

XVI. *On the action of finely divided Platinum on Gaseous Mixtures, and its Application to their Analysis.* By WILLIAM HENRY, M. D. F. R. S.

Read June 17, 1824.

SEVERAL years have elapsed since the President of the Royal Society, in the further prosecution of those Researches on Flame, which had already led him to the most important practical results, discovered some new and curious phenomena in the combustion of mixed gases, by means of fine wires of platinum introduced into them at a temperature below ignition. A wire of this sort being heated much below the point of visible redness, and immersed in a mixture of coal gas and oxygen gas in due proportions, immediately became white hot, and continued to glow until all that was inflammable in the mixture was consumed. The wire, repeatedly taken out of the mixture and suffered to cool below the point of redness, instantly recovered its temperature on being again plunged into the mixed gases. The same phenomena were produced in mixtures of oxygen with olefiant gas, with carbonic oxide, with cyanogen, and with hydrogen; and in the last case there was an evident production of water. When the wire was very fine, and the gases had been mixed in explosive proportions, the heat of the wire became sufficiently intense to cause them to detonate. In mixtures, which were non-explosive from the redundancy of one or other gas, the combination of their bases went on silently, and the

same chemical compounds were formed as by their rapid combustion.*

Facts analogous to these were announced, in the autumn of last year, by Professor DOBEREINER of Jena, with this additional and striking circumstance, that when platinum in a spongy form is introduced into an explosive mixture of oxygen and hydrogen, the metal, even though its temperature had not been previously raised, immediately glows, and causes the union of the two gases to take place, sometimes silently, at others with detonation. It is remarkable, however, that platinum in this form, though so active on mixtures of oxygen and hydrogen, produces no effect, at common temperatures, on mixtures of oxygen with those compound gases, which were found by Sir HUMPHRY DAVY to be so readily acted upon by the heated wire.† Carbonic oxide appears, indeed, from the statement of M. M. DULONG and THENARD,‡ to be capable of uniting with oxygen at the temperature of the atmosphere, by means of the sponge; but though this is in strictness true, yet the combination, in all the experiments I have made, has been extremely slow, and the due diminution of volume has not been completed till several days have elapsed. On mixtures of olefiant gas, of carburetted hydrogen, or of cyanogen, with oxygen, the sponge does not, by any duration of contact, exert the smallest action at common temperatures.

It was this inefficiency of the platinum sponge on the compounds of charcoal and hydrogen in mixture with oxygen,

* Philosophical Transactions, 1817, p. 77.

† DOBEREINER in *Ann. de Chim. et de Phys.* XXIV—XCVI.

‡ Ditto. XXIII. 442.

while it acts so remarkably on common hydrogen, and also, though slowly, on carbonic oxide, that suggested to me the possibility of solving, by its means, some interesting problems in gaseous analysis. I hoped, more especially, to be able to separate from each other the gases constituting certain mixtures to the compositions of which approximations only had been hitherto made, by comparing the phenomena and results of their combustion, with those which ought to ensue, supposing such mixtures to consist of certain hypothetical proportions of known gases. It might, for instance, be expected, that from a mixture of hydrogen and carburetted hydrogen with oxygen, the platinum sponge would cause the removal of the hydrogen, leaving the carburetted hydrogen unaltered. To ascertain this, and a variety of similar facts, I made artificial mixtures of the combustible gases in known volumes; and submitted them, mixed with oxygen, sometimes to contact with the sponge, and sometimes with the balls made of clay and platinum, described by Professor DOBEREINER.*

* The proportions which I used, but which perhaps are not of much importance, were two parts of fine china clay, and three parts of spongy platinum mixed with water into a paste, which was moulded into small spherules, about the size of peas. The sponge, best adapted to the purpose of acting on mixed gasses, is obtained by using a little pressure to the ammonia-muriate, after putting it into the crucible. If too light and porous, the sponge is apt to absorb mercury by being repeatedly passed through it, and to become amalgamated. In order that the balls or sponge might be removed after their full action, they were fastened to pieces of platinum wire.

SECTION I.

ON THE ACTION OF FINELY DIVIDED PLATINUM ON GASEOUS MIXTURES AT COMMON TEMPERATURES.

