XXI. *Conditions of Chemical Change in Gases: Hydrogen, Carbonic Oxide, and Oxygen.*

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INTRODUCTION,

THE influence of physical forces, of modes of aggregation and of mass, not only on the result, but on the manner of the transformation of one kind of matter into another kind—in brief, *the conditions of chemical change*—present a problem to the chemist which only of late years has been submitted to experimental investigation. The difficulties besetting this line of inquiry are many, but the greatest of them is the difficulty of finding a reaction that is simple in kind, that takes place between bodies which can be prepared in great purity, and that yields products which can be exactly measured. Several methods of investigation have been pursued. The course of a gradual change between two bodies has been followed step by step, either by measuring the amount of residue still remaining undecomposed after successive equal intervals of time, or by measuring the time required for the successive formation of equal quantities of one of the products of the reaction. Such was the method employed by BERTHELOT, who measured the rate of etherification of an alcohol by an acid, and by HARCOURT and ESSON, who measured the rate of decomposition of hydric peroxide by hydric iodide. Unluckily but few of the reactions, which occur slowly enough for such investigation, appear to be of a simple nature; examination reveals the fact that, in most cases, the change from the initial substances to the final product does not take place in one stage, but is a complex reaction brought about by the successive formation and decomposition of intermediate compounds at rates which severally vary with the conditions of the experiment.

Another method of investigation is that of comparing the rates of two opposite changes taking place simultaneously in a homogeneous mixture. When two bodies enter into double decomposition to form two new bodies which are themselves capable, under the conditions of the experiment, of re-forming the original substances by a reverse change, a mixture of the four bodies is produced, and an equilibrium is finally established when the rate of decomposition of one pair of the reacting bodies is exactly equalled by the rate of decomposition of the other pair. Were it possible to measure accurately the quantities of four reacting bodies which preserve such an equilibrium, the precise relative rate of the two changes would be obtained. But in most cases it is impossible to make accurate measurements of one of the constituents of a mixture without separating it from the others, and thus disturbing the equilibrium; so that some indirect method of measurement becomes necessary in experiments of this nature. Changes of colour, of temperature, of volume, of magnetic and optical properties, have afforded indirect methods of measuring the amount of particular bodies present in such a mixture without separating the constituents. By these means measurements of the rate of chemical change have been made by GLADSTONE, THOMSEN, OSTWALD, GULDBERG and WAAGE, and other chemists.

Again, when one body is presented to two others which are in excess, with each of which it is capable of uniting to form a stable compound, it divides itself between the two in proportions depending upon the relative rates at which the two reactions take place. Measurements of the masses of the reacting substances present at the beginning of the experiment and of the products finally formed give data for calculating the relative rates of the two changes. The incomplete combustion of a mixture of hydrogen and carbonic oxide by a small quantity of oxygen seemed to present a case of this kind suitable for investigation. The gases could easily be prepared in a pure state; the measurement, explosion, and subsequent analysis could be readily performed in a eudiometer. By the study of this reaction, BUNSEN, with the refined apparatus devised by himself for the manipulation of gases, made the first attempt to elucidate the laws of chemical change. His experiments form the starting-point of several long series of observations by E. von MEYER, HORSTMANN, and other chemists, and led me to make a careful investigation of the conditions which affect the chemical changes occurring during the explosion of these gases. An account of this investigation, carried on during several years, I venture to bring before the Royal Society, in the belief that the results obtained clear up some discrepancies between the observations of previous workers, and prove that, under the simplest conditions, the division of the oxygen is determined by the reciprocal reaction of two pairs of gaseous bodies, forming a system in mobile equilibrium capable of exact expression by a simple formula.

HENRY'S *experiments*.

The first experiments on the incomplete combustion of hydrogen and carbonic oxide were made by HENRY. In a memoir printed in these Transactions (1824), HENRY compared the action of the electric spark and of platinum sponge on mixtures of carbonic oxide and electrolytic gas. He discovered the fact that the lower the temperature at which the reaction occurs the greater is the proportion of carbonic acid produced.

He writes: "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 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.

TABLE I.

	Before firing.			After firing.	
	CO.	H.	O.	Oxygen to CO.	Oxygen to H.
Experiment 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 temperatures, 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."

BUNSEN'S *experiments.*

BUNSEN thus states the problem :—*

"The proportion in which one body divides itself between two others—present in large excess over it—does not depend merely on the relative strength of their

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* BUNSEN, 'Ann. Chem. Pharm.,' 85, 137.

chemical attraction, but also on the relative quantities of them present. If a and b represent the *masses* of two bodies A and B capable of combining with C to form compounds AC and BC, and if x and y represent the affinities of A and B for C respectively, then the proportion of the compound AC formed to the compound BC formed will be expressed by the equation

$$\frac{AC}{BC}=\frac{ax}{by}$$

"It follows from this that any alteration in the mass of either A or B will cause a corresponding alteration in the proportion of the compounds AC and BC formed."

This Law of Mass, commonly attributed to BERTHOLLET, was tested by BUNSEN in the following way:—*

He exploded in a eudiometer different mixtures of carbonic oxide and hydrogen with a quantity of oxygen insufficient to completely burn them. In the explosion a portion of the carbonic oxide was burnt to carbonic acid, and a portion of the hydrogen was burnt to steam. If the above law of mass held good, the relative quantities of carbonic acid and steam formed would alter in a regular manner with the relative quantities of carbonic oxide and hydrogen taken. Partly owing to the paucity of his experiments, and partly owing to an undetected source of error, BUNSEN wrongly concluded that the law of mass was modified in a particular way by the tendency of the atoms to form simple hydrates of carbonic acid. "This catalytic action which the excess of molecules present, taking no part in the decomposition, exert upon the combining molecules is seen in a most remarkable manner in the volumetric relation between the products formed by the combustion, and brings to light a singular law which appears to be of fundamental importance in the mode of action of affinity. If the particles a in a homogeneous gaseous mixture have the choice of combination between the particles b and c of two other gases present in excess, a certain equilibrium ensues between the attractions of all the particles, so that the compounds $(a+b)$ and $(a+c)$, formed by the union of a with b and c, stand in a simple relation to one another, dependent on the amount of the particles remaining uncombined, and undergoing discontinuous alteration on gradual increase of these particles."

BUNSEN'S experiments, made by exploding electrolytic gas with varying proportions of carbonic oxide, gave numbers, representing the relation between the carbonic acid and steam formed, which almost exactly corresponded with the six most simple hydrates of carbonic acid. In his first paper he showed that a variation of pressure from 317 millims. of mercury to 726 millims. did not materially alter the proportion in which the oxygen divided itself, and that the same result was obtained whether the explosion was made in the sunlight or in the dark. In the first edition of the

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* BUNSEN, 'Gasometry,' 1857.

'Gasometrische Methoden,' published in 1857, some further experiments were added, which are included in the following table :—*

TABLE II.—BUNSEN'S Experiments.

No. of experiment.	Temp. C.	Pressure.	Gases present before explosion.			Oxygen divides itself,		Ratio of carbonic acid to aq. vapour in the hydrates of carbonic acid.
			Oxygen.	Hydrogen.	Carbonic oxide.	To carbonic oxide.	To hydrogen.	
	°	Millims.						
1	22·3	734	100	200	794	67	33	$2CO_2$, H_2O - - 67 : 33.
2	3·3	453	100	200	595	50	50	CO_2, H_2O - - 50 : 50.
3	22·5	395	100	200	449	49	51	" "
4	4·7	381	100	200	295	34	66	CO_2, $2H_2O$ - - 33 : 67.
5	22·6	723	100	200	147	25	75	CO_2, $3H_2O$ - - 25 : 75.
6	2·6	352	100	200	119	24	76	" "
7	2·3	344	100	200	81	19	81	CO_2, $4H_2O$ - - 20 : 80.
8	22·0	720	100	370	315	20	80	" "
9	7·0	321	100	200	74	17	83	CO_2, $5H_2O$ - - 17 : 83.

These experiments remained without confirmation until 1874, when E. von **MEYER** published a paper on the "Incomplete Combustion of Gases,"† in which he pointed out that when mixtures of carbonic oxide and hydrogen were exploded with progressively increasing quantities of oxygen, the proportion in which the oxygen divided itself altered *per saltum*, and that this proportion might always be expressed by whole numbers.

v. MEYER regarded his experiments as confirming BUNSEN'S law, but as HORSTMANN subsequently pointed out, the whole numbers, expressing the ratios between the amounts of carbonic acid and steam formed, were in some cases so large that the difference between one such whole number and the next above or below it, fell within the limits of experimental error. The ratio of the volume of steam formed per unit volume of hydrogen present to the volume of carbonic acid formed per unit volume of carbonic oxide present, was called by v. MEYER the coefficient of affinity of hydrogen for oxygen compared with that of carbonic oxide for oxygen. Taking the affinity of carbonic oxide for oxygen as the unit, the coefficient for hydrogen and oxygen is given by the equation

$$\frac{H_2O}{H_2} : \frac{CO_2}{CO} = \alpha : 1$$

This "coefficient of affinity" according to v. MEYER is not a constant, but varies *per saltum* within small limits on account of the discontinuous alteration in the proportion of carbonic oxide and hydrogen burnt. It is greatest when the quantity of oxygen

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* This table is affected by two or three small errors of calculation, which bring the numbers, expressing the ratio of carbonic acid to steam formed, nearer to the theoretical numbers than they should be. These errors are corrected in the second edition of BUNSEN'S 'Gasometrische Methoden.'

† 'Journal für praktische Chemie' (2), 10, 273.

used is as small as possible, and the mixture therefore approaches the limit of inflammability. As the quantity of oxygen is increased, he says, the proportion of steam to carbonic acid produced must necessarily approximate to the proportion in which the hydrogen and carbonic oxide are originally present, although this proportion is never actually reached, because, when the oxygen is nearly sufficient for complete combustion, the hydrogen is all burnt while some carbonic oxide remains unoxidized. The true coefficient of affinity, according to v. MEYER, is that obtained with the minimum quantity of oxygen.

There is an obvious objection to this use of the term "coefficient of affinity." The smallest proportion of oxygen used by v. MEYER was that which was just necessary to produce an explosion. He gives no proof that, if this proportion were diminished still further, the ratio of carbonic acid to steam produced would be unaltered. The limit of inflammability is not necessarily the limit of the exercise of chemical affinity. If we assume that oxygen unites with the excess of carbonic oxide and hydrogen according to the equations—

$$2CO+O_2=2CO_2$$

$$2H_2+O_2=2H_2O$$

then the divison of the oxygen between the carbonic oxide and the hydrogen depends on the rate at which oxygen unites with carbonic oxide, and the rate at which it unites with hydrogen, under the conditions existing at each moment from the beginning of the change until the last molecule of oxygen is broken up. These conditions change at each moment (without reference to the changes of temperature and pressure), since the carbonic oxide and the hydrogen are attacked at unequal rates, and therefore the proportions of carbonic oxide and hydrogen remaining unconsumed vary continually during the combustion. In this case, the final division of the oxygen represents the sum or net result of its dividing itself between the two combustible gases in a series of different ratios during a series of successive moments. Its division would represent the actual ratio of two constant rates only if one of two conditions were fulfilled. First, if the ratio of the combustible gases in the original mixture were the same as the ratio of carbonic acid and steam formed; or, secondly, if the proportion of oxygen were so small that the subtraction, by combustion, of the corresponding quantities of the combustible gases would not materially alter their ratio. The first condition can only be fulfilled by burning all the combustible gases. The second involves the measurements of such small quantities that the errors of experiment become important. Practically, the limit of inflammability of the mixture imposes an inferior limit to the reduction of the quantity of oxygen which prevents the second condition being fulfilled.

The effect produced by the presence of an inert gas, nitrogen, which takes no part in the chemical action, on the division of the oxygen between the two combustible gases was also studied by v. MEYER. He found that on addition of nitrogen the coefficient of affinity was altered, *more* carbonic oxide and *less* hydrogen being burnt. When similar mixtures were exploded in tubes of different diameter, v. MEYER in most cases found that the coefficient of affinity was altered. In a large tube of 20 millims. diameter more carbonic oxide and less hydrogen were burnt than in narrower tubes of 12·5 millims. and 5·5 millims. diameter. With one mixture, however, v. MEYER found no alteration of the coefficient whether the explosion was made in the largest tube or the smallest. This change of affinity he attributed to the increased friction of the gases in the narrower tubes, which he says always tends to increase the relative affinity of hydrogen for oxygen. In most cases this increase of affinity is sufficient, according to v. MEYER, to cause a *leap* in the proportion of hydrogen to carbonic oxide burnt, but in a few cases, where the equilibrium is more stable, this increase of affinity does not suffice to alter the ratio of the gases burnt.

In the summer of 1876, at the suggestion of Mr. VERNON HARCOURT, I began experiments in the Christ Church laboratory to test the truth of BUNSEN'S law. I was ignorant at the time of the paper HORSTMANN had published in a local journal* at Heidelberg in the spring of the same year.

Description of the apparatus.

The apparatus employed in the earlier experiments detailed in this paper was devised by Professor McLEOD and erected by him in the LEE'S laboratory at Christ Church, Oxford. The construction of this instrument is too well known to require description.

The later experiments were made in the laboratory of Balliol College with an apparatus devised by Professor F. D. BROWN for measuring the tensions of saline solutions. The only alterations I found necessary to make were (1) the substitution of a eudiometer (with a bent capillary tube and steel cap) in place of the shorter tension-tube, (2) the adjustment of a movable shelf to two of the iron uprights to hold a mercury trough for the laboratory tube.

A general view of this instrument and details of the connections are given in Plates 41 and 42.

The framework of the instrument is very strongly constructed of iron, screwed up firmly together. The jacket surrounding the eudiometer is of copper, with a wooden casing. The jacket has a door near the bottom, and a movable plate at the top, both made of gun-metal. The windows are of plate glass. The liquid employed in the jacket is water for temperatures below 100°, and a mixture of glycerin and water for higher temperatures. A screw-stirrer is made to revolve in the liquid. In an annular pipe, outside the jacket, and opening into it near the top and bottom, the liquid is heated and a continuous circulation maintained. Two thermometers graduated to tenths of degrees are placed at different heights in the jacket. The mean of their readings is taken as the temperature of the gas in the eudiometer.

The barometer tube is surrounded with a water-jacket. An enlargement at the top

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* Verh. des Heidelb. naturf. med. Vereins, N.S., I., 3.

diminishes the error due to residual air. The heights of the mercury in the eudiometer and barometer are read off by a cathetometer. The whole apparatus stands on a stone floor in a cellar underground.

