Experiments on the analysis of the heavy inflammable air / by William Austin.

EXPERIMENTS

ON THE

ANALYSIS

OF THE

HEAVY INFLAMMABLE AIR.

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EXPERIMENTS, &c.

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IN a Paper read before the Royal Society in the year 1788, I ſuggeſted an idea, that the heavy inflammable air is a compound of the light inflammable and phlogiſticated airs. At that time I had obſerved, that the heavy inflammable air, or at leaſt fixed air, is formed upon the decompoſition of nitrous ammoniac by heating it in cloſe veſſels; and that this air is affected by the electrical ſhock, like other elaſtic fluids into whoſe compoſition the light inflammable air enters. The concluſion which I then drew from thoſe facts ſeems to be ſupported by ſeveral ſubſequent experiments, which I now take the liberty of laying before the Royal Society. Should it hereafter be found, that the real conſtitution of the heavy inflammable air differs from what I conceive to be the reſult of the facts below recited, the facts themſelves may ſtill have their uſe, as they exhibit ſeveral properties hitherto unobſerved of the moſt extenſive compound body we know, excepting water.

Several elaſtic fluids containing the light inflammable air, as the hepatic and alkaline airs, being decompoſed by the electric ſpark, I was induced to try it on the heavy inflammable

air, as ſoon as I ſuſpected that it contained the lighter air as a conſtituent part. Agreeably to my expectation, this experiment immediately detected the light inflammable air; for ſuch an expanſion took place as could not ariſe from any other known ſubſtance. Thus the heavy inflammable air was ſometimes expanded to twice its original volume; and yet, upon examining the air ſo expanded, not a ſixth part of the whole was found to have undergone a decompoſition: for inſtance, when two meaſures and three quarters were expanded to ſix, it appeared by experiment, that nearly two meaſures and a half remained in their original ſtate.

After the inflammable air has been expanded to about double its original bulk, I do not find that it increaſes further by continuing the ſhocks. Conceiving that the progreſs of the decompoſition was impeded by the mixture of the other airs with the heavy inflammable, I paſſed the ſpark through a mixture of the heavy inflammable air and of the light inflammable air, obtained from diluted vitriolic acid and iron filings; but the expanſion ſucceeded nearly as well as when the heavy inflammable was electrified alone. This is an almoſt inſurmountable obſtacle to this mode of inveſtigation: yet it has ſuch advantages in other reſpects, the air to be analyſed being unmixed with other ſubſtances, and only in contact with the glaſs and quickſilver by which it is confined, that I determined to proſecute the ſubject in this manner as well as I could.

From this partial decompoſition of the heavy inflammable air we obtain a mixture of the two inflammable airs with phlogiſticated air; that is, of the heavy inflammable air not decompoſed, of the light inflammable air diſengaged by the ſpark, and of phlogiſticated air. How much of this phlogiſticated air pre-exiſted in the heavy inflammable air, and how much

much was diſengaged during the operation, it is not eaſy to determine. Neither are we acquainted with any ſubſtance which will ſeparate the two kinds of inflammable air by combining with the one and leaving the other: but we know that dephlogiſticated air will combine, in certain proportions, with each of them, either mixed or ſeparate; that with one of them it forms fixed air, with the other water. Therefore, by inflaming dephlogiſticated air with a mixture of theſe two airs, and obſerving the quantity of dephlogiſticated air conſumed, and the quantity of fixed air produced, we diſcover the exceſs of dephlogiſticated air conſumed above what is ſufficient for the production of the fixed air; and may conclude, that this exceſs of dephlogiſticated air has combined with light inflammable air. This concluſion is further confirmed by attending carefully to the contraction which takes place upon inflaming theſe airs, which is much greater in proportion to the quantity of fixed air produced, when a mixture of the two inflammable airs is inflamed, than when the heavy inflammable air is burnt alone. It is well known, that in all experiments of this kind, what remains after the combuſtion of the airs mixed together in due proportion, and after the ſeparation of the fixed air, is chiefly phlogiſticated air. From a conſiderable number of experiments, conducted with great care and attention to all theſe circumſtances, I have endeavoured to approximate to the quantities of the phlogiſticated and light inflammable airs diſengaged, when a given quantity of the heavy inflammable air was decompoſed. But all that can be attained to, is only an approximation to truth. The quantity of air decompoſed by this method is ſo ſmall, and the ſeparation of the different parts into which it is reſolved is attended with ſuch difficulties,

that

that an accurate analyſis of the heavy inflammable air can never be obtained in this manner.

