XIX. *Sequel to an Essay on the Constitution of the Atmosphere, published in the Philosophical Transactions for* 1826; *with some Account of the Sulphurets of Lime.* *By* JOHN DALTON, *D.C.L., F.R.S., &c.*

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IN an essay of mine on the constitution of the atmosphere, which was printed in the Transactions for 1826, I signified my intention of following it with a sequel of experiments to ascertain if possible which of the two views therein developed was most countenanced by facts. I now proceed to give an account of such investigations relating to this subject as have engaged my attention during a long period of years.

It may be needful to premise certain facts which are, I believe, universally admitted as indisputable; namely, that the atmosphere consists principally of two elastic fluids, azote and oxygen, either mixed by some mechanical law, or otherwise combined by a chemical principle in proportion nearly as four parts of the former to one of the latter in volume; that the two elastic fluids may be obtained separately in a state of purity; that when thus obtained they may be mixed in all possible proportions; and that the aggregate volumes in such cases are just equal to the sum of the two volumes of the ingredients: also, that any body which has a chemical affinity for either of them so as to combine with it in a separate state, will also combine with it in the mixed state.

It is also pretty generally admitted that oxygen and azote are capable of chemical combinations in five or more definite proportions, namely,

2 vol. of azote with 1 vol. of oxygen—forming 2 vol. of nitrous oxide.
1 vol. of azote with 1 vol. of oxygen—forming 2 vol. of nitrous gas.
1 vol. of azote with $1\frac{1}{2}$ vol. of oxygen—forming $1\frac{1}{2}$ vol. of hyponitrous acid.
1 vol. of azote with 2 vol. of oxygen—forming 2 vol. of nitrous acid vapour.
1 vol. of azote with $2\frac{1}{2}$ vol. of oxygen—forming $2\frac{1}{2}$ vol. of nitric acid.

There does not appear to be a doubt of the reality of five combinations, but all chemists are not agreed as to the proportions of the volumes being precisely as above specified, chiefly because no general law has been found to obtain in such gaseous compounds.

These compounds are never formed nor decomposed without manifest chemical agency; they all contain oxygen, but no portion of it can be abstracted from any one of them without some chemical operation; whereas nitrous gas will immediately seize the oxygen from any of the aforementioned mixtures, the same as if it was alone, whatever may be the proportions. Atmospheric air itself, or any artificial mixture of the two gases in the same proportion as common air, is equally affected by nitrous gas and by every other agent.

Waving at present any consideration as to the nature and properties of the above chemical compounds, I shall now proceed to state the means by which the proportions of oxygen and azote in mixtures of these two gases may best be determined. Having been engaged in this investigation occasionally for more than forty years, I may be entitled to give my opinion on this important subject in practical chemistry.

Various methods of analysing common air have been discovered in the last fifty years. I have principally directed my attention to three, namely, (1.) by the use of VOLTA's eudiometer and hydrogen, or (2.) by nitrous gas, or (3.) by quadrisulphuret of lime, to abstract the oxygen from the azote.

First Method, by VOLTA's *Eudiometer.*

Mr. CAVENDISH was one of the first to investigate the changes produced by firing mixtures of hydrogen and common airs in various proportions. (Vid. Philos. Trans., 1784.) The following Table will exhibit a lasting monument of his skill in effecting such an investigation. Many have attempted since to improve the methods of analysis, and have brought out results widely differing from those to be derived from his table; but it is now universally allowed that his results are nearer approximations to the truth than most of those we have seen since.

His method was to take 100 measures of common air and mix them with various proportions of hydrogen, beginning with upwards of 100, and gradually descending till about 20; then, firing each mixture by an electric spark, he marked the diminution of the mixture each time as under.

The following results are extracted from Mr. CAVENDISH's Table, except the last column, "Amendment," which I have attached, for reasons assigned below.

Exp.	Common Air.		Inflammable Air.		Diminution on firing.	Amendment.
1.	100	measures mixed with	124·1	gave	68·6	66·3
2.	100	——	105·5	——	64·2	65·8
3.	100	——	70·6	——	64·7	64·9
4.	100	——	42·3	——	61·2	60·6
5.	100	——	33·1	——	47·6	47·4
6.	100	——	20·6	——	29·4	29·5

In the first three experiments no oxygen was found in the residuary gas; in the fourth a trace of oxygen was found; and in the fifth and sixth, considerable quantities of oxygen were found in the residues.

It is obvious that Mr. CAVENDISH began intentionally with an overdose of hydrogen, probably expecting the diminution to be a constant quantity till the hydrogen became deficient, and then of course the diminution must be lessened; this was not the case exactly; but the reason is easily discovered, and it proves the accuracy of the observations.

Hydrogen gas is rarely obtained quite pure: it frequently holds two or three per cent. of common air, detached from the water through which it bubbles and by other means; this air increases as more water enters the hydrogen bottle, till sometimes it amounts to ten per cent. at the last, as every one knows who has had a due share of experience. Now as Mr. Cavendish does not mention the purity of his hydrogen, we must try it by the means now generally known, as the reported results will guide us in the investigation.

