

XIV. *Continuation of the Experiments and Observations on the Specific Gravities and Attractive Powers of various Saline Substances.* By Richard Kirwan, Esq. F. R. S.

Read April 11, 1782.

**B**EFORE I enter into a detail of the new experiments I have made in the prosecution of this subject, I must beg leave to rectify some mistakes I have fallen into in my last paper.

1. In computing the quantity of acid taken up by 10,5 gr. of mild vegetable fixed alkali, I made no allowance for the small quantity of earth it contains, *viz.* 0,7035 of a grain; but in large quantities of alkali, this proportion is considerable, and occasioned a small but sensible error in my subsequent calculations of the proportion of ingredients in neutral salts, the quantity of alkali being, by that fraction, less than I supposed it in 10,5 gr. This correction being made, it will be found, that 100 gr. of perfectly dry vegetable fixed alkali (abstracted from the quantity of earth) generally contain 22,457 gr. of fixed air instead of 21, as I before determined; yet the former determination is right, where the earth is not separated, yet may well be supposed to exist, as in the alkali of pearl-ash, purified by three repeated calcinations and solutions. Hence also 100 gr. of such alkali, free from earth, water, and fixed air, take up 46,77 gr. of the mineral acids, that is, of the mere

A a 2

acid

acid part; and 100 gr. of common mild vegetable alkali take up about 36,23 of real acid.

100 gr. of perfectly dry tartar vitriolate contain 30,21 of real acid, 64,61 of fixed alkali, and 5,18 of water. Crytallized tartar vitriolate loses only 1 *per cent.* of water in a heat in which its acid also is not separated in any degree, and therefore contains 6,18 of water.

100 gr. of nitre, perfectly dried, contain 30,86 of acid, 66 of alkali, and 3,14 of water; but in crytallized nitre the proportion of water is somewhat greater; for 100 gr. of these crytals, being exposed to a heat of 180° for two hours, lost 3 gr. of their weight, without exhaling any acid smell; but when exposed to a heat of 200°, the smell of the nitrous acid is distinctly perceived. Hence 100 gr. of crytallized nitre contain 29,89 of mere acid, 63,97 of alkali, and 6,14 of water.

100 gr. of digestive salt perfectly dry contain 29,68 of marine acid, 63,47 of alkali, and 6,85 of water. 100 gr. of crytallized digestive salt lose but 1 gr. of their weight before the smell of the marine acid is perceived; and hence they contain 7,85 gr. of water.

But the mistake which cost me most time and pains to correct was that which I fell into when I imagined, that the mixtures of oil of vitriol and water, and spirit of nitre and water, had attained their maximum of density when they had cooled to the temperature of the atmosphere, which at the time I made my experiments stood between 50 and 60° of FAHRENHEIT. The former I had even suffered to stand six hours, which was much longer than was necessary for its cooling; but when the acid was so much diluted as to cause little or no heat, I allowed it to stand but for a very little time before I examined its density: yet several months after I found many of these mixtures

mixtures much denser than when I first examined them, and that at least twelve hours rest was requisite before concentrated oil of vitriol, to which even twice its weight of water is added, attains its utmost density, and still more when a lesser proportion of water is used: thus, when I made the mixture of 2519,75 gr. of oil of vitriol, whose specific gravity was 1,819, with 180 of water, I found its density six hours after 1,771; but after twenty-four hours it was 1,798: and hence, according to the reasoning in the former paper, the accrued density was at least ,064 instead of ,045 as I had formerly found it. But by using oil of vitriol still more concentrated, whose specific gravity was 1,8846, I was enabled, by a similar train of reasoning, to make a still nearer approximation, and found that the accrued density of oil of vitriol, whose specific gravity is 1,819, amounts to 0,104; and consequently its mathematical specific gravity is 1,715. 6,5 gr. of this oil of vitriol contained, as I before found, 3,55 of mere acid, and the remainder water, then the weight of an equal bulk of water is 3,79 gr.; and subtracting from this the weight of the water that enters into the composition of the oil of vitriol, it will be found, that the weight of a bulk of water, equal to the acid part, is 0,84, and consequently the specific gravity of the pure and mere acid part is 4,226. Upon this ground, and constantly allowing the mixtures to rest at least twelve hours (until the oil of vitriol was diluted with four times its weight of water, and then often only six hours) before their density was examined, I constructed the table hereto annexed; the temperature of the room I constantly kept between 50 and 60°.

Oil of vitriol.	Acid.	Water.	Accrued density.	Mathemat. sp. gravity.	
Grains.					
1000	--	387,95	,07	1,877	1,846
1100	--	487,95	,104	1,738	1,844
1200	--	587,95	,105	1,637	1,742
1300	--	687,95	,144	1,561	1,705
1400	--	787,95	,144	1,500	1,644
1500	--	887,95	,137	1,452	1,589
1600	--	987,95	,137	1,412	1,539
1700	--	1087,95	,130	1,379	1,509
1800	--	1187,95	,124	1,350	1,474
1900	--	1287,95	,116	1,326	1,442
2000	--	1387,95	,116	1,304	1,420
2100	--	1487,95	,112	1,286	1,398
2200	--	1587,95	,112	1,269	1,381
2300	--	1687,95	,108	1,254	1,362
2400	--	1787,95	,104	1,241	1,345
2500	--	1887,95	,104	1,229	1,333
2600	--	1987,95	,101	1,219	1,320
2700	--	2087,95	,096	1,209	1,307
2800	--	2187,95	,091	1,200	1,291
2900	--	2287,95	,090	1,192	1,282
3000	--	2387,95	,090	1,184	1,274
3100	612,05	2487,95	,090	1,177	1,267
3200	--	2587,95	,090	1,170	1,260
3300	--	2687,95	,089	1,164	1,253
3400	--	2787,95	,084	1,159	1,243
3500	--	2887,95	,083	1,150	1,233
3600	--	2987,95	,073	1,149	1,222
3700	--	3087,95	,073	1,144	1,217
3800	--	3187,95	,071	1,140	1,211
3900	--	3287,95	,071	1,136	1,208
4000	--	3387,95	,071	1,132	1,204
4100	--	3487,95	,070	2,128	1,198
4200	--	3587,95	,070	1,125	1,195
4300	--	3687,95	,070	1,121	1,191
4400	--	3787,95	,070	1,118	1,188
4500	--	3887,95	,070	1,115	1,185
4600	--	3987,95	,070	1,113	1,183
4700	--	4087,95	,070	1,110	1,180
4800	--	4187,95	,070	1,107	1,177
4900	--	4287,95	,070	1,105	1,175
5000	--	4387,95	,070	1,103	1,172
5100	--	4487,95	,069	1,100	1,169

Oil of vitriol.	Acid.	Water.	Accrued density	Mathemat. sp. gravity.	
Grains.					
5200	- -	4587,95	,069	1,098	1,167
5300	- -	4687,95	,069	1,096	1,165
5400	- -	4787,95	,069	1,094	1,163
5500	- -	4887,95	,068	1,092	1,160
5600	- -	4987,95	,067	1,091	1,158
5700	- -	5087,95	,067	1,089	1,156
5800	- -	5187,95	,067	1,087	1,154
5900	- -	5287,95	,065	1,086	1,151
6000	- -	5387,95	,064	1,084	1,148
6100	612,05	5487,95	,064	1,082	1,146
6200	- -	5587,95	,063	1,081	1,144
6300	- -	5687,95	,062	1,080	1,142
6400	- -	5787,95	,062	1,078	1,140
6500	- -	5887,95	,061	1,077	1,138
6600	- -	5987,95	,060	1,076	1,136
6700	- -	6087,95	,060	1,074	1,134
6800	- -	6187,95	,060	1,072	1,132
6900	- -	6287,95	,060	1,070	1,130
7000	- -	6387,95	,059	1,069	1,128

With regard to the nitrous acid, I found also I had been a little too precipitate as to the time of examining its density after it had been mixed with water. Hence, making use of some whose specific gravity was 1,474, I allowed the mixtures to rest twelve hours, until it was diluted with twice its weight of water, and the subsequent mixtures six hours at least; by the former process of reasoning, I found the specific gravity of the mere nitrous acid to be 5,530.

Spirit of nitre.	Acid.	Water.	Accrued density.	Mathemat. sp. gravity.	Physical sp. gravity.
900	-	507	-	1,557	1,557
1000	-	607	-	1,474	1,474
1100	-	707	,035	1,413	1,448
1200	-	807	,056	1,367	1,423
1300	-	907	,075	1,329	1,394
1400	-	1007	,095	1,298	1,363
1500	-	1107	,077	1,273	1,350
1600	-	1207	,082	1,251	1,333
1700	-	1307	,082	1,233	1,315
1800	-	1407	,083	1,217	1,300
1900	-	1507	,083	1,204	1,287
2000	-	1607	,096	1,191	1,269
2100	-	1707	,088	1,181	1,254
2200	-	1807	,071	1,176	1,247
2300	-	1907	,068	1,162	1,230
2400	-	2007	,068	1,154	1,222
2500	-	2107	,067	1,147	1,214
2600	-	2207	,065	1,141	1,206
2700	-	2307	,063	1,135	1,198
2800	-	2407	,061	1,129	1,190
2900	-	2507	,058	1,124	1,182
3000	-	2607	,055	1,120	1,175
3100	393	2707	,054	1,116	1,170
3200	-	2807	,054	1,111	1,165
3300	-	2907	,053	1,108	1,161
3400	-	3007	,052	1,104	1,156
3500	-	3107	,050	1,101	1,151
3600	-	3207	,048	1,098	1,146
3700	-	3307	,047	1,095	1,142
3800	-	3407	,045	1,092 or 3	1,137
3900	-	3507	,043	1,089	1,132
4000	-	3607	,040	1,087	1,127
4100	-	3707	,037	1,085	1,122
4200	-	3807	,035	1,083	1,118
4300	-	3907	,034	1,080	1,114
4400	-	4007	,032	1,078	1,110
4500	-	4107	,029	1,077	1,106
4600	-	4207	,027	1,075	1,102
4700	-	4307	,025	1,073	1,098
4800	-	4407	,022	1,072	1,094
4900	-	4507	,020	1,070	1,090
5000	-	4607	,018	1,068	1,086
5100	-	4707	,015	1,067	1,082
5200	-	4807	,012	1,066	1,078
5300	-	4907	,008	1,066	1,074

The foregoing experiments were made at the temperature of between 50 and 60° of FAHRENHEIT; but as it may be suspected, that the density of the above acids is considerably altered at degrees of temperature considerably different, I endeavoured to find the quantity of this alteration, and to calculate what this density would be at 55°, that the quantities of acid and water may thereby be investigated.