I therefore attempted to decompoſe the heavy inflammable air by means of ſulphur, which readily unites with the light inflammable air in a condenſed ſtate, and with it forms hepatic air. Having introduced ſome ſulphur into a retort, filled with heavy inflammable air, and applied a ſufficient heat to melt and ſublime it, I found, that a conſiderable quantity of hepatic air was formed. After this air was abſorbed by water, I could not perceive that the remaining air differed from the heavy inflammable air before the operation. Sulphur mixed with powdered charcoal, upon being heated, yields hepatic air in great abundance, almoſt the whole of which is abſorbed by water. The ſmall unabſorbed reſidue, which does not exceed a hundredth part of the bulk of the whole air, appears to be phlogiſticated air.

In whatever manner the heavy inflammable air was decompoſed, whether by paſſing the electrical ſpark through it, by melting ſulphur in it, or by heating ſulphur and charcoal together, an appearance conſtantly occurred, which ſeemed to indicate, that volatile alkali is formed, whenever the heavy inflammable air is decompoſed. The circumſtance is this: a ſmall piece of paper, ſtained with any blue vegetable ſubſtance, is turned green by ſtanding in the air during any of theſe proceſſes; and this green is changed to red upon the addition of an acid. The inflammable air had been very long expoſed to water, and had no ſuch effect upon blue vegetable ſubſtances before the operation.

I have concluded theſe analytic attempts with ſeveral obſervations on the formation of fixed air from ſome ſubſtances, which conſiſt only of the light inflammable, phlogiſticated, and dephlogiſticated airs, and from others, in which theſe three

airs

airs are combined with ſuch matters as cannot be ſuſpected of having any place in the compoſition of fixed air.

I proceed now to a detail of the experiments, upon which theſe obſervations are founded.

Exp. 1. A bent glaſs tube, one-third of an inch in diameter, open at both ends, being filled with, and inverted in quick-ſilver, $2\frac{4}{5}$ meaſures of heavy inflammable air were thrown into it, and electrical ſhocks were paſſed through this air till it meaſured $4\frac{1}{2}$.

Lime water being then thrown up to it was not rendered in the leaſt degree turbid.

During the operation a thin depoſit, of a whitiſh or aſh colour, appeared upon the inſide of the glaſs tube and quick-ſilver. This was a common appearance, for which I can give no reaſon.

The meaſure, made uſe of in this and in all the following experiments, is $\frac{1}{4}$ of an inch. The air being thrown into the tube, the length of the column of air was meaſured by a moveable ſcale thus graduated. Some objection may be made to ſo ſmall a meaſure; but it is really unavoidable on this occaſion, on account of the great difficulty of decompoſing the heavy inflammable air in larger quantities. I attempted it upon a larger ſcale in a jar perforated with braſs rods, ſuch as is uſed for inflaming airs; but after having worked for many hours, in paſſing electrical ſhocks through air confined in one of theſe jars, it was not expanded more than one quarter of its original bulk. A piece of paper, coloured with a blue vegetable ſubſtance, was turned green by ſtanding in the air during this operation.

It was a very tedious work to throw airs into the ſmall tube in ſuch quantities as could be expreſſed in integer numbers of the

the meaſure: I have therefore generally been contented to uſe fractional numbers, and have been ſtudious only to introduce ſuch quantities of the airs as were convenient for the experiments.

The inflammable air uſed in all theſe experiments was obtained from foliated tartar. I have alſo paſſed electric ſparks through inflammable air from pit-coal, and found that it expanded in the ſame manner. Dr. HIGGINS * has ſhewn, that 5,5 of inflammable air from foliated tartar inflamed with 7,5 of dephlogiſticated air, form 5 meaſures of fixed air. Dr. PRIESTLEY † has deduced nearly the ſame proportions of the dephlogiſticated and fixed airs, by combining the dephlogiſticated and inflammable airs in a condenſed ſtate. In the following combuſtions of theſe airs, after accounting for the phlogiſticated air in the reſidues, the quantity of fixed air produced ſeems to be equal in bulk to the inflammable air combined; and the dephlogiſticated air to be to the fixed air, or to the inflammable, in the ratio of 7 to 5; or, in other words, when 5 meaſures of fixed air are formed, it appears, that very nearly 5 of inflammable air and 7 of dephlogiſticated air have diſappeared. But in burning different airs there will be conſtant variations in the reſults, ariſing from the very different ſtates of the heavy inflammable air; and therefore, in theſe obſervations, I am obliged to follow the proportions which took place in my own experiments.