On looking at the column headed "diminution on firing" it is easy to see there is a discrepancy in the first three experiments in that column; if the hydrogen used contained any oxygen the diminution on firing ought to have continually decreased, whereas it was greater in the third than in the second experiment. This it must be allowed is a proof of inaccuracy in one or both of the experiments; but it is no greater error than usually occurs if we trust to a single experiment with any gaseous mixture. The average of two or three experiments on mixtures of the same proportions should be taken. The fourth experiment clearly shows that the hydrogen contained oxygen as well as azote; for a diminution of 61·2 would denote the union of 20·4 oxygen with 40·8 hydrogen; hence there must have been 1·5 common air in the hydrogen. I have formed the column "amendment" by assuming the hydrogen in all the experiments to contain 4½ per cent. common air. If we combine the results of the third and fourth experiments, either by assuming Mr. Cavendish's diminution or that of the amendment, we shall obtain a very good approximation to the quantity of oxygen in atmospheric air, the former experiment giving too great diminution by reason of the excess of hydrogen and that containing some oxygen, and the latter giving too little diminution for want of the requisite quantity of hydrogen; the former will give 20·98 per cent. oxygen, and the latter 20·92 per cent. oxygen in atmospheric air. If any doubt should remain as to Mr. Cavendish's hydrogen containing oxygen, it is removed by the consideration that his first experiment would indicate 22·9 oxygen per cent. in air, which cannot be allowed; and his last experiment that 8·8 oxygen must have combined with 20·6 hydrogen instead of 17·6, which is equally inadmissible.

Since the period 1784 it has been found by various chemists that in mixtures of oxygen and hydrogen, as well as in other similar ones, the electric spark does not always cause an explosion, and when it does a complete combination does not always take place, but that in the residue sometimes portions of both the ingredients may be found. The limitations and restrictions are now pretty generally known; and with regard to the mixtures of common air and hydrogen, I published a letter in the 10th volume of the Annals of Philosophy, (New Series) page 304, in which I showed the limitations found by my own experience to be as under:

Common air and hydrogen in which the oxygen is only $\frac{1}{15}$th, or from six to seven per cent. of the whole mixture, do not explode.

Common air and hydrogen in which the oxygen is only $\frac{1}{14}$th, or seven per cent., explode imperfectly, leaving both oxygen and hydrogen.

Common air and hydrogen in which the oxygen is from $\frac{1}{13}$th to $\frac{1}{6 \cdot 86}$th, or from eight to fourteen or fifteen per cent., fire leaving hydrogen and azote only.

Common air and hydrogen in which the hydrogen is $\frac{1}{3 \cdot 38}$th to $\frac{1}{7}$th, or from fourteen to thirty per cent., fire and leave oxygen and azote only.

Common air and hydrogen in which the hydrogen is $\frac{1}{8}$th to $\frac{1}{14}$th, or from eight to twelve per cent., fire imperfectly, and leave oxygen, hydrogen, and azote.

Common air and hydrogen in which the hydrogen is $\frac{1}{15}$th or less than seven per cent., do not explode.

It should be observed that when one of the gases is so far deficient as not to allow of an explosion by a single spark, the effect may be obtained by a current of sparks for a longer or shorter period, accompanied by the requisite diminution of volume. In such instances where the effect is produced only by a current of sparks it may be proper here to suggest the reason. When mixtures explode perfectly but feebly, we see the flame, lighted by the spark, to run down the eudiometer till it reaches the water; when they explode still more feebly, the flame runs perhaps half way down the tube and is extinguished before it reaches the water. There scarcely can be a doubt that the extinction must be occasioned by the cooling effect of the eudiometer and of the intermixture of the mass of air which has to be heated by the feeble flame. Another spark in its passage will re-alight the flame, to suffer a quicker extinction, and so on till at length the combustion is complete. This reason will also explain the excessively slow combustion of azote by the electric spark, as ascertained by Mr. CAVENDISH, and as I have found by repeated experience. Query, might not this experiment succeed better by heating the eudiometer?

From what we have stated it must be obvious that in order to secure the complete abstraction of either oxygen or hydrogen from mixtures by VOLTA's eudiometer, we should avoid too near an approach to the limitations we have pointed out; or if that cannot be, we should carefully examine the residue for both gases. The best test for very small portions of oxygen is undoubtedly nitrous gas; for somewhat larger portions of oxygen or hydrogen, additions of those gases might be made so as to bring the mixtures into proportions capable of being exploded.

Second Method, by Nitrous Gas.

The nitrous gas eudiometer is of singular utility on many occasions. No other can exceed it in accuracy when mixtures contain very little, as one or two per cent. of oxygen; or on the other hand when nearly the whole of the gas is oxygen. But when the mixture of gases contains from twenty to eighty per cent. of oxygen, as in the case of common air, it is not the best when great exactness is required. The reason is well known; when oxygen and nitrous gas combine, the combination is not like that of oxygen and hydrogen, in uniform proportion. We may take one third of the diminution for oxygen, when mixed over water; but this can be considered only as a first approximation. One hundred parts of oxygen may combine with 130 or 360 parts, or any intermediate quantity of nitrous gas, according to circumstances. When only 1 or 2 per cent. of oxygen are expected I put in 5 or 10 per cent. of nitrous gas, and take one third of the diminution for oxygen. When the oxygen (freed from carbonic acid) is judged to be 90 or more per cent. pure, I put 100 parts of nitrous gas of known purity (say 98 ±) to 100 of the oxygen, and mark the diminution; I next put in 40 nitrous and mark the diminution, and so on, till there is manifestly a slight portion of nitrous left; then this is to be removed by a small portion of oxygen; finally, knowing the quantity of azote which was in the nitrous gas, the rest must have been introduced by the oxygen.