I. *Mixtures of Hydrogen and Olefiant Gases with Oxygen.*

When to equal volumes of olefiant gas, and an explosive mixture (which is to be understood, whenever it is so named, as consisting of two volumes of hydrogen and one of oxygen gases) one of the platinum balls, recently heated by the blow-pipe, and allowed to cool during eight or ten seconds, is introduced through mercury, a rapid diminution of volume takes place; the whole of the hydrogen and oxygen gases is condensed; but the olefiant gas is either not at all, or very little acted upon. In a few experiments, when the tube was narrow, and the quantity of mixed gases small, the olefiant gas escaped combustion entirely; but, in general, an eighth or tenth of it was converted into water and carbonic acid. It is difficult, however, to state the precise proportion of any gas which, when added to an explosive mixture, renders the latter insensible to the action of the balls or sponge; for much depends on their temperature when introduced into the gaseous mixture, the diameter of the containing vessel, and other circumstances, which, in comparing different gases, should be so regulated as to be equal in every case.

When the proportions of the gases are changed, so that the explosive mixture exceeds in volume the olefiant gas, there is a more decided action upon the latter, manifested by an increased production of carbonic acid. Thus, for example, the explosive mixture being to the olefiant as $2\frac{1}{2}$ to 1,

about one-fourth of the olefiant gas was consumed ; and by increasing the proportion of the explosive mixture, the olefiant gas was still more acted upon. On using oxygen sufficient to saturate both the hydrogen and the olefiant gases, the ball acted much more rapidly ; in several instances it became red hot ; all the hydrogen was consumed ; and the whole of the olefiant gas was changed into water and carbonic acid. In this case the use of the sponge is inadmissible, as it kindles the gases, and occasions their detonation.

II. *Mixtures of Hydrogen and Carburetted Hydrogen Gases with Oxygen.*

When carburetted hydrogen, procured from stagnant water, was added to an explosive mixture, in various proportions between equal volumes, and ten of the former to one of the latter, the action of the hydrogen and oxygen on each other took place as usual, on admitting one of the balls. When, reversing the proportion, the explosive mixture was made to exceed the carburetted hydrogen, but not more than four or five times, the latter gas was entirely unchanged. With a larger proportion of the explosive mixture carbonic acid was always found to have been produced ; but still the carburetted hydrogen was very imperfectly consumed, and fully three-fourths of it were generally found to have escaped unburned.

When, to a mixture of hydrogen and carburetted hydrogen, oxygen enough was added to saturate both gases, the effect of the sponge was found to vary with the proportion of the simple hydrogen. In several cases, where the hydrogen did not exceed the carburetted hydrogen more than four times, the latter gas remained unchanged ; when in

larger proportion, there was a decided action upon the carburetted hydrogen. But it was much more easy to regulate the action of the balls upon such a mixture so as to act upon the hydrogen and oxygen only, than in the case of olefiant gas, which, under similar circumstances, is always more largely converted into water and carbonic acid.

III. *Mixtures of Hydrogen and Carbonic Oxide with Oxygen.*

The addition of one volume of carbonic oxide to two volumes of an explosive mixture produces a distinct effect in suspending the action of the platinum balls, and even of the spongy metal itself. The action of the gases upon each other still, however, goes on slowly, even when the carbonic oxide exceeds the explosive mixture in volume; and after the lapse of a few days, the oxygen is found to have disappeared, and to have partly formed water, and partly carbonic acid. I made numerous experiments to ascertain whether the oxygen, under these circumstances of slow combustion, is divided between the carbonic oxide and the hydrogen, in proportions corresponding to the volumes of those two gases. The combustible gases being in equal volumes, and the oxygen sufficient to saturate only one of them, it was found that the oxygen, which had united with the carbonic oxide, was to that which had combined with the hydrogen, as about 5 to 1 in volume. Increasing the carbonic oxide, a still larger proportion of oxygen was expended in forming carbonic acid. On the contrary, when the hydrogen was increased, a greater proportional quantity of oxygen went to the formation of water. But it was remarkable, that when the hydrogen was made to exceed the carbonic oxide four or five times, less

oxygen in the whole was consumed than before ; the activity of the carbonic oxide appearing to have been diminished, without a corresponding increase in that of the hydrogen.