The platinum wires are sealed into the eudiometer close to the shoulder, and are passed through two small glass prominences, over each of which an india-rubber tube surrounding the wire is stretched so as to prevent contact between the wire and the water in the jacket. By this device a spark can be passed between the wires without lowering the water in the jacket. The lower ends of the eudiometer and barometer are not contracted. They are fastened gas-tight into steel blocks by a collar and nut compressing three or four india-rubber rings. The details of these junctions and of the 3-way steel cock are given in the diagrams (Plate 42.) By this arrangement the eudiometer and barometer can easily be removed and cleaned out with a long brush.

I have found the steel caps joining the eudiometer and laboratory tube to answer their purpose most admirably. In eight years' work I have never known an experiment to be lost on account of any failure of this joint.

The readings of the instrument are made by artificial light. On the further side of the jacket a screen, half of translucent paper and half of black paper, with their line of demarcation horizontal, was made to slide up and down close to the window.

Behind this screen and moving with it an argand burner, connected by a flexible tube with the gas supply, is adjusted; with this artificial illumination more concordant readings are obtained than with variable daylight, and the experiments can be carried on at all hours.

Repetition of BUNSEN'S *experiment.*

I commenced by repeating BUNSEN'S experiments with carbonic oxide and electrolytic gas. The gases were exploded over mercury in a wet eudiometer, and the calculations made according to the directions in BUNSEN'S "Gasometry." In the following table the results of this first series of experiments are given side by side with BUNSEN'S results, and expressed in a similar manner for the purpose of comparison. The explosions were made under pressures varying from 200 to 300 millims. of mercury, and between the temperatures of 15° and 17° C.

TABLE III.—Experiments with Carbonic Oxide and Electrolytic Gas in a Wet Eudiometer.

Number.	DIXON'S experiments.			BUNSEN'S experiments.			Number.
	100 volumes of the combustible gases contain		Ratio of carbonic acid to water formed	100 volumes of the combustible gases contain		Ratio of carbonic acid to water formed	
	CO	H_2	$\frac{CO_2}{H_2O}$	CO	H_2	$\frac{CO_2}{H_2O}$	
1	80·3	19·7	2·83				
				79·9	20·1	2·04	1
2	79·5	20·5	2·65				
3	79·3	20·7	2·03				
4	79·2	20·8	2·26				
5	78·7	21·3	2·34				
6	75·7	24·3	1·62				
7	75·3	24·7	1·46				
				74·2	25·8	·89	2
8	73·6	26·4	1·40				
9	71·4	28·6	1·07				
10	70·2	29·8	1·08				
11	69·2	30·8	1·00	69·2	30·8	·95	3
12	69·1	30·9	1·00				
13	60·2	39·8	·62				
				59·6	40·4	·51	4
14	48·2	51·8	·44				
15	46·8	53·2	·39				
16	46·6	53·4	·39	46·5	53·5	·34	5
17	45·8	54·2	·39				
				37·4	62·6	·29	6
18	28·3	71·7	·22	28·8	71·2	·24	7
				27·0	73·0	·20	8

These experiments gave no indication of any sudden change in the proportion of carbonic oxide and hydrogen burnt. They neither agreed well with BUNSEN'S results, nor were they concordant one with another. In the first five experiments the proportion of carbonic oxide to hydrogen taken was nearly the same as in BUNSEN'S first experiment, but the ratio of carbonic acid to steam formed varied from 2·8 to 2. In the 9th, 10th, 11th, and 12th experiments the proportion of carbonic acid to hydrogen taken was nearly the same as in BUNSEN'S 3rd experiment; the results were concordant and agreed with BUNSEN'S. Between these two sets, according to BUNSEN, the sudden change from 2 : 1 to 1 : 1 occurs. Experiments 6, 7, and 8, intermediate between these two sets, gave intermediate ratios for the carbonic acid and water formed. Experiment 13 did not agree with BUNSEN'S 4th, nor Experiments 15, 16, and 17 with BUNSEN'S 5th.

These discrepancies, greater than could be accounted for by any error of manipulation, led to a more minute examination of the conditions affecting the chemical change.

The re-action between carbonic oxide and oxygen.

In the first place the question presented itself—Is the action between a small quantity of oxygen and an excess of combustible gases always complete, or is it possible that a certain number of oxygen molecules may during the moment of explosion remain in equilibrium between the attractions of the other molecules around them and so remain uncombined ?

To solve this question a mixture of carbonic oxide with one-third its volume of oxygen was fired in a wet eudiometer at 15° C. and under a pressure of 300 millims.

Carbonic oxide	75 volumes.	
Oxygen.	25 „	
Before explosion	100 „	
After explosion	75·9 „	Contraction = 24·1.
After absorption	25·1 „	Absorption = 50·8.

The contraction on explosion was found to be less than the original volume of oxygen by ·9 volume, and the absorption was found to be more than double the original volume of oxygen by ·8 volume. Since more carbonic acid was produced than could have been formed by the oxygen taken, it was evident that the carbonic oxide must have been oxidized to some extent by the steam present in the eudiometer. Now for every molecule of carbonic oxide so oxidized, a molecule of free hydrogen must be liberated, and the place of the decomposed molecule of steam would be filled by the volatilization of a molecule of water from the sides of the tube. In this experiment the oxygen, if completely consumed, would oxidize 50 volumes of carbonic oxide to carbonic acid, but since 50·8 volumes of carbonic acid were formed, ·8 volume of carbonic oxide must have been oxidized by the steam. This reduction of ·8 volume of steam, producing an equal volume of hydrogen, would make the contraction on explosion ·8 volume less than it would have been had no such secondary action taken place. The observed contraction agreed with this. A repetition of the experiment gave a similar result.

Volume of carbonic oxide	=	73·24	
„ oxygen	=	26·76	
Total volume before explosion	=	100	
„ after explosion	=	74·02	Contraction = 25·98.
„ after absorption	=	19·70	Absorption = 54·32.

Here the volume of carbonic acid formed is more than twice the volume of oxygen taken by ·8 volume, and the contraction on explosion is less than the volume of oxygen taken by ·78 volume. By an analysis of the residual gases the liberated hydrogen was directly estimated, and its volume and was found to be exactly ·78 volume.

Volume of residual gases = 19·70
,, On addition of oxygen = 51·12
,, After explosion = 40·49 2nd contraction = 10·63
,, After absorption = 21·58 2nd absorption = 18·91
CO = 18·91
$H_2 = \frac{2}{3}\left\{10{\cdot}63 - \frac{18{\cdot}91}{2}\right\}$
$= {\cdot}78$

It was evident from these experiments that the results obtained with carbonic oxide and electrolytic gas were affected by the presence of the aqueous vapour. Since at the temperature reached in the explosion the excess of carbonic oxide reacts with the steam, forming carbonic acid and liberating hydrogen, the presence of aqueous vapour appears to increase the affinity of carbonic oxide for oxygen and diminish that of hydrogen. Such an effect is exactly the opposite of that produced by adding carbonic acid to the mixture before explosion. Bunsen showed in his first paper that when an excess of hydrogen is exploded with oxygen in presence of some carbonic acid, some of the latter is reduced by the excess of heated hydrogen to carbonic oxide. Thus the previous addition of aqueous vapour, one of the products of the reaction, alters the apparent division of the oxygen, just as the previous addition of carbonic acid, the other product of the reaction, alters it in an opposite direction. This fact accounts in part for the discrepancies observed in comparing my experiments with Bunsen's, for while my explosions were made at an initial temperature varying between 15° C. and 17° C., Bunsen made one set of explosions between 22° C. and 23° C., and the other set between 2° C. and 5° C., so that very different quantities of aqueous vapour were present in the different experiments. In order, therefore, to make the experiments a real test of the law of mass, it was necessary to perform the explosions with dry gases in a dry eudiometer.

Before proceeding to repeat the experiments with dry carbonic oxide and electrolytic gas, another attempt was made to determine whether, in a dry eudiometer, oxygen is completely burnt when exploded with a large excess of carbonic oxide. This experiment led to the important discovery that dry carbonic oxide and oxygen do not combine when submitted to the electric spark. A mixture containing 3 volumes of carbonic oxide to 1 of oxygen was brought over into the dried eudiometer, and a spark from a Leyden-jar was passed through it without causing explosion. A little more oxygen was added, and the spark again passed without result.

A fresh charge of the carbonic oxide, prepared from recrystallized oxalic acid, was next brought into the dried eudiometer and mixed with an excess of oxygen. The following numbers taken from my laboratory note-book are the measurements made in this experiment with McLeod's form of gas analysis apparatus.

	Line in eudiometer.	Barometer.	Temp. C.	Difference.
		millims.	°	millims.
Dry vacuum	5	536·2	14·13	12·0
[Wet vacuum	5	548·2]		Table 12·0
				Aq. tens.=0·0
On adding carbonic oxide .	5	663·7	14·16	
On adding oxygen	5	905·3	14·18	
This mixture would not explode when sparks were passed through it.				
On adding carbonic oxide .	5	991·4	12·4	
This mixture would not explode when sparks were passed through it.				

A second sample was then brought into the eudiometer—

	Line in eudiometer.	Barometer.	Temperature.	Difference.
		millims.	°	millims.
Dry vacuum	5	537·0	13·4	11·2
				Table 11·4
On adding carbonic oxide .	5	696·2	13·45	
On adding oxygen	5	910·9	13·0	

This mixture would not explode. It was then passed into the laboratory tube and allowed to stand for a few seconds over a drop of water. On returning it to the eudiometer, and again sending a spark through, the mixture exploded.

Since it had been already shown that carbonic oxide is oxidized by steam at a high temperature, it seemed possible that carbonic oxide is incapable of direct union with oxygen, but is burnt indirectly by steam with liberation of hydrogen. The steam would act as a carrier of oxygen to the carbonic oxide by a process of alternate oxidation and reduction, somewhat analogous to that undergone by nitric oxide in the sulphuric acid chamber. I have made many experiments to test this hypothesis, both on account of the interest attaching to such a "catalytic" decomposition among the simplest gaseous bodies, and of its important bearing on the mode of division of the oxygen between the hydrogen and carbonic oxide in incomplete combustions of these gases.

The carbonic oxide used in these experiments was prepared by gently heating recrystallized sodic formate with concentrated sulphuric acid in a glass flask. The gas was passed (1) through a wash-bottle containing a strong solution of potash, (2) through a wash-bottle containing concentrated sulphuric acid, (3) through a U-tube containing fragments of solid caustic potash, and (4) through a U-tube containing fragments of pumice saturated with concentrated sulphuric acid. It was collected over mercury in glass cylinders which had been heated and filled while hot with hot mercury. On exploding 100 volumes of the gas in a wet eudiometer with 156·3 volumes of oxygen a contraction of 50·17 volumes was observed, and on treating the residual gases with potash a further contraction of 100·00 volumes was observed.

The oxygen was prepared by heating re-crystallized potassium chlorate in a piece of combustion tubing drawn out and bent, so that the drawn out end formed a delivery tube which dipped under the surface of mercury. On exploding 100 volumes of the gas with excess of hydrogen a contraction of 300·02 volumes was observed.

The following experiments were conducted in McLeod's form of gas analysis apparatus. A mixture of the two gases in the proportion of 2 volumes carbonic oxide to 1 volume oxygen was kept in a glass cylinder over mercury in contact with a stick of potash. The apparatus, after dried air had been drawn through all its parts for twelve hours, was charged with hot mercury, and then specially dried in the following manner. The water in the glass jacket surrounding the eudiometer and barometer was kept for some hours at a temperature of 90°–95° C., while air, drawn through a nearly horizontal drying tube containing sulphuric acid, was passed by means of a bent glass tube dipping under the surface of the mercury in the trough, through the laboratory tube, eudiometer and barometer, to the top of which an aspirator was attached. The mercury from the reservoir was run up several times into the hot tubes, so as to transfer to the glass any traces of moisture it might carry with it, and more dry air was drawn through the tubes after the mercury had been returned to the reservoir. By reversing the inclination of the sulphuric acid drying tube, the air in the eudiometer was expelled through it without disconnecting the laboratory tube. Finally the bent tube was removed, the air in the laboratory tube drawn over into the eudiometer, and the former, when completely filled with mercury, closed by its stopcock. The laboratory tube and eudiometer were then disconnected, the air in the latter expelled by running up the mercury until drops issued from the steel cap, when the stopcock was turned and the laboratory tube connected up again. The mixture of carbonic oxide and oxygen, prepared as above, was transferred from the glass cylinder to the laboratory tube, and thence was drawn into the eudiometer and placed under a pressure of 250 millims. of mercury, at a temperature of 17° C. On passing a spark from a Leyden-jar through the gases they did not ignite. Several powerful sparks were passed without result, and then the rapid succession of sparks from a Ruhmkorff's coil was employed. At the first discharge the gases ignited and burnt slowly down the tube. The eudiometer was then further dried by drawing through it at 100° C. air which had been passed through two horizontal drying tubes freshly charged with sulphuric acid. Some of the mixture used in the last experiment was passed into the eudiometer, and put under a pressure of 100 millims. (temp. 17°·2 C.). Sparks from the Ruhmkorff coil were passed through it without igniting it. The gases were tested under 150 millims. pressure with the same result. Under 200 millims. the gases did not ignite when a continuous succession of sparks was passed, but the platinum wires became red hot, showing that some local action was produced. Under 250 millims. pressure the gases ignited on passing the spark. The disc of flame took about three seconds to travel down the half-metre of tube filled with the mixture. Some of the same mixture, standing in the laboratory tube, was charged with aqueous vapour by passing a drop of water to the surface of the mercury. It was drawn over into the vacuous eudiometer and put under 150 millims. pressure. On passing a spark from the coil the gases exploded suddenly down the tube. The passage of the flame was too quick to be followed by the eye.

Into a small straight eudiometer, heated and filled while hot with hot mercury, some of the same gaseous mixture was passed up. A little phosphoric oxide [powder] was then introduced into the tube, which was shaken so that the oxide adhered to the sides of the glass. The gases were left standing in the tube for an hour. A spark from a Leyden-jar was then passed between the platinum wires without effecting the ignition of the gases. The gases were under a pressure of 700 millims. Several powerful sparks were passed without any result. A discharge from the coil ignited the gases. This experiment was repeated with the following modifications. Into the gaseous mixture in the small eudiometer was passed up a stick of phosphoric oxide, made by pressing the powder into a short glass tube closed at one end with a cork. To pass up this stick, the glass tube was depressed under the end of the eudiometer, the cork removed, and the phosphoric oxide pushed up by a glass rod. The gases were allowed to stand for two days in contact with the phosphoric oxide, the eudiometer being clamped down on to a caoutchouc cushion under mercury. On passing a spark from a Leyden-jar, no combustion took place. The pressure was 700 millims. The first discharge from the coil caused a very slight combustion near the wires. On loosening the clamp the mercury rose about 2 millims. in the tube. No further combination took place on passing a succession of sparks from the coil. A little water was then introduced by a pipette. The heat evolved on contact of the oxide with the water caused the mixture to explode with a bright and sudden flash.