In this way I find a perfect agreement, whether the nitrous test or the hydrogen is used; but with common air the residue is so enlarged with azote as to render the measuring of it not so accurate.

Third Method, by Quadrisulphuret of Lime.

Quadrisulphuret of lime is an excellent test for oxygen, and may be applied to common air or to other mixtures of which oxygen is a part, up to the purest oxygen. As this and other similar compounds seem to me destined to act an important part in chemical operations, it may not be improper here to give some account of their origin and their constitution, as far as actual experiments have demonstrated.

The alkalies and the alkaline earths that are soluble in water have been long known to combine with sulphur, both in the dry and humid way. In the last century they went by the name of *hepar sulphuris*, or liver of sulphur, from their colour.

SCHEELE was the first to use the quadrisulphuret of lime to abstract oxygen from atmospheric air. LAVOISIER also made use of the same article; but it was to DE MARTI of Spain we owe the most successful attempt with the quadrisulphuret of lime to abstract the oxygen from atmospheric air. His memoir, printed in 1795, and reprinted in the Journal de Physique, vol. lii., 1801, may still be read with interest. All the *hepars*, when dissolved in water, have usually gone by the harsh name of *hydroguretted sulphurets* in our English works of chemistry since the commencement of the present century.

In 1798 BERTHOLLET published an essay on the nature and combinations of sulphuretted hydrogen, with reference to the part it acts in the sulphurets. PROUST afterwards controverted some of BERTHOLLET's opinions in the 59th volume of the Journal de Physique, 1804. GAY-LUSSAC, in the 78th volume of the Annales de Chimie, 1811, gives some important results on the mutual action of metallic oxides and alkaline hydrosulphurets; he finds amongst other results that no *sulphates* are formed, that water is formed, that sulphites or sulphuretted sulphites, and often metallic sulphurets are formed; and that consequently it is not possible to obtain the simple metallic bases of hydrosulphurets by means of hydrosulphurets of their oxides;

and that when a sulphuret is dissolved in water, no sulphate is ever formed, as is commonly imagined, but sulphites and sulphuretted sulphites. Some proofs are afterwards given[*]. VAUQUELIN, in the 6th volume of the Annales de Chimie et de Physique, 1817, presents us with a laboured series of experiments on the alkaline sulphurets, the chief object of which is to ascertain the state of the alkali in the sulphuret, whether it is that of a metal or of an oxide. After many experiments on the sulphurets of potash, soda, and lime in the dry way, and one on sulphuret of lime in the humid way, the author sums up, and notwithstanding his leaning to the opinion that the alkalies exist in sulphurets in the state of *metals*, he is obliged at last to acknowledge "that it is probable, *but not yet demonstrated*, that in all the sulphurets formed by means of the alkaline oxides by a red heat, these last lose their oxygen, and are united to sulphur in the metallic state, as is the case with the other metals." GAY-LUSSAC, in the sequel of the same volume, page 322, in a memoir, animadverts on the before-cited paragraph; and allowing that sulphuric acid is formed when a sulphuret of potash made by a red heat is dissolved in water, he contends, according to a suggestion of BERTHOLLET, that the acid is formed in the instant of solution from the reciprocal action of the sulphuret and the water, rather than from the oxygen of the potash and sulphur. This opinion is countenanced by several combinations of a similar nature, which he has adduced, and which are worth the attention of chemists.

Without adverting at present to my own experiments, I may observe that Sir JOHN HERSCHEL, in an essay in the first volume of the Edinburgh Philosophical Journal, 1819, was the first writer who published an atomic view of the class of salts called sulphuretted sulphites, or hyposulphites, that accorded with what I had long entertained and demonstrated by reiterated and decisive experiments[†]. In the above-mentioned essay he showed clearly that the hyposulphurous acid is composed of two atoms of sulphur and two of oxygen, which united to one atom of base, as potash or lime, compose an atom of a hyposulphite. The formation of those of lime, potash, soda, barytes, and some metallic oxides is more particularly explained. A saturated solution of hyposulphite of lime at 50° he found to be 1·30 specific gravity[‡].

In the 14th volume of the Annales de Chimie et de Physique, GAY-LUSSAC has given the principal results of HERSCHEL's essays on the hyposulphurous acid with some judicious remarks, but he leaves the subject as one requiring further investigation.

In 1822 BERZELIUS published a memoir on the alkaline sulphurets. The results of his experiments seemed to him confirmatory of the previous notion of VAUQUELIN. Those experiments were on the sulphurets of potash and lime made in the dry way; he made only one on lime, which agreed very well with the theory; but this very

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[*] See also vol. lxxxv. p. 199.

[†] See New System of Chemical Philosophy, vol. ii. Preface, and p. 105.

[‡] Dr. THOMSON, in a paper on the compounds of chromium in the Transactions of the Royal Society for 1826, disputes the accuracy of this constitution of hyposulphurous acid. I have never had any doubt concerning it since 1815.

delicate experiment was not enough to establish so important a law of combination, and I do not find that any one besides has obtained the same result*.

Though I am not prepared to deny that sulphurets of potassium and calcium can be obtained by the process of BERZELIUS, I am quite satisfied that sulphurets of potash and lime, &c. may be easily procured in the dry way: of that of lime I have had numberless instances. As the compounds of sulphur and the alkaline earths have been very little subjected to investigation by chemists in general, we find great vacancy in the accounts given of them by the modern compilers of chemical books. For this reason I shall introduce here a few of the results I have obtained in a long series of experiments on this branch of chemical inquiry.

