the bent tube was immerſed, into them, if I had not inſtantly turned it out of the water, and admitted the air through it.

In diſtilling any body which contains water, it is to be obſerved, that the air included in the retort and recipient will be dilated and expelled for the greater part, if not totally, by the watery vapour; and when that vapour no longer iſſues in due quantity, to fill the veſſels and counteract the preſſure of the atmoſphere, the external air preſſing on the veſſels, will preſs into them, wherever it finds admittance; but if the communication is intercepted only by water, or any other fluid, that will be preſſed into the recipient, and even into the retort, ſo ſoon as the emiſſion of hot vapour from the charge is inſufficient to fill the ſpace which the vapour formerly occupied, after expelling the air.

If external air be admitted to prevent the water from being preſſed into the recipient, the quantity of it will be equal to that formerly expelled, provided the diſtillation be very ſlowly conducted, as in the preſent inſtance. Therefore rejecting from the following meaſurement the air heretofore expelled, ſince it was not altered in any conſiderable degree, we are now to conſider the charge as conſiſting of 7680 grains of the ſalt expoſed to 346.50 cubic inches of atmoſpheric air; both which amount to 7813.4 grains.

When the freſh emiſſion of air took place, and amounted to 40 cubic inches, I began my reckoning in the following manner:

	Cub. Inch. contained.	Of fixed Air.	Of Phlogiſticated.	Of Inflam.
Firſt	40	6	30	4.0
Next	160	26.7	100	33.3
	160	32.	80	48.
	160	40	40	80

The

The water now saved amounted to 340 grains, and ethereal oil began to condense with the last portions of it, for no more water, separable from the oil, appeared after this period.

Cub. Inch. contained.	Of fixed Air.	Of Phlogisticated.	Of Inflam.
Next 160	40	20	100
320	80	10	230
320	80	0	240
320	53.5	0	266.5
320	46.	0	274
320	45.7	0	274.3
320	45.7	0	274.3
320	45.7	0	274.3
320	40.	0	280
320	35.5	0	284.5
320	32.	0	288.
320	32	0	288.
320	21.3	0	298.7

Before this period, the distillation of oil had ceased, and now I drew off all that was condensed. It weighed 180 grains.

160	8	0	152
64	2.1	0	61.9

The

The laſt portion of elaſtic fluid iſſued ſo ſlowly, although the fire was augmented, and the retort ſhewed a bright red heat, that very little more was to be expected: I therefore withdrew the fire. The elaſtic fluid left in the retort and recipients meaſured, when cold,

Cub. Inch. contained.	Of fixed Air.	Of Phlogiſticated.	Of Inflam.
277	15	0	262
Total 5021	727.2	280	4013.8

The inflammable air thus produced, differs greatly in ſpecific gravity from that of metallic ſolutions; the firſt portions expelled by moderate heat are much heavier ſpecifically than thoſe which follow at diſtant intervals, and thoſe that are expelled by the greateſt heat at laſt, are the lighteſt, but yet greatly exceed the inflammable air from metals, in denſity and weight.

As it is not neceſſary to my preſent purpoſe, that my menſurations ſhould be perfectly accurate, I ſhall not inſiſt further on theſe differences of the ſpecific gravity of the inflammable air of acetous ſalt, than to remark, that a mixture of the firſt and laſt portions is, according to my experiments, to atmoſpheric air, in ſpecific gravity, as 19 to 28.84189, and that a cubic inch of this mixture weighs .261 gr. when it is freſh, but freed from fixable air by lime liquor.

	Gr.
Stating a cubic inch of this inflammable air at - - -	0.261
A cubic inch of phlogiſticated air, according to Fontana, at - -	.377
A cubic inch of common air, at -	.385
A cubic inch of pure air, called dephlogiſticated air, at - -	.42
And a cubic inch of fixable air, at	.57

	Grains.
In the products of the acetous ſalt, I find, of fixable air -	414.504
Of phlogiſticated air - -	105.56
And of inflammable air - -	1047.6018
Total	1567.6658

On the firſt emiſſion of fixable and inflammable air, a denſe white fume fills the long neck and receivers; and theſe elaſtic fluids,

fluids, as they iſſue through the water into the meaſures, fill theſe laſt with fume of the ſame kind, but not equally opaque. But when the elaſtic fluids have ſtood a few minutes, a very ſmall quantity of oily and aqueous matter is depoſited, and they become tranſparent. The quantity of oily matter depoſited by 100 cubic inches, was too ſmall to be meaſured, but ſome allowance is to be made for it.

During this proceſs, the long neck was cool to the touch within ſix inches of the luting, at the mouth of the retort, and in all diſtillations that I have made, in which elaſtic fluids of any kind are ſlowly expelled, the heat extends very little farther in the receiving veſſels than it would by the approximation of ſuch veſſels to the heated retort, if it were quite empty; but condenſible vapour carries the heat with it to a conſiderable diſtance, and as far as it extends in the ſtate of vapour, from the retort into the extreme condenſing veſſels. Hence it appears, that elaſtic fluids retain the fire which iſſues with them, in a ſtate of combination, and by virtue of the attraction which caufes this union, prevent the efcape or diffufion of this fire into the neighbouring bodies or fpaces; and as this phenomenon is common to all the elaftic fluids, and almoft all experiments in which they are flowly produced, it ftrongly indicates that a great quantity of fire is combined in every one of them, and is to be confidered as a conftituent principle and active ingredient.

On breaking the retort, I found a fpongy mafs, of a black or deep blue colour on the upper furface, and dark grey in the mafs, refembling in all refpects the black alkaline coal of tartar. It adhered to the glafs, and when feparated by folution, was found to weigh 5524 grains; but as the glafs had been manifeftly corroded in feveral places, it muft have contributed to this weight.

The folution of this alkali fhewed a confiderable bulk of light black coaly matter, which

which was eaſily ſeparated by filtration from the alkaline liquor which paſſed limpid, and when waſhed and dried, weighed 86 grains. It was very like lamp black, catched fire readily like tinder, and burned without ſmoak or flame to grey aſhes, which by calcination grew whitiſh, or pale yellow, and melted in a weak red heat. The melted matter conſiſted of vegetable alkali and a little fixable air, and weighed 8 grains; therefore the quantity of volatile combuſtible matter was about 78 grains.

The filtered alkaline ſolution from which the coaly matter was ſeparated, was milder and ſeemed to contain more fixable air than is in ordinary ſalt of Tartar. In divers experiments it appeared to differ in nothing elſe from purified ſalt of Tartar; and even before the coaly matter was ſeparated, it did not act like phlogiſticated or Pruſſian alkali. By neutralizing it with diluted vitriolic acid, I expelled from it 1858 cubic inches of fixable air = 1059.06 grains, which added to 414.504 obtained in the diſtillation, make 1473.564 grains.

Of

Of 346.5 cubic inches of atmoſpheric air included in the veſſels, $\frac{4}{5}$ were phlogiſticated air, the weight of which is 104.5 grains; and the weight of the pure air in this quantity of atmoſpheric air is 29.1 gr.: but ſince this quantity of phlogiſticated air is almoſt equal to that which was expelled along with the inflammable, and we know that phlogiſticated air is in no reſpect altered or active in proceſſes of this kind, we ſhall reject it as well from our ſtatement of the charge, as from that of the products; and ſay, that the charge conſiſting

	Grains.
Of mere vegetable alkali - -	3862.994
Of acetous acid and water -	3817.006
Of pure air - - -	29.1
And altogether amounting to	7709.100
Yielded of mere alkali - -	3862.994
Of fixable air - - -	1473.564
Of inflammable air - -	1047.6018
Of oily matter held in the black coal - - -	78.
Of oil - - -	180.
Of water condenſed - -	340.
Theſe amount to - -	6982.1598

 Which

	Grains.
Which is leſs than the charge by	726.9402

This deficiency puzzled me exceedingly, until by repeated experiments ſimilar to this, I found that it is always owing to the water and oil, and chiefly to the water which follows the ſtream of elaſtic fluids, and of which a ſmall part remains ſuſpended in them for a conſiderable time after they acquire the temperature at which I meaſured their bulk, but not their weight.

Applying theſe experiments to my preſent purpoſe, I may, wthout any conſiderable error, ſtate the quantity of water carried off in vapour, and not included in the foregoing weight, at 700 grains; and the quantity of oil carried off in the ſame way, at 26.9402 grains.

The quantity of water which the 29.1 grains of pure air can furniſh in theſe circumſtances, is too ſmall to be regarded on this occaſion; and therefore we may ſay that the acetous ſalt contained 340 + 700 = 1040 grains of water, and conſequently

2777.006

2777.006 of mere acid, or mere acid and fixable air: for I ſtrongly ſuſpect that in the mere evaporation and exſiccation of the ſalt, ſome fixable air is formed from the acetous acid where it is expoſed to the air.

It is to be obſerved, that the inflammable air, oil, and phlogiſtic part of the black coal, amount to 1332.542 grains; and the fixable air to 1473.564 grains; the total of which differs from 2777.006, the computed quantity of mere acid, only by the weight of the pure air, which never fails, with ignited acetous ſalts, to make fixable air. From all which I conclude, that the quantity of matter, in acetous acid thus treated, which is expended in the formation of inflammable air and oil, is not much leſs than that which is expended in making fixable air; and for the reaſon above-mentioned, I am of opinion that the weight of theſe would be equal, if the acetous ſalt were prepared without expoſure to air, which ſo far as it enters will make fixable air, as will be ſhewn hereafter.

In

In this experiment we remark the moſt illuſtrative phenomena of a great many more which I have made on ſalts and vegetable ſubſtances, containing the principles of acetous acid; in all which it appears that phlogiſton enters the compoſition of acetous acid in great quantity; that acetous acid detained by its attraction to a fixed body, until it is ignited to a certain degree, forms new compounds; that fire is the only matter which it receives in this circumſtance; that it abſorbs and combines with this fire, and fixes it; that ſome principle or principles of the acetous acid combined with fire make fixable air, whilſt ſo much of the remainder as combines in like manner with fire makes inflammable air; and that which eſcapes the neceſſary ignition makes oil; or that which is obſtinately retained in a fixed body makes a coaly combuſtible ſubſtance.

But above all things we are to obſerve, concerning the diſtillations in which acetous acid is ſubmitted to the action of fire, that no part of it either in this or any ſimilar experiment is expelled from acetous ſalts duly prepared, in the form of acetous acid, and that the acidulous liquor, which is ſaid by chemical writers to be diſtilled in ſuch proceſſes, is not truly acid, but a mixture of water, fixable air, and the ethereal oil of the ſubſtance ſubmitted to the diſtillation.

Finally, it is to be remarked, that in this or in any of the diſtillations of acetous compounds, made by the ableſt chemiſts, there is no increaſe of weight in conſequence of the new compounds formed by the acetous acid and fire; and conſequently all ſuch experiments tend to ſhew that the matter of fire does not gravitate ſenſibly.

SECT. IV.

Experiments ſhewing that in the Tranſmutation of Acetous Acid into the Elaſtic Fluids and Oil, there is no intermediate Form of it, and tending to eſtabliſh the foregoing Inductions.

IN diſtilling 16 ounces Troy of acetated vegetable alkali in a glaſs retort ſet in a ſand pot, the abſorption of air took place in the manner deſcribed in the preceding experiment. Fixable and inflammable air iſſued alſo after the ſalt had been compleatly fuſed, and the abſorption had ceaſed, but the proportion of fixable air was ſomewhat leſs relatively to the inflammable air, from the beginning to the 2340 cubic inch of the mixed elaſtic fluids; which I impute to the different application of heat.

For here any fixable air, detached from the hotteſt part of the charge near the bottom of the retort, muſt paſs through the

frothy

frothy and colder parts, in which a great part of it may be retained, whilſt the inflammable air which is leſs forcibly attracted by the alkaleſcent charge, eſcapes through it undiminiſhed.

When about 3000 cubic inches of elaſtic fluid were expelled, the quantity of water and oil was nearly the ſame as appeared at the like period of the former experiment; and now the charge boiled over the helm.

This inconvenience was repeatedly experienced in diſtilling the ſame ſalt in this manner, although I had uſed retorts capable of holding ſix times the charge, and had regulated the fire with the greateſt caution.

The part of the charge which had not boiled over, was a black ſpongy alkaline maſs, which, when diffuſed in water, eaſily depoſited a black coaly matter, like that deſcribed in the foregoing experiment, on the filter, whilſt the alkaline ſolution paſſed through quite colourleſs.

This filtered ſolution evaporated to dryneſs, yielded pure white and very mild fixed vegetable alkali, which on the affuſion of vitriolic acid, yielded a greater proportion of fixable air than is above deſcribed, as might be expected in conſequence of the heat which it ſuſtained being much weaker and of ſhorter duration.

The portion which boiled over, and conſequently ſuſtained the leaſt heat, was as deliqueſcent as the acetated alkali employed, and was of a dark brown colour, as if ſtained by the oil expelled from the part of the ſalt which occupied the bottom and hotteſt part of the retort. The ſolution of it paſſed ſlowly through the filter, and was opaque, olive-coloured and greaſy, by reaſon of the oil. The dry ſalt got from it by ſlow evaporation, was plainly impregnated with oil, which gave it the colour of pale yellow ochre. Its weight was exactly half that of the white alkaline ſalt got from the other part of this charge; and with vitriolic acid it yielded fixable air and acetous acid, which left a reſidue of vitriolic ſalt, blackened by the oily matter. Therefore, the part of the acetous acid which was sufficiently ignited, was all transmuted into elastic fluids and oil, and the remainder retained the form and characters of this acid; and in the transition of acetous acid to form fixable and inflammable air and oil, there is no intermediate form of it; and as the oil may by fire alone be turned into inflammable air, the part which appears in the oily form differs from the inflammable air chiefly in its having escaped the necessary ignition, and consequent disunion of its parts, which must precede its combination with the quantity of fire essential to the elastic form of inflammable air.

In repeating this experiment with 64 ounces of acet. veg. alkali, I observed the same phenomena on a larger scale, and did not obtain one drop of acid. But yet the water impregnated with fixable air and ethereal oil had a pungent acidulous taste; which has misled chemists to consider the like product of acetous salts and vegetable substances as an acid spirit.

In

In these circumstances, the acetous acid does not part in its proper form and constitution from the alkali; but remains in it, until by the access of a certain charge of fire, it forms the new products which pass off in distillation.

In the foregoing manner, 32 ounces Troy of my acetated vegetable alkali were distilled, very slowly, and yielded the water, oil, fixable air, and inflammable air, already described; until, at the expiration of six hours, the charge begun to froth and rise towards the helm: then the retort was quickly raised out of the hot sand, without exposing its contents to the atmospheric air. When the matter had subsided a little, and concreted by cooling, it was very spongy at the upper part, but as compact as the foliated Earth of Tartar at the bottom, and equally crystaline, foliated, and deliquescent; but it was of a dark grey colour, and weighed 26 ounces: therefore, only six ounces were expelled in the forms above-mentioned: but in reducing the acetous salt to this state, all the water that could have been withdrawn without decompoſing it totally, was taken from it.

To theſe 26 ounces I added, very ſlowly, through a ſeparating funnel, in a tubulated retort fitted to the apparatus deſcribed in the Third Section, 26 ounces of the moſt dephlegmated vitriolic acid, every part of which excited heat, where it acted on the ſaline maſs. By diſtillation in a ſand heat, I obtained firſt, three ounces of dephlegmated acetous acid; then as much more of weaker acetous acid; then two ounces, of which one-third was water; and laſtly, an ounce of acid, equal to dephlegmated acetous acid mixed with its weight of water.

During the diſtillation of the acid, a denſe white vapour flowed down along the lower ſide of the long neck and receiver, conſiſting chiefly of acetous and oily vapour and fixable air; and the elaſtic fluid which iſſued through the bent tube of the lower recipient, after the atmoſpheric air was expelled, conſiſted of fixable air blended with a little of the oily and acetous vapour. After this,

half

half an ounce of water, impregnated with vitriolic and ſulphureous acid, was diſtilled, and then the ſulphureous or volatile acid, in its elaſtic ſtate, iſſued rapidly. At this moment I raiſed the retort out of the hot ſand, and ſuffered it to cool quickly, without admitting any air to it.

The quantity of water thus procured from the mixture of the moſt dephlegmated vitriolic acid with highly dephlegmated acetous ſalt, from either of which ſeparately, no water can be procured by heat, is worthy of notice. The true reaſon of it will appear hereafter; but when the experiment was made, I imputed it to the agency of Phlogiſton, which in divers experiments appeared to facilitate the extrication of water from acids, air, and other bodies; and although I could not determine whether the water was only liberated, or was really formed, I made practical uſe of the obſervation; for ever after, in preparing the ſtrongeſt acetous acid, I was little ſolicitous about the dryneſs of the acetous ſalt, or ſtrength of the vitriolic acid, and truſted

 chiefly

chiefly to the volatility of the acetous acid, by reafon of which, the firft portions diftilled from a great charge are as ftrong as acetous acid can be procured from the drieft materials.

The denfe white vapour which occurs in the diftillation of this and other acetous compounds, runs diftinct under the air left in the veffels, as water runs under oil, and confifts of fixable air blended with oily vapour. Whilft the acid arifes highly dephlegmated, this fine oil is freely imbibed by it, to a certain quantity; but the diluted acid which follows, becomes turbid with the oil, becaufe it is foluble in water only, in fmall quantity.

Hence we learn, that the oil or moft phlogiftic part of acetous acid will unite with the like acid, although the phlogiftic part, which has acquired the form of inflammable air, will not. And as this oil may be tranfmuted into inflammable air by fire only, the agent which gives the elaftic form is fire, and that which prevents the phlogiſtic part of acetous acid from uniting with the like acid again, is nothing elſe but fire.

The ſaline maſs, conſiſting of vitriolic acid and vegetable alkali, was found ſtrongly impregnated, and quite blackened with coaly matter, like that already deſcribed; whence it appears, that vitriolated Tartar, with exceſs of vitriolic acid, will retain, like alkali, a portion of the Phlogiſton of acetous acid in a conſiderable heat, and will form with it a black coaly ſubſtance.

The ſulphureous acid ſhews that the phlogiſtic matter of acetous acid, volatile ſulphureous acid, ſulphur, and other bodies, is identical.

From this and the foregoing experiments we may infer, that the fire expended in decompoſing acetous acid, paſſes off along with the products in a fixed ſtate, ſince they iſſue cold; and that every portion of the acetous acid requires its due charge of fire, before it can be tranſmuted by it; ſince by withdrawing the charge of acetous ſalt from the fire, at any time before the whole of its acid is transformed, whatever part of it remains, is ſtill poſſeſſed of every property of acetous acid, and affects no condition intermediate between this and the ſubſtance of elaſtic fluids, which with a due charge of fire it never fails to form.

This is manifeſtly true, with reſpect to the part of the acetous acid which is expended in the formation of fixable air; but as ſome of the phlogiſtic part of the acetous acid is expended in forming oil, whilſt the remainder of its phlogiſtic matter, in new combination, forms inflammable air, the part which is turned into inflammable air, may be ſaid to affect an intermediate form of oil, although the ſame may not be ſaid of the acetous acid; but ſtill the oil appears to be nothing more than the ſubſtance of inflammable air before it combines with fire; for this oil puſhed through red hot ſand or glaſs, or clay, or detained in porous bodies by capillary attraction, until it can be duly ignited, is almoſt wholly con-

vertible

vertible into inflammable air, like that expelled from the acetous ſalt.

In due time, we ſhall diſcover the reaſon why one part of the acid is expended in making fixable air, whilſt the remainder forms a combuſtible elaſtic fluid or oil, ſo different from acetous acid or fixable air.

In theſe diſtillations of acetated vegetable alkali, and in thoſe of other acetous ſalts, in glaſs veſſels, I have always found that more of the fixable air is retained in the alkaline or earthy reſidue, than is expelled along with the inflammable air.

In fixable air, whoſe parts are detained and approximated by an alkaline ſalt, as in our mild alkaline reſidues of acetous ſalt; or by earth, as in chalk or magneſia; the matter of fire does not ſeem to be combined in ſo great a quantity as in that which aſſumes the elaſtic form; but ſtill we may be allowed to call it, even in the fixed ſtate, by the uſual name, and in the latitude of ſpeech which muſt be admitted in the infancy of

this

this knowledge, we may ſay, that fixable air never becomes elaſtic, until it is ſaturated with fire, and unreſtrained by other matter; for in detaching it from alkalies, chalk, magneſia, or any other body, ſo as to produce it in the elaſtic ſtate, we are obliged to uſe fire; we obſerve a great expenditure of fire, becauſe the body thus yielding fixable air, never conceives near ſo much heat, whilſt it emits fixable air, as it would in the ſame fire, if it contained none of this matter; and the fire which thus accompanies fixable air does not deſert it, becauſe it does not warm the veſſels through which the fixable air runs with a rapid ſtream: or if we attempt the extrication of fixable air by any other means, we find that nothing void of fire will anſwer the purpoſe. Acids cauſe great heat, and conſequently emit a great quantity of fire in combining with pure alkalies, pure calcareous earth, calcined magneſia and divers other bodies; therefore they contain fire abundantly: but when acids are employed to detach fixable air from theſe bodies, little or no heat is diſcoverable, no fire is emitted to waſte, but all that belonged to the acid or alkali, or lime or magnesia, and which cannot be retained in the saline compound, is transferred to the fixable air and combines with it; for otherwise, it would issue hot, and gradually impart this heat to the neighbouring bodies.

Whenever any heat is discovered in the solution of bodies which yield fixable air, and very little else, it implies no more than that the menstruum and solvend together emit more fire in the approximation and union of their parts, than is necessary to the constitution of that quantity of fixable air which issues in the elastic form.

SECT.

SECT. V.

Analyſis of Acetous Calcareous Salt by Fire, illuſtrated with general Obſervations.

I HAVE purpoſely omitted the doubts which may be entertained concerning the foregoing inferences, left they ſhould perplex the reader, and reſerved the diſ-cuſſion of them for the ſubſequent pages, in which I am to relate the experiments made for this and other purpoſes.

Suſpecting that the alkali of the acetous ſalt might have contributed to the formation of the elaſtic fluids, and of the oil eſpecially, by ſome other means than the mere detention of the acetous acid, until it receives a greater charge of fire than that by which it may be diſtilled alone without decompoſition ; and intending that the meaſures, by which the real agency of the alkali might be aſcertained, ſhould at the ſame time afford ſome further elucidation of the nature

of

of this acid, I made the following experiments with new acetous compounds.

Into a cylindrical glaſs veſſel, filled with mercury, and inverted in a baſon of the ſame, I introduced 240 gr. of powdered lime, and when it had all riſen above the quickſilver, I added 720 gr. of concentrated acetous acid, which with a glaſs rod I mixed briſkly with the lime. A heat exceeding 212 degrees was immediately excited, and the mercury was depreſſed conſiderably.

The matter which depreſſed it, occupied a ſpace of 18 cubic inches, under the mean preſſure of the atmoſphere, whilſt it was hot; and was chiefly acetous vapour; for the ſpace leſſened quickly as the veſſel cooled, and the mercury ſoon roſe to its former heighth.

By this experiment I diſcovered the cauſe of the great waſte of acetous acid which I had often experienced, in attempting to make acetous calcareous ſalt without uſing water, in order to ſave the trouble of evaporation, or to know the degree of concentration or ſtrength at which the acid was contained in the ſubject to be ſubmitted to the action of fire: even when the acid diluted with an equal weight of water was mixed with quicklime, I obſerved a conſiderable waſte of the former in pungent vapour, expelled by the heat of the ſlaking lime, before the intended combination could take place.

When I diluted concentrated acetous acid with equal parts of water, and diſſolved a little lime in this weakened acid; and then, in order to have a dry ſalt directly, poured it on quicklime, I obſerved that the parts of the lime which were moſt heated grew black. This is analogous to the change which acet. calc. ſalt undergoes in the like heat in cloſe veſſels; and hence I learned, that in compoſing this ſalt, the lime ought to be previouſly ſlaked and cooled, and a quantity of water, more than is ſufficient for the ſolution of the calc. ſalt, ought to be employed, as in the following experiment:

 I ſlaked

I ſlaked four ounces Troy of pure lime, and when it was quite cold, I added 30 ounces and 8 pennyweights of water, and then 11 ounces 4 pennyweights of concentrated acetous acid: theſe being the neceſſary proportions for ſaturation and ſolution in the degree of heat excited during the union of the acid and ſlaked lime, which was about 100 of Farenheit.

I evaporated the ſolution ſlowly to dryneſs, never exceeding 200 degrees of heat; and obſerved that it exhaled acetous acid ſenſibly throughout the evaporation, and copiouſly, when the ſaline matter grew conſiſtent and approached to dryneſs, although at this time the heat did not exceed 100. I therefore dried it no further than to render it compleatly pulverable and fit to be eaſily introduced into a retort, without waſte. In this ſtate it weighed 11 oz. 4 dwts. 4 gr. =

	Grains 5380
So it conſiſted of lime - - -	1920
Of acetous acid and water - -	3460
And the loſs of acid by evaporation was about - - - -	1916

or

or near $\frac{1}{5}$ of the acid employed: and hence it appears, that near $\frac{1}{5}$ more of the acid is required for the ſolution of lime, than is retained in the dry calcareous ſalt; or, that dry acetous calcareous ſalt retains the acid in a more concentrated ſtate than we have it in the pureſt concentrated acetous acid. But the exhalation of acid throughout the evaporation, and the quantity of acetous acid obtainable from acetous calcareous ſalt, when decompoſed by nitrous and other ſtrong acids, ſhew that there is a real loſs of near $\frac{1}{5}$ of the acetous acid in evaporating this ſolution to dryneſs.

I have often obſerved, that acetous calcareous ſalt, which felt perfectly dry and was kept in paper looſely folded, ſmelled of acetous acid whenever the paper was opened, during two or three months. For this reaſon, and becauſe the acid varies in quantity as the ſalt is more or leſs dried, I noted the quantity of calcareous earth and acid in the calcareous ſalt, at the time of my uſing it in any experiment, from which I intended to learn the quantity of fixable

and

and inflammable air, and of oil and water, which could be produced from it in diftillation.

Of the calcareous falt thus prepared, I introduced 3965 gr. containing 1438 of lime, and 2527 of acid and water, into a glafs retort well coated, and placing it in a reverberatory furnace, in which the heat might act equally on the upper and lower parts of the charge, I adapted a condenfing apparatus, fimilar to that already defcribed. The retort and recipients contained 231 cubic inches of common air = 88.935 gr. and the meafures in which the elaftic fluids were to be received, contained 37 cubic inches each.

When fire was applied, the elaftic fluids expelled were ftated thus:

Cub. Inch.

1. 37 were atmofpheric air.
2. 37 were atmof. air more phlogifticated.

A portion of water and colourlefs ethereal oil was now drawn off, and marked N° 1, and a white vapour appeared in the receiver.

	Cub. Inch. contained.	Fixed Air.	Phlogiſtic. and Inf.
3.	37	5	32
4.	37	6	31

Before this time, a portion of clear oil, inclining to yellow, was ſaved apart, and marked N° 2.

5.	37	12	25

Another portion of yellow oil was now withdrawn, and marked N° 3.

			Inflam. chiefly.
6.	37	11	26
7.	37	10	27

Now the oil N° 4 was drawn off.

8.	37	9	28
			Inflammable.
9.	37	8	29
10.	37	7.5	29.5
11.	37	7.5	29.5
12.	37	7.5	29.5
13.	37	7.5	29.5
14.	37	7.5	29.5
15.	37	7.5	29.5
16.	37	7.5	29.5
17.	37	7.5	29.5
18.	37	7.5	29.5
19.	37	7.5	29.5

	Cub. Inch. contained.	Fixed Air.	Inflammable.
20.	37	7.5	29.5
21.	37	7.5	29.5
22.	37	7	30
23.	37	6.5	30.5
24.	37	5.5	31.5

No oil appeared to have been diſtilled ſince the twentieth meaſure; I therefore drew off all that was in the recipient, and got none afterwards; this was marked N° 5.

25.	37	5.3	31.7
26.	37	5	32
27.	37	4.9	32.1
28.	37	4.8	32.2
29.	37	4.7	32.3
30.	37	4.6	32.4
31.	37	4	33
32.	37	3.5	33.5
33.	37	3.5	33.5
34.	37	3.4	33.6
35.	37	3.4	33.6
36.	37	3.3	33.7
37.	37	3.2	33.8
38.	37	3.1	33.9
39.	37	3.1	33.9
40.	37	3	34

	Cub. Inch. contained.	Fixed Air.	Inflammable.
41.	37	3	34
42.	37	3	34

Ever after the diſtillation of oil had ceaſed, the vapour in the veſſels was leſs opaque.

43.	37	3	34
44.	37	3	34
45.	37	3	34
46.	37	3	34
47.	37	3	34
48.	37	3	34
49.	37	3	34
50.	37	3	34
60.	370	30	340
61.	37	3	34
62.	37	3	34
63.	37	3·1	33·9
64.	37	3·5	33·5
65.	37	4	33
66.	37	5	32
67.	37	6	31
68.	37	7	30
69.	37	8	29
70.	37	8.5	28.5
71.	37	9	28
72.	37	9·5	27·5

73.

	Cub. Inch. contained.	Fixed Air.	Inflammable.
73.	37	9.9	27.1
74.	37	10.2	26.8
75.	37	10.5	26.5
80.	185	52.5	132.5
81.	37	10.5	26.5

At this time the retort was ready to melt, and it was neceſſary to withdraw the fire. What iſſued afterwards was retained in a bladder, faſtened to the diſcharging tube of the ſeparating funnel, and theſe veſſels, when cold, contained 232 cubic inches of air, chiefly inflammable, the calcareous earth, or wet bladder, having imbibed the fixable air, if any iſſued, about the time when the fire was withdrawn.

	Gr.
The ſum of the cubic inches of elaſtic fluids was - -	3229
Of which the atmoſpheric air, unaltered, made - - -	74
The fixable air - - -	456.2
The inflammable and the phlogiſtic air - - -	2698.8

It is to be obſerved, that in this diſtillation, no air in addition to that contained in the recipients was admitted; for as there was no danger of boiling the calcareous ſalt over the helm, the retort was quickly heated, and if any abſorption of the air happened, its place was ſupplied immediately by the vapours and elaſtic fluids which iſſued early and continually from the charge.

By long experience in operations of this kind, I have been convinced that the quantity of fixable air, which the water can imbibe during the meaſurement, is not conſiderable, when it is thus mixed with inflammable air, and when the quantity of water employed is not above $\frac{1}{50}$ of the bulk of the elaſtic fluids. What is thus imbibed and gradually emitted to waſte from the water is, to my apprehenſion, barely ſufficient to compenſate for an inaccuracy, in the menſuration, of a contrary tendency, by which we are led to over-rate the quantity of fixable air. For in the agitation of the mixed elaſtic fluid with lime liquor, the quantity of this laſt which enters the meaſure denotes not only the quantity of fixable air

air imbibed, but the quantity of phlogiſtic and inflammable air which is entangled in minute bubbles in the mixture of water and lime; and therefore, if we ſtate the bulk of the fixable air to be equal to that of the liquor which enters the meaſure, we aſſume a greater than the real quantity. When the buſineſs is ſteadily conducted, theſe oppoſite errors correct each other ſufficiently, with regard to the fixable air.

Concerning the inflammable air which is thus loſt during the ſeparation of the fixable air, it is to be obſerved, that it is barely equivalent to the bulk by which we are apt to over-rate the quantity of this elaſtic fluid, in meaſuring it ſoon after it has iſſued. For in a mixture of fixable and inflammable airs, iſſuing with a temperature exceeding 52 by a few degrees, the inflammable air is more dilated than the other, or requires a longer time to accommodate itſelf to the denſity proper to its mean temperature. Therefore, in meaſuring it ſoon after its egreſs from the charge, I conſider the bulk left in the lime liquor as equal or almoſt equal to that by which the inflammable air in the meaſure exceeds the volume to which it would in due time contract in a temperate medium.

By frequent compariſons of the bulks of ſuch elaſtic fluids, meaſured at various temperatures, with their bulks at 52, I aſcertained the quantity that ought to be deducted from the meaſures taken at any temperature, exceeding 52; and this was eſpecially neceſſary in warm weather, or when the laboratory was heated. But in making this deduction from the meaſured bulk, I found it not expedient, for the reaſons already mentioned, that it ſhould be greater with regard to the inflammable than the fixable air.

Theſe obſervations are applicable eſpecially to the preſent experiment, in which the elaſtic fluids were neceſſarily meaſured before they had acquired that temperature to which I confine myſelf in calculating their weight.

Deducting then $\frac{1}{9}$ of the measured bulk of the elastic fluids of this distillation, I stated the mean bulk of the fixable air at 405.512 cubic inches; and that of the inflammable and phlogistic, at 2398.934.

Of 231 cubic inches of air included in the retort and receivers, 74 were expelled without alteration, and 157 only are to be accounted for: but of this quantity 125.6 cubic inches is the bulk of phlogisticated air, which is merely passive, and about 31.4 cubic inches of pure air operate in the process. Deducting, therefore, 125.6 cubic inches from the volume of the inflammable and phlogistic air, which was 2398.934, we shall find the cubic inches of inflammable air alone to be 2272.434.

The pure air measuring 31.4 cubic inches, and weighing 13.188 gr. and being an active matter, is to be considered as a part of the productive charge, which consisting of 3965 gr. of calcareous salt, and 13.188 gr. of pure air, amounts to 3978.188 gr.

On

On opening the retort when it was cold, I perceived that it had been melted, but the coating had preſerved the form of it. The maſs contained in it was almoſt equal in bulk to the calcareous ſalt employed: it was black and ſpongy in all parts, except at the bottom, which preſented a circular ſurface, about 1 $\frac{1}{2}$ inch in diameter, grey near the centre, but declining to blackneſs towards the circumference, and the greyneſs extended to the depth of $\frac{1}{10}$ of an inch at the central part only.

This grey part being contiguous to the ſand bed which preſerves a red heat for hours after the fire is withdrawn, was longeſt expoſed to the heat; and the change of colour is nothing more than the whole maſs would have undergone by a further continuance of the fire, as will appear in ſubſequent experiments.

The whole weighed 2191 gr. and exceeded the weight of the lime contained in it by 753 gr. Diſſolved in dilute marine acid, it afforded 1160.157 cub. inch. of fixable

able air, and 11.5 of denſe inflammable air, which, I believe, was held in the ſpongy maſs by capillary attraction: and in the ſolution it appeared that two or three grains of the glaſs adhered to the calcareous maſs. Thus the whole of the fixable air meaſured 405.512 + 1160.157 = 1565.669 cub. inch. weighing 892.4313 gr. And the inflammable meaſured 2283.934 cub. inch. weighing 596.1067 gr.