It appears from these experiments that the greater the degree of dryness reached, the greater pressure the gases can withstand without entering into explosive combination when an electric spark is passed through them.

An attempt was next made to dry the gases and tubes more thoroughly. A mixture of the two gases in the same proportions, and prepared in the same way, was placed in a glass gasholder over concentrated sulphuric acid. The explosion tubes, each drawn out at one end, and fitted at the other with a caoutchouc stopper and glass tube, were joined together by short pieces of india-rubber tubing. They were then strongly heated, while air, previously dried by passing through a horizontal sulphuric acid tube, was aspirated through them. When cool, the stopper of each was removed, a plug of freshly-packed phosphoric oxide quickly pushed in, and the stopper immediately replaced. The tubes were then drawn out near the stoppered end in the blow-pipe flame. They were then reconnected by short pieces of tubing. Between the gasholder and the first explosion tube a drying tube packed with phosphoric oxide was placed; the last explosion tube was connected with a delivery tube, opening under strong sulphuric acid in a wash-bottle. The mixture of gases was then forced through the tubes, and when about a litre had been allowed to escape from the wash-bottle, the counterpoise of the gasholder was so adjusted that the pressure in the tubes was a little less than the pressure of the atmosphere. A fine BUNSEN flame was then brought to bear upon the capillary portions of the tubes until the sides fell in under the external pressure, whereupon the glass was melted and drawn out. This operation was found to be far from easy; more than half the tubes so charged were fired during the sealing, owing to the contact of the insufficiently dried gases with the heated glass. I tried in vain to seal up damp tubes filled with the same mixture; the gases always exploded when the fine glass tubes got red hot. About half the samples of carbonic oxide and oxygen sealed up with phosphoric oxide were unaffected when a succession of sparks from a coil was passed through them a few hours afterwards.* The other half ignited after the discharge had been passing for a few seconds. In some cases this appeared to be due to some phosphoric oxide having been shaken on to the platinum wires, which gave off moisture when heated by the discharge. In other cases, I believe, the ignition was due to the platinum wires themselves, when heated by the discharge, giving up occluded hydrogen, which uniting with the oxygen present supplied the steam necessary for the combustion.

An easier method of drying the gases was next adopted with complete success. A glass tube about 600 millims. long was closed at one end, and at a point 100 millims. from the open end it was bent at an angle of 60°. Near the closed end two long and thick platinum wires, ending in balls of platinum about 2 millims. in diameter, were fused through the glass. Between these balls sparks could be passed from a jar or a coil without appreciably raising their temperature. The bent tube was heated and filled with hot mercury. The mixture of carbonic oxide and oxygen was then introduced from the gasholder by a fine glass tube passing down through the mercury in the shorter arm. When the longer arm was nearly filled with the mixture, a freshly packed stick of phosphoric oxide was introduced into the gases, and the open end closed with a caoutchouc stopper. The mixture of gases was thus separated from the air by some six or eight inches of mercury and the caoutchouc stopper. After standing for twenty-four hours, the mixture was unaffected by a torrent of sparks from a powerful coil. In one of these tubes I have submitted the gases to a pressure of 800 millims., and passed a discharge without igniting them. On passing up some water through the mercury by a pipette and allowing the vapour to diffuse, the mixture was rendered explosive.

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* Four of these tubes were exhibited before the Chemical Section of the British Association at Swansea in 1880. When tested with sparks from a Leyden-jar no action was observed; with a discharge from the coil the wires became red-hot, but the gases did not explode.

I gratefully acknowledge the valuable help given me by Mr. S. E. MILLER, laboratory assistant at Christ Church, in charging these tubes.

Dr. BÖTSCH* in a dissertation read at Tubingen has denied the fact (briefly announced by me in 1880) that the absence of steam prevents the combination of carbonic oxide and oxygen by the spark. He states that he has repeated the experiment, and the mixture exploded, "even when dried by phosphoric oxide." He found that by sufficiently reducing the pressure he could prevent the propagation of the explosion, both in the wet and dry gases. He suggests as an explanation of my results that the dry gases were tested under a less pressure than the wet gases. From the detailed account I have given above, it is evident that Dr. BÖTSCH's explanation does not account for the facts observed. I conclude that he failed to obtain the same result by not leaving the mixture long enough in contact with dry phosphoric oxide. I may add that during the last two years, several of my pupils have repeated the experiment in the Balliol College laboratory, so that the fact of the non-inflammability of the dry gases when submitted to an electric spark under ordinary pressure and temperature, may fairly be considered beyond the possibility of doubt.

Experiments have already been described in which the addition of water to a non-explosive mixture of carbonic oxide and oxygen has rendered it explosive. Into one of the explosion tubes above described a piece of potash (previously fused and heated to redness in a silver boat, and allowed to cool in a desiccator) was introduced. It was fused to the glass at the top of the tube above the platinum wires. The phosphoric oxide was then introduced, the tube was drawn out to a capillary end in the blowpipe and charged with the mixture. It was then sealed up in the flame and allowed to stand. After two days the gases were tested with a succession of sparks without exploding. The potash was then gently warmed by applying a BUNSEN flame to the top of the tube. On passing a spark, a flame passed up from the platinum wires to the top of the tube. After standing an hour it was again tested with a spark. No explosion took place. On heating the potash rather strongly and passing another spark a flame passed up from the platinum wires to the top of the tube, and downwards about half the length of the tube. After the tube had stood about two hours longer, a third flame was produced on reheating the potash and passing a spark.

To try what effect the admixture of small quantities of different gases had on the determination of the explosion, some of the mixture of carbonic oxide and oxygen previously used was brought over into the eudiometer of McLEOD's apparatus, which had been dried at 100° C. Under 300 millims. pressure the mixture did not explode on passing through it a succession of sparks. A little carbonic acid gas, dried over phosphoric oxide, was introduced. The spark was passed without causing an explosion. A fresh charge of carbonic oxide and oxygen was brought into the eudiometer, and a small quantity of cyanogen, dried over phosphoric oxide, introduced. The spark did not cause an explosion under 300 millims. pressure. A fresh portion of the same mixture, with a small quantity of dry air, was tested under the same pressure with

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* LIEBIG's Annalen, 1882.

the same result. Similarly, small quantities of dry nitrous oxide and dry carbon bisulphide were found not to render the mixture inflammable. A small quantity of hydrogen dried over phosphoric oxide, occupying about $\frac{1}{800}$ of the total volume of the gases, was next introduced into a fresh portion of the dry mixture. On passing a spark under 300 millims. pressure, the gases ignited and burnt rather slowly down the tube. After the apparatus had been re-dried some of the same mixture of carbonic oxide and oxygen was introduced into the laboratory tube, and a portion of it was drawn over into the eudiometer and tested by a spark under 300 millims. pressure, without ignition. A drop of ether was then passed up into the laboratory tube; a very small quantity of the mixed gases, charged with ether vapour, was drawn over into the eudiometer. After the gases had been allowed to interdiffuse for an hour, the passage of the spark caused an explosion under 250 millims. pressure. Similarly a trace of the vapour of the hydrocarbon pentane rendered the mixture explosive. In the same way I have found that both a trace of dry hydric chloride gas and a trace of dry sulphuretted hydrogen gas render a non-inflammable mixture of carbonic oxide and oxygen explosive.

From these experiments it appears that the non-explosive mixture of carbonic oxide and oxygen is rendered explosive not only by the presence of a trace of steam, but by traces of other bodies containing hydrogen which react with oxygen to produce steam. Nitrogen, cyanogen, nitrous oxide, carbon bisulphide, and carbonic acid do not confer inflammability on the mixture. To test the effect of the presence of steam on other gaseous mixtures, I made some comparative experiments on dry and wet mixtures of hydrogen and oxygen obtained by the electrolysis of dilute sulphuric acid. Into the carefully dried eudiometer of McLEOD's apparatus a mixture of equal volumes of air and electrolytic gas, which had been standing for some days over phosphoric oxide, was introduced. Beginning at 20 millims., the pressure was increased 5 millims. at a time until the gases exploded. The dry mixture did not explode under 70 millims.; it did explode under 75 millims. The residue was run out and a fresh portion of the same mixture introduced into the damp tube. Beginning at 20 millims., the pressure was increased by 5 millims. at a time until the gases exploded. The damp mixture did not explode under 70 millims.; it did explode under 75 millims.* The union of oxygen and hydrogen is therefore not affected by the presence or absence of water. On the other hand, a mixture of cyanogen with ten volumes of air, which had stood over phosphoric oxide, did not explode when the pressure was raised step by step from 100 millims. to 800 millims. in the dry eudiometer. On addition of aqueous vapour the mixture did not explode under 300 millims., but did explode under 305 millims. I am inclined to think that cyanogen undergoes oxidation in the same way as carbonic oxide, through the medium of steam.

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* *Note added Dec.*, 1884.—LOTHAR MEYER and K. SEUBERT (Journ. Chem. Soc., Oct., 1884) find that electrolytic gas is only partially burnt when a spark from a RUHMKORFF coil is passed through it under a pressure of 70·5 millims.; at 72 millims. pressure the combustion is complete.

Mention has been made of the slowness with which the flame travels down the explosion tube when a mixture of carbonic oxide and oxygen in a state of comparative dryness is ignited. To obtain some idea of the rate of propagation of explosion under these conditions, some of the mixture of carbonic oxide and oxygen was brought into the well-dried eudiometer of the gas apparatus. A loud-beating seconds' pendulum was set going close by, and a spark sent from the coil as a second struck. By watching at the level of the mercury below and listening to the beats of the pendulum, the passage of the flame could be roughly timed. Beginning at 260 millims., the pressure was raised 20 millims. between each passage of the spark. The gases withstood 480 millims. pressure without igniting; at 500 millims. pressure they ignited. The flame was timed to pass down the 360 millims. between the wires and the surface of the mercury in $2\frac{1}{4}$ seconds. The eudiometer was re-charged, a drop of water passed over and the gases fired under 500 millims. pressure. The passage of the flame appeared instantaneous.

An attempt was made to measure the effect of different quantities of steam on the rate of propagation of the explosion. This was done by comparing the pressures produced in the tube when equal masses of carbonic oxide and oxygen were successively exploded at the same temperature and pressure with different amounts of aqueous vapour. Since the total quantity of heat evolved in each explosion was the same, and the cooling surface was the same in each experiment, a quicker explosion would bring the column of gases to a higher average temperature than a slower explosion, and would therefore cause a sharper push on the mercury column. If a sufficiently sensitive gauge were attached to the eudiometer, its readings would give comparative indications of the rate of explosion of the carbonic oxide and oxygen. Near the bottom of the eudiometer in which the gases were exploded, a self-registering pressure gauge was attached by a strong glass tube. The gauge (of 1 millim. bore) contained air in the closed limb over mercury. An index, similar to those used in SIX's thermometer, was carried up and left at the highest position reached by the mercury. Near the bend of the gauge two bulbs were blown in the tube as reservoirs, enabling the mercury to be lowered in the eudiometer without permitting the air to escape from the closed limb of the gauge. This gauge was found to be not very sensitive, but the difference between its readings (1) with the slow combustion of the nearly dry gases, and (2) with the rapid explosion of the gases saturated with steam, was well marked.

In two experiments a trace only of aqueous vapour was present. The eudiometer was dried at 80° C., by drawing through it for half an hour air which had passed through two long sulphuric-acid drying tubes and a small tube containing phosphoric oxide. It was found that by this method of drying just sufficient aqueous vapour remained in the tube to enable the combustion to take place slowly when sparks from a RUHMKORFF's coil were passed through the gases. In the first experiment several sparks were passed before the gases took fire. In both experiments the disc of flame occupied about two seconds in passing down the length of 500 millims. occupied by the gases in the eudiometer. In three other experiments measured quantities of aqueous vapour were added short of saturation; in the last two experiments the aqueous vapour was at maximum tension, and the sides of the eudiometer were wet. Before each explosion the mercury in the gauge was brought to the mark 229 on the scale, which indicated a pressure of 533 millims. of mercury on the air in the closed limb.

The following table gives the quantities of aqueous vapour in each experiment, the readings of the pressure gauge, and the pressures corresponding to those readings.

TABLE IV.—Pressures produced by the explosion of carbonic oxide and oxygen with varying quantities of steam.

No.	Tension of carbonic oxide and oxygen.	Tension of aqueous vapour.	Reading of pressure gauge before explosion.	Reading of pressure gauge after explosion.	Increase of pressure registered in gauge.	Temperature of gases.	Length of column of gases exploded.
	millims.	millims.			millims.	° C.	
1	200	Trace	229	236	29	33	500
2	,,	Trace	,,	236·2	30	33·2	500
3	,,	8·7	,,	249·2	87	33	505
4	,,	9·4	,,	249·6	89	33·5	505
5	,,	15	,,	249·4	88	34	514
6	,,	38	,,	252·6	105	33·3	524
7	,,	40	,,	252·6	105	34	525

These experiments show very plainly the increased rapidity of the propagation of the explosion produced by the addition of steam to the mixture of carbonic oxide and oxygen. With the exception of the 5th experiment the pressures registered mount up regularly with the increase of aqueous tension in the eudiometer.

During the last three years several most interesting and ingeniously devised series of experiments have been brought before the French Academy of Sciences by MM. BERTHELOT and VIEILLE, and by MM. MALLARD and LE CHATELIER on the velocity of explosion of gases. They have shown the velocity to be far in excess of the rates previously assigned. The old determinations of BUNSEN gave for the velocity of explosion of electrolytic gas 34 metres per second, and for carbonic oxide and oxygen 1 metre per second. These numbers must be multiplied a thousandfold. MM. BERTHELOT and VIEILLE * have shown that the explosion of any particular mixture of gases in a tube begins slowly, increases in velocity, and finally gives rise to an "explosive wave," which is propagated at a uniform rate. This rate is independent of the pressure and the diameter of the tube, but varies when different explosive mixtures are used. The experiments were made on different explosive mixtures in a tube 40 metres long. They found the velocity of the explosive wave to be a close approximation to the mean velocity of translation of the molecules in the gaseous products of combustion calculated from the formula of CLAUSIUS.