Exp. 2. Three meaſures and one-third of inflammable air were expanded to $5\frac{1}{2}$: the difference is $2\frac{1}{6}$. To this air were added $3\frac{1}{2}$ meaſures of dephlogiſticated air, which increaſed the column of air to 9 meaſures. One electrical ſpark reduced them to 4.

* HIGGINS on Acetous Acid, p. 288, 289.

† PRIESTLEY, Vol. VI. p. 27.

Lime

Lime water being then thrown up left only three meaſures of air. A ſolution of liver of ſulphur did not reduce it further. The remaining air inflamed upon being brought near a candle in the open air.

In order to account for this, it muſt be obſerved, that, before the inflammation, the airs occupied the ſpace of 9 meaſures, and were reduced by combuſtion and lime water to 3. The contraction is 6 meaſures. Of theſe the meaſure of fixed air accounts for 2,4, allowing 1 meaſure of inflammable air and 1,4 of dephlogiſticated air to produce 1 meaſure of fixed air, according to the proportion ſtated in the laſt page; 2,4 meaſures, which thus went to form fixed air, being taken from 6, which is the whole contraction, leave 3,6. If we ſuppoſe this contraction of 3,6 to have ariſen from the union of the light inflammable and dephlogiſticated air, very nearly 2,4 meaſures of the former muſt have combined with 1,2 of the latter. This explains, with a tolerable degree of exactneſs, both the contraction which takes place, the reſidue after combuſtion, and the quantity of dephlogiſticated air combined. For without any expanſion, the reſidue from $3\frac{1}{3}$ meaſures of inflammable air and $3\frac{1}{3}$ of dephlogiſticated air, after forming 1 meaſure of fixed air, would be 4,43, which exceeds the reſidue in the experiment by 1,43. Some dephlogiſticated air muſt therefore be combined, beſides what enters into the fixed air: and with what other ſubſtance but the light inflammable air could it combine, ſo as to occaſion a contraction of 3,6 meaſures?

The dephlogiſticated air being in this inſtance inſufficient to ſaturate the inflammable airs, it could not be aſcertained how much of the heavy inflammable air was decompoſed, and how much remained in its original ſtate. The two following experiments were therefore made in order to determine, in what

proportion the dephlogiſticated air is ſufficient to ſaturate this inflammable air, and what quantity of fixed air they produce when inflamed.

Exp. 3. In a large exploding jar I mixed $4\frac{3}{4}$ meaſures of heavy inflammable air with $7\frac{1}{4}$ of dephlogiſticated air. After exploſion theſe airs meaſured ſomething more than $6\frac{1}{3}$, and were reduced by lime water to rather leſs than $2\frac{1}{2}$. In this reſiduary air a candle burnt with an increaſed flame, as in dephlogiſticated air.

Thus very nearly 4 meaſures of fixed air were produced from $4\frac{3}{4}$ of heavy inflammable air.

Exp. 4. Into the ſmall bent tube, which was employed in the firſt and ſecond experiments, I introduced $3\frac{2}{3}$ meaſures of inflammable air, and $5\frac{2}{3}$ of dephlogiſticated air. Theſe were reduced by inflammation to $5\frac{1}{3}$, and by lime water to $2\frac{1}{3}$.

In this experiment, 3 meaſures of fixed air were produced from $3\frac{2}{3}$ of inflammable air.

In the third experiment, the quantity of fixed air produced is 4 meaſures very nearly. The reſiduary air is rather leſs than $2\frac{1}{2}$. If to $2\frac{1}{2}$ we add a quantity of inflammable air equal to the bulk of fixed air, that is, very nearly 4 meaſures, it will amount to $6\frac{1}{3}$ full meaſure; and if we further add 5,6, which is the quantity of dephlogiſticated air neceſſary to form 4 meaſures of fixed air, we ſhall have 11,93, which is within ſeven hundredths of a meaſure of the original quantity of the two airs.

In the fourth experiment, 3 meaſures of fixed air are produced, which require 3 of inflammable air, and 4,2 of dephlogiſticated air; theſe, added to the $2\frac{1}{3}$ meaſures of reſiduary air amount to 9,53, which is two-tenths of a meaſure more than the original quantity.

It

It appears from theſe obſervations, that the proportion of dephlogiſticated and inflammable air, in the conſtitution of fixed air, above ſtated, agrees very nearly with experiment. In one inſtance, the quantity ariſing from calculating after this proportion exceeds the real quantity by two-tenths of a meaſure; and in the other, it falls ſhort of it by ſeven hundredths of a meaſure.

