

E S S A Y S,

ON THE

EFFECTS PRODUCED BY VARIOUS PROCESSES ON

ATMOSPHERIC AIR;

WITH A PARTICULAR VIEW

TO AN INVESTIGATION OF THE

CONSTITUTION OF THE ACIDS.

BY M. L A V O I S I E R,

Member of the ROYAL ACADEMY of SCIENCES at PARIS, &c.

TRANSLATED FROM THE FRENCH,

BY THOMAS HENRY, F. R. S.

Member of the *Medical Society of LONDON*, and of the *Literary*
and Philosophical Society of MANCHESTER.

W A R R I N G T O N,

P R I N T E D B Y W. E Y R E S,

For J. JOHNSON, N^o. 72, St. Paul's Church-Yard, LONDON.

M D C C L X X X I I I.

THE TRANSLATOR's

P R E F A C E.

IN a volume of Essays Physical and Chemical, written by M. Lavoisier, which I translated and published a few years since, a number of additional essays were announced, on various important subjects, with which that ingenious philosopher promised soon to favour the public. Other avocations, it should seem, have prevented the fulfilling of his engagement, and he appears to have been principally occupied in an attempt to overthrow Stahl's doctrine of phlogiston, and in an investigation of the nature and

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constitution of the acids. The result of his inquiries he has communicated to the royal academy of sciences in a series of memoirs, a translation of which is now presented to the public.

PHLOGISTON had been so much talked of, though never seen, by chemists, being cognisable only by its effects, that many began even to doubt its existence, and to regard it rather as a creature of the imagination, than as a real and powerful agent, concerned in some of the most important operations of nature. Among others, our author had entertained these doubts; and, imagining he saw strong objections to Dr. Priestley's theory of the phlogistication of air, he thought the changes effected in it, by various processes, might be accounted for on different principles.

DR. PRIESTLEY had supposed that fixed air is one of the constituent parts of

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of common air, and that, whenever a quantity of phlogiston is thrown into the latter, it separates the fixed air, and becomes united to the remainder, which has a greater affinity to it than to the fixed air, and forms phlogisticated air.

M. LAVOISIER however contends that this is not the case; that atmospheric air consists of about $\frac{1}{2}$ of very pure air, and $\frac{1}{2}$ of mephitic gas, which, when detached from its purer portion, is no longer fit for the purposes of air; and he denies that any fixed air is naturally contained in atmospheric air, but asserts that it proceeds from the union of coaly matter with the above pure part or Dr. Priestley's dephlogisticated air, a term which M. Lavoisier is not altogether disposed to admit.

ANOTHER objection of M. Lavoisier to Dr. Priestley's theory of the phlogistication of air, was founded on the different

views in which these two philosophers beheld the phænomena which take place during the calcination of metals, and their subsequent reduction to a metallic form. Dr. Priestley had supposed that a separation of the fixed air being effected by the phlogiston, this air is united to the metallic calx, and that, during the reduction, the calx recovers its phlogiston, and parts with the fixed air. On this M. Lavoisier observes, that it is probable the air absorbed is not fixed, but pure air, and that, could we reduce the calxes without addition, it would be separated again pure. This is actually the case with the calx of mercury, which requires no addition for its reduction, and yields pure dephlogisticated air when it recovers its metallic form. But the other calxes requiring the addition of some coaly matter, this, he imagines, debases the pure air, and changes it into fixed air. The agency of phlogiston, therefore, in this case also, he regards as gratuitous, and not sufficiently founded on facts.

THE

THE existence of phlogiston, however, has not only been proved, but Dr. Priestley has clearly shewn that phlogiston and inflammable air are the same thing, with this difference only, as Mr. Kirwan remarks, that when, in a state of elasticity, it possesses so much fire as is requisite to give it the form of vapour, and that this air is capable of being wholly absorbed in the reduction of metals, and of restoring to the calxes their pristine metallic splendor and malleability.*

THERE can be little doubt, therefore, that the phlogistication of air really takes place in many processes; but perhaps it may produce its effects in a manner somewhat different to what Dr. Priestley originally imagined. The idea of that excellent philosopher seemed at first well

* I AM informed that Dr. Priestley has delivered an account of his interesting experiments and remarks, on this subject, to the Royal Society.

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founded; but recent facts have thrown a different appearance on the subject. Of these none are more convincing than the experiments of M. Lavoisier on the combustion of pyrophorus, by which almost the whole of the dephlogisticated air employed, instead of being phlogisticated in the sense of Dr. Priestley's term, was converted into fixed air.

Now as the being of phlogiston can be no longer doubted; as Dr. Priestley has literally given "*to airy nothing a local habitation and a name*;" and has embodied and rendered visible this Proteus which has so long eluded the grasp and sight of the chemist; the truth may, perhaps, without much difficulty, be found, by changing M. Lavoisier's term coaly matter, *matière charbonneuse*, for that of phlogiston; and allowing that, instead of wholly uniting with the residuum, it partly combines with the pure or dephlogisticated portion of the common air, and thereby

thereby forms the aërial acid or fixed air, which is, in fact, a true phlogisticated acid.

THE other objection has been answered by Mr. Kirwan, in his admirable paper on the specific gravities, &c. of saline substances.* Mercury affords inflammable air, and consequently contains phlogiston. This phlogiston must fly off during the calcination, and form fixed air, which will be absorbed by the calx. And though the calx, when reviving, yields dephlogisticated air, this may depend upon the mercury's attracting the phlogiston from the air, and applying it to its own reduction.

THAT fixed air contains phlogiston has been proved by Mr. Kirwan, and he has even determined the amount of it to be in the proportion of 14,661 grains of

* Phil. Trans. Vol. LXXII. p. 227.

phlogiston,

phlogiston, and 85,339 of pure air in 100 grains of that gas. And he computes that 100 cubic inches of dephlogisticated air are converted into fixed air by 7,2165 grains of phlogiston, and will then be reduced to the bulk of 86,34 cubic inches; and that, reciprocally, 100 cubic inches of fixed air being decomposed, will afford 115,821 cubic inches of dephlogisticated air, and part with 7,2165 grains of phlogiston, supposing the decomposition to be complete, or, in other words, the dephlogisticated air to be quite pure.*

WE therefore seem to be arrived at a pretty perfect knowledge of the constituent parts of one of the acids, viz. the aërial, which appears to be compounded

* Phil. Trans. Vol. LXXII. p. 236.—Mr. Kirwan also mentions Dr. Priestley's very candid approbation of his account of the constitution of fixed air, though so contrary to opinions which the Doctor had advanced in his last publication. An instance of philosophical candour highly to be admired and worthy of imitation.

of the pure part of atmospheric air, united with phlogiston, and, in its elastic state, also containing a portion of latent heat, or as M. Lavoisier, perhaps as properly calls it, fixed fire.

MANY of the ensuing essays strongly tend to demonstrate that this pure air enters, also, as a principal component part, into the constitution of the other acids;* but we yet remain unacquainted with the true nature of the other portion, by the variety of which, each acid seems to be distinguishable from the others. M. Lavoisier has supposed the vitriolic acid to be formed by the junction of sulphur to pure air, and that sulphur is formed by depriving vitriolic acid of this air. Should we not rather say, that when vitriolic acid is formed, the

* THE Abbé Fontana and Mr. Berthollet had before shewn, that the acid of ants and the vegetable acids consist of fixed air, or are, at least, resolvable into it. Vide Cavallo's Treatise on Air, p. 607.

fulphur

sulphur throws off its phlogiston, a part of which, joining with the pure portion of the atmosphere, is again attracted by the basis of the sulphur, and, thus combined, forms the acid ; and, on the contrary, that when this acid is reconverted into sulphur, the basis parts with the pure air, and recovers its phlogiston ?

AN experiment of Dr. Priestley's, which he lately communicated to Dr. Percival, greatly elucidates and almost confirms this opinion. Having mentioned his having formed sulphur by the union of inflammable air with vitriolic acid, as a proof of the identity of that air with phlogiston ; he adds, that he had also proved, more unexceptionably than before, that the electric matter contains phlogiston, by making it to pass through the air, confined by the acids, in a syphon. " When," says he, " I use the " dephlogisticated marine acid, the air is " diminished by the process, and dephlo-
" gisticated.

“ gisticated. If I use the phosphoric acid
“ or the phlogisticated alkali, the air is first
“ diminished, and then increased by an
“ addition of inflammable air. If I use
“ VITRIOLIC ACID or the NITROUS ACID,
“ there is a production of DEPHLOGIS-
“ TICATED AIR, faster than the electric
“ city can injure it.” Now, from whence
can this dephlogisticated air proceed,
but from a decomposition of the acids by
the phlogiston of the electric matter, in
which the pure air is separated, while
the phlogiston, combining with the
remaining part or basis of this acid, forms
a sulphur?

WHETHER the phlogiston, by means
of which the pure air is separated, and
which uniting therewith forms fixed air,
be admitted into the composition of the
acid, or rejected when that air loses its
elasticity, is not as yet ascertained. It is
probable, that the acid not only receives
its acidifying principle from the pure air,
but

but also its fire or absolute heat. Now though Dr. Crawford has shewn that bodies which contain much phlogiston possess little absolute fire (these substances repelling each other; so that the addition of phlogiston to any substance expels from it a part of its fire, and, on the other hand, the addition of fire separates a part of its phlogiston) yet it appears that their coexistence is not incompatible; inflammable air, as was before observed, owing its elasticity to a portion of fire with which it is combined.* Now as a small portion of phlogiston, added to vitriolic acid, makes volatile vitriolic acid, and a larger dose fixes it and forms sulphur, perhaps a very minute quantity may be necessary to the composition of the acid.

M. LAVOISIER objecting, and with some reason, to the appellation of fixed

* Kirwan, Phil. Trans. Vol. LXXII. p. 209.

air,

air, has, in the subsequent essays, denominated it, the *chalky aërisform fluid or acid*; and the academy not satisfied with this name, as being too confined, have preferred that of *gaseous air*. But, as the customary term is best known to English readers, I have thought proper to retain the use of it, till philosophers, in general, have agreed upon the adoption of a new one.

T H E
C O N T E N T S.

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E S S A Y I.

E X P E R I M E N T S

ON THE

R E S P I R A T I O N O F A N I M A L S,

AND ON THE CHANGES EFFECTED ON THE

AIR IN PASSING THROUGH THEIR LUNGS.

OF all the phenomena of the animal œconomy, none is more striking, none more worthy the attention of philosophers and physiologists than those which accompany respiration. Little as our acquaintance is with the object of this singular function, we are satisfied that it is essential to life, and that it cannot be suspended for any time, without exposing the animal to the danger of immediate death.

B

IT

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IT is universally known that air is the agent, or rather the subject of respiration; but at the same time all sorts of air, or more generally speaking, all sorts of elastic fluids, are not proper for the purpose, nay, there are many kinds which animals cannot breathe, without perishing, at least, as soon, as if they had no air to respire.

THE experiments of some philosophers, and especially those of Messrs. Hales and Cigna, had begun to afford some light on this important object; and, Dr. Priestley has lately published a treatise, in which he has greatly extended the bounds of our knowledge; and has endeavoured to prove, by a number of very ingenious, delicate, and novel experiments, that the respiration of animals has the property of phlogisticating air, in a similar manner to what is effected by the calcination of metals and many other chemical processes; and that the air ceases not to be respirable, till the instant when it becomes surcharged, or at least saturated, with phlogiston.

HOWEVER probable the theory of this celebrated philosopher may, at first sight, appear; however

however numerous and well conducted may be the experiments by which he endeavours to support it, I must confess I have found it so contradictory to a great number of phenomena, that I could not but entertain some doubts of it. I have accordingly proceeded on a different plan, and have found myself led irresistibly, by the consequences of my experiments, to very different conclusions. It will not be necessary, at present, to discuss, particularly, each of Dr. Priestley's experiments, nor to shew how they all contribute to confirm the opinion which I am proceeding to communicate in this memoir: it will be sufficient to relate my own, and to give an account of their results.

IN a convenient apparatus, which it would be difficult to describe without the aid of engravings, fifty cubic inches of common air were inclosed, to which I introduced four ounces of very pure mercury, which I proceeded to calcine by keeping it, during twelve days, in a degree of heat almost equal to that which is necessary to make it boil.

NOTHING remarkable occurred during the first day: the mercury, though it did not boil,

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was in a continual state of evaporation, small drops of it, which were at first very minute, lined the inside of the vessels, and gradually increasing till they acquired a certain bulk, fell again by their own gravity to the bottom. On the second day I could observe some small red particles swimming on the surface of the mercury, which, in a few days, increased both in number and bulk. On the twelfth day, having extinguished the fire and suffered the vessels to cool, I observed that the air, which they contained, was diminished to the amount of from eight to nine inches, viz. about $\frac{1}{5}$ of its volume: at the same time a considerable portion of mercurius precipitatus per se, or calcined mercury, was formed, which I computed to be about forty-five grains.

THIS air, which had been thus diminished, did not precipitate lime-water; but it extinguished candles, and animals, immersed in it, perished in a short time: it no longer afforded red vapours, when mixed with nitrous air, nor was diminished by it. In short, it was absolutely reduced to a mephitic state.

IT

It has been proved by Dr. Priestley's, and also by my own, experiments, that calcined mercury is merely a combination of that metal with about $\frac{1}{2}$ part of its weight of air, much better and more respirable, if the expression may be allowed, than common air: it should appear then, as proved, that, in the preceding experiment, the mercury, as it calcined, had absorbed the best and most respirable part of the air, and left only the mephitic or unrespirable part. The following experiment confirmed me more and more in the truth of this opinion.

I CAREFULLY collected the forty-five grains of calcined mercury which had been formed in the preceding experiment; and putting it into a very small glass retort, the neck of which was turned up so as to pass under the edge of a bell-glass, filled with, and inverted into, water, I proceeded to reduce it without addition. By this operation I recovered nearly the same quantity of air which had been absorbed during the calcination; namely, between eight and nine cubic inches, which, when recombined with the air which had been vitiated by that process, re-

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stored the latter, pretty exactly, to the same state in which it had been, previous to the calcination being performed in it, viz. that of common air; for now candles were not extinguished in it; animals no longer perished in it, and it was nearly as much diminished as atmospheric air, by the addition of nitrous air.

We have here the most complete proof, that chemistry can afford, of the decomposition and recombination of air; from whence it evidently results, 1st. that $\frac{1}{5}$ of the air which we breathe, are mephitic, or incapable of supporting the respiration of animals, or the inflammation and combustion of bodies: 2dly. that the surplus, or $\frac{4}{5}$ only of the volume of atmospheric air, is respirable: 3dly. that, in the calcination of mercury, this metallic substance absorbs the salubrious part, leaving only the mephitic portion of the air: 4thly. that by reuniting these two portions which had been separated, we can recompound air, similar to that of the atmosphere.

THESE preliminary truths, relative to the calcination of metals, tend to lead us to plain consequences

sequences concerning the respiration of animals; and as the air, which has served some time for this vital office, has much relation to that in which metals have been calcined, our knowledge, relative to the one, leads us naturally to an application of it to the other.

I PLACED a sparrow under a glass receiver, filled with common air and standing in mercury, capable of containing thirty-one cubic inches: the bird did not seem at all affected at first, except that it was a little stupefied: in a quarter of an hour it began to be agitated; its respiration became laborious and rapid; and, from this instant, the symptoms of distress increased, till, at the end of fifty-five minutes, it died convulsed.—Notwithstanding the heat of the animal, which necessarily, at first, rarefied the air in the receiver, there was a sensible diminution of its bulk, which at the end of fifteen minutes amounted to about $\frac{1}{40}$; but instead of increasing afterwards, the diminution became something less in about half an hour; and when the animal was dead, and the air in the receiver had recovered the temperature of the room where the experiment

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was made, the diminution did not appear to be more than $\frac{1}{65}$.