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* Comptes Rendus, xcv., 151.

$$v = 29\cdot354 \sqrt{\frac{\tau}{\alpha}}$$

where τ is the absolute temperature, calculated on the assumption that the molecules contain all the heat disengaged in the reaction, and α is the mean density of the gases remaining after combustion.

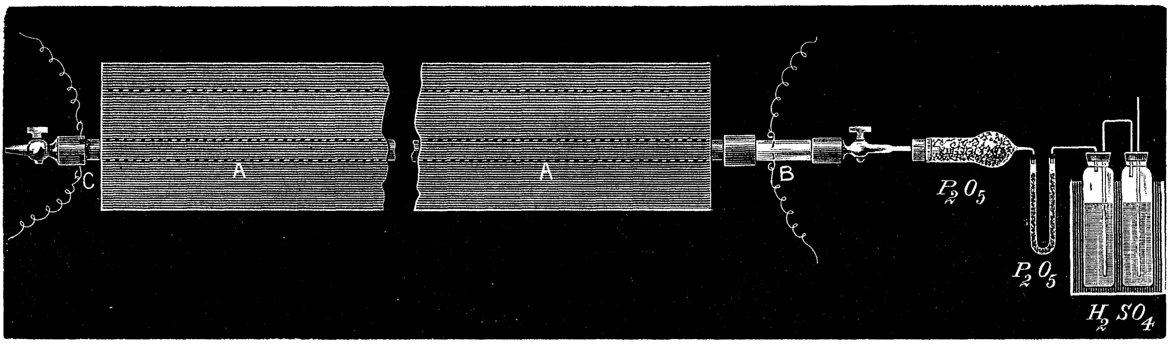
The rate of explosion and the calculated velocity of the gaseous molecules agree fairly well in the case of hydrogen and the simpler hydrocarbons exploded with oxygen. For instance, they find the velocity of explosion of electrolytic gas to be 2810 metres per second, the "theoretical velocity" being 2831 metres per second. But with carbonic oxide the velocity observed is only 1090 metres per second, the calculated velocity being 1940. This gas they consider, therefore, to be an exception to the general rule. When, however, a mixture of carbonic oxide and hydrogen is exploded with oxygen, they find the observed velocity of explosion to approximate to the calculated velocity, and explain the fact by supposing the hydrogen to communicate to the carbonic oxide a law of detonation analogous to its own. With mixtures of carbonic oxide and nitrous oxide, a similar divergence between the calculated and observed velocities of explosion is found, whereas with hydrogen and other gases containing hydrogen, exploded with nitrous oxide, there is a very close agreement between the observed and calculated velocities. BERTHELOT *and* VIEILLE *dried the explosion tube before each experiment, and employed dry gases.* In their experiments with hydrogen and oxygen they found that the rate of the explosive wave was independent of the material of the tube, and of its diameter above 5 millims. The velocity was the same whether the tube was curved or straight. The maximum velocity was attained only after the explosion had travelled between 50 and 500 millims. from the spark. The "variable state" preceding the régime of the explosive wave differed according to the strength of the spark employed to fire the mixture. The velocity of explosion was determined by making the flame break two thin strips of tin, stretched across the explosion tube near either end, each strip forming part of one of the circuits of a BOULENGÉ chronograph. A grain of fulminate was folded in the strips to ensure their being broken by the flame. BERTHELOT and VIEILLE have published no experiments on the duration of the variable state preceding the establishment of the explosive wave with carbonic oxide and oxygen.

Measurement of the initial velocity of explosion of carbonic oxide and oxygen.

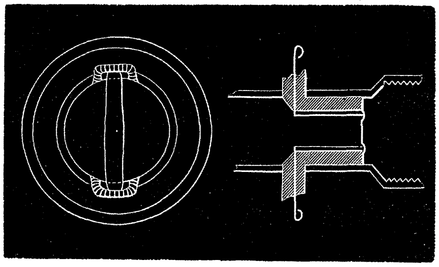
To determine directly the initial velocity of explosion of carbonic oxide and oxygen from the point of ignition, with varying quantities of aqueous vapour, the following apparatus was employed :—

A is a brass pipe of 13 millims. internal diameter soldered into a metal trough, so that each end projected a short distance from the end of the trough. To one end of the brass tube the firing piece B was cemented. This consisted of a short thick glass tube in which were sealed two platinum wires connected with the secondary coil of a large

Ruhmkorff, and of a short brass tube and tap for admitting the gases. To the other end of the brass pipe was screwed the cap C containing the metallic bridge to be broken by the explosion: this consisted of a thin strip of silver foil soldered with fusible metal on to two insulated brass pieces let into two vulcanite plugs, one on each side of the cap. The silver strip was sufficiently thick to convey the current of one Grove cell without becoming heated. No fulminate or other explosive was employed. The silver strip was invariably broken by the flame. The distance from the platinum wires to the silver bridge was 1·049 metre. In the circuit, of which the silver strip formed a portion, a chronograph was inserted. This consisted of two small electromagnets which, when the current was flowing, held down a style against a spring. The chronograph was adjusted so that the end of the style pressed lightly against the blackened surface of a glass plate carried by a heavy pendulum. The pendulum, at the lowest point of its swing, overturned a brass upright moving on a horizontal axis, and so broke the primary coil of the Ruhmkorff, inducing a direct current in the secondary coil. This induced current caused a spark between the platinum wires which fired the explosive mixture. Until the explosion reached the silver foil the style continued to describe an arc of a circle on the moving blackened plate. When the silver was broken, the style, released from the magnet, sprang upwards, marking the moment of interruption. To correct for the error due to the retardation of the chronograph a blank experiment was always made immediately before firing the mixture. The wires of the chronograph were attached to the break of the primary coil of the Ruhmkorff, so that the circuit was completed through this break instead of through the silver foil.



Arrangement of Explosion Tube.



Plan of cap C. Section of cap C.

On allowing the pendulum to fall the style registered a mark on the moving plate when the circuit was broken. Without moving the chronograph the wires were readjusted, and the explosion made. The distance between the two marks on the blackened plate gave the time which elapsed between the breaking of the primary coil of the RUHMKORFF and the rupture of the silver foil by the explosion, independently of the error of the chronograph; for the position of both marks was affected equally by the retardation of the electro-magnet. The rate of the pendulum, and therefore the interval of time corresponding to the two marks, was determined by taking the trace of a standard tuning fork on the blackened plate allowed to fall from the same height. By filling the trough with water and heating it with two argand burners, the explosion tube could be kept at any desired temperature.

Three sets of experiments were made, one at 10° C., the second at 35° C., and the third at 60° C. The mixture of gases, containing two volumes of carbonic oxide to one volume of oxygen, was contained in a copper holder over water. After the explosion tube had been dried by heating and drawing through it for some hours air which had passed through three long tubes containing pumice saturated with oil of vitriol, the mixture of carbonic oxide and oxygen was driven slowly into the tube, (1) through two sulphuric acid drying tubes, and (2) through two long tubes containing anhydrous phosphoric acid. When two or three litres of the mixture had been driven through the tube, the stopcocks at both ends were closed and the mixture fired at a temperature of 10° and under the atmospheric pressure. The interval between the spark and the rupture of the silver foil was found to be ·0291 second, giving a mean velocity of 36 metres per second. The tube was then heated to 35° by means of warm water in the trough, and some more of the same mixture was driven in through the same drying tubes. The gases fired at 35° had a mean velocity of explosion of 69 metres per second. On recharging the drying tubes with fresh phosphoric acid and repeating the experiment at 35° the mean velocity of explosion was found to be 44 metres per second. With the same drying tubes as in the last experiment the mean velocity at 60° was found to be 53 metres per second.

When the mixture was made to bubble through two sulphuric acid wash-bottles only, a far higher velocity was obtained. At 10° C. the mean velocity was found to be 119 metres, at 35° C. 103 metres and 102 metres, and at 60° C. 120 metres per second.

When the mixture was exploded at 10° C. and saturated with steam at that temperature a mean velocity of 175 metres was reached. At 10° C., therefore, the velocity of explosion of carbonic oxide and oxygen under atmospheric pressure is greatest when it is saturated with steam. At 35° C. a similar result was found. In three successive experiments the mixture was driven into the warm tube through a wash-bottle containing water at 6°, 8°, and 12° C. respectively. The velocity of explosion increased with the quantity of steam present. When saturated with steam at 35° C. the mixture gave a velocity of 225 metres per second. When the tube was heated to 60° C., and the mixture driven in over water at different temperatures, the velocity of explosion increased with the quantity of steam added. When the mixture was saturated with steam at 60° C. the mean velocity was 317 metres per second. The following table gives the results of these experiments :—

TABLE V.—Mean rate of explosion of carbonic oxide and oxygen through one metre with different quantities of aqueous vapour under atmospheric pressure.

Exploded at 10° C.		Exploded at 35° C.		Exploded at 60° C.	
Hygrometric state.	Rate in metres per second.	Hygrometric state.	Rate in metres per second.	Hygrometric state.	Rate in metres per second.
Dried by passing slowly over fresh P_2O_5	36	Dried by passing slowly over fresh P_2O_5	44	Dried by passing slowly over P_2O_5 used before	53
		Dried by passing slowly over P_2O_5 used before	69		
Dried by bubbling through two bottles of H_2SO_4	119	Dried by bubbling through two bottles of H_2SO_4	102	Dried by bubbling through two bottles of H_2SO_4	120
		” ”	103		
		Saturated at 6° . . .	129		
		” ” . . .	123		
		Saturated at 8° . . .	155	Saturated at 8° . . .	158
				” ” . . .	166
Saturated at 10° . . .	175				
” ” . . .	176				
		Saturated at 12° . . .	200	Saturated at 12° . . .	211
		Saturated at 35° . . .	225	Saturated at 35° . . .	244
		” ” . . .	226		
				Saturated at 50° . . .	289
				Saturated at 60° . . .	317

In each series of experiments the *initial velocity* of explosion of a mixture of carbonic oxide and oxygen is seen to increase with successive additions of steam. It is this initial velocity with which we have to deal in experiments with an ordinary eudiometer. When a mixture composed of two volumes of carbonic oxide and one volume of oxygen, saturated with steam at 10°, is exploded under atmospheric pressure, the velocity of the explosion increases rapidly from the point of inflammation. In a tube of 13 millims. diameter and 55 metres long the rate of explosion is found to be constant after travelling 700 millims. along the tube; the constant velocity of the "explosive wave" attained under these conditions being rather over 1500 metres per second. At the extremely high temperature accompanying the explosive wave, carbonic oxide is possibly decomposed; after the explosion the tube is found coated with a very fine layer of carbon. Whether under these conditions steam is necessary for the propagation of the explosive wave is doubtful, it is possible that the initial reaction between the carbonic oxide, steam, and oxygen increasing in velocity as the flame travels down the tube, produces at last a temperature at which a new reaction is determined. But such conditions do not occur in the partial burning of the comparatively short columns of gases that have been employed in researches on the incomplete combustion of gases.

The result of these various experiments may be thus summarised:—

1. The drier the mixture of carbonic oxide and oxygen, the greater the pressure it can withstand without igniting when a spark is passed through it.

2. The addition of a trace of aqueous vapour to the non-inflammable mixture causes it to become inflammable, all other conditions remaining the same.

3. The addition of a trace of hydrogen or of a volatile body containing hydrogen causes the dry mixture to become inflammable, all other conditions remaining the same.

4. The rapidity of explosion of the mixture in a tube one metre long is greater with a large quantity of aqueous vapour than when only a trace is present.

These well-established facts, coupled with the fact that carbonic oxide does decompose steam at a high temperature, appear to me to show conclusively that in the ordinary explosion of carbonic oxide and oxygen, the union is not a direct one, but is effected indirectly by the agency of hydrogen.

In a paper on the alkaline peroxides,* the late Sir B. Brodie has thus described such an indirect action:—"The alkaline peroxides have a double function, and can be used as agents either of oxidation or of reduction. By certain modifications of the conditions of the experiment, we can produce separately either result. It is not unreasonable to suppose that, among the numerous and varied forms of chemical decomposition, instances would be found in which these phenomena would occur simultaneously. If this were to be the case the result would be what is termed a contact or catalytic decomposition, but caused by two successive changes of a normal chemical character."

The action of steam in determining the union of oxygen with carbonic oxide is of this kind; that is to say, when carbonic oxide and oxygen are exploded in a eudiometer, the heat of the spark causes the carbonic oxide in its immediate neighbourhood to decompose the steam usually present, and the hydrogen, liberated by this reaction, unites with the oxygen to re-form steam. The steam so formed reacts with more carbonic oxide, and so the alternate changes go on until all the carbonic oxide is oxidized according to the two equations

$$\begin{aligned} CO + H_2O &= CO_2 + {}_2H \\ 2H_2 + O_2 &= 2H_2O. \end{aligned}$$

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* Phil. Trans., 1860.

The ignition of a mixture of hydrogen and oxygen and of other explosive mixtures by an electric spark, may be stopped either by sufficient rarefaction or sufficient dilution with a neutral gas such as carbonic acid or nitrogen. Probably, in the first case, the mean distance of the molecules is increased to such an extent that the necessary molecular disturbance cannot be communicated from molecule to molecule, and the combustion is confined to the space between the platinum wires; in the second case, the neutral gas both increases the mean distance of the reacting molecules, and also decreases the temperature by absorption of heat. In the reaction under consideration —viz., in a mixture of two volumes of carbonic oxide and one of oxygen—although a single molecule of water should suffice theoretically for the oxidation of any number of carbonic oxide molecules, it is evident that the explosion cannot be propagated unless a certain minimum number of steam molecules are present. For when the mean distance between the water molecules reaches a certain magnitude, each molecule of water becomes surrounded by a crowd of carbonic acid molecules, the product of its action on the carbonic oxide and oxygen under the influence of the electric spark; and the incipient combustion dies out, because fresh molecules of carbonic oxide and oxygen do not come in contact with it while it has still enough kinetic energy to react with them. The slow rate of propagation of explosion in a nearly dry mixture is also readily explained. The carbonic oxide molecules have to wait their turn. Though probably an enormous number of steam molecules are present in the tube, yet since they are *comparatively* very few, each one must do duty a vast number of times. Each steam molecule must in turn present an atom of oxygen to as many molecules of carbonic oxide as the number of times the volume of carbonic oxide exceeds the volume of the steam. Since each reduction and each oxidation of the oxygen-carrier takes time, a given number of carbonic oxide molecules takes longer to burn in presence of a comparatively small than in presence of a comparatively large number of steam molecules.

Explosion of dry carbonic oxide and electrolytic gas.