To this end I took some dephlogisticated spirit of nitre, and examined its specific gravity at different degrees of heat, and found it as follows :

Deg.	-	Sp. gravity.
at { 30	-	1,4653
46	-	1,4587
86	-	1,4302
120	-	1,4123

Therefore, the total expansion of this spirit of nitre from 30 to 120°, that is, by 90° of heat, was 0,0527; for 1,4650 - 1,4123 = 0,0527, by which we see that the dilatations are nearly proportional to the degrees of heat: for beginning with the first dilatation from 30 to 46°, that is, by 16° of heat  $\div 90 \cdot 0,0527 :: 16 \cdot 0,0093$ ; but in reality these 16° of heat afforded a dilatation equal only to 0,0063; for 1,4650 - 1,4587 = 0,0063; so that the difference betwixt the calculated and observed dilatations is only  $\frac{3}{10000}$ , a difference of no consequence in the present case, and that might arise from the immersion of the cold glass ball filled with mercury in the liquor, it being the solid I use to try the specific gravity of liquids. In the next case the difference is still less; for  $\div 90 \cdot 0,0527 :: 56 \cdot 0,0327$ ; but 56° of heat produced in reality a dilatation of 0,0348 for 1,4650 - 1,4302 = 0,0348, so that the calculation is deficient only in  $\frac{2}{10000}$ .

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I afterwards tried another, and somewhat stronger, spirit of nitre, whose specific gravity was.

	Deg.	-	Sp. gravity.
at {	34	-	1,4750
	49	-	1,4653
	150	-	1,3792

Here also the expansions are nearly proportional to the degrees of heat; for 116° of heat (the difference between 34 and 150) produce an expansion of 0,0958; and 15° of heat (the difference between 34 and 49) produce an expansion of 0,0097, and by calculation 0,0123, which last differs from the truth only by  $\frac{2.6}{100000}$ .

By this experiment we see, that the stronger the spirit of nitre is, the more it is expanded by the same degree of heat: for if the spirit of nitre of the last experiment were expanded in the same proportion as in the first, its dilatation by 116° of heat should be 0,0679, whereas it was found to be 0,0958.

As the dilatation of spirit of nitre is far greater than that of water by the same degree of heat, and as it consists only of acid and water, it clearly follows, that its superior dilatability must be owing to the acid part; and hence, the more acid is contained in a given quantity of spirit of nitre, the greater is its dilatability. We might therefore suppose, that the dilatation of spirit of nitre was intermediate betwixt that of the quantity of water it contains and that of its quantity of acid; but there exists another power also which prevents this simple result, namely, the mutual attraction of the acid and water to each other, which makes them occupy a less space than the sum of their joint volumes, which condensation I have therefore called their *accrued density*. Taking this into the account,



we may consider *the dilatation of spirit of nitre as equal to those of the quantities of water and acid it contains minus the condensation they acquire from their mutual attraction, and this rule holds as to all other heterogeneous compounds.*

To find the quantities of acid and water in spirit of nitre, whose specific gravity was found in degrees of temperature different from those for which the table was constructed, *viz.* 54, 55, or 56° of FAHRENHEIT, the surest method is to find how much that spirit of nitre is expanded or condensed by a greater or lesser degree of heat, and then, by the rule of proportion, find what its density would be at 55°; but if this cannot be done, we shall approach pretty near the truth, if we allow  $\frac{1}{1000}$  for every 15° of heat above or below 55° of FAHRENHEIT, when the specific gravity of spirit is between 1,400 and 1,500; and  $\frac{2}{1000}$  when the specific gravity is between 1,400 and 1,300.

As to oil and spirit of vitriol I found the dilatations exceeding irregular, probably by reason of a white foreign matter, which is more or less suspended or dissolved in it, according to its greater or lesser dilution. This matter I would not separate, as I intended trying the density of this substance in the state in which it is commonly used. In general I found, that 15° of heat cause a difference of about  $\frac{2}{1000}$  in its specific gravity when it exceeds 1,800; and of  $\frac{3}{1000}$  when its specific gravity is between 1,400 and 1,300, its dilatation is greater than that of water, and so much greater as it is stronger.

The dilatations of spirit of salt are very nearly proportional to the degrees of heat, as appears by the following table.

	Deg.		Sp. gravity.	
at	{	33	-	1,1916
		54	-	1,1860
		66	-	1,1820
		128	-	1,1631

Hence  $\frac{6}{1000}$  should be added or subtracted for every 21° above or below 55° in order to reduce it to 55°, the degree for which its proportion of acid and water was calculated. The dilatibility of this acid is much greater than that of water, and even than that of the nitrous acid of the same density.

I now proceed to examine the quantity of pure acids taken up at the point of saturation by the various substances they unite with.

## OF THE MINERAL ALKALI.

That which I made use of was procured from Mr. TURNER, who by a peculiar and ingenious process extracts it in the greatest purity form common salt.

Of this alkali I rendered a portion tolerably caustic in the usual manner, and evaporating 1 oz. of the caustic solution to perfect dryness, I found it to contain 20,25 gr. of solid matter. I was assured, that the watery part alone exhaled during the evaporation, as the quantity of fixed air contained in it was very small, and to dissipate this a much greater heat would be requisite than that which I used. This dry alkali I immediately dissolved in twice its weight of water, and saturating it with dilute vitriolic acid, found it to contain 2,25 gr. of fixed air, that being the weight which the saturated solution

lution wanted of being equal to the joint weights of the water, alkali, and spirit of vitriol employed.

The quantity of mere vitriolic acid necessary to saturate 100 gr. of pure mineral alkali I found to be 60 or 61 gr. the saturated solution, thus formed, being evaporated to perfect dryness weighed 36,5 gr.; but of this weight only 28,38 were alkali and acid, therefore the remainder, that is, 8,12 gr. were water. Hence, 100 gr. of GLAUBER'S salt, perfectly dried, contain 29,12 of mere vitriolic acid, 48,6 of mere alkali, and 22,28 of water; but GLAUBER'S salt crystallized contains a much larger proportion of water; for 100 gr. of these crystals being heated red-hot lost 55 gr. of their weight. This loss I suppose to arise merely from the evaporation of the watery part, and the remaining 45 contained alkali, water, and acid, in the same proportion as the 100 gr. of GLAUBER'S salt, perfectly dried, abovementioned; then these 45 contained 13,19 gr. of vitriolic acid, 21,87 of fixed alkali, and 9,94 of water; consequently 100 gr. of crystallized GLAUBER'S salt contain 13,19 of vitriolic acid, 21,87 of alkali, and 64,94 of water.

I also saturated this alkali with the dephlogisticated nitrous acid, and found that 100 gr. of the alkali took up 57 of the mere nitrous acid in the experiment I most depended on; but this quantity varied in some experiments a few grains, being sometimes 60, and sometimes 63 gr.; so that I conclude the proportion of this acid, taken up by the alkali, is nearly the same as that of the vitriolic acid. Supposing this quantity to be 57 gr. then 100 gr. Cubic nitre, perfectly dry, contain 30 of acid, 52,18 of alkali, and 17,82 of water; but Cubic nitre crystallized contains something more water; for 100 gr. of these crystals lose about 4 by gentle drying; therefore 100 gr.

of

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of the crystallized salt contain 28,8 of acid, 50,09 of alkali,  
and 21,11 of water.

Of mere marine acid, 100 gr. of this alkali required from 63  
to 66 or 67 gr.; perhaps one reason of this variety is, that it is  
exceeding hard to hit the true point of saturation. Allowing it  
to be 66 gr. then 100 gr. of perfectly dry *common salt* contain  
nearly 35 of real acid, 53 of alkali, and 13 of water; but  
100 gr. of the crystallized salt lose 5 by evaporation; then 100  
gr. of these crystals contain 33,3 of acid, 50 of alkali, and  
16,7 of water.

The proportion of fixed air, alkali, and water, in crystal-  
lized mineral alkali, I investigated thus: 200 gr. of these crys-  
tals were dissolved in 240 of water; the solution was saturated  
by such a quantity of spirit of nitre as contained 40 of mere  
nitrous acid; hence I inferred, that these 200 gr. of alkali  
contained 70 of real alkali. The saturated solution weighed  
40 gr. less than the sum of its original weight, and that of the  
spirit of nitre added to it; therefore it lost 40 gr. of fixed air.  
The remainder, therefore, of the original weight of the crys-  
tals must have been water, that is, 90 gr.; consequently 100  
gr. of these crystals contained 35 of alkali, 20 of fixed air,  
and 45 of water.

This proportion is, particularly with regard to the alkali,  
very different from that found by Mr. BERGMAN and LAVOI-  
SIER, which I impute to their having used soda recently crys-  
tallized. Mine had been made some months, and probably  
lost much water and fixed air by evaporation, which altered  
the proportion of the whole. According to the calculation of  
these philosophers 100 gr. of this alkali takes up 80 of fixed  
air.

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The specific gravity of the crystallized mineral alkali weighed in æther I found to be 1,421.

## OF THE VOLATILE ALKALI.

It is not possible by the old chymical methods to find the proportion of the ingredients in volatile alkalies, whether in a liquid or in a concrete state; seeing that, though it may be separated from fixed air, yet it cannot from water, on account of its extreme volatility. Then to find this proportion we must recur to the experiments of Dr. PRIESTLEY, who by his new analysis produced this alkali free from the ærial acid and water in the form of air: and in the third volume of his Observations, p. 294. informs us, that 1<sup>o</sup> measures of alkaline air take up, and are saturated by, 1 measure of fixed air. Let us suppose the measure to contain 100 cubic inches; then 185 cubic inches of alkaline air take up 100 of fixed air; but 185 cubic inches of alkaline air weigh, at a medium, 42,55 gr.; and 100 cubic inches of fixed air weigh 57 gr.; then 100 gr. of pure volatile alkali, free from water, take up 134 of fixed air.

On expelling its ærial acid from a parcel of this alkali in a concrete state, and formed by sublimation, I found 100 gr. of it to contain 53 of fixed air, and therefore, according to the preceding reasoning, 39,47 of real alkali and 7,53 of water *per cent.*

Saturating a solution of this alkali with the vitriolic, nitrous, and marine acids, I found, that 100 gr. of the mere alkali take up 106 of mere vitriolic acid, 115 of the nitrous, and 30 of the marine.

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The specific gravity of the concrete volatile alkali weighed in æther was 1,4076.

The proportion of water in the different ammoniacal salts I have not been able to find, on account of their volatility; but believe it to be very small, as volatile alkali and fixed air crystallize without the help of water, when both are in an aërial state.

## O F C A L C A R E O U S E A R T H.

I first dissolved this earth in the nitrous acid, and found that, after allowing for the loss of fixed air and the quantity of water I formerly mentioned, 100 gr. of the pure earth take up 104 of mere nitrous acid. Instead of dissolving this earth immediately in the vitriolic acid, I precipitated its solution in the nitrous by the gradual addition of the vitriolic, and found that to effect this 91 or 92 gr. only of mere vitriolic acid were required.

100 gr. of this pure earth demand for their solution 112 of mere marine acid. The solution, which is at first colourless, grows greenish on standing. Natural Gypsum varies in its proportion of acid, earth, and water, 100 gr. of it containing from 32 to 34 of acid, and also of earth, and from 26 to 32 of water. The artificial contains 32 of earth, 29,44 of acid, and 38,56 of water; when well dried it loses about 24 of water, and therefore contains 42 of earth, 39 of acid, and 19 of water *per cent.*

100 gr. *nitrous selenite*, carefully dried, contain 33,28 of acid, 32 of earth, and 34,72 of water.