THIS air, which had been respired by the sparrow, was become very different from that of the atmosphere: it precipitated lime-water; extinguished candles, and suffered no diminution by the test of nitrous air: another bird, introduced into it, existed but a few moments: it was, in short, entirely mephitic, and, in that respect, appeared much similar to that in which mercury had been calcined.

BUT a more attentive examination discovered to me two very remarkable differences between the two airs: 1st. the diminution of that, in which the sparrow had died, was much less than that of the air which had been employed for the calcination; and, 2dly. the respired air precipitated lime-water, on which the other produced no change.

THIS difference between these two airs, on the one part, and, on the other, the great analogy which appeared between them, in many respects, led me to presume, that two causes are complicated

cated in respiration, of which probably I was hitherto acquainted only with one; and to clear up my suspicions on the subject, the following experiment was made.

INTO a jar filled with mercury, and inverted into the same, were passed twelve inches of air, vitiated by respiration; and a thin stratum of caustic fixed alkali was introduced to the surface of the metal. I might have made use of lime-water, but the necessary quantity of it would have been too considerable, and would have impeded the success of the experiment.

THE effect of the caustic alkali was to occasion a diminution in the volume of this air, of nearly $\frac{1}{6}$; while, at the same time the alkali had, in part, lost its causticity, and acquired the property of effervescing with acids; it also crystallised within the glass, even under a very regular rhomboidal form; properties which we know could not be communicated to it, but by combining it with that species of air or gas, known by the name of fixed air: from whence it appears that air, vitiated by respiration, contains nearly $\frac{1}{6}$ of an aeriform acid, perfectly similar to that obtained from chalk.

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THE air, thus deprived of its fixable part by the caustic alkali, was so far from being re-established in the state of common air, that, on the contrary, it approached nearer to that of the air which had been employed in the calcination of mercury, or, more properly, was exactly the same ; for neither candles could burn, nor animals live in it ; nor could I perceive, from any experiments I made, the least difference between the two airs.

Now air which has served for the calcination of metals, is, as we have already seen, nothing but the mephitic residuum of atmospheric air, the highly respirable part of which has combined with the mercury, during the calcination : and the air which has served the purposes of respiration, when deprived of the fixed air, is exactly the same ; and, in fact, having combined, with the latter residuum, about $\frac{1}{4}$ of its bulk of dephlogisticated air, extracted from the calx of mercury, I re-established it in its former state, and rendered it equally fit for respiration, combustion, &c. as common air, by the same method as that I pursued with air vitiated by the calcination of mercury.

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THE result of these experiments is, that to restore air that has been vitiated by respiration, to the state of common respirable air, two effects must be produced: 1st. to deprive it of the fixed air it contains, by means of quick-lime or caustic alkali: 2dly. to restore to it a quantity of highly respirable or dephlogisticated air, equal to that which it has lost. Respiration, therefore, acts inversely to these two effects, and I find myself in this respect led to two consequences equally probable, and between which my present experience does not enable me to pronounce.

AFTER what we have seen, it may be concluded, that one of the two following effects is produced by respiration: either the highly respirable portion contained in common air, is converted into fixed air, in passing through the lungs, or else an exchange is made in that viscus; on one part the dephlogisticated air is absorbed, and on the other, the lungs throw out a portion of fixed air, nearly equal in bulk to the other.

THE first of these opinions is supported by an experiment which I have already communicated

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nicated to the academy. For I have shewn in a memoir, read at our public Easter meeting, 1775, that dephlogisticated air may be wholly converted into fixed air by an addition of powdered charcoal ; and, in other memoirs, I have proved that this conversion may be effected by several other methods : it is possible, therefore, that respiration may possess the same property, and that dephlogisticated air, when taken into the lungs, is thrown out again as fixed air. But, on the other hand, strong analogies seem to militate in favour of the second opinion, and lead us to believe that a portion of the pure air remains in the lungs, and is combined with the blood. We know that it is one property of this air to communicate a red colour to bodies, and especially to metallic substances, with which it is combined : mercury, lead, and iron furnish examples of this fact. These metals form, with highly respirable air, beautiful red calces, the first under the name of calcined mercury, or red precipitate of mercury ; the second under that of minium ; and the third, of colcothar. The same effects, the same phenomena, are observable, in the calcination of metals and in the respiration of animals ; all the circum-

circumstances are the same, even to the colour of the residuums. May we not then suppose that the red colour of the blood depends on the combination of dephlogisticated air, or, to speak more accurately, of its basis with an animal fluid, in the same manner as the colour of red precipitate of mercury and minium is owing to the combination of this basis with a metallic substance? Though this consequence has not been deduced by Mr. Cigna, Dr. Priestley, and other moderns who are occupied on this object, I will venture to say that there is none of their experiments that do not tend, in appearance, to confirm it; nay, they have proved, and more especially Dr. Priestley, that the blood is red only in proportion as it is continually in contact with atmospheric, or with dephlogisticated air; that it becomes black in fixed air, in nitrous, in inflammable, and in all unrespirable airs, and also in the exhausted receiver of an air-pump: that on the contrary it recovers its red colour, when placed again in contact with air, and especially if it be dephlogisticated, and that this restoration of colour is constantly attended by a diminution in the volume of air. Does it not then follow, from all these facts, that this pure species of air has
the

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the property of combining with the blood, and that this combination constitutes its red colour. But whichever of these two opinions we embrace, whether that the respirable portion of the air combines with the blood, or that it is changed into fixed air in passing through the lungs; or lastly, as I am inclined to believe, that both these effects take place in the act of respiration, we may, from facts alone, consider as proved,*

1st. THAT respiration acts only on the portion of pure or dephlogisticated air, contained in the atmosphere; that the residuum or

* THAT truly ingenious philosopher Dr. Crawford has proved that dephlogisticated air contains a large proportion of absolute heat, and on this fact has founded a very probable theory of the cause of animal heat. He supposes that this pure part of atmospheric air has a greater affinity to phlogiston than to heat, and therefore that when a quantity of atmospheric air is inspired by the lungs, the pure part receives the phlogiston which is continually throwing off from the blood, by means of the bronchial vesicles, and in return parts with a quantity of absolute heat, which is absorbed by the blood. In every process in which there is an emission of phlogiston, fixed air is formed, and seems to consist of phlogiston united to the pure part of the atmosphere. T. H.

mephitic

mephitic part is a merely passive medium which enters into the lungs, and departs from them nearly in the same state, without change or alteration.

2dly. THAT the calcination of metals, in a given quantity of atmospheric air, is effected, as I have already often declared, only in proportion as the dephlogisticated air, which it contains, has been drained, and combined with the metal.

3dly. THAT, in like manner, if an animal be confined in a given quantity of air, it will perish as soon as it has absorbed, or converted into fixed air, the major part of the respirable portion of air, and the remainder is reduced to a mephitic state.

4thly. THAT the species of mephitic air, which remains after the calcination of metals, is in no wise different, according to all the experiments I have made, from that remaining after the respiration of animals; provided always, that the latter residuum has been freed from its fixed air: that these two residuums may be substituted for each other in every experiment,

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ment, and that they may each be restored to the state of atmospheric air, by a quantity of dephlogisticated air, equal to that of which they had been deprived. A new proof of this last fact is, that if the portion of this highly respirable air, contained in a given quantity of the atmospheric, be increased or diminished, in such proportion will be the quantity of metal which we shall be capable of calcining in it, and, to a certain point, the time which animals will be capable of living in it.

THE limits which I have prescribed to myself in this memoir, will not permit me to enter on many other experiments which tend to the support of the theory I have advanced. Of this number, is a part of those which Messrs. Trudaine, de Montigny, and myself have lately made, in the Montigny laboratory. There is reason to hope that these experiments will throw still additional light, not only on the respiration of animals, but also on combustion: operations which have a much stronger relationship to each other, than we may, at first sight, believe.

ESSAY

E S S A Y II.

ON THE COMBUSTION OF CANDLES
IN ATMOSPHERIC AIR AND IN
DEPHLOGISTICATED AIR.

IT having been sufficiently proved that the air of the atmosphere is not a simple substance or element, as the ancients believed, and has been imagined even in our own time; but that it is composed in part only of very pure or dephlogisticated air, and that the remainder, which is perhaps still a compound, is mephitic, and incapable of supporting either animal life, combustion, or flame; it will be necessary, in order that this essay may be intelligible, to distinguish four species of aëriform fluids.

1st. ATMOSPHERIC air, in which we live, respire, &c.

C

2dly. PURE

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2dly. PURE or dephlogisticated air, which forms about $\frac{1}{4}$ of the composition of atmospheric air.

3dly. THE mephitic part of atmospheric air, which forms $\frac{3}{4}$ of its composition; with the nature of which we are as yet wholly unacquainted.

4thly. FIXED air, as it is commonly called, which may exist either in a state of elasticity, or quiescent and united with other bodies.

THOSE who have been employed in making experiments on the burning of candles, have been convinced that a considerable diminution took place, during the combustion, in the volume of air. To prove this, a very simple but inconclusive experiment has been made. A lighted candle has been placed on the plate of an air-pump, and being covered with a receiver, it has been observed that the candle was soon extinguished, and that as soon as the vessels were become cold, the receiver adhered to the plate. But this effect could not be produced except the volume of air, remaining in the receiver after the combustion, were smaller than it was

previous

previous to the introduction of the candle. But attention has not been paid to this circumstance, that a candle cannot be placed under a receiver, but the contained air must be heated at the instant when the candle is introduced, and before the receiver can be applied to the plate. The air included in the receiver therefore being hot, it will diminish in bulk as it grows cool; and this may account for the adhesion of the receiver to the plate, when the candle is extinguished and the vessels cooled.

It is proper also to remark, that there are few air-pumps which do not admit of the passage of some portions of air, between the leather and the edges of the receiver; especially when the receiver, so far from adhering to the plate, is rather pushed from it, by the rarefaction of the internal air; consequently, there is almost always an escape of air while the candle continues to burn; and as there will not remain a sufficient quantity under the receiver to balance the pressure of the atmosphere, another cause is formed of the receiver's adhering to the plate.

EXPERIMENTS made in jars immersed in water are equally unsatisfactory. 1st. The air is rare-

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fied when the candle is introduced, and continues to dilate during the combustion, and; therefore, a considerable portion of it escapes at the rim of the jar. Hence it is impossible to ascertain the quantity of air on which we operate, nor the real amount of the diminution in its bulk. adly. The burning of candles has the property of changing a part of the atmospheric air into fixed air ; and as the latter is capable of combining with water, supposing a diminution in the bulk of the air to have been caused by the combustion, and taken place during the experiment, it is impossible to distinguish it from that which proceeds from the combination of the fixed air with the water.

THESE reflections induced me to take another method, and convinced me of the necessity of operating over mercury. I accordingly began by immersing a glafs jar, at the same time inclining it to a certain angle, into a basin of mercury ; and then setting it upright, I marked the place which answered to the surface of the quicksilver, and repeated this trial so often, that I was assured that the mercury corresponded very nearly each time with the mark I had first made on the jar.

BEING

BEING thus convinced of the practicability of always inclosing the same quantity of air under the jar, by sufficient care and attention; I proceeded in the same manner, holding the jar inclined and partly plunged in quicksilver in my left hand, and, with my right, introducing under it, very quickly, a small lighted wax candle. The introduction of the candle, the immersion and elevation of the jar, ought to be performed in an instant, and it will be necessary to practise these evolutions, till such a degree of dexterity be acquired by the experimenter, as to enable him to perform all these operations in an almost indivisible space of time.

IN a few moments after the candle has been inclosed in the jar, it begins to give a weaker light, and, in a short time, is extinguished. The mercury, as might be expected, descends, at first, rapidly, owing to the heat and rarefaction of the confined air; but when the candle is extinguished, and the vessels are perfectly cooled, it returns pretty exactly to the mark which had been made before the introduction of the candle. I have used the expres-

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sion *pretty exactly*, as it is impossible to answer for very trifling differences in this experiment, because that slight errors, as to the height of the mercury, may be caused by some little variation in inclining the jar more or less, or by some circumstances attending its elevation.

THE result of this experiment did not convince me that the burning of a candle occasioned no sensible diminution in the volume of air; it was still necessary to determine the state of the air after the combustion, and the changes that might have been effected in it. I therefore introduced to the air in the jar, in which the candle had been extinguished, a small portion of a caustic lixivium of fixed alkali. The volume of air was presently diminished, and reduced from 26 to $23\frac{1}{2}$ inches; so that the diminution amounted to nearly $\frac{1}{6}$ of the original quantity of air. At the same time the caustic alkali had acquired the property of effervescing with acids; which proved that the diminution had been occasioned by the fixed air combining with the alkali: for when I added a small portion of vitriolic acid to the alkaline ley in the jar, a brisk effervescence ensued, the absorbed air was again

again separated, and the mercury redescended almost exactly to the mark which I had made on the jar.

THOUGH this experiment was perfectly conclusive in some respects, it was still insufficient to my views, relative to the diminution of the bulk of air by combustion, and there remained still something incomplete on this subject. For considerable differences in the experiment might be caused merely by inclining the jar more or less, and it was very possible that the diminution of the air might have been counterbalanced by some error in the process; I therefore resolved to take every precaution in my power, to obtain a result that should be more certain, and free from every kind of error; to which purpose the following experiment appeared to me likely to be more decisive.

IN the middle of a glass stand, was placed a small wax candle; and on the top of the wick, was fixed a small piece of Kunckel's phosphorus, weighing about $\frac{1}{10}$ of a grain. The stand was then placed in a basin of mercury and covered with a jar, and, by means of a syphon, I raised the mercury, by suction, to a certain

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elevation which I marked exactly with a slip of paper. Every thing being thus disposed, I made a piece of iron wire red hot, having first bent it for the purpose, and then passed it through the mercury, into the jar, so as to touch the top of the candle and set fire to the little piece of phosphorus. Though the wire must, necessarily, have been much cooled in passing through the mercury, it still retained sufficient heat to inflame the phosphorus, and by this means the candle was lighted, as I expected.

While the candle continued to burn, the air was rarefied; but when it was extinguished, the mercury mounted insensibly, in proportion as the vessels cooled, and became stationary a little above the mark I had made before the candle was lighted. From this it was evident, that a small diminution in the bulk of the air was effected, and being measured very precisely, it was found to amount exactly to $\frac{3}{4}$ of a cubic inch. But one grain of phosphorus absorbs, in combustion, three cubic inches of air, as has been established by several experiments.* The $\frac{1}{16}$ of a grain therefore should

* SEE Lavoisier's Essays, Physical and Chemical, translated by Henry, chapter ix.

absorb

absorb half an inch, which reduces the real diminution of the air, caused by the burning of the candle, to $\frac{1}{4}$ of an inch. The jar contained seventy-two cubic inches. On the supposition, therefore, that the diminution of $\frac{1}{4}$ of an inch was not to be attributed to some slight error with respect to the measures, the diminution occasioned by the burning of a candle in common air would not amount to above $\frac{1}{48}$ in, which may be regarded as a mere nullity, especially if it be considered that a very trifling change in the temperature of the room, is capable of producing this difference.

As the jar which I had used in this experiment was very long and narrow, I imagined that the candle might not have burnt so long as it would have done, if the vessel had been less lofty, and the circulation of air more easy. The experiment was therefore repeated in a vessel which was shorter and not capable of containing above thirty cubic inches.