Having determined the action of aqueous vapour on carbonic oxide at high temperatures, I began in Nov., 1876, a second series of experiments with dry carbonic oxide and electrolytic gas in a well dried eudiometer. After each explosion the residual gas was analysed. Only those experiments were accepted in which the residual analysis confirmed the first part of the operation. The gases were exploded under pressures varying between 200 millims. and 300 millims., and at temperatures between 6° and 11°. The following table gives the composition of the mixtures and the ratio between the carbonic oxide and hydrogen burnt in the several explosions.

TABLE VI.—Explosion of dry carbonic oxide and electrolytic gas.

No.	Combustible gases contain in 100 vols.		Ratio of carbonic acid to water formed $=\frac{CO_2}{H_2O}$.
	Carbonic oxide.	Hydrogen.	
1	83·7	16·3	2·07
2	81·8	18·2	1·77
3	80·8	19·2	1·62
4	78·1	21·9	1·29
5	77·6	22·4	1·27
6	77·4	22·6	1·31
7	75·8	24·2	1·08
8	75·5	24·5	1·05
9	73·4	26·6	·97
10	72·6	27·4	1·00
11	69·3	30·7	·74
12	68·9	31·1	·73
13	66·7	33·3	·74
14	53·5	46·5	·42

While I was making these experiments I heard that Professor HORSTMANN, of Heidelberg, had already published a paper[*] in which he had shown that BUNSEN'S results were vitiated through his having exploded the gases in a eudiometer saturated with aqueous vapour. HORSTMANN had repeated BUNSEN'S experiments using a dry eudiometer. With all mixtures he found less carbonic oxide and more hydrogen burnt than BUNSEN found with similar mixtures. He then made a series with a wet eudiometer and found that when water was present more carbonic oxide and less hydrogen was burnt than when the gases were dry. He concluded rightly that some of the steam already present was reduced during the explosion by the excess of carbonic oxide. He then showed, by making comparative experiments with and without the previous addition of carbonic acid, that a similar action takes place between the carbonic acid added and the excess of hydrogen. With mixtures of carbonic oxide and electrolytic gas, less carbonic oxide and more hydrogen is burnt when carbonic acid is added to the mixture before explosion.

In these experiments HORSTMANN proved conclusively that the alteration in the proportion of carbonic oxide and hydrogen burnt took place gradually and not *per saltum*. To compare HORSTMANN'S results with mine, I have interpolated from the curve given in his paper the ratios of carbonic acid to water formed by explosion of mixtures of similar composition to mine. These ratios I found to be always smaller than those I had obtained. In the last column of the table I have compared in a similar way the new set of experiments given by BUNSEN[*] in the second edition of his "Gasometry." This series was made with *dry* gases which were exploded by a chain of sparks simultaneously sent through the length of the eudiometer. By fusing short

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[*] Verh. des Heidelb. naturf. med. Vereins, N.S., I., 3.

[†] Gasometrische Methoden, II^{te}. Auflage. 1877.

pieces of platinum wire into small glass beads, BUNSEN constructed a chain of alternate links of metal and glass, each piece of platinum being insulated from its neighbours by a glass bead round which the spark passed when the two ends of the chain were connected with an electrical machine. This chain was fastened to two platinum wires fused through the glass near the top and bottom of the eudiometer. The object of this mode of ignition was to prevent the formation of an "air-wave" down the tube and the consequent compression of the still unburnt gases by the expansion of the burning gases above. The results obtained in this way by BUNSEN agree well with those obtained by HORSTMANN. My experiments show a greater proportion of carbonic oxide burnt in every case.

TABLE VII.—Explosion of dry carbonic oxide and electrolytic gas.

No.	Combustible gases contain in 100 vols.		Ratio of carbonic acid to water formed $=\frac{CO_2}{H_2O}$		
	Carbonic oxide.	Hydrogen.	DIXON.	HORSTMANN.	BUNSEN. (new experiments.)
1	83·7	16·3	2·07	..	..
2	81·8	18·2	1·77	1·52	..
3	80·8	19·2	1·62	1·43	..
4	78·1	21·9	1·29	1·14	1·15
5	77·6	22·4	1·27	1·09	1·12
6	77·4	22·6	1·31	1·08	1·11
7	75·8	24·2	1·08	·95	1·01
8	75·5	24·5	1·05	·94	·99
9	73·4	26·6	·97	·88	·89
10	72·6	27·4	1·00	·81	·84
11	69·3	30·7	·74	·70	·74
12	68·9	31·1	·73	·69	·73
13	66·7	33·3	·74	·63	·70
14	53·5	46·5	·42	·41	..

The chief differences in the condition of the gases in the three series of experiments tabulated above lay in the initial pressure under which they were exploded, and in the length of the path traversed by the flame from the point of ignition. In my experiments the pressures were between 200 millims. and 300 millims.; in HORSTMANN'S experiments the pressures were between 360 millims. and 480 millims.; and in BUNSEN'S between 600 millims. and 650 millims. To determine what difference, if any, is produced in the division of the oxygen by a variation of (1) the initial pressure, and (2) the length of the column of gases along which the explosion is propagated, a fresh series of experiments was begun in the autumn of 1877.

Experiments on the influence of initial pressure and of the length of the column of the gases on the division of the oxygen.

In the first experiment a mixture of carbonic oxide and electrolytic gas, containing 70 parts of carbonic oxide to 30 of hydrogen, was exploded in two portions, the first under 120 millims. pressure and the second under 400 millims. pressure. In the first portion the ratio of carbonic acid to steam produced was 1·2, and in the second portion ·8. A nearly similar mixture was divided into three portions. The first, exploded under 100 millims. pressure, gave 1·24 for the ratio $\frac{CO_2}{H_2O}$; the second, exploded under the same pressure, but only forming a column half as long as the first portion, gave 1·06 for the ratio $\frac{CO_2}{H_2O}$; the third, forming a column equal to the first, but exploded under 225 millims. pressure, gave ·85 for the ratio.

A set of experiments was then made with different portions of the same mixture under nearly constant conditions of temperature and pressure, but with variations in the length of the column of exploded gases.

In these and all the subsequent experiments the following method of drying the apparatus, charging the eudiometer and calculating the results, was adopted. The whole apparatus being emptied of mercury, air was drawn for twelve hours by a pump attached to the top of the barometer, through two long horizontal drying tubes charged with oil of vitriol, through a bent tube passing under the mercury in the trough and opening into the laboratory tube, thence through the capillary connecting tubes down the eudiometer and up the barometer. The taps at the top of the barometer and at the bottom of the eudiometer were then closed and the drying tubes were attached to the mercury reservoir. Dry air was then drawn for some hours through the reservoir and long connecting tube, and up the barometer. The mouth of the reservoir being closed, the drying tubes were again connected with the laboratory tube, and dry air was drawn through the eudiometer and barometer while the water in the jacket surrounding them was heated to 90°–100° C. After some time the tap at the top of the barometer was closed and hot mercury poured into the reservoir. By raising the reservoir the hot air in the eudiometer and barometer was expelled. The reservoir was lowered until the eudiometer and barometer were empty. As the mercury ran down, bubbles of air always rose from the sides of the tubes and from the lower tube connected with the reservoir. The lower stopcock being closed the air remaining in the laboratory tube was allowed to pass over into the eudiometer, the laboratory tube being thus completely filled with dry mercury. The mercury was again run up to the top of the eudiometer and barometer and the air expelled, and once more the mercury was run down to extract bubbles of air sticking to the glass. On again running up the mercury and letting it overflow from the barometer and eudiometer all traces of air were got rid of. The hot water in the jacket was then replaced by a constant current of cold water from the main, running into the cylinder near the bottom and being siphoned off at the top. In the experiments made at ordinary temperatures a drop of water was drawn into the top of the barometer and the space thus saturated with aqueous vapour, while the eudiometer remained dry. On lowering the mercury in the two tubes, the level stood lower in the barometer than in the eudiometer by the difference of aqueous tension in the two tubes. By comparing this difference with the values given in REGNAULT'S table for the aqueous tension at the particular temperature observed, the dryness of the eudiometer was verified.

The carbonic oxide was prepared from magnesium formate by the action of sulphuric acid. It was passed through a small wash-bottle containing a strong solution of potash, thence through a U-tube containing fragments of caustic potash, and collected over hot mercury in cylinders of glass containing phosphoric oxide. As I found that a trace of air was always introduced with the sticks of compressed oxide, I allowed the gas to stand some time in each cylinder with the oxide, and then poured it away by inclining the tube under the surface of mercury, leaving the stick of oxide in the tube. The tubes were then filled with the gas used in the experiments, and were used over and over again for collecting the gas without being recharged with phosphoric oxide. The hydrogen was prepared by the electrolysis of dilute sulphuric acid, an amalgam of zinc and mercury being employed for the positive electrode. The gas was collected and dried in the same way as the carbonic oxide. The oxygen was prepared by heating re-crystallised and well-dried potassic chlorate in a bent tube dipping under mercury. The oxygen and the electrolytic gas were collected over mercury and dried in the same way.

After the explosion of the gases and the absorption of carbonic acid formed, the residue was exploded with an excess of oxygen, and the contraction on explosion and subsequent treatment with potash observed. The two portions of the experiment together made a complete analysis of the original mixture, which served to control the result of each part of the experiment. In calculating the results, the measurement of the gases originally taken and the analysis of the residual mixture were taken to give an independent determination of the quantity of each gas burnt in the first explosion, and the mean of these two determinations was taken as the correct number.

The following table contains the results of the experiments made to test the effect of varying the length of the column of gases exploded:—

Composition of Mixture.

Carbonic oxide	67·10
Hydrogen	21·91
Oxygen	11·09
	100·00

TABLE VIII.

*Reference number.	Length of column.	Ratio $\frac{CO_2}{H_2O}$	Temperature.	Pressure.
	millims.		° C.	
1	200	1·17	10·5	210
2	300	1·17	9·7	210
3	300	1·19	11·1	210
4	400	1·21	10·5	210
5	400	1·21	11·1	210
6	600	1·24	10·3	210
7	800	1·32	10·3	200
8	400	1·33	85·	200

In this set of experiments the proportion of carbonic oxide burnt gradually increases as the length of the path of the explosion is increased. It is evident, therefore, that under pressures as low as 200 millims., one of the conditions which affects the division of the oxygen is the shape of the vessel containing the gases. In the last experiment the gases were fired at a temperature of 85° C. The increase of initial temperature acts in the same way as an increase in the length of the columns.

A second series of experiments was then made with another mixture containing equal volumes of carbonic oxide and electrolytic gas. Portions of this mixture were exploded alternately at the line 200 in the eudiometer and between the lines 700 and 800. The pressure in every case was 250 millims., the temperature near 10° C.

Composition of Mixture.

Carbonic oxide	49·60
Hydrogen.	33·52
Oxygen	16·88
	100·00

TABLE IX.

Reference number.	Length of column.	Ratio $\frac{CO_2}{H_2O}$	Temperature.	Reference number.	Length of column.	Ratio $\frac{CO_2}{H_2O}$	Temperature.
	millims.		° C.		millims.		° C.
9	200	·52	10·5	13	700	·55	9·6
10	200	·53	10·1	14	800	·54	10·5
11	200	·53	9	15	750	·545	9·5
12	200	·52	10·5				
	200	Mean ·525			Mean 750	Mean ·545	

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* In this and in the subsequent tables each experiment is marked by a "Reference number." Under the same number in the Appendix the details of that experiment will be found.

In this series a slight difference is produced by a change in the length of column. The difference is in the same direction, but not so well marked as in the previous experiments, in which the mixture was poorer in oxygen and was fired under 50 millims. less pressure. It seemed likely that with higher initial pressures or with more oxygen the difference would disappear altogether.

To test this point another mixture was made still richer in electrolytic gas, and was exploded alternately near lines 200 and 800 in the eudiometer, under 250 millims. pressure and between 6°·7 and 9° C.

Composition of Mixture.

Carbonic oxide	41·02
Hydrogen	39·28
Oxygen	19·70
	100·00

TABLE X.—AT 250 millims. pressure.

Reference No.	Length of column.	Ratio $\frac{CO_2}{H_2O}$	Temperature.
	millims.		° C.
16	200	·39	9·0
17	200	·385	7·4
18	800	·385	7·9
19	800	·39	6·7

These experiments show that with mixtures containing 20 per cent. of oxygen under 250 millims. pressure, the division of the oxygen is independent of changes in the length of the column of gases. But with a lower initial pressure, this mixture is susceptible to an alteration in the length of column, as is shown by the following experiments:—A portion of the mixture was exploded under 100 millims. pressure, at the line 300; and a second portion was exploded under 100 millims. pressure, at the line 800.

TABLE XI.—At 100 millims. pressure.

Reference No.	Length of column.	Ratio $\frac{CO_2}{H_2O}$	Temperature.
	millims.		° C.
20	300	·42	8·6
21	800	·45	9·8

It appears from these series of experiments that for a given mixture of carbonic oxide and electrolytic gas, a change in the length of column causes an alteration in the division of the oxygen between the combustible gases so long as the pressure is kept below a certain limit. The lower the pressure below this limit the greater is the change produced. The limit varies with different mixtures: when a small percentage of oxygen is present the limit is higher than when the mixture is richer in oxygen. With pressures in excess of this limit no alteration is produced in the division of the oxygen by changes in the length of the column.

To determine what is the effect produced by a change of initial pressure alone on the proportion of carbonic oxide and oxygen burnt with the same length of column and at the same temperature, a series of experiments was made with portions of one mixture, starting at the lowest pressure at which the explosion was propagated, and increasing the pressure up to 600 millims.

COMPOSITION of mixture.

Carbonic oxide	61·64
Hydrogen	25·50
Oxygen	12·86
	100·00

This mixture would not explode under 50 millims. or under 60 millims. pressure. It exploded under a pressure of 75 millims.

TABLE XII.—Experiments at different pressures. Length of column =450 millims.

Reference No.	Pressures.	Ratio $\frac{CO_2}{H_2O}$	Temperature.
	millims.		° C.
22	75	1·27	6·5
23	100	1·21	5·6
24	125	1·01	6·4
25	150	·95	6·5
26	200	·92	5·8
27	300	·85	6·9
28	425	·81	7·0
29	600	·82	6·4

From this table it appears that, as the pressure is increased, less carbonic oxide and more hydrogen is burnt until a pressure of about 400 millims. is reached, after which a further increase of pressure makes no difference in the division of the oxygen. To establish this important point more surely, a second series of experiments was performed in a similar way. Different portions of a mixture were exploded between the lines 400 and 500 on the eudiometer, under pressures varying from 75 millims. to 1000 millims.

COMPOSITION of mixture.