100 gr. *marine selenite*, well dried, so as to lose no part of the acid, contain 42,56 of acid, 38 of earth, and 19,44 of water.

## OF MAGNESIA OR MURIATIC EARTH.

This earth, perfectly dry and free from fixed air, could not be dissolved in any of the acids without heat. In the temperature of the atmosphere even the strongest nitrous acid did not act upon it in twenty-four hours; but in a heat of  $180^{\circ}$  these acids diluted with four or six times their quantity of water attacked it very sensibly; but as much of the acids is dissipated by heat, I could not judge of the exact quantity of acid requisite to dissolve a given quantity of it, any otherwise than by precipitating the solutions by another substance, whose capacity for taking up acids was known. The substance I used was a tolerably caustic vegetable alkali. By this method I found, that 100 gr. of pure magnesia take up 125 gr. of mere vitriolic acid, 132 of the nitrous, and 140 of the marine. None of these solutions reddened vegetable blues; all of them appeared to contain something gelatinous; that in the marine acid became greenish on standing for some time.

100 gr. of perfectly dry Epsom salt contain 45,67 of mere vitriolic acid, 36,54 of pure earth, and 17,83 of water; but 100 gr. of crystallized Epsom lose 48 by drying, and consequently contain 23,75 of acid, 19 of earth, and 57,25 of water. Common Epsom salt contains an excess of acid, for its solution reddens vegetable blues.

100 gr. of nitrous Epsom, well dried, contain 35,64 of acid, 27 of pure earth, and 37,36 of water.

The solution of marine Epsom cannot be tolerably dried without losing much of its acid, together with the water.

The specific gravity of pure muriatic earth is 2,3296.

## OF EARTH OF ALLUM OR ARGILLACEOUS EARTH.

This earth I found to contain about 26 *per cent.* of fixed air, though I had previously kept it red-hot for half an hour: this surpris'd me much, as most writers say it contains scarce any. It dissolv'd in acids with a moderate effervescence until the heat was rais'd to 220°, after which I found the solution lighter than the quantities employ'd in the proportion I mention'd.

100 gr. of this earth (exclusive of the fixed air) require 133 of the *mere* vitriolic acid to dissolve them. This solution I made in a very dilute spirit of vitriol, whose specific gravity was 1,093, in which the proportion of acid to that of water was nearly as 1 to 14. This solution contain'd a slight excess of acid, turning vegetable blues into a brownish red; but it crystalliz'd when cold, and the crystals were of the form of allum; so that I believe this to be nearly the proper proportion of its acid and earth; but there was not water enough to form large crystals. As this solution contain'd an excess of acid, I added more earth to it, but could not prevent its tinging blue paper red, until it form'd an insoluble salt, that is, one that required an exceeding large quantity of water to dissolve it, and while part was thus become insoluble, yet another part would still retain an excess of acid; so that at the same time part would be super-saturat'd with earth, and another with acid, if tinging vegetable blues be a mark of an excess of acidity, which indeed in this case seems dubious.

100 gr. of Allum, perfectly dried, contain 42,74 of acid, 32,14 of earth, and 25,02 of water; but crystalliz'd allum loses 44 *per cent* by desiccation; therefore 100 gr. of it contain 23,94 acid, 18 of earth, and 58,06 of water.



100 gr. of this pure earth take up as far as I can judge 153 of the mere nitrous acid. The solution still reddened vegetable blues; but after the addition of this quantity of pure earth, I think it was, that an insoluble salt came to be formed. The solution, when cold, grew turbid, and could not be wholly dissolved by 500 times its weight of water.

The same quantity of pure earth requires 173,45 of the mere marine acid for its solution; but the solution still reddens vegetable blues. After this an insoluble salt was formed; but the beginning of its formation is difficultly discovered both in this and in the former cases.

The specific gravity of argillaceous earth, containing 25 *per cent.* of fixed air, I found to be 1,9901.

## O F P H L O G I S T O N .

Before I proceed to investigate its proportion in various compounds, and particularly in phlogificated acids, it will be necessary to say something of its nature.

It is allowed on all hands, that fixed air, or the Aërial Acid, as it is more properly called, is capable of existing in two states; the one fixed, concrete, and unelastic, as when it is actually combined with calcareous earth, alkalies, or magnesia; the other, fluid, elastic, and aëriiform, as when it is actually disengaged from all combination. In its concrete and unelastic state it can never be produced single and disengaged from other substances; for the moment it is separated from them, it assumes its aërial and elastic form. The same thing may be said of phlogiston: it can never be produced in a *concrete state*, single and uncombined with other substances; for the instant it

is difengaged from them, it appears in a fluid and elastic form, and is then commonly called *inflammable air*. These different states of the same substance arise, according to the immortal discoveries of Dr. BLACK, from the different portions of elementary fire contained in such substance, and absorbed by it, whilst its sensible heat remains the same, and hence called its *specific fire*. For want of attention to these different states, the very existence of phlogiston as a distinct principle has been frequently called in question, and chemists have been required to exhibit it separate in its fixed state, without recollecting, that neither can fixed air be shewn separate in a concrete state, nor that phlogiston may also be in the same predicament; while others have totally mistaken the nature of inflammable air, and imagined it to be a combination of acid and phlogiston. The reason why fixed air cannot be separated from any substance in a concrete state is, because when it is separated, for instance by means of an acid, there is always a double decomposition, the acid yielding its specific quantity of fire to the concrete fixed air, which then assumes an aërial form, while the fixed air yields the substance it was combined with to the acid. This is so true, that though a solution of lime in the nitrous acid yields a considerable quantity of heat, yet a solution of chalk in that acid scarcely yields any; for all the fire that is set loose, and rendered sensible in the first case, is absorbed by the fixed air in the second case, being precisely that which converts it into an aërial form. The separation of phlogiston from a metallic earth in the form of inflammable air arises from the same cause, the dissolving acid yielding its fire to the phlogiston, which then assumes an aërial form, while the phlogiston yields the metallic earth to the acid. It is true, that much sensible heat is produced on this occasion, for which  
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three substantial reasons may be assigned; first, the proportion of fixed air in a given weight of crude calcareous earth, is much greater than that of phlogiston in any metal, as will hereafter be shewn, it being in the former one-third of the whole, and that of phlogiston in the latter for the most part not even one-sixth. Secondly, much of the phlogiston combines with the acid itself during the solution, and expels part of its specific quantity of fire, as Dr. CRAWFORD has shewn, and as I have since experienced; and this fire must occasion sensible heat. Thirdly, much of the phlogiston, during solution, unites to the surrounding atmosphere, expelling also part of its specific fire, and this also must occasion sensible heat; and hence it is, that metallic solutions *in vacuo* are generally attended with less heat, though with a more violent effervescence than in open air. The solution of metallic calces is not attended with as much heat as that of their respective metals, not only because neither the dissolving acids nor the surrounding air is much phlogisticated; but also because they contain an elastic fluid in a concrete state, which absorbs much of the fire given out by the dissolving acids, as it acquires an aerial state.

The origin and formation of inflammable air being thus explained, I now proceed to shew its identity and homogeneity with phlogiston. By phlogiston is generally understood that principle in combustible bodies on which their inflammability principally depends; that principle to which metals owe their malleability and splendor; that which combined with vitriolic acid forms sulphur; that which diminishes respirable air. Now inflammable air is that very principle which alone is truly inflammable, as Mr. VOLTA has elegantly shewn. In effect, combustible substances are either animal or vegetable,

as horns, hair, greafe, wood, &c.; from all of which Dr. HALES has extracted inflammable air; or charcoal, from which Mr. FONTANA has extracted it, as did Dr. PRIESTLEY from refins, spirit of wine, and æther, in all which it is the only principle that is inflammable, and they are inflammable only in proportion as they yield it; or phosphorus, from whose acid Dr. PRIESTLEY has obtained this air by means of minium, for it was the acid, and not the minium, that contained it, as Dr. PRIESTLEY rightly conjectured, the acid obtained by deliquescence being never thoroughly dephlogificated until heated and vitrified, as Mr. MARGRAAF has shewn; or they are mineral substances, as sulphur, from which inflammable air has been separated by means of fixed alkalies, and, according to Dr. PRIESTLEY, also by means of marine air, or bitumens or bituminous substances, all of which may be made to yield it; or metallic substances, as zinc and regulus of arsenic, both of which are inflammable; but neither of them is so when deprived of its inflammable air: this is, therefore, the true and only principle of inflammability in any substance. I acknowledge that the inflammable air, proceeding from almost all these substances, is exceeding impure; that it contains from some a mixture of aerial acid or of oil, and from all some part of the substance which yields it or expels it, and hence its smell is different, according to the class of the substances from which it is extracted; but it is equally true, that none of these substances contribute to its inflammability; on the contrary, it is so much the less inflammable (that is, requires so much more air to be mixed with it before it flames) as it contains more of these heterogeneous substances. Hence inflammable air of the morasses is never totally consumed\*; and, on the contrary,

\* 15 Roz. 146.

inflammable air, from metals which is the purest of all, is also the most inflammable.

Secondly, Inflammable air is also the principle which reduces metallic earths to a metallic state, and gives them their metallic splendor. This has been proved analytically and synthetically, and therefore may be said to be as completely demonstrated as any thing in natural philosophy: thus Dr. PRIESTLEY has extracted inflammable air from iron and zinc by heat alone; and the iron, thus stripped of its phlogiston, lost its splendor, and was of a black colour, which is that which iron, slightly dephlogisticated, always assumes, as appears by *martial æthiops*: so also zinc and regulus of arsenic, when once inflamed, lose their metallic appearance: so also a mixture of lead and tin inflames in a moderate heat, and then both are converted into a calx destitute of splendor and malleability. On the other hand, if a current of inflammable air, in the act of combustion, be directed on the calces of iron, lead, or mercury, they are immediately revived and restored to their metallic form, as appears by the experiment of Mr. CHAUSSIER\*. The following experiment is still more conclusive: if a polished plate of iron be put into a saturate and dilute solution of copper in the vitriolic or marine acids (I mention these because they are commonly used for the production of inflammable air, though the result is the same when other acids are used), no effervescence will arise, no inflammable air will be caught; but the iron will be dissolved, and the copper precipitated in its metallic form. Here inflammable air must be produced as usual, for the acid quits the copper and dissolves the iron; but this inflammable air instantly loses its aerial form, and unites to the copper, just as fixed air leaves alkalies to unite to lime

\* 10 Roz. 313.

without any effervescence; and by this same inflammable air is the copper evidently reduced, acquiring splendor, malleability, and every other metallic property. But if the solution of copper be not saturated with copper, a small quantity of inflammable air may be caught, as the excess of acid will disengage more of it from the iron than the calx of copper can take up. Inflammable air is then the principle that metallizes metallic earth; and if metals contain only a specific earth and phlogiston, inflammable air certainly contains nothing else but phlogiston. If iron and the arsenical acid be digested together, no inflammable air is produced; but the arsenical acid is, in great measure, converted into white arsenic, as Mr. BERGMAN has observed, and also Mr. SCHEELLE\*; what reason can be assigned why inflammable air is not produced by this as well as by all other acids; but that this metallic acid received it, and was by it reduced to a semi-metallic form, as by pure phlogiston? Yet this acid produces inflammable air, from zinc because zinc gives out more phlogiston than the regulus of arsenic can take up; but it attracts and is metallized by a part of it, and it is only the excess that appears in the form of inflammable air, as Mr. SCHEELLE has remarked. This inflammable air, indeed, is not pure, for it holds some of the regulus in solution; but this portion of regulus does not enter into its composition, as is very evident.