It is evident, that $3\frac{2}{3}$ meaſures of this inflammable air burnt in the ſmall tube are capable of forming 3 of fixed air. The fixed air, produced by inflaming the ſame airs in the large jar, bears rather a greater proportion to the inflammable air employed; for $4\frac{3}{4}$ meaſures of it produced almoſt 4 of fixed air. I tried many experiments on theſe airs mixed together in different proportions, and only in one inſtance found the product of inflammable air greater in proportion than 4 from $4\frac{3}{4}$; which I therefore conceive to be as much as this air is capable of producing, and ſuſpect, that a ſmall error muſt have been committed in that inſtance, which gave a greater proportion of fixed air. The $\frac{3}{4}$ of a meaſure which remain, are chiefly phlogiſticated air, mixed perhaps with a very ſmall quantity of inflammable air; as will appear from the reſidues in ſome of the following experiments, which contain about that quantity of phlogiſticated air more than they could derive from the dephlogiſticated air. Thus, for inſtance, in the third experiment, the reſiduary air meaſures $2\frac{1}{2}$, the quantity of dephlogiſticated air engaged in forming the fixed air is 5,6, which added together make 8,1; but the whole dephlogiſticated air amounts only to 7,25; the difference 0,85 is nearly equal to the phlogiſticated air, which I ſuppoſe to have been mixed with the heavy inflammable air.

Exp. 5. Three meaſures of inflammable air were expanded to $6\frac{1}{4}$, then $4\frac{1}{4}$ of dephlogiſticated air were added; after

inflammation they meaſured 4¾; lime water contracted them to 2½.

In this experiment 2¼ meaſures of fixed air were formed, which is nearly 0,28 leſs than the inflammable air uſed in this experiment is capable of producing. We have therefore only 0,28 to account for the expanſion; and we cannot ſay, that the whole of this was decompoſed, as the dephlogiſticated air, even in this experiment, was not quite ſufficient to ſaturate the two kinds of inflammable air; and therefore a ſmall quantity of heavy inflammable air might remain in the reſidue in its original ſtate.

Exp. 6. A quantity of heavy inflammable air, which meaſured between 3¼ and 3⅓, was expanded by about 300 electrical ſhocks to 6½ full meaſure. To theſe were added 5¼ of dephlogiſticated air. After inflammation they meaſured 4¾, and were reduced by lime water to 1$\frac{5}{6}$.

The inflammable air in this experiment was between 3¼ and 3⅓; we will therefore take 3,29, the arithmetical mean of thoſe numbers. The quantity of fixed air produced is leſs by 0,36 than could be produced from the ſame airs without electrifying.

It is probable, that a ſmall quantity of the heavy inflammable air may eſcape unaltered in each of theſe experiments; the following were therefore made with a ſtill greater proportion of dephlogiſticated air, and the reſidues were examined with more attention.

All the preceding experiments were made with the ſame airs; theſe being exhauſted, a freſh ſupply was procured for thoſe which follow. The purity of this dephlogiſticated air was ſuch, that one meaſure of it being mixed with 1¾ of nitrous air was reduced to 0,2 of a meaſure. The inflammable air was leſs pure than the former. In the two following

experiments

experiments 4,44 measures of fixed air were produced from 5,58 of the heavy inflammable; the remaining 1,18 must have been chiefly phlogisticated air.

Exp. 7. Inflammable air 2¾ and dephlogisticated air 4,58 were inflamed in the small tube. They then measured 4¼, and were reduced by lime water to 2⅙. After several bubbles of nitrous air, the residue was less than 2 by nearly ¼.

In this experiment 2,09 measures of fixed air were produced.

Exp. 8. In a large exploding jar, 2⅚ measures of inflammable air, and 4,17 of dephlogisticated air, were reduced by combustion to 4,· nearly, and then by lime water to 1,75. About a measure of nitrous air being then thrown up, the residuary air measured 1,5.

The quantity of fixed air produced in this instance is 2,35.

Exp. 9. Inflammable air 2⅚ measures were expanded by about 200 electrical shocks to 5 and not quite ⅙ more. To the air thus expanded, I added as much dephlogisticated air as increased the column of air to 9½; thus the dephlogisticated air was rather more than 4,09. After combustion, they measured fully 4; and, after being exposed to lime-water, rather less than 2. Nitrous air occasioned a small contraction further.

According to the proportion stated in p. 56. 2⅚ measures of this inflammable air contain 0,58 of phlogisticated air; 0,58 added to 2, which went to form fixed air, amount to 2,58. But the original quantity of inflammable air, *viz.* 2⅚ exceeds 2,58 by 0,25. What becomes of the 0,25 measures of inflammable air which thus disappear? I apprehend they must have undergone a decomposition, and have been expanded to 10 times their original bulk.