Sulphuret of Lime, in the dry way.

In 1806 I formed, for the first time, the protosulphuret of lime by heating 50 grains of fallen lime with 50 sulphur in a covered crucible not quite air-tight, so that the escape and combustion of the excess of sulphur might be allowed; when raised to a red heat an addition was made to the weight of the lime; by repeating the dose of the sulphur and heating, a further addition was made to the weight; but repeating the operation a third time seldom made any further addition. The weight of the compound was 65 grains; it was a white powder with a tinge of yellow, not caustic, but bitter to the taste.

In 1809 I examined this powder more minutely, and found it was best made by mixing equal weights of pure hydrate of lime and flowers of sulphur, putting the mixture into a covered crucible and heating it slowly to red; when the escape of the sulphur fumes ceases, cool the contents, and again mix them with the same weight of sulphur as in the first operation, and again heat it as above; at last it will be found that 32 parts of hydrate of lime = 24 lime have combined with 14 of sulphur, or one atom to one†. In the work referred to I have stated that pounded lime and sulphur scarcely form any union by this process, and carbonate of lime and sulphur still less. An ingenious pupil of mine, Mr. WILLIAM BARNETT WATSON of Bolton, has succeeded in uniting lime and sulphur by heat; instead of taking pounded lime, which has a harsh gritty feel, he takes hydrate of lime, and expels the water by a red heat continued till 32 parts of hydrate are reduced to 24; this is a fine soft powder; when 24 parts of this pure and finely divided lime freed from water are well mixed with 24 parts of sulphur and heated red in a covered crucible, a partial combination takes place, and an increase of weight to the lime; this operation is to be repeated till the additional weight becomes 14 grains, after which no further addition can be effected. Mr. WATSON found it require several repetitions. I have since found it may be effected by two or three only. This sulphuret is not used in eudiometry.

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[*] Annals of Philosophy, 1822.

[†] See New System of Chemical Philosophy, vol. ii. pages 99 and 102.

Quadrisulphuret of Lime, in the humid way.

When sulphur and hydrate of lime in almost any proportions are boiled together in water, quadrisulphuret of lime is formed and dissolved in the water; the solution is of a deep yellow colour, and has a very bitter taste. I have not seen in any author the proportion that ought to be used, nor the quantity and specific gravity of the liquid solutions. These are subjects which have engaged my attention. If lime is in excess, the liquid consists of *lime water* holding in solution quadrisulphuret of lime. If sulphur is in excess, the liquid consists of *water* holding in solution quadrisulphuret of lime. I have long known that the economical proportions to be used are 32 parts of dry hydrate of lime by weight with 56 of sulphur, that is, one atom of lime with four atoms of sulphur. If more lime than that above be used, it will be found prevalent in the residue; if more sulphur, then the redundant sulphur will be found in the residue. A few ounces of the mixed ingredients may be gently boiled in an iron pan for an hour or more, stirring the liquor occasionally, and covering the pan with a lid to prevent the too free admission of atmospheric air. Or, in order to prevent the action of oxygen on the liquid, a flask may be substituted for the pan; the materials may be put into the flask nearly filled with water, and the flask loosely corked may be immersed in a pan of boiling water so as to be almost covered by the water. The liquor to be preserved should be kept in green glass bottles nearly full, and having ground stoppers. After the boiled liquor has cooled and the sediment subsided, the clear liquor may be decanted; if it be strong or deep coloured the sediment may be washed with a little water, and another quantity of the liquor obtained of inferior strength. The sediment may be dried if necessary, and subjected to analysis, as I have mostly done. The quantity and specific gravity of the clear liquors should then be ascertained.

The first quadrisulphuret of lime I made was in 1804; it was very weak, since it only absorbed one fourth of its bulk of oxygen gas; the next that was made took its bulk of oxygen. The next, made in 1806, took 2½ times its bulk of oxygen. In these no account was taken of quantities or residues of lime and sulphur. After this I saw the necessity of investigating, (1.) the quantities of lime and sulphur mixed; (2.) the quantity and specific gravity of the liquid obtained; and (3.) the quantity and proportion of the materials left in the residue, in order that the rationale of the changes effected might be explained. From 1806 to the present time (1837) I have made no quadrisulphuret of lime without attending to all those particulars. In this period I have made it 23 times, six of which were in flasks, and the rest in iron pans covered as mentioned above; the difference of the two methods I found to be very little; it consisted chiefly in traces of sulphuret of iron being found in the residues when pans were used.

A few trials of the various liquids obtained soon furnished me with a formula for ascertaining the quantities of sulphur and lime in a liquid of given specific gravity;

namely, multiply the three leading decimals in the specific gravity of the liquid by 13, and the product will give the aggregate weight in grains of sulphur and lime in 1000 water grain measures of the liquid; of this aggregate $\frac{9}{13}$th will be sulphur, and $\frac{4}{13}$th lime.

With regard to the residue after boiling and its analysis, it is obvious the residue must consist chiefly of sulphur and lime, which for want of due continuance of the ebullition have escaped combination; and there may be some impurities in the sulphur, or the hydrate of lime may not be free from carbonate, &c.; but when the residue is comparatively small no material disturbance of proportions in the quadrisulphuret can take place. If the residue be chiefly sulphur, its quantity may be approximated by ignition; but if lime is in excess, it may be estimated by the quantity of muriatic acid required to saturate it.