Thirdly, Inflammable air is the substance which, with vitriolic acid, forms sulphur, for it is the very substance which the vitriolic acid separates from metals; and this substance, so separated, when in sufficient quantity, and in proper circumstances, unites to it in such proportion as to form common sulphur. Thus sulphur is formed by distilling concentrated vitriolic acid

\* 2 Nov. Act. Upsal. p. 210. Kon. Vetén. Accad. Handlingar, vol. 36. p. 288.

with

with iron or bismuth, or by distilling tartar vitriolate with regulus of antimony. It is this also that diminishes respirable air, as Dr. PRIESTLEY has clearly shewn in the 5th vol. of his *Observations*, p. 84.; for though in its complete aërial state, after it has absorbed that large quantity of fire requisite to its aërial form, it difficultly and slowly unites to respirable air in the heat of the atmosphere, their points of contact through their difference of density being very small, and there being no substance at hand to receive the large portion of elementary fire they both contain, and of which they must lose a large proportion before they can combine together; yet while inflammable air is (as Dr. PRIESTLEY elegantly expresses it) in its *nascent* state, before it acquires its whole quantity of specific fire, respirable air easily unites to it, and is diminished in proportion to its purity; but if to a mixture of both, igneous particles of sufficient density to be visible be introduced, a degree of heat is excited, which, as it rarifies the dephlogisticated part of respirable air to a greater degree than it can inflammable air\*, brings both into nearer contact, increases their attraction to each other, and both uniting give out their fire, or in other words *inflammate*, when in proper proportion to each other, without any decomposition of either, unless the loss of a great part of their specific fire be called a decomposition, which loss is not usually called a decomposition; for water is never said to be decomposed when it becomes ice, nor metals when they become solid on cooling.

In answer to all this it will be said, that inflammable air undoubtedly contains phlogiston, which produces all the before-mentioned effects; but that the phlogiston it contains is united to some other substance, which some will have to be an acid,

some an earth, and others respirable air. To these hypotheses I shall oppose one general observation, which is, that since inflammable air, when pure, that is, when disengaged from all heterogeneous substances which no way contribute to its inflammability, has always the same properties; it must, if it consists of phlogiston combined with any other substance, be always united to the same specific substance; that is, if this be an acid, it must be always the same species of acid, or if an earth, it must be always the same species of earth; for we find, that substances, which are only *generically* the same, always produce, with any other given substance, compounds whose properties are very different from each other. Thus we see that the different species of alkalis, or earths, or metals, produce with one and the same species of acid compounds essentially different. This is a rule which, as far as I know, admits of no exception: and if we apply it to the abovementioned suppositions it will intirely destroy them; for it is impossible to think, that the phlogiston can in every substance, that produces inflammable air, meet either the same acid, or earth, or any respirable air.

But to be more particular, the following reasons demonstrate that an acid of any sort cannot be the basis of inflammable air. 1<sup>st</sup>. Inflammable air has been, by Dr. PRIESTLEY, separated from metals by mere heat. Now metals contain no acid, except perhaps their dephlogisticated calx, which those eminent chemists, BERGMAN and SCHEELE, suspect to be of an acid nature; but these calces cannot enter into the composition of inflammable air, otherwise the inflammable air of each different metal would have different properties, as already *shewn*: *NOT* indeed are these the acids that have been supposed to enter into the composition of inflammable air; but rather those acids by  
 6 whose



whose means it is extricated. But as this air is extricated from metals, not only by acids, but also by alkalies\*, this supposition must vanish of course.

The same reasons militate with equal strength against the supposition that an earth of any kind enters into the composition of this air; nor is there an instance of any earth rendered permanently fluid by any means, except in sparry air. Besides, if it were a metallic earth, it must necessarily be supposed to be in a metallic state; and how then could it escape the action of all kind of acids? for no acid is capable of decomposing inflammable air. Lastly, respirable air cannot be said to be the basis of inflammable air, unless we suppose that respirable air enters into the composition of metals; for Dr. PRIESTLEY has, by solar heat, extracted inflammable air from them in a vessel full of mercury, into which respirable air had no access, and even *in vacuo*. Besides, respirable air and phlogiston form other compounds very different from inflammable air, *viz.* fixed and phlogisticated airs as will presently be seen.

It may also be fairly urged against all these suppositions, that they are not founded on any direct experiment, nor any known analogy, but merely gratuitous, or at least deduced from experiments inadequate to their support; whereas the opinion that inflammable air is nothing else than phlogiston thrown into a fluid form by elementary fire, is directly founded on that experiment whereby inflammable air is separated from metals by mere solar heat in the most perfect vacuum, just as fixed air united to marble and in a concrete state (in which it is nearly of equal density with gold) is separated from the marble, and thrown into a permanently fluid form by heat alone.

\* Mem. Par. 1776, p. 687.

In favour of the existence of an acid in inflammable air, it has been said, that if this air be passed through water tinged blue by litmus, it reddens instantly. I have seen this frequently happen when inflammable air has been extracted from iron by spirit of vitriol; but if this air be washed, by passing it through lime-water, and then passed through, or agitated in, an infusion of litmus, it will not discolour it in the least: this I have seen done by Mr. FONTANA in June 1779. It has also been said, that inflammable air and alkaline air, mixed together, form a cloud; but this has been fully disproved by Dr. PRIESTLEY, in the fourth volume of his Observations.

That an earth of any kind is essentially requisite to the constitution of inflammable air, seems to me utterly improbable; nor do I know of any experiment from whence it can be inferred. That metallic substances may be held in solution by inflammable air is certain; but it is equally so, that they no way contribute to its inflammability\*, and are quite distinct from it.

But the opinion, that inflammable air consists of respirable air super-saturated with phlogiston, is grounded on very specious arguments drawn from experiments to be found in various part of Dr. PRIESTLEY's works, which deserve so much the more attention as the facts mentioned by that excellent philosopher are not to be questioned. I shall endeavour to state them with accuracy; but shall at the same time accompany them with such remarks as seem to me to invalidate the conclusion that has been drawn from them.

In the first volume of Dr. PRIESTLEY's Observations it appears, that a quantity of strong inflammable air, having been agitated in a glass jar immersed in a trough of water,

\* 2 PRIESTLEY, 268.

the surface of which was exposed to the common atmosphere, after the operation had continued ten minutes near one-fourth of the quantity had disappeared; the remainder became fit for respiration, and yet was weakly inflammable. By further agitation it was diminished half, and then admitted a candle to burn in it though feebly; but, on continuing the agitation a little longer, it came to extinguish a candle. Upon this I shall remark, first, that it clearly follows, from this experiment, that if the external respirable air had no access to the inside of the jar, half nearly of the inflammable air was converted into, or consisted of, respirable air, since such quantity of air was found in it after the operation. Now it is absolutely impossible that either could happen; for inflammable air could not be converted into half nor even one-third or one-fourth of its volume of respirable air, as even one-fourth of respirable air contains more matter than four times its bulk of inflammable air; it is then evident, that the external air must have had access to it. Secondly, I agitated about half a pint of inflammable air, obtained from iron and previously passed through lime-water and kept over mercury, in about twelve times its bulk of water, out of which its air had been boiled in a glass bottle closed with a glass-stopper. The agitation continued at several times at least two hours. A large quantity of the air was indeed absorbed, as appeared by opening the bottle in water; but the remainder appeared, by the nitrous test, as noxious, and was also found to be as inflammable as at first. Even Dr. PRIESTLEY attests, that inflammable air, which had been united to water for one month, was afterwards as inflammable as ever 3 PR. 267.

The true explanation of the first experiment appears, therefore, to be the following: First, Water easily imbibes inflammable air, but does not combine with it; for after it has imbibed

bibed one-fourteenth of it, its taste is no way altered, as Dr. PRIESTLEY has observed. I PR. 196. Water also easily imbibes common air: when, therefore, inflammable air is agitated in water having a communication with the atmosphere, the inflammable air must necessarily be diminished by reason of its absorption, and the part so absorbed immediately escapes out of the water into the atmosphere, as is evident by the smell which is perceived when the quantity of inflammable air is considerable. This escape gives room for the further absorption of the inflammable air which then escapes in the same manner. In the mean time the common air under the jar rises into it, as appears by the direct experiments both of Dr. PRIESTLEY \* and Mr. FONTANA; and hence the air in the jar must appear by the nitrous slightly phlogisticated and respirable; but a further agitation will decompose the common air, as we shall soon see, and then a candle will be extinguished. The same process takes place when inflammable air stands long in water whose surface is exposed to the atmosphere.

Another experiment of the same tendency, but seemingly more decisive, is to be found in the 4th vol. of Dr. PRIESTLEY's Observations, p. 368. There it is related, that a portion of inflammable air, inclosed in a glass tube, hermetically sealed and heated until the glass was softened, stained the glass black, and the tube being opened, the air was found reduced to one-third of its bulk; and this residuum was found to be mere *phlogisticated air*, neither precipitating lime-water, nor being affected by nitrous air, or in the least inflammable. Yet decisive as this experiment appears, a little consideration will shew the absolute impossibility that inflammable air should consist of one-third phlogisticated air and two-thirds phlogiston;

\* I PR. 96. 159. 3 PR. 156. Phil. Transf. 1779, p. 443.

for, in the first place, one Cubic inch of phlogificated air weighs 0,377 of a grain: now let us suppose, that to this phlogificated air is added two-thirds of its bulk of phlogiston; and to make the supposition still stronger, let us also suppose, that phlogiston has no weight; then, by the supposition, this compound of phlogificated air and phlogiston will constitute inflammable air, and amount to a bulk of three Cubic inches, and these three Cubic inches will weigh no more than 0,377 of a grain; but if three Cubic inches of inflammable air weigh 0,377 of a grain, one Cubic inch should weigh 0,105 of a grain, which cannot be; for then inflammable air would be little more than one-third lighter than common air, contrary to all the experiments that have been hitherto made, and particularly those of Mr. CAVENDISH, FONTANA, and Dr. PRIESTLEY himself, which shew it to be about eleven times lighter than common air. Secondly, It is said, that the matter which stained the glass black was the true phlogistic part of inflammable air, and was afterwards separated by means of minium. This then contained no phlogificated air; but is it not certain, that if there had been enough of it, the minium would have been reduced and converted into lead? And might not inflammable air be again separated from that lead, though no phlogificated or common air were at hand to supply its other supposed constituent part? Thirdly, In one of Dr. PRIESTLEY'S experiments the inflammable air, contained in the glass tube which was most heated, was reduced to so small a bubble that no experiment could be made on it: therefore, in this, at least, the quantity of phlogificated air did not amount to one-third, but was quite inconsiderable; the remainder then being taken up by the calx of lead in the glass, was pure mere phlogiston, so that this experiment is a strong proof of my opinion.