In cases, where the proportion of the carbonic oxide to the explosive mixture was intentionally so limited, that the platinum ball was capable of immediately acting upon the latter, the carbonic oxide was always in part changed into carbonic acid, the more abundantly as its volume was exceeded by that of the explosive mixture. Increasing the oxygen, so that it was adequate to saturate both gases, and causing the hydrogen to exceed the carbonic acid in volume, a speedy action was always exerted by the ball, and the whole of the combustible gases was silently converted into water and carbonic acid. The introduction of the platinum sponge into such a mixture was almost always found to produce detonation.

IV. Mixtures of Hydrogen and Cyanogen with Oxygen.

When one of the platinum balls, after being recently heated, is introduced into cyanogen and explosive mixture in equal volumes, no apparent action takes place. With half a volume of cyanogen there is a slight diminution ; and as we reduce the proportion of that gas, the action of the elements of the explosive mixture on each other becomes more and more distinct. There is not, however, as with carbonic oxide, any production of carbonic acid ; but in the course of a few minutes the inside of the tube becomes coated with a brownish substance, soluble in water, and communicating to it the same colour ; having a smell resembling that of a burnt animal substance ; and yielding ammonia on the addition of a drop or two of liquid potash. It was produced in too small a

quantity to enable me to submit it to a more minute examination; but its characters appeared to resemble those of a product, obtained by M. GAY LUSSAC, by mixing cyanogen with ammoniacal gas.*

If oxygen be added to a mixture of hydrogen and cyanogen, in quantity sufficient to saturate both the gases, it is still necessary, in order that an immediate effect should be produced by the sponge, that the hydrogen should exceed the cyanogen in volume. A decided action then takes place; an immediate absorption ensues; fumes of nitrous acid vapour appear, which act on the surface of the mercury; and, after removing the nitrous acid by a drop or two of water, and transferring the gas into a dry tube, carbonic acid is found to have been produced, equivalent in volume to double that of the cyanogen.

V. *Effect of adding various other Gases to an Explosive Mixture of Hydrogen and Oxygen.*

It had been already ascertained by Professor DOBEREINER, that one volume of oxygen, diluted with 99 volumes of nitrogen, is still sensible, when mixed with a due proportion of hydrogen, to the action of the sponge.† Carbonic acid, also, even I find when it exceeds the explosive mixture ten times, retards only in a slight degree the energy of the sponge. Oxygen, hydrogen, and nitrous oxide gases, when employed

* Annales de Chimie, XCV. 196.

† In analyzing atmospheric air by adding hydrogen to it, and acting on the mixture by a platinum ball, I have generally obtained a diminution indicating more than 21 per cent. of oxygen. This I find to be owing to the absorption of a small quantity of nitrogen by the ball, especially when, after being heated, it has been rapidly passed hot through the mercury.

to dilute an explosive mixture, are equally inefficient in preventing the mutual action of its ingredients. Ammonia may be added in ten times the volume of the explosive mixture, and muriatic acid gas in six times its volume, with no other effect than that of rendering the action of the sponge less speedy.

VI. *Mixtures of Carbonic Oxide and Carburetted Hydrogen with Oxygen.*

When mixtures of these gases are exposed to the sponge, the carburetted hydrogen seems to stand entirely neutral. The carbonic oxide is converted into carbonic acid, in the same gradual manner as if it had been mixed with oxygen only, and the carburetted hydrogen remains unaltered.

VII. *Mixtures of Hydrogen, Carburetted Hydrogen, and Carbonic Oxide with Oxygen.*

In mixtures of these gases, it is of little consequence whether the oxygen be sufficient for the hydrogen and carbonic oxide only, or be adequate to the saturation of all three. The circumstance, which has the greatest influence on the results of exposing such mixtures to the sponge, is the proportion which the simple hydrogen bears to the other gases, and especially to the carbonic oxide ; for in order that there may be any immediate action, the former should exceed the latter in volume. In that case the hydrogen is converted into water, and the carbonic oxide into carbonic acid ; but the carburetted hydrogen, unless the excess of hydrogen be very considerable, remains unaltered. If the proportion of hydrogen be so small, that no immediate action is excited by the sponge,

the ingredients of the mixture nevertheless act slowly upon each other ; and after a few days, the whole of the hydrogen and carbonic oxide are found to have united with oxygen, and the carburetted hydrogen to remain of its original volume.