THE circumstances, under which the experiment was conducted, were exactly the same as in the former ones, and when the vessels were quite

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quite cold there was a diminution of the volume of air of $\frac{1}{4}$ an inch, which precisely corresponds with the quantity which might be supposed to be absorbed by $\frac{1}{16}$ of a grain of phosphorus, if burnt alone under a jar. The burning of the candle, therefore, had occasioned no sensible diminution in the bulk of air.

FROM these several experiments it may be regarded as certain, 1st. that the burning of candles does not sensibly diminish the volume of air in which they burn. 2dly. That this combustion has the property of converting into fixed air about $\frac{1}{16}$ of the original quantity of air. 3dly. That if the air in which a candle has burnt, be brought into contact with lime-water or caustic alkali, in that case the above diminution of $\frac{1}{16}$ is produced by these liquids absorbing the fixed air which has been formed during the combustion.

THE air in which candles have thus burnt, when deprived by water, or any other means, of the portion of fixed air, formed in it, is called by Dr. Priestley and several others, the phlogisticated part of the air. They are of opinion, that

that there arises from candles when burning, and from metals when calcining, &c. a phlogistic emanation which combines with and saturates the air. My sentiments of the case are different, and I have already given some proofs that the residuum of atmospheric air, after combustion, &c. is its mephitic portion, which forms three fourths of its composition, deprived in a greater or less degree of its pure, respirable part. And in fact, if we restore to the residuum of the original quantity of air this $\frac{1}{4}$ of pure air which it has lost, we thereby restore it to its former state. Now if, as Dr. Priestley supposes, this air were phlogisticated, or contaminated by some principle which rendered it unsalutary, it would not be sufficient to restore to it the portion of which it had been deprived, but, in order to re-establish it in the state of common air, it would be necessary also to separate this contaminating substance from it. Besides, as I am going to oppose, by a train of experiments, Stahl's doctrine of phlogiston,* the objections which I shall adduce on that occasion will militate equally against the supposed phlogistification of air.

* See the preface.

FROM

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FROM my account, atmospheric air consists of about $\frac{3}{4}$ of its bulk of pure respirable air. The combustion of candles converts only $\frac{1}{5}$ of it into fixed air; supposing, then, the volume of air to have been 100 before the combustion, there should remain, after the operation, seventy-five parts of mephitic, and fifteen of pure air: and we accordingly find that animals will live; or phosphorus burn, in this residuum, after a candle has been extinguished by it; and even after this proof, there will still remain five parts of pure air. This last portion is so firmly united to the mephitic part, that I know of no other means of separating it than by the combustion of pyrophorus; which will appear in a succeeding essay.

THERE remains nothing to complete what I have to say on the subject, except an account of the phenomena which attend the burning of candles in very pure air. These experiments will furnish me with fresh weapons against the gratuitous doctrine of the phlogistication of air.

INTO a glass jar, filled with very pure air, obtained from calcined mercury, a candle was introduced.

introduced. This jar was fixed in a basin of quicksilver. The candle burnt with a vivid light, an enlarged flame, and all the circumstances described by Dr. Priestley. The heat, during the combustion, was so great, that a portion of air passed by the rim of the jar, and escaped, but the quantity was not very considerable. When the candle was extinguished and the vessels cooled, I introduced some caustic fixed alkali, over the surface of the quicksilver in the jar. Immediately the fixed air was absorbed, and I found by this trial that two thirds of the pure air had been converted into fixed air by the combustion. But, what was still more interesting, the remaining third, after the absorption of the fixed air, was still almost pure: for having transferred it into a smaller jar, a candle was again lighted in it; it afforded an enlarged flame, and about one half of it was converted into fixed air. The remainder, after the absorption by caustic alkali, was nearly of the same goodness as common air.

• WHEN, therefore, a candle is made to burn in a jar containing one hundred parts of pure or dephlogisticated air, sixty-six parts are changed into

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into fixed air, and of the thirty-four remaining parts, twenty-one, and $\frac{1}{2}$, are still pure air, capable of being changed into fixed air. Out of 100 parts, only $12\frac{3}{4}$, or about $\frac{1}{8}$, remain of air capable of extinguishing a candle without producing any precipitation in lime-water, and this appears to have been a portion of mephitic air contained in the dephlogisticated air. Undoubtedly this portion would have been still smaller, if the air had been more pure.

Now if, as is supposed by the celebrated philosopher, Dr. Priestley, combustion were possessed of the property of phlogisticating air, the quantity of phlogisticated air, formed during the process, should be greater in proportion to the quantity of combustible matter consumed. For the combustion is almost four times as much in dephlogisticated, as in an equal bulk of common, air; and therefore four times as much phlogisticated air should be formed; whereas on the contrary we obtain nine times less. The disproportion, then, of what we really have, to that which we ought to expect, according to Dr. Priestley's opinion, is as 1 to 36.

LASTLY,

LASTLY, the residuum after the combustion of phosphorus, and especially of pyrophorus, in dephlogisticated air, is still less than that after the burning of candles, and may be considered as a mere nothing ; whereas, according to Dr. Priestley's theory, it ought to be more considerable. It cannot therefore be to the addition of phlogiston that the formation of the mephitic residuum of atmospheric air after combustion is to be attributed, and it therefore must have existed, as I have advanced, previous to the combustion.

THE preceding experiments seem therefore to have proved the following facts :

1st. THAT the mephitic portion which forms of the composition of atmospheric air, contributes nothing to the phenomena of combustion.

2dly. THAT the action of combustion is confined to the portion of pure or dephlogisticated air, which forms the other $\frac{1}{4}$ of atmospheric air.

3dly. THAT

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3dly. THAT only $\frac{2}{3}$ of this pure air can be converted into fixed air, by the burning of candles, and that the other $\frac{1}{3}$ remain united to the mephitic portion, without combustion having the power to separate them,

4thly. THAT phosphorus has a greater power than candles, as it is capable of separating $\frac{2}{3}$ of the pure air contained in atmospheric air,

5thly. THAT pyrophorus acts yet more forcibly, and seems to convert almost the whole portion of pure, into fixed air.

THESE consequences might be carried much further, and it might be shewn, that fixed air, which is formed during the combustion of candles, is nothing but the inflammable air separated from the candle, united with a greater proportion of the pure part of the air in which the combustion is carried on, and a smaller, though considerable, portion of the matter of fire which enters into the composition of both kinds of air. But the proofs which might be adduced of these assertions are such as my readers are not yet prepared to receive, and I must

must defer the elucidation of this theory, till, on one part, I have demonstrated the existence of the matter of fire in aëriform fluids, and have shewn in a future essay, that fixed air may be formed, by combining inflammable, with the basis of dephlogisticated, air.

ESSAY III.

ON THE COMBUSTION OF KUNCKEL'S
PHOSPHORUS, AND ON THE NATURE OF
THE ACID RESULTING FROM THE PROCESS.

SECTION I.

*On the Combustion of Phosphorus, and the Formation
of its Acid.*

I HAVE already related, in chap. IX. part II. of my Essays Physical and Chemical, some of the principal phenomena attending the combustion of phosphorus, and the formation of its acid; but the intelligence I have acquired, since the publication of that work, enabling me to give a more accurate account of the results, and to be more certain in my explanations, I shall resume the subject in a summary way, and shall first speak of the formation of the phosphoric acid, before I proceed to the relation of the

the results of its combination with different mineral and vegetable substances.

If Kunckel's phosphorus be lighted, by means of a burning glass, under a jar inverted into a basin of mercury, we observe, 1st. that only a given quantity of phosphorus can be burnt in a determined quantity of air, and that these proportions are about one grain of the former to from sixteen to eighteen cubic inches of air.

2dly. THAT as soon as this quantity is burnt, the phosphorus is extinguished, without any possibility of kindling it again, except by bringing it into contact with fresh air, which has not hitherto been employed for combustion.

3dly. THAT fresh phosphorus, introduced under the same receiver, does not burn better than the former.

4thly. THAT during the combustion, a large quantity of white flowers or flakes are formed, which resemble very fine snow, and attach themselves every where to the inside of the receiver. These constitute the concrete phosphoric acid.

D 2 5thly. THAT

5thly. THAT at the beginning of the combustion, the air in the receiver is considerably dilated, on account of the heat which is produced; but, in a very short time, its bulk becomes so much diminished, that, when the vessels are cooled, it occupies no more than about $\frac{4}{5}$ or $\frac{3}{4}$ of the space it filled previous to the combustion. If the flowers are collected and carefully weighed, before they come in contact with fresh air, or have attracted any moisture from it, they will be found to be $2\frac{1}{2}$ times the weight of the phosphorus employed for their formation; or in other words, with one grain of phosphorus there will have been formed $2\frac{1}{2}$ grains of concrete phosphoric acid.

THIS very extraordinary increase of weight is pretty exactly proportioned to the quantity of air absorbed; for the absorption is actually about three cubic inches of air for each grain of phosphorus that has been burnt; and as three cubic inches of air weigh about one grain and half, this weight, added to one grain of phosphorus, gives $2\frac{1}{2}$ grains, the weight which the flowers have been observed to possess.

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THE air thus reduced, as much as it can be, by the combustion of phosphorus, is so far from being more dense than atmospheric air, that its specific gravity is even rather diminished than augmented. It is no longer capable of serving for the respiration of animals, of supporting the combustion or inflammation of bodies, and, in short, is absolutely in a mephitic state, and therefore to avoid confounding it with any other species of air, I shall distinguish it, in this memoir, by the name of atmospheric gas: but if to this air, thus decomposed, and which no longer possesses the principal characteristics of common air, be added a quantity of dephlogisticated or highly respirable air, obtained from the calx of mercury or of lead, equal to the bulk of air which was absorbed during the combustion, it is again rendered capable of supporting the respiration of animals, the combustion of bodies, &c. and in a word re-assumes all the properties it possessed before the operation.

IF after the above described re-establishment of the air, the phosphorus be kindled again, exactly the same effects are observed as in the

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former combustion; and the air may be repeatedly reduced to a mephitic state, and restored to that of common air, by the same methods.

It is however proper to observe, that if we wish to carry this experiment to some length, it will be necessary to add, each time, a somewhat larger proportion of dephlogisticated air, than has been absorbed in the preceding combustion; because this air is never perfectly pure, but always contains a small portion of atmospheric gas, so that the quantity of the latter will be something increased, though very insconsiderably, during each combustion; and this increase will be less perceptible in proportion to the purity of the highly respirable air employed in the process; nay, we may arrive at such precision, in making the experiment, as to be able previously to determine the quantity of this pure air which will be required, according as its degree of purity has been ascertained by the test of nitrous air.

We know, from experiments, of which I have already given an account, that atmospheric air contains

contains about $\frac{1}{4}$ of dephlogisticated or highly respirable air. The absorption, however, which takes place, during the combustion of the phosphorus, never exceeds, and is generally less than, $\frac{1}{2}$, from whence it is evident, that the whole of this pure air, contained in the atmospheric air, is not separated by the combustion: frequently the remainder which is left mixed with the atmospheric gas, is $\frac{1}{4}$, and sometimes more; so that this air, which has been drained and rendered noxious by the above process, when it has been well washed, is capable of becoming again respirable, of supporting flame, &c. The following relation contains what has been done on this subject.

THOUGH the mephitic portion of atmospheric air does not easily combine with water, yet this combination is, in some degree, effected, if it be agitated for a considerable length of time in a large quantity of water. The highly respirable air is still less disposed to unite with that fluid. If therefore we agitate in the above manner the air in which phosphorus has been burnt, and which is composed, as has been seen, of $\frac{1}{2}$ of highly respirable air, and $\frac{1}{4}$ of atmo-

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spheric gas ; the highly respirable air, which at first formed only $\frac{1}{2}$, will be found to amount to a larger portion, and this will increase in proportion as the atmospheric gas is absorbed by the water. The air then which has served for the combustion of phosphorus, being washed and well agitated in a large quantity of water, must pass through all the intermediate states from that to which it was reduced by combustion, to that of dephlogisticated air. But the change cannot be effected, without a diminution of its volume, which is, for the most part, made at the expence of the noxious part.

THE whole of this theory, relative to the combustion of phosphorus, and the formation of its acid, is equally applicable to the combustion of sulphur, and the formation of the vitriolic acid ; with this difference only, that the combustion of sulphur, not being so easily supported, and this substance extinguishing more readily than phosphorus, it is more difficult to deprive a given quantity of air of its highly respirable part, by the one than by the other ; accordingly, as soon as $\frac{1}{6}$ or $\frac{1}{7}$ of the air is consumed, the sulphur ceases to burn ; whereas bodies such as phosphorus,

phosphorus, which are more combustible, and more susceptible of being kept in a state of ignition, will burn in it longer. By this difficulty I have been prevented from obtaining such exact results from the combustion of sulphur as from that of phosphorus, and I have therefore omitted, at present, to give the detail of them. But thus far I can assert, that if sulphur be burned in a glass jar, inverted into mercury, the diminution in the volume of air will be proportionable to the consumption of sulphur, and that a very concentrated vitriolic acid will be produced, which will be two or three times the weight of the sulphur employed to form it. This is a subject which I shall in future resume, and shall bestow upon it all possible accuracy.

I FLATTER myself that I am sufficiently authorised by the event of the preceding experiments, both on phosphorus and sulphur, to declare, 1st. that atmospheric air is composed of about $\frac{1}{4}$ of highly respirable or dephlogisticated air, and $\frac{3}{4}$ of mephitic, noxious air. 2dly. That phosphorus, during its combustion, acts only on the highly respirable part, leaving the mephitic, which may be considered as a mere passive medium,

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dium, unaltered. 3dly. That the phosphoric and vitriolic acids are composed, of above one half of their weight, of highly respirable air. I shall hereafter shew how these two acids may be decomposed, and in what manner we may recover, by means of combinations, this pure air which forms one of their component parts.

THE phosphoric acid, which is obtained by the above process, dissolves almost immediately on coming into contact with the air; and, by thus running ad deliquium, becomes a highly concentrated, heavy acid, possessing no more smell than concentrated vitriolic acid, resembling it in its oily appearance, and in every other point.

THIS is the acid which has been employed in all the experiments to be related in this memoir; but I have obtained it by a method somewhat more expeditious and convenient, which consists in burning the phosphorus under large glass jars, on the inside of which a little distilled water has been thrown. As soon as the vapours formed by the first combustion are dispersed, a fresh quantity of phosphorus is to be

be introduced and burnt in the same manner, and thus the process is to be carried on for several days, till a sufficient quantity of acid be obtained. It may be supposed that the acid procured by this means will be less concentrated than the former, as being diluted with water; but it is in other respects exactly of the same nature, and may be used in every experiment, where a highly concentrated acid is not requisite.

HAVING shewn in what manner this acid is produced, it remains to pursue it through the different unions which it is capable of contracting. To avoid confusion, and to facilitate the making of references to the experiments contained in the following part of this memoir, I shall divide it into different articles.

ARTICLE I.

Phosphoric Salt with a Calcareous Basis.

ON adding phosphoric acid, drop by drop, to lime-water, the water became turbid, and a white precipitate subsided, which at first sight appeared

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appeared to be similar to that produced by throwing fixed air into it; but on more close examination, the sediment was found to be of a crystalline form, a true neutral salt, not effervescing with acids, dissolving entirely in water, but requiring a much larger portion to keep it dissolved, than is requisite for selenite, or even lime. The water on evaporation afforded more of these crystals, the figure of which was not easy to be described.

A similar salt was obtained by adding the acid to quicklime and to chalk. The mixture with the latter was attended with effervescence; and in both cases the salt fell to the bottom of the vessel as fast as it was formed, owing to its difficult solubility.

THIS salt possessed several remarkable singularities: first, in whatever manner it was made, it always retained an excess of acid. So far from being able to give it a superabundance of calcareous earth, the attempt was vain to render it exactly neutral; and, by washing, the salt, with its superabundant acid, is dissolved in the water, whereas the excess of calcareous earth remains unchanged on the filter.