The dephlogisticated air was still further increased in the following experiment.

Exp.

Exp. 10. Three meaſures of inflammable air, after 150 electrical ſhocks, became 5,1. To this was added as much dephlogiſticated air as increaſed the column of air to $10\frac{5}{8}$. After inflammation it meaſured about 4,9; and was reduced by lime water to $2\frac{1}{4}$. This reſidue was not inflammable.

The contraction upon burning theſe airs was 5,93; and the quantity of fixed air appears to be 2,15. This fixed air requires 2,15 meaſures of inflammable air and 3,01 of dephlogiſticated air. Theſe deducted from the ſum of the contraction leave 2,92, above what is ſufficient to account for the fixed air produced. Suppoſing this contraction to have been occaſioned by the union of light inflammable and dephlogiſticated air, 1,94 of the former muſt have combined with 0,97 of the latter. It is evident, that the quantity of dephlogiſticated air uſed in this experiment is more than ſufficient to combine with both kinds of inflammable air.

The fixed air produced in theſe experiments is 0,23 leſs in proportion, than was produced, when the inflammable air was not decompoſed in the ſeventh and eighth experiments. It appears by calculation, that theſe 0,23 were expanded to about ten times their bulk. It is obſervable, that the expanſion in this caſe is 2,33; and that the quantity of light inflammable air which combined with the dephlogiſticated air, is only 1,97, which is 0,40 leſs. This proves, that it is very difficult, if not impoſſible, to unite the whole of theſe airs; and that a ſmall quantity will remain diffuſed in the reſidue, unleſs the airs be much purer than I have been able to procure them; yet it is not probable, that ſo large a proportion of light inflammable air as 0,40 ſhould eſcape combuſtion, over and above what eſcapes in ſimilar circumſtances, when no light inflammable air is preſent. The addition of light inflammable

air

air to a mixture of the other airs would rather contribute to render the combuſtion more general, and the reſidue conſequently leſs; for in all combuſtions, the union of the inflammable and dephlogiſticated airs is more complete, as the proportion of phlogiſticated air mixed with them is leſſened. In general, when air does not burn in ſuch circumſtances, we preſume, that it is phlogiſticated air; and upon this principle we muſt conclude, that a conſiderable part of thoſe 0,40 was phlogiſticated air.

I proceeded to repeat this experiment with a freſh ſupply of the two airs; but the tube burſting in the laſt exploſion, a ſmaller one was uſed in exp. 12, which however could not affect the reſult of the experiment.

Exp. 11. Four meaſures and a half of inflammable air and $6\frac{1}{2}$ of dephlogiſticated were reduced by inflammation to $5\frac{1}{2}$; and by cauſtic alkali to 2 and a very little more. The remainder was not inflammable.

The product of fixed air is $3\frac{1}{2}$ meaſures.

Exp. 12. Two meaſures and three quarters of inflammable air were expanded to 6; then, to reduce the column of air, one meaſure of dephlogiſticated air was added, and the electrical ſpark was paſſed through the two airs; afterwards 2 meaſures of dephlogiſticated air were added, and the electrical ſpark again paſſed through them; and, laſtly, 3,59 meaſures of dephlogiſticated air were thrown up, and the electrical ſpark repeatedly paſſed through this mixture of airs. After theſe exploſions the airs meaſured $5\frac{2}{3}$, and after the addition of cauſtic alkali 3,83.

The product of fixed air is 1,83; which is 0,30 leſs in proportion, than was produced in exp. 11. from the ſame inflammable air not electrified.

Not-

Notwithſtanding the utmoſt attention, we are liable to a ſmall error in each of theſe experiments; and there is conſequently a ſmall variation in the reſults; but, I think, they concur ſufficiently to juſtify the following concluſions.

1. That the heavy inflammable air contains the light inflammable air in great abundance.

I apprehend this light inflammable air was, before the application of the electrical ſpark, a conſtituent part of the heavy inflammable air; becauſe, if it were contained in the heavier air not as a conſtituent part, what ſhould hinder its being burnt when the heavy inflammable air is burnt? Can it be ſuppoſed, that the heavy inflammable air ſhould contain the light inflammable air in circumſtances of combuſtion, and that the light inflammable air ſhould eſcape the fire? And if the lighter air be burnt, the ſame quantity of dephlogiſticated air would be neceſſary to ſaturate it before as after its being electrified. But it is evident from the preceding experiments, that much more dephlogiſticated air is neceſſary to ſaturate the air, after it has been expanded by the electrical ſhock, than before.