VIII. *Mixtures of Hydrogen, Carbonic Oxide, and Olefiant Gases with Oxygen.*

When the oxygen, in a mixture of these gases, is sufficient to saturate the two first only, and the proportion of hydrogen is so adjusted that the action of the sponge is not very energetic, the hydrogen and carbonic oxide only are acted upon ; but if the diminution of volume, which the sponge produces, be rapid and considerable, part of the olefiant gas is converted into water and carbonic acid. This effect on olefiant gas takes place still more readily, if the oxygen present be adequate to the saturation of all three combustible gases.

It is remarkable, that if to a mixture of hydrogen, carbonic oxide, and oxygen, in such proportions that the sponge would act rapidly in producing combination, olefiant gas be added, the action of the gases on each other is suspended. Thus 20 measures of carbonic oxide, 31 of hydrogen, and 28 of oxygen, were instantly acted upon by the sponge ; but the addition of 20 measures of olefiant gas to a similar mixture entirely suspended its efficiency. By standing fourteen days, rather more than half the carbonic oxide was acidified, and about one-twelfth of the hydrogen was changed into water, but the olefiant gas remained unaltered.

IX. Mixtures of Hydrogen, Carbonic Oxide, Carburetted Hydrogen, and Olefiant Gases with Oxygen.

In mixtures of these four gases with oxygen, it was found, by varying the proportion of hydrogen, that hydrogen and carbonic oxide are most easily acted upon ; then olefiant gas ; and carburetted hydrogen with the greatest difficulty. When the action of the sponge was moderate, only the hydrogen and carbonic oxide were consumed, or at most the olefiant gas was but partially acted upon. Adding more hydrogen, so as to occasion a more rapid diminution, the olefiant gas also was burned ; but the carburetted hydrogen always escaped combustion, unless the hydrogen were in such proportion that the ball or sponge became red hot.

From the facts which have been stated, it appears that when the compound combustible gases mixed with each other, with hydrogen, and with oxygen, are exposed to the platinum balls or sponge, the several gases are not acted upon with equal facility ; but that carbonic oxide is most disposed to unite with oxygen ; then olefiant gas ; and lastly, carburetted hydrogen. By due regulation of the proportion of hydrogen, it is possible to change the whole of the carbonic oxide into carbonic acid, without acting on the olefiant gas or carburetted hydrogen. With respect indeed to olefiant gas, this exclusion is attended with some difficulty, and it is generally more or less converted into carbonic acid and water. But it is easy, when olefiant gas is absent, so to regulate the proportion of hydrogen, that the carbonic oxide may be entirely acidified, and the whole of the carburetted hydrogen be left unaltered. This will generally be found to have been

accomplished, when the platinum ball has occasioned a diminution of the mixture, at about the same rate as atmospheric air is diminished by nitrous gas, when the former is admitted to the latter in a narrow tube.

SECTION II.

ON THE EFFECT OF FINELY DIVIDED PLATINUM ON GASEOUS MIXTURES AT INCREASED TEMPERATURES.

The effect of varying the proportion of free hydrogen to the compound combustible gases, on the degree of action which is excited by the platinum sponge, will perhaps admit of being explained, by examining the facts that have been stated, in connection with the degrees of combustibility of the compound gases under ordinary circumstances. The precise degree of temperature at which any one of them burns is not known, on account of the imperfection of our present methods of measuring high degrees of heat. It has been ascertained, however, by Sir HUMPHRY DAVY,* that at a heat between that of boiling mercury, and that which renders glass luminous in the dark, hydrogen and oxygen gases unite silently, and without any light being evolved; that carbonic oxide is as inflammable as hydrogen; that olefiant gas is fired by iron and charcoal heated to redness; but that carburetted hydrogen, to be inflamed, requires that the wire should be white hot. Now this is precisely the order in which the three compound gases require hydrogen to be added to them, in order to be rendered susceptible of being acted upon by the platinum sponge; carbonic oxide being acted upon

* On Flame, 8vo. p. 72.

with the smallest proportion of hydrogen; olefiant gas requiring more hydrogen, and carburetted hydrogen a still larger proportion. It is extremely probable, then, that the temperature, produced by the union of the hydrogen and oxygen forming part of any mixture, is the circumstance which determines the combustible gases to unite, or not, with oxygen by means of the sponge. It was desirable, however, to ascertain the exact temperature at which each of those three gases unites with oxygen with the intervention of the spongy platinum. For this purpose the gases, mixed with oxygen enough to saturate them, were severally exposed in small retorts containing a platinum sponge, and immersed in a mercurial bath, to a temperature which was gradually raised till the gases began to act on each other. In this way the following facts were determined.