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It dissolved more readily in water to which some phosphoric acid had been added, than in simple water; but, on evaporation, it did not retain this additional acid, which was drained from it by means of brown paper, or washed away by water.

Its affinity to calcareous earths was weaker than to alkaline salts, on the addition of which the same appearances ensued, as when they are added to solutions of calcareous salts, formed with the other acids.

ON adding, drop by drop, a solution of silver in nitrous acid to a solution of this phosphoric salt, a greyish saline precipitate was immediately formed, which gradually became red, approaching the colour of keys of wine; but if added to a solution of quicksilver in the same acid, the precipitate was white and powdery.

NEITHER this salt, nor the phosphoric acid, communicates any particular couleur to the flame of spirit of wine: whereas phosphorus itself gives spirit of wine a light green colour. But it is remarkable that the phosphorus does not take

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take fire, as long as it is covered by the spirit of wine, and thereby defended from contact with the air, but immediately inflames as soon as so much of the spirit is evaporated, as to leave any part of the phosphorus uncovered.

A R T I C L E II.

Phosphoric Salt with Basis of Magnesia Alba.

ON throwing, gradually, some magnesia alba into weak phosphoric acid, it was dissolved with effervescence; but as the salt which was formed, possessed but a small degree of solubility, it precipitated, as fast as it was formed, to the bottom of the vessel. On adding distilled water, the precipitate was dissolved; and the solution being left to stand, all night, in a cold place, a great number of very small regular crystals of a flattish needle-like form, were found in the morning: they were many lines in length, cut off obliquely at each end, and resembled very exactly, in figure, the crystals which are obtained by a very slow and insensible evaporation of a solution of that kind of gypsum called lapis specularis: but on attempting

tempting to separate and dry them in a stove, they fell into powder. Nor was I able, by subsequent evaporation, to procure such regular crystals as these which were obtained spontaneously with a large portion of water. This salt was immediately decomposed by vitriolic acid, which, uniting with the magnesia, formed the bitter purging salt, commonly called Epsom salt.

ARTICLE III.

Phosphoric Salt with Basis of Fixed Alkali.

MINERAL fixed alkali was dissolved with effervescence in dilute phosphoric acid. The solution was not bitter, but rather agreeable to the taste, something like that of a solution of sea salt. The salt obtained by this union had not the least excess of acid; as is the case with almost all the other phosphoric salts. It refused to form into crystals, whatever degree of evaporation was used, and whether the solution were made superabundantly acid or alkaline. The result was, always, a tenacious, gummy residuum, which roped like thick turpentine, attracted moisture from the air, and deliquesced in it.

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THE vegetable fixed alkali dissolved also, in the phosphoric acid, with effervescence. When the combination was formed, it was set to evaporate, and, when grown cold, crystals were obtained of a columnar shape, perfectly square, terminated by a pyramid, having also four sides, commonly equal to each other, and corresponding exactly to the four sides of the crystalline column. Hot water dissolved nearly double the quantity of this salt that was capable of solution in cold water. The salt had a small degree of acidity. Thrown on burning coals it puffed up, but melted with difficulty; but as soon as it flowed, it lost all its saline taste. I have not yet pursued the investigation of this extraordinary circumstance, which affords a key to some interesting phenomena.

THIS salt gives a very slight red tinge to the flame of spirit of wine; whereas that with the mineral alkali affords no such appearance. They both precipitate silver from nitrous acid in form of a white powder, which is distinguishable from the precipitate produced by marine salts in being very much divided, and not collected in flakes or curds. They also separate mercury

mercury from that acid in form of a yellowish white, and lead in that of a white precipitate, the latter being rather saline.

ARTICLE IV.

Phosphoric Ammoniacal Salt.

THE concrete volatile alkali effervesces with phosphoric acid, and forms with it a neutral ammoniacal salty more soluble in hot than in cold water, the crystals of which have some similitude to alum; but as they are very complicated, it would not be easy to describe them without figures.

ARTICLE V.

Phosphoric Metallic Salts.

DILUTE phosphoric acid has no action on mercury in the cold. Globules of mercury have been kept several months in it without the least appearance of solution: perhaps if it had been very concentrated and strongly heated, its action might have been stronger; but I have not had an opportunity of making the trial.

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POURED on a solution of silver in nitrous acid, it produced no precipitate.

WHEN cold, it had little effect on iron, but when hot, a brisk effervescence ensued. A taper being plunged into the vacant part of the jar in which the combination had been effected, continued to burn as in common air, but with a lightish green flame. The solution being evaporated, yielded no regular crystals, but a saline mass, of a green colour, and very soluble in water.

M. SAGE has asserted in many of his works that the phlogisticated alkali, which is used for the preparation of Prussian blue, is only an alkali saturated with phosphoric acid, and has given his theory an air of probability which may tend to mislead. If the assertion were true, the phosphoric salts with alkaline bases should form Prussian blue when combined with martial vitriol.—But the contrary is the case. The precipitate is whitish, dissolves, though with difficulty, in acids, and leaves only a small insoluble portion, which has only a blueish tinge, scarcely perceptible.

SUCH

OF PHOSPHÓRUS. 51

SUCH are the experiments which the provision of phosphoric acid I had made, has enabled me to make. I wished to have gone further, and to have repeated the whole of them; but circumstances having led me to another kind of experiments, and the difficulty of procuring, for a long time, a sufficient quantity of pure acid, having deterred me from waiting, I have determined to give them to the society, as they are; and hope, that, though incomplete, they may be of some use to chemistry, either by establishing new facts, or by destroying false theories. I can answer for the accuracy of my experiments.

ESSAY IV.

ON THE EXISTENCE OF AIR IN THE NITROUS
ACID, AND ON THE MEANS OF DECOMPOSING
AND RECOMPOSING THAT ACID.

IN the first volume of my Physical and Chemical Essays, it was shewn, that when Kunckel's phosphorus was burnt under a glass jar inverted into water, about $\frac{1}{3}$ of the air contained under the jar was absorbed; and that this diminution of air was proportioned to the increase of weight in the phosphoric acid resulting from the combustion.* I therefore concluded that this acid was, in part, composed of air, or, at least, of an elastic substance contained in the air. As exactly the same phe-

See also the third Essay in this collection.

nomena

nomena take place in the combustion of sulphur, and the formation of the vitriolic acid, I had equal reason to conclude that air also enters into the composition of the latter.

THESE first steps led me to reflect on the nature of the acids in general, and on examining the circumstances of their formation, and destruction, I thought that I began to discover that they were all composed, in great measure, of air; that this substance was common to them all, and that they were varied from each other by the addition of different principles peculiar to each acid.

WHAT was at first only probable conjecture, was converted to sufficient certainty when experiment was applied to theory; and I am at present enabled to declare positively, not only that air, but the most pure part of the air, enters into the composition of all the acids without exception; and that on this substance their acidity depends, in so much that we may, at pleasure, deprive them of that quality or restore it to them again, according as we take away, or give to them, the portion of air essential to their composition.

BEFORE I proceed further on this subject, it seems necessary to inform the public, that one part of the experiments contained in this memoir are not properly mine; perhaps, strictly speaking, there is not one of which Dr. Priestley may not claim the original idea. But as similar facts have led us to somewhat different consequences, I trust, that if I should be accused of having borrowed my experiments from the works of that celebrated philosopher, I shall, at least, be allowed the merit of the conclusions.

IT is a generally known fact that elastic vapours are separated from almost all solutions of metals in acids, which form species of air, the properties of which vary according to the nature of the acids, by the assistance of which we are enabled to form them.

THESE different kinds of air by no means proceed from the metal, as I shall have frequent occasions to shew; they are to be attributed to the decomposition of the acid itself; and I imagined that from hence we might be supplied with a simple method of analysing the acids. It seemed probable, for instance, that by dissolving

solving mercury in nitrous acid, collecting the different elastic principles which escape from this combination, and attentively observing the phenomena which appear from the first instant of the solution, to the point, when the mercury, after having successively passed through the state of mercurial salt and red precipitate, reappears finally in its metallic form, I should infallibly acquire information concerning the nature of the principles which enter into the composition of nitrous acid.

THE experiments which I am going to relate might have succeeded equally with any other metal; but I gave the preference to mercury, because this metal possesses the property of being reduced without addition; and I therefore concluded that I should meet with less complication in the course of my experiments, and should be led, in a more simple manner, to the conclusions at which I wished to arrive.

I THEREFORE took a small matras, with a long narrow neck, which I bent in the flame of a lamp, so that the extremity might pass under a glass jar, filled with water, and plunged into a vessel

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containing the same fluid. Into this matras I introduced two ounces of nitrous acid, which smoked moderately, the specific gravity of which was to that of distilled water in the proportion of 131607 to 100000; and I added two ounces one drachm of mercury, heating the mixture gently in order to accelerate the solution.

As the acid was strongly concentrated, the effervescence was brisk and the separation of air very rapid. I received the disengaged air in different jars, that I might examine the varieties which might possibly occur between the parcels separated at the beginning, and those at the end of the effervescence. When the effervescence was finished, and the whole of the mercury dissolved, I continued to make the solution hot in the same vessel. In a short time the effervescence was succeeded by an ebullition, during which, the production of air continued almost as great as at first. The process was carried on, till, the whole of the fluid having been converted into air or watery vapours, I had nothing left in the matras but a white mercurial salt, of a pasty form, rather dry than moist, and beginning

beginning to turn yellow on the surface. The quantity of air, which had been already obtained, amounted to about 162 cubic inches. All this air was of the same nature, and in no respect differing from that to which Dr. Priestley has given the name of nitrous air.

THE operation being continued, I perceived red vapours to arise from the mercurial salt, similar to those of the nitrous acid; but this circumstance was not of long duration, and presently the air, contained in the upper part of the matras,* recovered its transparency. Having set apart the air, amounting to ten or twelve inches, which had passed during the continuance of the red vapours, it was found to be very different from that which had been hitherto collected, and not to differ from common air, except that candles burnt something better in it. At the same time the mercurial salt was changed

* THESE vapours owe their origin to a portion of nitrous air, and of highly pure air, which are disengaged at the same time from the mercurial salt, and combining together, form nitrous acid. This explanation will not be well understood till the whole of this Essay has been read.

into

into a beautiful red precipitate, and continuing to urge it with a moderate degree of fire, I obtained, in the space of seven hours, 234 cubic inches of air, much purer than common air; in which candles burned with a very enlarged flame, and which, by all its characters, convinced me that it was the same I had extracted from the calx of mercury, commonly called mercury precipitated per se, and which Dr. Priestley has obtained from a great variety of substances, by mixing them with spirit of nitre. In proportion as this air was disengaged, the mercury was reduced, and I recovered, within a few grains, the two ounces one drachm which had been employed in the solution. This trifling loss proceeded from a small portion of a yellow and red sublimate which adhered to the dome of the retort.

THE mercury having been recovered from this experiment, in its former state, without change either in its quality or weight, it is evident that the 426 cubic inches of air, which had been obtained, could not have been produced but by the decomposition of the nitrous acid. I had therefore reason to conclude that

two.

two ounces of nitrous acid are composed, 1st. of 190 inches of nitrous air; 2dly. of 12 inches of common air; 3dly. of 224 inches of air better than common air; 4thly. of phlegm. But, as it has been proved, by Dr. Priestley's experiments, that the small portion of common air I had obtained could be nothing but air better than common air, the superior quality of which had been altered by a mixture of nitrous air, in the transition from one to the other, I may re-establish the quantity of these two airs, as previous to their mixture, and suppose that the 12 inches of common air, which I obtained, proceeded from a mixture of 24 inches of nitrous air, and a like quantity of air superior to that of the atmosphere.

In thus re-establishing the quantities, we shall have, as the product of two ounces of nitrous acid,

	Inches,
Of nitrous air	196.
Very pure air.	246.
Total	442.

And for the product of one pound of the same acid,

Nitrous

	Inches.
Nitrous air	1568.
Very pure air	<u>1968.</u>
Total	3536.

If it were possible to know the absolute weight, as well as the bulk, of these quantities of air, it would be easy to determine the weight of phlegm; and we should then possess a complete analysis of the nitrous acid. The experiments of Dr. Priestley to this purpose are far from being satisfactory, and I confess that I have not been able to arrive at any certain conclusions. I shall, however, suppose here, as I have every reason to presume, that the pure air, obtained from mercury, is something heavier than common air, and that it weighs $\frac{5}{6}$ of a grain to the cubic inch. I shall also suppose, that nitrous air is something lighter than atmospheric air, and that its weight is $\frac{4}{5}$ of a grain to the cubic inch; on this supposition we shall find that a pound of nitrous acid, such as that employed, will be composed as follows, viz.

	Oz.	3.	Gr.
Nitrous air	1	5 $\frac{1}{4}$.	
Very pure air	1	7	$2\frac{1}{2}$.
Phlegm, or Water	13		18.

Total lbj.

Here,

Here, then, we are presented with a method of decomposing the nitrous acid, and demonstrating the existence of air, or rather of more pure and perfect air than that of the atmosphere; but a complete proof of this fact was obtained, when, after having decomposed the nitrous acid, I was able to recompose it by again combining the same materials. This is a power which I have actually attained; but previous to the relation of that experiment, it will be necessary to give some account of the nature of nitrous air.

THOSE who have not read the experiments related in Dr. Priestley's first volume on different kinds of air, and especially those of Mr. William Bewley, which are inserted at the end of that volume, may perhaps imagine nitrous air to be merely nitrous acid in the form of vapour. It will be sufficient, in order to overthrow this opinion, to make it appear that it is even doubtful whether nitrous air be in a state of acidity, and this the result of the following experiments tends to prove.

1st. NITROUS AIR is capable of passing through very considerable quantities of water, and

rating it with alkali, and evaporating the water, a true nitre was obtained.

With a view of obtaining the acid in a more concentrated state, I endeavoured to substitute mercury in the place of water, by forming the same mixture in a tube filled with, and inverted into, mercury, taking care to leave a small stratum of water over the surface of the metal. The penetration of the two airs was nearly as rapid in this as in the preceding experiment; the vapours of nitrous acid were condensed by the small portion of water contained in the tube, and by proportioning properly the quantity of water, I was capable of forming either a very smoking spirit of nitre, as strong as can possibly be made, or one that was more weak, and similar to that originally employed in the operation. This experiment should be made with all possible expedition, because the smoking spirit of nitre, which is formed and comes into contact with the mercury, acts upon the metal, dissolves it, and again forms fresh nitrous air. This last circumstance furnishes an additional proof of the re-composition of the nitrous acid.

It may perhaps appear surprising, that seven parts and $\frac{1}{3}$ of nitrous air, and only four parts of very pure air, are necessary to compose the nitrous acid; whereas in the decomposition of it, a somewhat larger quantity of pure than of nitrous air was obtained. I am uninformed of the cause of this circumstance, but the fact is certain, that the above proportions of nitrous and pure air exactly saturate each other: and consequently that by employing the very materials, which have been afforded by the nitrous acid in its decomposition, it is impossible to form again the quantity of acid which existed before the solution, and that a defect appears of nearly one half of the pure air.