Fourthly,

Fourthly, If phlogiston could be decomposed by heat, and then leave a residuum of phlogificated air, amounting to one-third of its bulk, the diminution arising from its inflammation with common or dephlogificated air could never be so great as it is found to be by repeated experiments; for when inflammable and common air are fired in the proportion of eleven of the latter to four of the former, a bulk equal to the whole of the inflammable air, and to one-fifth of the common air, disappears, according to Mr. VOLTA \*, and the diminution is about two-fifths of the whole, or more exactly out of fifteen measures, only 8,8 remain; but if the inflammable air were decomposed, and one-third of it, being phlogificated air, should remain, then not quite one-fifth of the whole would vanish, and the residuum should be 10,54 measures. This evidently proves, that pure inflammable air is never decomposed (unless the loss of its fire be called a decomposition); but in the act of inflammation is totally transferred upon the pure part of respirable air to which it unites. Fifthly, To obtain still a clearer insight into this matter, I intreated Mr. CAVALLO, who is very expert in the management of the blow-pipe, as well as in pneumatic experiments, to repeat this experiment in my laboratory. We accordingly filled a tube 10,5 inches long, and one-fourth of an inch in diameter, with inflammable air from iron received over mercury, and having made the tube red-hot throughout and black, and softened it so far as to endanger the escape of the air, we opened it on mercury. The air was diminished only one-tenth, and inflamed with an explosion as loud as an equal quantity of the same inflammable air that had not been heated.

\* Roz. April 1779, p. 295.

The only question that remains then is, whence the phlogificated air proceeded which Dr. PRIESTLEY mentions to have found? The circumstance of his experiment would furnish a plausible answer; but the doctor has lately informed me, that he believes the air was really inflammable, but being a very small quantity escaped before the flame could be applied.

It seems, therefore, sufficiently proved, that inflammable air purified from the acids or other substances that expel it from its basis, and also from all particles of the body to which it was originally united, such as inflammable air from metals received on mercury, and well washed in lime-water, is one and the same substance with phlogiston, differing only in quantity of fire, inflammable air containing nearly the same quantity of this element as the same bulk of atmospheric air, as Dr. CRAWFORD has found by some late experiments, an account of which will soon be laid before the public. This does not contradict that most important discovery of this ingenious philosopher, that fire and phlogiston repel each other: the meaning of this being only, that the addition of phlogiston to any substance, as to respirable air, dephlogificated acids, metallic calces, expels part of the fire already contained in such substance; and, on the contrary, by the removal of phlogiston from any substance, the quantity of fire absorbed by such substance is increased.

It may appear extraordinary, supposing inflammable air and phlogiston to be the same substance, that inflammable air should mix so easily with water, whereas phlogiston constantly repels and is repelled by it; but this intirely depends on the state of this same substance, which, when fixed and concrete, is called *phlogiston*, and, when rarified and aëriform, *inflammable air*. In this latter state it mixes with water in proportion to its rare-

faction, as it even does in the less dense forms of its concrete state: thus æther is totally absorbed by ten times its weight of water. The animal oil of Dippel mixes intirely with water; so does pure Petrol, and essential oils frequently distilled, and the spiritus rector of plants.

Much more remains to be said of the different states of phlogiston from its most rarefied known state, *viz.* that of inflammable air, to its most condensed state, that in which it is combined with metallic earths, &c. I have already distinguished eight intermediate states each differing from the other by the portion of elementary fire they contain, this quantity being, as far I can judge directly, as the rarefaction of the phlogiston; but these researches are foreign to my present subject. I shall only remark, that phlogiston, in a state perhaps 100 times rarer than inflammable air, and consequently containing much more fire, may possibly constitute the electric fluid.

P. S. Since I wrote the above, I have been honoured with a letter from Dr. PRIESTLEY, in which he informs me, that he has reduced the calces of iron, copper, lead, and tin, merely by melting them in inflammable air by means of a burning glass. A certain quantity of inflammable air was absorbed by each during their reduction; but the unabsorbed part was equally inflammable, so that there was no decomposition; but the remainder was of the same nature as the part absorbed. He also, by the same means, converted nitrous vapour into nitrous air, and the phosphoric acid into phosphorus. And since the communication of the last mentioned experiments, which seem to him also a direct proof of the identity of inflammable air and phlogiston, he has been so obliging as to inform me, that he has revived the calces of metals in *alkaline air* as well as



in *inflammable air*, and also formed a phosphorus; and that he has little doubt but that he shall be able to produce any thing else in which phlogiston is supposed to be concerned. This, he says, agrees with several of his former experiments, especially that in which he produces inflammable air from alkaline air, by means of the electric spark and volatile alkali from iron, superaturated with phlogiston by means of nitrous air, which he has repeatedly done since the publication of his last volume. This observation, he adds, may help to explain some things in the theory of chemistry, especially the affinity which all acids have both with *phlogiston* and with *alkalies*; but, he says, that alkaline air contains something else besides phlogiston; because when this air is used, there is always a residuum of something that is *neither alkaline nor inflammable air*; but he wants more sunshine to complete and extend his experiments on this subject\*.

## OF THE QUANTITY OF PHLOGISTON IN NITROUS AIR.

100 gr. of filings of iron being dissolved in a sufficient quantity of very dilute vitriolic acid produced, with the assistance of heat gradually applied, 155 cubic inches of inflammable air, the barometer at 29,5, and the thermometer between 50 and 60°. Now inflammable air and phlogiston being the same thing, this quantity of inflammable air amounts to 5,42 gr. of phlogiston.

Again, 100 gr. of iron, dissolved in dephlogisticated nitrous acid, in a heat gradually applied and raised to the utmost, afford 83,87 cubic inches of nitrous air. And as this nitrous air con-

\* Since this paper was committed to the press, I find that Mr. PELLETIER has reduced the arsenical acid to a regulus, by merely passing inflammable air through the solution of that acid in twice its weight of water. ROZ. Journ. February 1782.

tains nearly the whole quantity of phlogiston which iron will part with (it being more completely dephlogisticated by this acid than by any other means) it follows, that 83,87 cubic inches of nitrous air contain at least 5,42 gr. of phlogiston; but it may reasonably be thought that the whole quantity of phlogiston which iron will part with is not expelled by the vitriolic acid, and that nitrous acid may expel and take up more of it. To try whether this was really so, I calcined a certain quantity of green vitriol, until its ferruginous basis was quite insipid; I then extracted from 64 gr. of this ochre two cubic inches of nitrous air, consequently 100 gr. of this ochre would give 3,12 cubic inches of nitrous air; and if 83,87 cubic inches of nitrous air contain 5,42 of phlogiston, then 3,12 cubic inches of this air contain 0,2 of a grain of phlogiston; consequently, nitrous acid extracts from 100 gr. of iron two tenths of a grain more phlogiston than the vitriolic acid does; therefore 83,87 cubic inches of nitrous air, containing nearly all the phlogiston which iron gives out, contain 5,62 gr. of phlogiston.

Then 100 cubic inches of nitrous air contain 6,7 gr. of phlogiston, and since 100 cubic inches of nitrous air weigh 39,9 gr. they must also contain 33,2 gr. of nitrous acid.

Also, 100 gr. of nitrous air contain 16,792 of phlogiston, and 83,208 of acid.

When first I made these experiments I imagined, that the nitrous air thus expelled contained all the phlogiston of the metals dissolved in the nitrous acid, as this acid is well known to dephlogisticate metals as perfectly as possible; but I soon observed, as did Dr. PRIESTLEY and Mr. FONTANA, that the greater part of this air is reformed and detained in the solution, the acid and calx having, according to the beautiful remark of Mr. SCHEELLE, a greater attraction to phlogiston than either separately; yet that the  
 calculation

calculation is nearly just, will appear clearly in my next paper, by its coincidence with the quantity of phlogiston discovered in lead by Dr. PRIESTLEY and that which is contained very evidently in regulus of arsenic, silver, and quicksilver.

## OF THE QUANTITY OF PHLOGISTON IN FIXED AIR.

Before I attempt to determine this quantity, it will be necessary to prove that it contains any; and for this purpose minutely to examine its nature and origin.

Dr. PRIESTLEY first discovered that in all processes, wherein phlogiston is disengaged from any substance, as in *combustion, respiration, calcination of metals, putrefaction, decomposition of nitrous air by respirable air, &c.* fixed air is precipitated from the common or dephlogisticated air in which these processes are performed, and that these last airs are diminished both in weight and bulk, and are afterwards less fit, or absolutely unfit, for these processes, according to the quantity of phlogiston that was set loose. These facts are admitted by all, let their systems be what they may. However, Dr. PRIESTLEY thinks he has seen one exception to this general rule; for, he says, that in the combustion of inflammable and common air no fixed air is precipitated, 5 PR. 124. He also seems inclined to admit another exception in the case of the combustion of sulphur.

The questions that here arise are, first, whether the fixed air that appears in these circumstances proceeded from the respirable air or not? Secondly, If it proceeded from the respirable air, whether it pre-existed in that air; or whether it was generated

generated during the process that exhibits it? and if so, what are its constituent parts?

The first question is easily answered; for in such phlogistic processes as are attended with the destruction of the substances that are known to contain fixed air, as those of the animal and vegetable kingdom, the fixed air may be supposed to proceed in many cases, both from the decomposed substance and from the respirable air; and of this sort are the processes of combustion of most animal and vegetable substances, and fermentation; but the fixed air, that appears in such phlogistic processes as are performed on substances that contain no fixed air, must be deemed to proceed from the respirable air singly. And of this case we have four clear instances; the calcination of metals; the decomposition of nitrous air by respirable air; the diminution of common air by the electric spark; and, lastly, its diminution by amalgamation.

And first as to the calcination of metals, Dr. PRIESTLEY has observed, that by this operation respirable air (and only respirable air) is diminished between one-fourth and one-fifth, both in its weight and bulk; but Mr. LAVOISIER has demonstrated, that nothing is lost or escapes through the vessels (as Mr. SCHEELE would have it); for the weight and materials continue undiminished when the operation is performed in close vessels\*. That part, therefore, which the air loses is taken up by the metallic calx, which accordingly is found to gain the very weight which the air loses. Now the air contained in the calx is fixed air; for Mr. LAVOISIER also observed, that by the calcination of lead, by solar heat, over lime-water, the water was rendered slightly turbid †. It is true,

\* Mem. Par. 1774.