1st. Carbonic oxide began to be converted into carbonic acid at a temperature between 300° and 310° FAHRENHEIT. By raising the temperature to 340° , and keeping it at that point for 10 or 15 minutes, the whole of the gas was acidified, the condensation of volume in the mixture being equivalent to the oxygen which had disappeared.

2dly. Olefiant gas, mixed with sufficient oxygen, and in contact with the sponge, showed a commencement of decomposition at 480° FAHRENHEIT, and was slowly but entirely changed into carbonic acid by a temperature not exceeding 520° FAHRENHEIT. M M. DULONG and THENARD* state the same change to take place at 300° cent. = 572° FAHRENHEIT; but having repeated the experiment several times, I find no reason to deviate from the temperature which I have assigned.

* Ann. de Chim. et de Phys. XXIII. 443.

3rdly. Carburetted hydrogen, exposed under the same circumstances, was not in the least acted upon by a temperature of 555° FAHRENHEIT, the highest of which, by an ARGAND's lamp, I was able to raise the mercurial bath. This, however, must have been near the temperature required for combination; for on removing the retort from the mercurial bath, and applying a spirit lamp, at such a distance as not to make the retort red hot, a diminution of volume commenced, and continued till all the carburetted hydrogen was silently converted into water and carbonic acid.

4thly. Cyanogen, similarly treated, was not changed at a temperature of 555° FAHRENHEIT, and on applying the flame of a spirit lamp to the tube, it produced no action till the tube began to soften.

5thly. Muriatic acid gas, mixed with half its volume of oxygen, began to be acted upon at 250° FAHRENHEIT. Water was evidently formed; and the disengaged chlorine, acting upon the mercurial vapour in the tube, formed calomel, which was condensed, and coated its inner surface.

6thly. Ammonical gas, mixed with an equal volume of oxygen, showed a commencement of decomposition at 380° FAHRENHEIT. Water was also in this case distinctly generated; and at the close of the experiment, nothing remained in the tube but nitrogen and the redundant oxygen.

I proceeded, in the next place, to examine the agency of finely divided platinum at high temperatures, on those mixtures of gases, which are either not decomposed, or are slowly decomposed, at the temperature of the atmosphere.

When carbonic oxide and hydrogen gases, in equal volumes, mixed with oxygen sufficient to saturate only one of

them, were placed in contact with the sponge, and gradually heated in a mercurial bath, the mixture ceased to expand between 300° and 310° FAHRENHEIT, and soon began to diminish in volume. On raising the temperature to 340° , and keeping it some time at that point, no further diminution was at length perceptible. From the quantity of carbonic acid, remaining at the close of the experiment, it appeared that four-fifths of the oxygen had united with the carbonic oxide, and only one-fifth with the hydrogen. When four volumes of hydrogen, two of carbonic oxide, and one of oxygen, were similarly treated, the hydrogen, notwithstanding its greater proportional volume, was still found to have taken only one-fifth of the oxygen, while four-fifths had combined with the carbonic oxide. These facts show that at temperatures between 300° and 340° FAHRENHEIT, the affinity of carbonic oxide for oxygen is decidedly superior to that of hydrogen; as, from the experiments before described, appears to be the case, also, at common temperatures.

But a similar distribution of oxygen, between carbonic oxide and hydrogen, does not take place, when those three gases are fired together by the electric spark. This will appear from the following table, in which the three first columns show the quantities of gases that were fired, and the two last, the quantities of oxygen that were found to have united with the carbonic oxide and with the hydrogen.