After the fixable air was expelled, I ſeparated the marine ſolution from the undiſſolved coaly matter, which, after being well waſhed and dried, weighed 131 gr. and had great bulk for this weight. It was combuſtible, but not freely; for it could not catch fire from a flint ſpark. In the degree of ignition neceſſary for its combuſtion, in the ſlowneſs of it, and its affording no ſmoak or flame, it reſembled the powder of culm, which is the kind of mineral coal employed, not as fuel but as a phlogiſtic flux of the Corniſh ores of tin. By calcination and frequent agitation in a red heat for three hours, it was reduced to a grey powder, which clotted in its approach to whiteneſs, and was found to be calcareous earth, impregnated with a little of the marine acid, which was inſeparable, by waſhing, from the coaly matter. The calcareous earth weighed 41 gr. and therefore, 90 gr. of the coaly powder were diſſipated, during the combuſtion.

When the ſolution of acetous calcareous ſalt is inſpiſſated ſo far only as is neceſſary for introducing it into a retort, it will neceſſarily yield in diſtillation a little acetous acid, or nearly that quantity which would exhale in the exſiccation of it in open air, ſince it is a property of this ſalt to hold more acetous acid neutralized in conjunction with water, than it can hold in the dry ſtate. I have accordingly obſerved in divers diſtillations of acetous calcareous ſalt, the quantity of acid was greater from maſſes barely inſpiſſated, and leſs when the ſalt was better dried before the diſtillation, and leaſt of all, or next to nothing, when it was perfectly dried. But as this treatment was attended with waſte of the acid, I preferred the ſalt

here

here deſcribed for the beſt experiments; and in my deſcription of the phenomena, I am to obſerve, that a few drops of the water firſt diſtilled were ſour, but that the quantity of acetous acid which thus eſcaped undecompoſed, was too ſmall to require any further attention.

The portion of watery liquor firſt diſtilled, and marked N° 1, weighed 122 gr, was quite tranſparent and colourleſs, taſted pungent on the firſt impreſſion and then left a ſenſe of coldneſs on the tongue, like peppermint water, and ſmelled ſtrongly of the ethereal oil which next appeared ſwimming on the water. It did not catch fire when approached to flame; but when it was ſuddenly heated by pouring it into a hot ſpoon, the matter that exhaled from it was inflammable and preſented a weak diffuſive flame of very ſhort duration: It was nothing more than water ſlightly impregnated with the ſubſequent oily liquor.

The ſtraw-coloured oily fluid marked N° 2 weighed 252 gr, ſmelled like the former,

former, and had a pungent taſte, reſembling that of acetous ether, but approaching to cauſticity: advanced within a few inches of the flame of a candle, it catched fire, even when the air was cold, and burned with a durable denſe and bright flame, leaving after, ſlow combuſtion about $\frac{1}{10}$ of its bulk of water, which taſted and acted in all trials, like water very ſlightly impregnated with acetous acid.

The yellow tranſparent liquor marked N° 3 weighed 135 gr, ſmelled and taſted like N° 2, catched fire from a diſtant flame, and burned with a clear denſe and durable flame, until the whole was conſumed, or what remained after ſlower combuſtion was only ſufficient to bedew the ſpoon in ſome parts, or to ſtain them to a dull yellow colour.

In the diſtillation of oils expelled from different acetous ſalts, there is always a very ſmall reſidue of fixed matter, the quantity of which is greater as the proceſs for obtaining the oil is more rapidly conducted, and

and is greateſt in thoſe circumſtances in which the greateſt abraſion of the veſſels takes place; for glaſs veſſels ſuffer this abraſion from watery, oily, or any fluids long agitated in them during evaporation or diſtillation. In conſideration therefore of the fixed matter which may be protruded along with the oil from an acetous ſalt, by mere mechanical impulſe; and of the abraſion which tends to increaſe the quantity of matter left in the rectification or diſtillation of ſuch oil; I do not repreſent the reſidue in combuſtion as an eſſential part of the oil; and ſince the quantity of it was ſo inconſiderable, I ſhall take no further notice of it.

N° 4 weighed 178 grains, and differed from N° 3 chiefly in its richer yellow or ſaffron colour, being leſs tranſparent, and leaving a dew on the ſpoon after combuſtion, which was acidulous and very acrid.

The oil N° 5 weighed 168 gr. and differed in no particular worth notice from N° 4, except its greater opacity.

On

On pouring portions of theſe oils to meet in a cylindrical glaſs tube, and inverting the order of mixture, I could not obſerve the appearances which indicate a notable difference of ſpecific gravity, although the tenacity or ſpiſſitude of the oil laſt diſtilled was much greater than that of the firſt limpid portions, which certainly derive ſome part of their ſpecific gravity from the water contained in them.

That the oily vapour and oil expelled from acetous ſalts by fire, poſſeſs an inebriating and ſomniferous quality, I long ago ſuſpected and am now aſſured by repeated experience: for whenever I ſmelled the meaſures recently filled, and breathed the air contaminated with them, for half an hour or more, I felt theſe effects; but they ſoon ceaſed on my retiring into the freſh air.

	Gr.
It now appears, that the acetous calcareous ſalt, weighing -	3965.
And the pure air - - -	13.188
Both amounting to - -	3978.188

Gave the following products:

	Grains.
Fixable air - - - -	892.4313
Inflammable air - - -	596.1067
Oily matter of the black coal -	90.
Ethereal and yellow oil - -	733.
Water - - - -	122.
Lime - - - -	1438.
All amounting to - -	3871.538
The waſte of matter blown away along with the elaſtic fluids is equal to the difference between the ſum of the charge and that of the products, and is	106.65

The quantity of oil waſted in the ſtate of vapour out of the recipients along with the elaſtic fluids, was very ſmall; but in this and all ſuch experiments, the quantity of watery matter which paſſes off with them is conſiderable; and there is no reaſon to apprehend any important error in our ſtating the quantity laſt mentioned of 106.65 gr. as water: wherefore the whole of the water amounted to 228.65 Gr.

And the charge yielded of fixable air and water	1121.0813
Of inflam. air and oily matter	1419.1067.

It will appear hereafter that the pure air, weighing 13.188 gr, contributed to the fixable air and water only, and if we therefore deduct this quantity from 1121.0813, the remainder which is 1107.8933, is the quantity of fixable air and water; and 1419.1067 is that of the inflammable air and oily matter produced from the whole of the acetous acid. Thus it appears that the acetous acid and water, of the calcareous salt, weighing 2527 Gr.

	Grains.
Yielded fixable air and water	1107.8933
Inflamm. air and oily matter	1419.1067
And yielded in all these -	2527.

As the first portions of the oil were found miscible with water, like ether, and water was deposited in the combustion of them, and appeared in some other experiments made with the view of converting it into inflammable air, I am certain that water contributed considerably to the weight of the finer oil, if it be not an essential ingredient of it.

By a review of this experiment, and those of the Third and Fourth Sections, and due consideration

consideration of the established principles of chemistry, we are enabled to make the following observations and inferences.

First; The acid in the dried acetous calcareous salt retains much less water than is contained in dry acetated vegetable alkali; and this is perfectly consistent with the greater affinity of the latter salt to water; for bodies which contain much water, and yet are dry to the touch and pulverable, evidently hold it by chemical affinity. The quantity of water producible from different acetous compounds, may therefore vary considerably, but has no strict connexion with the conversion of the mere acid into fixable and inflammable air.

Secondly; The oily product is much greater from acetous calcareous salt than from acetated vegetable alkali, and the quantity of inflammable air is much smaller. This is to be expected from the weaker affinity of calcareous earth than of alkali to oil, and from the greater quantity of acid in the calcareous salt than in the acetated alkali.

In the firſt efforts of the fire to decompoſe or tranſmute the acetous acid, the fixable air firſt formed in contact with the lime, adheres to it, and makes mild calcareous earth or whiting, which having a very weak affinity with the phlogiſtic or oily part of acetous acid, makes little or no reſiſtance to its immediate eſcape: wherefore this oily part, having nothing capable of detaining it longer in order to ſubject it to the degree of heat in which it is convertible into inflammable air, paſſes off by moderate heat in its proper condition, as faſt as the part of acetous acid which forms fixable air is ſeparated from it.

In the mean time, as much of this latter part as the calcareous earth cannot retain in the degree of heat which it ſuſtains, paſſes off in form of elaſtic fixable air, and mixed with that part of the matter of acetous acid, which having been duly heated before its eſcape, forms inflammable air.

The ſmallneſs of the quantity of inflammable air from the acid of acetous calcareous

ſalt,

ſalt, comparatively with that which is producible from an equal quantity of the ſame acid detained by fix. veg. alkali, is a neceſſary conſequence of the greater quantity of oil, and ſhews that the inflammable air is furniſhed from the principles of the oil, and that the quantity of it is greater or leſs as the heat is, to which theſe principles are ſubjected before they eſcape from the baſis of the acetous ſalt; all which is conformable to the reſult of thoſe experiments in which inflammable air is made by heat alone from the oily product of every acetous ſalt.

Thirdly; The firſt effect of encreaſing heat, towards the converſion of acetous acid into other forms, is to turn a certain part into fixable air, which having no character of a phlogiſtic body, but all thoſe of an acid, ſhews that the part of the acid, which is turned into fixable air, conſiſts more of the acid than of the phlogiſtic matter. But as the remainder of the acetous acid, when deprived of a great quantity of the acid principle, forms oil and inflammable air; as the quantity of oil is greateſt when it is leaſt heated, and leaſt when moſt heated, or in the greateſt expenditure of it in the formation of inflammable air; we may without heſitation repeat the inductions of the former Sections, with this addition; that whilſt a part of the acetous acid is by the acceſſion of fire formed into fixable air, the remainder, depoſiting the greater part of the water proper to concentrated acetous acid or its ſalts, is diſpoſed to form oil; that the oleaginous matter, when ſufficiently charged with fire, depoſites its water, and forms inflammable air; but in as much as it is forcibly attracted by a fixed baſis, it contributes to the formation of coal.

Fourthly; In the compariſon of theſe experiments we obſerve, that the quantity of fixable air produced from acetous acid is leſs as that of the oil is greater; and from this alone we might expect that the oil, however different from acetous acid, contains a great part of the ſame acid principle which contributes to the formation of fixable air.

That this is at once a true inference and juſt expoſition of the phenomenon, will appear

pear in ſubſequent experiments; and here I ſhall only obſerve that, in diſtillation, we obtain fixable air from this oil in proportion to the quantity of pure air admitted to it, and the degree of heat to which we expoſe it: but when the oil, without being expoſed much to air, is duly heated, it becomes inflammable air, of which the acid principle is a conſtituent part. The quantity of fixable air, in this caſe, is inconſiderable; the quantity of water is greateſt from the firſt or colourleſs oil, and leaſt from the laſt portions diſtilled; and the reſidue is ſo ſmall, that we may ſay, the oil is wholly convertible into inflammable air, the water and fixable air being variable and ineſſential ingredients, which in my preſent uſe of theſe experiments merit no particular attention.

To transform this or any other eſſential oil into inflammable air, inſtead of an iron tube which from its own ſubſtance yields inflammable air, I uſe a glaſs tube hermetically cloſed at one end, ſtrongly coated with clay, and fitted at the mouth, by grinding, to a ſmaller bent tube, which forming an angle with the large one, may eafily tranfmit the product of the oil, through water, into the meafuring veffels. In introducing the oil, I take care that it fhall touch no part of the tube, except that which it fills to the heighth of one or two inches; and then I pour in a mixture of fine white fand and flint powder, in fufficient quantity to imbibe the oil. Placing a column of fand over this charge, to the length of 18 inches or more, I thruft the charged end into the fand-bed of a reverberatory furnace; inclining the tube fo, that the fealed end fhall be nine inches under the fand, the upper part of the charge about three, and that the greater part of the column of fand in the tube fhall emerge and be fully expofed to the action of the fire. In this way, the column of fand is made red-hot before the charge is heated, and when the fire penetrates the fand-bed, or the tube is drawn forward, the oil which expands flowly from the flint powder, is forced to pafs through the winding interftices of the reddened column of fand, and iffues through the bent tube in the form of inflammable air, carrying oily vapour, of which the quantity is inconſiderable when the operation is well performed.

The oils which yield a greater quantity of fixable air than can be imputed to what they have imbibed, or that which the air admitted can contribute to form, afford nothing contradictory to the foregoing expoſition; for I do not aſſert that oil may not combine with the principles of fixable air, in conſiderable quantity. On the contrary, I have formerly remarked that concentrated acetous acid unites with the oil of acetous ſalts, and I have no doubt that it may unite with others. But when any oil yields fixable air abundantly, along with the inflammable, I conclude that, like acetous acid, it contained the gravitating principles of fixable air, and not fixable air already formed; for ſo innumerable vegetable ſubſtances contain them; ſo mixtures of pure air and this inflammable air contain them, but not fixable air, until they are deflagrated.

Fifthly; Since nothing beſides fire is neceſſary to the converſion of the drieſt oil producible

producible from acetous acid, into inflammable air, and fixable air in ſmall and variable quantity; ſince nothing elſe is active in cauſing thoſe parts of matter, which in the oil were coherent and united, to repel each other and form an elaſtic fluid; and ſince from the ſame oil by the ſame fire we produce new compounds, viz. fixable air and inflammable air, between the diſſimilar parts of which there is alſo repulſion; we muſt in conformity to the general and beſt eſtabliſhed principles of chemical union, conclude that fire combines with ſome principles of the oil, with which it forms molecules, which repel each other by virtue of that fire, and conſtitute fixable air; that it alſo combines with the phlogiſtic part of the oil aſſociated with a portion of the acid principle, and in this combination forms inflammable air, whoſe molecules repel thoſe of fixable air by the agency of fire only.

Sixthly; From the experiment in which a ſolution of calcareous acetous ſalt, poured on freſh lime, is firſt dried, and then reduced to a black ſubſtance, ſimilar to the

reſidue

residue left in the distillation of this salt, we perceive that the matter of fire which quick-lime holds in combination, and which it emits on the affusion of water, but without exciting illumination, effects the transmutation of acetous acid in the same manner as fire issuing luminous from burning fuel; and therefore, that it is the mere matter of fire, and not a particular motion or modification of it, that produces these changes in the acetous acid.

Seventhly; The accension of the oil produced from acetous acid, by the flame of a candle approached within five or six inches of it, or indeed by a flame two or three feet distant from it in deep vessels, although it be a phenomenon common to many oils and ethers, is not to be disregarded.

Of these the characteristic and rarest oily matter owes its palpable form as much to the pressure of the atmosphere, as to the attraction of the molecules of such oil to each other: for when that pressure is averted, ethers and the finer oils expand, by a great

part

part or the whole of their matter, into the form of an aerial fluid. During this expansion cold is produced; that is to ſay, they imbibe and fix the uncombined fire of the ſpace through which they expand, and of the contiguous bodies. Thus it appears, that theſe oily bodies attract fire; that in their aerial or vaporous form, they can fix more of it than in their denſe ſtate; and that the powers which limit their union with fire in their ordinary condition, are the attraction of aggregation, and the concurrent preſſure of the atmoſphere. All which is exemplified in the rapid emiſſion of fixable air, or nitrous air, or marine acid, or volatile alkali, from water charged with either of theſe, ſo ſoon as we remove a part of the preſſure of the incumbent atmoſpheric air.

SECT. VI.

Experiments to determine whether the apparent conversion of Acetous Acid is not owing to the Abstraction of some Principle of it, as well as to the Accession of Fire.

ALL bodies that contain the acid and phlogistic principles of acetous acid, attract air, and by air duly administered, may be made to furnish salts possessing the acid character, but differing from each other according to the proportions in which these principles are held, and the basis that holds them in combination. Hence the saccharine and other new vegetable acids, which so far as they consist of the foregoing principles, are convertible by fire into fixable and inflammable air, leaving a small residue of the fixed matter peculiar to each of them.

This is our inference from the processes for making the new acids, and from all the experiments for decomposing vegetable substances

ſubſtances by fire, from the time of the learned Dr. Hales to the lateſt efforts of the aſſiduous and ingenious Fontana.

But ſince the works of ſo many able philoſophers tend to impreſs the notion, that the products of ſuch proceſſes exiſted already formed in the ſubjects, and that they are only liberated in conſequence of the abſtraction of the reſiduary fixed matter; and ſince the like reaſoning might be thought applicable to my experiments, and conſequently to weaken the foregoing inductions, I judged it neceſſary to make ſome efforts to prove the total converſion of the mere acetous acid by fire only, in experiments which the inaccuracies of the foregoing could not affect.

I ſoon found that a great part of what was done with this view, was applicable to greater uſes, and I now think that, to avoid repetitions, it ought to be reſerved for a future part of this Eſſay, as the following experiments ſeem fully ſufficient for our preſent purpoſe.

The

The earthen retorts generally uſed in London, are made of the common crucible compoſition, which conſiſts of powder of baked clay, made plaſtic with fat apyrous clay and water. Theſe are porous and ſpongy to a great degree, as may be eaſily ſeen by the quantity of water which they imbibe, and for this reaſon alone the products of acetous ſalts diſtilled in them, differ in quantity from thoſe which I have deſcribed.

The expedition with which operations muſt be conducted in my public courſes of chemiſtry, often required that red-hot earthen retorts ſhould be cooled quickly, in order to ſhew the reſiduary matter from which elaſtic fluids were expelled; and on theſe occaſions I obſerved, that whenever an ounce or more of water was thrown on the reddened veſſel, a conſiderable quantity of elaſtic fluid, mixed with condenſible watery vapour, iſſued from it. When the water was repeatedly thrown on, until the elaſtic fluid formerly contained in the retort and its lengthened neck were expelled, what followed as the proper aerial product of the water, or of the matter propelled out of the pores of the retort, was always found to be intermediate between atmoſpheric and phlogiſticated air. At firſt I uſed this phenomenon to exemplify the poroſity and imperfection of theſe retorts, and I endeavoured to explain it thus. The water is drawn by capillary attraction into the pores at the ſurface which it firſt touches, and as it enters theſe, drives before it to the oppoſite or internal ſurface of the veſſel, the air which had been lodged in them. This air having been expoſed to burning fuel, or meeting the fuliginous matter which the clay might have imbibed, is neceſſarily more phlogiſtic than that of the atmoſphere; and as the part of the water, which is firſt and moſt deeply imbibed, is ſooneſt and moſt heated, its vapour is determined to expand into the veſſel, by the power which propelled the air in the ſame courſe: to account for the quantity of air, I had recourſe to the obſervations mentioned in my Eſſay on Calcareous Cements, page 16.

To this evident permeability of the common retorts, I attributed the waſte of water and other products which always occurred in diſtilling acetous ſalts in them, but I could not ſo eaſily account for another phenomenon which conſtantly attended this waſte, namely, the extraordinary quantity of phlogiſticated air, and the increaſed proportion of the fixable air, relatively to the quantity of the inflammable.

My conjectures on this ſubject need not be now related, ſince Dr. Prieſtley's experiments, communicated to the Royal Society in 1783, relating to the air produced when porous retorts containing water are thus expoſed to heat, ſerve fully to explain theſe appearances. I was however fully convinced, that the retorts above deſcribed were utterly unfit for my chief purpoſe in theſe experiments, and I had recourſe to thoſe of a more compact kind, with which I was favoured by my moſt reſpectable neighbour, the ingenious Mr. Wedgwood.

With theſe retorts, which I wetted on the outſide with a ſtrong ſolution of borax, I found the acetous ſalts could be diſtilled, with very little variation of the products, in fixable and inflammable air eſpecially, from thoſe of the diſtillations in glaſs veſſels; and the reſiduary matter did not ſenſibly differ from what was left in the glaſs retorts, when the degree and duration of the heat was not greater than they had ſuſtained.

Having diſtilled acetated vegetable alkali in one of theſe compact retorts, to the point at which the emiſſion of elaſtic fluids had formerly ceaſed, and at which the reſiduary maſs was known to conſiſt of vegetable alkali, fixable air, and alkaline tinder, in the proportions already deſcribed; in order to learn what this would yield by mere ignition, I augmented the fire gradually; the effect of which was to expel the fixable air of the alkali, mixed with inflammable air of the ſame ſpecies with the former, but of a lighter kind. The quantity of fixable air was never leſs than $\frac{2}{3}$ of all that I had formerly obtained in the ſaturation of the like alkaline coal with marine acid; and the inflammable air bore the like, or rather a greater proportion to the phlogiſtic matter which was found to reſide in the alkaline tinder.

When the emiſſion became very ſlow, although the furnace was hot enough to melt caſt iron, I withdrew the fire; and in the cooled retort I found a ſolid maſs, taſting alkaline and cauſtic, of a reddiſh brown colour, and opaque; and the retort was manifeſtly corroded. The alkali had preyed upon the ſiliceous matter, and both theſe on the argillaceous and magneſian of the veſſel; and I make no doubt that if it had diſſolved more of the ſubſtance of the retort, it would have emitted more of its fixable air. This cauſtic maſs, compared with ſlags made of alkali and Devonſhire clay, ſlightly impregnated with charcoal powder, ſhewed clearly that its colour was owing to the ſmall remains of the phlogiſtic matter of the tinder above deſcribed; but that no ſubſtance decidedly combuſtible, could be ſeparated from it.

It would be a vain labour to look for any ſuppoſititious fixed matter of the acetous acid in this compound of alkali and earths; and ſo far as this experiment approximated the intended purpoſe, it ſhewed, that the part of the acetous acid, which in ſome experiments remains fixed in the ſolid combuſtible ſubſtance, only requires more heat to be extricated, and to form inflammable air.

With the ſame views I made the more ſatisfactory experiment following.

I expelled the uſual products from acetous calcareous ſalt, heated in a Wedgwood retort as much as the coated glaſs veſſels had formerly been; and when the emiſſion had ſlackened, or almoſt ceaſed for half an hour; at which time, I knew from former experiments, as well as by direct menſuration of the products, how much calcareous earth, fixable air, and coaly matter, was contained in the retort; I encreaſed the heat as in the laſt experiment. When no more elaſtic fluid could be expelled, I removed the retort out of the furnace, to prevent as much

as

as poſſible the vitrification of the calcareous earth.

The quantity of fixable air thus obtained by the ſecond or ſtrong heat, was nearly the ſame as was formerly expelled in the ſolution of the black reſidue of acet. calc. ſalt diſtilled in a glaſs retort; and allowing for the rarity of the inflammable air which iſſued along with the fixable, I found its weight to correſpond ſo nearly with that of the matter expelled in the calcination of the coaly ſubſtance which was ſeparated from the black reſidue of acet. calc. ſalt, by the ſolution of the mere calcareous part in marine acid, that I entertained no doubt of the total converſion of that matter which with calcareous earth makes the coal, into inflammable air.

On opening the retort, I found a part of the calcareous reſidue vitrified, as indeed I expected, where it touched the clay of the retort; but the upper and central parts, to which the vitrification did not extend, conſiſted of ſpongy friable calcareous earth,

 preſerving

preserving the figure of the pellets used in the charge, and rather grey and yellow than white. It was soluble without effervescence, excited heat, and flaked on the affusion of water, and possessed every character of pure lime, except its perfect whiteness; but this the best limestone never acquires, when it is reduced to lime in close vessels, for without the aid of air, the phlogistic matter cannot be totally expelled, or to speak in terms less exceptionable to some philosophers, the white colour cannot be attained.

Here I rested in full persuasion that the conversion of the acetous acid does not depend on the abstraction of fixed parts, or the mere expulsion of the volatile from them; but that it is effected by the accession of matter which can be no other than fire, since none other thus pervades glass and porcelain. And now I imagine the reader perceives more distinctly, that the fixable air is formed from acetous acid, so far as the gravitating principles of this air, in combining with fire, lose their former connexion with the other parts of acetous acid;

that

that the remainder of this acid, exclusive of water, either is converted into inflammable air, as fast as the fixable air is formed, or is totally convertible into inflammable air, by a due charge of fire; that the water of acetous acid, or its salts, is passive in these processes, or inessential to the fixable or inflammable airs; and finally, that the mere acetous acid contains nothing but the gravitating principles of fixable air and dense inflammable air, and requires nothing but fire to form these elastic fluids, whose parts repel each other by reason of the fire only; because previous to the decomposition, which is effected by an accession, and not by any loss of matter, they attracted and were coherent. Just so, the aerial principle of nitrous acid combines with fire, when a nitrous salt is heated to redness, and forms the elastic fluid called pure air, and easily deposites the concomitant acid, when this also is charged with fire and meets water.

It may not be improper on this occasion to observe, that in distilling acetated calcareous salt in a Wedgwood retort, and suffering the whole product of condensed water and ethereal oil to remain in the recipient, until the operation was finished, they presented two liquors, perfectly distinguishable, in comparing the upper oily part with the lowest watery fluid, but yet so far blended where they met each other, as to exhibit a gradation from the oily to the aqueous consistence. In pouring the whole into a funnel, in order to separate them, they blended together, and formed a semi-transparent liquor, from which not $\frac{1}{10}$ of that which before appeared like oil, was afterwards separable. This I attributed to the incapacity of the mild calcareous earth to detain the ethereal oil, until by the abstraction of water, it becomes fatter or more concentrated.

SECT. VII.

Experiments on Acetated Magnesia supporting the foregoing Inductions; and Observations on Fuel.

CONCENTRATED acetous acid has very little effect on magnesia, until water is added in sufficient quantity to dissolve the salt as fast as it is formed. When mild magnesia is gradually added to the acid moderately diluted, to the point of saturation, the solution has a gluey consistence, and retains a much greater quantity of fixable air than I have ever observed to be held by any other neutral liquor: it also retains this air with greater obstinacy, and sustains a boiling heat for some hours before it parts with the whole of it.

In boiling it froths to the heighth of a foot or 18 inches, with bubbles, many of them exceeding two inches in diameter, which endure for many minutes, and by their

their toughneſs and opacity, reſemble thin bladders.

This ſaline liquor taſtes like the yeaſt of ſweet ales, and in my opinion differs very little from it: for in a curſory analyſis, I find yeaſt to conſiſt of magneſia, combined with the phlogiſtic, acid and watery matter of acetous acid. By evaporation, this liquor becomes as tough as melted glue, and then dries to a ſemi-tranſparent horn-like ſubſtance, which adheres ſtrongly to glaſs or porcelain, and is deliqueſcent. All this time it exhales acetous acid; and like the calcareous ſalt, it is found, in its dry ſtate, to retain much leſs acetous acid than was neceſſary for the ſolution of the magneſia.

The continual frothing, and the agitation which is neceſſary during the evaporation and exſiccation of this acetated magneſia, muſt promote the abſorption of air, if it is diſpoſed to abſorb any; and it is with a view to the effects of this air, and the ſpontaneous eſcape of a certain part of the acid from this ſalt, that I notice theſe particulars.

The

The dry acetated magnesia thus prepared, and distilled in the manner of the calcareous salt, yielded in the same circumstances water, oil, fixable and inflammable air. But the quantity of fixable air, in distillation, was greater relatively to the inflammable; and much less fixable air remained in the residuary magnesia than in the black residue of the calcareous salt. No acetous acid was ever found in the first products of the dry magnesian salt; and the matter left in the retort, after the emission of air had slackened or ceased in a red heat, was black, spongy and friable, so that it could scarcely be handled, without falling into powder.

Vitriolic acid, diluted with an equal or any other quantity of water, shewed no action on this black matter for 30 or 40 seconds; but when the solution became perceptible, it proceeded and increased rapidly with considerable heat. Only a small quantity of fixable air, such as magnesia can retain in a red heat, was emitted during the solution, and a light coaly matter arose

towards

towards the ſurface, and remained undiſſolved in the acid liquor.

This vitriolic ſolution yielded by evaporation Epſom ſalt only; and the coaly powder, which reſiſted freſh vitriolic acid, and was then waſhed and dried, was found to vary in quantity, with the intenſity and duration of the heat to which it had been expoſed, and was always combuſtible and reducible to magneſia, in conſequence of the expulſion of its phlogiſtic matter. This magneſia contained fixable air when the combuſtion or calcination was ſlow; but in the contrary circumſtances, it was mere magneſia indurated by the heat.

In diſtillations by moderate heat, the black reſidue reſiſted the action of vitriolic acid for the longeſt time, where it appeared to be beſt impregnated and defended by the inſoluble coaly matter; but the reſidues which had ſuſtained greater heats, and which diſſolved ſlowly, ſeemed to reſiſt acids by virtue of their induration or aggregation only. This laſt is a well known property of magneſia indurated by intenſe heat.

In divers variations of my experiments on acetated magneſia, I obſerved the following particulars.

The drieſt ſort yielded more of its acid in the form of fixable air, than any ſuch ſalt leſs dried and leſs expoſed to air; and it afforded the ſmalleſt quantity of water and oil. When a moiſt ſalt was uſed, the firſt portions of water were ſlightly impregnated with acid, and the apparent quantity of oil was greatly augmented, for the true oil blended with a conſiderable quantity of the preceding or concomitant water.

This, like the oils formerly deſcribed, diffuſed itſelf in open air, and by its vapour catched fire from a lighted candle placed at ſome diſtance. For this, like other volatile oils and ethers, owes its aggregation partly to the preſſure of the atmoſphere, which it eſcapes when nothing intercedes them, becauſe it freely pervades the compreſſing column.

When

When the black coaly resſidue of the magnesian salt was urged with a very strong heat, it emitted a little fixable air, mixed with a much greater bulk of inflammable, and lost proportionably of its weight and blackness, until it became grey, and was reduced to the quantity, or to less than that, of the mere magnesia originally employed. In the fiercest heat it vitrified wherever it touched the earthen retort, and there formed a glassy grey or pearl-coloured slag, resembling that of talc.

When the black magnesian coal was heated to redness in contact with pure air, it entered into combustion, and formed fixable air, of which a part was retained in the magnesia, and the remainder was easily separable from the residuary pure air.

The quantity of fixable air expelled from the magnesian salt, relatively to that of the inflammable, is greatest in the early periods of the process, and gradually decreases to the end; for the magnesia can retain but a small quantity of fixable air in a weak red heat,

heat, but it obſtinately retains the matter which by due ignition forms inflammable air.

By the moſt careful examinations of the different reſidues of divers proceſſes, I could not diſcover any matter depoſited by the products already deſcribed in the magneſia, except the phlogiſtic, which in diſtillation formed inflammable air, and by calcination in contact with pure air, yielded fixable air.

From all this it appears, that any quantity of acetous acid that magneſia can detain, until it is ſufficiently charged with fire, undergoes the tranſmutation already deſcribed, and is totally converted, not by the depoſition of any matter in the magneſia, but by the acceſſion of fire; and the inferences formerly made, are all ſupported by theſe experiments, but need not be repeated here.

It is however expedient now to remark, that the very matter which in combination with fire, or by the mere action of fire,

makes

makes our inflammable air, is ſtrongly attracted not only by fixed alkali and lime, but by magneſia likewiſe, and with each of theſe, forms a ſpecies of coal or fuel. It is a fact likewiſe highly meriting our attention, that theſe moſt ſoluble ſubſtances, whoſe appetence of acids is of the ſtrongeſt kind, become inſoluble in their ordinary menſtrua, by this union with the matter of our inflammable air, which they thus appear to attract more powerfully than vitriolic acid, and which cannot be expelled from them, except by intenſe heat, or the concurrent action of fire and atmoſpheric air.

By thus making artificial fuel, ſimilar to charcoal or coke, and equally inſoluble in acids, although containing alkali or ſoluble earths, we are led to the knowledge of the conſtituent parts of native fuels. Theſe yield our inflammable air by heat, and contain little more than the gravitating matter of it, which with pure air yields abundance of fixable air, in the combuſtion of them. Therefore, if an acid principle is neceſſary to the conſtitution of fixable air, it is con-

tained

tained in this inflammable air, and conſequently, is united along with the phlogiſton in all thoſe bodies which are partially or almoſt totally convertible into this inflammable air by heat, or which in combuſtion yield fixable air abundantly. Thus charcoal will appear to conſiſt of phlogiſton and the acid principle of acetous acid, together with a ſmall quantity of fixed vegetable alkali and calcareous earth; ſince $\frac{19}{20}$ or more of common well burned freſh charcoal are convertible into that inflammable air: and our acid principle united with phlogiſton, requires very little, if any other matter, in order to form a body highly combuſtible where fire and air act on it; but otherwiſe durable, reſiſting acids, and conſiderably fixed in cloſe veſſels, yet unable even in this circumſtance to maintain its aggregation againſt the utmoſt force of fire.

SECT. VIII.

Phenomena of Acetous Acid in Mixtures with the Vitriolic, and Obſervations generalizing the foregoing Inductions.

WHEN acetated vegetable alkali is decompoſed by vitriolic acid, previouſly diluted with an equal quantity of water, and cooled, there is very little heat or intumeſcence during the mixture; and if the acetous ſalt employed for this purpoſe is neutral, no fixable or inflammable air appears, and little or nothing iſſues, until the charge is heated. In diſtillation, the firſt portion of acetous acid is ſtrong, but the ſucceeding are weaker, in regular gradation, until the acid ariſes, diluted with ſo much water as ſcarcely to be equal to diſtilled vinegar. The reſiduary maſs is vitriolated Tartar, and neither this nor the ſides of the retort contiguous to it, ſhew any blackneſs or ſigns of phlogiſtic matter.

When

When the acetated ſalt is decompoſed by the moſt concentrated vit. acid, and due care is taken, in the manner formerly deſcribed, that the heat excited during the mixture ſhall not exceed 100 degrees; the acid ariſes highly concentrated at firſt, but weaker afterwards, and the reſiduary vitriolated Tartar appears clean and white.

But when highly concentrated vitriolic acid and the drieſt acetated vegetable alkali in powder, are mixed in large quantity, and equal weight, as quickly as is poſſible, in earthen ware, a quantity of fixable and inflammable air is immediately diſcharged along with the acetous product, and is always proportionate to the heat excited in the mixture; the produce in acetous acid is at the ſame time leſſened, and is ſucceeded by volatile vitriolic acid in conſiderable quantity. If the fire be withdrawn when this volatile acid ariſes in thick white fumes, the reſiduary vitriolated Tartar with exceſs of vitriolic acid is found blackened with coaly or oleaginous matter, and the ſides of the retort ſhew an oily ſtain.