† L. LAVOIS. 291.

that Dr. PRIESTLEY, in a similar experiment, did not observe this turbidity; but he accounts for this circumstance very justly, by supposing, that the calx of lead absorbed the fixed air preferably to the lime. And this supposition is not gratuitous; for metallic calces, and particularly those of lead, are known to attract fixed air as strongly as quick lime, or rather more strongly\*: and what sets this matter beyond all doubt, the calces of lead all yield fixed air by heat, and the grey calx of lead, in particular, which was that produced by Dr. PRIESTLEY, in the experiment to which I allude, affords by heat fixed air only. Other calces of lead after fixed air afford also dephlogificated air; but this I shall shew also to have been originally fixed air. If filings of iron be mixed with water in close vessels, they will be converted into rust, and the incumbent air diminished one-fourth, as Mr. LAVOISIER attests †; but Dr. PRIESTLEY has shewn, that rust of iron yields scarce any other than fixed air, which may be expelled out of it by mere heat ‡. Nay, iron alone, exposed to common air over a vessel of water for three months, reduced this air one-fifth; and being exposed to dephlogificated air, over a vessel of mercury, it reduced it one-tenth in nine months §. In all these cases the fixed air could surely come from nothing else but the incumbent respirable air and the phlogiston of the metal.

Secondly, It is well known, that if nitrous air be decomposed by respirable air over lime-water, the lime will be precipitated ||. In this case also, the fixed air must proceed from the

\* VOGEL, § 599. 2 N. Act. Upsal. 240. IX Mem. Scav. Etrang. 544.

† 1 LAVOIS. 192.

‡ 2 PR. 112.

§ 2 PR. 182. 4 PR. 253.

|| 1 PR. 114. 3 PR. 30. 1 PR. 138.

respirable air and the phlogiston of the nitrous air; for it cannot proceed from the nitrous acid, as this acid is not decomposed, but is taken up by the water over which the mixture of both airs is made, as Mr. BEWLY has undeniably proved: and hence it is, that unless a large quantity of lime-water be used so as to contain enough for both the nitrous and aërial acids to act on, there will be no precipitation of lime, as Mr. FONTANA has observed; for the nitrous acid will seize on the lime preferably to the aërial. Dr. PRIESTLEY indeed observed, that if a bladder, filled with nitrous air, be dipped in lime-water, it occasions a precipitation of lime on the surface of the water. I PR. 213. But he elsewhere acknowledges, that this proceeds from the inability of the bladder to confine nitrous air. I PR. 76. and 128, which Mr. BAUME also long ago observed, without knowing any thing more of this air. BAUME *sur l'Æther*, 285. The phlogiston passes through the bladder, and unites to the common air contiguous to it\*. Besides, nitrous air acts on the bladder itself, and extracts fixed air from it. I PR. 214. Hence also, if rain-water carefully boiled, and freed from its own air, be made to absorb a quantity of nitrous air, it will again, on boiling, yield it back as pure as at first; but if common water be made to imbibe nitrous air in the same manner, it will, on boiling, yield also a portion of fixed air. 3 PR. 109. Does not this happen clearly because common water contains atmospheric air, or air somewhat purer, which is converted into fixed air by mixture with the nitrous air? This experiment also shews, that water itself never unites to phlogiston, since it does not take any from nitrous air, where the union of phlogiston to the acid is of the laxest kind.

\* 3 PR. 156.

Thirdly, If the electric spark be taken through common air, this air will be diminished one-fourth, and a solution of lime, if contiguous, will be precipitated, and a solution of turnsole tinged red. I PR. 184. 186. Whence could the fixed air here produced proceed, but from the common air, and the phlogiston of the metallic conductors? This excellent philosopher has even shewn it could proceed from nothing else; for after that air had contributed all it could to that production, that is, was diminished to the utmost, he changed the liquors, but could produce no change in their colour, nor the least sign of fixed air. This experiment has also been repeated in France, and the inside of the glass tube, in which the common air was contained, was moistened with a solution of caustic fixed alkali, and the alkali, after the operation, was found crystallized; but when the tube was exhausted of air, and the experiment repeated, no change whatsoever was found in the alkali. *Essai sur l'Electricité, par Mr. Le Comte DE LA CEFEDE*, vol. I. P. 155.

Fourthly, If lead and mercury be agitated in a phial, partly filled with common air, this air will be diminished one-fourth, and the residuum will be found completely phlogisticated. The diminution will be still greater if the phial contain dephlogisticated air. I PR. 149. The lead is converted into a calx, calcination being the known effect of the amalgamation of the base metals; and this calx absorbed the fixed air produced, for Dr. PRIESTLEY expelled this air from it. I PR. 144.; and hence an amalgama of lead and mercury decrepitates when heated\*. Whence could this fixed air proceed, but from the respirable air? For surely neither lead nor mercury contain any.

\* MALOQUIN. 105.

If the above experiments be attended to, the answer to the second question will be equally obvious. It is certain, that common air does not consist of one-fourth of its bulk of fixed air; for if it did, the remaining three-fourths must be dephlogisticated air: and if so, then the absolute weight of a mixture of three-fourths dephlogisticated air and one-fourth fixed air should coincide at least nearly with the absolute weight of an equal bulk of common air; but in fact it is very far from it: for four cubic inches of common air weighed 1,54 gr.; but a mixture of three cubic inches of dephlogisticated air and one of fixed air weighs 1,83 gr.; neither indeed has so large a portion of fixed air been ever supposed to exist in common air. Besides, if fixed air pre-existed in common air, it might be separated from it by lime-water, at least in some degree. I have mixed one part of fixed air with twenty of dephlogisticated air, and also with twenty of phlogisticated air in close vessels, and these mixtures did not fail to render lime-water turbid. But let common air be agitated in lime-water ever so long in close vessels, not the least cloudiness will appear; nor does quick-lime, in these circumstances, in the least affect common air, as Dr. PRIESTLEY has observed. 2 PR. 184. The spontaneous precipitation of lime-water arises therefore from an accidental diffusion of fixed air through common air, and the slowness of this precipitation shews its quantity to be very small. The inference from the above experiments will be much stronger against the pre-existence of fixed air in respirable air, if, instead of common air, dephlogisticated air be used; for there the diminution is so great, and the quantity of fixed air produced so considerable, that it can by no means be supposed to have pre-existed, its properties being so very opposite to those of dephlogisticated air.



To this it has been answered, first, that fixed air in common air is united to some unknown basis, which attracts it more strongly than quick-lime does; but that it is precipitated from that basis by the phlogiston set loose in phlogistic processes, which is still more strongly attracted by that basis; and, secondly, that the diminution both of the weight and bulk of respirable air in phlogistic processes does not arise intirely from the separation of fixed air, but from some other cause.

But neither of these answers is satisfactory: for the supposition of such a basis is evidently gratuitous, being supported by not one experiment. It is also contrary to analogy, there being no instance of the separation of fixed air, nor of any other acid, from any substance merely by the greater affinity of phlogiston to such substance. It is also insufficient for the purpose for which it was framed; for of dephlogisticated air 97 parts in 100 are reducible to fixed air by phlogistic processes; and can it be imagined, that 97 parts in 100 of it were mere fixed air united to less than three parts of an unknown basis? I say, less than three parts; for, according to the present supposition, this unknown basis took up the phlogiston of the substance that separated the fixed air from it, and yet it, and the whole quantity of phlogiston it took up, amounted but to three parts of an hundred; can it be supposed, that this vast proportion of fixed air would not in the least affect lime-water, as pure dephlogisticated air is known not to do? Can it be supposed, that such an immense quantity of fixed air, combined with any basis, would be so superlatively fitted for all phlogistic processes, while fixed air, in its disengaged state, is totally unfit for them? Besides, this unknown basis, after all, is nothing but phlogisticated air, with which fixed air is incapable of contracting any union; and if its phlogiston be washed away, it is not

found different from common air slightly injured. Accordingly, we find that this conjecture, first advanced by Dr. PRIESTLEY in the infancy of his researches, is now abandoned by him. Vol. V. p. 31. And he now justly thinks, that common air does not contain above  $\frac{1}{52}$  of its bulk of fixed air.

As to the diminution of bulk, it is certain, that the whole of it does not proceed from the separation of fixed air; for though no part of the fixed air should be absorbed, yet since part of the common air is converted into fixed air, there must be a diminution of bulk, since fixed air is specifically heavier than common air, and the bulks are inversely as the specific gravities; but the diminution of *mass* must wholly, and that of bulk must also for the greater part arise from the absorption of fixed air by water, or the substance from which the phlogiston proceeds. I have successively added six measures of nitrous air to two of dephlogificated air from precipitate *per se*, and after each addition transferred the mixture into fresh lime-water, and after each I found the lime precipitated until the whole was reduced to one-tenth nearly, so that nine-tenths of this dephlogificated air was evidently converted into fixed air; and since fixed air did not pre-exist in the dephlogificated air, it was evidently produced by the union of the phlogiston of the nitrous air with the truly dephlogificated part of the dephlogificated air.

Here we see how fixed air is generated in most other phlogistic processes, performed in common air. The phlogiston is attracted by the dephlogificated part of common air, unites to it, expels part of its fire, and so forms fixed air; yet a part of this pure air generally escapes the action of phlogiston, being protected from it by the quantity of phlogificated air which is always found in common air, and which forms about two-thirds of it, in the same manner as gold is protected by silver,

silver, and silver by gold, from the action of their respective menstruums; and this is the reason why, in some phlogistic processes, the diminution is greater than in others; and why the diminution continues to increase slowly for a long time.

Nor is the supposition, that common air consists of two fluids, one phlogisticated and the other dephlogisticated, gratuitous; it is pointed out by several experiments. If a mixture be made of three parts phlogisticated air and one of dephlogisticated air, it will exactly perform the functions of common air; a candle will burn in it, an animal will live in it, just as in common air\*. Besides, common air may in some measure be separated into these constituent parts by lying over pure water; for dephlogisticated air is much more miscible with water than common air, as Mr. FONTANA remarked, *Phil Trans.* 1779, p. 443. and 444 †, and SCHEELE on Fire, § 94. Hence, if common air be suffered to stand some time over pure water, it will be diminished, the purer part being in great measure absorbed by the water, and the remainder will be found to consist of so large a proportion of phlogisticated air that a candle will not burn in it. 1 PR. 158. 4 PR. 353. Mr. SCHEELE again expelled that part which the water had absorbed, and found it dephlogisticated. He also found, that phlogisticated air is not at all absorbed by water. *ibid.*

Hence we see, why the whole of any quantity of common air can never be converted into fixed air; for no part of it will unite with phlogiston, but the dephlogisticated part (which never exceeds one-third of the whole). This Mr. SCHEELE has decisively proved by exposing liver of sulphur to a mixture

\* *Mem. Par.* 1777, p. 191.

† He informed me, that water takes up one-fourteenth of its bulk of dephlogisticated air, and only one-twenty-eighth of common air.

of phlogificated and dephlogificated air; the mixture was diminished in the same proportion as it contained dephlogificated air, and no more. SCHEELE, § 43.

Phlogificated air, therefore, is not the usual product of common phlogistic processes; but the phlogificated residuum that is found after such processes must have pre-existed, as that evidently does which is found after the mixture of nitrous and very pure dephlogificated air, for almost the whole of this last is turned into air which is absorbed by water, and precipitates lime, as we have already seen, so that no part of it is converted into phlogificated air, this being immiscible with water. Now common air is affected by nitrous air just in the same manner, and differs only in degree; therefore the phlogificated air, which is found after its phlogification in the usual processes, was not produced by those operations, but pre-existed.