Carbonic oxide	63·31
Hydrogen	24·40
Oxygen	12·29
	100·00

Experiments at different pressures. Length of column =450 millims.

TABLE XIII.—Pressure 75 millims.

Reference No.	Pressure.	Ratio $\frac{CO_2}{H_2O}$	Temperature.
	millims.		° C.
30	75	1·36	15·7
31	,,	1·46	16·6
32	,,	1·43	15·0
33	,,	1·38	14·3
34	,,	1·45	14·0
35	,,	1·36	13·2
36	,,	1·35	14·2
37	,,	1·37	14·5
	75	Mean 1·395	

TABLE XIV.—Pressure 100 millims.

Reference No.	Pressure.	Ratio $\frac{CO_2}{H_2O}$	Temperature.
	millims.		° C.
38	100	1·40	14·4
39	,,	1·42	13·3
40	,,	1·39	14·8
	100	Mean 1·403	

TABLE XV.—Pressure 125 millims.

Reference No.	Pressure.	Ratio $\frac{CO_2}{H_2O}$	Temperature.
	millims.		° C.
41	125	1·19	14·9
42	,,	1·15	14·9
	125	Mean 1·17	

TABLE XVI.—Pressures from 75 millims. to 1000 millims.

Reference No.	Pressure.	Ratio $\frac{CO_2}{H_2O}$	Temperature.
	millims.		° C.
	75	*mean* 1·395	
	100	*mean* 1·403	
	125	*mean* 1·17	
43	150	1·07	15·1
44	175	1·03	15·2
45	200	·99	15·1
46	250	·94	15·0
47	300	·92	11·7
48	400	·91	15·3
49	700	·90	14·9
50	1000	·90	15·7

Under very small pressures considerable differences were found in the ratio $CO_2 : H_2O$, in several experiments repeated under the same conditions. Thus under 75 millims. pressure this ratio was found to vary from 1·35 to 1·46 in eight experiments. These discrepancies may partly be accounted for by errors of manipulation, for on the very small masses of gases employed at this pressure, the error of experiment becomes serious. If the mean value of the ratios found in the several experiments made at the lower pressures be taken as correct, we see that the ratio rises very slightly as the pressure is increased from 75 millims. to 100 millims., and then falls abruptly as the pressure is increased to 150 millims., after which the fall is more gradual, until at about 400 millims. the ratio becomes constant. This result entirely confirms the previous series of experiments, and proves that for a mixture of carbonic oxide and electrolytic gas containing 12 per cent. of oxygen, there is a "critical pressure;" below this critical pressure alterations of pressure affect the division of the oxygen, above it alterations of pressure have no effect.

In working at low pressures, therefore, there are two sources of variation to be taken into account: one springing from changes of pressure, the other from changes in the length of the column of gases exploded.

We have seen above that changes in the length of the column cease to have any effect on the ratio of the products of combustion, when a mixture containing 19 per cent. of oxygen is exploded under a pressure only as high as 250 millims. The question arises, what is the "critical pressure" for such a mixture? To determine this point a series of experiments was made at different pressures with a mixture of the following composition.

COMPOSITION of Mixture.

Carbonic oxide	58·47
Hydrogen	22·54
Oxygen	18·99
	100·00

TABLE XVII.—Length of column = 400 millims.

Reference No.	Pressure.	Ratio $\frac{CO_2}{H_2O}$	Temperature.
	millims.		° C.
51	75	1·54	18·8
52	100	1·40	18·2
53	125	1·29	16·2
54	200	1·19	12·6
55	400	1·19	13·7
56	500	1·19	8·8

For a mixture containing 19 per cent. of oxygen the critical pressure is about 200 millims. Now since a mixture containing 19 per cent. of oxygen was found to be unaffected by changes in the length of column under 250 millims. pressure, it seemed likely that in other mixtures changes in the length of column would cease to affect the division of the oxygen as soon as the critical pressure was reached. The critical pressure for the mixture containing 12 per cent. of oxygen is 400 millims. The following experiments with some of this same mixture show that at this and higher pressures changes in the length of column have no effect.

TABLE XVIII.—Pressure = 400 millims.

Reference No.	Length of Column.	Ratio $\frac{CO_2}{H_2O}$	Temperature.
	millims.		° C.
57	200	·905	13
58	200	·88	9·5
48	450	·91	15·3

TABLE XIX.—Pressure = 1000 millims.

Reference No.	Length of Column.	Ratio $\frac{CO_2}{H_2O}$	Temperature.
	millims.		° C.
59	100	·89	10·4
60	100	·92	12·9
50	450	·90	15·7

The critical pressure of a mixture may therefore be defined as the lowest pressure at which any further increase of pressure or any change in the length of the column of exploded gases ceases to affect the ratio of the products of combustion. The critical pressure is lowered as the quantity of oxygen in the mixture increases.

These facts account for the agreement of HORSTMANN'S first series of experiments and those made by BUNSEN with his chain of sparks given in Table VII. Although the path traversed by each flame from the point of ignition is very small in BUNSEN'S experiments compared with HORSTMANN'S, yet since the pressures employed by both experimenters were near to or above the critical pressures of the mixtures exploded, this great difference in the length of column had no effect on the division of the oxygen. The same facts also account for the disagreement between my experiments and those of BUNSEN and HORSTMANN. For since the first ten experiments in my series were made at pressures below the critical pressure of the respective mixtures, both the lower pressure and the longer column increase the proportion of carbonic oxide burnt. In the four last experiments of this series the increase in the quantity of oxygen taken brings the critical pressure below the pressure employed. The results are in close accordance with those of BUNSEN and HORSTMANN.

A third series of pressure experiments was next made with a mixture containing only 8 per cent. of oxygen.

COMPOSITION of Mixture.

Carbonic oxide	66·28
Hydrogen	25·66
Oxygen	8·06
	100·00

This mixture would not explode under 100 millims. pressure. It exploded under 125 millims.

TABLE XX.—Length of column = 400 millims.

Reference No.	Pressure.	$\frac{CO_2}{H_2O}$	Temperature.
	millims.		° C.
61	125	1·02	11·3
62	150	1·08	11·2
63	175	1·09	11·2
64	200	1·09	12·5
65	250	1·09	7·8
66	300	1·04	8·6
67	400	1·03	14·5
68	600	1·00	12·4
69	1000	·98	10·0

In this series the proportion of carbonic oxide burnt increases at first with increase of pressure, reaches a maximum, and then falls continually. No critical pressure appeared to be reached as far as the pressure was pushed. If the critical pressure for a mixture containing only 8 per cent. of oxygen is above 1000 millims., it follows that under this pressure a change in the length of column will affect the division of the oxgyen. The following experiments, in which some of the same mixture was exploded under 1000 millims. with a short column, prove this to be the case.

TABLE XXI.—Pressure = 1000 millims.

Reference No.	Length of Column.	Ratio $\frac{CO_2}{H_2O}$	Temperature.
	millims.		° C.
70	25	·90	8·0
71	50	·91	8·4
69	400	·98	10·0

As the general result of these pressure experiments, it appeared that the law of mass might be tested by the incomplete combustions of carbonic oxide and hydrogen, provided that each mixture of gases was exploded above its critical pressure. It will, perhaps, be most convenient, before proceeding to describe the experiments made with this view, to give here an account of HORSTMANN's second paper, which advanced the inquiry another stage.

HORSTMANN's *experiments.*

HORSTMANN[*] having shown that no sudden alterations occur in the ratio of carbonic acid and water produced by the combustion of carbonic oxide and electrolytic gas mixed in various proportions, and that BUNSEN's earlier experiments were vitiated by the presence of varying proportions of aqueous vapour in the eudiometer, proceeded to repeat v. MEYER's experiments, in which mixtures of carbonic oxide and hydrogen were exploded with successively increasing quantities of oxygen.

HORSTMANN found in these experiments that, for a given mixture of carbonic oxide and hydrogen, the proportion of carbonic acid formed gradually diminishes at first with increase of oxygen, reaches a minimum when between 30 and 40 per cent. of the combustible gases is burnt, and then gradually increases towards the limit that would be reached if all the gases are burnt. Nowhere did he find any alteration *per saltum* in the proportion of the products of combustion. But an examination of the numbers given by these experiments led HORSTMANN to detect a remarkable relation between the ratio of the unburnt carbonic oxide to the unburnt hydrogen, and the ratio of the burnt carbonic oxide to the burnt hydrogen. He found that when mixtures of carbonic oxide and hydrogen in any proportions are exploded with the same quantity of oxygen, the ratio between the quantities of the two gases burnt is proportional to the ratio between the quantities of the two gases left unburnt. Thus, if A and B are the quantities of carbonic oxide and hydrogen in any mixture exploded with a certain quantity of oxygen, then the quantity of carbonic acid formed (a) and the quantity of steam formed (b) are given by the equation

$$\frac{A-a}{B-b} = \frac{a}{b} \times \kappa$$

where κ is a constant depending on the quantity of oxygen taken.

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[*] Verh. des Heidelb. naturf. med. Vereins., N.S. II., 1; LIEBIG's Annalen, 190-228.

Horstmann states his results in the following way: "*The law by which the division of the oxygen between the combustible gases is governed, can be expressed as follows: The ratio of the resulting water-vapour to the resulting carbonic acid is equal to the ratio of the unburnt hydrogen, to the unburnt carbonic oxide, multiplied by a 'coefficient of affinity,' which is independent of the proportion of the combustible gases, but which changes with the relative mass of the oxygen added.*" With equal quantities of oxygen the "coefficient of affinity" remains constant, not only when the ratio of the hydrogen to the carbonic oxide is altered, but also when the unburnt portion of the combustible gases is replaced, entirely or in part, by an indifferent gas of a similar physical constitution, such as nitrogen.

The numbers from which Horstmann deduces this law are only fairly concordant. From the ten series of experiments made with different mixtures I have placed together, for the purpose of comparison, those in which nearly equal proportions of oxygen were taken. The first series, which Horstmann regards as incorrect, is omitted. In the following table the mean ratio of the oxygen to the combustible gases, the composition of the mixtures, the percentage burnt, and the "coefficient of affinity" calculated from these experiments are given.

Table XXII.—Horstmann's Experiments.

Mean ratio of oxygen to combustible gases. $O_2 : (H_2 + CO)$.	Ratio of combustible gases before explosion. $H_2 : CO$.	Percentage of combustible gases burnt.	Coefficient of affinity.
·11	·3648	22·0	4·30
	·6142	22·0	3·81
·127	·3648	25·1	4·28
	·6142	25·8	4·43
	1·2035	25·7	4·48
	1·0392	24·9	4·78
·192	·9061	38·4	6·35
	3·0308	38·4	5·44
·245	·9061	48·0	5·94
	1·0392	48·5	5·92
	1·2035	48·7	5·47
	3·0308	48·9	5·86
	·6142	49·4	6·03
	·7247	49·7	5·67
	·3648	49·8	5·25
·268	·9061	52·2	5·09
	1·2035	53·9	5·85
	3·0308	54·7	4·86
·320	·9061	63·3	5·34
	3·0308	63·8	4·91
	·3493	64·1	5·00
	·3648	64·3	4·17

A glance at the last column in this table shows that for equal quantities of oxygen, Horstmann's coefficient of affinity is fairly constant: in the third, fifth, and sixth sets the extreme values differ by about 20 per cent.; the other sets show a better agreement.

In a later paper Horstmann gives the following table of the coefficients of affinity corresponding to different percentages of the combustible gases burnt.

Table XXIII.—Horstmann's new table of coefficients.

Percentage of combustible gases burnt.	Coefficient of affinity.
15	2·68
20	3·8
25	4·83
30	5·65
35	6·16
40	6·35
45	6·12
50	5·88
55	5·64
60	5·38
65	5·11
70	4·85

The alteration in the coefficient of affinity, with increase of oxygen, Horstmann attributes (1) to the increased temperature of combustion, and (2) to the alteration of pressure and physical characteristics of the whole mixture produced by the combustion. He was led to this conclusion by the following experiments: Different mixtures of hydrogen and carbonic oxide were exploded with air. In each experiment, therefore, a certain quantity of nitrogen was present. The "coefficients of affinity" were found to agree approximately with those previously obtained in explosions with mixtures containing the same percentage of oxygen, and not with mixtures containing the same relative proportion of oxygen and combustible gases.

For instance, 100 volumes of carbonic oxide and hydrogen were mixed with 76 volumes of air containing 16 volumes of oxygen. In the explosion, therefore, 32 *per cent. of the combustible gases* is burnt, but only 20 per cent. of the mixture of carbonic oxide, hydrogen, and nitrogen. From the previous experiments the coefficient of affinity corresponding to a combustion of 32 per cent. is 5·9, and for a combustion of 20 per cent. it is 4·0. The coefficient found is 3·7.

TABLE XXIV.

Volume of nitrogen added to 100 volumes of carbonic oxide and hydrogen.	Volume of burnt gases in 100 volumes of carbonic oxide, hydrogen and nitrogen.	Coefficient of affinity.		
		Found.	Calculated.	
60	20	3·7	4·0	$\frac{H_2}{CO}=\cdot96$
75	23	4·3	4·4	
113	28	5·1	5·3	
70	22	4·4	4·3	$\frac{H_2}{CO}=3\cdot03$
90	25	5·2	4·7	
115	28	5·8	5·2	
59	20	3·7	3·9	$\frac{H_2}{CO}=1\cdot04$
80	23	4·7	4·5	
99	26	4·8	4·9	
114	28	6·2	5·2	
125	30	5·3	5·3	

These coincidences, HORSTMANN considers, prove that the presence of the nitrogen affects the coefficient in the same way as the presence of an equal quantity of carbonic oxide or hydrogen, and point to the conclusion that the constancy of the coefficient of affinity in the different experiments depends upon a *similarity of physical conditions.*

In two later papers HORSTMANN* has shown that when carbonic acid is added to the mixture previous to explosion, more hydrogen and less carbonic oxide is burnt than when the mixture is fired without carbonic acid. When a mixture of carbonic acid and hydrogen is exploded with insufficient oxygen to burn all the hydrogen some of the carbonic acid is reduced to carbonic oxide.