HAVING shewn that the principles of the nitrous acid are capable of disunion and recombination, it remains for me to demonstrate that we may produce the same effect with materials which are not all derived from the nitrous acid. Instead of very pure air, procured from the red precipitate of mercury, atmospheric air may be employed. But a greater proportion of it will be necessary, and instead of four, nearly sixteen parts will be wanting to saturate seven parts and $\frac{1}{3}$ of nitrous air. The whole

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of this last is destroyed or condensed in this, as in the preceding experiment; but that is not the case with the common air, of which not above $\frac{1}{3}$ or $\frac{1}{4}$ is absorbed, and the remaining part is no longer in a state fit for the support of flame, or the respiration of animals. It should appear to be proved, therefore, that the air which we breathe contains only $\frac{1}{4}$ of real air; and that this true air is mixed, in our atmosphere, with $\frac{3}{4}$ of noxious mephitic air, which would be fatal to most animals, were its quantity a little more considerable. The deleterious effects of the vapour of charcoal, and of several other exhalations, are further proofs how nearly this fluid approaches the boundaries beyond which it would become mortal to animals. I hope soon to be able to discuss this idea, and to give ocular demonstration to the academy of the experiments on which it is founded.

FROM the experiments, contained in this memoir, it appears, that when mercury is dissolved in nitrous acid, the metal attracts the portion of air contained in the acid which constitutes its acidity: on one part the metal, combined with the air, is reduced to a calx; and, on the other, the acid, deprived of its air,
is

is expanded and forms nitrous air. That these things really happen, during the operation, is proved by the mixture of the two airs, which originally entered into the composition of the nitrous acid, again forming pure nitrous acid similar to what it was previous to the separation of its principles.

NITROUS acid then consists of nitrous air combined with $\frac{5}{7}$ of its bulk of the purest part of common air, and a considerable portion of water. It will, doubtless, be asked, whether the phlogiston of the metal may not contribute something in the operation? Without presuming to decide on a question of such great consequence, I shall only answer, that as the mercury is left, after the process, precisely the same as before, it does not appear that it has either lost or recovered its phlogiston; except it can be supposed that the phlogiston necessary to the reduction of the metal had passed through the vessels: but this is to admit of a species of phlogiston different from that of Stahl and his disciples, and to return to the principle of fire; to fire combined in bodies; a system of greater antiquity than that of Stahl, and very different from it.

I SHALL conclude this memoir, as I began it, by acknowledging my obligations to Dr. Priestley for the greatest part of what interesting matter it may contain. But the love of truth, and the promotion of science, to which all our efforts ought to be directed, oblige me at the same time to take notice of one error into which he has fallen, and to which it might be dangerous to accord. This justly celebrated philosopher having observed that, by combining nitrous acid with any kind of earth, he constantly obtained common air, or air of even a purer nature than common air, believed that it might therefore be concluded that atmospheric air is compounded of nitrous acid and earth. This theory will be sufficiently confuted by the experiments contained in this memoir. It is evident that it is not the air that is composed of nitrous acid, as the Doctor has imagined; but, on the contrary, the nitrous acid which is composed of air; and this remark alone supplies a key to a great number of experiments contained in Dr. Priestley's second, third, fourth, and fifth volumes on air.

E S S A Y V.

ON THE SOLUTION OF MERCURY IN
VITRIOLIC ACID.

HAVING shewn in former essays that nitrous acid is the result of a combination of a certain proportion of dephlogisticated, with nitrous, air; that sulphur and phosphorus are incapable of acquiring acidity but in proportion as they are combined with a very considerable portion of dephlogisticated air; and having declared that it is possible to discover, in the vitriolic acid, by chemical experiments, the dephlogisticated air which entered into its composition in the combustion of the sulphur: I shall proceed in the present essay to prove, by means of analysis, what I have hitherto only accomplished by means of composition.

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FOUR ounces of mercury, and six ounces of vitriolic acid, were put into a small glass retort, and gradually heated by an open fire in a reverberatory furnace. The extremity of the retort, the neck of which was very long, was immersed in a basin of mercury, and the air, in proportion as it arose, was received into tall narrow jars filled with, and inverted into, mercury. The solution was effected with considerable effervescence, during which, a very considerable quantity of volatile vitriolic air was separated, which, as long as it is confined in mercury, and does not come into contact with water, preserves its elasticity, and is incapable of either rarefaction or condensation, except by various degrees of compression or heat.

THIS air, when exposed to water, is but slowly absorbed, and the combination is attended with sensible heat. The water which has been thus impregnated is clear and limpid, and forms what we call volatile, sulphureous, or vitriolic, acid. But the quantity of this air, absorbable by water, varies considerably, according to the different temperature, and is greatest when the water is coldest; whereas, on the

the contrary, when the water is nearly boiling, it is incapable of absorbing a particle of it. I could not possibly determine with accuracy how much of this air would be necessary to saturate a given quantity of water in different degrees of temperature. But thus far is certain, that the water is capable of absorbing a greater portion of this, than of fixed air, but much less than of marine acid air.

If it be desired to collect the whole of this vitriolic air, it will be only necessary to adapt, to the retort, a tubulated receiver, similar to that described by Mr. Woulfe and improved by Mr. Bucquet; by which means we catch in the receiver, the sulphureous acid, in the highest state of concentration, and that, which cannot be condensed, is found united to the water in the bottles connected with the receiver.

THE first portions of volatile vitriolic air are very pure, but, as the process advances, it becomes mixed with common air, and even with some portions of dephlogisticated air. These may be separated by placing the whole in contact with caustic alkali, for the vitriolic air will

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be instantly absorbed, and the common or the dephlogisticated air left behind.

If when the mercury is almost reduced to dryness, the fire be urged rather more briskly, a small portion of volatile vitriolic air still continues to pass; but the quantity of dephlogisticated air which comes over, at the same time increases continually; and when the residuum is quite dry, it is necessary to change the apparatus, because the fire necessary to the success of the operation would melt the retort if it were not placed in sand.

An aperture was therefore made in a Paris crucible, which might admit the neck of the retort to pass through it. The crucible was used as a sand bath, in which the retort was placed, having its upper part thinly coated with moist refractory clay, to prevent the glass being affected by the cold air, as it ought to be equally heated in every part, and also that the retort might be less exposed to be broken.

INTO an apparatus, such as is now described, I put two ounces of mercurial vitriol, dry and deprived

deprived of the greater part of its water of crystallization, and the product of the preceding operation. A brisk fire was applied. The process continued above an hour and half, and during the whole course of it, there were collected, 1st. a small portion of volatile vitriolic air, which was absorbed in the water of the tub into which the neck of the retort was immersed: 2dly. eighty inches of dephlogisticated air, which was of such a degree of purity, that four parts of it required for its saturation seven parts or measures of nitrous air, and the whole eleven measures were reduced to $1\frac{1}{2}$. So that the dephlogisticated air obtained from mercurial vitriol approaches much nearer to absolute purity than any we have hitherto possessed.

In proportion to the separation of the volatile vitriolic, and dephlogisticated air, the mercury, which had been combined with them in the mercurial vitriol, was revived, recovered its form, and passed over in distillation as running mercury. This however was not wholly the case, for two species of calx of mercury sublimed into the neck of the retort. The one was white and had a saline appearance; the other was grey.

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grey. I shall take an opportunity of examining these calxes, which are such as M. Beaumé has declared to be incapable of being reduced without addition. When the operation was finished, nothing remained in the retort.

ON calculating the products of this last operation, and comparing them with those I had obtained from an equal quantity of mercurial vitriol, in a common apparatus for distillation, I found that two ounces of this metallic compound yield,

	3.	3.	Grs.
1st. Of water or phlegm		1	
2d. Running mercury	6		12
3d. White calx of mercury, sublimed	3		18
4th. Grey calx of mercury		40	
	1	2	70
Total	1	2	70
The quantity of mercurial vitriol was 2			
The loss therefore amounted to	0	5	2

THIS loss may doubtless be accounted for, by the eighty cubic inches of dephlogisticated air which were collected, and by the volatile vitriolic air which was absorbed by the water.

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IN VITRIOLIC ACID. 75

It is apparent that as no other substance was employed in this operation but vitriolic acid and mercury, and as the latter is recovered in its original metallic form, the dephlogisticated air could only proceed from the vitriolic acid; and, according to the opinion I had advanced, the dephlogisticated air, which had been absorbed during the combustion of the sulphur, is found by analysis in the vitriolic acid.

ANOTHER fact, which it is impossible to deny, after the experiments that have been related, is, that volatile vitriolic acid is common vitriolic acid, deprived of a part of its dephlogisticated air.

ESSAY

ESSAY VI.

EXPERIMENTS ON THE COMBUSTION
OF ALUM WITH PHLOGISTIC SUBSTANCES,
AND ON THE CHANGES EFFECTED ON AIR IN
WHICH THE PYROPHORUS HAS BURNED.

AS it will be needless to repeat every thing that has been written on the subject of Homberg's pyrophorus, and to discuss the various opinions which have, successively, prevailed concerning the cause of its spontaneous inflammation, I shall confine myself to recurring to a memoir of Mr. Homberg, which is printed among those of the Academy of Sciences for the year 1718, page 238, and especially to that of M. de Suvigny, published in the third volume of Memoirs of Mathematics and Physics, presented to the academy by learned foreigners.

IT will be proper on this occasion to recollect, that it has been proved by the experiments

ments of M. de Suvigny, 1st. that not only alum, but also all the vitriolic salts with a basis of fixed alkali, such as Glauber's salt, vitriolated tartar, &c. mixed with a proper proportion of any light porous matter containing phlogiston, and urged by a degree of fire sufficient to bring the mixture to a red heat, leave a residuum of a blackish hue, which has the property of taking fire spontaneously in the air.

2dly. THAT in all these operations the vitriolic acid is converted into sulphur, so that it may be said that Homberg's pyrophorus, and all those formed by M. de Suvigny on similar principles, are merely phlogistic hepars of sulphur with either a fixed alkali or aluminous earth for their basis.

3dly. THAT it is a proof of the conversion of vitriolic acid into sulphur in the formation of the pyrophorus, that in whatever manner this substance be analysed, not an atom of vitriolic acid, nor of the vitriolic salts which had been employed in the operation, is to be found, but only liver of sulphur and sulphur.

4thly.

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4thly. THAT very good pyrophorus may be formed without making use of any vitriolic salt, by a combination of sulphur, alkali, and powdered charcoal; a fact which proves most incontrovertibly that pyrophorus is a true hepar sulphuris.—Having stated these preliminaries, I shall proceed to give an account of my own experiments.

Two parts of alum and one part of sugar were mixed together, and the mixture calcined in an iron ladle, without making it red hot, till the sugar was entirely converted into charcoal, and neither smoke nor vapour continued to rise.

I TOOK two ounces of this calcined mixture, and placing it in a glass retort, in a sand heat of a reverberating furnace, the fire was raised, and the air which separated was received into jars filled with water. About 120 inches of fixed air first passed, then about 160 inches of air composed of equal parts of fixed, and of inflammable air; and the last product obtained consisted of 180 inches of air, three fourths of which were inflammable, and one fourth only fixed

fixed air; and the last portions were only pure inflammable air.

THE fixed air may be separated from the inflammable, either by suffering them to remain for some days together in the jars, standing in water, when the fixed gas will be absorbed, leaving the inflammable, which does not readily unite with water; or the absorption may be accelerated by placing them in contact with a lixivium of caustic alkali, or over lime-water. This liquor entirely and rapidly absorbs the fixed air, and the inflammable air which remains will be quite pure. By these methods I have discovered that of 460 cubic inches of elastic fluid which were obtained in this operation, 215 were inflammable, and 245 fixed air. But this calculation of the product must not be regarded as quite exact, with respect to the fixed air, because this acid being obliged to pass through a considerable quantity of water in its way to the upper part of the jar, a part of it was necessarily absorbed by that liquid during the course of the operation, and before its bulk could be determined. This circumstance may be supposed to have occasioned a loss of at least a fourth

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a fourth or a sixth of the quantity of fixed air, so that the whole that was separated in the process must have amounted to, at least, 300 inches.

DURING almost the whole course of the experiment, a considerable quantity of sulphur was separated, part of which was sublimed and condensed in the neck of the retort, and part, passing in vapours through the water, was deposited on its surface in form of a fine powder. The operation continued about an hour and half.

THE residuum in the retort was Homberg's pyrophorus, was very good and strong, and flamed as soon as it came into contact with the air.

THE quantities and qualities of the air discharged in the operation being sufficiently determined, I proceeded to the following experiments.

Two drachms of this pyrophorus were placed on the scale of a very sensible balance, and I observed, that it began to increase in weight
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the moment the combustion commenced, and that this augmentation continued to take place for several minutes: in order to discover the cause on which it depended, it was thought proper to observe all the circumstances of the combustion with the utmost attention.

I ACCORDINGLY began by introducing successively two drams of pyrophorus into different jars filled with fixed air, and with nitrous air. It did not give any light, nor afford any remarkable phenomenon.

BUT the case was different when I placed the pyrophorus under jars filled with common, or with dephlogisticated air; and as the circumstances of these experiments are very remarkable, I shall give a full relation of them.

ABOUT half an ounce of pyrophorus was put into a small glass bottle, which was covered with a little glass cover, and the junctures being luted so that the whole apparatus might be passed through water without any of the water getting into the bottle, it was conveyed under a jar filled with common air, and I accurately

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marked the height at which the water stood in the jar. Then introducing my hand under the jar, I removed the cover that was affixed to the bottle, and made a free communication between the pyrophorus and the air of the jar. A considerable degree of heat was immediately produced without combustion, and, at the same time, a diminution of the quantity of air took place, which was, at first, pretty rapid, but abated in about five minutes; yet did not entirely cease till after the space of between forty-five minutes and an hour had elapsed.

THIS diminution of the volume of air was greater than any I had hitherto observed, and bore the proportion of 100 to $72\frac{1}{2}$, or to more than $\frac{1}{4}$; whereas, in almost all operations of this kind, it scarcely amounts to a fifth.

WHEN the experiment was made over lime-water, instead of common water, the diminution was the same; and, as it advanced, I observed a precipitation of the lime to be formed, which evinced that one of the causes of this diminution was owing to the conversion of a part of the air in the jar, into fixed air, which was absorbed by the lime-water.

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THIS experiment induced me to repeat the experiment in dethylgisticated or highly respirable air ; but I perceived the necessity of making use of a much larger jar, that the phenomena might be more distinguishable ; in other respects I conducted the operation much in the same manner as before.

As soon as the little cover was detached from the bottle, and the pyrophorus came into contact with the pure air, it took fire, and burned with a sparkling and decrepitation, and particularly with a very splendid light and extreme rapidity. In a short time, the violence of the combustion abated, and the light began insensibly to diminish, till, in some minutes, it was entirely extinguished.

THE pyrophorus, in this experiment, must not be put into a glass bottle, but into a small vessel made of tin, and without solder, on account of the great degree of heat which is produced, and would break the glass, or melt the solder.

AT the first instant, the great heat produced a small increase in the volume of air contained

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in the jar, but it was presently succeeded by a rapid diminution which also abated in about a quarter of an hour, but did not wholly cease till the air was reduced to a seventh of the space it occupied previous to the combustion of the pyrophorus; nor was it diminished so far as it was capable of being, for, when lime-water was admitted, it was again reduced, nearly one half, so that the remainder did not amount to above a twelfth or thirteenth part of the original volume of air.

THE remaining parcel of air was still almost pure or dephlogisticated, and by continuing to burn fresh phosphorus in it, I at length succeeded in rendering $\frac{143}{144}$ of the original quantity of air absorbable by water.

THIS experiment was frequently repeated, and particularly in presence of Dr. Franklin and several members of the academy; the circumstances having been varied by sometimes employing common water, and sometimes lime-water; and I am convinced that in the combustion of pyrophorus, very pure or dephlogisticated air is changed into fixed air, except the portion which is absorbed by the pyrophorus itself,

itself, as I shall presently shew, and that this fixed air combines with the water.