Phlogificated air consists of fixed air super-saturated with phlogiston, as sulphur does of volatile vitriolic acid super-saturated with phlogiston; and as sulphur is not generally formed when the vitriolic acid unites to phlogiston, but only volatile vitriolic acid, so neither is phlogificated air each time that pure air unites to phlogiston, but rather fixed air, I say *super-saturated*, because it contains such a quantity of phlogiston as to be insoluble in water. Many experiments of Dr. PRIESTLEY clearly point out this composition. Thus that celebrated philosopher has found, that if phlogificated air be agitated in water, out of which its air had been boiled, and whose surface is exposed to the atmosphere, it will be in great measure purified (just as sulphur is decomposed by trituration in water), and if then it be passed through lime-water two or three times, it renders it turbid. 2 PR. 218. Here then the excess of phlogiston, by reason of its repulsion from water, is easily

easily attracted by the dephlogificated part of the common atmosphere, which is immediately imbibed by the water out of which its air had been boiled; the phlogificated air is thereby decomposed and partly turned into fixed air, which makes the lime-water turbid. Part also of the fixed air is decomposed as will presently be seen, and hence the degree of purity which it acquires. Further, if the electric spark be taken in fixed air, three-fourths of it will be rendered insoluble in water, and the whole will probably become so if the operation be long enough continued. I PR. 248. This insoluble residuum Mr. FONTANA found to be phlogificated air; and that, if this phlogificated air be agitated in water (whose surface is exposed to the atmosphere) it will become again common air. *Recherches Physiques*, 77. That is, it will acquire a degree of purity nearly the same as that of common air. This fully confirms all that has been hitherto said concerning these airs; so also, if a mixture of filings of iron and sulphur, made into a paste, be exposed to fixed air, and made to ferment, part of the fixed air will be turned into phlogificated air, 3 PR. 257. Just as in another equally curious experiment he found, that vitriolic air was converted into sulphur by the gradual exhalation of phlogiston from a solution of that air in water, and as it daily happens in the hot baths at Aix la Chapelle. And hence we see, that fixed air, even in its elastic state, is capable of taking an excess of phlogiston, when this last is insensibly separated from any substance, and then becomes phlogificated air. Phlogificated air may also be formed by a rapid and copious affluence of phlogiston, in certain circumstances, as we shall soon see. I should not omit, that phlogificated air, after it has been purified from phlogiston by agitation in water, is again diminishable by phlogistic processes, and that fixed air is precipitated

pitated from it as usual. 2 PR. 219. A circumstance which at that time was thought inexplicable, and which indeed is so, on any other principles but those here laid down, of which it is an immediate consequence.

Having thus far synthetically proved the constituent parts of fixed air to be pure elementary air and phlogiston, I shall now endeavour to do the same by its analysis: and, in the first place, that it contains phlogiston, and even in such quantity as to deserve to be classed among the phlogisticated acids, appears by its action on *black manganese*. This semi-metallic calx, as has been proved by that admirable chemist Mr. SCHEELE, is completely soluble only in phlogisticated acids, and is precipitable from them by fixed alkalies in the form of a white calx. He also found, that this manganese is also soluble in water strongly impregnated with fixed air, and is also precipitable from it in the form of a *white calx*. 35 Mem. Stock. p. 96.

If fixed air be repeatedly dissolved in, and expelled from water, it leaves each time a residuum which is insoluble in water, diminishable by nitrous air, and capable of supporting animal life. Hence it is evidently decomposed, the phlogiston separating from it, and gradually uniting to the common atmosphere by reason of the repulsive power betwixt it and water. Dr. PRIESTLEY indeed found, that a candle would not burn in it; but this arises only from a mixture of a small quantity of fixed air not yet decomposed, of which, according to the experiments of Mr. CAVENDISH, one-ninth is sufficient to extinguish a candle\*.

Again, Mr. ACHARD has converted fixed air into air of nearly the same purity as common air by passing it five or six times through melted nitre. Mem. Berlin. 1778. Mr. CAVALLO

\* 1 PR. 34. 40. 2 PR. 219, 220.

passed it but once through melted nitre, and yet found it considerably meliorated, for it was diminished by nitrous air. In this case the nitrous acid attracted the phlogiston; for it is known to become phlogisticated by the fusion of nitre, so as to be expellable even by the vegetable acids. 2 N. Act. Upf. 171. And aqua regia may be made by mixing nitre with marine acid.

I shall now briefly consider what may be said in opposition to this doctrine.

In the first place it may be difficult to conceive, that the addition of phlogiston should render any substance more soluble in water, as it is known to render most acids less soluble in that liquid; but a little attention will shew, that phlogiston does not always render substances less soluble in water than they were before; for the acid of sugar is less soluble in water than sugar itself, though sugar consists of that acid united to phlogiston. The dephlogisticated marine acid unites more difficultly with water than the same acid does when phlogisticated, as the illustrious BERGMAN has observed\*. Caustic volatile alkali has been decomposed by Mr. SCHEELE, and found to consist of an air insoluble in water, and phlogiston; so that it is rendered soluble in water only by union with phlogiston. It would be foreign to the subject to enter into the reason of these exceptions, but the facts are certain.

Another objection may be drawn from a remarkable experiment to be found in the fifth volume of Dr. PRIESTLEY'S observations, where it is said, that inflammable air and common air being fired by an electric spark over lime-water, the diminution took place all once, and the lime was not precipitated; but as it is equally true, that fixed air is precipitated by other phlogistic processes, this experiment proves only, that in these

\* Anleitung, § 333.

particular circumstances, where a large quantity of phlogiston is suddenly heated and transferred all at once upon the dephlogisticated part of common air, phlogisticated air may be formed as sulphur and volatile acid is formed, when a large quantity of hot phlogiston is united all at once to the vitriolic acid.

Analogous to this is another experiment of Mr. CAVALLO's, where he found, that, by the explosion of gunpowder, a large quantity of phlogisticated air is produced \*; and also another of Dr. PRIESTLEY's, wherein he found, that by firing a mixture of equal parts, sulphur and nitre, only one-twelfth of the air produced was fixed air, the remainder being phlogisticated air. But I own the circumstances of the former experiment are not as yet well known to me, not having been able to repeat it in such a manner as to remove all doubt either of the escape of the air through the cement which fixes the wire that conducts the electric fire, during combustion; or that the small quantity of inflammable air used prevents the fixed from being sensible. It may also happen, that to the production of fixed air it is necessary that the phlogiston be condensed to a certain degree, as it is in common cases; and perhaps, when exceedingly rarified, as it is in inflammable air from metals, it forms some other, as yet unknown, compound. Thus much is certain, that all other inflammable air, fired with the electric spark, produces fixed air; and all other inflammable air is specifically heavier than the metallic, and before inflammation evidently contains no fixed air. Mr. WARTIRE, after burning metallic inflammable air, found a *white powdery substance* (probably a calx) which may have absorbed the fixed air.

However, in the common process of combustion of animal and vegetable substances it is certain, that fixed air is separated

\* CAVALLO ON Air, p. 812.

from



from common air, and that the whole diminution is owing to its production and absorption. Mr. LAVOISIER has set these points in the clearest light. He introduced a lighted candle into a receiver standing on mercury: the air at first expanded by reason of the heat, and the candle was shortly after extinguished; but when all was cold, there was scarcely any diminution. He then introduced, under the receiver, a caustic fixed alkaline liquor: the air was immediately diminished, and the diminution reached nearly one-ninth of the whole. He then introduced a small quantity of vitriolic acid; the alkali immediately effervesced, gave out its fixed air, the mercury re-descended, and the air in the receiver occupied the same space as at first; so that this experiment is perfectly conclusive. He also lighted a candle in dephlogisticated air, and when it was extinguished, introduced a caustic fixed alkaline liquor, and then, and only then, this air was diminished two-thirds, by which it is evident, that two-thirds of it were converted into fixed air; but the remaining third was so far from being phlogisticated air, that a candle burned in it as well as ever, and after it went out half of this air was absorbed by a caustic fixed alkali, and the remainder was still little worse than common air. Mem. Par. 1777, p. 195, &c.

Yet Mr. LAVOISIER thinks, that by the calcination of metals fixed air is not produced; but that the metals absorb the dephlogisticated part of common air, and are thereby converted into a calx. And on this is founded his extraordinary opinion of the non-existence of phlogiston; whereas it is evident, that even mercury affords inflammable air, and consequently contains phlogiston, and that it loses part of this during calcination, and consequently fixed air must be produced, as he himself acknowledges it to be during combustion, by the union of inflam-

mable air and the dephlogisticated part of common air, which after this union is absorbed by the calx. It is true, that the mercurial calx, and also the calces of lead, and many others, yield dephlogisticated air; but then the mercury is always revived, so that it is evident, it retakes the phlogiston from the fixed air, of which nothing then remains but the dephlogisticated part, which accordingly appears in the form of dephlogisticated air. Dr. PRIESTLEY never found the whole of the mercury revived, and accordingly he recovers a little fixed air from the mercurial calx. 2 PR. 217. But Mr. LAVOISIER finds the whole of the mercury revived, and for that reason finds no fixed but all dephlogisticated air; thus their different results are clearly explained, and probably proceed from the different degrees of heat they employed, and the different phlogistication of their acids. The dephlogisticated air that is extracted from *minium* proceeds also from a partial revivification of the lead, which always takes place\*: nor is it wonderful, that this calx should dephlogisticate fixed air, since it dephlogisticates the marine acid also, as Mr. SCHEELÉ has observed †.

To this it will probably be objected, that dephlogisticated air must pre-exist in the *minium*, since it is expelled by the marine acid; but this does not follow; for if manganese be dissolved in the common marine acid which is phlogisticated, and afterwards expelled from it by the vitriolic, it will also be found dephlogisticated.

I shall now proceed to investigate the proportion of phlogiston and elementary or respirable air in fixed air.

Dr. PRIESTLEY, in the fourth volume of his Observations, p. 380. has satisfactorily proved, that nitrous air *parts* with as

\* BEAUME, 7. 1 Pott. Lithog. 29. 3 Dict. Chy. 205.

† KON. Vet. Acad. Handling. vol. XXXV. p. 193.

much phlogiston to common air as an equal bulk of inflammable air does when fired in the same proportion of common air. Now, when inflammable air unites with common air, its whole weight unites to it, as it contains nothing else but pure phlogiston; since, therefore, nitrous air phlogificates common air to the same degree that inflammable air does, it parts with a quantity of phlogiston equal to the weight of a volume of inflammable air similar to that of nitrous air. Now 100 cubic inches of inflammable air weigh 3,5 gr.; therefore, 100 cubic inches of nitrous air part with 3,5 gr. of phlogiston when they communicate their phlogiston to as much common air as will take it up. I say, that nitrous air *parts* with *as much* phlogiston, because it is certain, that it does not part with the *whole* of its phlogiston to common or dephlogificated air, for it contains much more, as already shewn, and, as appears by the red colour, it constantly assumes when mixed with common or dephlogificated air, which colour belongs to the nitrous acid combined with its remaining phlogiston, and not to the fixed air then produced, nor to the phlogificated air remaining, as is very evident. Hence the acid, thus formed, is volatile.