The following Table exhibits a selection of the principal varieties in the proportions of ingredients and products obtained so as to illustrate the foregoing statements.

Table of Proportions in Quadrisulphuret of Lime.

	Quantities of hydrate of lime and sulphur mixed.	Proportions of lime and sulphur.	Quantity of liquor obtained in water grain measures, and quantities of lime and sulphur in it.	Measures of oxygen required to saturate 100 liquid.	Quantity of residue when dried.
	Hydrate. Sulphur.	Lime. Sulph.			
1	120 = 90 lime + 210	4 : 9⅓	3100 of 1·056 containing 70 lime + 156 sulph.	900	56 = 16 lime + 40 sulph.
2	50 = 37½ lime + 50*	4 : 5⅓	2200 of 1·0240 containing 21 lime + 47 sulph.	400	20 = 12 lime + 4 sulph. + loss.
3	150 = 112½ lime + 200	4 : 7+	1450 of 1·146 containing 85 lime + 190 sulph.	2350	†20 = 7 lime + 13 sulph.
4	96 = 72 lime + 168 sulph.‡	4 : 9⅓	2800 of 1·056 containing 63 lime + 141 sulph.	900 §	34 = 9 lime + 25 sulph.
5	35 = 26 lime + 140 sulph.	4 : 21·6	1600 of 1·037 containing 23·7 lime + 53·3 sulph.	600 §	83 all sulph.

On the Quantity of Oxygen in the Atmosphere.

Since the commencement of the present century it has been ascertained beyond dispute that the chief constituents of the atmosphere, oxygen gas and azotic gas, are in the same proportion in all countries and at all times, except when influenced by local circumstances; namely, 21 per cent. of volume of oxygen, and 79 per cent. of azote, neglecting fractions: other elements are found in the atmosphere, but they are comparatively insignificant in quantity, namely aqueous vapour, carbonic acid, &c. The experiments have generally been made on air collected at the surface of the earth; and it may be remembered that I have endeavoured to prove in various essays that the diffusion of gases one amongst another as well as in *vacuo*, is owing to the repulsive powers peculiar to the particles of each particular gas, otherwise we

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* Boiled in a flask loosely corked.

† Lost some of the ingredients by boiling over; hence a deficiency.

‡ Boiled in a flask with great care.

§ The oxygen was determined by especial care in these two cases.

should never have the feeble efforts of carbonic acid and aqueous vapour diffusing those elements against the immense pressure of the atmosphere. The principle I contend for has, I believe, obtained general assent; but I apprehend few have been aware of the consequences. If we suppose a carbonic acid atmosphere of 15 inches of mercury pressure and a hydrogen atmosphere of the same pressure, together constituting a mixture of the two amounting to 30 inches of pressure, were to surround the earth, I think no one would hazard a conjecture that these two would be found in equal proportions at every elevation in the atmosphere; yet a similar supposition seems prevalent with regard to our present atmosphere of oxygen and azote. It has been an object of investigation with me for many years to find how the fact stands in this respect; that is, whether the oxygen is more abundant relatively in the lower strata of the atmosphere than in the higher, as it ought to be in a stagnant column; or whether the constant agitation of the atmosphere and the predominant mechanical power of the azotic part of it do not prevent that equilibrium which a stagnant mixture of aerial fluids of different specific gravities would effect. From the experiments about to be related, I have reason to believe that the higher regions of the atmosphere are somewhat less abundant in the proportion of oxygen than the lower, though the reverse might be expected from the enormous consumption of oxygen by daily processes on the surface of the earth, when we know of no proportionate consumption of azote. It appears, however, that the disproportion of the two elements at different elevations is by no means so great as theory requires; and therefore we must conclude the unceasing agitation of the atmosphere by currents and countercurrents is sufficient to maintain an almost uniform mixture at the different elevations to which we have access.

The subject is one involving an important principle. I have kept it continually in view for the last forty years, and have made innumerable experiments with a view to its elucidation. As the value of such experiments depends much upon a thorough acquaintance with the nature of the operations and the several sources of error to which they are liable, it may be needful to point out certain particulars, which, as long experience has taught me, require attention in order to secure a due approximation to accuracy. I allude more particularly to the use of VOLTA's eudiometer as applied to determine the proportions and quantities of oxygen and hydrogen gases.

1. Hydrogen gas procured over water is sure to contain some common air, whether the water has been previously boiled or not; it arises out of the water and may amount to 1 or 2 per cent.; the same observation applies to oxygen gas; the proportion of oxygen and azote is usually that in common air nearly. When a phial of hydrogen gas, by long keeping or by accident, has acquired a portion of common air, and then stood some weeks after, the oxygen seems to diminish, either by slow combustion or by absorption in the water, and so leaves the azote and oxygen in another proportion to that of common air. Before using such hydrogen the oxygen in it should be tested by nitrous gas, and the percentage of hydrogen by oxygen gas.

It is best not to rely too much upon hydrogen taken from a bottle half filled with water.

2. Oxygen gas, and others, will show carbonic acid by sending them up through a narrow eudiometer tube filled with lime-water, provided the acid gas amounts to $\frac{1}{2}$ per cent. of the original; but it does not show any carbonic acid in this way in atmospheric air, though the acid is always present to the amount perhaps of $\frac{1}{1000}$th part. The proportion of pure oxygen in any sample containing from 90 to 100 per cent. of that gas, may be found either by hydrogen gas or nitrous gas; and if great accuracy is required, I recommend testing it both ways, as has already been mentioned under the head nitrous gas.