In divers experiments of this kind, the acetous acid was expoſed to the action of diſengaged vitriolic acid, and of the ſame diluted with water, and never appeared to ſuſtain any change from the mere action of that powerful mineral acid. But when great heat was excited, and this fire co-operated, a part of the acetous acid was transformed into fixable and inflammable air, as it would have been by fire any other way adminiſtered, whether the vitriolic acid was uſed in exceſs, or only in the quantity neceſſary for ſaturating the alkali of the acetous ſalt; and at the ſame time a portion of oily matter was detained in the vitriolated Tartar, or phlogiſticated the diſengaged part of its acid, as any other oil or as charcoal would do. From all which I inferred that phlogiſton is attracted more forcibly by the acid principle of acetous acid than by the vitriolic acid in its ordinary form; that this converſion of acetous acid, in the preſence of the vitriolic, is effected, not by this laſt, but by the fire emitted during the union of vitriolic acid with the vegetable alkali; and that in conſequence of the ſeparation of the matter expended in the formation of fixable air, the residuary more phlogisticated matter of the acetous acid, forms inflammable air, so far as it meets a due quantity of fire, but otherwise preserves the oily form. A portion of this oil follows and blends with the acetous acid which escapes the decomposition, and the remainder detained in the residuary vitriolic mass, forms a coaly substance, as it does with divers other bodies, or meeting disengaged vitriolic acid, gives the same products as are always observed in the distillation of this acid with oils or charcoal, or any vegetable or other substance which yields fixable air in combustion, and thus appears to contain the acid as well as the phlogistic principle of acetous acid.

To try the validity of these inductions, and the truth of my interpretation of the phenomena, I made the following experiments.

With 16 ounces of the oil of vitriol of the manufacturers, I mixed the same quantity of concentrated acetous acid, whoſe ſpecific gravity ſhewed that it contained an ounce of water beyond the quantity which the ſtrongeſt acetous acid uſually holds.

The heat excited was about 200 degrees, and the mixture in a few hours acquired a pale ſtraw colour. The firſt 10 ounces of acetous acid diſtilled from it did not differ in any thing remarkable from concentrated acetous acid, and the reſidue was tranſparent, but amber-coloured. Along with the eleventh ounce, volatile ſulphureous acid iſſued, mixed with a very ſmall quantity of inflammable air, and phlogiſticated air; but as the quantity of this laſt decreaſed very quickly, it was conſidered as the atmoſpheric air included in the veſſels at the commencement of the operation, the pure air of which was expended on the charge, or in the ſulphureous acid which imbibes pure air in the preſence of water. Now the liquor in the retort became reddiſh brown and opaque, and during the diſtillation of another ounce, which was received apart, the elaſtic fluids iſſued more copiouſly.

These

These consisted of volatile vitriolic acid, mixed with about $\frac{1}{8}$ part in bulk of fixable air, and a quantity scarcely worth notice of inflammable air. The weight of the elastic fluids, acid, water and residuary matter, was very little less than that of the materials of the charge and the pure part of the air of the vessels, and I had no reason to doubt that the small deficiency was owing to the watery vapour which was blown away along with the elastic fluids. Rejecting the last ounce of distilled acid, because it was chiefly water, I saved the preceding 11 ounces for future use.

The residuary acid in the retort was now of a dark red colour, by transmitted light, where it was made to spread thinly on the sides of the vessel; but the whole mass by reflected light looked black, and perfectly opaque.

I mixed the foregoing 11 ounces of acetous acid with 11 of oil of vitriol, by which heat was excited as before, to about 200 degrees. In distilling nine ounces of colourleſs acetous acid from the mixture, I obtained the ſame products and noticed the ſame phenomena as appeared in the former proceſs. Reſerving this acid, I proceeded until another ounce, conſiſting of weak acetous acid, impregnated with volatile vitriolic, was collected, and in the mean time, the quantity of elaſtic ſulphureous acid and fixable air, mixed with a little inflammable air, was encreaſed. The bulk of the fixable air was about $\frac{1}{6}$ of that of the volatile vitriolic acid as formerly. I then withdrew the retort from the hot ſand, and found the acid in it to have all the appearances already deſcribed. The weight of this and of the foregoing products was almoſt equal to that of the acids employed; the deficiency not exceeding what ought to be allowed for the watery vapour blown away along with the elaſtic fluids.

The nine ounces of acetous acid laſt mentioned being diſtilled again with the ſame quantity of the moſt concentrated vitriolic acid, preſented the ſame phenomena, with this difference only, that fixable air and volatile

volatile ſulphureous acid and inflammable air were produced in greater proportion, relatively to the acetous acid: and as the acetous product was next diſtilled with a double quantity of concentrated vitriolic acid to the ſame effect, except that the quantity of elaſtic fluids was augmented, I ceaſed when the acetous acid was reduced to three ounces, in order to examine it; being already convinced that the whole of acetous acid by this treatment may be reduced to the forms of fixable and inflammable air, and oil capable of affecting the vitriolic acid like other oils and combuſtible ſubſtances.

Theſe three ounces of acetous acid, combined with fixed vegetable alkali, made a fine white foliated ſalt, as purified acetous acid would do. And this ſalt in diſtillation yielded water, oil, fixable air, inflammable air, and a black coaly reſidue in the proportions formerly deſcribed in the diſtillation of acetated vegetable alkali; and the coaly alkaline reſidue in like manner yielded fixable air, and the black combuſtible ſubſtance reſembling lamp-black.

The

The several portions of vitriolic acid, which was thickened and rendered opaque in these distillations, were mixed and distilled, and the condensible product was saved in three separate and equal parts. The first consisted of oil of vitriol, weakened with about two ounces of water, and impregnated with sulphureous acid, and during the distillation of this part, a great quantity of volatile vitriolic acid, mixed with $\frac{1}{18}$ of its bulk of fixable air, was emitted.

The second portion was oil of vitriol, smelling of sulphureous acid, but clear and colourless, and along with this issued elastic sulphureous acid, mixed with much less fixable air than was in the former; the third portion was like the second, but was not accompanied with so much volatile sulphureous acid: and in the retort I found six ounces of a dark red opaque liquor, of the consistence of treacle, whilst hot, but which concreted in cooling into a wet saline mass, such as might be expected from oil of vitriol, stained by oil, and imbibed by a salt irregularly crystalized. I afterwards found

found that this was nothing more than the vitriolated Tartar, Selenite and Epsom salt, which accompany all the oil of vitriol of the modern manufactories, impregnated with the oleaginous matter of the acetous acid, which every body hitherto tried appears to retain, until it is violently heated or calcined in contact with air.

In all this we see nothing like a dephlogistication or decomposition of the acetous acid by the vitriolic. On the contrary, the acetous acid which arises by moderate heat from the vitriolic, suffers no change; but that quantity of it which can be detained in vitriolic acid, until it sustains greater heat, undergoes the very same transmutation that fire alone always produces, whatever the substance may be that fixes the acetous acid.

We now well know the reason why some part of the decomposed acetous acid became fixable air; why in the moderate heat very little appeared as inflammable air, and much more assumed the oily form; and if the question,

queſtion, implying ſome fallacy in this reaſoning, were propoſed, viz. why does the vitriolic acid become phlogiſticated? I ſhould anſwer firſt, the vitriolic acid becomes volatile or phlogiſticated in diſtillation with any of the ſubſtances which yield ſuch inflammable air by heat as the oil of acetous acid affords: all oils and vegetable ſubſtances, not excepting the drieſt, or the charred coal of them, have this effect with vitriolic acid: in other and more general terms, all bodies that contain the ſame phlogiſtic and acid principles that reſide in acetous acid, render vitriolic acid volatile in diſtillation: and ſecondly, without affecting the validity of this anſwer, founded on known facts, I ſhould ſay that in all the phlogiſtications of vitriolic acid that I ever ſaw, pure air is withdrawn from it: and as in the inſtance before us, the oleaginous part of the acetous acid forms fixable air, whilſt the vitriolic acid becomes volatile, and pure air would alſo form fixable air with the ſame oleaginous matter thus heated; I conclude that pure air is more forcibly attracted by this laſt than by the acid prin-

ciple

ciple of ignited vitriolic acid, and consequently that this acid, by the subduction of the pure air, and the substitution of phlogiston from the oleaginous matter, makes volatile sulphureous acid. This is sufficient for the present occasion; for it would lead me too far from the objects of this Essay, to enumerate the experiments by which I have been induced to believe that volatile vitriolic acid consists of the vitriolic acid principle combined with phlogiston and fire, whilst the ordinary vitriolic acid is composed of the same acid principle, pure air and water, with less of the matter of fire.

The phenomena of these experiments on mixtures of acetous and vitriolic acid, impressed me with some doubts, which I have not introduced in the relation, because such measures only serve to perplex the reader, in exhibiting the sagacity of the experimenter. To remove these scruples, and look for something further, I varied the experiments in the following manner.

I mixed 24 ounces of strongest acetous acid with 48 of my strongest oil of vitriol.

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The mixture became hot as in the former experiments, and in a few hours had a light ſtraw-colour. In diſtilling 13 ounces of clear colourleſs acetous acid from it, the quantity of elaſtic fluid emitted was not conſiderable; after the thirteenth ounce, the acid diſtilled grew gradually and uniformly weaker, and the emiſſion of elaſtic fluids encreaſed.

The next ſeven ounces conſiſted of acetous acid and about an equal quantity of water conſiderably impregnated with vitriolic and volatile vitriolic acid; and the next 17 ounces conſiſted chiefly of vitriolic acid mixed with water and a little volatile vitriolic acid; and during the diſtillation of theſe, volatile vitriolic acid in the elaſtic form iſſued in conſiderable quantity, mixed with fixable air and a little inflammable air. The bulk of the fixable air was, as formerly, about $\frac{1}{8}$ of the inflammable.

As the acid laſt diſtilled at this period, was as ſtrong as oil of vitriol, I removed the veſſels from the fire. The matter remaining

maining in the retort was opaque, and of the conſiſtence of ſyrup, when cold, and looked black in the maſs; but where it was made to ſpread thin on the retort, it looked ſemi-tranſparent and of a livid red colour.

Rejecting the portions of acid laſt diſtilled, becauſe they were diluted with the water which appertained formerly to the part of the acetous acid that was thus decompoſed, and with the water which was formed, as will be fully ſhewn hereafter, by the union of the mere phlogiſton of acetous acid with the pure air of the vitriolic, I took the 13 ounces of acetous acid firſt drawn off, and mixing them with the livid vitriolic reſidue in the retort, proceeded to diſtillation. The heat excited during the mixture was not, to my feeling, ſo great as before, and very little of any elaſtic fluid iſſued from the charge, until about nine ounces were diſtilled; but in drawing off the tenth ounce, volatile vitriolic acid iſſued copiouſly and mixed with about $\frac{1}{2}$ of its bulk of fixable air and a little more in-

 flammable

flammable air than had appeared in former experiments.

The diſtillation was continued, with the ſame phenomena, until the matter in the retort was reduced to 24 ounces; and the product, collected after the nine ounces of acetous acid, conſiſted of vitriolic acid much weakened with water, and ſlightly impregnated with acetous and volatile vitriolic acid.

Now one purpoſe of this trial was accompliſhed; for acetous acid, weighing 13 ounces, and which had been previouſly expoſed to the action of 48 ounces of concentrated vitriolic acid, was as much decompoſed in the mixture with the blackened reſiduary vitriolic acid of the former diſtillation, as ever the acetous acid had been by an equal quantity of freſh vitriolic acid; and thus the decompoſition appeared to have been effected by fire, and not by the vitriolic acid, except ſo far as it ſerved to detain the acetous acid. The ſurplus of inflammable air which appeared above the quantities noticed in former diſtillations, was owing to nothing more than the incapacity of the blackened oil of vitriol to furniſh ſo much atmoſpheric air as is contained in the pure and colourleſs; for the ſame matter which yields inflammable air, always affords fixable air when under due ignition it meets pure air.

The nine ounces of acetous acid firſt drawn off in the foregoing diſtillation, appeared on divers trials to be acetous acid unaltered in every reſpect, except that it was impregnated with a little of the vitriolic, and contained more water than is proper to our concentrated acetous acid: for in mixture and diſtillation with freſh concentrated oil of vitriol, it preſented the phenomena deſcribed in the beginning of this Section; and the portion of it that was diſtilled unaltered in this proceſs, being divided into two parts; one of them combined with calx of lead and diſtilled, gave the ſame products as are obtainable from the like calx combined with my pure acetous acid; and the other part, combined

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with fixed vegetable alkali, made acetated vegetable alkali, which yielded water, oil, fixable and inflammable air, and a black alkaline coal, like those of pure acetated vegetable alkali: and in these trials the vitriolic impregnation was found to be so small as scarcely to deserve any notice.

Wishing to know the condition of the matter that gave the blackness and spissitude to the vitriolic acid remaining in the retort, and which, as I have already shewn, would be expended, if the distillation were continued, in the production of volatile vitriolic acid and fixable air; I diluted the 24 ounces of this acid with 16 of distilled water. In so doing, I observed the same hissing, heat, and pungent vapour as occur in mixing water with concentrated colourless vitriolic acid. But the diluted acid remained opaque, and the opacity was plainly owing to large particles of black flacculent matter, which were diffused through it, and were not disposed to separate by subsidence, or by rising to the surface: in order therefore to effect a separation, by making the diluted acid paſs through a filter without corroding it, I added a quart more of water.

The filtrated liquor ſhewed a pale yellow colour, and when reduced to eight ounces, or leſs, by evaporation in the open air, became opaque and livid, as if a part of the oleaginous matter had paſſed along with the acid and water, through the filtering papers: it alſo depoſited ſome ſaline matter, but this was only what originally was contained in the oil of vitriol employed. The matter left on the filter was like lamp-black wetted with weak vitriolic acid, and felt as if it were in a ſtate intermediate between oil and coal. A ſmall portion of it expoſed to heat, firſt exhaled water and vitriolic acid, then became red, and entered into combuſtion, but without any appearance of flame. By the reſidue it appeared to contain ſome ſalts of the vitriolic acid which might be waſhed away from it. I therefore waſhed the maſs left on the filter with a quart of water, which being uſed in ſucceſſive portions, left the black matter free from vitriolic acid, or at leaſt inſipid.

The water thus employed being evaporated to an ounce, left about half this quantity of vitriolic acid, which was blackened by the oily matter that followed it through the filter conſiſting of good paper in four folds, and in cooling depoſited ſome ſalt of the ſame kind with that laſt mentioned.

I had often before obſerved, that the black reſidues of acetous ſalts impregnated the water with which they were waſhed, ſo far that in evaporation the laſt portions of it appeared turbid and black; and I attributed this to the imperfection of the filters; but in theſe laſt experiments, and others which they ſuggeſted to me, I found that the coaly matter, left in the reſidue of divers acetous ſalts decompoſed by heat, is in a ſmall degree ſoluble in water, like ſelenite or lime, and ſtill more when the water is acidulated.

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The black coaly matter that remained on the filter after the ablutions above mentioned, when dried to the confiſtence of ſoap, blackened and ſtrongly adhered to every ſubſtance on which it was rubbed, and neither alkalies nor any of the mineral acids could efface the traces made with it, but aqua regia ſeemed to weaken them. It floated in a mixture of equal parts of oil of vitriol and water, but was not diſſolved by this, or nitrous, or marine acid; aqua regia ſeemed to alter the colour of it ſuperficially, but did not act as a ſolvent. Its weight was three ounces, of which about $\frac{3}{4}$ were water, which exhaled in drying it to 15 dwts. with a pleaſant acid ſmell, towards the concluſion.

When it was well dried, it reſembled Indian ink in the cake, both in the colour and texture as well as in the traces made with it. When it was further heated, the ſmell was not diſagreeable; it contracted to $\frac{1}{4}$ of its bulk before it catched fire; and this did not happen until it was heated to redneſs in the open air: then it flamed in an inſtant, and glowed with a bright red heat; but in the next inſtant, the flame, which was thin and ſmall, diſappeared. On withdrawing it from the fire, the redneſs and combuſtion ſuddenly ceaſed, as it happens to culm and other bodies which require great heat and ventilation for their combuſtion. It took two hours calcination, and free expoſure to air by frequent agitation, to deprive it of the coaly character, and to reduce it to a grey incombuſtible powder, which weighed 48 grains, and by divers trials conſiſted of magneſian earth.

From the facts related in this and the foregoing Sections, it appears that acetous acid is decompoſed in vitriolic acid, in quantity proportionate to the capacity of the vitriolic acid to retain it until it ſuſtains the heat which alone is neceſſary for the decompoſition of acetous acid. That this capacity of vitriolic acid to retain the acetous is as the relative quantity of the former, and depends on a general law. For ſo vitriolic acid retains water in a degree of heat much greater than water alone can abide,

abide, under the ſame atmoſpheric preſſure; ſo all bodies, from which any thing can be expelled by fire, retain the laſt portions of the volatile matter more obſtinately than the firſt, and compel them to ſuſtain the greater heat. It alſo appears that when acetous acid is decompoſed by fire, in the freeſt expoſure to vitriolic acid, the matter which is capable of forming inflammable air, and which conſiſts, as will fully be ſhewn in the ſequel, of the phlogiſton united with ſome of the acid principle of acetous acid; unites with magneſian earth in preference to the vitriolic acid, and forms with it a coaly maſs, which may in the common ſenſe of this word be ſaid to be inſoluble. Having in former experiments ſeen magneſia containing only a little of this matter, and perfectly ſoluble, ſave only the parts ſtrongly impregnated with it; and now finding that one part of mere magneſia can retain 20, if not any quantity of it, and that the ſubſtance thus formed is of the fixed, rather than of the very volatile kind, we readily conceive how this ſame matter forms ſuch a variety as occurs in nature of combuftible bodies, according to the kind and quantity of other matter with which it is combined in them; and why all fuch bodies, whether fpirits, ethers, oils, gums, refins, vegetable extracts and falts, wood, charcoal, mineral fuel, coke, or fubftances referable to thefe heads, yield fixable air in combuftion, and by due ignition in clofe veffels, denfe inflammable air, which likewife yields fixable air in combuftion: and alfo why fixable air is always produced in the phlogiftication of vitriolic acid by the oleaginous part of acetous acid, or by any vegetable, animal or mineral fubftance, containing the acid and phlogiftic principles of acetous acid, and capable of yielding our denfe inflammable air.

In former experiments, the quantity of water that blended with the oil, or was wafted away with the elaftic fluids generated from acetous acid by fire, was variable; and there was room for doubting whether the water proper to concentrated acetous acid or its falts, was all depofited during the converfion of the mere acid, or

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did not contribute to the fixable and inflammable air: but in theſe experiments with vitriolic acid, wherein the quantity of water left by the decompoſed acetous acid could be meaſured by the ſpecific gravity of the acids diſtilled compared with that of theſe acids in the concentrated ſtate in which they were mixed; I was fully perſuaded that the acetous acid depoſites its water, previous to the converſion into fixable and inflammable air, or into that compound which with divers bodies forms coal; and that water is not a neceſſary ingredient in any one of thoſe. But I do not inſiſt on this ſubject at preſent, becauſe ſuch menſuration would appear exceptionable, not only by reaſon of the errors to which it is liable, but becauſe it ſhews a quantity of water which could not, conſiſtently with my former experiments, exiſt in the concentrated acetous acid. The cauſe of this phenomenon will be conſidered hereafter.

In the laſt mentioned diſtillation of acetous from vitriolic acid, I was amuſed with a phenomenon which brought to my recollection

lection ſome appearances of the ſame kind which I had noticed on former occaſions. When the quantity of acetous acid amounted to about three ounces, and roſe in the receiver ſo high that the diſtance between its ſurface and the nozel of the long ſlender neck of the retort, did not exceed a quarter of an inch, and when the drops fell at the interval of three or four ſeconds, each of them, rebounding after the fall, and ſtill preſerving the globular form, rolled on the acid liquor; and then, after floating in a quieſcent ſtate, for five or ſix ſeconds, burſt ſuddenly and ſpread upon it. Some of theſe globules in their motion ſtruck the preceding ones, and frequently the motion was communicated without either of them burſting for ſome ſeconds after they became quieſcent.

Afterwards, when the acid in the receiver roſe, and was not diſtant from the nozel of the retort by more than the diameter of a large drop, the liquor which trickled down, did not diſcharge itſelf into the acid, either in the foregoing manner, or in that of a co-

lumn;

lumn; but it formed globules of ſix times the former bulk; each of which, preſerving its proper form, ſunk by half its diameter into the acid liquor, without mixing with it; but when the ſize of any globule encreaſed to exceed $\frac{3}{10}$ of an inch in diameter, it then parted from the nozel and ſpread on the liquor.

All this looked as if each drop carried its proper atmoſphere of repellent matter, which it retained for a conſiderable time, with a force greatly ſuperior to the weight of a grain, for the drop could not, by reaſon of its mere aggregation, rebound from liquor of the ſame kind, and roll on it, and dip and ſwell in it without mixing.

I immediately attempted to produce the like phenomena in diſtilling water, under the ſame circumſtances preciſely; but without ſucceſs; neither could I find them in treating ſpirit of wine in the ſame way.

Upon a review of all the phenomena of this kind that I had ever noticed, I am perſuaded that the drops of all inelaſtic fluids carry their refpective atmofpheres of fome repellent matter which is of the fiery kind; and that in moft fluids, the denfity of thefe atmofpheres is rarely fufficient to refift the approximation or union of the drops with fuch force as to exhibit the appearances above defcribed: but that bodies, whofe principles feverally attract fire fo forcibly as to form elaftic fluids with it, maintain denfer atmofpheres of this matter around their parts or drops, which then repel with greater force; and that the effect of this repulfion is greateft and moft durable, when the drops carry with them any elaftic fluid, exceeding the quantity which they can retain when cooled. The electricity producible in diftillations and evaporations, and the quick evaporation, if not the convertibility of water into an aerial fluid, by the electric matter, are things not repugnant to this notion; which I mention only for its confonance with the agency of fire that occurs in all our experiments.

The mixed elaftic fluids lately defcribed were feparated and meafured in the following manner.

Receiving the ſucceſſive portions through quickſilver, in cylindrical graduated glaſs tubes of known capacity, I noted the ſpace occupied by each of them, when the mercury within the tube was level with that in the baſon in which the tube ſtood. I then transferred the tube into ſtrong lime water, and admitted as much of it as could, with the aſſiſtance of agitation, be employed in abſorbing all the volatile vitriolic acid without becoming turbid. Guided by ſome trials of known mixtures, and contenting myſelf with an approximation to accurate meaſurement, I ſtated half the bulk of the water ſo admitted to be equal to the whole of the volatile vitriolic acid, eſpecially when there was a reſidue of fixable air; for the water thus impregnated with ſulphureous ſelenite and acid, did not in theſe circumſtances appear to imbibe more than half its bulk of fixable air. By waſhing the remaining elaſtic fluid in lime liquor, I ſaw the quantity of reſiduary air or inflammable air; and deducting the bulk of this and of the volatile vitriolic acid from that of the mixed elaſtic fluids, I found the meaſure of the fixable air.

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At intervals, I received the mixed elaſtic fluids in a veſſel containing a column of water above the quickſilver; and as the water in this circumſtance imbibed a great quantity of volatile vitriolic acid, and retained little or no fixable air when fully ſaturated with the acid, the bulk of fixable air emitted in a certain time, was ſeen; and in comparing this with the meaſure of mixed elaſtic fluids which were expelled in the like time of uniform diſtillation, I approximated the true proportions of the different elaſtic fluids; but not before I had treated the fixable air with lime water in the foregoing manner, in order to ſeparate the volatile vitriolic acid which it carried with it through the column of water, at the period of ſaturation: Then the fixable air was eaſily withdrawn from the inflammable, with which it was generally impregnated.

SECT.

SECT. IX.

Experiments on Mixtures of Acetous and Nitrous Acid.

TO any man that confiders the varieties in fmell, tafte, medicinal effect and technical ufe of the fubftances, whofe products, by the fole action of fire, differ in little or nothing except the proportion of them to each other, as appears in the works of Geoffroy, Hales, Newman, Cartheufer, Fontana and others; it is manifeft, that our knowledge of the principles of vegetable fubftances and of bodies which refemble them in compofition, has been remarkably defective: and the experiments which throw new light on a fubject fo extenfive in nature, and fo interefting to medical practitioners, as well as to divers artifts, muft appear highly important.

With thefe impreffions I undertook many experiments which the avowed purpofes of this

this Eſſay did not ſeem to require; but of which I think a few ought to be related as follows, in order to ſhew their conformity with the foregoing doctrines, and to generalize the inductions which ſeem to demand our chief attention.

To four ounces of acetated vegetable alkali I added gradually eight ounces of the ſtrongeſt nitrous acid; for as ſtrong nitrous acid excites conſiderable heat in mixing it with water only, and the acetous ſalt always retains ſome water, the ſudden mixture of the nitrous acid with the acetous ſalt would from this cauſe alone, cauſe a degree of heat ſufficient to expel ſome of the acetous acid.

Notwithſtanding this precaution, the heat amounted to about 150 degrees, and ſome nitrous air and vapour was emitted, but the quantity did not much exceed what might be expelled from the ſame nitrous acid by heating it. In diſtillation I obtained eight ounces of acid; of which the four firſt were chiefly acetous and the reſt nitrous acid. The colour of the mixed acids was yellower than

than that of the nitrous acid ufed, and refembled that of nitrous acid flightly phlogifticated. The dry mafs in the retort weighed about four ounces, was perfectly white, diffolved and cryftalized like nitre, and in divers trials was found to be true nitre, with excefs of nitrous acid.

As the quantity of nitrous acid was twice greater than what was neceffary for the decompofition of the acetated falt; and as the acetous acid, in the inftant of its expulfion from the alkali, was fully expofed to an equal quantity of ftrongeft nitrous acid, and thefe acids were expofed in vapour to each other, it was imagined that fome change might be produced in the acetous by virtue of the attraction of its phlogifton to the air of the nitrous acid, and that the nitrous acid, thus deprived of its air in the prefence of phlogiftic matter, would form nitrous air.

But fince the quantity of acetous acid was as great as the acetated falt can be made to yield in any decompofition, and the quantity of nitrous air or vapour was too ſmall to be imputed to any other agency than that of the fire, by which alone the nitrous acid would yield as much as appeared in this experiment; and as the reſiduary ſalt, conſiſting of half the nitrous acid combined with the vegetable alkali of the acetous ſalt, ſhewed nothing phlogiſtic or oleaginous; it appeared that the acetous acid, which can ſo eaſily be decompoſed by heat, undergoes no ſuch change in the fulleſt and moſt advantageous expoſure to the ſtrongeſt nitrous acid.

To be more fully aſſured of this I diſtilled the nitrous acid of the foregoing proceſs, with four ounces of acetated vegetable alkali, and obtained the whole of the acetous acid quite clear and colourleſs: the matter in the retort was white, and conſiſted of true nitre ſuper-ſaturated with nitrous acid only. Thus the nitrous acid was found to have undergone no material alteration or loſs; and the acetous acid, being afterwards tried in divers combinations, and laſtly by fire, ſhewed no appearance of dephlogiſtication

or

or decompoſition by the action of the nitrous acid.

With the views already expreſſed, I mixed eight ounces of acetated lime with the ſame quantity of ſtrong nitrous acid, and after drawing off the acetous acid and ſo much of the nitrous as was uſed in exceſs, I diſtilled theſe with four ounces of the acetous calcareous ſalt. The phenomena were ſuch as may be expected by any perſon acquainted with the foregoing experiment, and gave no indication of material alteration in the nitrous acid, or of any decompoſition of the acetous by the mere action of the former. A ſmall portion, indeed, of nitrous and fixable air appeared; but from the quantity of it, and the period of the diſtillation, in which it was produced, it was manifeſtly owing to the heat which the charge ſuſtained at the bottom of the retort, where it had clotted, and was moſt expoſed to the fire, after the chief part of the liquid matter had been expelled.

I then wetted 16 ounces of dried and pure nitre in powder, with four ounces of

 ſtrongeſt

ſtrongeſt acetous acid, and added eight ounces of the ſtrongeſt oil of vitriol, in a glaſs retort. The phenomena attending the mixture did not differ in any thing remarkable from thoſe which accompany the mixture of ſuch oil of vitriol with dry nitre, except that the vapour which iſſued was mixed with perhaps a little more nitrous air.

In diſtilling four ounces of acid liquor from the charge, about $\frac{2}{3}$ of the common air of the veſſels iſſued, and carried with them about an equal bulk of nitrous vapour, mixed with a quantity of fixable air, too ſmall to deſerve particular notice. The condenſed liquor conſiſted of acetous and nitrous acid, and had a high orange colour. After the fourth ounce, the ſubſequent acid fell in a ſlender column, almoſt as fine as horſe-hair, from the nozzel of the retort, through the liquor in the recipient which it touched, to the bottom of it; ſhewing this product to be chiefly nitrous acid; and this laſt gradually diluted the colour of the firſt four ounces of acid until it became yellow.

When

When the whole of the diſtilled acids amounted to five ounces, and acetous acid no longer iſſued along with the nitrous, from the charge, the nitrous acid next diſtilled was green, as phlogiſticated nitrous acid mixed with water always is; and an elaſtic fluid began to iſſue in notable quantity. This conſiſted of four parts in bulk of dephlogiſticated air, mixed with one of nitrous vapour and nitrous air. But this is the proper produce of that part of the nitre which was conſiderably heated without meeting vitriolic acid in ſufficient quantity to detach its acid in the ordinary ſtate of nitrous acid. For ſome time afterwards, the proportions of dephlogiſticated air and nitrous vapour varied as the heat extended higher in the charge; and as no phenomenon occurred except what is proper to nitre and vitriolic acid ſtrongly heated in theſe proportions, I put an end to the operation.

The mixed acids thus obtained were kept ſix months in a cloſe veſſel, and diſtilled by a gentle heat. The portion firſt condenſed to the amount of two ounces was orange-

 coloured,

coloured, and confifted of acetous acid, impregnated with nitrous acid and nitrous phlogiftic vapour, which made it look rather opaque, and inclining to olive-colour; but by the fucceeding portions of acid, it was diluted to its former yellow colour, and the whole paffed over, the laft portions being entirely nitrous, without leaving a ftain behind. About half a pint of elaftic fluid in the mean time iffued from the recipient through quickfilver, and confifted of phlogifticated air and nitrous air, mixed with that of the veffels, the bulk of which laft is not included in the half-pint. This quantity is too fmall to denote any notable change of the acids in the diftillation, for the mixed acids could retain fo much nitrous elaftic fluid from the former procefs, and the phlogiftication of the air of the veffels, is the well known refult of the abforption of its dephlogifticated part by the nitrous air or vapour.

In this experiment the acetous acid was firft expofed to the action of the vitriolic in its moft concentrated ftate; and when this

this was expended in decompoſing the nitre, it was expoſed to the ſtrongeſt nitrous acid in ſubſtance and in vapour; and as the diſtillation advanced, a part of the acetous acid was expoſed at once to nitrous acid in hot vapour, and to the pure air of that part of the nitre, which by reaſon of the deficiency of vitriolic acid, and its vicinity to the hotteſt part of the ſand, was decompoſed by heat alone: and as no more cf the acetous acid was decompoſed or expended in making the nitrous acid red and elaſtic, than appears always to be when it is retained in ſuch heat; we may truly infer that the acetous acid cannot be decompoſed by the mere action of the nitrous, and that in the preſence of the water which is a conſtituent part of theſe acids in their ordinary condition, the nitrous acid cannot draw the phlogiſton from the acetous, ſo as to exhibit it in a dephlogiſticated ſtate.

As water weakens the action of divers bodies on each other, and eſpecially that of acids on inflammable liquors, I had reaſon thus to impute the inactivity of the nitrous acid in theſe diſtillations, to the water inſeparable from both acids in their ordinary form; but in order to try the validity of this notion, I made divers experiments with the ſtrongeſt nitrous acid and the moſt dephlegmated oil diſtilled from acetated vegetable alkali: for ſeeing that acetous acid may be reſolved by fire into fixable air, water and oil; that the two former are not affected by nitrous acid ſo as to afford new compounds, and that the latter is; I conſidered this as the only part of the acetous acid on which the nitrous is apt to act, and the moſt likely to indicate the effects which nitrous acid would produce with the acetous, if it could be procured quite free from water.

The reſult of the mixture of theſe was, that when the oil was ſlowly added to the nitrous acid, and gradually blended with it by agitation in iced water, ſo that no ſenſible heat was excited, they mingled freely and perfectly, without emitting or exhaling any thing conſiderable, except what they ſeverally exhale into the air included with them, previous to any mixture of this kind. The firſt drops of oil gave the nitrous acid a yellow colour, the next orange; with more it acquired a claret colour, which grew deeper and darker as the quantity of oil encreaſed. The acid nevertheleſs ſeemed to have truly diſſolved its bulk of the oil, for in a column of a quarter of an inch in diameter, the mixture appeared uniform and tranſparent. When it was removed from the iced water, and acquired the temperature of the air, which was 36° at this time, it began to diſcharge bubbles, which aroſe very ſmall from the bottom, and grew larger in their progreſs upwards through the liquor, as it happens in making nitrous ether; and in the courſe of twelve hours, a quantity of elaſtic fluid was emitted, meaſuring upwards of thirty times the bulk of the mixture. Three-fourths in volume of this elaſtic fluid were fixable air, and the remainder was inflammable air mixed with nitrous air, the former of which ſeemed to be nothing more than the proper exhalation of that part of the oil which had eſcaped the action of the nitrous acid, or which having

having depoſited its water in the acid, aſſumed this form, as the ethereal part of alkohol is diſpoſed to do in theſe circumſtances.

On the application of heat, the mixture emitted a great deal more of the like elaſtic fluids; and when phlogiſticated nitrous vapour aroſe in conſiderable quantity, I withdrew the fire, knowing from other experiments what the ſubſequent product would be, and ſatisfied already in this proof, that the nitrous acid needs no heat beyond 36 degrees in order to act forcibly on this oil.

When the acid and oil were quickly mixed in any order, or in any quantity exceeding a dram of either, the heat and intumeſcence were very great, and the quantity of elaſtic fluid ſuddenly emitted was proportionate to theſe directly. After it had depoſited the condenſible phlogiſticated nitrous vapour which iſſued along with it from the boiling mixture, it was found to conſiſt chiefly of fixable and inflammable air mixed with nitrous and phlogiſticated air;

 but

but the proportions of theſe varied in different experiments with the circumſtances of them. By attending to theſe, I perceived that the inflammable air was produced from the volatile oil which had received the heat of the mixture, but eſcaped the action of the acid, and that the quantity of fixable air was directly proportionate to the phlogiſtication of the nitrous acid. Therefore this acid and our oily matter mutually decompoſe each other, and form new compounds, by virtue of the elective attractions of their principles, and without the aid of extraneous fire; and as a great quantity of fire is emitted during the action of the oil and acid on each other, the quantity of it that exiſts concentrated and combined in theſe, is much greater than can be retained in their new products.