2. That no fixed air is formed during the ſeparation of the lighter air from the heavy inflammable air.

Here it ſhould be obſerved, that if the conſtitution of the heavy inflammable air depended on an union of the light inflammable and fixed airs, as ſome have ſuppoſed, we ſhould certainly diſcover the fixed air, when the other part was ſeparated from it. Or, ſhould it be conjectured, that the light inflammable air is ſeparated from water ſuſpended in the heavy inflammable air, in that caſe, would not fixed air be formed from the other conſtituent part of the water uniting with the heavy

heavy inflammable air in conſequence of the repeated electrical ſhocks?

3. That the electrical ſhock ſeparated a ſubſtance from the heavy inflammable air, which has ſome leading characters of an alkali.

When inflammable air is decompoſed by ſulphur, or when hepatic air is made from charcoal and ſulphur, we have the ſame appearance of an alkali. That this is the volatile alkali is evident from its evaporation, when hepatic air is made from ſulphur and charcoal.

4. That the heavy inflammable air, through which the ſpark has been repeatedly paſſed, when burnt with any proportion of dephlogiſticated air, does not produce ſo much fixed air, as the ſame quantity of inflammable air not electrified.

Hence it is evident, that a part of the air is actually decompoſed by the ſpark. Hence alſo we may infer, that the decompoſed air is not reſolved into light inflammable air and charcoal, of which ſome chemiſts have ſuppoſed it to conſiſt, becauſe the charcoal would combine with dephlogiſticated air after its ſeparation from light inflammable air, and we ſhould not have ſuch a defect of fixed air..

6. That the reſidues, after inflaming the decompoſed air, are generally greater than thoſe from the air in its natural ſtate, or than can be accounted for from the mixture of the heavy inflammable and dephlogiſticated airs.

This affords a ſtrong preſumption, that phlogiſticated air is extricated from the decompoſed heavy inflammable air in a ſeparate ſtate, beſides what enters into the volatile alkali, which is formed at the ſame time. If light inflammable air only were diſengaged during the decompoſition, the reſidues would certainly not be greater after inflammation with a ſuffi-

cient quantity of dephlogiſticated air; on the contrary, if the inflammable air were increaſed in proportion in the mixture, the combuſtion would be more complete, and the reſidues leſs.

Having obſerved, that ſulphur readily combines with light inflammable air, if preſented to each other at the inſtant that the inflammable air is detached from other bodies, before its particles have receded from each other, and that hepatic air is generally formed in this manner, I introduced ſome ſulphur and heavy inflammable air into a glaſs retort, firſt filled with, and inverted in quickſilver, and applied a ſufficient heat to melt it. The heat was continued till the ſulphur was ſublimed. The melted ſulphur ſoon acquired a dark reddiſh colour; as it ſublimed, it became quite black, and every part of the retort was covered with a black cruſt. On the depending part of the retort, where the melted ſulphur lodged, and where the heat was ſtrongeſt, there remained a black mark, which could not be removed by a much greater heat than that by which the ſulphur was ſublimed. The bulk of the air was not materially altered by this operation. A little blue paper being thrown up to the air after the operation, became green. Water abſorbed about one-third of it, and acquired a ſtrongly hepatic ſmell. The inflammable air was carefully waſhed, ſo as to ſeparate from it all the hepatic air. I then mixed this inflammable air with dephlogiſticated air, and inflamed them, expecting to find a greater quantity of phlogiſticated air in the reſidue, than when the inflammable air was burnt, which had not been ſubjected to this proceſs. But the difference of the reſidue does not exceed $\frac{1}{113}$ the quantity of air decompoſed in this manner, if we may judge from the following experiment.

Expe-

Experiment. Inflammable air, from which hepatic air had been made, and had been ſeparated by expoſure to water, $4\frac{1}{2}$, and dephlogiſticated air $6\frac{2}{3}$, were inflamed in a large exploding jar. After the inflammation they meaſured 6; and after being agitated with lime water $2\frac{1}{4}$. This reſidue burnt with increaſed flame.

The airs uſed in this experiment were the ſame as thoſe in the ſecond experiment. The quantity of fixed air generated is only 0,035 leſs in proportion than was produced in the third experiment from the air in its original ſtate.

The reſidue is only 0,17 more than it ſhould be by calculation, allowing the dephlogiſticated and inflammable airs to enter into fixed air in the proportion of ſeven to five.