THESE effects of the combustion of pyrophorus in dephlogisticated air, throw great light on the phenomena attending the combustion of that substance in common air. The effects are nearly the same, but with this difference, that atmospheric air not containing above $\frac{1}{4}$ of pure, genuine air, no more than that quantity of fixed air is formed and absorbed. The remaining $\frac{3}{4}$ are the mephitic part of the air, the nature of which is not as yet at all understood, and which, as I have demonstrated on another occasion, is utterly incapable of supporting either animal or vegetable life.

WHAT has been hitherto said, relates only to that portion of pure air which is converted into fixed air, during the combustion of the pyrophorus. It remains that I should give an account of some circumstances which, to me, appear to prove, that a considerable portion of this air is absorbed by the pyrophorus, while burning, and combines with it; and that it is the surplus only that is changed into fixed air.

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AND, 1st. the diminution of the volume of de-phlogisticated air, at the beginning of the combustion of the pyrophorus, is much greater than could proceed from the mere combination of fixed air with water. It is well known that this combination is not, in general, effected very readily, without agitation, whereby the points of contact between the fixed air and the water are multiplied. These circumstances do not take place under the jar where the combustion of the phosphorus is carried on, and, on the contrary, the great degree of heat which is excited is an almost insurmountable obstacle to the union of the air and water.

2dly. It is a known fact that pyrophorus increases in weight while burning; that this augmentation is very rapid, and nearly equal to the portion of air which we may reasonably imagine to be absorbed in this process. It is true that those who have observed that pyrophorus thus increases in weight, have attributed the increase to the moisture of the air which they supposed it to attract, and indeed it must be allowed, that this is likely to happen at first; but when once the pyrophorus is strongly heated,
when

when it is become red and burns with violence, we cannot then suppose that it attracts moisture from the air, for it is evident that this great heat must, on the contrary, dispel and reduce it into vapour, if it existed in the pyrophorus.

It seems certain, therefore, from both these considerations, that the pyrophorus absorbs and fixes a considerable portion of pure air during its combustion.—It may perhaps be asked what becomes of this air, and what alteration does it produce in the nature of the pyrophorus? This I intend to explain in the remaining part of this essay, and hereby to prove, in a more convincing manner, that there is really an absorption and combination of air in the combustion of this substance.

If pyrophorus be tasted previous to its combustion, we perceive nothing of the stypticity of alum, but a very disagreeable taste of hepar sulphuris: when, on the contrary, it has burned in pure air, all the coaly part is consumed, it is perfectly white, it has a part of the stypticity of alum, and on dissolving and evaporating it, we obtain an alum, supersaturated with

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earth, such as Mr. Beaumé has described in his Chemistry.

THIS last observation discovers to us every thing which happens in the formation and combustion of pyrophorus. We clearly perceive that the vitriolic acid of the alum passes into the state of sulphur while the pyrophorus is forming; whereas it changes again to the state of vitriolic acid when the pyrophorus is burning. Now we have been informed by the experiments related in former essays, that sulphur is vitriolic acid deprived of its dephlogisticated air, or, what is much the same, that the vitriolic acid is a combination of sulphur with that air, or, what will perhaps approach more nearly to accuracy, with the basis of this pure air. Vitriolic acid therefore cannot be changed from a state of acidity to that of sulphur, without a separation of dephlogisticated air being produced, and, on the other hand, sulphur cannot pass from its own form to the state of vitriolic acid, without a fixation of this air being effected; and this has been actually observed in the experiments related in this essay. For we have seen that from a mixture of burnt alum and charcoal,

charcoal, amounting to the weight of two ounces, about 400 cubic inches of air were separated, a part of which was fixed, and the other part inflammable air. But the pyrophorus, on the contrary, when in combustion, absorbed a very large quantity of pure air; which facts fully confirm the theory I have advanced. It will undoubtedly be asked, if the vitriolic acid of the alum contains pure air, why do we principally obtain fixed air during the calcination of the alum and charcoal, and also from whence proceeds the inflammable air which passes with it? To the first question it is answered, that the pure air, or its basis, is converted into fixed air, by uniting with the coaly substances. Of this we have a proof in the reduction of the calx of mercury: if it be reduced without addition, it yields only dephlogisticated air; but if charcoal or any phlogistic substance be added, we obtain fixed air.

As to the inflammable air, the quantity separated in this operation is not constantly the same, but is proportionable to the quantity of charcoal employed. Nor is this air of the same nature as that we obtain from the solution of certain

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certain metallic substances in the vitriolic and marine acids; it is less inflammable, burns with much more difficulty, and makes very little explosion when mixed with two thirds of common air.

THIS inflammable air possesses one remarkable property, viz. that of being changed into fixed air by combustion. The other inflammable airs which are obtained by the solution of metals, either in the vitriolic or marine acids, differ in this respect, and instead of being converted into fixed air, at the time they are inflamed, appear to yield acids similar to those by which they have been extracted. These considerations, and some others which it would be improper to introduce in this essay, lead me to suspect that there may be three species of inflammable air, viz. vitriolic, marine, and fixed inflammable. That which is separated during the combustion of the pyrophorus is of this last species. And as this inflammable air produces exactly the same effects, in burning, on the pure part of atmospheric air, as charcoal does, I am strongly inclined to believe that it is the substance of the charcoal itself reduced to

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to vapour, and in the form of air. For the same reason the two other inflammable airs appear to me to be, the one, a species of vitriolic sulphur, the other of marine sulphur in an aërisome state. But as my experiments are not quite complete, I must content myself with this transient view of the subject.

ESSAY

ESSAY VII.

ON THE VITRIOLISATION OF MARTIAL PYRITES.

THE pyrites which are the subject of this memoir, are the common vitriolic martial pyrites, of the most common species, which are frequently found in chalk, and in almost all clays, &c. with the nature of which we are well acquainted. But with respect to my present views, it will be only necessary to consider them as compounded of iron and sulphur.

If pyrites be distilled in an earthen retort, with a red heat, a considerable quantity of sulphur is sublimed, and collected in the neck of the retort.

If, on the contrary, these pyrites remain in a warm moist air, they crack on their surface, split, fall in pieces, and become covered with vitriolic efflorescences. And, when they have been exposed for a sufficient time to the air, if

if they be lixiviated, they yield a great quantity of martial vitriol ; but if distilled in this state, not a particle of sulphur will be obtained.

THE intervention of air is indispensibly necessary to the vitriolisation of pyrites, which may be preserved in their original state as long as they can be protected from the action of that fluid. A slight covering of oil is sufficient for this purpose ; and we find by experience, that they may be kept unchanged under water.

SINCE pyrites, therefore, are composed of sulphur and iron before their efflorescence, and, after it, of vitriolic acid and iron, it is evident that the sulphur is converted into that acid, by the effect of the vitriolisation.

Now as I have declared, and, I trust, proved, in the essays on the combustion of sulphur, and phosphorus, vitriolic acid is compounded merely of sulphur saturated with very pure or dephlogisticated air ; or in other words, that sulphur is vitriolic acid deprived of part of its dephlogisticated air, and vitriolic acid is sulphur with an over-proportion of the same air : the sulphur of pyrites, therefore, cannot be changed into vitriolic acid without absorbing pure air.

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THE necessity of exposure to the air for vitriolising pyrites, was a strong presumption in favour of the theory ; but as it was possible to confirm it by experiments, and as, in chemistry, we should never be content with reasoning, when we may prove by facts, I proceeded in the following manner.

I KEPT some martial pyrites in a moderately warm place, till they began to effloresce, when they were immediately removed and placed under a glass receiver, plunged in water. The progress of the vitriolisation went on at first as rapidly as in the open air ; it afterwards abated, and at the end of eighteen or twenty days, was entirely suspended. During all this time the water continued to rise in the jar, in proportion to the rapidity of the vitriolisation, and on the eighteenth day began to remain stationary.

THE air, in which the pyrites had been confined, extinguished candles, but it neither precipitated lime-water, nor united with alkalies. It was reduced to that state which I have denominated the mephitic portion of the atmosphere, which had lost about $\frac{1}{3}$ of dephlogisticated air ; so that the pyrites in acquiring a vitriolic

a vitriolic property, had absorbed a portion of pure air, from the atmospheric air under the receiver, and the transition of the sulphureous part of the pyrites to vitriolic acid is subject to the same law, and cannot take place, but by the union of dephlogisticated air with the sulphur.

THE progress of the vitriolisation of pyrites is much more rapid, if the operation be carried on in dephlogisticated air. But as I have not pursued this experiment with sufficient attention, I shall postpone giving a particular account of it.

THE vitriolisation of pyrites therefore depends on the addition of dephlogisticated air or its basis to the sulphur of the pyrites, whereby the vitriolic acid is formed, which meeting with iron in a state of very minute division, must necessarily attack and dissolve it as fast as it is formed; and from this union proceeds martial vitriol.

E S S A Y VIII.

GENERAL CONSIDERATIONS ON THE NATURE
OF THE ACIDS, AND ON THE PRINCIPLES
OF WHICH THEY ARE COMPOSED.

WHEN the ancient chemists had arrived at the power of reducing a body into oil, salt, earth and water, they believed that they had attained the utmost bounds of chemical analysis, and they accordingly bestowed, on salt and oil, the appellation of chemical principles.

BUT as the art was continually improving in its progress, succeeding chemists perceived that the substances which they had been taught to consider as principles, were still capable of decomposition; and they soon discovered that all the neutral salts, for example, were formed by

by the union of two substances, viz. of some acid, with a saline basis of either an earthy or metallic nature.

HENCE the whole theory of neutral salts, which engaged the attention of chemists for above an age, is at present brought to such a degree of perfection, that it may be regarded as the most certain and complete part of chemistry.

IN this state, in which the science of chemistry has been delivered to us by our predecessors, it remains for us to perform, on the *constituent parts* of neutral salts, what preceding chemists have effected on those salts themselves;—to examine the acids and the bases of which they are composed, and to advance this kind of chemical analysis somewhat farther beyond its present limits.

IN the foregoing essays I have endeavoured to prove as clearly as is possible by physics and chemistry, that the very pure air which Dr. Priestley has denominated *dephlogisticated air*, enters, as a constituent part, into the composition of several acids, and especially into that of the phosphoric, vitriolic, and nitrous acids.

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MANY additional experiments enable me to generalise this doctrine, and to declare that this pure and highly respirable air, is the constitutive principle of acidity ; that this principle is common to all the acids ; and that the difference by which they are distinguished from each other is produced by the union of one or more principles besides this air, so as to constitute the particular form under which each acid appears.

THESE facts being, in my opinion, firmly established, I shall in future distinguish dephlogisticated or highly respirable air, in a state of combination or fixity, by the name of the *acidifying principle*, or, if any person prefer to express the same signification by a Greek word, the *oxyginous principle*. This name will prevent circumlocution, give more exactitude to my mode of expression, and enable me to avoid those errors, which might be continually occasioned by using the word *air*. For this name, since the modern discoveries, is become a generic term, and is moreover applicable to substances in an elastic state ; whereas at present we are to consider them as combined, and either in a liquid or concrete form.

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WITHOUT repeating the particular details which I have before related, I shall only in a few words, and in the new terms I have adopted, call back the recollection of the academy to the following positions :

1st. THAT the acidifying or oxyginous principle, combined with the matter of fire, of heat, and of light, forms pure or dephlogisticated air. It must be allowed, that this first proposition is not strictly proved, and perhaps is not capable of absolute demonstration. I have therefore advanced it merely as an idea which I apprehend is very probable; and it must not be confounded with the following, which are supported by experiment and positive proofs.

2dly. THAT the same acidifying principle, combined with phlogistic substances or charcoal, forms fixed air.

3dly. THAT with sulphur it forms vitriolic acid.

4thly. THAT with nitrous air it forms nitrous acid.

5thly. THAT with Kunckel's phosphorus it forms phosphoric acid.

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6thly.

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6thly. THAT with metallic substances in general it forms metallic calces, saving the exceptions which I shall mention in this or some future essay.

THUS far then does our present knowledge, of the combination of the acidifying principle with the various substances in nature, extend; and it is not difficult to perceive that there is still a vast field left to be traversed; that there remains a part of chemistry which is quite new and hitherto entirely unknown, and which cannot be complete, till we are able to determine the degree of affinity which this principle bears to all the substances with which it is capable of combining, and to know the different species of compounds, which result from those combinations.

EVERY chemist is sensible that the more simple the bodies are on which we operate, and the nearer approaches we make in the reduction of substances to their elementary atoms, the more difficult become the means of their decomposition, and recomposition. We know, therefore, that to decompose and recompose

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recompose the acids, must be attended with much greater difficulties than the analysis of the neutral salts, into the combination of which they enter. I hope, however, to be able to shew, in future, that there is no acid, that of sea salt perhaps excepted, which may not be decompounded and recompounded, and which we cannot deprive of the principle of acidity, and restore it again whenever we please.

THIS kind of experiment requires great variety of method; and the processes necessary to perform the combination vary according to the different substances on which we are to operate. In some cases we are obliged to have recourse to combustion, either in atmospheric or very pure air, as when sulphur, phosphorus or charcoal are the objects. These substances, during the combustion, absorb the acidifying principle, and by its accession are converted into vitriolic, phosphoric, and aerial acid or fixed air. With respect to other substances, the mere exposure to the air, aided by a moderate degree of heat, is sufficient to produce the combination; and this happens to all vegetable substances, that are capable of

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passing to the acid fermentation. In every operation of this kind, there is an absorption of the pure part of the atmospheric air, and the acidifying principle forms as many particular acids as there are substances capable of passing to the acid fermentation. After all, we are obliged, in most cases, to have recourse to the science of affinities, and to employ the acidifying principle which is previously engaged in another combination.

THE example of this nature, which I design to adduce, is one taken from an experiment which has been very well known for some years, and related in Mr. Bergman's memoirs, viz. the formation of the acid of sugar. This acid, according to the experiments which I am going to relate, appears to me to consist only of the sugar *itself* combined with the acidifying or oxyginous principle: and I intend to demonstrate, in several successive memoirs, that we may, by processes analogous to this, unite this principle with the horn of animals, with silk, with animal lymph, with wax, essential oils, expressed oils, manna, starch, arsenic, iron, and, probably, with many other substances of the

the three kingdoms, which are thereby converted into true acids.

BEFORE we proceed farther, it may be necessary to recollect that the nitrous acid, as appears from the experiments I have formerly related, is the result of the combination of nitrous air with the acidifying principle; that the proportion of these two principles varies in different parcels of nitrous acid; that, for example, the smoking acid is supersaturated with nitrous air; so that we may consider the smoking spirit of nitre as a nitrous acid impregnated and overcharged with nitrous air; whereas, on the other hand, that which yields white vapours is supersaturated with dephlogisticated air. To these opinions I shall add that from a number of experiments I have made since the publication of my former memoir on this subject, I am convinced that the nitrous acid, which I have employed on these occasions, and which was constantly the same, contains about 240 cubic inches of aëriform fluid in every ounce, viz. 120 inches of nitrous, and about an equal quantity of dephlogisticated air, which is nearly equal in weight to 48 grains of nitrous air, and 60

H 4 grains

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grains of the acidifying principle to each ounce.—The whole of the remainder consists of phlegm or water.

FROM these premises it may be always concluded, that whenever I have introduced, into a combination, one ounce of nitrous acid, and have obtained, in the course of the operation, 120 inches of nitrous air, there will remain in the combination 120 inches of very pure air, or 60 grains of the acidifying principle. Let us then apply these facts to the combination of nitrous acid with sugar.