In metallic ſolutions, and in all others, in which the nitrous acid is phlogiſticated; in all combuſtions of phlogiſtic bodies, in which nitrous acid or nitrous ſalts, by virtue of the air contained in them, perform the office of the pure part of atmoſ-

pheric

pheric air in calcining, deflagrating or detonating these substances; and in every known instance of the phlogistication of nitrous acid, and of the formation of nitrous air from it; the acid principle loses a part or the whole of its pure air, and by receiving phlogiston instead of it, becomes nitrous air. The quantity of disengaged nitrous air that appears in any of these cases depends on the capacity of the materials employed, to retain the pure air of the nitrous acid in preference to the nitrous air, and in these the consequent predominance of pure air may easily be found: hence the nitrated calces of metals yield abundance of pure air and little or no acid, as Mr. Cavendish has well shewn in the instance of Mercurius corrosivus ruber. Of all the experiments which clearly evince this deposition of pure air by the nitrous acid, when it becomes phlogisticated, and forms nitrous air, we need only to mention the following.

Nitrous air, whether procured in detonation, in the solution of metals, vegetables, or other phlogistic substances, or in the action of the nitrous acid and oils on each other, on the admixture of pure air becomes nitrous acid somewhat phlogisticated; and a great part of the pure air thus administered, is actually expended in the formation of the acid, whilst the remainder contributes to the formation of water. In this as well as every other instance of the entry of pure air into a phlogistic body, heat is generated or fire is emitted, shewing that the nitrous air and pure air severally, are capable of holding more fire, than the nitrous acid and water, which they form, can retain.

Aided by these general observations, we may interpret the phenomena of the mixtures of nitrous acid and oil in the following manner.

Whilst the phlogiston of the oil unites with the acid principle of the nitrous acid, the pure air of the latter is transferred to the vegetable acid principle of the oil, and contributes towards the acid characters, which then become as apparent in the fixable air, as the privation of them is manifest in in the nitrous air. That this expoſition is true will appear from theſe conſiderations; that the nitrous air thus formed, requires only pure air to become nitrous acid, and that diſengaged pure air, however procured, together with this oil, in the act of combuſtion in cloſe veſſels, yield fixable air and water, and nothing elſe, (except that quantity of the fire formerly combined in the oil and pure air, which the fixable air and water cannot retain: for I purpoſely reject from our preſent conſideration a ſmall and variable quantity of the elaſtic fluid called phlogiſticated air, which always appears in the above-mentioned proceſſes, and ſhall be noticed in due time.

SECT. X.

Experiments and Obſervations relating to the Principles of Acetous Acid and Fixable Air, and the Bodies from which Fixable Air is not only extricated but formed; with general Interpretations of divers intereſting Phenomena.

IN addition to the curſory obſervations formerly made, I am now briefly to relate the general reſult of the experiments which exhibit the agency of air on acetous compounds.

Having tried every one of the tinder like and coaly ſubſtances heretofore deſcribed as conſiſting of oily matter of acetous acid fixed by earth or alkali or neutral ſalts, by calcining or burning them in contact with pure air; I found the quantity of fixable air produced in theſe proceſſes to bear a direct proportion to that of the pure air expended in them reſpectively. In burning the oils of acetous acid with pure air from nitre, the

product

product was fixable air and water, exclusive of the fire emitted and a small and variable quantity of phlogisticated air; and when the oils containing the smallest quantity of water were used, the weight of the fixable air equalled or exceeded that of the oil. In burning the inflammable air expelled from acetous acid, the fixable air always greatly exceeded the inflammable air in weight, as will be shewn hereafter; and in all these cases the quantity of fixable air was directly proportionate to the expenditure of pure air.

By these experiments I was thoroughly persuaded that some gravitating matter of pure air contributes to the formation of fixable air, and that every combustible product of acetous acid, contains the acid principle of fixable air as well as phlogiston. As the phlogistic products of acetous acid, when it is decomposed by fire, require no other matter but pure air in order to yield fixable air in consequence of their reciprocal decomposition, and this acid affords nothing but water and fixable air, exclusive of these

phlogistic

phlogiſtic compounds, I could no longer doubt of the exiſtence of the gravitating matter of pure air in acetous acid which yields fixable air; and the induction that acetous acid conſiſts of water, acid, air and phlogiſton, ſeemed to me fully eſtabliſhed.

By the abſtraction of fixable air, and conſequently of the pure air of acetous acid, we deprive the remainder of this acid of every property that characterizes an acid, and by the due agency of air we reſtore to a conſiderable part of this ſame remainder, the decided acid characters of fixable air. Therefore one of the principles of fixable air reſides as well in our oil, tinder, coal or inflammable air, as in concentrated vinegar, although it ſhews no property of an acid until it is combined with air.

Although the phenomena of combuſtion were inexplicable, they furniſh no juſt argument in contradiction of theſe inferences concerning acetous compounds and air, ſince by the experiments of the laſt Section we find that nitrous acid acting on the oil of the acetous and ſupplying pure air, contributes to the formation of fixable air, without the aid of fire or the proceſs of combuſtion, which has nothing peculiar to it except the illumination; for fire is emitted wherever fixable air is formed from the materials above-mentioned; and is as manifeſt in its eſcape from the mixture, which impreſs us only with the ſenſe of heat, and from which it iſſues ſlowly and progreſſively, as in the combuſtion in which the ſame matter, iſſuing more rapidly, and meeting no denſe medium to alter or reſtrain its motion before it is propagated to our viſual organs, excites in us the ſenſe of illumination. Thus I endeavour to expreſs facts to which we muſt preſently have recourſe, without involving them in any theoretic interpretation.

This recent knowledge of acetous acid, oily matter, fixable air, and denſe inflammable air, opens to us a new proſpect of many intereſting phenomena, which have perplexed and miſled the moſt ingenious Experimenters. A conciſe and general explanation

planation of theſe, according with our interpretation of the phenomena already noticed, will now I hope be acceptable to the reader.

In diſtillations of the acetous acid alone, no change is produced in it, becauſe there is nothing to facilitate an abſtraction of its water, or to detain any of its principles in preference to the others, and becauſe the volatility of this compound of water, acid air, and phlogiſton, limits the heat which it ſuſtains in this proceſs. But when the ſame acetous acid is detained by any body which facilitates the abſtraction of its water which ſerves as the intermedium of the union of the other principles, and in conſequence of this detention is duly ignited, the acid principle ſo far as it meets air, forms fixable air, but meeting phlogiſton only, forms with it an inflammable body, which in the circumſtances reſpectively deſcribed, appears in the form of oil, tinder, artificial fuel, or of denſe inflammable air.

In accounting for the production of fixable air, and of oil and inflammable air,

 which

which in combuſtion yield fixable air, from the dephlegmated and ignited acetous acid, we furniſh an eaſy explanation of the phe-nomena which occur in the diſtillation and combuſtion of all the vegetable and other ſubſtances which yield fixable air, oil, and our inflammable air, in various proportions; and we ſhew at the same time that however they may vary in their other principles, and conſequently in their properties, they all contain our vegetable acid principle aſſoci-ated with phlogiſton. The nature of the coaly and charred reſidue left in the diſtil-lation of vegetables and divers combuſtible mineral ſubſtances, is clearly ſhewn by the like reſidues of acetous compounds; for ſo far as all theſe yield denſe inflammable air by mere ignition, or fixable air in com-buſtion, the exiſtence of our acid principle in each of them is manifeſted.

When we conſider that in every dephleg-mation of the acetous acid a great deal of oil is formed, and that all oils in their com-buſtion ſhew, by the quantity of fixable air, that they conſiſt chiefly of our acid principle

principle and phlogiston detained, in some instances, by a little earth or other fixed matter, and associated, in others, with a little water; and when we also observe that waxy, resinous, bituminous, and divers other solid combustible bodies may, by distillation and the abstraction of earthy matter, be reduced to the state of oil; we find sufficient reason to conclude that the form and characters of oil are those which our acid principle and phlogiston, abstracted from other matter, are most disposed to assume; and as no oil or ardent spirit, or resinous or camphorated or coaly substance, exists without them, and nothing else is common to all the bodies that are combustible; I shall for the future express the compound of our acid principle and phlogiston by the term of oily or coaly matter, rather than introduce new terms.

As the most dephlegmated acetous acid sustains certain degrees of heat, and may be distilled without decomposition, for the reasons above-mentioned, we readily conceive how ardent spirits and the purer oily bodies retain their form and characters after the like treatment, and how camphorous bodies, flowers of Benzoin, and others, consisting chiefly of our oily or coaly matter, may be sublimed unaltered; and for the same reasons that acetous acid duly heated, undergoes the changes already described, ardent spirits, oils, and all the volatile bodies which abound in our oily or coaly matter, are convertible, to the amount of this matter, into inflammable air, when they are detained by any body, or pushed through red-hot tubes, in order to undergo the necessary ignition.

A cursory review of the particulars comprehended under these general observations, is sufficient to shew how copiously and extensively our acid principle is diffused through the animal and mineral as well as through the vegetable creation, how constantly it attaches itself either to the gravitating matter of air, or to phlogiston, and why in all our attempts to expel it from fixed bodies, we find it compounded in the form of fixable air, inflammable air, or oil, which

which laſt bears the ſame relation to our acid principle that ſulphur has to that of vitriolic acid, or phoſphorus of Kunkel to that of the phoſphoric acid.

The fixable air, inflammable air and oil, procured in the diſtillation of wood, peat, bitumens and foſſile coal; and the fixable air which is produced abundantly in the combuſtion of ſuch native ſubſtances, or of their oil or inflammable air, ſhew clearly that theſe fuels differ from each other only in the quality and quantity of earthy ſaline and other matter combined in them with the principles of our vegetable oil, which thus appears to be common to them all, and to conſtitute the greater part of them abſtracted from their water. Thoſe who wiſh to trace mineral fuel to a vegetable origin, will find the characteriſtic matter of it abounding in all organized bodies on earth, and even in their relicks after rotting, and may obſerve that black peat ſtrongly compreſſed, differs very little from mineral coal, either in the appearance, or analyſis, or products of combuſtion: and the circulation of the ſame oily matter to vegetables again, is exhibited in the practice of huſbandry. Virgin mould, however richly impregnated with the matter of the vegetables which have periſhed on it, is exhauſted by the repeated removal of heavy crops, and cannot by any culture or mixture be enriched again for vegetation, without receiving, in ſome form, our oily matter, which we thus trace into the crops, until the exhauſted ſoil can bear no other than ſtunted vegetables ſubſiſting chiefly on the nouriſhment conveyed to them by the air or rain.

The agency of water in vitriolic acid is by all allowed to be the ſame as we deſcribed it in regard to the acetous: hence it happens that water impedes the action of vitriolic acid on all bodies by which it can be phlogiſticated, and that vitriolic acid and acetous acid, which however concentrated, contains a great quantity of water, produced little or no effect on each other, when they were mixed in equal quantities. But when the proportion of water in the mixture

mixture was leſſened by adding only a little of the acetous acid to a great quantity of the moſt dephlegmated vitriolic acid; and when the acetous acid, detained in the vitriolic, diveſted of water, and conſiderably heated at the ſame time, was deprived of that part of it which iſſued in the form of fixable air, the remainder then conſiſting only of phlogiſton aſſociated with the vegetable acid principle, was expoſed at once to the action of fire and vitriolic acid, which, as we ſhall preſently ſhew, contains pure air, and always depoſites it in the act of combining with phlogiſton, to form volatile ſulphureous acid. Then whilſt the vitriolic acid became phlogiſticated, its air acting as uſual on the hot oily matter, contributed to the formation of fixable air. But in proportion to the water which yet remained to impede this decompoſition, a part of the oleaginous matter eſcaped in the form of ether or inflammable air, and a portion of the vitriolic acid remained imperfectly phlogiſticated.

The action of vitriolic acid on ardent ſpirits, oils, and all the bodies which contain our oily matter, is of the ſame kind: for weak ſpirits are not ſenſibly affected by this acid, and to produce the greateſt alteration in both, we muſt mix them in their moſt dephlegmated ſtate. Then the water, which is a conſtituent part of alkohol, being detained by the vitriolic acid, and ſome part of the acid principle of the alkohol being expended in the formation of fixable air which eſcapes, ſo much of the acid principle of the ſpirit as can be ſaturated with its phlogiſton to form an oily liquor, paſſes off in diſtillation, under the name of ether. This is followed by the water impregnated with ſome concomitant ethereal and oily matter; and ſo much of this laſt as the vitriolic acid can detain, is afterwards expended in phlogiſticating this acid by one of its principles to form volatile vitriolic acid, and contribute by its acid principle to produce the fixable air which accompanies the vitriolic acid air.

In the mean time a part of the oily matter thus heated, eſcaping the action of the vitriolic, is expelled in the form of inflammable air, to which this oily matter is always convertible by heat alone: and with regard to the thick livid refiduary matter, we need only obferve that it contains a confiderable quantity of vitriolic acid unaltered, and derives its fpiffitude and colour from the falts of the vitriolic acid and the faccharine matter of the fpirit entangling a portion of oil: but as the faccharine matter itfelf confifts chiefly of the acid and phlogiftic and aerial principles of acetous acid, the produce from this refidue by diftillation to drynefs, is vitriolic acid, vitriolic air, fixable air, and inflammable air in fmall and variable quantity, for the reafons already mentioned.

In acetous acid and ardent fpirits the acid principle predominates over the phlogiftic, and is accompanied with fome air; for otherwife they could not yield fixable air, as they do, in divers proceffes, without the aid of pure air; and fpirits could not render falt of Tartar mild and cryftalizable, as they ufually do in digeftion or diftillation. But in oils, the acid principle appears to be faturated

turated with phlogiſton, and the quantity of water which ſuch a compound can retain or unite with is, in all caſes, proportionate to the quantity by which our acid principle predominates in the oil; except when ſome other matter ſerves like this as the medium of union between the oil and water.

This being the nature of oils, ſo far as we can briefly expreſs it in general terms, we are next to conſider the phenomena which vitriolic acid and oily bodies have been obſerved to produce.

When diluted vitriolic acid is preſented to an oil, they produce little or no effect on each other, for the reaſons above-mentioned: but when the dephlegmated acid is uſed, its firſt action is to abſtract the water and thicken and char the oil. The products are afterwards fixable air, inflammable air, vitriolic air, leaving a coaly reſidue proportionate to the heterogeneous ſalts in the acid and the proper earthy or other fixed matter of the reſpective oils.

To account for theſe products, we need only make the obvious application of what has been ſaid with regard to vitriolic acid and acetous acid in diſtillation.

In like manner, the production of fixable and vitriolic air, and all that occurs when we mix or diſtil vitriolic acid with any vegetable or other ſubſtance abounding with our acetous principle and phlogiſton, are eaſily explicable, under due conſideration of the matter combined in theſe ſubſtances reſpectively with our oily matter, and of the predominant acid, in ſome inſtances, which with the concomitant air will afford fixable air to which the aerial principle of the vitriolic acid may not yet have contributed.

As to the heat produced, on the mixture of vitriolic acid with oily and other bodies abounding with our acid and phlogiſtic matter, it is manifeſtly owing to the capacity of the phlogiſtic compound and of the vitriolic acid ſeverally to retain more fire combined in their ſubſtance, than can be afterwards engaged

engaged as a component principle of the fixable air, vitriolic air, or other product of the process: and that the degree of heat should be proportionate to the expenditure of the air of the vitriolic acid in the formation of fixable air, will not appear singular, when it is considered that in the deflagration of our inflammable air with pure air, fire is most copiously emitted, and nothing remains but fixable air and water, except a small and uncertain quantity of phlogisticated air, as will more fully appear hereafter.

In comparing the inactivity of nitrous and acetous acids on each other, with the phenomena attending the mixtion of nitrous acid with the oil of the acetous, we discover the agency of water in all similar mixtures: for the acetous acid differs from this oil, in nothing that affects the nitrous acid, except water. The elective attractions of the phlogistic and acid principles of the acetous acid, and the aerial and acid principles of the nitrous, the consequent decompositions and new products are therefore sufficiently exhibited

bited in mixtures of this oil with nitrous acid, and ſerve to explain many phenomena which have occurred to Experimenters in their trials of nitrous acid with bodies containing the acid principle of acetous acid as well as phlogiſton.

So far as the principles of our oil and nitrous acid were duly applied to each other, and unreſtrained by water, the phlogiſton of the former attached itſelf to the acid principle of the latter, and made nitrous air, whilſt the nitrous acid depoſited and transferred its air to be expended chiefly in the formation of fixable air: and as the new products could not retain all the fire originally combined in the oil and nitrous acid, a conſiderable quantity of it neceſſarily eſcaping, acted in its proper character, heating and expanding the mixture and the contiguous bodies. But inaſmuch as the principles of the oil and acid were accompanied with water, and were reſtrained by it, or in imperfect mixture eluded each other, we had inflammable air or oily vapour in conſequence of the heat, and nitrous vapour or acid partially phlogiſticated.

In this manner and even in these terms we can easily account for the products and phenomena of nitrous acid with divers vegetable and animal substances, which contain our acid principle and phlogiston, viz. the heat, the intumescence, the nitrous and fixable air, the escape of inflammable air and oily vapour, and the semi-phlogisticated state of some part of the nitrous acid.

Many experiments admitting or requiring this explanation, may be met in the works of the latest writers on chemical subjects, and particularly in Dr. Priestley's second volume of Experiments and Observations on Airs: but in every exposition of this kind, due care should be taken that the fixable air which the phlogistic body alone may yield, be not confounded with that to which the air of the nitrous acid contributes.

In explaining the phenomena attending the mixture of nitrous acid with bodies consisting chiefly of our oily matter and water, the agency of this last is especially to be considered. The first effect of the nitrous acid in in theſe caſes is, like that of the vitriolic, to abſtract the water, and then act like diluted nitrous acid on the other matter of theſe bodies: ſo nitrous ether is made from ſpirit of wine and this acid, of which ſome part remains in the water abſtracted from the ethereal or oily matter, another part blends with the ether, when heat is avoided, whilſt a portion of the pure or empyreal air is expended in the generation of fixable air; and proportionate to this expenditure we find nitrous and phlogiſtic air, the quantities of which are greateſt when, by extraordinary dephlegmation of the acid and ſpirit, or by the heat of haſty mixture, or the want of due compreſſion, the action of theſe laſt on each other is rather promoted than moderated.

Subſtances which conſiſt almoſt entirely of our oily matter, and afford little or no water to dilute the nitrous acid and moderate its action, produce the greateſt quantity of fixable and nitrous air; which are expelled with ſuch impetuoſity as to blow a great part of the ingredients away, before they can be blended ſufficiently for their mutual decompoſition. This happens in mixtures of nitrous acid and eſſential oils, which always emit a great quantity of fire, generally burſt forth into flame, and burn with great rapidity. When the decompoſition is partial or incomplete, the fire emitted is partly wafted away with the elaſtic fluids newly compoſed, and partly expended in vaporizing the undecompoſed parts of the ingredients; but when neither water nor any other matter gives any conſiderable impediment, and the circumſtances favour the action of ſuch bodies on each other, they are almoſt wholly expended in forming the new compounds of firable air, nitrous air, phlogiſtic air, and water; and the vivid flame and intenſe heat ſhew that the fire which was lodged in the oily matter, and in the air of the nitrous acid, is for the greater part liberated to act in its proper character on the neighbouring bodies.

All the phenomena that accompany the action of nitrous acid on other bodies, which like theſe contribute to the formation of fix-

fixable air, are similar to, and intermediate between those of solutions, of the processes for ether, and of the inflammation of oils, and differ from them in nothing that can embarrass an experienced chemist.

Notwithstanding the attractive power with which nitrous acid is combined in alkalies earths and metals, the force wherewith its empyreal air is drawn to the principles of our coaly matter, is always sufficient under due ignition, to produce the effects lately described, and particularly the formation of fixable air and nitrous air, which is often accompanied with a considerable quantity of phlogistic air. This last indeed varies greatly, as the circumstances of the process and the subjects of it are varied; but does not require immediate attention.

The rapid combustion and explosive power of compounds, consisting of nitrous salt, well mixed in due proportion with charcoal or any other substance consisting chiefly of our acid principle, combined with phlogiston, are necessary consequences of those attractive forces which tend to the formation of fixable air, nitrous and phlogistic air and water, and to the liberation of the matter of fire. Our recent knowledge of these subjects is chiefly derived from that important discovery of Mr. Cavendish, of the emission of fire and formation of water, from the gravitating matter of empyreal and light inflammable air; and any person who may hereafter compose a theory of combustion and detonation, will find the chief difficulty to consist in the attempt to shew why a combustable mixture, whether elastic, fluid, or solid, requiers ignition in some part before the intended decomposition can take place. My conjectures on this subject will appear in a subsequent section.

A great many different pyrophori are made by mixing earthy, metallic, or alkaline bodies, with vegetable or animal substances consisting chiefly of our oily matter, and then expelling their moisture and superfluous oily or acidulous matter, by ignition in close vessels. Nothing but this oily or coa-

coaly matter is common to all the pyrophori, which by mere expoſure to pure air, imbibe it ſuddenly, enter into combuſtion, and yield fixable air; which, if it be not copiouſly emitted during the combuſtion, is found to be detained in the earth or alkali of the pyrophorus, from which, previous to the admiſſion of air, little or no fixable air could be obtained. The fixable air formed in all inſtances of this kind, is manifeſtly the product of the oily or coaly matter, and pure or empyreal air; and the fire liberated and ſpontaneous accenſion, ſhew clearly that one or both of theſe contained a much greater quantity of fire, than the new products, conſiſting of fixable air water and reſiduary groſs matter, can retain.

After this manner, we may eaſily explain the phenomena of fixable air and heat wherever they are produced, during the action of empyreal air, (or atmoſpheric air which contains it) on ſubſtances containing our oily or coaly matter; and the ſame interpretation is applicable, wherever we ſee fixable air formed, and fire extricated

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during the action of nitrous salts, black wad, or of other bodies containing empyreal air, on combustible bodies holding our oily or coaly matter. But since mixtures of solid bodies containing empyreal air intimately combined in them, with other solid bodies containing our oily matter, emit fire abundantly, and burn most vehemently, so soon as the action of the aerial matter of one, on the oily matter of the other, commences, whether spontaneously, or by the excitation of a flint spark; we cannot doubt that the empyreal air, or oily matter, or both, retain a vast quantity of fire fixed in the solid substance and as much neutralized as acid is in a neutral salt: and in comparing the action of the elastic fluid called empyreal air, in the combustion of phlogistic bodies, with the like effect of nitrous and other solid bodies, which act in combustions by virtue of their pure air, we find no ground for supposing that much more of the matter of fire is necessary to the elastic condition of pure air, than can be retained by it in the closer approximation of its parts, in bodies to whoſe maſs and weight it greatly contributes; unleſs we admit, that fire is combined in much greater quantities in phlogiſtic bodies than in any other; in direct contradiction to the opinion of the ingenious Dr. Crawford, who very juſtly conſidered the empyreal air as the vehicle of fixed fire; but will now, on a review of the ſubject, if I miſtake not, admit, that phlogiſtic bodies alſo contain fire, and emit it in combuſtion. But the vivid combuſtions of *light inflamable* air, ſulphur, zinc, and other bodies, with pure air, in which little or no fixable air is formed, as that excellent philoſopher Mr. Cavendiſh has ſhewn; teach us that fixable air is not a neceſſary product of combuſtion, nor of the union of air with phlogiſton: And now we ſee, that it cannot be produced by the union of air with any known matter, except the acid principle manifeſtly contained and diſguiſed by phlogiſton, in the bodies comprehended under the general heads already ſpecified, and conſequently in ſubſtances whoſe varieties, diſtinguiſhed only by the names, would fill a volume.

The proceſſes of fermentation, putrefaction and reſpiration, which laſt, as Dr. Crawford very ſagaciouſly obſerves, generates animal heat, are all productive of fixable air, of which, a great part is actually formed from principles which before were otherwiſe engaged and compounded in the reſpective inſtruments of theſe operations; and theſe proceſſes are all attended, like thoſe above deſcribed, with the emiſſion of fire, But as I intend to ſpeak of theſe ſubjects elſewhere, I ſhall not inſiſt on them here for the mere purpoſe of ſhewing, what the reader anticipates, their conformity with the notions ſo often tried in the interpretation of the phenomena which accompany the formation of fixable air in various proceſſes.

The appearance of ſmall quantities of fixable air, in proceſſes which do not rank under any of the forgoing heads, is generally

rally owing to the following circumſtances: The common nitrous acid of the ſhops is diſtilled from rough nitre, and exclusive of water, carries with it ſome of the vegetable oily matter, which colours it, and in every circumſtance of deplogmation and ignition, yields fixable air. In the refining of nitre, we approximate the intended purity, but never attain it perfectly; and therefore find ſome fixable air mixed with the firſt product of nitre diſtilled even in glaſs veſſels. The moats alſo, or duſt and fibres, whether animal or vegetable, that are wafted every where in the air, and adhere to our veſſels and inſtruments, never fail to impregnate the ſubjects of our experiments, and to yield fixable air, when expoſed to heat and the action of air or of bodies containing this matter. Coarſe earthen veſſels generally retain in their ſubſtance ſome of our oily or coaly matter; the imperfect metals are ſeldom free from it; and a grain is ſufficient in the recited circumſtances, to produce ſome cubic inches of fixable air, as will be ſhewn hereafter. It is not, there-

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fore a matter of ſurpriſe, that in the in-conſiderate uſe of impure materials, earthen veſſels, dirty gun barrels, and by expoſure to the common air, many ſubſtances ſhould have appeared to yield variable quantities of fixable air, which in the contrary circumſtances could have afforded nothing of this kind.

We cannot yet ſpeak with certainty of the character of the mere acid matter of each of the chemical acids, abſtracted from phlogiſton and every other kind of gravitating matter. In each of the ſubſtances, which we conſider as a certain acid ſaturated with phlogiſton, the acid matter is as much diſguiſed as it can be in a neutral ſalt: This appears in the compariſon of ſulphur with vitriolated tartar, of phoſphorus with microſmic ſalt, of regulus arſenic, with neutral arſenical ſalt, &c. all which differ very much from their reſpective acids. But as empyreal air is adminiſtred in every proceſs in which we are ſuppoſed to dephlogiſticate the mere acid matter, and this laſt is not known to us in the ſtate in-

intermediate between that of its combination with phlogiſton and this laſt in which it is certainly combined with gravitating matter of empyreal air, we cannot pretend to deſcribe any mere acid matter in its uncombined ſtate; nor is it yet demonſtrated, that the empyreal air, which is a conſtituent part of each of the acids of the chemiſts, expells or extricates in every inſtance, all the phlogiſtic matter which was formerly combined in the ſubject from which the acid is prepared. There is, however, in the preparation of every acid, ſufficient evidence either of the expulſion of ſome phlogiſtic matter, or of its union with the pure acid matter being diſſolved in conſequence of its being expended in the formation of water, of which a part, or the whole in moſt inſtances, is retained in the body which we are ſaid to dephlogiſticate.

Whenever vitriolic acid is employed in the formation of ſulphur, its empyreal air is expended in forming fixable air or water; the acid character of the reſidue is loſt in the

the union with phlogiſton, and cannot be reſtored until empyreal air is adminiſtred in ſome ſhape to combine with the mere acid matter and with a part if not the whole of the phlogiſton, which with a pro-tion of the empyreal air forms water.

This agency of empyreal air appears in every proceſs for making vitriolic acid from ſulphur and nitrous acid or nitrous ſalt, or ſulphur and empyreal air, whether admi-niſtered pure, or blended with phlogiſtic air, as it is in atmoſpheric air; and the extri-cation of the empyreal air from the other matter of vitriolic acid, whilſt it is em-ployed in the formation of ſulphur, is equal-ly apparent in every experiment in which artificial ſulphur is formed in conſiderable quantities, as in making liver of ſulphur with charcoal and vitriolated tartar or glau-bers ſalt, or in making pyrophorus with alum and flower or ſugar; for in theſe in-ſtances, and in every diſtillation of vitrio-lic acid or vitriolic ſalt with charcoal, coak, bitumens, oils, reſins, and divers ſubſtances which ſeverally yield little or no fixable

air

air or water until empyreal air acts on them during ignition, the quantity of fixable air and water produced during the intended formation of ſulphur, ſhews that the proper air of the vitriolic acid, is excluded from the ſulphureous compound.

Although vitriolic acid be diveſted of water in the long continued fuſion of glaubers ſalt, it obſtinately retains the greater part of its empyreal air; and until this is engaged and expended in the formation of fixable air and water, the vitriolic ſalt cannot make liver of ſulphur with charcoal or the other ſubſtances that abound with our coaly matter. The agency of this laſt in the extrication of the empyreal air of glaubers ſalt, is the ſame as in metallic reduction; and the liver of ſulphur thus made by fuſion, ſhews how much the acid character of vitriolic acid depends on its empyreal air: For the ſaline maſs now containing almoſt all the mere acid matter which belonged to the Glaubers ſalt, but deprived of the air, is no longer neutral and mild, but taſtes ſtrongly alkaline and cauſtic,

tic, and is deliquefcent. Expofed to empyreal air it imbibes it greedily, and without meeting any other matter, refumes the characters of Glaubers falts. Vitriolated tartar treated in the fame way, affords the fame phenomena and inferences.

The nitrous acid, in like manner, lofes its acid characters, and acquires thofe of nitrous air, when it is deprived of the empyreal air, and is fuppofed to receive phlogifton, in metallic folutions, or in combuftions and detonations. When the quantity of nitrous air is confiderable, the empyreal air which had been detached from it in fuch proceffes, is eafily traced in the bodies which effected the feparation, as in the nitrated calces, or in the water formed, or in the fixable air; and the nitrous air never refumes the true characters of nitrous acid, until it meets empyreal air, with which it recompofes nitrous acid and its water.

It is not to be denied that in proceffes of this kind, as well as in the expulfion of empyreal air from nitre, a confiderable quan-

quantity of phlogiſtic air appears, of which I cannot yet ſpeak with preciſion, although I am certain there is nothing in it repugnant to theſe notions of acids.

Phoſphorus of Kunkel, as the celebrated Scheele and Lavoiſier have ſhewn, imbibes empyreal air in great quantity. During its ſaturation with the air, nothing but fire is perceptibly emitted, and this which has been called dephlogiſtication, is really effected without any emiſſion of the phlogiſtic matter, becauſe there is no loſs of weight, and water is manifeſtly formed.

In the phoſphorus, the acid matter is totally diſguiſed by the combination with phlogiſton; in the tranſition to phoſphoric acid it may be equally diſguiſed, becauſe it combines with the gravitating matter of empyreal air; but it is only in this combination with air that it forms a ſubſtance poſſeſſing the common chemical characters of an acid.

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How the mere acid principle of phoſphorus would act, if it were perfectly freed from phlogiſton and empyreal air, I know not; but I am aſſured that the empyreal air is not all expended in forming water with the phlogiſton of the phoſphorus, and that it does not act merely by diſſolving the union between the phlogiſton and acid principle, which in the latitude of ſpeech may ſtill be called dephlogiſtication; for the aſtoniſhing quantity of empyreal air which phoſphorus imbibes in combuſtion, to the amount of about twice its own weight, is not all emitted in the form of water, but ſerves as well as diſengaded empyreal air, for the greater part, to compoſe fixable air, when the phoſphoric acid is formed into phoſphorus again, by diſtilling it with charcoal or other ſubſtances containing the acid principle of fixable air.

Arſenical matter combined with phlogiſton to form Regulus of arſenic, has more of the character of a combuſtable metallic ſubſtance than of an acid; and it is only by by abſorbing empyreal air in due quantity, that it acquires the general properties of a chemical acid. That this empyreal air is not wholly expended in abſtracting the phlogiſton, but that it actually contributes to the formation of the acid, may eaſily be ſhewn, 1ſt, by the fixable air which is produced in great quantity during the reduction to the reguline ſtate by ſuch phlogiſtic ſubſtances as contain our oily or coaly matter; 2dly, by the empyreal air which this acid emits when it is ſtrongly ignited and ſublimed into the form of white arſenic; and 3dly, by the rapid combuſtion of zinc fuſed in this acid, as Mr. Scheele has obſerved.

In the preparation of the acid of ſugar and of other factitious vegetable acids, all the phenomena correſpond with theſe notions of the acids in general, and with no others. The nitrous acid employed in ſuch proceſſes is wholly expended thus: its empyreal air in forming water and the vegetable acid, whilſt the remainder of it eſcapes in the form of nitrous air, if not of phlogiſtic air: The empyreal air thus depoſited in the ſaccharine or other vegetable acid, is demonſtrable, in the greater quantity of fixable air that may be expelled by mere ignition from ſuch an acid, than from an equal weight of the ſugar or other ſubſtance which was formerly ſuppoſed to contain ſuch acid diſguiſed only by phlogiſton.

We are indebted to the ingenious Mr. Scheele and Mr. Lavoiſier for many excellent experiments and obſervations, which illuſtrate all that is here advanced concerning the matter of acids and pure air, although their concluſions concerning phlogiſton and fixable air are exceptionable, as is the uſe of the term oxygenous principle; for as empyreal air is common to many other bodies as well as to the chemical acids, and contributes to the formation of acid, only when it combines with and dephlogiſticates ſome particular kind of matter, the term oxygenous principle is applicable rather to this laſt than to the empyreal air, and it is only in this latter ſenſe that we want it.

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The marine acid eludes this analogy in no other particular than the ſtronger adheſion of the empyreal air, which we cannot ſeparate totally from the acid matter by any art yet diſcovered.

When dephlogiſticated marine acid is prepared, by mixing the nitrous with the common marine acid, the change produced in this laſt, is proportionate to the quantity of nitrous air which is always produced and emitted from the mixture, and conſequently to the quantity of pure air which is drawn by the marine acid from the nitrous: thus, dephlogiſticated marine acid made in this way, appears to conſiſt of marine acid ſaturated with empyreal air: and as the menſtrual power of every acid is abated by phlogiſton, and encreaſed by the acceſſion of empyreal air; ſo the fully aerated marine acid becomes a ſolvent of bodies which reſiſt the ordinary marine acid.

But independent of the intenſity which an acid ſolvent acquires by the acceſſion of air, the nature of metallic ſalts and calces, re-

requires that the ſolvent ſhould ſupply pure air abundantly; for, as this air is a neceſſary conſtituent principle of ſuch bodies, the tranſition from metal to ſalt or calx, can take place only as the menſtruum ſupplies air. Hence the efficacy of nitrous acid in calcining metals, and of the dephlogiſticated marine acid in diſſolving thoſe which reſiſt the common ſpirit of ſalt.