The remaining heavy inflammable air is therefore very little altered as to its quality by this operation, though it is much leſs in quantity than can be accounted for from the production of hepatic air. For the light inflammable air in the conſtitution of hepatic air is expanded to the ſame degree as in its ſimple ſtate; and an expanſion might be expected, when the hepatic air is generated from the heavy inflammable, juſt as when the lighter air is ſeparated from the heavy by the electrical ſhock; but no expanſion is obſerved in this inſtance. I therefore ſuſpect, that, when hepatic air is formed in the heavy inflammable air, the heavy air is imperfectly decompoſed; that only a part of the light inflammable air is combined with ſulphur; and that the remaining parts are precipitated in a ſtate analogous to charcoal, and blacken the ſulphur. Upon applying heat to the ſulphur thus blackened, I have perceived an hepatic ſmell. This blackened ſulphur is not entirely diſſolved, like pure ſulphur, by being boiled in cauſtic alkali, but a black powder remains. In one inſtance, this black ſubſtance diſappeared

peared after long boiling in ſtrong nitrous acid. More experiments, than it is in my power to make at preſent, are neceſſary to determine fully the nature of it.

The analogy between the heavy inflammable air and charcoal is illuſtrated by the formation of hepatic air from charcoal and ſulphur. Theſe ſubſtances, heated in a ſmall glaſs retort, yield hepatic air in great abundance. The blue vegetable colour is turned green by expoſure to this air. After hepatic air had been generated for a long time from the ſame materials, without admitting any common air into the retort, ninety-nine parts in a hundred of the air which came over laſt were abſorbed by water. The inſoluble part appeared to be phlogiſticated air. Thus ſulphur and charcoal, heated in a glaſs retort, yield hepatic air, phlogiſticated air, and volatile alkali, or a ſubſtance very analogous to it.

As far as I have been able to diſcover by experiments, the heavy inflammable air and charcoal conſiſt of the ſame elements in different proportion. The application of heat to pure charcoal confirms this opinion; for the production of heavy inflammable air from charcoal, by mere heat, is conſtantly accompanied with a production alſo of phlogiſticated air. I apprehend, that in theſe caſes the charcoal is decompoſed and reſolved into theſe two parts. Whenever charcoal, or any ſubſtance containing it, is decompoſed by heat only, the phlogiſticated and heavy inflammable airs are produced; and when the heat is intenſe, Dr. HIGGINS has obſerved *, that the air produced from theſe ſubſtances becomes rarer; as I imagine, in conſequence of a portion of the heavy inflammable air itſelf being reſolved by heat into its conſtituent parts. I would not lay much ſtreſs on the appearance of phlogiſticated air from

* HIGGINS on Acetous Acid, p. 293.

the

the compound forms of vegetable, animal, and bituminous ſubſtances, all of which yield phlogiſticated air and volatile alkali in great abundance; yet when the more ſimple modifications of the heavy inflammable air, as charcoal, vinegar, and, if Dr. PRIESTLEY is not miſtaken, fixed air, give out phlogiſticated air, when decompoſed in cloſe veſſels, I cannot but infer, that phlogiſticated air is an eſſential part of that peculiar ſubſtance which exiſts in all theſe ſtates, whether that ſubſtance be called charcoal, or the gravitating matter of heavy inflammable air.

Hence it appears, that the phlogiſticated and heavy inflammable airs combined, conſtitute charcoal; and that the mere application of heat always reſolves charcoal into theſe two ſubſtances. But the heavy inflammable air is itſelf a compound of the lighter inflammable and phlogiſticated airs. If phlogiſticated air be combined with the heavy inflammable, or, which is the ſame thing, if light inflammable air be taken from it, charcoal is re-produced; therefore, when ſulphur is melted in the heavy inflammable air, and hepatic air formed in it, the remaining parts of the heavy inflammable air return to the ſtate of charcoal. And laſtly, when ſulphur is melted in contact with charcoal, the decompoſition is complete; and the charcoal is reſolved into its ultimate particles, the phlogiſticated and light inflammable airs, with a ſmall admixture of volatile alkali.