3. The gradual deterioration of oxygen, hydrogen, nitrous gas, common air, &c., when by use the phial becames $\frac{1}{4}$, $\frac{1}{2}$, or $\frac{3}{4}$ filled with trough water, is a circumstance by no means to be overlooked. The entrance of water that has been sometime stagnant in the cistern, though preserved carefully from any material impurities, always affects the remaining air, though the phial be well corked and immersed in a cup of water. The cause is obvious to those acquainted with the laws that regulate the absorption of gases by water. The common air in the water (the quantity of which varies much as to the oxygen part) is continually either making its escape into the incumbent air of the phial, or this last air is entering the water, so that the degree of purity is continually changing in a small degree. This renders it necessary to test the actual state of this gas after it has been some time in the phial, before we recommence the use of it. A phial of air may be pure at first, and only 90 per cent. at its conclusion. I have known samples of common air kept in bottles at first containing 21 per cent. of oxygen, and after some months a small residue was found to contain only 19 per cent.

4. It may not be improper here to relate some unpublished results which I formerly obtained when experimenting on subjects here discussed. In my memoranda for 1816, I find that I took water well boiled (supposed $\frac{1}{4}$ of an hour or more) and then poured it gently into a Florence flask, filling it up into the narrowest part of the neck, and left it so, exposed to the atmosphere for three days without any agitation. At the end of this, 2700 grains of water imbibed 49 grain measures of atmospheric air by agitation, which is about $\frac{4}{5}$ of a full share; hence $\frac{1}{5}$ of a full share must have been, both the air that was left in after boiling, and that acquired from the atmosphere in three days by absorption from the small exposed surface.

Water boiled in a kettle for three or four minutes, then suddenly cooled and transferred without agitation into a bottle containing 2700 grains, and then agitated with atmospheric air, imbibed 32 measures, which are about half a charge; whence it may be inferred that water boiled for three or four minutes loses about half of its air.

I boiled a kettle full of water for a quarter of an hour; let it stand a day or two to cool, then transferred it carefully by a siphon into a cylindric jar of 8 inches diameter and 10 inches deep; afterwards drew off daily by a siphon 2700 grain measures from the middle or near the bottom of the jar, and charged it with air to the full by agitation. The bottle of water imbibed

The first day . . .	16 measures.	
The second day . .	15 measures.	
The third day . .	12 measures.	
The fourth day . .	10 measures.	
The fifth day . . .	10 measures.	
The sixth day . .	9 measures.	
The seventh day. .	4 measures.	The water taken near the surface.
The eighth day . .	7 measures.	These portions taken up consisted nearly one half of oxygen.
The ninth day . .	9 measures.	
The tenth day . .	7 measures.	
The fifteenth day .	2 or 3 measures.	

From these experiments it would appear that by boiling water briskly for three or four minutes, about half of the atmospheric air previously in the water escapes along with the steam. But it requires much longer boiling and keeping the atmospheric air as much as possible from the surface of the water to get the rest of the air expelled. It is never all expelled by boiling, except in the construction of a good water hammer. Any one air not chemically combined with water is easily and effectually expelled from it by repeatedly agitating the water with another kind of air.

It also appears that water deprived of its atmospheric air, if kept at rest, acquires the air again slowly, and more so if the surface exposed is small. But if violent agitation of the water, so as to mix the atmospheric air and it intimately together, be used, the full impregnation is effected in one or two minutes, as I have elsewhere shown.

Trough waters being mentioned above (3.) it may be well to explain some of the circumstances affecting it. The waters I use for the chemical trough is *rain-water;* it is preferable to pump water by its freedom from carbonic acid and earthy salts; it is slightly coloured at first when drawn from the cistern, but it soon becomes clarified by standing: my trough contains about nine gallons when in work. I take great care to put nothing in it which can materially affect its purity; small portions of lime water and of some iron and other salts are the chief impurities which are admitted; no sulphurets or hydrosulphurets are allowed to enter, and very little of either acids or alkalies. I examine the state of the water occasionally; lately, after it had been more than half a year in the trough, though not very frequently used, I had the curiosity to examine its state before the trough was emptied. The water was neutral by the colour test; it contained about 50 grains of saline matter in the gallon; it was transparent, but slightly milky; prussiate of potash gave sensible blue; oxalate of ammonia, muriate of barytes, and carbonate of soda produced a white precipitate. The taste was like that of earthy pump water. It had its full share of azotic gas, but rather less than half of its share of oxygen gas; that is, it had about 4 or 5 cubic inches of azote in the gallon, and only 1 cubic inch of oxygen.

In the following train of experiments on the oxygen in the atmosphere I have mostly used from 50 to 70 measures of hydrogen for 100 air, unless otherwise mentioned. Possibly this may not be thought the best proportion for securing the complete abstraction of the oxygen. The limits are, 100 air with 42 of hydrogen for the minimum, and 100 air with 170 hydrogen for the maximum. In the former case the hydrogen is barely sufficient for the oxygen; in the latter case the oxygen is barely enough to admit of a complete combustion, being only $\frac{1}{13}$th of the mixture. Perhaps the best proportion would be 100 air to 100 hydrogen to ensure complete combustion, because it is about the mean of the two extremes; but it must be considered that if the hydrogen should contain even a very small portion of oxygen, the whole of it in 100 measures would be included in the atmospheric oxygen, so that in practice it would probably be safest to use a mean between 40 and 100 of hydrogen. I have mostly endeavoured to keep between 50 and 70 of hydrogen for 100 air.