On theſe conſiderations, the marine acid does not yet appear as an exception to theſe notions of the agency of empyreal air in acids; nor will it afford any ſtronger objection to them, after the relation of the following phenomenon, which has not, to my knowledge, been noticed by any chemiſt.

The acid elaſtic fluid which iſſues when two pounds of mangancſe are mixed and diſtilled with two or three of ordinary ſpirit of ſea ſalt, may all, except a ſmall portion of phlogiſtic air, be condenſed in a ſolution of fixed vegetable alkali; and the

ſolution

ſolution thus impregnated, yields a conſiderable quantity of nitre, which cryſtalizes in the ordinary form, and detonates on red hot coals. The ſolution at the ſame time yields regenerated ſea ſalt.

It is to be obſerved, that manganeſe, by mere ignition, yields a great quantity of empyreal air with phlogiſtic air, as nitre does; and from theſe facts I conclude, that manganeſe contains nitrous acid or the principles of it in great quantity.

But red lead, and the calcis which ſerve to dephlogiſticate the marine acid, or to produce the change in it that is expreſſed by that word, alſo yield empyreal and phlogiſtic air by ignition; and I venture to prognoſticate, that nitrous acid will alſo be found in theſe caſes to make aqua regia with marine acid, excluſive of any change producible in the marine acid, by its union with empyreal air ſupplied from the calx.

Since air then is a conſtituent principle of all theſe, and neceſſary towards their acid character, and ſince the marine acid affords no contradictory inſtance, it is perfectly conformable tot he tenour of nature, that acetous aced ſhould contain air and poſſeſs the acid character, as much by virtue of this air as of any other matter of it; and as the union of a ſpecific matter with phlogiſton, makes ſulphur, but with air, vitriolic acid; or as the union of a certain kind of matter with phlogiſton, makes phoſphorus, but with air, phoſphoric acid; it is perfectly conformable to the known nature of acids, that the peculiar matter which diſtinguiſhes the acetous from other acids, ſhould attract phlogiſton, and in this union exhibit none of the acid characters, but appear as an oily or camphorous or reſinous ſubſtance, bearing ſtrong reſemblance, in divers properties, to ſulphur or phoſphorus, and a weaker ſimilitude only when it is overwhelmed with other matter, as it is in ſpirits, ſugar, gums, vegetables, foſſile coal, &c.; and finally that by receiving

empyreal

empyreal air, and depositing a part of its phlogistion, it should assume the acid characters that appear in acetous and other vegetable acids and in fixable air.

In speaking of sulphur, the subjects which claimed my chief attention, did not require that I should deviate from the common notion of its being composed of mere acid matter and phlogiston; but it is now expedient to declare that in a great number of experiments it appears to me that sulphur contains a small portion of our oily matter; and it is owing to the prevalence of the vitriolic acid, that the small quantity of fixable air, which is formed during the combustion of sulphur, does not shew itself by the test of lime water presented to the acid vapour.

Inductive reasoning is ever liable to error, but approaches the nearer to be conclusive, as the induction is more general, free from experimental exception, and applicable in the solution of phenomena, which do not appear to be explicable upon any other general ground. The matter of this ſection then is to be conſidered rather as a teſt and probation of my notions concerning acetous acid, fixable air, oil, and denſe inflammable air, than as an attempt towards explaining, in ſo ſmall a compaſs, all the phenomena that have been noticed on this occaſion.

The terms which have been hitherto uſed by chemical writers, are in many inſtances utterly unfit for theſe diſcuſſions, and render them as embarraſſing to the writer, as they may be obſcure to an inattentive or captious reader. The moſt correct of our writers have felt this inconvenience; and until the new notions are adopted by general conſent, philoſophers will rather continue to read with candour and indulgence, than encourage the premature introduction of new terms.

SECTION XI.

Experiments and Obſervations on Acetous Compounds Containing Volatile Alkali; and Reflections on the Varieties Analyſis and Products of divers Subſtances.

THE new and unexpected appearances which occurred to me in my firſt experiments on acetated volatile alkali, prompted me to repeat them often on a very large ſcale, and to vary them ſo much, that a full detail of all that relates to them cannot be introduced in this eſſay. I ſhall however give a ſummary view of the particulars which ſeem to be remarkable, either for their novelty or their aptitude to our purpoſe of tracing the principles and properties of acetous acid.

The water inherent in the concentrated acetous acid and in the rectified volatile alkaline ſalt of ſal ammoniac, is ſufficient to keep the neutral ſalt which they form, in perfect ſolution. But the neutral li-

 quor

quor ſhews a conſiderable degree of tenacity or ſpiſſitude, although it be colourleſs and tranſparent.

In neutralizing the acid with a cauſtic volatile alkaline liquor, conſiſting of ſix parts of water and one of mere alkali, the heat excited amounts to 150°; and as the alkali uſed is ſtronger the heat is greater. The denſe white fume which clouds the veſſels in which this mixture is made, conſiſts chiefly of neutral ſalt formed by the union of the acid vapour with the alkaline air which continually iſſues from the alkaline liquor when it is preſſed by the atmoſphere only, without any intermediate impervious body.

The uncommon duration of this denſe white vapour, or the ſlow condenſation of it into a neutral ſalt, implies a ſlow extrication of the proper fixed fire of the acid vapour and alkaline air in conſequence of the counteraction of contrary powers. For the parts of the acid and alkali tend to retain their reſpective portions of fire, though

though not ſo ſtrongly, as the attraction which draws them into contact, tends to exclude the greater part of it, as it happens in the formation of the neutral ſalt.

When the acid is neutralized by concrete mild volatile alkaline ſalt, of which it requires about an equal weight, the mixture is rather cooled than heated in temperate weather; ſhewing that the fixable air expelled from the alkali, engages and carries off with it, in a ſtate of combination, all the fire which otherwiſe would ſhew itſelf under its proper characters.

In diſtilling the neutral liquor, the firſt effect of the heat is to expel a conſiderable part of the alkali in the cauſtic and aerial ſtate, and the emiſſion of alkaline air continues until the liquor condenſed in the recipient, amounts to one fourth of the bulk of the charge.

This being drawn off and examined is found to conſiſt of water ſaturated with cauſtic volatile alkali, and impregnated with

with a part of the neutral ſalt which paſſes over along with the watery vapour, and of which the quantity is greateſt in quick diſtillation, but rarely exceeds one eighth of the neutral ſalt employed.

What follows, is for a moment neutral, but after a few drops, iſſues ſtrongly acid to the taſte, and conſiſts of water, acetous acid and neutral ſalt, a part of which cryſtalizes in the acid liquor, in cooling; and the product is of this kind, until the original charge is reduced to about half its bulk.

After this, the matter in the retort becomes neutral, and then concrete and cryſtaline by cooling: But by ſlow ſublimation it forms long ſlender flatted cryſtals terminating in ſharp points, ſhooting from the ſides of the veſſels in divers directions, irregularly piled on each other, but leaving large interſtices, and having no predominance of acid or alkali, to the taſte: Their hue is pearly white, and their length ſeldom

dom exceeds an inch and eight tenths, but is much leſs in haſty ſublimation.

The cryſtals which form towards the concluſion of the proceſs are not ſo white as the former, and the laſt of all are yellow, as if ſtained with oil. A very thin cruſt of fixed black matter always remains at the bottom of the retort, adhering firmly to it, and too ſmall in quantity to admit of ſtrict examination.

The white cryſtals have a peculiar ſmell, which differs conſiderably from that of the yellow, which is a little offenſive, and not unlike that of the ſmoak that iſſues during the combuſtion of ſucculent vegetables for potaſh. Thus the neutral liquor affords firſt the volatile alkaline odour, then the acid variouſly modified, then divers gradations in the ſmell of the neutral ſublimate, until it becomes empyreumatic.

When a weak ſolution of acetated volatile alkali in water, ſuch as may be made with acetous acid and the cauſtic volatile

ſpirit

ſpirit of ſal ammoniac, is ſlowly diſtilled, the volatile alkari ariſes in greater quantity, in the beginning of the diſtillation, and requires ſome water to be preſented in the receivers, in order to condenſe it, until a ſufficient quantity of watery vapour iſſues along with it from the charge. This alkalized water ſerves to neutralize the acid liquor which follows it, until the matter remaining in the retort becomes neutral. Although the greater part of the acetated volatile alkaline ſalt is thus decompoſed in diſtillation with water, yet a conſiderable ſhare of it may, in this proceſs, be dephlegmated, becauſe it is leſs volatile than water. But for this purpoſe the diſtillation muſt be very ſlow; otherwiſe the difference in volatility is not ſufficient to to prevent the ſalt from paſſing over along with the water.

The whiteſt cryſtals, heated again in cloſe veſſels, melt and ſublime into white cryſtals like the former, until the charge is reduced to about $\frac{1}{5}$ or leſs; then the ſublimate ſhews a yellowiſh tint, which

encreaſes

encreaſes to the end, and a black ſtain is left on the bottom of the retort, but nothing elſe that merits any conſideration in regard to the quantity of the charge.

The yellow cryſtals ſublimed again, afford a white ſublimate at firſt; but towards the middle of the proceſs the cryſtals laſt formed incline to yellowneſs, which encreaſes gradually in every ſucceſſive crop. The bottom of the retort ſhews a ſtain or film which blackens it, but not any quantity of fixed reſidue that the tendereſt balance could ſhew in weighing the whole charge.

About this period of the proceſs, the air in the veſſels becomes impregnated with fixable air mixed with a ſmall quantity of inflamable air, the cauſe of which will be conſidered hereafter.

The ſame phenomena occur in the fifth ſixth and ſeventh ſublimation of theſe cryſtals, by a very gentle and ſteady heat.

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The quantity of alkali predominating in the firſt product by diſtillation from the acetated volatile alkaline liquor, is greater as the diſtillation is more ſlowly conducted. In this caſe, that part alſo which diſtills with exceſs of acid is greater, and becomes ſtrong even to cauſticity about the time when the neutral dephlegmated reſidue is fit to concrete by cooling: and the portion of neutral ſalt, which riſes along with the alkaline and acid liquors, is, in this circumſtance, ſmaller than it ever is found in quick diſtillations.

Acetated volatile alkali, in its dry cryſtaline form, and perfectly purified by five ſublimations, melts at the temperature of 170, and ſublimes at 250 or thereabouts. It is combuſtible, very deliqueſcent, and impreſſes the tongue firſt with a ſenſe of coldneſs and then of ſweetneſs, which is ſoon followed by the kind of taſte that may be given by a mixture of nitre and ſugar, in which the ſweet is not to predominate over the mawkiſh taſte of nitre.

The

The laſt ſallow cryſtals obtained in the ſublimation of large quantities of acetated volatile alkali, have a taſte not unlike that of ſugar made brown and empyreumatic by fuſion, are odorous in their drieſt and coldeſt ſtate, and ſmell like the yeaſt of fermenting melaſſes.

As the neutral cryſtals of acetated volatile alkali may be heated and ſublimed repeatedly without loſing the alkali, and the ſolution of the ſame ſalt undergoes a partial decompoſition in diſtillation, the firſt product being alkaline, the ſecond acid, and the dephlegmated remainder neutral; water appears to be the chief agent in this decompoſition, and to have conſiderable effect in weakening the union of the acid and alkali.

This acetated volatile alkaline ſalt copiouſly precipitates nitrous ſolution of ſilver, by virtue of compound affinities, and a conſiderable predominance of acetous acid will not prevent this effect. This fact demands confiderable attention, in the ordinary ufe of the folution of filver, to detect marine and vitriolic impregnations.

The falt compofed of acetous acid and volatile alkali, can not be decompofed by lime as it is reprefented in Bergman's Tables.

A fmall portion of lime combines with the falt, and expells a little of that part of its volatile alkali which is fo weakly retained in the acetous falt, that it iffues, as we have obferved, even before the water, in the diftillation of folutions of this falt.

Every ounce of the neutral falt combines with a penny-weight of the lime, and the liquor holding a falt of three chemical principles, viz. acetous acid, volatile alkali, and lime, may be evaporated to the confiftence of olive oil, without depofiting any lime or lofing any of the faline ingredients. The tafte of the neutral falt is totally altered by this affociation with lime; and the lime may be recovered by

precipitation

precipitation with fixed alkali, and will then form ſelinite with vitriolic acid; ſo that it undergoes no alteration.

Magneſia operates in a ſimilar manner, with the acetated volatile alkali; and when the ſalt of three principles, whether holding lime or magneſia, is gradually heated in cloſe veſſels, the chief part of the acetated volatile alkali ſublimes, white at firſt and afterwards coloured; but that part which is detained in the earthy matter until it ſuſtains a greater heat, is partially at firſt, and towards the end totally decompoſed, when the heat is increaſed. The volatile alkali mixes with the oily and watery product, which is ſimilar to that of acetous acid in other experiments; and the quantity of fixable and inflammable air, is proportionate to that of the acid detained, until it ſuſtains that heat which alone is in all caſes ſufficient for the converſion of acetous acid to water, oil, fixable and inflammable air.

In this treatment of acetated volatile alkali, the ſmell and taſte are incredibly varied, with every change of proportion and of the degree of heat which the principles of it undergo.

The reſiduary lime or magneſia in ſuch diſtillations, has all the appearances and properties of the like reſidues from acetous calcareous ſalt or acetated magneſia.

The facility with which volatile alkali eſcapes, in a very weak heat, from acetous acid, when their union is weakened by water, implies that the like decompoſition may more eaſily be effected when the acid is held by matter which attracts it more forcibly than water, and the alkali meets fixable air or other matter, ſo that the extrication of the acid from the alkali may be effected by compound affinities: and on this ground we may account for the product of volatile alkali in the diſtillation of muſtard, opium, tobacco, and of divers other vegetable ſubſtances, whoſe decoctions and infuſions are neutral, and which certainly contain all the principles of acetous acid, becauſe they yield fixable air, inflammable air, and oil in diſtillation.

The ſame properties of acetated volatile alkali, and its extreme volatility in diſtillation coction or ſublimation, aſſiſts us in explaining the changes which, to the ſurprize of the ableſt chemiſts, are produced by the coction or diſtillation of divers vegetables, particularly thoſe arranged in the Materia Medica under the head of Antiſcorbutics, and lead us to a true analyſis which ſhall exhibit the quantity of this volatile ſalt or of its principles, as well as that of the earthy watery and fixed ſaline matter already diſcovered in vegetable bodies. We ſee that the purer oily matter of vegetables, conſiſting of phlogiſton and the acid principle of acetous acid, and which ſpontaneouſly exhales and diffuſes itſelf in air, maintains a great part of its volatility and odoriferous quality even in conjunction with volatile alkali; and nothing but experiment is wanting to ſhew volatile alkali, or other matter, acting a

 ſimilar

ſimilar part in the compoſition of the oily ſublimates reſembling camphor, or benzoin flowers, and in the more ſaline ſublimates from vegetable ſubſtances, all of which abound with our oily matter.

The appetence of fire which we conſtantly experience in fixable air, and the conſequent facility with which it is expelled from bodies by fire; the like appetence of the phlogiſtic and acid matter of acetous acid, and the incapacity of even fixed alkalies to retain them under the impreſſion of fire; the eſcape of acetous acid during the coction of the ſolution of acetated vegetable alkali; and in a word the recited properties of acetated volatile alkali, point out to us the laws of attraction, or ultimate reaſon in natural philoſophy, by which we are to account for the alkaline, acid, neutral, aerial, and fixed products, ſo diſſimilar in property and quantity, which the very ſame ſubſtances have been found to yield in coction, fermentation, putrefaction, diſtillation *per-ſe*, and in other proceſſes.

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The ſingular relation of acetous acid to volatile alkali, lime, and magneſian earth, whereby three or more of theſe may be held in the ſame ſalt, is to be conſidered only as one of many inſtances of the capacity of this acid to form ſaline bodies uncommonly compounded, inſeparable by the uſual arts of cryſtaliſation, and partially or totally convertible by heat. This is to be enumerated amongſt the cauſes which produce that wonderful variety in ſubſtances, every one of which abounds with the principles of acetous acid; and it is alſo to be ranked amongſt the impediments to a compleat analyſis of vegetable bodies.

But although volatile alkali, induces the varieties and appearances lately mentioned in acetous compounds, it is to be obſerved, that it is not more effectual than water in impeding the converſion of the acetous acid by fire; for ſo much of the acetated volatile alkali, as is duly igitned in any proceſs, undergoes the ſame decompoſition that happens to other acetous compounds; and nothing has yet been diſcovered that can prevent this converſion of the acetous acid by fire.

There is no difficulty, therefore, in accounting for the ſtain left on the retort in ſubliming acetated volatile alkali; for the moats and duſt which it muſt neceſſarily catch from the air, in charging, or from the retort, however clean it may appear, added to the matter abraded from the glaſs during the operation, and aided by the attraction of the veſſel to the ſalt, are ſufficient to detain a ſmall quantity of the acetous compound, until it acquires the heat in which every fixed matter becomes ſtained with the reſiduary oily matter of ignited acetous acid. This notion of the phenomenon is ſupported by the appearance of fixable air mixed with a little inflammable air, at this period of the proceſs.

The varieties of ſmell and taſte which an acetous ſalt exhibits in conſequence of variations in the proportions of its principles, ſerve to ſhew, that in the analyſis of vegetable and other bodies which differ greatly in ſmell, taſte, and appearance, we are not to expect as great a difference in the kinds of matter of which they are compoſed, but are more likely to find in thouſands of them, little or nothing more than a certain earth, and alkali, and phlogiſton with one or both of the gravitating principles of fixable air. This expreſſion to preclude the conſideration of the matter of fire, may be conveniently uſed, until we find by direct experiment that this matter gravitates.

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SECTION XII.

Preparatory Experiments on red Lead, Lithrage and Lead, and Eſtimate of the matter imbibed or expelled in calcination and reduction.

WITH a view to the following experiments with calces of lead and acetous acid, I made very accurate aſſays of lithrage and red lead, the particulars of which I omit, as it will be ſufficient for my preſent purpoſe to ſtate the following facts.

The ordinary red lead of our manufactories, muſt be ſlowly dried in a heat not exceeding 150 degrees, before the weight can be aſcertained with accuracy. After this the quantity of water that can be obtained from it in a greater heat is very inconſiderable, even when the heat is ſufficient to expel ſome of the fixable, phlogiſtic, andempyreal air of this calx. For experimental uſe, it is therefore ſufficient to expoſe it

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in thin ſtrata to the heat above mentioned for five or ſix hours; but then it ought to be ſifted through a fine lawn ſieve, in order to ſeparate the half calcined lead that is generally to be found in it; becauſe, ſome particles of the metal, during the calcination, incruſt themſelves with the calx, and eſcape the action of the air, and the ſparks and coal duſt blown from the fire, fall on the red lead during the proceſs, and revive it ſuperficially wherever they meet it duly heated. For this reaſon the quantity of lead found in the beſt aſſays of ordinary minium is variable, and is always greater than that which the ſame red leads affords, after it has been duly ſeparated from the uncalcined part.

7680 grains, or 16 ounces of red lead, yield 6835.2 grains of lead in reduction; and therefore 844.8 grains are, in this tranſition, expended in the aerial and aqueous products of the proceſs; provided the reduction is effected by the mere abſtraction of the matter which was imbibed during the calcination, and does not require any ſupply of phloſton towards thevivid lead. But if any of the phlogiſton employed in the revival, is imbibed by the metallic earth and retained in the lead, then the quantity of aerial and watery matter expelled from 7680 grains of minium muſt exceed 844. 8 grains, by this quantity of phlogiſton. Whether any, or what quantity of phlogiſton is expelled in the calcination of lead, is a queſtion which cannot yet be anſwered with preciſion. According to the opinion of Mr. Lavoiſier, who doubts of the exiſtence of phlogiſton, the calcination is effected by the mere entry, and combination of empyreal air with the whole matter of the lead, and the reduction muſt then be conſidered as the reſult of the mere abſtraction of this air. Mr. Kirvan, and moſt other able philoſophers, incline to the opinion that the greater part, though not the whole of the phlogiſton, is expelled in the calcination, and muſt be ſupplied again from a phlogiſtic ſubſtance during the reduction.

After due conſideration of the facts on which theſe different opinions have been founded,

founded, and of my own experiments, I am persuaded that there is no good reason for doubting the existence of phlogiston in this and other calcinable metals: but contrary to the opinion which I had entertained for many years, I am forced to adopt a new motion, that the air imbibed during the calcination of lead, unites with the phlogistic and earthly matter, but expells little or none of the former, and that little or none of the phlogiston used in the reduction of minium, enters into, or contributes to the weight of the lead, but that it is almost wholly expended in combining with the pure air of the calx and facilitating the expulsion of it.

Mr. Cavendish's experiments shew, that the gravitating matter of light inflammable air is phlogiston; and the elasticity of this fluid, as well as the fire emitted during the union of its gravitating matter with empyreal air to form water, shew its affinities to fire and empyreal air, and its aptitude to render those bodies combustible, that hold it in combination. But as lead, like other metals, is combustible, though

not

not in ſo high a degree as zinc, and as it yields inflammable air in ſolution, though not ſo copiouſly as zinc or iron, it manifeſtly contains phlogiſton.

In the calcination of mercury in contact with emp. air, the latter is imbibed to a quantity equal to $\frac{1}{8}$ of the weight of the mercury, as Mr. Lavoiſier has ſhewn; but during the calcination nothing is emitted, and by the expulſion of the emp. air, and without any aid of phlogiſtic matter, the mercury recovers its former metallic condition. Mercury in theſe experiments, and the noble metals in others, are found capable of imbibing air and becoming calciform without loſing any phlogiſton; and all the appearances that have been thought to indicate the expulſion of phlogiſton, during the ſolution of mercury and of the perfect metals, are fallacious, ſince we know that the abſtraction of the pure air from the acid employed, leaves the remainder of it in that ſtate which we have been uſed to call phlogiſtic, if not truly phlogiſticated.

Lead diffuſed in quick-ſilver, was found by Dr. Prieſtly to phlogiſticate atmoſpheric air, and this is now known to imply that the lead imbibed empyreal air. Lead thus deprived of its aggregation, as it is in fuſion, and freely expoſed to pure air by agitation, becomes calciform whilſt it imbibes the air, but emits nothing that glaſs can retain, and conſeqnently nothing of the phlogiſtic kind.

Omitting other analogies and arguments, I am now to obſerve that I have frequently endeavoured to calcine lead in contact with pure empyreal air, and to trace the phlogiſton which is generally ſuppoſed to be expelled. But inſurmountable difficulties attended every attempt, and this one particularly, that the calx firſt formed precluded the air from the melted lead. So far however as the experiment ſucceeded, I found an abſorption of air, but no emiſſion of any thing like inflammable air, nor of any notable quantity of water, which was indeed the expected product.

The freer and more rapid combuſtion of zinc, indicates a greater quantity of phlo-

giſton

giſton than is held in lead; and yet in burning zinc with pure air, I could never diſcover, by any water ſeparable from the calx, that its phlogiſton was diſengaged or expelled.

I do not depend on the accuracy of theſe experiments, ſo far as to affirm that no water is formed during the calculations of lead or of other metals, and that none of the phlogiſton is detached in conſequence of the formation of water; and I am aware, that in the calcination of thoſe metals, particularly iron, which contain ſome of our oily matter, ſome fixable air is formed. But ſince we are not authoriſed by general analogy to ſuppoſe that lead loſes any notable quantity of its phlogiſton by the calcination, ſince even in ſolution it yields very little inflammable air; ſince it does not detonate with nitre; and yet in the experiments above mentioned certainly imbibe air without yielding any quantity of phlogiſtic matter or water that might deſerve notice in the following experiments; I

ſhall

ſhall not heſitate in aſſuming the lead of 7680 grains of minium at 6835, 2 grains, and the other matter at 844, 8 grains: and I may on the ſame grounds conſider the reduction as effected by the mere expulſion of aerial matter, without inducing any conſiderable error in the following eſtimations.

Dr. Prieſtley has ſhewn that lead expoſed to the heat neceſſary for its compleat fuſion, becomes lithrage in conſequence of the emiſſion of a certain quantity of fixable air and of purer reſpirable air than that of the atmoſphere. We now expreſs the fact in other words and ſay, in the tranſition to lithrage, red lead yields fixable air and empyreal air mixed with phlogiſtic air in quantities which vary in the ſucceſſive portions.

As the relative quantity of fixable air is greateſt at the commencement of the proceſs, and gradually becomes leſs as that of the empyreal air encreaſes; and as this and other metalic calces are always found to hold empyreal air more obſtinately than fixable or phlogiſtic air, under ignition, we may ſafely conclude that well fuſed lithrage retains as much, or very nearly as much empyreal air along with a ſmall quantity of phlogiſtic air, as it exceeds its proper lead in weight.

By the aſſay I find that 7680 grains of lithrage yield 6924 of lead; and for the reaſons above mentioned, this quantity of lead, together with 756 grains of empyreal and plogiſtic air are ſufficient to compoſe 7680 grains of lithrage. According to this proportion, 6835. 2 grains of lead belong to 7581. 5 of Lithrage, as well as to 7680 grains of read lead, which has been found to contain this quantity of lead; and therefore the quantity by which 7680 grains of red lead exceed 7581. 5 grains of lithrage, in both of which the weight of lead is the ſame, is the quantity of aerial matter which is acquired in the tranſaction of the lithrage to red lead, or of that which is expelled by fuſing the red lead until it becoms lithrage, viz. 98. 5 grains, grains, of which I find

24 or leſs to be fixable air, and about 74.5 to conſiſt of empyreal air mixed with the phlogiſtic.

Before I diſmiſs this ſubject I muſt obſerve that lithrage by due calcination forms red lead, and that I have ſeen this proceſs conducted on the great ſcale of a manufactory. I alſo can affirm from experience, that by diſtillation in glaſs veſſels, we cannot diſcover all that red lead emits during the fuſion and tranſition into the form of lithrage, becauſe the veſſel is always corroded and perforated, before the central parts of the charge can be compleatly melted. When an earthen retort is uſed, the red lead corrodes it and expels ſome aerial matter from it, and the part of the lithrage which inſinuates itſelf into the pores of the veſſel, being heated more than the reſt of the charge, and employed in vitrification, loſes ſome of the proper air of lithrage. In trials of this kind, the quantity of aerial matter expelled during the fuſion of red lead into lithrage, is much greater than in the former, and exceeds that which we have ſtated by eſtimation from the beſt aſſays.

On due conſideration of the nature of acids, and of the agency of empyreal air in metallic ſolutions and ſalts, and of the capacity of Phoſphorus to imbibe empyreal air; the experiments of Mr. Sage for the revival of metals from diluted ſolutions by phoſphorus, will be found to exhibit nothing repugnant to thoſe notions, although he gives a different interpretation of the phenomena. On the contrary we may diſcover in theſe precipitations the ſtricteſt conformity with our doctrine, ſince thoſe are the moſt conſpicuous and compleat, that are effected in the ſolutions of the perfect metals which loſe no phlogiſton by ſolution, or in the ſolutions of imperfect metals which yield the ſmalleſt quantity of inflamable air or phlogiſton in ſolution. Mr. Pelletier's experiment for precipitating reguline arſenic from the ſolution of acid of arſenic, by paſſing inflammable air through it, ſhews the agency of phlogiſton and empyreal air in the humid way, but does not prove that the privation

of

of the phlogiſton reduces arſenic to an acid, or that the addition of freſh phlogiſton is neceſſary to reſtore the arſenic to the reguline ſtate; much leſs does it ſerve to ſhew that lead in calcination loſes its phlogiſton, or that calx of lead muſt imbibe and retain the phlogiſton of a reducing flux, before it can form lead.

In like manner Dr. Prieſtly's ingenious experiment for reviving the calx of lead by light inflammable air, does not prove that any of the inflammable air unites with he lead, but ſhews that the phlogiſton of the inflammable air, ſerves to extricate the empyreal air of the calx; and from the experiments of Mr. Cavendiſh on empyreal and inflammable air, as well as thoſe which follow, this extrication ſeems to be effected by the converſi on of the empyreal air into water, by means of the phlogiſtic matter of the inflammable air.

I mention theſe particulars in order to excite chemiſts to a reviſion of the phenomena on which the doctrine of phlogiſtication and dephlogiſtication of metals has been

 founded,

founded, and to caution them againſt a precipitate condemnation of the notion that lead loſes little or no phlogiſton in calcination, and that its calx imbibes as little from any phlogiſtic body during the reduction. If it were neceſſary to the purpoſes of our preſent enquiry that I ſhould expreſs my opinion, all that happens to lead during the calcination and reduction, I ſhould ſay, the empyreal air imbibed in calcination, is retained along with the proper phlogiſton of lead, in a ſtate approaching to that of water, in the calx; and when bodies which can engage this empyreal air, and form it into water or fixable air, are duly adminiſtered, it is detached, and leaves the proper phlogiſton of the lead to be retained in its former ſtate of combination. But if this is not ſtrictly true in regard to the whole of the phlogiſton of lead, it approximates the truth ſufficiently for every purpoſe of our preſent enquiry.

SECTION XIII.

Distillation of two pounds of red lead with half a pound of acetated vegetable alkali.

HAVING found by former experiments that concentrated acetous acid, whether directly mixed with a triple or quadruple quantity of lithrage or red lead, or applied to these by mixing the acetated vegetable alkali with them, revived the whole of the lead, and yielded at the same time a great quantity of dense inflammable air along with the fixable; and wishing to know, first, the result of trials with smaller quantities of the acetous acid, and then the smallest quantity with which the reduction can be effected without waste of inflammable air or phlogistic matter, I proceeded as follows.

Two pounds averdupoise=13999 grains of sifted red lead and half a pound,=3499·75 of my driest acetated vegetable alkali, were ground together, and distllied in a Chelsea retort. A more compact vessel was not necessary, because I did not intend to measure the water, nor aim at any great accu-

racy

racy in regard to the quantity of elaſtic fluids. The meaſures in which theſe were received from the neck of the retort which was lengthened with a ſlender glaſs tube, contained each 8. 5 cubic inches, and the quantity of atmoſpheric air included in the neck of the retort and glaſs tube, was ſo ſmall as not to be regarded in ſo great a charge. The following table exhibits the meaſured bulks of the recent elaſtic fluids expelled during the proceſs. The firſt column ſhews what meaſures were actually examined; the ſecond repreſents the number of cubic inches of elaſtic fluid emitted at any period after the preceeding meaſure had been examined: the third ſhews the bulk of fixable air contained in the correſponding meaſure of the mixed airs, and the fourth ſhews the cubic inches of phlogiſtic and inflammable air which iſſued along with the correſponding quantity of fixable air. It is to be obſerved however, that the two laſt columns are formed on the ſuppoſition that the proportions of the elaſtic fluids to each other in the meaſures which were examined, did not differ much from thoſe of the intermediate portions which were not tried.

Meaſures.		*cub. in.*		*cub. in. of fix. air.*	*Cub. inches of inflammable and phlogiſtic air.*	
Firſt 3	=	25.5	contained	6	19.5	inflammable air with ſome phlogiſtic
the 5th	=	17		8	9	inflammable with ſome phlogiſtic.
10th	=	42.5		21	21.5	inflammable with ſome phlogiſtic.
20th	=	85		42	43	————
40th	=	170		85	85	————
100th	=	510		255	255	————
120th	=	170		113	57	inflammable air with ſome phlogiſtic air,
180th	=	510		340	170	————
250th	=	595		396	199	————
300th	=	425		282	143	------------
350th	=	425		282	143	inflammable with leſs phlogiſtic air
400th	=	425		212	213	inflammable with ſtill leſs phlogiſtic air

These laſt portions iſſued ſlowly, and the retort was now heated to redneſs throughout.

450th	425	212	213	inflammable air with more phlogiſtic
455th	42.5	21.5	21	almoſt all phlogiſtic, and iſſuing very ſlowly
460th	42.5	28.5	14	almoſt all phlogiſtic, iſſuing very ſlowly

The heat of the charge was now ſufficient to compleat the reduction of red lead

465th	42.5	30.5	12	all phlogiſtic, iſſuing quicker
470th	42.5	33.5	9	all phlogiſtic, iſſuing ſlow
475th	42.5	34.5	8	all phlogiſtic, iſſuing very ſlowly.
Total 475	4037.5	2402.5	1635	

Some watery vapour iſſued at every period of the proceſs, excluſive of that which was quickly diſtilled at the commencement from the acetous ſalt; and of the mixed inflammable and phlogiſtic airs, about 200 cubic inches were phlogiſtic, and 1435 inflammable air.

When I had thus expelled 475 meaſures or 4037. 5 cubic inches of elaſtic fluid, and could obtain no moreby a heat ſufficient for the compleat reduction of red lead, and continued for more than 15 minutes, I quickly drew away the fire, in order to prevent the waſte of lead or eroſion of the retort. When all was cooled, I found the alkali of the acetous ſalt lying over the lead, and taſting cauſtic, but yet containing 174 grains of fixable air, and perhaps a little of the matter of the retort which the lithrage might have corroded before it was revived. The lead which formed a maſs at the bottom, together with the globules that adhered to the ſides of the retort and could be collected, weighed 12439 grains; but as the lead ought to have weighed 12459. 1 according to former experiments, the ſmall particles that could not be detatched and collected, weighed about 20 grains.

The lead of the minium employed in this experiment, being 12459. 1 grains, the whole of the aerial matter of the red lead was 1539. 9; and allowing 43 grains for

for fixable air, and 30 at the utmoſt for phlogiſtic air, for reaſons which will appear hereafter, the empyreal air of the minium amounted to 1466. 9 grains. The fixable air of the meaſures which were examined, was neceſſarily imbibed into lime liquor, and thus meaſured before it had cooled to the mean temperature, at which it would meaſure leſs by a ſeventh, and weigh 1043. 372 grains. This and 174 grains retained in the alkaline ſalt make 1217. 372 grains of fixable air, to which the red lead alone contributed 43 grains; and thus the product of fixable air, from the acetous ſalt and empyreal air of the red lead, appears to be 1174. 372 grains.

The art of meaſuring the phlogiſtic air that was mixed with the inflammable air will be ſhewn hereafter; here I am only to obſerve, that the utmoſt weight of the phlogiſtic air of this experiment did not exceed 37. 7 grains, of which the minium alone might have yielded 30 grains, and the acetous ſalt furniſhed the remainder.

The

The 1535 cubic inches of inflammable air were not of the heavieſt kind; but at a medium of the heavy which iſſued firſt and the lighter which was laſt expelled, the whole weighed about 300 grains.

In the acetous ſalt employed, the acid and water amounted to 1739. 396 grains, and the utmoſt quantity of acid, abſtracted from water, was ſcarcely 869. 698 grains. But of this quantity 7. 7 grains were of phlogiſticated air and 300 grains were expended in making inflammable air, and only 561.998 grains contributed to the formation of 1174. 372 grains of fixable air produced from the the acid, and the empyreal air of the red lead.