Thus far I have proceeded in the decompoſition of the heavy inflammable air. The formation of this air, on many occaſions, confirms what has been ſaid concerning its analyſis. In the reſolution of compound bodies into their conſtituent parts, it may always be ſuſpected, that the whole is not accounted for, that ſome part may have eluded obſervation, till the very

parts

parts we aſſign are put together, and the ſame compound is produced from them. The frequent production of fixed air, from ſubſtances generally not ſuppoſed to contain the heavy inflammable air, has lately given riſe to a new ſyſtem in chemiſtry. The author of this ſyſtem has the merit of pointing out the appearance of fixed air in almoſt all phlogiſtic proceſſes, in the combuſtion of various ſubſtances, in the reduction of metals, and in the decompoſition of acids; phænomena which cannot otherwiſe be accounted for, than by ſhewing that the ſpecific matter of charcoal is a compound body; that its component parts are preſent in all theſe proceſſes; and in ſome of them nothing elſe, if we except dephlogiſticated air.

I have already taken notice of the formation of fixed air from nitrous ammoniac, which is now well known to contain nothing, but the phlogiſticated, light inflammable, and dephlogiſticated airs. This ſalt, heated in cloſe veſſels, yields dephlogiſticated nitrous air in great abundance, mixed with a ſmall proportion of fixed air. I have often repeated this experiment with nitrous ammoniac, which indicated no trace of fixed air either with lime water, or with acids, before its decompoſition; but, when the ſalt was decompoſed by heat, I always found lime water rendered turbid by the generated air; and, upon adding an acid to the turbid lime water, have obſerved air bubbles to be produced in it.

When the three elementary airs are in a condenſed ſtate, and are ſet free from any combinations, they unite and form fixed air without the aſſiſtance of heat. Thus fixed air is generally produced when metals are diſſolved in the nitrous acid. In theſe ſolutions, the component parts of nitrous acid and the light inflammable air, being extricated at the ſame time, unite before they have acquired the aëriform ſtate, and conſtitute fixed air.

Objects

Objects are often too common or too near for our obſervation. Phlogiſticated air preſents itſelf in the decompoſition of ſo many bodies, that its appearance excites no enquiry; and it is not regarded as eſſential to the chemical conſtitution of the bodies which yield it, excepting in the inſtances of nitrous acid and volatile alkali, two ſubſtances of very ſmall extent in the ſcale of natural bodies. The calces of metals are well known to contain phlogiſticated air; yet the effect of this air on calcination in general, and how far the very different calces of the ſame metal are influenced in colour or other properties by the different proportions of phlogiſticated air, has never been conſidered. Fixed air is often formed from the calces of metals, mixed with water, or with ſome other ſubſtance containing light inflammable air *. Red precipitate mixed with iron filings yielded very pure fixed air. Braſs duſt mixed with red precipitate, likewiſe gave out fixed air, though in leſs quantity. Turbith mineral and iron filings, treated in the ſame manner, afforded much leſs fixed air than the red precipitate and iron filings. It is probable, that the turbith mineral contains leſs phlogiſticated air, than the red precipitate. The fixed air in all theſe experiments was mixed with phlogiſticated and dephlogiſticated air. Mr. KIRWAN † found, that the ſimple calx of mercury with iron filings and water produced fixed air. The ſame author alſo obſerved, that iron calcined with nitrous acid gave out, upon being heated, fixed air; and he found the production of this air renewed upon the addition of water. Dr. PRIESTLEY ‡ obtained fixed air from iron converted into ruſt by expoſure to nitrous air. In all theſe experiments the

* PRIESTLEY, VI. p. 253, 254.

† Eſſay on Phlogiſton, p. 114.

‡ Ibid. p. 52.

three

three elementary airs are preſent, and, being expelled by heat from the metals with which they were combined, unite with each other, and form fixed air. It is not material to the preſent argument, whether the light inflammable air be ſuppoſed to be furniſhed from water, or from the regulus of a metal: it is enough for our purpoſe, that none of the ſubſtances employed in theſe experiments, contain heavy inflammable air or charcoal, in ſufficient quantity to account for the fixed air produced, as Dr. PRIESTLEY * has juſtly obſerved.

The growth of plants affords a ſtrong proof of the formation of charcoal from the ſubſtances which have been aſſigned. If we may believe experiments, water and air alone are neceſſary to this natural proceſs; yet vegetation is the great ſource of charcoal or heavy inflammable air. This enquiry is ſtill in its infancy; but from the beſt experiments that have been made it ſhould ſeem, that plants grow beſt in phlogiſticated air; that they take in phlogiſticated air, and give out dephlogiſticated air. Theſe phænomena cannot be accounted for but by ſuppoſing, that water is decompoſed by growing plants; that part of its dephlogiſticated air is diſcharged into the atmoſphere; and that the other conſtituent part of water, with phlogiſticated air, is taken into the growing ſubſtance. Thus the phlogiſticated and light inflammable airs are brought together by the proceſs of vegetation.

* PRIESTLEY, VI. p. 319.