Experiments on the Quantity of Oxygen in Atmospheric Air.

Air from the Summit of Helvellyn[*], July 14, 1824.

A phial, containing about half a pint, was filled with water at a clear rivulet on the ascent; this was emptied at the summit and well corked; the cork was drawn at the foot of the mountain in a trough of clear running water, when a quantity of water was found to enter corresponding to the increased pressure of the atmosphere. The phial was then corked and inverted in a cup of water, and the air analysed a week afterwards.

Average of four experiments on this air with hydrogen, about 50 to 100 air, gave	20·70 oxygen per cent.
Average of four experiments of the common air taken in Manchester at the time of the analysis, and with same phial of hydrogen and same proportion, gave	20·88 oxygen per cent.
Average of seven experiments on Helvellyn air made a day afterwards, gave	20·58 oxygen per cent.
Average of seven experiments on air from an open place in the town next day with same hydrogen, gave	21·1 oxygen per cent.
Average of eight experiments on the country air three miles from Manchester, July 29, with same phial of hydrogen, which now manifested a very slight trace of oxygen, gave	21 oxygen per cent.

1824, November 23.—Barometer 28 inches, very low. Apprehending that this

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[*] This mountain, situate at the head of Ullswater, separates Cumberland from Westmoreland; its height above the sea, which lies to the S.W., and from which it is distant about 20 miles, is upwards of 3000 feet; it is surrounded by other mountains, mostly of less elevation.

circumstance, attended by rain and a high wind S.E., might have some influence on the proportions of the atmosphere, I made the following experiments.

Average of six experiments gave 20·75 oxygen per cent.

When the remainder of this air had been kept five months in the bottle, it then yielded on an average of three experiments 20·67 oxygen per cent.

1825, January 8.—Barometer 30·94, extremely high, after a week of calm weather. Filled a bottle with air from the town.

Average of four experiments with two parts air and one hydrogen gave 21·12 oxygen per cent.

The remainder of this air, kept till August same year, gave 21·1 oxygen per cent.

June 8.—Average of four experiments from air in the town gave 20·97 oxygen per cent.; barometer 29·90.

June 10.—Air from a field near the town, barometer being 30·30, thermometer 70°, wind S.W.; sunny and sultry. Two parts of the air with one of pure hydrogen being mixed, the average of six experiments gave 20·58 oxygen per cent.

June 14.—Mixed some pure azotic gas with oxygen gas, which was marked 90 per cent. pure, in such proportions as to make a mixture of 21 per cent. oxygen. On trial with hydrogen the mixture gave, first experiment 21 + oxygen per cent.; the second experiment 20·9 oxygen per cent.

November 3.—Air in the town, barometer 28·76, thermometer 46°, rainy, with S.W. wind. Average of ten experiments gave 20·6 oxygen per cent.

Air from the Summit of Snowdon, 3570 feet above the sea, taken by John Blackwall, Esq., May 14, 1826, at 7 p.m.; wind N.E. light, barometer 26·20, thermometer 42°.

May 28.—Average of ten experiments gave 20·65 per cent. oxygen.

Country air three miles from Manchester, analysed the same day, average of six experiments gave 20·8 per cent. oxygen.

Again, Snowdon air in six experiments gave 20·66 oxygen per cent.; but the bottle being now half full of water, I did not examine the rest.

Another bottle of air was taken at the summit on another occasion, May 18, by the same gentleman; wind S.W., light.

May 25.—Analysed; average of six experiments gave 20·59 oxygen per cent.

Country air near Manchester at same time gave average 20·7 per cent.

A second bottle of air from Snowdon, taken at the same time, May 18, gave on an average of four experiments 20·9 oxygen per cent.

Air from the town at the same time, on an average of five experiments, gave 21·04 oxygen per cent.

1826, July, Air from the Summit of Helvellyn.

Average of ten experiments gave 20·63 oxygen per cent.

Average of the town air found at same time was 20·73 oxygen per cent.

Air taken in an Aerial Voyage over Cheshire.

Mr. Grafton was so good as to procure me a bottle of air taken in an aerial voyage over Cheshire with Mr. Green, June 26, 1827; height 9600 feet above the sea*. The air was transferred into two phials.

First Phial.

June 27.—	Average of seven experiments of balloon air gave	20·7 oxygen per cent.
	Average of seven experiments on town air gave .	20·83
July 2.—	Average of eight experiments of balloon air gave	20·2†
	Average of eight experiments on town air gave .	20·8

The second phial of balloon air was carefully preserved, the phial being filled and having a ground stopper. It was analysed.

1828, May 28.—	Average of three experiments balloon air gave	20·70 oxygen per cent.
	Average of three experiments town air gave .	20·80
Aug. 5.—	Average of thirteen experiments, being the whole of the balloon air, gave	20·52
	Average of thirteen experiments on town air gave	20·92

On the last-mentioned day I received a bottle of air from the summit of Snowdon through the care and attention of my friend and pupil Mr. John Hall. It was corked and well sealed with wax; when opened under water a due portion of that fluid entered.

The average of the first two experiments gave 20·44 oxygen per cent.