As the experiment and menſuration could not, for the foregoing reaſons, go further than to approximate the truth, I contented myſelf with the following inferences.

As the quantity of the acid which contributed to the formation of fixable air, ſcarcely amounted to 561. 9 grains, and the quantity of fixable air produced from this

and

and the empyreal air of the red lead, was 1174. 3 grains, this laſt air muſt have entered into the compoſition of the fixable air and formed one half of its maſs and weight, or a great deal more. But ſince the portion of acid thus expended, could yield, by mere ignition and without the acid of the empyreal air of the red lead, a great quantity of fixable air, by reaſon of the empyreal air which is a conſtituent principle of acetous acid; the empyreal air muſt have made near $\frac{2}{3}$ of the weight of the fiaxble air found to have been formed of the mere acid and the empyreal air of the red lead.

As the gravitating matter of empyreal air makes about $\frac{2}{3}$ of the weight of the fixable air, and as 1466. 9 grains of empyreal air could not have been expended in making 1174. 3 grains of fixable air, of which a part is certainly derived from the mere acetous acid; and as none of the empyreal air iſſued unaltered, and the whole of it was expended in forming new compounds; a conſiderable part of it muſt have been employed in the

the formation of water, which iſſued in vapour at every period of the proceſs.

In this water we trace, in conformity to the experiments of Mr. Cavendiſh, the phlogiſton of that part of the acetous acid which was expended in the fixable air; and then infer that phlogiſton is not a neceſſary conſtituent principle of fixable air.

Finally, ſince there was a great ſurplus of inflammable air, but none of empyreal air, it is certain that the quantity of acid employed could have reduced much more red lead, and engaging more empyreal air, could have aſſiſted in forming a much greater quantity of fixable air and water.

SEC-

SECTION XIV.

Diſtillation of eight ounces of lithrage, with two of acetous acid previouſly dephlogiſticated conſiderably by vitriolic acid; and formation of fixable air, from acetous acid and empyreal air, without ignition.

BY repeated digeſtions and diſtillations of acetous acid, from oil of vitriol, I endeavoured to diveſt it of ſuperfluous oil or phlogiſtic matter, as far as might be done without decompoſing the acid totally. Eight ounces averdupoiſe=3499.75 grains of lithrage were ground with four of water, and two ounces=874. 94 of this acid were gradually added.

A ſlight intumſcence enſued, and ſome acid vapour and elaſtic fluid eſcaped; but this laſt was chiefly the interſticial atmoſpheric air of the powdered lithrage, and the quantity of the former was too ſmall to be regarded on this occaſion. The heat did not

not exceed 96 degrees; for the acid was added in ſucceſſive portions, and much weakened by the water previouſly mixed with the lithrage.

In the courſe of two hours, during which the mixture was frequently agitated and ground in a porcelain mortar of Mr. Wedgwood's excellent manufacture, the lithrage became white, and indeed formed white-lead. A Wedgwood retort, which could retain elaſtic fluids, or any charge, better than the common Chelſea retorts, was charged with the mixture, ſo that none of it was left adhering to the neck; and my aparatus for ſaving the condenſible vapour and the elaſtic fluids, being fitted to it, the diſtillation was carefully conducted, but at the ſame time as quickly as the menſuration of the elaſtic fluids would permit.

When the atmoſpheric air included in the retort and receivers, was almoſt all expelled, along with the four ounces of water uſed in the mixture, the ſubſequent products were meaſured thus.

cub.

cub. in.	fixable.	phlogiſtic	
firſt 8	4	4	————————
next 8	6	2	————————
8	7	1	————————
16	15	1	phlog. and inflam.
16	15	1	————————
16	15	1	————————
16	15.2	8	————————
16	15.2	8	inflammable with
16	15.2	8	ſome phlogiſtic.
16	15.2	8	————————
8	7.6	4	————————
80	75.6	4.4	————————
80	75.6	4.4	————————
80	75.6	4.4	————————
80	77.8	2.2	————————
80	77.8	2.2	inflam. with
80	77.8	2.2	very little of the
80	77.8	2.2	phlogiſtic.
80	75.6	4.4	————————
80	75.6	4.4	————————
80	71.2	8.8	all imflam.
80	71.2	8.8	————————
40	35.6	4.4	————————
total 1064	997	66.4	————————

The

The laſt portions iſſued very ſlowly, and the emiſſion ceaſed when the charge was heated ſufficiently for the reduction of lithrage; and in the middle and latter meaſures, the elaſtic fluids carried with them ſome aqueous vapour.

Neither the firſt, nor any ſubſequent portion of the water collected during this diſtillation, ſhewed any ſign of acid; but it was ſtrongly impregnated with ethereal oil of acetous acid, ſome of which floated diſtinct on it, and ſome was expended in greaſing the Recipients. By a trial to be related hereafter, I found that the quantity of oil was not leſs than 10 grains.

The quantity of water was greater than was employed in the experiment, including that of the acid; but the encreaſe was not meaſured, becauſe an earthen retort admits of no accuracy in this particular, unleſs it be of true porcelain well glazed.

On opening the retort, a large maſs of lead was found at the bottom, which with the globules collected from the ſid s, weighed

3125 grains; and from the appearanc of the ſmaller globules which I could not detach without waſte, it was manifeſt that the whole of the lead was revived, and that if there had been no waſte, it would have weighed 3155. 242 grains, which is the whole quantity of lead obtainable from the 3499. 75 of lithrage; the aerial matter of which amounts to 344. 506 grains. By firing the mixture of inflammable and phlogiſtic air, with as much empyreal air as was barely ſufficient for the combuſtion of the inflammable part, and meaſuring the bulk of the reſiduary phlogiſtic air, I found that the 66. 4 cubic inches of the mixed airs conſiſted of 20 of phlogiſtic air and 46. 4 of inflammable air.

Deducting 7. 54 grains which is the weight of the 20 cubic inches of phlogiſtic air, from 344. 506 the weight of all the aerial matter of the lithrage, we find the empyreal air of the lithrage to be 336. 966 grs.

Of the inflammable air which iſſued at the commencement of the proceſs, a cubic inch weighed 260; but a cubic inch of that which was laſt expelled by the greater heat, weighed leſs than 2. grs. and by the noticed decreaſe of the ſpec. gravity; I was aſſured that the mean weight of 23 grains in a cubic inch might be aſſumed in computation, and that the 46. 4 cubic inches weighed 10. 672.

The inflammable and phlogiſtic airs were meaſured at the due temperature; but the fixable air, being meaſured as it iſſued warm from the extremity of the recipient, contracted in cooling to the mean temperature, by one fifth of its bulk, and in this laſt ſtate would weigh 454. 632 grains.

According to Mr. Kirvans eſtimation; the mere acid is to the concomitant water of concentrated acetous accid, nearly as 19. to 49: But I have reaſon think we are leſs liable to error in ſtating them as 20 to 48; and by this rule, the acid employed, amounting to 874. 94, contained of mere acid and its phlogiſton 257. 335 grains, and of water 617. 604 grains.

As the inflammable air and oil were derived from the acetous acid alone, and weighed 20. 672 grains, the quantity of the mere acid otherwiſe expended was 236. 663 grains.

The phlogiſtic air inflammable air and oil being thus accounted for, the empyreal air of the lithrage, weighing 336. 966, with 236. 663 of the acetous acid abſtracted from water, were expended in the formation of 454. 632 grains of fixable air, and a quantity of water not aſcertained by direct menſuration, but which muſt be nearly 118. 997 grains, becauſe this and the fixable air make the weight of the empyreal air and efficient acid laſt mentioned.

Now it is to be conſidered that the acetous acid, when by mere ignition a part of it is converted into inflammable air and oil, yields a great quantity of fixable air, which for the reaſons formerly ſtated, is proportionate to the quantity of empyreal air which the acid contained. In this caſe, the quantity of fixable air producible from the mere acid,

acid, by heat alone, is not leſs than one third of its weight; and therefore, without any aid of the empyreal air of the lithrage, the whole of the acid employed in the experiment, may be ſaid to have yielded out of its proper matter 85. 778 grains of fixable air, and the quantity of this laſt which was not merely extricated, but formed with the aſſiſtance of the empyreal air, was about 368. 854 grains; for this with the laſt mentioned proper fiaxble air of the acetous acid, makes the whole of the fixable air obtained.

Deducting the inflammable air and oil, the quantity of the mere acid otherwiſe expended, appears to be 236. 663 grains; and deducting from this the proper fixable air of the acetous acid 85. 778 grains, we find the quantity of the mere acetous acid, which was expended in the formation of fixable air with empyreal air, and in the formation of water and revival of the metal, to be 150. 885 grains. Thus it appeared that the utmoſt quantity of acid matter derived from the acetous acid, in 368. 854 grains of the fixable air did not amount to 150. 885 grains, but fell ſhort of this weight by as much as the proper fixable air of the acid exceeded 85.77 grains, and by the whole quantity of phlogiſton expended in the formation of water. Deducting this phlogiſtic matter, which could not be leſs than 17 grains, the acid matter in 368. 854 grains of the fixable air, did not amount to 133.885 grains. Hence it was inferred that when the acid matter of acetous acid is employed *in exceſſive quantity* to form fixable air with the empyreal air of lithrage, the fixable air may conſiſt of a little more than one part of the acid matter combined with two of the empyreal air. By a more accurate eſtimate of the fixable air taken at 85 grains, it is moſt probable that the proportions would be found to be accurately two to one, provided fixable air, like other acids, may not ſubſiſt with various proportions of the empyreal air.

In this view of the ſubject, I could not perceive that the lithrage imbibed any conſiderable quantity of phlogiſtic matter from the acid employed; for admitting that in the fixable air formed, the quantity of matter derived from the acetous acid, was no more than one third of the weight of that fixable air, and consequently only 122 grains instead of 133 as it was stated; no more than 11 grains of the acid employed remain unaccounted for; and it is by no means probable that the phlogistic matter appertaining this quantity, could have produced any considerable effect on eight ounces =3499·75 grains of calx of lead, if it had been really dephlogisticated during the calcination. It was therefore inferred that lead loses little or none of its phlogiston in calcination, and imbibes none during the reduction; but that in this latter process, the calx of lead is divested of the empyreal air together with the small portion of phlogistic air which it imbibes in the calcination.

From some of the phenomena of this experiment, I suspected that the acetous acid could be totally converted into fixable air and water, by combining with empyreal air, and without the aſſiſtance of fire. I therefore triturated this acid diluted with a quadruple quantity of water, with lithrage in various proportions; and found that the quantity of mere acid that was barely ſufficient, by frequent trituration, to make the lithrage look white in the courſe of two days, united with the empyreal air of the lithrage, and in the new forms of fixable air and water, formed with the lead a calciform maſs, which after being duly dried and powdered, yielded no acetous acid either in diſtillation or in ſolution in vitriolic acid, but afforded fixable air in abundance, and mixed only with a very ſmall quantity of inflammable air.

The weight of the fixable air was always twice greater than that of the mere acid abſtracted from water; and in ſome experiments it was ſtill greater. Thus it appeared that fixable air may be made of its conſtituent principles, without the aid of ignition, when they meet unreſtrained by any counteracting power; and that when acetous vapour or denſe inflammable air meet empyreal air without forming fixable air, the counteracting agent is no other than the matter of fire, which cauſes the repulſion of their parts, and conſequently the elaſticity of theſe fluids.

SEC.

SECTION XV.

Reduction of lithrage and red lead by acetous acid, and the products.

TO prevent the waſte of acetous acid during its action on lithrage, I poured two ounces troy=960 grains of the ſtrongeſt concentrated vinegar recently procured from acetated vegetable alkali and retaining all its phlogiſton, into four ounces=1920 grains of diſtilled water and adding this gradually to 14 ounces=6720 grains of lithrage, I ground them together. The heat of the mixture did not exceed ſeventy degrees, and little or nothing was emitted, except the intereſtitial air of the lithrage powder, which cauſed a ſlight intumeſcence.

The mixture was at firſt quite ſoft; but after being ground for about half an hour in a porcelain mortar, it grew ſtiff, and in two hours it was ſufficiently dry to be cut

into

into ſlices which were rather friable than plaſtic. The water then ſeemed to have been engaged in the ſaline maſs, as the proper water of its cryſtals.

Having obſerved in former experiments that this acid required a good deal of time to combine intimately with the lithrage and to form a maſs reſembling white-lead in colour, I left it cloſely covered for 24 hours, and then found it ſo hard and dry as to require ſome force in cutting out that part which had not formerly been looſened from the mortar. The whiteneſs which appeared in the ſuperficial parts on the firſt action of the acid, gradually improved as the maſs dried, and at laſt was almoſt equal to that of white-lead, with ſcarcely any appearance of the lithrage colour. It was then diſtilled in a Wedgwood retort, and the products being meaſured and examined at ſhorter intervals than thoſe expreſſed in former experiments, were ſtated thus.

The fixable air weighed	658	grains
The phlogiſtic air	20	
The inflammable	3	

No

No oil appeared in this experiment, and the quantity of water was not aſcertained, becauſe in the quick emiſſion of the elaſtic fluids a great quantity of the watery vapour was wafted along with them, and more was condenſed in the meaſures than remained in the recipient.

In the revival of lithrage by means of acetous acid, charcoal, and other ſubſtances, I had repeatedly obſerved that the quantity of phlogiſtic air was not as that of the phlogiſtic matter employed, but as the quantity of the calx reduced to lead, and concluded that the phlogiſtic air proceeded from the lithrage chiefly. By experiments of this kind I am now perſuaded that in the calcination or ſcorification of lead, the calx imbibes not only the empyreal air, but ſome part of the phlogiſtic air of the atmoſphere, and that the quantity of this laſt varies in different parcels of lithrage, from ten grains in 16 ounces to 20 or more, which laſt was the quantity in this diſtillation.

In the retort I found a mafs of lead covered with fmall grains and globules of of the fame metal, without any perceptible admixture of unreduced lithrage, all together weighing 6034. 5 grains. The lead which adhered in thin plates and fmall globules to the fides of the retort, and could not eafily be detached or weighed, was eftimated at 24 grains; becaufe this quantity with the former makes 6058. 5 grains, the proper lead of the 14 ounces of lithrage.

By the rule formerly eftablifhed the aerial matter difcharged during the reduction of 14 ounces of lithrage, amounted to 661 .5 grains; and as 20 of this quantity confifted of phlogiftic air, the empyreal air weighed 141. 4 grains. But as none of this efcaped unaltered, it muft all have been expended in the formation of fixable air and water; and as none of the acetous acid efcaped unaltered, that part of it which was not neceffary towards the formation of water, was expended in the fixable air; and the greater part, if not all the phlogifton of the

acetous

acetous acid, except that of the inflammable air which eſcaped, appears to have been employed in the formation of water. As this acetous acid was of the ſtrongeſt kind, and neither aerated nor deprived of any oily matter by diſtillation with vitriolic acid we cannot, conſiſtently with the experiment of the laſt ſection, eſtimate the quantity of mere acid and phlogiſtic matter at leſs than 293 grains, or the water at more than 667. But as three grains of the former were expended in inflammable air which eſcaped the lithrage, 290 grains of mere acid and 641. 5 grains of empyreal air were expended in the formation of 658 grains of fixable air, and of water whoſe quantity was 273, provided no part of the phlogiſtic matter of the acid entered into the lead.

This quantity of water required 39 grains of phlogiſton, which is almoſt a ſeventh part of the acid; and about one fourth of that part of the acid which forms inflammable air by mere ignition: and in this view of the ſubject we find no reaſon for ſuppoſing that any of the phlogiſton of the acid entered the lead or fixable air, or that

it

it was otherwiſe expended than in the formation of water.

If the quantity of water amounted to 273, not leſs than 234 grains of empyreal air, were expended in the formation of it, and the remainder of the empyreal air, viz. 407. 5 grains, was employed in the formation of fixable air, the quantity of which would be 611. 2 grains, provided the empyreal air be to the other matter of fixable air as two to one. But the whole of the fixable air produced was 658 grains, if not more; and this exceſs is to be imputed to the fixable air which the acetous acid alone is capable of producing when ignited, by reaſon of that empyreal air which is a conſtituent principle of this as well as of other acids.

In the haſty diſtillation of recent mixtures of lithrage and acetous acid, I have often had a greater waſte by the eſcape of inflammable air, and ſome part of the lithrage remaining unreduced, whether the quantity of acetous acid was greater or leſs

than

than is here repreſented; and in repeated experiments I have obſerved that the intended expenditure of the acid was beſt effected, by ſinking the bottom of the retort an inch or two in the ſand-bed of a reverberatory furnace, and thus cauſing the fire to act from above downwards.

Having mixed concentrated acetous acid duly diluted with water, with red lead in various proportions, and heated theſe mixtures in the manner already deſcribed, I found the products and phenomena to differ from thoſe lately mentioned in nothing but what might have been expected from the greater quantity of phlogiſtic and empyreal air contained in red lead with the portion of fixable air already noticed.

The quantity of inflammable air was ſmalleſt when the weight of the red lead was to that of the acid as 16 to 2, and then did not exceed five grains. The greateſt quantity of lead reduced by two ounces of the acid did not exceed eleven ounces and a quarter; and whenever more red lead

was

was uſed than the acid could reduce, the ſuperfluous part formed lithrage by the fuſion, and emitted the quantity of fixable phlogiſtic and empyreal airs which it uſually yields in the tranſition to lithrage, as we have ſtated in the 12th ſection.

In theſe experiments it always appeared that much more acid was neceſſary towards the revival of a given weight of lead from red lead, than was required in precipitating the ſame quantity from lithrage: and as the calx which contained moſt air and leaſt lead, required the greater quantity of acid for its reduction, I had this additional ground for the opinion that the acetous acid acts rather by facilitating the expulſion of aerial matter from ſuch calces, than by contributing any thing conſiderable towards the maſs or weight of the revived lead.

It is ſcarcely to be doubted that this doctrine is applicable in other metalic reductions effected by fuel or ſubſtances containing our oily or coaly matter; and that the quantity of empyreal air in any calx, may be determined by the quantity of fixable air and water emitted during the fusion with fuel previously divested of fixable air and water.

SEC-

SECTION XVI.

Distillation of lithrage with acetous acid, with a view to the mensuration of the water formed, as well as to the other products.

HAVING observed that water thrown on a hot earthen retort of the kind usually sold in London, is absorbed into its whole substance; and that the part of the water which penetrates towards the internal surface, is expelled through it, into the annexed receivers, where it may be condensed; I could not rely on any experiments made in such retorts, in regard to the aqueous products of the charges, since it was to be apprehended that the water, impelled by the excentric pressure of vapour and elastic fluids, might be expelled through the retort much quicker than it is found to enter when poured on the heated vessel: and as the more compact retorts of Mr. Wedgwood might be suspected of imbibing some water, and perhaps of tranſmitting it, be-cauſe they were not glazed; I made the following experiment, with a view chiefly to the water producible in conſequence of the union of the empyreal air with the phlogiſtion of the acid.

I mixed an ounce=480 grains of my ſtrongeſt concentrated acetous acid with four ounces=1920 grains of water, and this I ground ten ounces 4800 grains of lithrage. Having uſed the precaution of tying a bladder over the veſſel in which the mixture was made, I was aſſured that there was no waſte by the evaporation of the acid, or the emiſſion of any elaſtic fluid different from the interſticial air of the lithrage, which the water alone would have expelled; and I could not perceive that the mixture was diſpoſed to drink in any of the atmoſpheric air included in the bladder.

In this confined ſituation, it became conſiſtent enough in 7 or 8 hours, to be formed into pellets; but to make them paſs

freely

freely and without waſte through the long and ſlender neck of a glaſs retort, I left them expoſed to the air for 24 hours, in which time they dried ſufficiently, and loſt 168 grains of the water employed. The glaſs retort, well coated, was filled to the helm with theſe pellets, and heated on the ſand bed of a reverberatory furnace, from which its neck extended two feet, before it entered the receiver, to which it was well faſtened with glue lute. The atmoſpheric air of the veſſels is not regarded in the following account, becauſe it paſſed off with the watery vapour, before any conſiderable quantity of fixable air was emitted.

cub. in.	fixable	phlogiſtic
1ſt. 25	13	12 with very little
next 25	19.5	5.5 ditto [inflam.
25	21.5	3.5 ditto
25	22.1	2.9 ditto
25	23.3	1.7
25	23.3	1.7 ditto

At this period the retort was not in the leaſt reddened in any part.

cub. in.	fixable	phlogiſtic
25	23.7	1.3 ditto
25	24.1	9
25	24.1	9 ditto
25	24.2	8
25	24.2	8 with more in-(flam.
25	24.5	5
25	24.6	4
25	24.6	4

The mixed airs as they iſſued ſmelled like acetous Ether or nit Ether, and water trickled ſlowly all the time from the neck of the retort, but there was no appearance of oil.

25	24.6	4 ditto

The retort was not yet reddened.

25	24.6	4 ditto
25	24.6	4 ditto
25	24.8	2
25	24.8	2 ditto
25	24.9	1

The retort was now red hot, and water iſſued ſlowly.

25	24.9	1
25	25	0

The

The retort was hotter than would be neceſſary for the fuſion of lithrage, during the emiſſion of the two laſt meaſures, which was very ſlow; and no more could be procured by an encreaſe of heat until the retort was ready to melt, when I quickly withdrew the fire, and left the veſſels to cool gradually. The elaſtic fluid left in them was fixable air and meaſured fifty cubic inches, which with the former quantity make 600 cubic inches.

Of this bulk, the fixable air, which was meaſured as it iſſued, made 564. 9 cubic inches; but at the mean temperature it would have meaſured 484. 2 cubic inches, weighing 275. 994 grains.

Of the phlogiſtic and inflammable air, meaſured at the mean temperature, after the fixable air was withdrawn from them, there were 35. 1 cubic inches at leaſt, and by the method already deſcribed, I found the bulk of phlogiſtic air to be about 30. 1 cubic inches, weighing 11. 347 grains, and that of the inflammable about 5 cubic

 inches

inches weighing at the utmoſt 1. 305 grains. The diſtillation was ſlowly and ſteadily performed, and laſted four hours in the month of Auguſt 1783, from the time when the fixable air appeared until the fire was withdrawn.

The water condenſed in the recipient was not in any ſenſible degree oily, or impregnated with acetous acid, but ſmelled, not unpleaſantly of the inflammable air. It was quite limpid, and including ten grains which adhered to the veſſels, it weighed 2107 grains. Of the water mixed with the acid and lithrage, only 1752 grains were included with the charge, becauſe 168 grains had exhaled. In the acid employed the water did not exceed 335 grains, the mere acid being eſtimated at 145 grains in 480 of this concentrated acetous acid. The whole of the water therefore included with the charge amounted to 2087 grains; which is leſs than the quantity found in the receiver, by twenty grains. From this alone it appears that a conſiderable quantity of water was actually formed, and conſequently that ſome of the empyreal air of the lithrage, with phlogiſton from the acetous acid, was expended in this way: And the emiſſion of water, during the whole of the proceſs, and long after the charge had ſuſtained a heat ſufficient for the fuſion of lithrage, cannot be ſatisfactorily accounted for on any other ground. But it is further to be obſerved, that a great quantity of watery vapour was wafted out of the receiver, along with the warm elaſtic fluids; for whenever I applied a cold and dry veſſel to receive them, it was bedewed, and plainly ſhewed that much more water was really formed in the manner already mentioned, than was aſcertained by direct menſuration.

On opening the retort, I found ſome of the pellets retaining their figure; but thoſe which lay contiguous to the veſſel and were heated more, were altered in this reſpect. The former exhibited in a diſtant view, a ſallow green colour; but on cloſer inſpection, this appeared to be compounded of the dark blue of minute globules of lead, interſperſed with the yellow of lithrage.

The

The other pellets ſunk into a maſs conſiſting of large globules of lead bedded in melted lithrage. A more compleat fuſion of the lithrage and ſubſidence of the lead, in the heat above deſcribed, thus appeared to have been prevented by the expenditure of the fire in the formation of the elaſtic fluids continually emitted from the charge.

The whole maſs, carefully ſeparated from the glaſs, weighed 4560 grains, and therefore the lithrage which was reduced to lead yielded 240 grains of aerial matter; for this lithrage by the mere expoſure to the like heat was found to yield little or nothing.

Of the 240 grains, 11. 347 may be conſidered as the weight of phlogiſtic air; and 228. 653 grains, is the quantity of empyreal air.

Out of 145 grains of mere acid, 1. 305 were expended in inflammable air; but in conſideration of the ſmell of the water, we may ſtate the expenditure at 2 grains; and

then

then it will appear that from 143 grains of mere acid and 228. 6 of empyreal air, 275. 9 of fixable air were formed, and the water compofed at the fame time was not lefs than 95. 7 grains, although fcarcely a fourth part of this quantity was faved in the recipient.

According to this eftimation 82 grains of the empyreal air were expended in forming water, and the remainder of the empyreal air=146. 6 grains, was employed in the formation of fixable air. But if the materials of fixable air be to each other in the proportion laft ftated, this quantity of empyreal air was expended in forming 219. 9 grains of fixable air, and the acid furnifhed the remainder, by virtue of its proper empyreal air.

Now, in comparing the products of different experiments, and allowing duty for inaccuracies, we find ftrong grounds for fufpecting that the proportion of empyreal air to the other matter in fixable air, is variable; and that this, like other acids, may fubfift

with

with different doſes of empyreal air, and may vary in this reſpect, according to the circumſtances under which it is formed. This is, at leaſt, a conſideration not to be neglected by future experimenters.

S E C-

SECTION XVII.

Regulization of Arſenic by acetous acid.

THE flame of burning regulus of arſenic, and the facility with which it enters into combuſtion in a moderate heat, impreſſed me with the opinion that it contains more phlogiſton than is held in lead or metals which exhibit no flame or vivid ſparks during the calcination, and that if there is any loſs of phlogiſton during the calcination of either, that of the arſenic muſt be greateſt. In this caſe, the calx of arſenic would not only require a greater quantity of phlogiſticated acid for its reduction to the reguline ſtate, but would yield a ſmaller proportion of fixable air; ſince the fixable air which is formed by the aſſiſtance of empyreal air in reductions, is five or ſix times greater in quantity than that which the acetous acid alone can yield by ignition: But if, on the other hand, the calx of arſenic

ſhould

ſhould be found to require but a ſmall quantity of acid, in order to form the combuſtible regule; and if the quantity reduced to the reguline ſtate ſhould be proportionate, rather to the quantity of empyreal air expelled from it, than to the quantity of phlogiſton derived from the acid, this would ſhow that this regule loſes little or none of its phlogiſton during the combuſtion, and receives as little in the reduction.

With theſe views, and not without expectation of ſhewing the great quantity of empyreal air which this regule imbibes during the deflagration, without any conſiderable loſs of phlogiſtic matter, and alſo of proving the greater affinity of empyreal air to the acid of fixable air, than to that of arſenic, I made the following experiment.

I mixed 1749. 88 grains of my acetated vegetable alkali, whoſe acid and water weighed 869. 715 and its alkali 880. 165 grains, with 6999. 5 grains of cryſtaline white arſenic, and gradually heated the mixture in a glaſs retort placed in a ſand pot and connected with the uſual apparatus for meaſuring the elaſtic fluids. Rejecting the atmoſpheric air of the veſſels, I ſtated the product thus.

	cub. in.	fix. air	phlogiſtic
firſt	9	1.8	7.2
next	9	4	5 phlogiſtic
	9	4.5	4.5 ditto
	9	5.5	3.5 ditto
	9	6	3 ditto
	9	6.5	2.5 ditto
	9	6.8	2.2 ditto
	9	7.2	1.8 ditto
	9	7.6	1.4 ditto
	9	8	1 ditto
	45	43	2 ditto
	45	43.5	1.5 ditto
	90	88	2 ditto
	90	88.5	1.5 ditto
	90	88.5	1.5 ditto
	90	88.6	1.4 ditto
	90	88.4	1.6 ditto

90	87	3	ditto
90	85.5	4.5	phlogiftic
90	84.5	5.5	ditto with very little inflam.

Water ftill continued to trickle from the retort, and rolled down in round globules over a thin coat of reddifh brown arfenical fublimate, which lined the lower part of the neck of the retort through its whole length, and was afterwards found to be regulus of arfenic chiefly. The elaftic fluids carried with them a denfe white vapour which foon condenfed into white, and partly into reguline arfenic; but ftill fo much arfenic was permanently retained, that the elaftic fluid fmelled horribly arfenical.

90	84.3	5.7	ditto
90	84.3	5.7	
90	84.2	5.8	ditto
90	84.1	5.9	ditto
90	84	6	ditto
90	84	6	ditto
90	84	6	ditto
90	84	6	ditto

90	84	6	ditto
90	84	6	ditto
450	420	30	weakly inflam.
90	84	6	ditto.

The emiſſion of air being very ſlow, although the heat was encreaſed until the retort was red hot, very little more was to be expected, and I withdrew the fire to ſave the retort and its contents.

Of the air left in the retort and recipients 33. 6 were fixable air and 2. 4 cub. inches were phlogiſtic mixed with a very ſmall quantity of inflammable air. The ſum of the cubic inches of warm airs

was	2376
of warm fixable air	2221. 9
the phlog. and inflam. air at the mean temperature meaſured	154. 1
the fix. air contracted in cooling by $\frac{1}{8}$ of its bulk and meaſured	1851. 584
weighing	1055.403 gr.
The phlogiſtic air weighed	56 grains
and the inflammable air about	2 grains.

The water ſaved in the recipient weighed 460 grains, although the acetous ſalt, which was dry, could not have yielded more than 430. 7 grains. Of the water formed during this proceſs, we may ſay that about 30 grains were ſaved: but a much greater quantity was manifeſtly waſted away along with the fixable air, which iſſued warm, and depoſited moiſture, as often as the ſucceſſive portions of it were tried by cooling them in dry veſſels.

In the retort I found 3900 grains of reguline arſenic ſublimed and adhering near the helm. The neck of the retort was alſo lined with the like matter in a powdery form, which with the ſmall portion blown forth into the receiver, weighed 37 grains: and the whole of the reguline arſenic did not exceed 3937 grains.

The maſs remaining at the bottom of the retort ſhewed a granuilar texture, like that of fine ſugar, and had a pearly whiteneſs. It appeared to have been in a ſtate

of

of perfect fusion, and tasted like neutral arsenical salt. The retort suffered some superficial erosion at the bottom. I seperated this saline arsenical substance into two parts; one consisting of the calx of arsenic unaltered, the other of such arsenical salt as I had often made by digesting white arsenic with caustic vegetable alkaline lixivium; for it became liquid in a boiling heat, plastic and repoy in a weaker heat, and quite hard, like glue, in cooling.

Thus it appeared that the acetous acid was expended in reducing a great part of the arsenic to the reguline state, and in extricating its aerial matter, which the quantity of fixable air shewed to be of the empyreal kind. But as no empyreal air was emitted uncombined; and as the residuary arsenic, whether we consider the portion combined with the alkali, or that which was only detained, remained unaltered; we may conclude that this part contributed little or nothing towards the elastic fluids expelled from the charge, and that 3937 grains of regule of arsenic, in the transition to calx of arſenic or white arſenic, imbibe about 56 grains of phlogiſtic air, and as much empyreal air as is neceſſary for forming 1055. 4 grains of fixable with the quantity of acetous acid here employed. This quantity was eſtimated at 439 grains of mere acid abſtracted from water; but as two grains were expended in inflammble air, only 437 had been employed in forming 1055. 4 grains of fixable air.

In conſideration of the fixable air alone, 3937 grains of regulus yielded 618. 4 grains of empyreal air; but in conſideration of the water formed, we muſt allow a much greater quantity of empyreal air to white arſenic, together with the proportion of phlogiſtic air already mentioned. If the proportion of aerial to reguline matter, were the ſame in white arſenic and in red lead, the regulus in this experiment could have held or yielded only 486. 5 grains of air.

This looſe compariſon of the neceſſary quantities of acetous acid, and of the aerial matter extricated during the converſion of white arſenic into combuſtible regulus, and calx of lead into metal, and the expenditure of the phlogiſton in forming water, in both inſtances, are ſufficient to ſhew that the alteration is effected in one as well as in the other by the abſtraction of aerial matter; ſince the expenditure of the phlogiſtic body is as the quantity of aerial matter extricated, and not as the weight of the reguline or metallic maſs produced in theſe experiments. For theſe reaſons, the gradations we obſerve in the combuſtion of metals, regulus of arſenic and phoſphorus, depend rather on the quantity of the gravitating matter of empyreal air, which they reſpectively imbibe, and of the fire conſequently extricated, than on any circumſtance of dephlogiſtication. Finally, ſince acetous acid duly applied is as effectual in the formation of phoſphorus and ſulphur, with their reſpective acids, as in that of regulus of arſenic, and in metallic reduction, the attraction of empyreal air to the acid matter of fixable air, is of the ſtrongeſt kind, and muſt render the decompoſition of fixable air excedingly difficult.

SECTION XVIII.

Products of 16 ounces of lithrage and one of charçoal, during the reduction.

SELECTED pieces of well burned charcoal of oak were put into a deep earthen veſſel called a long pot, and covered to the depth of an inch with powdered charcoal. The pot was well cloſed with a luted cover, and kept two hours in a heat ſufficient to melt ſilver. Then it was placed in ſuch a manner that the powder might remain red hot for ſome time after the pieces next the bottom had cooled. This was done, in order to perfect the charring, to make the lower pieces imbibe only the proper inflammable air of charcoal, ſince they muſt imbibe ſomething in cooling to prevent their abſorbing atmoſpheric air, and eſpecially to prevent any of the empyreal part of atmoſpheric air from entering into them.

ſome

Some of theſe pieces being briſkly reduced to fine powder in a covered mortar, 480 grains of this powder were immediately mixed with 7680 grains of powdered lith-rage, and inſtantly charged into a coated glaſs retort, for in other experiments I had obſerved that ſuch charcoal, more freely and longer expoſed to the air in powder, drinks in water from the atmoſpheric air, and that 480 grains of the powder could imbibe four or five grains from the air in half an hour.

The retort being placed in a reverbera-tory furnace, with its bottom ſunk two inches in the ſand, the fire was made to act ſlowly on it from above downwards. The products during the reduction, exclu-ſive of the dilated air of the veſſels, were noted as follows, the fixable air having been meaſured warm, the reſt at the mean tem-perature.

cub. in.	fix. air	phlogiſtic.
17	5	12 ditto
17	11	6 ditto

cub. in.	ſixable	phlogiſtic
17	16.5	0.5 ditto
17	16.7	0.3 dirto
17	16.8	0.2 ditto
17	16.8	0.2 ditto
17	16.8	0.2 ditto

Thirty grains of water are now ſaved in the recipient.