INTO a small glass retort were put four drachms of sugar, to which were added two ounces of water, and two ounces of the nitrous acid, I have above described. The retort was placed over an open fire in a small reverberatory furnace, and to its neck, which was very long, a bottle, with two necks, was adapted, into which were introduced eight ounces, seven drachms, and twenty-four grains of distilled water. To the second neck of the bottle a glass tube was luted, and communicated with a common chemico-pneumatic apparatus standing in water,

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It is plain that by these dispositions I had a double advantage; on the one hand that of retaining, in the intermediate bottle, whatever might pass in distillation, and be capable of being condensed: and, on the other, that of receiving in the jars, the different kinds of air which might be separated; so that there could be no defect in ascertaining the whole amount of the products of the operation.

ALL the junctures were carefully luted with fat lute, which was covered with slips of cloth spread over with a mixture of white of egg and fallen lime; and as soon as this exterior covering had become so dry as to be sufficient to secure the fat lute, in case of its growing moist, some lighted coals were put under the retort.

AT first the sugar dissolved quietly; but as soon as the liquor had acquired forty or forty-five degrees of heat, by Reaumur's thermometer, a very brisk ebullition, or rather effervescence ensued, which proceeded from a very rapid separation of nitrous air, the purest and strongest I had ever obtained. It is necessary to proceed
very

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very gradually in this operation, otherwise the acid of sugar itself would be decomposed, and, instead of obtaining pure nitrous air, we should have a considerable mixture of inflammable and fixed air. It will be necessary therefore to withdraw all the fire, the moment the ebullition commences, and to replace it only in such portions as may be necessary to keep up the boiling. When the operation is advanced one half or two thirds, the nitrous air no longer passes so pure; it at first becomes mixed with a small portion of fixed air, which keeps continually increasing, and a little inflammable air; and, when nothing passes but these two species of air, the operation may be considered as finished.

HAVING divided, into a great number of portions, the aëriform fluids which had been separated during the process, I proceeded to examine their nature, by the different methods with which we are supplied by modern chemistry, and I found that the two ounces of nitrous acid, and the four drachms of sugar, which had been employed, had yielded

Of

		Inches.
Of nitrous air,	-	190.
Fixed air,	-	90.
Inflammable air,	-	25.
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When I had separated the vessels, there were found in the retort, two ounces, six drachms, and eighteen grains of a transparent colourless acid, similar to that described by Bergman, except that it was liquid; and the water in the intermediate bottle was increased in weight one ounce, two drachms and twelve grains, was moderately acid, and had a slight nitrous odour.

It will readily be understood, that in order to be accurate in the account of the products of this experiment, it was necessary that the quality and quantity of the acid, which had been distilled and condensed in the intermediate bottle, should be clearly ascertained, as no exact calculation could be made without deducting this from the whole quantity of acid employed. For this purpose I gradually dropped, into the acid liquor of the intermediate bottle, an alkaline lixivium, composed of five parts of water, and

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and four of very pure fixed vegetable alkali. The quantity necessary to produce an exact saturation amounted to six drachms twelve grains. I then determined by another experiment, how much of the original acid would be required to saturate an equal portion of the alkaline liquor, and found the quantity to be three drachms fifty-six grains and $\frac{1}{3}$. And therefore, of the two ounces of nitrous acid employed, three drachms, fifty-six grains had passed unchanged into the receiver, and consequently not above one ounce, four drachms, fifteen grains $\frac{1}{3}$ had really contributed to the other products of the experiment.

Now one ounce of nitrous acid is composed, as has just been observed, of 240 cubic inches of aëriform fluids, viz. of 120 cubic inches of nitrous air, and 120 inches of very pure or de-phlogisticated air, so that in the above experiment I had actually combined with the sugar 183 cubic inches of nitrous air, and the same quantity of very pure air, which amount in weight to somewhat more than one drachm of nitrous air, and nearly one drachm and half of the acidifying principle. It has been seen that

that during the combination there were separated 190 inches of nitrous air, which amounts to the whole quantity employed: there remained therefore combined 183 inches of pure air; and in the composition of two ounces, six drachms, eighteen grains of saccharine acid remaining in the retort, were contained four drachms of sugar and 183 inches, or one drachm thirty grains of very pure air, or the acidifying principle; exclusive of the portion of fixed air, which was separated towards the conclusion of the process, and proceeded, as will be presently shewn, from the decomposition of the saccharine acid itself.

MR. BERGMAN, and all subsequent writers on this subject, have therefore been mistaken in considering the saccharine acid as the result of the decomposition of the sugar; for it appears certain, on the contrary, that this acid is formed by the combination of the sugar with nearly $\frac{1}{2}$ of its weight of the acidifying principle.*

Not wishing to depend on this first experiment, I was desirous of knowing the difference

It is, notwithstanding, probable that the phlogiston of the sugar, at least, in part, unites with a portion of the nitrous acid, to form the nitrous air. T. H.

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in the results, when different portions of sugar and nitrous acid might be used; and I therefore repeated the experiment with the same circumstances, and the same quantities of nitrous acid and water, but with only three, instead of four, drachms of sugar, and I obtained

		Inches
Of nitrous air,	- - -	176.
Fixed air,	- - -	127.
Inflammable air,	- - -	17.
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		320.

I impute the greater portion of fixed air obtained in this process to the fire having been raised rather more towards the conclusion, and having been continued for rather a longer time, than in the former experiment.

THE operation being finished, and the vessels unluted, the retort was found to contain one ounce, seven drachms, forty-eight grains of liquid saccharine acid, and proceeding in the same manner as before, there appeared to have passed by distillation, into the intermediate bottle, four drachms, nine grains and half of the nitrous acid originally employed; so that the quantity

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of nitrous acid, which had actually entered into the experiment, amounted to no more than one ounce, three drachms, sixty-two grains and half; which, according to the above determined proportions, should contain 178 inches of nitrous air, and as much pure air; from whence it appears, 1st. that the whole of the nitrous air had been thrown off, the pure air or acidifying principle only remaining. 2dly. That the three drachms of sugar employed had attracted, during the effervescence, eighty-nine grains of the acidifying principle, and that these two substances, when united, and combined with phlegm, formed together the quantity of one ounce, seven drachms, forty-eight grains of saccharine acid.

INDEPENDENT of the information, which experiments of this kind afford, upon the nature of acids, they furnish us with a new method of analysing animal and vegetable substances; and though I have nothing quite complete to present on this subject, I shall proceed to give an account of the first essay which I have made upon sugar.

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IN the same apparatus that was used in the preceding experiments, I mixed two ounces of nitrous acid, with an equal quantity of water and six drachms of sugar, and proceeded in the same manner, receiving, in an intermediate bottle, the nitrous acid, which came over in distillation. When no more nitrous air was separated, and nothing remained in the retort, but the saccharine acid, the vessels were unluted, the intermediate bottle was removed, and I continued to keep up a gentle fire under the saccharine acid, receiving the air, which was separated, directly into jars, till at last, having raised the fire a little higher, towards the end, there was left only a small coaly residuum in the retort. I divided, into ten parts, the elastic fluid which had been disengaged during the operation, and very attentively and accurately separated the different kinds which I had obtained. The following table presents the whole results of the experiment.

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An Account, in Cubic Inches, of the Kinds and Quantities of the different Aëriform Fluids obtained in the Combination of Two Ounces of Nitrous Acid, and Six Drachms of Sugar, the Operation being carried on to Dryness.

Portions.	Nitrous Air.	Fixed Air.	Inflammable Air.	Total.
First	56 $\frac{1}{3}$	--	--	56 $\frac{1}{3}$
Second	49 $\frac{6}{10}$	6	--	55 $\frac{6}{10}$
Third	23 $\frac{1}{2}$	22 $\frac{1}{2}$	4 $\frac{2}{3}$	50 $\frac{2}{3}$
Fourth	21 $\frac{4}{10}$	30 $\frac{2}{3}$	4 $\frac{1}{3}$	56 $\frac{4}{10}$
Fifth	14 $\frac{6}{10}$	45 $\frac{1}{2}$	2 $\frac{9}{10}$	63
Sixth	15	39 $\frac{1}{4}$	7 $\frac{1}{2}$	61 $\frac{3}{4}$
Seventh	--	28 $\frac{1}{8}$	8 $\frac{1}{4}$	36 $\frac{3}{8}$
Eighth	--	48	11 $\frac{4}{10}$	59 $\frac{4}{10}$
Ninth	--	32 $\frac{4}{10}$	8	40 $\frac{4}{10}$
Tenth	--	25 $\frac{4}{10}$	17	42 $\frac{4}{10}$
Totals	180 $\frac{1}{3}$	277 $\frac{1}{2}$	74 $\frac{1}{2}$	522 $\frac{1}{2}$

I, AT this time, put no water in the intermediate bottle; and when the operation was finished, there were found in it two ounces and half of weak nitrous acid, which, from the quantity of alkaline liquor saturated by it, answered to four drachms, seventeen grains of

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the original acid used in the experiment. From hence it appears, that only one ounce, three drachms, fifty-five grains of nitrous acid had been decompounded: and this quantity is composed, according to the foregoing proportions, of about 177 inches of nitrous air, and an equal portion of pure or highly respirable air.

It is apparent from a view of the above table, that the nitrous air which had entered into the combination as one of the constituent parts of the nitrous acid, was thrown off in the form of gas, or in an aërisome state; but it may be asked what is become of the pure air or acidifying principle, which constituted the other principle of the nitrous acid? We have seen, from the preceding experiments, that it, at first, entered into combination with the sugar, in order to form with it a particular acid; and from the present experiment, we learn, that if, after the saccharine acid has been formed, the fire be moderately raised, the acid is almost wholly resolved into fixed and inflammable air. For what is fixed air? I have demonstrated, in another place, that it is the result

sult of a combination of phlogistic matter with the acidifying principle; from whence it should seem that sugar is composed of a small portion of inflammable air and much coaly matter. The latter uniting with the acidifying principle of the nitrous acid, forms with it the large quantity of fixed air which is obtained towards the end of the operation. I intend, by further experiments, to illustrate any obscurity which may attend this mode of analysis.

EVERY thing I have related as to sugar, may, as I have already remarked, be applied to a great number of animal and vegetable substances; from almost all of which, by combining them with nitrous acid, or, more properly, with the acidifying principle contained in that acid, we obtain particular acids, many of which have, indeed, some properties in common, but afford distinct characters in the result of their combinations. Here, therefore, we have a new road opened in chemistry; and that part of this science which treats of salts, to which some German chemists have given the name of *halotechnic*, instead of employing five or six acids, is now possessed of more than double

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that number, reckoning only those of which I have already acquired a knowledge; and it is not to be doubted, but the number will be, in future, considerably increased.

FROM all these reflections, and from the experiments contained both in this essay and some of the preceding ones, it results,

1st. THAT when the acidifying principle is combined with any body without decomposing it, (excepting, however, most metallic substances,) it converts such substance into a particular acid, which, exclusive of the general properties which are common to all the acids, has others which are peculiar to itself.

2dly. THAT, with respect to metallic bodies, it forms, with most of them, compounds known by the name of metallic calces. It must however be added here, that, even in this class of substances, there are some, as arsenic, iron, and perhaps several others, which, when combined with the acidifying principle, to a certain degree of supersaturation, not only assume a saline character, but even acquire properties common to the acids, and, like them, become true solvents.

3dly. THAT

gdly. THAT the acidifying principle, like all the others, has its different degrees of affinity; and possesses, for instance, a much stronger affinity to sugar and most animal and vegetable substances, than to nitrous air; and that it is in consequence of this preference that it quits the latter to form, with different substances, various kinds of acids.

4thly. THAT the number of acids, which may be formed, is as yet wholly indeterminate, as we are unacquainted with the whole of the substances which are susceptible of combining with the acidifying principle; and we are still less informed of the means which may be used to effect this combination.

5thly. THAT the nature of the nitrous acid appearing to be better known, at present, than it was formerly; and two distinct principles, viz. nitrous air, and pure air, or the acidifying principle, being proved, almost to demonstration, to exist in that acid; it affords to chemists a valuable means of analysis, and is capable of throwing considerable light on that of vegetable substances.

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6thly. THAT it seems not altogether impossible, especially from the last experiment related in this essay, that the phlogistic matter is wholly formed in vegetables, and is not, as chemists have hitherto imagined, the effect of fire.

ALL these conclusions will be illustrated and more firmly established by examples, which I design to adduce in a subsequent train of memoirs on this subject.

ESSAY

E S S A Y IX.

ON THE COMBINATION OF THE MATTER OF
FIRE WITH EVAPORABLE FLUIDS;
AND ON THE FORMATION OF ELASTIC
AÉRIFORM FLUIDS.

I SHALL suppose in this essay, that every part of the planet we inhabit is surrounded with a very subtle fluid, which penetrates, without any apparent exception, all the bodies which compose this globe; that this fluid, which I shall call the *igneous fluid*, the *matter of fire*, of heat and of light, has a tendency to place itself in equilibrium in all bodies, but is not capable of penetrating all, with equal facility; and that it exists, sometimes in a state of liberty, and sometimes in a fixed form and combined with other substances.

THIS opinion, of the existence of an igneous fluid, is so far from being new, that it was embraced by many philosophers among the ancients ; and it will therefore be unnecessary that I should relate the facts on which it is founded : especially as the future memoirs which I have to present on the subject, will serve as proofs of its reality. Indeed if I shew that this theory is universally agreeable to all the phenomena, and explains all the circumstances attending experiments in physics and chemistry, it will almost amount to demonstration.

WHENEVER we form certain combinations in water ; when, for example, we unite a fluid acid, that is, an acid dissolved in water, with a fixed alkali, also, in a state of solution, a neutral salt is formed, and, if the quantity of water be sufficient, the salt is kept dissolved.

IN every experiment of this kind, the water acts in two distinct ways. One part is absorbed by the saline combination, and is called, by chemists, the water of composition ; another part takes the name of the water of solution, and keeps the particles of the salt so equally

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equally separated from each other, that every portion of the liquor is equally impregnated with them.

THE same phenomena prevail relative to the igneous fluid. As all the bodies in nature are immersed in this fluid, and have imbibed some of it, there is scarcely any combination whatever but contains a greater or smaller quantity of the matter of fire. We should therefore distinguish, in bodies, between the fire of solution, and the fire of combination; between fire in a state of freedom, and fire when combined; in the same manner as was above observed, with respect to water, in the solution of salts.

AFTER this explanation, it will not be difficult to give a precise idea of what we understand by heat. Its intensity is measured by the quantity of free and uncombined igneous fluid contained in bodies. Though we have no exact scale to determine the proportion of igneous matter, we are at least possessed of methods of estimating it. These means are supplied by the dilatation of bodies, which is effected merely by introducing into them a greater quantity of the matter of fire.

fire. Thus, when a thermometer is heated, and made to rise, we only mix a greater quantity of that matter with the liquor in the tube; for it is not at all surprising, that in mixing two fluids together, the mixt should occupy a greater space than was held by one of the ingredients only.

WITH regard to the impression which the igneous fluid makes on our organs—an impression pleasant and reviving when moderate, but painful and destructive when it exceeds certain limits—it proceeds entirely from the tendency in that fluid to combination. We shall presently see that besides the power of penetrating into bodies, and separating their particles, it possesses the property of converting fluids into vapour, when combined with them in certain proportions; and this conversion into vapour necessarily implying a destruction of organisation, must consequently occasion a painful sensation.

HAVING thus sufficiently defined what I mean by the matter of fire, or rather by free fire, and by fire in a state of combination, it remains for

for me to add some general reflections upon what must necessarily happen in the different combinations.

We know that every mixt, every compound, has its own proper portion of igneous fluid; a kind of exact point of saturation: for the law of saturation seems to be general in every physical and chemical combination. From whence it follows, that whenever mixts and compounds are brought together, so that decompositions and new compositions are the result, one or other of the three following cases takes place: either the quantity of fire, which enters into the combination, will be the same as before, or there will be a decrease, or lastly, an increase of it. It is evident, that in the first case neither a separation or absorption of the matter of fire is effected; or, in other words, that there is neither any portion of free fire which passes into a state of combination, nor any fire that has escaped from a combined, to a free, state.