	Before firing.			After firing	
	Measure of Carb. Oxide.	Measure of Hydrog.	Measure of Oxygen.	Oxygen to Carb. Oxide.	Oxygen to Hydrogen.
Exp. 1	40	40	20	6	14
2	40	20	20	12	8
3	20	40	20	5	15

When equal volumes of carbonic oxide and hydrogen gases, mixed with oxygen sufficient to saturate only one of them, were exposed in a glass tube to the flame of a spirit lamp, without the presence of the sponge, till the tube began to soften, the combination of the gases was effected without explosion, and was merely indicated by a diminution of volume, and an oscillatory motion of the mercury in the tube. At the close of the experiment, out of twenty volumes of oxygen, eight were found to have united with the carbonic oxide, and twelve with the hydrogen, proportions which do not materially differ from the results of the first experiment in the foregoing Table. At high temperature, then, the attraction of hydrogen for oxygen appears to exceed that of carbonic oxide for oxygen : at lower temperatures, especially when the gases are in contact with the platinum sponge, the reverse takes place, and the affinity of carbonic oxide for oxygen prevails.

Extending the comparison to the attraction of olefiant and hydrogen gases for oxygen at a red heat, I found that when six volumes of olefiant, six of hydrogen, and three of oxygen were heated by a spirit lamp till the tube softened, a silent combination took place as before; all the oxygen was consumed; but only half a volume had been expended in forming carbonic acid, which indicates the decomposition of only one quarter of a volume of olefiant gas. On attempting a similar comparison between carbonic oxide and olefiant gas, by heating them with oxygen in the same proportions, the mixture exploded as soon as the glass became red hot, and burst the tube.

The property inherent in certain gases, of retarding the

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action of the platinum sponge, when they are added to an explosive mixture of oxygen and hydrogen, is most remarkable in those which possess the strongest attraction for oxygen; and it is probably to the degree of this attraction, rather than to any agency arising out of their relations to caloric, that we are to ascribe the various powers which the gases manifest in this respect. This will appear from the following Table, the first column of which shows the number of volumes of each gas required to render one volume of an explosive mixture of hydrogen and oxygen unflammable by the discharge of a Leyden jar; while the second column shows the number of volumes of each gas necessary, in some cases, to render one volume of an explosive mixture insensible to the action of the sponge, and in other cases indicates the number which may be added without preventing immediate combination. In the first column, the numbers marked with an asterisk were determined by Sir HUMPHRY DAVY; the remaining numbers in that column, and the whole of the second, are derived from my own experiments.

1 vol. of Explosive Mixture was rendered incapable of being inflamed by Electricity, when mixed with		Effect of adding the same Gasses to 1 vol. of Explosive Mixture on the action of the Sponge.
* About 8	vol. of Hydrogen . . .	not prevented by many vols.
6	Nitrogen . . .	ditto.
* 9	Oxygen . . .	not prevented by 10 vol.
* 11	Nitrous Oxide . .	ditto.
1.5	Cyanogen . . .	prevented by 1 vol.
* 1	Carbonized Hydrogen	not prevented by 10 vol.
4	Carbonic Oxide . .	prevented by $\frac{1}{2}$ a vol.
* 0.5	Olefiant Gas . . .	prevented by 1.5 vol.
* 2	Muriatic Acid . .	not prevented by 6 vol.
2	Ammonia . . .	not prevented by 10 vol.
3	Carbonic Acid . .	ditto.

From the foregoing Table it appears, that carbonic oxide produces the greatest effect, in the smallest proportion to an explosive mixture of oxygen and hydrogen, in preventing the action of those gases on each other, when exposed to the sponge at temperatures below the boiling point of mercury. In general, those gases which either do not unite with oxygen, or unite with it only at high temperatures, have little effect in restraining the efficiency of the sponge. There is an apparent exception, however, in cyanogen, which it would require more research than I have yet had time to devote to an object merely collateral to reconcile it, if it be capable of being reconciled, with the general principle.

From the fact that carbonic oxide, olefiant gas, and carburetted hydrogen, when brought to unite with oxygen by means of the platinum sponge assisted by heat, undergo this change at different temperatures, it seemed an obvious conclusion, that by exposing a mixture of those gases with each other and with oxygen to a regulated temperature, the correct analysis of such mixtures might probably be accomplished. Mixtures of two or more of the combustible gases were therefore exposed, in contact with oxygen gas and the platinum sponge, in tubes bent into the shape of retorts, which were immersed in a mercurial bath. This bath was gradually heated to the required temperatures, and by proper management of the source of heat, was prevented from rising above that degree.