17	16.8	0.2 ditto

The retort is almoſt red hot.

17	16.8	0.2 ditto
17	16.8	0.2 ditto
85	84.6	0.4 ditto

The Retort is red hot throughout.

85	84.7	0.3 ditto

Water drops ſlowly from the nozzle of retort, and the quantity now collected in the recipient is about 40 grains.

85	84.9	0.1 ditto
85	84.9	0.1 ditto

The

The elaſtic fluids now iſſue very rapidly.

cub. in.	fix air	phlogiſtic
85	84.9	0.1 ditto
85	84.8	0.2 ditto
85	84.8	0.2 ditto

The elaſtic fluids iſſue by pulſes and the watery vapour is viſible at its exit from the nozzle of the retort.

85	84.7	0.3 ditto
85	84.7	0.3 ditto
85	84.6	0.4 ditto

The elaſtic fluid continues to iſſue rapidly, and to carry watery vapour, and more water is collected in the recipient, amounting in the whole to ſeventy grains or more.

85	84	1	containing a little inflam.
85	83	2	equal parts of phlog. and inflam.
85	79	6	almoſt all inflam.
85	74	11	ditto
85	68	17	ditto
34	22	12	all inflam.

In

In this laſt is comprehended the elaſtic fluid left in the veſſels. Although the heat was greatly augmented, the emiſſion was now ſo ſlow, that nothing more could be expected by any degree of heat that the retort could ſuſtain; I therefore withdrew the fire. The cubic inches of hot fixable air were 1407. 6; of phlogiſtic and inflammable airs 71. 4, of which 44 were inflammable and 27. 4 phlogiſtic air.

By cooling ſeveral portions of the fixable air, at different periods of the proceſs, and allowing . 57 gr. to each cubic inch of it in the temperate ſtate, I eſtimated the weight at 650 grains. The 27. 4 cubic inches of phlogiſtic air weighed 10. 329 gr. But as it had been exceſſively agitated with water unuſually thickened with lime, I ſuſpected that ſome of it was entangled in the lime, and had eluded the menſuration. It is therefore expedient to ſtate the phlogiſtic air at 20 grains, ſince this will better accord with other experiments, and will create the leaſt error here.

The inflammable air meaſuring 44 cubic inches, was eſtimated at ſeven grains, for it was lighter ſpecifically than any that had been expelled from acetous compounds.

The elaſtic fluids, as they iſſued, ſmelled agreeably of fixable air, and of nothing elſe until the inflammable air appeared, which imparted its peculiar ſmell to the fixable air that accompanied it. There was not a particle of oil; and eighty grains of water were ſaved in the recipient, although a conſiderable quantity was certainly wafted away along with the fixable air; for dry meaſures were ſoon bedewed with it in cooling.

When the helm of the retort was broken off, the globular part with its coating appeared like an earthen veſſel well glazed on the inſide. The glaſs was not much corroded, but was indented, near the upper part of the charge, by maſſes of lead: Theſe incircled a much greater quantity of the metal, divided into grains and drops of va-

rious

rious ſizes, by the interpoſed charcoal powder.

Having carefully ſeparated the lead and charcoal from the glaſs, I found their weight to be 7200 grains, of which the charcoal made more than half the weight of the quantity employed; but how much more I could not aſcertain ſatisfactorily, becauſe a little of the lead adhered to that which I ſeparated mechanically, and ſome of the charcoal followed the lead and was waſted in the fuſion of it. Another circumſtance contributed likewiſe to prevent my knowing the exact weight of the reſiduary charcoal; for it had imbibed, in cooling, ſome of the fixable air remaining in the receiver, and perhaps a little atmoſpheric air.

As the charcoal expended in this operation was certainly much leſs than half an ounce, = 240 grains, and I had found by other experiments ſimilar to that which is next to be related, that 7680 grains of lithrage require only 213. 7 of charcoal

for

for the reduction, I have no doubt that this laſt was the quantity expended.

The quantity of earth and alkali in 213. 7 of charcoal being too ſmall to claim our attention in this place; and the phlogiſtic air of the lithrage, and the inflammable air of the ſuperfluous charcoal, having contributed nothing to the other products; we may ſay the empyreal air of the lithrage, weighing 736 grains, together with 213. 7 grains of expended charcoal, produced 650 grains of fixable air, and a quantity of water greatly exceeding that which was ſaved: and ſince the weight of the efficient charcoal and of the empyreal air, making 949. 7 grains, exceeds that of the fixable air by 299. 7 grains, this laſt appears to have been the quantity of water formed, though not all condenſed, in this operation.

To form this quantity of water 42. 8 grains of phlogiſton are neceſſary, according to the admirable experiments of Mr. Cavendiſh; and as there is no reaſon for ſup-

ſuppoſing that the charcoal contained more than this quantity, which is $\frac{1}{5}$ of its weight, of phlogiſton, no part of this laſt appears to have entered the lead, or contributed to the fixable air, or to have been otherwiſe expended than in the formation of water. By this computation, no more than 171 grains of the expended charcoal, was employed in the formation of the fixable air; and as 256. 8 grains of the empyreal air, were expended in the water, no more than 479. 2 grains contributed to the fixable air; and in 650 grains of it, the empyreal air was to the acid matter as 479. 2 to 170. 8 or as 2. 8 to 1.

This proportion differs conſiderably from that which was computed, in regard to the fixable air from acetous compounds; but whether the difference is owing to an erroneous eſtimation of the mere acid in acetous acid, and of the quantity of fixable air which it can yield by heat alone; or to a capacity of the principles of fixable air to unite in different proportions, when they meet in different circumſtances, or with a great exceſs of one or the other, I cannot yet determine.

SECTION XIX.

Products in the reduction of lithrage and calx of mercury with the smallest quantity of charcoal.

IN order to avoid the inconveniences arising from an excess of charcoal, and to find the greatest quantity of lithrage that can be reduced by a known weight of it, as well as the produce in fixable air and water, I made the following experiment with 120 grains of charcoal, and 7680 grains of lithrage, prepared and mixed in the manner already described.

A small retort, well coated, and charged to the helm with the mixture, was placed in an earthen vessel, and surrounded with as much sand as filled the space between them, and was sufficient to cover the helm and a part of the neck.

The retort thus ſecured, was made to ſtand high above the bed of the furnace, in order that the fire might act equably around the charge, and fuſe the lead into one ſolid maſs, of which no part ſhould be loſt, although the glaſs ſhould be penetrated by it. Theſe meaſures were alſo intended to produce a ſteadier emiſſion of the elaſtic fluids than happened in the preceeding experiment.

Rejecting the atmoſpheric air of the veſſels, I meaſured the products of the charge gradually heated, thus.

cub. in.	fixable air.	phologiſtic air	
firſt 18	5	13	
next 18	13.2	4.8	phlog air with $\frac{1}{10}$ of emp. air.
next 18	15.6	2.4	phlog. with $\frac{1}{6}$ of emp. air.
18	17.4	0.6	phlog. with $\frac{1}{5}$ empyreal air.
18	17.8	0.2 ditto	
18	17.9	0.1 ditto	
18	17.91	0.09	phlog. with $\frac{1}{4}$ of emp. air.

After the 32 cubic inch of emitted airs, ten grains of water were ſaved in the recipient, and after this laſt meaſure about 25 grains were ſaved.

54	53·73	0.27 ditto
90	89·55.	0.45 ditto
90	89·55	0.45 ditto

Each of theſe portions in paſſing in large columns into the common air through water, ſhewed watery vapour ſuſpended in them, and bedewed the veſſels in which they were cooled.

90	89·55	0.45	ditto
90	89·55	0.45	ditto
90	89·55	0.45	ditto
90	89·55	0.45	ditto
90	89·55	0.45	ditto
90	89·55	0.45	phlog. with $\frac{1}{3}$ empyreal air.
36	35·8	0.2	equal parts of theſe.

In

In this last is included the air left in the vessels whilst they were hot. Towards the end, the emission gradually decreased in velocity, and it ceased at the last cubic inch, although the heat had been more than sufficient for the reduction of litharge, for 15 minutes. The fire was now withdrawn.

The sum of the cubic inches

Of hot fixable air was,	910.74
Of temperate phlogistic air	23.09
Of temperate empyreal air	2.17

The water saved amounted to 49 grains, although a great quantity was certainly carried off by the fixable air, notwithstanding every endeavour to moderate and equalize the heat.

The fixable air, when it had contracted by cooling to the mean temperature, was estimated at 384 grains, at the rate of .57 gr. to a cubic inch; but I strongly suspected that the specific gravity of this fixable air was not so great, and consequently that the abſolute weight was leſs than 384. The phlogiſtic air weighed 8.704 grains, and as ſome part of it proceeded from the unreduced litharge, which preyed on the veſſel, and yielded ſome of its empyreal air, the phlogiſtic air appertaining to the revived litharge may be ſtated at 8 grains. The empyreal air weighed 0.911 grains.

In the retort I found a cake of litharge, a quarter of an inch thick, vitrified into an opaque yellow ſlag with part of the glaſs of the retort, and the eroſion extended in ſome parts through the coating as far as the ſand; but yet the toughneſs of the ſlag prevented all tranſpiration in this quarter, for the reſiſtance to the paſſage of the elaſtic fluids into the meaſures, was only an half inch column of water.

Under the litharge I found a maſs of lead, and a few large grains which had bedded themſelves in the glaſs, all together weighing 3888 grains. There was not the ſmalleſt veſtige of charcoal; and as the earthy

earthy and alkaline parts of it, were inconſiderable, and were vitrified in the maſs already mentioned, they did not retain any aerial matter of charcoal; for by repeated experiments I have found that ſuch vitreous maſſes, and even the fineſt flint glaſs, retain nearly the whole of the empyreal air of litharge, but cannot, in perfect fuſion to fluidity, hold any conſiderable quantity of fixable air.

Not a particle of inflammable air was expelled in this experiment, becauſe the litharge, in the degree of heat neceſſary for expelling inflammable air from charcoal, furniſhed empyreal air enough to unite with the inflammable air, and contained a redundancy of air beyond what the inflammable matter of the charcoal required. A little of this ſurperfluous air was expelled by the great heat to which the litharge was expoſed and in the act of vitrification, for when litharge forms glaſs with clay or ſand, it parts with a little of its emp. air.

As the lead weighing 3888 grains, yielded 424. 513 of air, of which eight may be accounted phlogiſtic, the empyreal air of the reduced lithrage, amounted at leaſt to 416. 513. gr. and this quantity with 120 grains of charcoal, making 536. 513 gr. afforded ſcarcely 384 grains of fixable air, and a quantity of water, which was not leſs than 152. 513 grains, but might have been more. Towards the formation of this water, from 22 to 24 grains of phlogiſton were neceſſary, which laſt is a fifth part of the weight of the charcoal, by this approximation we account for as much phlogiſton as the charcoal can well be ſuppoſed to contain. As the water engaged at leaſt 130 grains of empyreal air, if not more; the fixable air engaged about 287 of empyreal air, and derived about 96 or 97. 5 of acid matter from the charcoal. Thus the empyreal air ſeemed to be to the acid matter in this fixable air, nearly as 3 to 1; and if the weight of the fixable air had been taken at leſs than 57 grains in a cubic inch, or its abſolute weight had not been overrated by aſſuming a greater ſpecific gravity than it really poſſeſſed

possessed, the proportion of the empyreal air to the other matter of *this* fixable air would be perhaps accurately 3 to 1. Regarding all this only as an approximation to the truth, and trusting that the errors cannot be so great as the difference between 3 and 2, I am of opinion that fixable air formed in these circumstances, contains more empyreal air than is in the ordinary sort, and that whilst some specimens of fixable air have but $\frac{2}{3}$ of their weight of empyreal air, others have $\frac{3}{4}$ and differ in specific gravity; the circumstances which afford this latter proportion being, strong heat, and redundancy of empyreal air.

As empyreal air is a common principle of fixable air and of water; and as it actually makes water with the phlogiston of charcoal, at the same moment that the like empyreal air engages other matter of charcoal, and makes fixable air with it, there is no ground for the opinion that phlogiston is a necessary principle of fixable air; but all our experiments conspire to shew, that it consists of the gravitating matter of empyreal air, combined with that acid principle which is common to acetous acid, oils, coal, vegetables, denſe inflammable air, &c.

But as every acid may ſubſiſt partially phlogiſticated and imperfectly impregnated with empyreal air, ſo may fixable air; and it is to be expected that future experiments will ſhew conſiderable varieties in fixable air, ariſing from theſe cauſes, and diſcoverable by the ſpecific gravity, the menſtrual powers, and the different bulks imbibed by water.

By the quantity of elaſtic fluids and water, and the total expenditure of the charcoal in the formation of them, it is now pretty certain that litharge loſes its aerial matter, but receives nothing in the reduction, and conſequently loſes none of its phlogiſton in calcination: It is therefore highly probable that all calcinations and reductions of metals are effected in the ſame way.

In

In the reduction of mercurius calcinatus by charcoal, I have found that water is formed as well as in the reduction of litharge, beſides the fixable air which Mr. Lavoiſier had noticed. But this fixable air did not appear to contain more than $\frac{2}{3}$ of its weight of empyreal air: and in this inſtance it is certain that no part of the phlogiſton of the charcoal is neceſſary towards the metallization, becauſe the empyreal air can be expelled, and the mercury may be revived, without charcoal, and by heat alone.

It is impoſſible for a man who muſt employ the greater part of his time in the duties of a profeſſion which allows no vacation, to ſuperintend ſuch experiments as thoſe on which the foregoing eſtimations have been founded, from the commencement to the termination; and being thus circumſtanced, I think it neceſſary to obſerve, that ſome part of every one of theſe experiments and menſurations, was committed to the care and fidelity of my operator. If any unintentional errors on his part ſhould happen to conſpire to the encreaſe of mine, my eſtimations may be very incorrect in regard to the proportions; but I have no reaſon to doubt that the notions of metallic reduction, of the principles of fixable air and denſe inflammable air, and of all that does not depend on accurate proportion, will abide the teſt of future experience.

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SECTION XX.

Phenomena of the combuſtion of denſe inflammable air, and of ſubſtances containing the acetous and phlogiſtic principles; and menſuration of the products.

IN order to fire large charges of inflammable air without waſte or danger, I provided glaſs jars that were ſtrong enough to bear an exploſion equal to that of a piſtol charge of gunpowder. The cylindrical cavity of each was ten inches in length and one in diameter; and at the diſtance of $\frac{2}{10}$ of an inch from the bottom, two holes were drilled at right angles with the axis of the cylinder. Into each of theſe holes a piece of braſs wire, $\frac{1}{10}$ of an inch in diameter, rounded at one end and ringed at the other, was cemented, ſo that the diſtance between the rounded ends within the veſſel did not exceed $\frac{1}{5}$ of an inch, and that the

the ring of each wire did not project above $\frac{3}{10}$ of an inch, for longer pieces were found to be inconvenient.

By these means I could make the electrical spark taken between the wires, to be great or small, according to the size or charge of a Leyden jar, employed for this purpose. That part of each exploding jar, which was to be occupied by an elastic fluid previous to the ignition by the electric spark, was graduated, in order to shew any errors in the mensuration, or waste in the introduction of them; and also to shew the quantity of elastic fluid remaining after an explosion.

By repeated trials I found that a cubic inch of the due mixture of inflammable and empyreal air, was the greatest quantity that could be fired at once, in an exploding jar of this kind, without waste of the quicksilver in which it stood inverted, and which was impressed and agitated violently at each explosion; or without manifest loss of the inflamed and dilated airs: And I

was

was convinced that the braſs wires had no ſenſible effect in any of the experiments that I am now to mention.

To hold the exploding jar in the required poſition, a braſs collar was faſtened to it by ſcrewing the ends of the collar together, and a piece of braſs projecting from the collar, and ſliding into a heavy frame of iron, connected the whole, ſo that the exploding jar might recoil an inch or a little more; but not without moving the whole frame, which reſiſted with a force of 14 pounds.

After ſome trials in this inſtrument, I obſerved that the inflammable air which was firſt expelled from an acetous ſalt by the weaker heat, required almoſt double its bulk of empyreal air for its combuſtion, by reaſon of the ethereal vapour mixed with it, or of its extraordinary denſity. But that the inflammable air expelled laſt by the ſtronger heat, and duly ſeparated from the fixable air, required much leſs empyreal air, and was of a rarer kind, a cubic

inch

inch of it weighing ſcarcely $\frac{2}{10}$ of a grain. Even this inflammable air ſuffered a conſiderable diminution of its bulk by repeated agitation with lime liquor, and by long expoſure to water.

The diſpoſition of the inflammable air from acetous ſalts, to vary thus by time, by the unavoidable waſhing, and the expoſure to water, as well as by the degree of heat in which it is procured, is apt to perplex and miſlead the experimenter; for a ſlight error in regard to the ſpecific gravity of the inflammable air, induces great errors in his eſtimation of the products after combuſtion, as may be gathered from the following experiment.

In the exploding jar I fired a mixture conſiſting of 5. 5 cub. inches of inflammable air of the pureſt kind from acetous calcareous ſalt and which had been well waſhed in lime liquor, and of 7. 5 cub. inches of empyreal air, in ſeparate charges of a cubic inch each, and transferred the reſiduary air of each exploſion into a reſer-

voir,

voir, through mercury. This air meaſured five cubic inches and was fixable air, which lime liquor readily imbibed, leaving a ſmall bubble of phlogiſtic air, not worth notice in regard to the weight.

In each exploſion the concuſſion of the apparatus was violent, and the vivid red flame ſhewed that the charge had at this inſtant expanded to eight times its former bulk, and depreſſed the mercury ſo far, although in the next inſtant, and quicker than the eye could trace it, the reſiduary air meaſured only half the charge: ſoon after it contracted further by cooling.

The internal ſurface of the jar, as far as the mercury had been depreſſed, was moiſtened; and this with the water which encircled the mercurial column at its ſurface and contiguous to the jar, ſhewed clearly that the water formed was a conſiderable part of the exploded airs. Until it appears that fire gravitates ſenſibly in the quantity here emitted, we muſt conſider the quantity of water thus formed, to be equal to

that

that by which the weight of the mixed airs exceed that of the fixable air.

The weight of the empyreal air at 42 : grains in the cubic inch was - -	3. 15 gr.
That of the inflammable, at . 2 gr. in the cubic inch was -	1. 1
And the weight of both	4. 25
The fixable air, at .57 gr. to the cubic inch, weighed -	2. 85
Consequently the water weighed	1. 4
Mr. Cavendish's ingenious and accurate experiments shew that one seventh of water is phlogiston, and the remainder empyreal air.	
In the formation of 1. 4 gr. of water, the quantity of phlogiston expended was -	.2
And the empyreal air expended was - -	1. 2
The part of the empyreal air which entered in the composition of the fixable air, thus appeared to be -	1. 95

And

And the quantity of matter furnifhed by the inflammable air towards the finable air was about - 0. 9 gr.

By other experiments and the fame kind of eftimation, the empyreal air appeared to conftitute more than two thirds of the fixable air, and in fome it feemed to be accurately $\frac{2}{3}$; but after all I continued to fufpect that the proportions of the principles are not the fame in every fpecimen of the elaftic fluid which we confider as fixable air. When the denfe inflammable air firft expelled from charcoal was ufed, the refult was nearly the fame. And from the whole I conclude, that when as much inflammable air of this kind is employed, as can be converted, in the explofion, by the empyreal air, the fixable air confifts of one part by weight of the acid matter of acetous acid or charcoal, and nearly or accurately two parts of empyreal air; and almoft $\frac{1}{7}$ of this kind of inflammable air is phlogifton, and the remainder mere acid bafis of fixable air, and of acetous acid, charcoal, oils, fpirits, and of all ſubſtances that yield acetous acid or denſe inflammable air abundantly.

Nothing appears to warrant the current opinion that fixable air contains phlogiſton; but on the contrary the water ſhews that the attractive forces conſpire to the union of the phlogiſton with empyreal air, to form water, even in the preſence of the principles of fixed air; and the quantity of phlogiſton which we trace in the water, being $\frac{1}{3}$ of the weight of the inflammable air, is as great as can by any experiment hitherto made, be ſhewn to exiſt in inflammable air of this ſpecific gravity.

When I uſed the heavier inflammable air carrying ethereal vapour, it required more empyreal air to burn the whole of it, ſo that no inflammable reſidue ſhould appear after the fixable air had been abſorbed by lime-liquor; and then the bulk of fixable air was greater in relation to that of the inflammable.

When no more than the neceſſary quantity of empyreal air was uſed, the quantity of phlogiſtic air that appeared after the exploſion, did not differ ſenſibly from that which appeared, by other experiments, to have been introduced in the empyreal air or the inflammable air: It was greateſt when I uſed inflammable air that had iſſued at the commencement of a diſtillation, or that had been long expoſed to water; or when I uſed the impure air expelled from nitre; and it was leaſt when the pureſt airs were uſed. Therefore the invariable and proper products in the combuſtion of denſe inflammable air with empyreal air, are fixable air, water and fire, and nothing elſe.

It is well known that charcoal continues to yield denſe inflammable air, as long as it is urged with intenſe heat; and if the experiment were purſued to the utmoſt extent, the whole of it, except the earth, might be converted into this kind of air. But even from charcoal, the air firſt expelled by the weaker heat, is heavier than that which is afterwards procured by intenſe heat. And as the heavieſt inflammable air from charcoal or acetous compounds, yields the greateſt quantity of fixable air in combuſtion; whilſt the light inflammable air of metallic ſolutions yields none, as Mr. Cavendiſh truly maintains; and as it is certain that phlogiſton is a common principle of both, the greater ſpecific gravity of the former is to be imputed to the acid mattter.

It ſeems therefore that the proportions, in which the acid and phlogiſtic matter are combined, in different ſpecimens of inflammable air expelled from vegetable ſubſtances, do vary conſiderably, and that the denſer air, containing the greater quantity of acid matter, is more eaſily expelled than the rarer, which not only holds phlogiſton in greater proportion, but is perhaps more fully ſaturated with the matter of fire, in conſequence of the predominance of phlogiſton, and the intenſer heat in which it is always formed.

To theſe cauſes I would impute the great ſpecific gravity of the inflammable air of oils, ſpirits, Ether, reſinous ſubſtances, and of that which mineral fuel emits at firſt in diſtillation; and the ſingular levity of the inflammable air expelled from coal by intenſe heat.

In the combuſtion of divers ſpecimens of inflammable air, with the ſole view of ſatisfying myſelf that they all could yield fixable air and water, I occaſionally uſed air expelled from nitre by heating it in a coated glaſs retort. Finding that the firſt gallon or the ſecond was not ſo pure as the four ſubſequent gallons emitted from a pound of the pure ſalt, and that in the ſubſequent meaſures the impurity encreaſed, I reſerved the beſt for uſe; but even in this the phlogiſtic air made $\frac{1}{14}$ of the bulk; for this quantity appeared by Dr. Prieſtly's teſt of nitrous air, and by expoſing the empyreal air to the ſolution of calcareous liver of ſulphur.

In the uſe of this air, or of inflammable air equally impure, I found that the phlogiſtic air introduced in either, ſuffered little or no diminution in conſequence of the explosion, when the quantity of inflammable air was great enough to employ the whole of the empyreal in the formation of fixable air and water; but when the empyreal air exceeded this proportion, a part of the phlogistic air disappeared: this was found by exposing the products of the explosion, first to lime liquor, in order to separate the fixable air, and then to the solution of calcareous liver of sulphur, which after imbibing the empyreal air, shewed the quantity of the phlogistic.

When I had used the proportions in which of the greatest diminution of the phlogistic air had taken place; the water formed at the same time acquired an acid impregnation, acted on the mercury, and became turbid with it. The most favourable circumstances to the production of this phenomenon were, the redundancy of empyreal air, and the repeated exposure of the whole residue of an explosion, to the shock and flame of subsequent charges.

From these phenomena I concluded two years ago, that the gravitating matter of phlogistic air is contained in nitrous acid, and that phlogistic air in the circumstances now described, contributes to the formation of an acid strongly resembling the nitrous. This did not amount to a clear knowledge of the subject.

But Mr. Cavendish, by a happy train of reasoning from experiments devised by himself, and knowing nothing of those which I have now related, has clearly shewn in the last volume of the Philosophical Transactions, that empyreal and phlogistic air exposed to electric sparks, form nitrous acid; and it is no longer to be doubted that the phlogistic air was thus expended in my experiments, which now serve only to suggest an easy and expeditious method of making nitrous acid from empyreal and phlogistic air, and to shew that flame or due ignition serves as well as the electric spark for this purpose.

But as there was no appearance of nitrous acid whilst the inflammable air predominated in the charge, we may infer, that empyreal air is attracted more forcibly by the acid matter of denſe inflammable air, or of the bodies which yield it, than by that of phlogiſtic air; and that it is by virtue of this ſuperior affinity, that all vegetable and other ſubſtances, abounding in our acid matter, and deflagrated with nitrous ſalt, engage the empyreal air of the nitrous acid in the formation of fixable air and water, and leave the reſiduary matter of the nitrous acid in the form of nitrous air or phlogiſtic air.

Tin imbibes more air in calcination than any other metal, unleſs we except regulus of manganeſe or iron, which I have not tried. Sixteen ounces of tin encreaſe in weight to 20 ounces by calcination: But in calcining filings of tin with empyreal air I could not diſcover any conſiderable quantity of fixable air, and iron produced but a little. As we do not find fixable air in the combuſtions of zinc, or phoſphorus of Runkel, or light inflammable air, altho' theſe are vivid in the higheſt degree, our acid matter is not a neceſſary agent in combuſtion, but rather ſeems to moderate it; for the bodies which yield the greateſt quantity of fixable air in combuſtion, afford the weakeſt heat and illumination; and this correſponds with the capacity of fixable air to retain a great part of the matter of fire which belonged to its principles, and the inability of water to fix any conſiderable quantity of the matter of fire belonging to empyreal air and phlogiſton ſeverally. Hence it happens that coak makes a much ſtronger fire than charcoal, altho' the former contains ten times more cineritious matter than the latter; for coak yields lighter inflammable air, and affords leſs fixable air, and conſequently contains leſs acid relatively to its phlogiſton, than charcoal.

In the combuſtion of charcoal with empyreal air, the expenditure of the latter, in fixable air and water, was always found to be more than thrice the weight of the charcoal. I could now eaſily aſcertain the proportions of theſe, and even the quantity of of the acid and phlogiſtic matter in this and other bodies; but as my preſent purpoſes are anſwered by approximation, I think it unneceſſary to detain the reader any longer on this ſubject.

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SECTION XXI.

Primary notions of the matter of Fire.

IN order to suggest a more extensive use of the foregoing observations, and to facilitate the explanation of certain phenomena which are yet to be considered, I am now to propose a few necessary notions of the matter of fire.

1. *The kind of matter which impresses us with a sense of heat, and which is capable of expanding and pervading all known bodies, is subject to laws of attraction, which fixes and disguises a certain quantity of it in divers substances; and this matter produces the effects which we call heat, and acts as fire, only when it is extricated from other kinds of matter.*

This notion needs no illustration or support; for the phenomena which conspire to to impreſs it, are very numerous; and Black, Bergman, Cavendiſh, Crawford, Prieſtley, Kirvan, Lavoiſier, and other diſtinguiſhed philoſophers, have adopted it.

2. *The homogeneal parts of the matter of fire repel each other.*

This repellent property is apparent in all the proceſſes in which the matter of fire is extricated from the groſſer and gravitating parts of bodies. The chief of theſe proceſſes are the mixtures producing heat, the abſorptions of divers cold elaſtic fluids cauſing heat, vitriolizations, incalaſcence of pyrophori, reſpiration, putrefaction, fermentation, and combuſtion. In all theſe, the matter of fire, ſo ſoon as it is liberated, is found by its peculiar effects, and the menſurable decreaſe of heat at encreaſed diſtances from the ſource of emiſſion, to move excentrically from that ſource, and to decreaſe in denſity. But as this happens, whether the extrication of it be attended with illumination or not, it indicates nothing that is conſiſtent with

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the tenour of nature, or that may be ſuggeſted by analogy, except that the parts of the matter of fire repel each other, although they certainly are attracted by other kinds of matter. This repellent property is equally apparent in every inſtance of the formation of elaſtic fluids from aggregate bodies; and eſpecially when this is done by mere ignition. But as theſe inſtances afford another inference of equal uſe, I ſhall ſubjoin them to the following notion.

3. *The matter of fire, by virtue of the repulſion ſubſiſting between its homogeneal parts, and of their attractions to the parts of other matter, is the cauſe of the elaſticity of aeriform fluids.*

This notion is neceſſary to the ſolution of the phenomena, and is ſupported by direct evidence, of which the following part will be ſufficient.

Oils, Reſins, vegetable acids, charcoal, and divers other bodies, are almoſt totally convertible into fixable air, and inflamma-

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ble air by fire. Nitrous acid may be decomposed and converted, in part, into empyreal air, in the remainder into phlogistic or nitrous air, by the agency of fire. The whole substance of solid nitrous ammoniac is convertible into fluids permanently elastic, by the mere action of fire. From the solid aggregation in manganese and other metallic calces and in divers salts, the gross matter of empyreal air may be propelled, to form an elastic fluid, by fire; so may that of dense inflammable air from coak and divers hard bodies; that of fixable air from stony concretes; that of alkaline air from ivory, Prussian blue, and microcosmic salt; that of vitriolic, or of marine, or of hepatic air, from divers solid, saline, or sulphureous compounds. All this is done by fire; and being best effected in vessels that are impervious to every other known matter, amounts to a satisfactory proof that the matter of fire is the only accessary and agent in the conversion of solid bodies into elastic fluids, and in the maintenance of their elasticity.

The electric matter is not to be mentioned in objection, until it is proved that it does not itself consist of the matter of fire, in a certain modification of it, depending on the repulsive property, and the relations to gross matter, which we are now describing.

Seeing this extensive agency of the fiery matter; that we can not only trace it into the subjects which thus become permanently elastic, but that it gives a temporary elasticity to vapours and sublimates; seeing that these resume their aggregation as fast as it escapes from them; that its union in the fluids, to which it gives permanent elasticity, may be further proved by the extrication of it from every one of them; and that, in these liberations of it which are daily experienced, in the absorptions of elastic fluids, in combinations, and in combustions of them, the emission is so copious as to remove all doubt of their having held it in great quantity, united with their respective separated parts, and restrained during that union from acting like liberated fire;

fire; obſerving alſo that as faſt as the fire is liberated or excluded, the diſtant groſſer parts of elaſtic fluids ruſh together or into other bodies; as when empyreal and nitrous air make nitrous acid, or empyreal and light inflammable air make water which cools to ſolid ice, or marine and alkaline air make ſal ammoniac; or as when acid or alkaline airs ruſh into water, or empyreal air into phoſphorus; we cannot now heſitate in admitting that the groſſer parts of elaſtic fluids, as well as thoſe of vapour, are made to recede from each other contrary to their inherent and inceſſant attractive powers, by virtue of their reſpective charges of the repellent matter of fire, and conſequently by the repulſion of the parts of fire to each other.

4. *The charges of repellent matter, by which attractive and gravitating particles form elaſtic fluids, are diſtinct atmoſpheres of fiery matter, in which the denſities are reciprocally as the diſtances from the central particles, in a duplicate or higher ratio.*

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This is an evident consequence of the former notions, and the prevalence of the repulsive over the attractive forces; and the terrestrial atmosphere, in which the density is inversely as the squares of the distances from the earth, shews that it is the natural and necessary effect of such forces, to form the charges of fiery matter which the particles engage, into the described atmospheres. The further evidence of the truth of this notion arises from phenomena, which I am presently to consider and explain, and which are not inexplicable by any other condition or agency of the matter of fire, that has been hitherto suggested.

5. *The repulsion of the homogeneal parts of the mattter of fire, limits the quantity that can be engaged by bodies, and tends to diffuse the remainder equably in space.*

This notion needs no illustration.

6. *The matter of fire limits the quantities, in which aeriform fluids, and bodies*

dies containing it, can combine chemically.

In the converſion of ſolid bodies into elaſtic fluids, we perceive the repulſive forces of the matter of fire reſiſting and overpowering the reciprocal attractions of the groſſer parts; and in mixtures of empyreal and inflammable air, and in divers other mixed airs, we ſee this matter reſiſting the attractions which tend ſtrongly to the chemical combination of the heterogeneal gravitating particles.

In ſuch inſtances it is manifeſt that the ſum of the repulſive forces, exceeds that of the attractive.

When aeriform fluids condenſe each other, or are concentrated and aggregated by bodies, it is equally evident that the attractive forces, although reſiſted by the repulſive, are prevalent.

These, and divers other phenomena ſhew, that the natural power, whether attractive or repulſive, of each part of matter, is limited; and therefore the ſum of the powers which any body can exert in regard to another, is by a law of nature as the number of its active parts, or in other words, as its quantity of matter.

In conſequence of this law, the ſum of the repulſive forces, which reſiſt the approximation of the gravitating parts of an elaſtic fluid, and their union with thoſe of a body which alſo holds ſome of the matter of fire, is as the quantity of that fluid; and no more than a determinate portion of it can be aggregated and combined in the body whoſe quantity of matter and attractive powers are limited.

By the ſame law it is determined that elaſtic fluids ſhall unite with each other in limited proportions only, to form denſer fluids or ſolid bodies, and that the ſuperfluous quantities ſhall remain elaſtic and unaltered.

As the matter of fire is manifeſtly the agent which reſiſts the coaleſcence and union of attractive particles in theſe caſes; and as the ſame matter demonſtrably exiſts in all bodies that unite only in limited proportions, we muſt aſcribe to this only competent and manifeſt agent, all thoſe limitations which we experience, in regard to the proportions in which bodies can be chemically united, and which we briefly expreſs by the word *ſaturation*.

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SECTION XXII.

Applications of the foregoing notions in the explanation of divers phenomena.

AS the limits of this Eſſay do not permit me to make extenſive applications of the foregoing notions, I ſhall endeavour, in the expreſſion of a few, in this and the following ſection, to ſuggeſt every thing that ſeems neceſſary towards explaining the moſt intricate phenomena of the matter of fire.

In regard to the apyrous bodies, ſuch as the pure earthy ſubſtances, I would infer from theſe notions that they chiefly conſiſt of parts which do not attract the matter of fire with forces ſufficient to cauſe a diſunion of them, and an interpoſition of this matter in ſuch quantity as to induce ſoftneſs or fluidity.