The rest of the air after these two experiments was divided into two portions, and entered into two phials for examination. These were analysed a week or two afterwards.

Average of five experiments with first phial gave 20·25 oxygen per cent.

Average of four experiments, which emptied the first phial, gave 19·98 oxygen per cent.

Average of seven experiments of second phial gave 20·3 oxygen per cent.; and a considerable portion was left.

Average of the town air was during these experiments nearly 21 oxygen per cent.

I am not aware of any cause why this air was so much inferior in oxygen to that on former occasions.

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[*] Height found as under:

Capacity of bottle	10·47 ounces.
On drawing the cork under water there entered . .	2·77 ounces.
Left . . .	7·7 ounces of air.

Also height of barometer and thermometer below given.

[†] The whole air in the first phial was spent in these fifteen experiments. The deterioration of the air in the first phial, by being kept half full of trough water for five days, is remarkable.

1831, July 4.—Helvellyn air brought down from the summit by me; wind S.W., with rain and fog.

1. July 21.—Mixed two ounce measures of this air with one of hydrogen, so as to make six separate and successive explosions; the hydrogen had $\frac{4}{10}$ths of a grain measure per cent. of oxygen, and this is allowed for in the corrected results. These results on the average gave 20·57 oxygen per cent.; the highest was 20·68, and the lowest was 20·43.

The residues of the six explosions were collected, and found to have 5 per cent. of hydrogen and 1 in 120 of oxygen.

2. Mixed *equal volumes* of this Helvellyn air and the same bottle of hydrogen used above, and fired the mixture in successive portions. The average of six experiments gave 20·8 per cent. of oxygen. No oxygen was found in the residue.

By comparing the results of 1 and 2, it would seem that more oxygen is reduced from common air by firing equal volumes of common air and hydrogen than by firing one volume of common air with half a volume of hydrogen.

August 23.—Mixed 100 measures of town air and 120 of new pure hydrogen; this fired gave 21·5 oxygen per cent.; there was no oxygen in the residue. This would seem to point out $\frac{1}{240}$th of oxygen in the hydrogen, yet nitrous gas scarcely manifested so much.

1832, July 26.—Mr. GREEN, jun., and Mr. JOHN TAYLOR of the Manchester gas works, ascended in a balloon from Manchester after 6 P.M., a fine, clear, calm evening, barometer being 30 inches, thermometer 65°; the balloon took a south direction, and landed in Cheshire about fourteen miles off. Mr. TAYLOR took a bottle of air when at the highest elevation, when the barometer stood at 16·8 inches, thermometer 55°; whence the altitude must have been about 15,000 feet.

Capacity of the bottle = 2406 grains of water.

On opening it under water in temp. 64° there entered 884 grains of water.

The air was soon after its reception on the 27th transferred into two small phials for examination.

The first phial was mixed with 60 per cent. of hydrogen, and fired in five portions; it yielded 20·59 oxygen per cent.

The second phial, mixed in like proportion, gave 20·65 oxygen per cent.

Air from the town the next day, fired with the same phial of hydrogen as the preceding, gave 20·95 on the average of five experiments.

Air from Switzerland, &c.

In the autumn of 1835 I was favoured with three samples of air taken in elevated situations in Switzerland by my friend W. D. CREWDSON, jun. Esq., of Kendal. Each of these was taken in a two ounce phial by pouring out the contained water and corking the phial immediately, leaving only a drop or two of water within. The cork was then well closed with sealing-wax. No. 1 was taken on the *Mer de Glace*, August 21, estimated at the height of 6000 feet above the sea; the second on the pass of the *Simplon*, August 29, at the height of 6174 feet above the sea; and the third on the *Wengern Alp* on the 15th September, at the height of 6230 feet. These airs were analysed in October with the following results.

Mer de Glace.—	Average of four first experiments	20·2	oxygen per cent.
	Average of four last experiments	19·4	oxygen per cent.
Simplon.—	Average of four first experiments	19·98	oxygen per cent.
	Average of four last experiments	19·53	oxygen per cent.
Wengern Alp.—	Average of four first experiments	20·45	oxygen per cent.
	Average of four last experiments	20·11	oxygen per cent.

It may not be amiss to subjoin a few experiments on air in close chambers, where a number of people have been congregated for two hours, the air being taken at the moment of breaking up.

1802, March 6.—Got a 20-ounce phial filled at the close of a congregation of 500 people assembled for two hours with 50 candles burning; the air completely neutralized 150 grains of lime water, but took very little more; this accords nearly with 1 per cent. of carbonic acid gas. The oxygen was not examined.

1824, November 28.—Examined the air at the close of an ordinary congregation, perhaps 200 people, retained for two hours.

Average of five experiments gave the oxygen 20·42 per cent.

1826, March 16.—Examined the air from a crowded congregation after two hours' confinement, but some doors open.

Average of four experiments gave the oxygen 20·23 per cent.

There was a very slight appearance of carbonic acid each time a charge was passed up through lime water, a phenomenon never observed in ordinary atmospheric air.

The general conclusions, it seems to me, to be drawn from these experiments are, that the proportion of oxygen to azote in the atmosphere on the surface of the earth is not precisely the same at all places and times; and that in elevated regions the proportion of oxygen to azote is somewhat less than at the surface of the earth, but not nearly so much so as the theory of mixed gases would require; and that the reason for this last must be found in the incessant agitation in the atmosphere from winds and other causes.

June 6, 1837.