1st. By subjecting 25 measures of carbonic oxide, 15 of olefiant gas, and 57 of oxygen, in contact with the sponge, to a heat which was not allowed to exceed 350° FAHRENHEIT till the diminution of volume ceased, all the carbonic oxide

was converted into carbonic acid, and the olefiant gas remained in its original volume.

2d. By exposing in a similar manner 20 measures of carbonic oxide, 21 of carburetted hydrogen, and 36 of oxygen, to a temperature below 400° FAHRENHEIT, the carbonic oxide was entirely acidified; and on washing out the carbonic acid by liquid potash, the carburetted hydrogen was found unaltered, mixed with the redundant oxygen.

3d. A mixture of 10 measures of olefiant gas, 10 of carburetted hydrogen, and 58 of oxygen, being heated in contact with the sponge to 510° FAHRENHEIT, the olefiant gas was silently but entirely changed into carbonic acid, while the carburetted hydrogen was not at all acted upon.

4th. By acting with the sponge upon 42 measures of carburetted hydrogen, 22 of carbonic oxide, 22 of hydrogen, and 28 of oxygen, first at a temperature of 340° FAHRENHEIT, which was raised gradually to 480°, all the carbonic oxide was changed into carbonic acid, and all the hydrogen into water; but the carburetted hydrogen remained undiminished in quantity, and was found, after removing the carbonic acid, mixed only with the redundant oxygen. In this experiment, the diminution of volume had continued some time before there was any perceptible formation of water, the attraction of carbonic oxide for oxygen appearing to prevail over that of hydrogen. The same precedency in the formation of carbonic acid is always apparent, when carbonic oxide and hydrogen, mixed even with oxygen enough to saturate both gases, are raised to 350° FAHRENHEIT.

By thus carefully regulating the temperature of the mercurial bath, the action of oxygen upon several gases, (carbonic

oxide, olefiant, and carburetted hydrogen for example) may be made to take place in succession; and by removing the carbonic acid, formed at each operation, it may be ascertained how much of each of the two first gases has been decomposed. The carburetted hydrogen indeed always remains unchanged, and its quantity must be determined by firing it with oxygen by the electric spark. If hydrogen also be present, it is difficult to prevent the olefiant gas from being partially acted upon; but this is of little consequence, as I had shown that it is easy to remove that gas in the first instance by chlorine.* It may be remarked, that this method of operating on the aëriform compounds of charcoal gives more accurate results than rapid combustion by the electric spark, being never attended with that precipitation of charcoal, which is often observed when the gases are exploded with oxygen. A regulated temperature, also, effects the analysis of such mixtures much more correctly than the action of the sponge or balls, because in the latter case the heat produced is uncertain; and though sometimes adequate to the effect, yet there is always a risk that it may exceed, or fall short of that degree, which is required for the successful result of the analytic process.

From the facts which have been stated, I derived a method of obtaining carburetted hydrogen gas perfectly free from olefiant gas, hydrogen, and carbonic oxide, and mixed only with a little oxygen, which, had it been necessary to my purpose, might also have been separated. The early product of the distillation of pit-coal was washed with a watery solution

* Philosophical Transactions, 1821, p. 147.

of chlorine, and afterwards with liquid potash, to remove a little chlorine that arose into the gas from the solution. The residuary gas was next heated with one-fourth its volume of oxygen, at the temperature of 350° FAHRENHEIT, in contact with the sponge; which converted the carbonic oxide into carbonic acid, and the hydrogen into water. The carbonic acid being removed by liquid potash, there remained only the carburetted hydrogen, the redundant oxygen, and a very minute quantity of nitrogen introduced by the latter gas. Hitherto, I have prepared this gas only in a small quantity, but it would be easy to extend the scale of the operation, and to remove the excess of oxygen by obvious methods.

SECTION III.

APPLICATION OF THE FACTS TO THE ANALYSIS OF MIXTURES OF THE COMBUSTIBLE GASES IN UNKNOWN PROPORTIONS.

At an early period of the investigation described in the first section, I proceeded to apply the facts of which I was then possessed, to the analysis of a mixture of gases in unknown proportions. For this purpose, I caused a quantity of gas to be collected from coal, by continuing the application of heat to the retorts two hours beyond the usual period, and receiving the gas into a separate vessel. Gas of this quality was purposely chosen, because, from former experience, I expected it to contain free hydrogen, carbonic oxide, and carburetted hydrogen, but no olefiant gas, the production of which is confined to the early stages of the progress. After washing it, therefore, with liquid potash to remove a little carbonic acid, and ascertaining its specific gravity when thus

washed to be 308, I proceeded at once to subject it to the new method of analysis.