Concerning fuſible bodies which concrete in cooling, I would in the next place infer, that they conſiſt chiefly of parts which attract the matter of fire with forces ſomewhat greater than thoſe laſt mentioned, and ſufficient to effect the ſolution of them in the fiery fluid, but not for the permanent retention of it: That bodies of this claſs exclude the ſolvent by virtue of the prevalent attractions which tend to reunite their groſs parts; but that they receive and tranſmit the matter which cauſes heat, more freely, and they retain it longer, than the former can in ſimilar circumſtances, by reaſon of the ſtronger attractions.

The bodies which, like oils or water, form elaſtic vapour, when duly charged with the matter of fire, conſiſt chiefly of parts which attract it with forces ſtill greater, and ſufficient to compel atmoſpheres around the diſtant molecules; but yet not ſufficient to retain theſe atmoſpheres after the influx of fire ceaſes, and in oppoſition to the mutual attractions of their central molecules, and the tendency of the fiery matter to diffuſe itſelf equably in the neighbouring ſpaces. As the ther-

thermometer ſhews no more than the relative quantities of the free matter of fire in bodies, theſe lately mentioned require a greater quantity of the fiery matter than the former, before they exhibit an equal temperature by the thermometer, for the reaſon already mentioned.

It is alſo by virtue of this ſuperior attraction to the fiery matter, that ice, reſin, fats, and other vapourable bodies, become fluid by moderate incaleſcence, but not before they have received a great quantity of fire; and that they reſpectively evaporate with leſs ignition or incaleſcence, in veſſels which avert the preſſure of the aerial atmoſphere, than where that, or any equivalent compreſſion, conſpires with their aggregate attractions, to reſiſt the influx of fire and the disjunction of their parts.—Thus water, or ſpirit, moderately heated, and placed in the receiver of an air-pump, boils when a part of the air which compreſſes it is drawn out, and ceaſes as often as the preſſure is reſtored.

Still ſtronger attractions of the matter of fire, comparatively with the forces which tend to the excluſion of it, are ſeen in ethereal oils and Ethers: For their vapours cannot be condenſed without the aid of compreſſion; and when they are thus condenſed and aggregated, their molecules, by attracting fiery matter and compelling it into atmoſpheres, with forces ſuperior to thoſe with which they attract each other, are made to recede, and form aeriform fluids, in the loweſt temperatures, ſo ſoon as the preſſure of the almoſphere is averted.

That the expanſion of ſuch ethereal fluids into the aerial form, in the exhauſted receiver of an air-pump, is owing to the tendency of their molecules to attract the matter of fire and to form atmoſpheres of it around them ſeverally, and that it is not effected by any other agency, is apparent from the concomitant phenomenon of *cold:* For as faſt as they aſſume the aerial form, they engage and fix the free fiery matter which belonged to the ſpaces into which

they

they expand; and this privation or deficiency of disengaged fiery matter, is what we call cold.

The bodies which by ignition may be partially or totally converted, even under the atmospheric pressure, into fluids permanently elastic, shew the kinds of matter by which that of fire is attracted in the supreme degree.

For the elasticity which subsists under immense pressure, argues a stronger attraction of the particles to their respective repellent atmospheres, than that which we last noticed; but that this stronger attraction compels denser and deeper atmospheres, may not only be argued a priori, but is experimentally demonstrable by the bulk, which in elastic fluids is the measure of the atmospheres, compared with the gravity, which is the measure of the gross particles; and it is also apparent in the extraordinary quantity of the fiery matter that escapes in the instant of the aggregation of these elastic fluids, or rather of their particles, to to form confiftent bodies; As when empyreal air is rapidly imbibed by phofphorus, Pyrophorus, Hepar fulphuris, or iron filings and fulphur; when alkaline air, and divers acid airs, are abforbed by water, or when they condenfe each other; or when the rare inflammable air and empyreal air make water, and exclude their matter of fire.

From all this it may be inferred, that in any future table of the affinities of the matter of fire, *pure phlogifton* ought to rank above every other kind of matter; inftead of being omitted, as it is in Bergman's tables, or fuppofed to have repugnance or apathy to the matter of fire, as Dr. Crawford formerly conjectured. But when this precedence is given to phlogifton, by reafon of the extreme levity of the purer inflammable air of metallic folutions, and of the quantity of fiery matter which it emits in the inftant of its union with empyreal air, the gravitating matter of this laft air muft not be placed beneath any other that is now known; becaufe no air that is free

from

from phlogiston, is lighter specifically than empyreal air; or emits more fire in the instant of aggregation.

I consider the specific gravity as a safe guide in our investigations of these affinities and of their order, in regard only to the elastic fluids which seem to consist of no more than one kind of gravitating matter engaged in the repellent atmosperes: And of fixable air, dense inflammable air, acid airs, the phlogistic alkaline air, and others, I would observe, that the atmosperes include molecules instead of solitary ultimate parts; for without this chemical union of heterogeneal parts, and the formation of molecules, an elastic fluid of the kind that I now speak of, could not differ, as it does, from either kind of matter of which it is composed.

From this consideration of the attractive forces which tend to form molecules, and of the atmospheres which, in compound elastic fluids, encompass the molecules, but not the ultimate parts severally, we derive an easy explanation of the phenomenon so often noticed in the preceding pages; I mean the conversion of a substance, not into one, but into two or three different elastic fluids, by mere ignition.

When elastic fluids are formed in solutions and other processes, in which the subjects are not ignited, it is to be observed that the gravitating parts of the emitted elastic fluid, were distant from each other, by reason of the interposed matter, at the instant of their extrication, and that at this distance there is a great dimunition of the powers which restrain them in their tendency to engage all the matter of fire that the menstruum or solvent could extricate during their union. Thus it happens, as Dr. Black originally suggested, and as Bergman has observed in his excellent Dissertation on Elective Attractions, that caustic alkali, in the union with an acid, excites great heat, that is to say, in their union they exclude a part of the matter of fire which they severally held in a fixed state; but mild alkali, in uniting with an acid

acid, gives little or no heat, and for this reaſon; that the gravitating parts of the fixable air, engage all the liberated matter of fire in forming atmoſpheres around its molecules. This expoſition is applicable to every other elaſtic fluid that is extricated in ſolutions or combinations attended with little or no incaleſcence.

Since the particles which attract the matter of fire, exclude a part of their reſpective charges in the inſtant of their cloſe approximation or contact, there is no difficulty in accounting for the cold produced in ſolutions, expanſions, and evaporations; in every one of which, the particles which reſume the matter of fire, and in fixing it produce the cold, are previouſly removed to ſome diſtance from each other, either by the interpoſition of the parts of a menſtruum, as when ice is diſſolved by nitrous acid, or by the prevalent powers of their proper fixed fire, of which we have an inſtance in Ether placed in the exhauſted receiver of an air-pump.

As the mere acetous acid consists of the gravitating parts of empyreal air, of phlogiston, and the acid principle of vegetables, and by the accession of the matter of fire only, makes two different elastic fluids, namely fixable air, and dense inflammable air, it follows from these notions, that the gravitating parts of these two airs would make acetous acid again, with water, if the matter of fire could be withdrawn from them; and I venture to prognosticate that this, or something equivalent, will be done by the first ingenious experimenter that attempts it, either by the means of a body which may absorb the gravitating matter of both, and exclude their atmospheres, or by breaking the atmospheres in the manner which I am to describe in the next section.

There is undoubtedly a natural limitation, as we formerly observed, of the forces with which the gross parts of divers elastic fluids compel, and are compelled by their respective atmospheres; but still these forces are so great, that we cannot form adequate ideas of them, without reflect-

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ing on the resistance which they give, even in small quantities of the elastic fluids, to any pressure which tends to condense them, and cause an approximation of their parts; or without adverting to the operations which shew the ability of these forces to maintain the elasticity of divers aeriform fluids, in opposition to the greatest mechanical powers hitherto employed to subdue them. The air-gun, and other instruments exhibit these forces in atmospheric air, and chemical operations and explosive compositions too often shew them in the other elastic fluids.

Although the force of chemical attraction reaches not far from the particles, with any sensible effect, we are not thence to conclude that the attractive virtue ceases at any distance. But from all the known phenomena we may infer, that the attractive forces, tending to the approximation and cohesion of gross particles, decrease in a duplicate, or some higher ratio of the distances, reciprocally; that the natural resistance to the interposition of the fiery matter, is leſſened at the ſmalleſt, and totally overpowered at ſmall diſtances which no eye can meaſure; and finally, that *where the ſenſible effect of attraction ceaſes, there repulſion ſucceeds.*

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SECTION XXIII.

Interpretations of the moſt important phenomena of combuſtion, according to the foregoing notions.

AS the atmoſpheres by which the groſs parts of an elaſtic fluid are made to recede from each other, contrary to their reciprocal attractions, extend into the minute ſpaces between them, with decreaſing denſity; and as the powers which form theſe appropriated charges, compell the ſeveral groſs parts to the centers of their reſpective atmoſpheres, and regulate the poſition of theſe parts relatively to each other, as well as their diſtances; the aerial form is maintained, not by the mere interpoſition of the matter of fire, but by the intervention of it in the deſcribed ſtate of denſity near the groſs particles and extreme rarity at the coincidence or contiguity of the atmoſpheres.

The nature of the ſubject admits no inference repugnant to this; for in a medium of uniform denſity, the groſs particles would be impelled or drawn by equal and contrary powers of the medium, and meeting no reſiſtance in it, to the attractive powers which tend to unite them, they would form an aggregate excluding every part of the medium, except thoſe that might be abſolutely coherent with the groſs particles and chemically combined.

Therefore, to deſtroy the elaſticity, and to effect the aggregation and union of the groſs parts of an aeriform fluid, or of any mixture of different airs, nothing more is neceſſary than to break or blend the atmoſpheres into a medium of equal denſity in the ſpaces between the particles; and although this cannot be done by mechanical compreſſion, it is eaſily effected by repleniſhing the minute ſpaces, in which the atmoſpheres extend, with a denſer fiery fluid.

As the ſmalleſt ſpark affords that denſer fluid, in quantity ſufficient to repleniſh

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many of theſe minute ſpaces, the fiery matter there expelled, in the inſtant of the union of the groſs parts, extends the neceſſary ignition through the neighbouring atmoſpheres, and thus a mixture of empyreal and rare inflammable air, by the momentary agency of a flint-ſpark, is rapidly expended in the formation of water and the emiſſion of a denſe fiery fluid.

As the adventitious fire requiſite for exciting the combuſtion, muſt have denſity exceeding that of the atmoſpheres in their interior denſeſt parts, it is ſcarcely to be doubted that the greateſt denſity in the atmoſpheres is almoſt equal to that of the fiery fluid iſſuing from a red-hot maſs of iron or of earth; for any incombuſtible body leſs heated, will not excite combuſtion in the mixture of inflammable and empyreal air. In this view of the ſubject, the quantity of fiery matter engaged in the atmoſpheres, appears adequate to the experienced elaſticity of theſe aeriform fluids, and to all the heat and flame of their combuſtion.

As the diſtances of the groſs parts of a mixture of empyreal and inflammable air, and the depth and denſity of their atmoſpheres, are encreaſed by heating the mixture gradually, in veſſels which do not effectually prevent the expanſion of it, the ignition of the veſſels to redneſs, or to any degree hitherto experienced, is found inſufficient for the inflammation of the mixture; for the obvious reaſon of the denſer or deeper atmoſpheres: and on the conſideration of all theſe particulars, I ſhould expect to find a greater degree of ignition, or a larger ſpark, whether of the electric fluid, or from a burning body, neceſſary towards the accenſion of inflammable with empyreal air, when by averting the preſſure of the aerial atmoſphere, we ſuffer the mixed airs to expand conſiderably, than the ſame mixture would require in the ordinary ſtate of denſity.

To avoid the tedious enumeration and diſcuſſion of phenomena of this kind, I would offer this general rule concerning them: The ignition neceſſary towards the accenſion cenfion of inflammable air or vapour, in empyreal air, is directly as the denfity of the repellent atmofpheres, and inverfely as the attractions of the gravitating parts to each other, for the reafons abovementioned.

In the mixture of inflammable with empyreal air, which do not in the leaft affect each other, but remain unaltered for any length of time, we fee nothing like aggregation to refift the union of their grofs attractive parts; and we perceive that the powers which impede their union, are totally different from thofe by which the grofs parts are aggregated into folid bodies. We muft therefore refufe our affent to the Chemifts who fay that the ufe of ignition in exciting combuftion, is to weaken the aggregation of the combuftible fubftance.

That aggregation retards the progrefs of combuftion, is not to be difputed; but to fhew why a confiftent fubftance, fuch as refin or charcoal, may perfift in contact with empyreal air, without combuftion; and why due ignition caufes the inflammation of it, I would ſay firſt, in conformity with all the foregoing notions, that phlogiſtic bodies, whether fluid like oil, or ſolid like charcoal or reſin, contain the matter of fire in a fixed ſtate, and in great quantity; ſecondly, that although it is thus fixed by prevalent attractive forces, it ſtill repels the like matter of fire appertaining to the empyreal air; becauſe this natural power exiſts, as well when it is counteracted and ſubdued, as when it acts unreſtrained; thirdly, that the groſs parts of empyreal air are prevented from uniting with thoſe of charcoal, oil or reſin, by their reſpective charges or portions of the matter of fire; and laſtly, that the effect of ignition is, in regard to the commencement of the combuſtion, to break and blend the charges of fiery matter which impede the union of the groſs particles, as well as to weaken the aggregation of the conſiſtent ſubſtances. All this is applicable, in reſpect to the ignition of nitre with combuſtible bodies, and the ignition of fulminating powder, fulminating gold, and other fulminating compoſitions, which require to be be heated to a certain degree, before they enter into combuſtion.

When we inflame a combuſtible elaſtic fluid or vapour, contained in a veſſel, and meeting the open air in a narrow aperture, the progreſs or velocity of the combuſtion is as the area of the aperture; becauſe the empyreal part of the atmoſpheric air is applied in ſmall portions, ſucceeding each other, but interrupted in the ſucceſſion by the fixable air or water newly formed. For the ſame reaſon the combuſtion of any aggregate is, in velocity, as the ſurface preſented to air is, in extent; and as the retardation of combuſtion is not as the hardneſs of the combuſtible body, the aggregation is only a ſecondary impediment.

After adopting theſe notions of the agency of ignition, and of the cauſes by which combuſtion is retarded, we ſhall find no dif-difficulty in anſwering the following queſtions:

Why do light inflammable air and empyreal air, mixed in due proportions, deflagrate totally, and to our ſenſe inſtantaneouſly, on the application of a ſpark or of a body ignited to redneſs; but not without this ignition? And why are the emiſſion of fire and the formation of water ſimultaneous?

Why does a mixture of heavy inflammable air and empyreal air, require the like ignition for its aſcenſion, and then deflagrate totally and inſtantly, and yield fixable air as well as water and fire?

Why does any exceſſive quantity of empyreal or of inflammable air, beyond the determinate proportions in which their groſs parts can combine, remain elaſtic and unaltered, or not altered in any conſiderable part of it, after the combuſtion?

Why do the nitrous alkaline and ſulphureous particles of fulminating powder, remain quieſcent in the contact of them, until ſome part of the powder is duly ignited;

nited; and why does the combuſtion excited by ſuch ignition, proceed ſlowly through mixture? Why do the ſame materials, when they are more perfectly mixed by fuſion, deflagrate with inſtantaneous and dreadful exploſion, in the inſtant of the contact of a ſpark with the melted maſs? And why does this maſs, when cooled and concreted, deflagrate by the contact of a ſpark, rapidly indeed, but not ſo inſtantaneouſly as the melted mixture.

Why does fulminating gold, which contains empyreal air, and the phlogiſtic matter which the volatile alkali introduces, require ignition for its aſcenſion; and why is the deflagration of it inſtantaneous?

Why, in all mixtures of ſolids, containing phlogiſton and empyreal air; or in gunpowder, which contains empyreal air and phlogiſton along with the acid principle of fixable air; the due ignition of any part is ſucceeded by the deflagration of the whole? And why is the combuſtion the more rapid, as the mixtion and proximity

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of the foregoing active ingredients, are made to approach nearer to perfection, by mechanical comminution and distribution of the subjects containing them.

In replying to these questions, we necessarily furnish answers to thousands that might be proposed, concerning combustions excited by ignition, and regulated by wicks or other means, or accelerated by arts that speed the influx of empyreal air.

In the ignitions that are necessary for the accension of different bodies, we observe many gradations, from that which iron demands, down to the weakest, which is sufficient for exciting combustion in phosphorus of Kunkel, and which, in fair trials of dry and comminuted phosphorus, scarcely exceeds 60 degrees of Farenheit. But in these gradations, we discover nothing but what is referable either to the elective attractions of empyreal air and phlogiston to other gross bodies and to each other; or to the aggregation of the combustible substances; or finally to the incapacity of fire

to

to blend the atmoſpheres and charges already deſcribed, unleſs it equals or exceeds them in their greateſt denſity.

With regard to the combuſtions which commence in the coldeſt air, and without the aid of adventitious fire, we need now ſay nothing more than that the pyrophori are compounds, which by reaſon of their extreme ſpongineſs, preſent ſurfaces of the greateſt extent, to the empyreal air of the atmoſphere, and at theſe ſurfaces expoſe to it, in the ſame inſtant, the two kinds of matter, namely phlogiſton and our acid principle, that attract it with the greateſt forces; and that the ſum of theſe forces exerted in ſuch favourable circumſtances, is ſufficient to overpower the reſiſtance of the atmoſpheres, and to expel them along with the proper fiery matter of the pyrophori.

In accounting for the ſpontaneous accenſion of certain mixtures, ſuch as that of black wad and linſeed oil, we are to advert firſt to the elective attractions of the empyreal

pyreal air, which one of the ingredients always supplies; next, to the phlogiſtic and acid matter preſented by the other ingredient; and laſtly to the prevalence of the attractive forces which tend to the formation of water and fixable air and to the excluſion of the matter of fire.

In theſe curſory interpretations, I have purpoſely avoided the electrical phenomena; not becauſe they ſhew any thing repugnant to theſe notions; nor becauſe they afford no ſimilitudes of the repellent atmoſpheres, or of the deſcribed condition of the matter of fire on the ſurfaces of bodies, or of the agency of air; nor in conſideration of any ſtrong doubt ariſing in my mind, concerning the identity of the *matter* of fire and the *pure* electrical fluid; but for this reaſon, that the electrical phenomena are intricate in themſelves, and unfit for the explanation of others. The ſame motives have diſſuaded me from the introduction of the phenomena of heat and combuſtion, producible by friction and percuſſion.

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SECTION XXIV.

Of Light.

IN attempting a concise and general exposition of the phenomena which depend on the agency of the matter of fire, I have found it expedient to advert first to those which fall within the chemical department of Natural Philosophy, and to reserve the consideration of Light for this place.

Nothing is more evident than that the fire emitted, during the deflagration of bodies, is a cause of illumination, and that wherever illumination subsists, there is matter in motion. But philosophers do not agree in their opinions of the kind of motion and of the nature of the matter itself.

To exhibit, in a few words, the fallacy of some recent doctrines concerning the mat-

matter of fire and light, and at the same time to remove the chief objections which have prevailed with many, as they formerly did in my mind, against the Newtonian Theory of Light, the following observations seem to be sufficient.

In the fiery fluid which is expelled in the manner already described, during the solution or combination of divers bodies; or which is emitted from heated bodies, in consequence of its tendency to equable diffusion, and of the prevalent forces with which the gross parts of such bodies tend to resume their former aggregation; we find every degree of density or heat, from that which corresponds with 540 degrees, at which lead may be melted, down to that of 60 in Farenheit's scale. All this occurs in processes and subjects different from those of combustion; and therefore a great variety, as well as a great number of instances can be produced, to shew that the fiery fluid may flow from bodies, with the smaller or the greater of these densities, without exciting any sensible illumination, or giving light.

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From another train of obſervations we learn, that light may be produced by the emitted fire, in every ſtate of denſity, from that which we call temperate, to that of the moſt brilliant combuſtions. For light is produced, not only by the vivid deflagration of zinc, iron, or coke, or during the languid combuſtion of ſulphur; but is alſo ſenſibly propelled during the ſlow abſorption of empyreal air by cold phoſphorus, and the indiſputable emiſſion of ſucceſſive portions of the matter of fire.

The legitimate inference from theſe phenomena is, not that the matter of light differs from that of fire, but that *Fire* ſubſiſts by the proximity, and *Light* by the rapid projectile motion of parts of the ſame kind of matter: For the latter inference agrees with all the phenomena, whilſt the former is repugnant to our experience of the effects of light concentrated by reflection or refraction.

In *Fire*, there is always a motion of the parts, by reaſon of their tendency to recede

cede from each other, and of their attractions to bodies; but it may subsist by the density without the motion; whilst light subsists by the projectile motion, in every density or diffusion of the luminous fluid.

When we consider that the elasticity of aeriform fluids, is owing to the matter of fire; that a cannon-ball is propelled only by the excess of the repellent powers of parts of this matter, above the forces with which they are attracted by the gross parts of gunpowder, or of the airs emitted during the deflagration of it; that the velocity of the ball is incomparably less than it would be if it were shot through an unresisting medium; and that even this latter velocity would be an inadequate representation of that, with which the parts of the fiery matter are shot forth, in the first instant of their liberation from the combustible body which held them closely approximated; we find the natural powers already described, sufficient in themselves, for the projection of these parts, with all the velocity ex-

experienced in the light of flaming bodies on earth, and to every diſtance at which it has been perceived.

In regard to the light of the ſun, we need imagine nothing more than the ſame matter propelled by the ſame powers, in greater quantity, and with greater vigour, by reaſon perhaps of a purer and denſer atmoſphere, and of a greater proportion of the fiery matter relatively to the reſt of his ſubſtance; for in ſuch circumſtances we produce the moſt rapid and luminous combuſtions of ſolid bodies.

In combuſtions effected by the incumbent air, this acts on the combuſtible bodies in ſucceſſive portions, and the matter of light is neceſſarily projected in like manner, and the parts which ſucceed each other in the ſame lines, anſwer to Newton's definition of a ray of light.

In the rays of light then, we find matter and motion enough to produce all the effects hitherto noticed, on chemical substances, on water, on vegetables, and on solar phosphori.

Having thus traced the matter of fire in various states, to that condition in which it coincides with Newton's character of light, it is unnecessary to insist on the conformity of the foregoing notions with the optical phenomena, further than by remarking that the ethereal medium which affects the surfaces of bodies, and to which he ascribes divers effects, does not appear to consist of any other than the matter of fire, which by the same powers that form atmospheres around the solitary gross parts, must necessarily form a dense elastic medium on the surces of their aggregates.

As I have frequently distinguished the parts of other matter from those of fire, by the term *gravitating parts*, it is necessary now to say, that this mode of expression, is not intended to convey an opinion that the matter which attracts so many bodies, does

does not gravitate to the aſſemblage of them in our earth, but relates to the *ſenſible* gravitation of any quantity that we can ſubmit to mechanical trials.

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SECTION XXV.

Of fermentation, putrefaction, and respiration.

THE phenomena of fermentation, putrefaction, and respiration, agree so strictly with these notions, and are so easily explained by them, that it is altogether unnecessary, in the following sketch, to notice any other than the objects of the greatest importance.

Mr. Cavendish has shewn, that from one hundred parts of sugar duly fermented, fifty-seven are expelled in the form of fixable air. Therefore, unless we suppose that the water used in the process is decomposed, which is by no means probable, the conversion of sugar into spirit is effected by the abstraction of 38 parts, or thereabouts, of empyreal air and 19 of acid matter; and the spirit consists of about 43 of phlogiſtic and acid matter, combined with ſome of the water employed in the proceſs: For we need not, at preſent, regard the ſmall quantity of precipitated earthy matter. The ſpirit then conſiſts of the vegetable acid principle more fully ſaturated with phlogiſton than it is in ſugar, and aſſociated with water; and the ſuperfluous acid matter together with the empyreal air, engaging a part of the matter of fire that is liberated in conſequence of theſe new unions by the mediation of water, eſcape by reaſon of the repellent atmoſpheres.

This perfectly correſponds with the nature of the products of ſugar by ignition; for the fixable air which it yields abundantly, ſhews that empyreal air enters into its compoſition; the inflammable air, oil, and combuſtible coal, which it affords, ſhew all the acid matter and phlogiſton that we find in the ſpirit; and in the earthy part of the charred coal of ſugar, we account for that which ſubſides in the fermented liquor, or may be abſtracted in diſtillation.

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The ſubſidence of earthy matter from a limpid ſolution of ſugar, during the fermentation and new combinations, is eaſily accounted for in this conſideration; that the empyreal air, which is the cauſe of the menſtrual power of acids, is carried off along with that part of the acid principle that is not engaged with phlogiſton to form ſpirit; and that the reſiduary ſpirit, or any ſaccharine acid that may remain, cannot hold the earth in ſolution.

Theſe general inferences are true, altho' the fixable air might have been over-rated, by its being meaſured along with the watery vapour which it always carries with it, in theſe circumſtances.

This repreſentation alſo correſponds with every thing that is worth notice in the preparation and properties of the acid of ſugar; for it is prepared in nitrous acid by the abſtraction of ſome of its phlogiſton, and by ſupplying empyreal air to the reſiduary matter; and the acid of ſugar thus conſtituted, cannot be made

to

to ferment and yield ardent ſpirit, or any ſuch quantity of oil or inflammable air, as may be had from the ſugar.

The changes producible by fermentation, in farinaceous ſubſtances, admit of the ſame conciſe explanation in regard to the acid and empyreal air extricated, the retention of all the phlogiſton with the reſiduary acid matter in the form of ſpirit, and the feculent ſubſidence conſiſting of earthy, ſaline, and inſoluble fatty matter, or of farina which has eluded the decompoſition.

A ſpirituous liquor, conſiſting of water and acid matter ſaturated with phlogiſton, contains every principle of acetous acid, except the empyreal air. But this is ſtrongly attracted by the acid and phlogiſtic matter of the ſpirit; and therefore by due expoſure to atmoſpheric air or pure empyreal air, or even to that which is held in nitrous acid, the ſpirituous liquor becomes vinegar, either in the acetous fermentation, or in chemical proceſſes, ſuch as the ingenious and indefatigable *Scheele* has deſcribed.

And now the reaſon is obvious, why vinegar may be made of wine, but no wine of vinegar, by ordinary fermentation; and the anſwer is eaſy, in regard to every queſtion that has ever been agitated on the ſubject of fermentation, unleſs we except that concerning the agency of yeaſt and leaven.

Yeaſt is not always neceſſary to the vinous fermentation; but when it is uſed to inſure it, under unfavourable circumſtances of cold air, imperfect ſolution of farinaceous matter, or vicidity of the fermentable liquor, it ſeems to ſerve only, like the partial ignition formerly deſcribed, to give in ſome part of the maſs, a certain preponderance of the forces which tend to the new combinations, over thoſe of the chemical attractions, gravitation, aggregation, and *inertia*, which conſpire to maintain the fermentable liquor unaltered. The matter which gives this preponderance, might eaſily be aſcertained by an accurate analyſis of yeaſt. It ſeems to be acetous acid, already formed, and engaged in magneſian earth and oil, beyond the quantity neceſſary

neceſſary for the ſaturation of the former: for this correſponds with an imperfect analyſis of yeaſt, that I made many years ago; and with the common practice of accelerating the fermentation of ales, by ſoured ale; and with the uſe of ſour bread or leaven in exciting a ſpeedy fermentation in dough; and with the effect of ſour ſtalks or huſks of grapes, or ſoured caſks, in exciting the acetous fermentation ſpeedily, in a vinous liquor; and with the uncommon efficacy which I have experienced of bread ſoaked in concentrated vinegar, in expediting the converſion of wine to vinegar; the change induced in the vicinity of a ſmall piece of it, being found, in due expoſure to the common air, to extend quickly through the whole of the vinous liquor.

The phenomena of putrefactive fermentations vary, with the kinds of matter in the ſubjects, with the proportions of theſe, the quantity of water, and the circumſtances which contribute to the retention or diſſipation of the liberated matter of fire: amongſt

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these circumſtances we muſt rank the partial or free concurrence of the atmoſpheric air. But neither the incaleſcence, nor the fixable air, or the denſe inflammable air emitted, nor the diſſolution of the organiſed bodies, nor the waſte of their volatile parts, nor the combuſtions and conſumptions which happen in ſome inſtances, ſhew any thing that is not eaſily deducible from the foregoing notions.

Finally, with the proceſſes, in which fixable air is not only extricated but formed, and in which the matter of fire is at the ſame time liberated, I muſt rank that of reſpiration; in which the thin *reticular* bronchial membrane, rather promotes the agency of the air on the circulating blood, than prevents it by interceding them.

As all the ſaccharine, farinaceous, herbaceous, and oily vegetable ſubſtances, that are uſed as food, and all the eſculent animal ſubſtances alſo, abound with the ſame acid and phlogiſtic principles that are contained in our ethereal oil and in-

flammable

flammable air of acetous acid and ardent ſpirits; as theſe principles form a conſiderable part of the blood, and are well known to attract empyreal air, even when they are diffuſed in water and combined with other matter, as it happens in the vinous and acetous fermentations, in putrefactions, and in other proceſſes analagous to theſe; the aptitude of the blood to act on empyreal air, might be argued a priori, tho' not ſo fairly proved as it has been by the experiments firſt made by Dr. Prieſtley, and afterwards proſecuted by the Abbe Fontana and Mr. Lavoiſier.

An experiment which I made in May 1785, in my public courſe of Chemiſtry, and which I afterwards repeated, with the precaution of expiring all the air that I could from my lungs, and of breathing for a while ſuch air as I intended to try, ſeems to have cleared away all the doubts that attended this ſubject. It conſiſted in breathing two gallon meaſures of empyreal air from nitre, in a glaſs veſſel, poiſed and moveable in lime-water, ſo that the air within

within was always equally compreſſed by the atmoſphere, under every diminution of bulk by inſpiration, and the reſpiration was made without labour.

The lime water, in which the veſſel floated, was further impregnated with perfect lime, and this liquor was conſtantly daſhed and ſprinkled through the reſpired air, by the hand of an aſſiſtant, to accelerate the abſorption of the fixable air from the reſiduary elaſtic fluid; and thus I was enabled to continue the reſpiration much longer, wirhout interruption, or preparing my lungs anew, than I could otherwiſe have done. Notwithſtanding all this, I could not continue the reſpiration to the total conſumption of the empyreal air, but was obliged to deſiſt at intervals, and to return repeatedly to the reſpiration, with my lungs prepared as formerly, after the whole of the fixable air had been abſorbed by the lime liquor from the remaining empyreal air.

The decreaſe in the bulk of the reſpired air, not at all correſponding with the real

con-

consumption of empyreal air, and the quantity of phlogisticated air greatly exceeding that which might have eluded my previous trials of the empyreal air, both contributed to shew that some phlogistic air was produced or detached during the process: And now that Mr. Cavendish's experiments prove that the phlogistic air could not have been formed of the empyreal air, I do not hesitate in concluding, that the former was expelled from the lungs during the respiration, along with the matter which contributed to the formation of the fixable air. It therefore is not to be regarded in the present consideration of the expenditure of the empyreal air.

As the pursuit of this last was my chief purpose, and I have not room now for a circumstantial detail of particulars, I shall confine myself to the following report:— After the last respiration, which was maintained with great difficulty and anxiety, the empyreal air disappeared totally, the residue being mere phlogistic air, and the fixable air was not equal in weight to the expended empyreal air; therefore one-third of the empyreal air muſt have been otherwiſe engaged.

But from the moſt general analogy, and from the quantity of watery vapour that iſſues from the lungs at every expiration, whether we breathe empyreal air or atmoſpheric air, we may conclude that whilſt about two-thirds of the empyreal air were employed in forming fixable air with the acid principle of the oleaginous part of the blood, the remainder of the empyreal air was expended in the formation of water, or perhaps, by ſome ſmall part of it, in entering the blood: and ſince a great quantity of the matter of fire is detached, in every proceſs, whether of the mixture of elaſtic fluids, or putrefaction, or fermentation, or of the ſolutions of vegetable or animal ſubſtances in nitrous acid, or of combuſtion; whenever empyreal air is expended in the formation of fixable air or water, and eſpecially when both are compoſed at the ſame time; I ſee no reaſon to doubt of the truth of Dr. Crawford's opinion,

nion, that animal heat is generated in the lungs, and diſtributed from thence to the reſt of the body by the circulating blood: And thus the phenomena of reſpiration agree perfectly with the foregoing notions of matter.

F I N I S.

CORRECTIONS:

Page.	Line.	
8	2	*for* luminated *read* laminated
21	19	*dele* and weight
23	15	*for* are *read* were
—	16	*for* extends *read* extended
29	2	*for* more *read* others
30	8	*read* the more accurate diſtillations
—	14	*after* fire *add* in ſuch quantity
38	15	*dele* comma *after only*
39	2	*dele* elſe
—	9	*for* will *read* [illegible]
—	10	*for* phlogiſton *read* oil
—	11	*dele* will
—	22	*for* acetous *read* mere
45	18	*for* heighth *read* height
84	2	*read* ſuppoſitious
—	24	*for* fire *read* the matter of fire. *The like correction is to be made wherever it is admiſſible.*
95	8	*for* phlogiſtic *read* oleaginous
114	21	*for* flacculent *read* flocculent
133	10	*for* nitrous *read* phlogiſtic
138	3	*for* alkohol *read* oil
144	6	*for* equaled *read* greatly
146	14	*for* viſiuial *read* viſual
154	20	*for* contribute *read* contributes
171	9	*for* expells *read* expels
172	5	*for* protion *read* portion
174	4	*for* ſalts *read* ſalt
188	15	*for* cryſtaline *read* cryſtalline
192	6	*for* diſtills *read* diſtils
199	8	*and wherever it occurs for* cryſtalization *read* cryſtallization
202	—	*and wherever it occurs for* lithrage *read* litharge
204	1	*for* vivid *read* revived
—	17	*and elſewhere for* Kirvan *read* Kirwan
205	6	*for* motion *read* notion
208	8	*for* calculations *read* calcinations
—	21	*for* imbibe *read* imbibes
210	22	*for* tranſaction *read* tranſition
214	8	*for* , all *read* of all
219	20	*for* detatched *read* detached
225	15	*ftr* aparatus *read* apparatus
229	18	*for* think *read* to think
246	10	*for* this *read* with this
253	20	*for* duty *read* duly
260	22	*for* granuilar *read* granular
261	3	*for* ſeperated *read* ſeparated
—	10	*for* repoy *read* ropy
291	3	*for* finable *read* fixable
296	14	*dele* of
302	13	*for* incalaſcence *read* incaleſcence