But the second case will be different; for a smaller quantity of the matter of fire enters into

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into the new combination, than existed in the former one; so that a part of the igneous fluid, which was combined, previous to the decomposition, will become free fire after the recombination, will recover its properties, and produce the effects which we call heat, and be dissipated by dividing itself insensibly among all the surrounding bodies, till an equilibrium be formed.

In the third case, in which a greater quantity of the matter of fire enters the new, than existed in the former, combination; the igneous fluid of the surrounding bodies will be absorbed, and be changed from the state of free, to that of combined, fire. The consequence of which will be a diminution of free fire in those bodies, which will be perceptible by the degree of cold which takes place; which cold will continue till all the surrounding bodies have severally supplied the deficient portion of free fire, so as to restore an equilibrium.

Thus we are furnished with a very sensible and plain criterion, by which we may determine

mine whether an absorption or separation of the matter of fire has taken place in any combination. In the first case, cold will be produced in the surrounding bodies; in the second, there will be an augmentation of heat.

We know how impossible it is, from the property of free fire to penetrate all substances, and from its tendency to preserve an equilibrium, to attain to any great accuracy in this kind of experiments. We can easily measure, in a jar, the air which is separated during the forming of any combination; but as we have no vessels which can contain, without loss, the matter of free fire; as jars, and, in general, all vessels, are so porous as to admit of a free access of it; all we can do is to judge, whether, in a short given time, there be any, or no efflux of the matter of fire; for, if it were possible to estimate its quantity, it could only be effected by means of a very complicated approximation. I do not, however, despair of making some use, even of these methods.

THESE principles, once established, it will not be difficult to apply them to the formation of

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of vapours, and of aëriform, or elastic fluids, in general.

We have just seen that whenever there is an absorption of the matter of fire in any combination, a certain degree of cold is produced in the neighbouring bodies.

THEREFORE, reciprocally, whenever cold is produced, we may equally conclude, that a portion of free fire has passed into a state of combination, or in other words, that the compound has absorbed a portion of the matter of fire or igneous fluid.

If, therefore, I prove that whenever there is a formation of vapours, cold is produced, I shall also have proved that there is an absorption of the matter of fire in the formation of vapours, or, what amounts to the same thing, that vapours are the result of a combination of the matter of fire, with the fluid, in a highly rarefied state.

I FIND my only embarrassment to proceed from the great choice of proofs of this position, and

and I might transcribe every thing that has been written on the subject of cold, arising from evaporation, by Messrs. Richman de Mairan, Cullen, and Beaumé.

It will be unnecessary to give a particular account of the experiments of these philosophers. They merit to be read and attentively considered in the original works. It will be sufficient to remark that they have shewn, 1st. that if a thermometer be immersed into any evaporable fluid, and then suddenly withdrawn, the thermometer will descend, several degrees, during the time the ball of it is drying, and that it ascends again insensibly as soon as all the fluid is evaporated, till it has recovered the exact temperature of the air and of the surrounding bodies in general. 2dly. That as the degree of cold produced is in proportion to the evaporability of the fluid, so the descent of the thermometer is less rapid, and does not proceed so far when the bulb is moistened with water, as when spirit of wine, volatile alkali, or especially æther, is employed. 3dly. That if the evaporation be accelerated by any other means than of heat, the increase of cold will be

pro-

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proportionable; so that not only all evaporation is attended with cold, but even the cold produced is governed by a certain law proportioned to the rapidity of the evaporation. That by continuing to moisten the bulb of the thermometer, as fast as it becomes dry, with evaporable fluids, the cold is increased more and more, because the efficient cause is hereby continued.

If the temperature of all bodies depends, as we have endeavoured to prove, merely on the quantity of the matter of fire, or free igneous fluid which they contain, it will follow that when the bulb of a thermometer is moistened with an evaporable fluid, the descent of the mercury which ensues is occasioned by no other cause, but because the fluid at the time it is reduced into vapour, carries off from the mercury a part of the matter of free fire which kept it elevated to the degree at which it before stood. Fluids, therefore, when they evaporate, deprive the surrounding bodies of a part of their matter of fire; and consequently vapours, and, in general, all aëriform bodies, are composed of some fluid, dissolved and combined with the matter of fire.

ALL

ALL the phenomena relative to cold may be rendered more evident, by placing the evaporable fluids in such circumstances as may be favourable to, and accelerate the formation of vapours ; as, for instance, in the vacuum of an air-pump. What I am going to relate on this subject, is extracted from a very considerable work, undertaken jointly by M. de la Place and myself, of which the academy has been already informed, and from a memoir which was read at the public meeting, last Easter.

ONE experiment alone, which I shall relate, goes to prove three points : 1st. that the resistance of the atmosphere is a resistance to be overcome, a force in opposition to the evaporation of fluids ; 2dly. that as soon as this compressing power is removed, the evaporable fluids expand and are changed into elastic aëriform fluids, or species of air ; and 3dly. that the transition of common fluids to a state of elasticity, is accompanied by an absorption of the matter of fire, which is taken from all the surrounding bodies.

LET a small bottle, or merely a glass tube of three or four lines in diameter, be filled with

K æther,

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æther, and covered with a wet bladder, which is to be fastened closely by passing several rounds of thread about it, and for greater security a second covering may be fastened in the same manner. The bottle, or tube, is to be so filled with æther, as to admit of no portion of air between the liquor and the bladder. Let it then be placed upon a good air-pump, the receiver of which must be furnished at top with a leathern covercle, penetrated by a shank, to which an awl or some other sharp-pointed instrument is to be firmly attached, for the purpose of pricking the bladder which covers the bottle at the instant it appears proper.

EVERY thing being thus disposed, let the receiver be exhausted, till the mercury in the barometer of the pump descend to two or three lines of its scale, and then let the bladder, which covers the bottle, be punctured.

IMMEDIATELY the æther will begin to boil, to evaporate with surprising rapidity, and to be converted into an elastic fluid, which, in the winter, will keep the barometer up to eight or ten inches, and, in very hot summer weather, to twenty or twenty-five inches.

If

If a small thermometer be introduced into the bottle containing the æther, the fluid in it descends considerably during the evaporation, on account of the great quantity of free fire which passes, in this experiment, into a state of combination, in order to reduce the æther into vapour.

If the air be permitted to re-enter, the thermometer recovers its ordinary height, viz. about 28 inches. But it is very remarkable that the æther, thus mixed with atmospheric air, is not thereby condensed, but remains as a permanently elastic fluid, and forms a particular kind of inflammable air, which I have not hitherto had an opportunity of examining.

THIS experiment succeeds with all evaporable fluids, with spirit of wine, and even with water; but, with this difference, that the atmosphere of spirit of wine, which is formed in the receiver of the air-pump, can only elevate the mercury one inch in winter, and four or five in summer, and the quantity of vapour is less than when æther is employed: consequently, the absorption of igneous fluid, and the degree

K 2 of

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of cold produced will be smaller. But it is not from hence less certain that, in all these experiments, the cold which is observed, with different fluids, is always nearly proportioned to the quantity of fluid evaporated.

THE above phenomena are less striking when, instead of putting the fluid into a bottle closely covered with a bladder, an open vessel is used ; but as this manner of conducting the experiment, gives rise to particular observations, which may afford great light to the subject in question, it seems necessary to give some account of it.

LET us suppose spirit of wine to be the fluid, the quantity of it, employed in the experiment, to be but small, and the temperature to be fifteen degrees. As soon as the barometer of the pump has descended to nineteen lines of its scale, the spirit of wine will begin to boil, but the ebullition will not continue, as in the former experiment: it will cease, on the contrary, for two reasons, as soon as we discontinue the pumping: 1st. because the spirit of wine, as it evaporates, is transmuted into an elastic fluid;

fluid; which, forming a kind of atmosphere that presses on the surface of the spirit, resists the progress of the evaporation; and 2dly. because at the instant of ebullition a portion of free fire passes into the state of combined fire, in order to constitute the elastic fluid which is formed, and this circumstance necessarily occasions a cooling of the whole quantity of spirit of wine, the necessary effect of which must be to retard its ebullition: so that supposing, as we have, that the fluid has, at first, begun to boil, the barometer being at nineteen lines, it should not boil, after it has been cooked by the first ebullition, till the barometer has descended to eighteen lines.

IF, after the first ebullition of the spirit of wine, which has been produced under the receiver, the working of the pump be continued, the spirit will not again boil so rapidly as at first, because no greater quantity of spirit will evaporate at each stroke of the piston, than will be necessary to replace what has been carried off through the capacity of the piston; so that this ebullition will always be stronger in proportion as the body of the pump is larger.

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THESE phenomena respecting the evaporation of volatile fluids in *vacuo*, are similar with the volatile alkali, æther, and several others: but one very important circumstance is worthy of observation, viz. that all these fluids evaporate, principally, from the bottom of the vessel, or in other words, that it is from thence the bubbles are separated. These bubbles mount up, and burst upon the surface, like those of water when boiling in a kettle. The cause of this phenomenon appeared to me, at first, to be an immediate consequence of the ensuing facts, and I reasoned as follows: in proportion as any fluid evaporates, it is cooled, as has been already shewn, and does not recover the temperature of the place in which the operation is performed, till the surrounding bodies have resupplied the quantity of free fire, of which the fluid has been deprived. It necessarily follows therefore, that the fluid confined under the receiver of an air-pump must be colder than the vessel which contains it. But the hottest parts should be the first which evaporate, and those will be the hottest which are in contact with the sides and bottom of the vessel, as receiving heat from it. In a word, it is at the surface

surface that the fluid is cooled, and, on the contrary, it is at its bottom, and by its contact with the containing vessel, that it recovers the igneous fluid from the surrounding bodies: it is consequently from the bottom that the ebullition must proceed. But however plausible this explanation may appear, I confess that some experiments have rendered it doubtful, and it is not without great hesitation that I have now related it.

BUT to resume, in few words, the whole theory of evaporation in *vacuo*; it appears certain that the transmutation of liquids into elastic aërisform fluids is subject to two laws, the effects of which are opposite to each other. On the one part, the degree of heat, to which they are exposed, tends to evaporate them; on the other, the pressure of the atmosphere resists their evaporation; insomuch that they are either in an elastic or liquid state, according as one or other of these powers becomes prevalent. But this theory will be greatly elucidated by the experiments which I am now employed in making, in concert with M. de la Place, an account of which I hope soon to be able to lay before the academy.

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BEFORE I conclude this essay, it may be proper to obviate one objection which the favourers of a different opinion will certainly deem unanswerable. If, as has been declared, elastic or aërisome vapours consist of the matter of fire combined with an evaporable fluid; and if no air or aërisome fluid can be formed without a portion of free fire passing to a state of combination; it ought to follow that, in every formation of air, cold should be produced; and it will not fail to be remarked that, when calcareous earth and alkalies are combined with acids, so far from cold, a sensible degree of heat is often observable during the *separation*; or rather during the *formation* of the air. An examination of what happens, on this occasion, instead of weakening, is the strongest proof of the truth of, this theory.

It must be allowed, that in the combination of acids with alkalies or calcareous earths, we sometimes observe heat. But this circumstance only proves that a greater portion of the matter of fire is disengaged in these combinations, than is necessary to the formation of the fixed air, which then recovers its elasticity. This assertion

assertion will be proved, by shewing that we can, at pleasure, increase or diminish the heat, in proportion to the increase or diminution of the quantity of fixed air contained in the alkaline basis. The following experiments are, in my opinion, indisputable proofs of the fact.

IN five separate bottles were placed as many mixtures, each consisting of four drachms of concrete volatile alkali dissolved in two ounces of distilled water. This alkali was nearly saturated with fixed air. To the first of these bottles was added one drachm, to the second, two, to the third, three, and, to the fourth, four drachms of quicklime ; the fifth was left without any addition. As soon as the lime was mixed with the alkaline solution, it attracted, from its superior affinity, the fixed air of the volatile alkali, and was precipitated to the bottom of the vessel, in the state of chalk or effervescent calcareous earth. All these liquors being decanted, were placed in as many glass bottles, and when they had recovered the same degree of temperature, they were saturated with nitrous acid, moderately

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moderately diluted, and the change of temperature occasioned by the effervescence, was observed by means of one of M. de Luc's mercurial thermometers. The following is an exact relation of the results.

THE volatile alkali, to which no addition had been made, and which had been deprived of no part of its air, so far from producing any heat, during its saturation with the acid, on the contrary, lowered the thermometer two complete degrees.

THE alkaline solution which had been deprived of a portion of its fixed air, by the addition of one drachm of lime, afforded two degrees of heat ; that to which two drachms of lime had been added gave three degrees ; that with three drachms, four degrees ; and, lastly, by that with four drachms of lime, four degrees and half of heat were produced.

THIS last alkaline solution, though deprived of more of its fixed air than the others, still contained sufficient to form a brisk effervescence with the nitrous acid, though not

not nearly so much as the solution to which no lime had been added.

THESE augmentations of cold or heat would have been more sensible, if the alkaline solutions had contained a greater quantity of salt, but the concrete volatile alkali not being soluble, in cold water, in greater proportion than that of one part of salt in four of water, it was not possible for me to procure a solution more strongly saturated. In order to complete my experiment therefore, I was obliged to have recourse to volatile alkali obtained by distillation with quick-lime; and though this alkali was not so far concentrated as it might have been, its combination with diluted spirit of nitre produced 27 degrees of heat. For the thermometer, which before stood at 16, suddenly rose to 43 degrees, at the instant of the combination.

THE phenomena are similar, if fixed alkali be employed. A solution of this salt, entirely divested of fixed air, or in a state of causticity, produces, with weak nitrous acid, a degree of heat, nearly equal to that of boiling water, whereas

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whereas a solution of the same alkali, saturated with fixed air, produces 6 degrees of cold.

It is proved, then, that pure alkaline salts, whether fixed or volatile, generally produce heat when combining with nitrous acid; but that the heat diminishes in proportion to the greater quantity of fixed air they contain; insomuch that when they are saturated with air, some degrees of cold are produced. Fixed air, therefore, in passing from a concrete state to that of vapour or elastic fluid, carries off with it a part of the matter of fire or igneous fluid, which is naturally disengaged whenever an alkali is united with an acid; and we may conclude that this igneous fluid enters into the composition of the fixed air, as into that of all vapours and elastic fluids, of every kind.

Of this assertion, give me leave to add a yet stronger demonstration. A very weak solution of fixed alkaline salt, nearly saturated with fixed air, was put into a bottle of strong flint-glass, into which a small thermometer was

was introduced ; a quantity of spirit of nitre was added, and the bottle immediately stopped. The pressure, effected by the want of communication with the atmosphere, soon abated the effervescence, and consequently heat was produced, and the mercury in the thermometer mounted several degrees ; whereas it would have descended if the experiment had been made in the open air. Having unstopped the bottle, after some minutes, and agitated the liquor, the effervescence which had been before prevented, and, as it were, suffocated, recommenced. In some time, the heat, which had been acquired while the bottle was closed, was dissipated, and the mercury of the thermometer settled somewhat below the degree of temperature of the external air.

FROM all these facts, I conclude, as has been already declared, that all vapour, air, and in general, every elastic aërisome fluid, is a combination of the matter of fire with a fluid, or even with any volatile solid body ; and that volatility is nothing else, but the property, which bodies possess, of being, in some manner, dissolved, of combining with

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with the igneous fluid, and, with it, forming aërisome fluids. Experiments, which I design, in future, to publish, on this subject, will serve to elucidate my theory in a more clear and perfect manner.

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