Having ascertained, by a previous experiment with VOLTA'S eudiometer, that 10 volumes of the gas required for saturation 9 volumes of oxygen, I mixed 43 measures with 43 of oxygen (= 41 pure) and passed a platinum ball, which had been recently heated, into the mixture. An immediate diminution of volume took place, attended with a production of heat, and formation of moisture. The residuary gas, cooled to the temperature of the atmosphere, measured 43.5 volumes. Of these 4.5 were absorbed by liquid potash, indicating 4.5 carbonic acid, equivalent to 4.5 carbonic oxide; the rest, being fired in a VOLTA'S eudiometer with an additional quantity of oxygen, gave 11 volumes of carbonic acid; the diminution being 22 volumes, and the oxygen consumed 22 also, circumstances which prove that 11 volumes of carburetted hydrogen were consumed by this rapid combustion. But of the loss of volume first observed, (viz. $86 - 43.5 = 42.5$) 2.25 are due to the carbonic acid formed; and deducting this from 42.5, we have 40.25, which are due to the oxygen and hydrogen converted into water; and $40.25 \times \frac{2}{3} = 26.8$ shows the hydrogen in the original gas. But the sum of these numbers ($26.8 + 4.5 + 11$) being less by 0.7 than the volume of gas submitted to analysis, we may safely consider that fraction of a measure to have been nitrogen. The composition then of the mixture will stand in volumes as follows:

Hydrogen	.	.	.	26.8	.	.	.	62.32
Carbonic oxide	.	.	.	4.5	.	.	.	10.50
Carburetted hydrogen	11.0	25.56
Nitrogen	.	.	.	0.7	.	.	.	1.62
				<u>43.0</u>				<u>100. 0</u>

On calculating what should be the specific gravity of a mixture of gases in the above proportions, it was found to be .303,* which coincides, as nearly as can be expected, with the actual specific gravity of the gas submitted to analysis, viz. .308. To place the correctness of the results beyond question, I mingled the gases in the above proportions, and acted on the artificial mixture in the same manner as on the original gas, when I had the satisfaction to find that the analytical process again gave the true volumes with the most perfect correctness for the hydrogen and carbonic oxide, and within the fraction of a measure for the carburetted hydrogen. Notwithstanding this successful result, which was twice obtained, I should still prefer, for the reason which has been stated, having recourse to a temperature carefully regulated, for the analysis of similar mixtures, in all cases where the hydrogen is in moderate proportion, and where great accuracy is desirable. Whenever (it may again be remarked) olefiant gas is present in a mixture, it should always be removed by chlorine, before proceeding to expose the mixture to the agency of the spongy metal.

It can scarcely be necessary to enter into further details respecting methods of analysis, the application of which to particular cases must be sufficiently obvious, from the experiments which have been described on artificial mixtures. The apparatus required is extremely simple, consisting, when the balls are employed, of graduated tubes of a diameter between 0.3 and 0.6 of an inch ; or, when an increased temperature is used, of tubes bent into the shape of retorts, of a diameter

* In this estimate, the specific gravity of hydrogen is taken at .0694 ; that of carbonic oxide at .6722 ; of carburetted hydrogen at .5555 ; and of nitrogen at .9728.

varying with the quantity of gas to be submitted to experiment, which may be from half a cubic inch to a cubic inch or more. These, when in use, may be immersed in a small iron cistern containing mercury, and provided with a cover in which are two holes, one for the tube, and the other for the stem of a thermometer, the degrees of which are best engraved on the glass.

By means of these improved modes of analysis, I have already obtained some interesting illustrations of the nature of the gases from coal and from oil. I reserve, however, the communication of them, till I have had an opportunity of pursuing the enquiry to a greater extent, and especially of satisfying myself respecting the exact nature of the compound of charcoal and hydrogen, discovered some years ago by Mr. DALTON, in oil gas and coal gas, which agrees with olefiant gas in being condensible by chlorine, but differs from it in affording more carbonic acid and consuming more oxygen.

Manchester, 6th June, 1824.