The influence of carbonic acid, he says, is not the same as that of nitrogen, but resembles it; direct experiments show that it is impossible to replace the excess of combustible gases in part by carbonic acid, without altering the coefficient of affinity. Carbonic acid, which has a higher specific heat than the simpler gases, produces a greater effect than an equal volume of nitrogen, hydrogen, or carbonic oxide. This fact confirms the earlier conclusion that the coefficient not only depends upon the percentage of oxygen, but also on the temperature of combustion. Steam acts in a manner analogous to carbonic acid. Such are HORSTMANN'S conclusions as to the function of inert gases in the explosive mixture. But in one paragraph he views the reaction in a different light:—

"The *burning* appears as a preliminary of secondary importance, through which are established the conditions antecedent to the reactions coming particularly into consideration. The chemical equilibrium is brought about by the two reciprocal transformations between carbonic acid and hydrogen on the one hand, and carbonic oxide

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* Ber. Deut. Ch. Ges., x., 1628; xii., 64.

and steam on the other, which can take place at the high temperature produced by the combustion."

This view of the final result of the reaction, which appears to me to be substantially correct, seems difficult to reconcile with HORSTMANN'S previous conclusions as to the function of nitrogen and carbonic acid in the explosive mixture. For if the final result depends upon an equilibrium being established between the reduction of the carbonic acid by the hydrogen and the oxidation of the carbonic oxide by the steam, how is it possible for nitrogen to take the place, and play the part, of an equal quantity of hydrogen or carbonic oxide ?

The following is HORSTMANN'S conclusions with regard to the variation of the coefficient with the percentage of oxygen taken :—

"The coefficient is probably dependent alone upon the temperature. The influence of the temperature is of a complicated kind. A portion of the carbonic acid and steam is dissociated at the temperature reached. As the temperature sinks, the equilibrium alters with it. The composition of the mixture corresponds therefore to an equilibrium for some unknown middle value between the temperature of combustion, which varies with the composition of the mixture, and the lower limit of temperature, at which the mutual action of the gases is just possible. This lower limit of temperature is the same with all mixtures."

From his latest experiments (not yet published) HORSTMANN concludes that the values of the coefficient, which by the earlier experiments fell between 4 and 7, may be much lower at low temperatures: for the lowest temperatures even less than 1. This shows that, contrary to what is found at high temperatures, the affinity of oxygen for carbonic oxide at low temperatures is greater than for hydrogen ; a result which confirms the statement of E. von MEYER that in the slow combustion effected by platinum at ordinary temperatures more carbonic oxide is burnt than hydrogen.

I shall show later that the proportionality discovered by HORSTMANN between the ratios of the unburnt gases and the products of combustion is a fact independent of the percentage of combustible gases burnt, and dependent only on the conditions (1) that a sufficiently high temperature should be reached in the explosion, (2) that none of the reacting molecules should be withdrawn from the sphere of action during the chemical change, and (3) that no indifferent gas should be present.

Experiments with dry gases above the critical pressure.

To test the accuracy of HORSTMANN'S conclusions, the following experiments were made with dry gases exploded at high pressures. A dry mixture of carbonic oxide and oxygen and a dry mixture of hydrogen and oxygen, each containing 12·4 per cent. of oxygen, were made. Varying proportions of each of these mixtures were brought together in the eudiometer and exploded under 1000 millims. pressure. In these experiments the ratio of carbonic oxide and hydrogen is varied ; about 12·4 per cent. of oxygen is employed in each case ; and the pressure is such that no increase of pressure or variation in the length of column makes any difference in the result. For the purpose of comparing the experiments one with the other, the volume of the combustible gases before the explosion is taken as 100 in each case; then the volumes of gases left unburnt and the volume of the burnt gases together make up 100. In the following table these volumes are given in separate columns. In the first column is given the "reference number," in the second the temperature of the mixture before explosion.

TABLE XXV.—Pressure = 1000 millims.

Reference No.	Temp.	Before Explosion.			After Explosion.				a.
		Oxygen.	Carbonic oxide.	Hydrogen.	CO.	CO_2.	H_2.	H_2O.	
	°C								
72	14·6	14·0	13·46	86·54	12·33	1·13	59·72	26·82	4·90
73	14·4	14·1	30·13	69·87	27·14	2·99	44·63	25·24	5·14
74	15·2	14·1	40·63	59·37	36·07	4·56	35·66	23·71	5·26
75	13·6	14·2	52·46	47·54	45·31	7·15	26·28	21·26	5·13
76	13·4	14·25	66·34	33·66	55·04	11·30	16·42	17·24	5·11
77	14·7	14·25	77·57	22·43	61·39	16·18	10·06	12·37	4·76
78	15·6	14·25	83·60	16·40	64·58	19·02	6·91	9·49	4·67
	14·5 Mean temp.								Mean coefficient 5·00

Of the four reactions, namely, the two *direct* reactions symbolised by the equations

$$(1)\ 2\,H_2 + O_2 = 2\,H_2O$$

$$(2)\ 2\,CO + O_2 = 2\,CO_2$$

and the two *indirect* reactions symbolised by the equations

$$(3)\ H_2O + CO = H_2 + CO_2$$

$$(4)\ H_2 + CO_2 = H_2O + CO$$

It has been shown that both the indirect and only one of the direct actions actually occur under the conditions of the experiments. Mr. ESSON,* who discussed the results of these experiments, found that the numbers obtained agree with the theory that the final division of the oxygen depends upon an equilibrium being established between the two reverse changes 3 and 4. The quantities found in these experiments satisfy the equation

$$\frac{k' \times h}{k \times h'} = \alpha$$

where h and h' represent the volumes, or the number of molecules, of steam and hydrogen remaining at the end of the reaction, and k' and k represent the number of molecules of carbonic oxide and carbonic acid remaining at the end of the reaction. *The product of the steam and carbonic oxide molecules bears a constant ratio to the product of the hydrogen and carbonic acid molecules.* Each experiment gives a value

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* *Vide* Mr. ESSON'S Note at the end of this paper.

for α. These values are given in the last column of the table. The mean of the seven experiments gives $\alpha = 5$. From this mean value the quantity of hydrogen and carbonic oxide burnt in any given mixture can be calculated. In the following table the quantities of hydrogen burnt, calculated for the mixtures employed in these experiments, are compared with those actually observed.

TABLE XXVI.—Volume of hydrogen burnt.

Reference No.	Calculated.	Observed.
78	9·7	9·5
77	12·6	12·4
76	17·1	17·2
75	21·3	21·3
74	23·5	23·7
73	25·2	25·2
72	26·9	26·8

According to this theory, the chemical changes vary as the explosion proceeds. The explosion starts with the direct union of oxygen and hydrogen, the change proceeding until all the oxygen is converted into steam, according to equation (1); as soon as steam is formed by this union it begins to oxidize the carbonic acid, according to equation (3); the carbonic acid so produced is in turn reduced to carbonic oxide by free hydrogen, according to equation (4). The heat developed by the direct union of the oxygen and hydrogen raises the whole body of the gases to incandescence. After all the oxygen is converted into steam, four gases remain at a high temperature—hydrogen and steam, carbonic oxide and carbonic acid. Of these four gases, one pair, hydrogen and carbonic acid, react at the high temperature to form the other pair, steam and carbonic oxide; but steam and carbonic oxide themselves react to form the first pair, hydrogen and carbonic acid, so that two reverse changes take place simultaneously in the mixture. The quantity of each pair present at any moment during the reaction depends on the relative rates at which the two changes proceed. Possibly these rates may vary with the temperature as the whole body of gases cools down. The quantities actually measured are those in equilibrium at the moment the gases cool to the temperature at which the reaction ceases. But since in the fall from the highest temperature reached in any explosion to the lowest at which reaction occurs there is a large range of cooling common to all the experiments, the relative rate of the two changes observed is in all cases that which is found under similar conditions of temperature.

According to HORSTMANN the coefficient varies with the proportion of oxygen employed, at first increasing with the increase of oxygen, reaching a maximum when from 15 to 20 volumes of oxygen are mixed with 100 of the combustible gases, and finally diminishing gradually as the oxygen is increased beyond this point. The volume of oxygen added to 100 volumes of the combustible gases was 14·2 in my experiments. The number found ($\alpha = 5$) is considerably below the maximum observed by HORSTMANN. To observe the effect of an increase of oxygen, a second series of experiments was made similar in all respects to the first, but with 17·7 volumes of oxygen instead of 14·2 added to 100 volumes of the combustible gases. The gases were exploded under 1000 millims. pressure in each experiment.

TABLE XXVII.

Reference No.	Temperature.	Before the explosion.			Coefficient α.
		Oxygen.	Carbonic oxide.	Hydrogen.	
	° C.				
79	13·4	17·7	83·9	16·1	4·8
80	13·4	"	79·8	20·2	5·0
81	12·6	"	78·2	21·8	4·9
82	13·6	"	68·7	31·3	5·3
83	13·0	"	45·4	54·6	5·2
84	13·2	"	35·9	64·1	5·2
85	13·7	"	15·8	84·2	5·0
	Mean 13·3				Mean 5·06

These experiments entirely confirm the previous series; the proportion of gases burnt is expressed by the equation

$$\frac{k' \times h}{k \times h'} = \alpha$$

and the mean value of α closely approximates to the value previously found. No appreciable rise in the coefficient is produced by increasing the amount of oxygen from 14·2 to 17·7 volumes. These experiments are therefore at variance with HORSTMANN'S conclusion.

To test this point further a mixture was made containing 15·9 vols. of oxygen to 100 volumes of the combustible gases. Two experiments were made with portions of this mixture; then more oxygen was added to the remainder and two more experiments made.

TABLE XXVIII.—Pressure = 1000 millims.

Reference No.	Temperature.	Before the explosion.			Coefficient α.
		Oxygen.	Carbonic oxide.	Hydrogen.	
	° C.				
86	6·7	15·9	73·2	26·8	5·7
87	8·9	"	"	"	5·6
88	8·8	24·3	73·2	26·8	5·6
89	8·0	"	"	"	5·5
	Mean 8·1				Mean 5·6

No difference was found in the coefficient whether 15·9 or 24·3 volumes of oxygen were used, but the mean value of the coefficient in these four experiments was appreciably higher than in the two previous series, which gave 5 for the value of α both with 14·2 and 17·7 volumes of oxygen. Apart from the variation of the oxygen, the only other difference between these and the previous experiments was a small difference in temperature amounting to some five or six degrees. In the first series the gases were exploded at a mean temperature of 14°·5, in the second series at a mean temperature of 13°·3, and in the last four experiments at a mean temperature of 8°·1. On calculating out the coefficient α from BUNSEN's later experiments,* and omitting the first as being below the critical pressure, its mean value is found to be 5·8 for a mean temperature of 7°·2.

TABLE XXIX.—BUNSEN's experiments with dry gases.

Temperature.	Oxygen.	Carbonic oxide.	Hydrogen.	Coefficient α.
°C.				
10·3	10·7	78·6	21·4	4·9
4·6	12·5	74·9	25·1	5·6
5·3	14·5	70·9	29·1	5·8
7·3	14·1	71·8	28·2	6·2
8·7	16·9	66·1	33·9	6·0
10·	20·7	58·5	41·5	5·5
Mean 7·2				Mean 5·8

Here a high value for the coefficient is also accompanied by a low temperature. It appeared possible then that a variation of a few degrees in the temperature of the gases before the explosion might materially alter the result. A few experiments showed this to be the case.

Experiments on the influence of initial temperature.

Portions of a mixture of the dry gases were exploded successively under 1000 millims. pressure at different temperatures. In the first two experiments the eudiometer was cooled down by placing ice water in the jacket, in the other experiments the eudiometer was warmed by hot water.

The mixture was of the following composition :

Carbonic oxide	70·8
Hydrogen	29·2
	100·0
Oxygen added . .	16·8

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* "Gasometrische Methoden, II^{te} Auflage."

Table XXX.—Pressure = 1000 millims.

Reference No.	Before the explosion.			After the explosion.				Temperature.	Coefficient a.
	Oxygen.	Carbonic oxide.	Hydrogen.	Carbonic oxide.	Carbonic acid.	Hydrogen.	Steam.	° C.	
90	16·8	70·8	29·2	55·3	15·5	11·3	18·0	3	5·7
91	,,	,,	,,	54·9	15·9	11·7	17·6	19	5·2
92	,,	,,	,,	54·8	16·1	11·8	17·3	20	5·0
93	,,	,,	,,	53·9	16·9	12·1	17·1	40	4·5
94	,,	,,	,,	53·1	17·7	12·8	16·3	60	3·8

These experiments show that a small change of initial temperature makes a very considerable difference in the division of the oxygen. To carry the range of temperature further, portions of a similar mixture were exploded under 1000 millims. pressure at temperatures ranging from −10° to 120° C.

Table XXXI.

Reference No.	Before the explosion.			After the explosion.				Temperature.	a.
	Oxygen.	Carbonic oxide.	Hydrogen.	Carbonic oxide.	Carbonic acid.	Hydrogen.	Steam.	° C.	
95	17·5	73·3	26·7	56·3	17·0	8·6	18·1	−10	7·0
96	,,	,,	,,	54·0	19·3	11·2	15·5	60	3·9
97	,,	,,	,,	53·6	19·7	11·4	15·3	80	3·7
98	,,	,,	,,	53·7	19·6	11·4	15·2	100	3·7
99	17·6	73·4	26·6	53·6	19·9	11·3	15·3	120	3·7

In the last two experiments the eudiometer was heated by hot glycerin in the jacket.

These additional experiments confirm the previous series; a change of initial temperature greatly influences the division of the oxygen. But they also bring to light a very important fact. The coefficient of affinity does not materially alter when the temperature is raised from 60° to 120°. The coefficient found at these two temperatures in the second series is also the same as that found at 60° in the first series. The two sets together show a progressive diminution of the coefficient as the temperature is raised from −10° to 60° and a nearly constant value between 60° and 120°.

Another mixture was now made containing about three times as much hydrogen as carbonic oxide; portions of this mixture were exploded successively under 1000 millims. pressure at 0°, 70°, 80° and 100°. A nearly similar mixture was exploded at 125°.

TABLE XXXII.

Reference No.	Before the explosion.			After the explosion.				Temperature.	*a.*
	Oxygen.	Carbonic oxide.	Hydrogen.	Carbonic oxide.	Carbonic acid.	Hydrogen.	Steam.		
								° C	
100	17·3	24	76	21·4	2·6	44·1	31·9	0	5·9
101	,,	,,	,,	20·5	3·4	44·7	31·3	70	4·2
102	,,	,,	,,	20·4	3·5	44·7	31·3	80	4·0
103	,,	,,	,,	20·4	3·6	44·4	31·6	100	4·0
104	15·9	24·5	75·5	21·2	3·3	47·0	28·5	125	4·0

Between 0° and 70° a large fall of the coefficient occurs; between 70° and 80° there is a slight fall; from 80° to 125° it remains constant. The high temperature constant with this mixture is rather higher than with mixtures containing excess of carbonic oxide.