4 PR. 267.

One measure of the purest dephlogificated air and two of nitrous air occupy but  $\frac{3}{5}$ th parts of one measure, as Dr. PRIESTLEY has observed, vol. IV. p. 245. Suppose one measure to contain 100 cubic inches, then the whole very nearly of the nitrous air will disappear, its acid uniting to the water over which the experiment is made, and 97 cubic inches of the dephlogificated air, which is converted into fixed air by its union with the phlogiston of the nitrous air; therefore 97 cubic inches of dephlogificated air take up all the phlogiston which 200 cubic inches of nitrous air will part with; and this we have

have

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have found to be seven grains; therefore, a weight of fixed air equal to that of 97 cubic inches of dephlogificated air and 7 of phlogiston, will contain 7 gr. of phlogiston. Now, 97 cubic inches of dephlogificated air weigh 40,74 gr.; to which, adding 7 gr. we have the whole weight of the fixed air equal 47,74 gr. = 83,755 cubic inches; and consequently 100 cubic inches of fixed air contain 8,357 gr. of phlogiston, and the remainder elementary air.

100 gr. of fixed air contain 14,661 of phlogiston and 85,339 of elementary air; which, when stripped of phlogiston, and impregnated with its proper proportion of elementary fire, becomes again dephlogificated air. Hence also, 100 cubic inches of dephlogificated air are converted into fixed air by 7,2165 gr. of phlogiston, and will be then reduced to the bulk of 86,34 cubic inches.

And reciprocally, 100 cubic inches of fixed air, being decomposed, will afford 115,821 cubic inches of dephlogificated air, and part with 7,2165 gr. of phlogiston, supposing the decomposition to be complete; that is, the dephlogificated air absolutely pure.

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Having read the foregoing account of the nature of fixed air to Dr. PRIESTLEY, I had the satisfaction to find it met with his entire approbation, which he authorized me to mention, notwithstanding what he had advanced to the contrary in his last publication.

## OF THE QUANTITY OF PHLOGISTON IN VITRIOLIC AIR.

The method I pursued was this :

1st, I found the quantity of nitrous air a given weight of copper afforded when dissolved in the dephlogisticated nitrous acid, and by that means how much phlogiston it parts with.

2dly, I found the quantity of copper which a given quantity of the dephlogisticated vitriolic acid could dissolve; and observed, that it could not dissolve the greatest quantity of copper without dephlogisticating a further quantity which it does not dissolve.

3dly, I found how much it dephlogisticates what it thoroughly dissolves, and how much it dephlogisticates what it barely calcines.

4thly, How much inflammable air a given quantity of copper affords when dissolved in the vitriolic acid to the greatest advantage.

5thly, I deduct from the whole quantity of phlogiston expelled by the vitriolic acid the quantity of it contained in the inflammable air; the remainder shews the quantity of it contained in the vitriolic air.

The particulars were as follows :

1st, 100 gr. of copper dissolved in the dephlogisticated nitrous acid afforded me 67,5 cubic inches of nitrous air, which, according to the before mentioned calculation, contain 4,52 gr. of phlogiston.

2dly, 100 gr. of real vitriolic acid take up or dissolve 54,73 of copper, and 100 gr. of copper require about 182,714 gr.  
of

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of real vitriolic acid to dissolve them. Again, 100 gr. of copper, when dissolved in the vitriolic acid, retain only as much phlogiston as is contained in three cubic inches of nitrous air, that is, 0,2 of a grain; therefore, since 100 gr. of copper give out 4,52 of phlogiston, the vitriolic acid strips it of 4,52 - 0,2, that is, 4,32 gr. of phlogiston.

3dly, To dissolve 70 gr. of copper in the vitriolic acid, to the greatest advantage, 20 more must be slightly dephlogisticated; therefore, to dissolve 100 gr. of copper in this acid, 28,6 more must be slightly dephlogisticated. 8 grs. of this slightly dephlogisticated calx afforded 4 cubic inches of nitrous air; therefore, 28,6 would afford 14,3, which contain 0,958 gr. of phlogiston; but 28,6 gr. of copper, before any dephlogistication, contain 1,292 gr. of phlogiston; therefore, they lose by this slight dephlogistication 0,344 of a grain of phlogiston. Hence, when 100 gr. of copper are dissolved in the vitriolic acid, the quantity of phlogiston expelled is  $4,32 + 0,34 = 4,66$  gr.

4thly, The quantity of inflammable air afforded by the most advantageous solution of 100 gr. of copper in the vitriolic acid is 11 cubic inches, which amount to 0,385 of a grain of phlogiston

5thly, The solution of 100 gr. of copper in the vitriolic acid afforded over mercury 75,71 cubic inches of air; but of this only 11 cubic inches were inflammable air, the remainder therefore was vitriolic acid air, amounting to 64,71 cubic inches.

6thly, Then the whole quantity of phlogiston expelled during the solution of 100 gr. of copper in the vitriolic acid is 4,66 gr.; of this inflammable air contains but 0,385 of a grain: the remainder therefore, which consists of 4,275 gr. must be con-

tained in the 64,71 cubic inches of vitriolic air: therefore, 100 cubic inches of vitriolic air contain 6,6 gr. of phlogiston, and 71,2 gr. of acid, and 100 cubic inches of this air weighing 77,8 gr. 100 gr. of this air contain 8,48 gr. of phlogiston and 91,52 of acid.

## OF THE QUANTITY OF PHLOGISTON IN SULPHUR.

This I endeavoured to find by estimating the quantity of fixed air produced during its combustion.

To the top of a glass bell, which was open, I firmly tied and cemented a large bladder, destined to receive the air expanded by combustion, a quantity of which generally escapes when this precaution is not used. Under this bell, which contained about 3000 cubic inches of air, I placed a candle of sulphur, weighing 347 gr.; its wick (which was not consumed) weighed half a grain: it was supported by a very thin concave plate of tin, to prevent the sulphur from flowing over during the combustion, and both were supported by an iron wire, fixed on a shelf in a tub of water. As soon as the sulphur was fired with a very feeble flame, it was covered with the bell, the air being squeezed out of the bladder. The inside of the bell was soon filled with white fumes, so that the flame could not be seen. In an hour after, the fumes thoroughly subsided, and all was cold. The water rose within the bell to a height equal to 87,2 cubic inches; whence I deduce that 87,2 cubic inches of fixed air were produced, which contain 7,287 gr. of phlogiston, which separated from the vitriolic acid, and united to the dephlogisticated part of the common air under the bell.

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The candle of fulphur being weighed, was found to have lost 20,75 gr.; therefore, 20,75 gr. of fulphur contain 7,287 gr. of phlogiston, besides the quantity of phlogiston which remained in the vitriolic air. This air must have amounted to  $20,75 - 7,287 = 13,463$  gr. which contain 1,141 gr. of phlogiston; therefore, the whole quantity of phlogiston in 20,75 gr. of fulphur is 8,428 gr.; therefore, 100 gr. of *fulphur contain 40,61 gr. of phlogiston and 59,39 of vitriolic acid.*

Several attempts have hitherto been made to determine the proportion of the constituent parts of fulphur; but all were evidently defective. The first was that of STAHL, who calculated the quantity of phlogiston from that of the acid remaining after slow combustion; but as much, both of acid and phlogiston, was dissipated, and as the remaining acid was also phlogisticated, and attracted much of the moisture of the air, no conclusion whatever could be drawn from this experiment. The second method was, to form a liver of fulphur, and convert this by a gentle long continued heat into a tartar vitriolate, and then calculate the weight a given quantity of alkali would gain by this operation. This was also devised by STAHL, and followed by BRANDT and NEWMAN, and by it they determined the proportion of phlogiston to that of acid to be nearly as 1 to 16. But during the formation of the liver of fulphur, whether in the moist or dry way, much of the phlogiston and acid is dissipated, as is evident by the vapour and smell that proceed from it, their alkali also contained fixed air, which it lost during the operation, and of which they kept no account, as they were ignorant of its existence; and the tartar vitriol formed by them or sal polycreste retained much undecomposed sulphur, as always happens when it is not strongly heated; so that this method also was very imperfect, however some subsequent



several chemists who made the experiment with more care concluded from it, that sulphur contained one-seventh of phlogiston. EXLEBEN, § 760.

By weighing flowers of sulphur in a perforated brass box in water, I found its specific gravity to be 1,924. It remained in the water a quarter of an hour before any air issued from it, and then some bubbles arose; but when I opened the box, I found the middle part of the flowers quite dry, so that I make no doubt but some air still remained, and that its specific gravity is still greater. Mr. PETIT weighed it in oil, and found its specific gravity 2,344, which I believe to be nearly the truth.

## OF THE QUANTITY OF PHLOGISTON IN MARINE ACID AIR.

8 gr. of copper dissolved in colourless spirit of salt afforded but 4,9 cubic inches of air, when the air was received over water, and this air was inflammable.

8,5 gr. of copper being dissolved in the same quantity of the same spirit of salt, and the air received over mercury, afforded 91,28 cubic inches of air; but of these only 4,9 cubic inches were inflammable air; the remainder, therefore, *viz.* 86,38 were marine air, which weigh 56,49 gr.

Now, as spirit of salt certainly does not dephlogistate copper more than the vitriolic acid does, it follows, that these 4,9 cubic inches of inflammable air, and 86,38 cubic inches of marine air, do not contain more phlogiston than would be separated from the same quantity of copper by the vitriolic acid: and since 100 grains of copper would yield to the vitriolic

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acid 4,32 gr. of phlogiston, 8,5 gr. of copper would yield 0,367 of a grain of phlogiston; this then is the whole quantity extracted by the marine acid, and contained in 91,28 cubic inches of air, and deducting from this the quantity of phlogiston contained in 4,9 cubic inches of inflammable air ( $=0,171$  of a grain), the remainder, *viz.*  $0,367 - 0,171 = 0,196$  is all the phlogiston that can be found in 86,38 cubic inches of marine air. Then 100 cubic inches of marine air can contain but 0,227 nearly of a grain of phlogiston 65,173 of acid.

Hence we see why it acts so feebly on oils, spirit of wine, &c. having a very small affinity to phlogiston; and why it is not dislodged from any basis by uniting with phlogiston, as the vitriolic and nitrous acids are, its affinity to it being inconsiderable.



## AMENDMENT to P. 191. L. 12.

I have lately repeated this experiment, and found that one measure of alkaline air is saturated by less than half of one measure of fixed air, but more than one-third, conformably to Dr. PRIESTLEY's first experiment, p. 293.; by which it appears, that 100 gr. of alkaline air require about 120 of fixed air to saturate them: and hence 100 gr. of concrete volatile alkali contain about 53 of fixed air, 44 of mere volatile alkali, and 3 of water.