A fourth mixture, containing about equal volumes of carbonic oxide and hydrogen, was next exploded at 70°, 80°, and 120° under 1000 millims. pressure. For the purpose of comparison an experiment previously made with a nearly similar mixture at 14° is included in the table.

TABLE XXXIII.

Reference No.	Before the explosion.			After the explosion.				Temperature.	*a.*
	Oxygen.	Carbonic oxide.	Hydrogen.	Carbonic oxide.	Carbonic acid.	Hydrogen.	Steam.		
								° C.	
75	14·2	52·5	47·5	45·3	7·2	26·3	21·3	14	5·1
105	15·4	51·7	48·3	42·7	8·9	26·0	22·3	70	4·1
106	,,	,,	,,	42·9	8·7	26·6	21·8	80	4·0
107	,,	,,	,,	42·8	8·8	26·4	21·9	120	4·0

Between 14° and 70° there is a large fall in the coefficient; between 80° and 120° the coefficient remains constant.

It is difficult to assign the marked change in the coefficient, as the initial temperature is raised from 0° to 60°, to a higher temperature being reached in the combustion when the eudiometer is warmed. In the first place if the temperature of the flame is increased by the whole amount of the initial warming of the gases, this increase is not more than 2 or 3 per cent., whereas the coefficient is altered some 40 per cent.; and secondly if such a small increase in the temperature of the flame affects the coefficient, we should expect the small further increase in the temperature of the flame by heating the eudiometer from 60° to 120° to make a further change in the coefficient. No change in the coefficient occurs as the temperature of the eudiometer is raised from

60° to 120°. The cause of the change must be sought in some condition present up to 60° and absent at higher temperatures. There is such a condition—the condensation of the steam by the sides of the vessel during the progress of the chemical change. By this condensation one of the reacting bodies is removed from the sphere of action. If we conceive the gases to be composed of a vast number of molecules moving in straight lines and coming into collision one with another and with the sides of the vessel, and that an appreciable time elapses during which the gaseous molecules are in sufficiently rapid motion to change atoms when they come into collision, then it must happen that while the change is proceeding a number of steam molecules strike the sides of the vessel. Now a vapour diffused through a gaseous mixture is condensed to a liquid by a cool surface when the pressure of the vapour in the mixture is greater than the tension exerted by the liquid at the temperature of the cool surface. On the contrary, when the surface is at such a temperature that a liquid film upon it exerts a tension greater than the pressure of the vapour of that liquid present in the atmosphere in contact with it, the liquid volatilizes from the surface. Under the latter conditions no vapour would be condensed from a gaseous mixture. For a surface at a given temperature, condensation depends upon the tension of the vapour in the mixture, and for a given tension of the vapour, condensation depends on the temperature of the surface.

These facts permit the question to be readily tested by experiment. In the first series of temperature experiments, if 3·7 be taken as the constant coefficient at high temperatures, then in the last experiment the tension of the steam formed by the unimpeded reaction would be 162 millims. at 60°. At this temperature the tension exerted by a film of water is about 150 millims. During the explosion, therefore, the sides of the vessel might condense a small quantity of steam, and the coefficient might in consequence be slightly raised. In the previous experiment at 40°, the tension of steam formed by the unimpeded reaction would still be 162 millims. at 40°; but at this temperature the tension exerted by a film of water is only 55 millims. So that a considerable condensation might take place, and the coefficient be considerably raised. At lower temperatures the effect would be greater still. In the same way, if 3·7 be taken as the constant coefficient in the second series of temperature experiments, then in the second, third, fourth, and fifth experiments the tension of steam formed by the unimpeded reaction would be 152 millims. at 60°, 80°, 100°, and 120° respectively. At 80° the maximum tension of aqueous vapour is 355 millims., so that at 80° and at higher temperatures no condensation could take place; but at 60° a slight condensation might occur. The two series of experiments show therefore that the coefficient remains constant when no condensation is possible during the reaction: with decrease of initial temperature the coefficient begins to increase as soon as condensation becomes possible. Similarly in the third series of experiments, if we take 4 as the constant coefficient, no condensation could take place at 80° or higher temperatures; at 70° some condensation might occur. The coefficient begins to increase as soon as condensation is possible. In the fourth series the maximum tension of aqueous vapour at 70° (233 millims.) is just greater than the tension of steam formed (219 millims.). Perhaps incipient condensation accounts for the very slight rise in the coefficient observed.

Now by varying the initial pressure the point of possible condensation can be altered without varying the temperature of the vessel. For instance, by reducing the initial pressure from 1000 millims. to 500 millims. in the two first series, the tension of the steam formed in the unimpeded reaction would have been reduced to 81 millims. and 76 millims. respectively; no condensation could therefore have taken place under these conditions until the temperature had been reduced below 50°, and so on for other initial pressures. By changing the initial pressure the truth of the hypothesis can therefore be tested; if the condensation of steam interferes with the reaction in the manner indicated, the increase of the coefficient will always occur when the tension of steam formed is equal to the maximum tension of aqueous vapour at the temperature of the eudiometer. Some of the mixture containing 73·4 parts of carbonic oxide and 26·6 parts of hydrogen in 100, was exploded under 400 millims. pressure and at different temperatures with the following results.

TABLE XXXIV.—Pressure = 400 millims.

Reference No.	Before the explosion.			After the explosion.				Temp.	*a.*
	Oxygen.	Carbonic oxide.	Hydrogen.	Carbonic oxide.	Carbonic acid.	Hydrogen.	Steam.	°C.	
108	17·6	73·4	26·6	54·0	19·6	10·7	16·0	40	4·1
109	,,	,,	,,	53·5	19·9	11·2	15·3	50	3·7
110	,,	,,	,,	53·5	19·9	11·2	15·5	100	3·7

In these experiments the tension of steam formed by the unimpeded reaction is only 62 millims. The maximum tension of aqueous vapour at 50° is 92 millims. and at 40° it is 55 millims. If condensation causes the increase in the coefficient, this increase should not take place until the temperature is reduced below 50°. The coefficient is found to be the same at 50° as at 100°, whereas at 40° a distinct increase is observed. When this same mixture was exploded under 1000 millims. pressure the steam produced had a tension of 153 millims., and at 60° where the maximum tension of aqueous vapour is 149, the coefficient began to rise. These experiments also show that the coefficient is the same whether the gases are exploded under 400 millims. or 1000 millims., provided that no condensation takes place.

Again, the same mixture was exploded under 100 millims. pressure at varying temperatures.

TABLE XXXV.

Reference No.	Before the explosion.			After the explosion.				Temp.	*a*.
	Oxygen.	Carbonic oxide.	Hydrogen.	Carbonic oxide.	Carbonic acid.	Hydrogen.	Steam.	° C.	
111	17·6	73·4	26·6	53·5	19·9	11·7	14·8	16	3·4
112	,,	,,	,,	52·2	21·2	12·8	13·8	30	2·7
113	,,	,,	,,	52·1	21·4	12·6	14·0	60	2·7
114	,,	,,	,,	52·0	21·4	12·7	13·9	100	2·7

The maximum tension of aqueous vapour at 16° is 13½ millims., at 30° it is 31½ millims.; the tension of the steam produced in the unimpeded reaction is 14 millims. As the temperature is reduced from 100° to 30°, no alteration is found in the coefficient; at 16° the coefficient is distinctly raised. The constant coefficient under 100 millims. is lower than that under 400 millims.

From all the experiments made at various temperatures, it follows that *when the steam formed during the reaction is more than sufficient to saturate the space at the temperature of the enclosing vessel, some of the steam is condensed on the sides of the vessel during the progress of the chemical change.*

By the removal of a portion of the steam during the reaction, more steam and less carbonic acid are found after the explosion than if all the steam had remained as a gas capable of reacting with the carbonic oxide.

When no condensation occurs, a change of initial temperature has no effect on the division of the oxygen in the explosion.

Experiments on the "critical pressure" at high temperatures.

In the experiments previously described, in which portions of a mixture were exploded under increasing pressures at ordinary temperatures, it was found that the ratio of carbonic acid to steam formed continually diminished until at about 400 millims. pressure it became constant. The lowest pressure at which the ratio became constant varied in different mixtures. The larger the percentage of oxygen taken, the lower the critical pressure was found to be. In these experiments, condensation of steam occurred during the reaction, and in consequence the ratio $\frac{CO_2}{H_2O}$ was diminished. In the temperature experiments last described, it was seen that this ratio varied with the pressure when no condensation took place. To determine the amount of this variation, and the "critical pressure," with different mixtures, three series of explosions were made under successively increasing pressures, at a temperature sufficiently high to prevent any condensation of steam. In the first series a mixture of nearly equal volumes of carbonic oxide and hydrogen was taken. 100 volumes of this mixture were exploded with 15·4 volumes of oxygen at 80°.

TABLE XXXVI.—Temperature of Eudiometer = 80° C.

Reference No.	Before the explosion.			After the explosion.				Pressure.	a.
	Oxygen.	Carbonic oxide.	Hydrogen.	Carbonic oxide.	Carbonic acid.	Hydrogen.	Steam.	millims.	
115	15·4	51·7	48·3	42·0	9·7	27·4	20·9	150	3·3
116	„	„	„	42·1	9·6	26·7	21·6	200	3·6
117	„	„	„	42·7	8·9	26·6	21·8	300	3·9
118	„	„	„	42·5	9·1	26·1	22·2	400	4·0
106	„	„	„	42·9	8·7	26·6	21·8	1000	4·0

This mixture would not explode when the spark was passed under 100 millims. or 125 millims. pressure. At 150 millims. it exploded. *The critical pressure is found to be between* 300 *millims. and* 400 *millims. Below the critical pressure a different equilibrium is established.* The constant coefficient for this mixture is the same as that for a mixture containing three volumes of hydrogen to one volume of carbonic oxide.

From the experiments previously given the following table is made up.

TABLE XXXVII.—Temperature of Eudiometer = 100° C.

Reference No.	Before the explosion.			After the explosion.				Pressure.	Co-efficient. a.
	Oxygen.	Carbonic oxide.	Hydrogen.	Carbonic oxide.	Carbonic acid.	Hydrogen.	Steam.	millims.	
114	17·6	73·4	26·6	52·0	21·4	12·7	13·9	100	2·7
110	„	„	„	53·5	19·9	11·1	15·5	400	3·7
98	„	„	„	53·7	19·6	11·4	15·2	1000	3·7

This mixture exploded under 100 millims. pressure at 100°. The "critical pressure" is below 400 millims.

Another set of experiments was made with a mixture containing about three times as much hydrogen as carbonic oxide. To 100 volumes of the combustible gases, 15·8 volumes of oxygen were added.

TABLE XXXVIII.—Temperature of Eudiometer = 100° C.

Reference No.	Before the explosion.			After the explosion.				Pressure.	Co-efficient. a.
	Oxygen.	Carbonic oxide.	Hydrogen.	Carbonic oxide.	Carbonic acid.	Hydrogen.	Steam.	millims.	
119	15·8	24·5	75·5	20·4	4·1	48·6	26·9	100	2·8
120	„	„	„	21·2	3·3	47·2	28·3	300	3·8
104	„	„	„	21·2	3·3	47·0	28·5	1000	4·0

The critical pressure is above 300 millims.

Experiments were next made with smaller quantities of oxygen. To 100 volumes of a mixture containing nearly equal quantities of carbonic oxide and hydrogen, 8·5 volumes of oxygen were added. Portions of this mixture were exploded under increasing pressures at 90° C. The coefficient continued to increase as the pressure was raised up to 2000 millims. of mercury.

TABLE XXXIX.—Temperature of Eudiometer = 90° C.

Reference No.	Before the explosion.			After the explosion.				Pressure.	a.
	Oxygen.	Carbonic oxide.	Hydrogen.	Carbonic oxide.	Carbonic acid.	Hydrogen.	Steam.		
								millims.	
121	8·5	48·2	51·8	43·6	4·7	39·3	12·5	400	2·9
122	"	"	"	43·9	4·3	39·1	12·6	800	3·3
123	"	"	"	43·8	4·5	38·7	13·0	1000	3·3
124	"	"	"	43·9	4·4	38·6	13·1	1500	3·4
125	"	"	"	44·1	4·2	39·0	12·8	2000	3·5

The critical pressure of this mixture is above 2000 millims. Another mixture, containing 10·2 volumes of oxygen to 100 volumes of the combustible gases, was exploded in a similar way under increasing pressures at 90° C. The coefficient continued to increase as the pressure was raised up to 2000 millims.; but in each case the coefficient was higher than under the same pressure with the lower proportion of oxygen.

TABLE XL.—Temperature of Eudiometer = 90° C.

Reference No.	Before the explosion.			After the explosion.				Pressure.	a.
	Oxygen.	Carbonic oxide.	Hydrogen.	Carbonic oxide.	Carbonic acid.	Hydrogen.	Steam.		
								millims.	
126	10·2	53·2	46·8	47·1	6·1	32·5	14·3	400	3·4
127	"	"	"	47·3	5·9	32·1	14·6	1500	3·6
128	"	"	"	47·5	5·8	32·1	14·7	1750	3·7
129	"	"	"	47·6	5·7	32·1	14·6	2000	3·8

The critical pressure of this mixture is above 2000 millims.

A third mixture with rather more oxygen was exploded in a similar way.

TABLE XLI.—Temperature of Eudiometer = 90° C.

Reference No.	Before the explosion.			After the explosion.				Pressure.	a.
	Oxygen.	Carbonic oxide.	Hydrogen.	Carbonic oxide.	Carbonic acid.	Hydrogen.	Steam.	millims.	
130	11·5	46·7	53·3	41·1	5·6	35·7	17·5	400	3·6
131	,,	,,	,,	41·3	5·4	35·6	17·7	600	3·8
132	,,	,,	,,	41·4	5·3	35·5	17·8	800	3·9
133	,,	,,	,,	41·4	5·3	35·4	17·8	1000	3·9

The "critical pressure" of this mixture is near 1000 millims.

From these series of experiments at a high temperature it appears that when the proportion of oxygen is low, the division of the oxygen varies with changes of pressure even beyond 2 metres of mercury. As the proportion of oxygen is raised, the point is sooner reached at which no further increase of pressure affects the result. In these experiments no condensation of steam was possible during the reaction.

These experiments also show that a variation in the quantity of oxygen from 11·5 to 15·4 (for every hundred of the combustible gases) has no effect on the coefficient a. According to HORSTMANN this coefficient varies from 3·8 to 5·6 when the proportion of oxygen is increased from 10 to 15 parts for every 100 of combustible gases. In the following experiments larger proportions of oxygen, increasing from 17·5 to 38·6 parts, were exploded with a mixture containing three of carbonic oxide to one of hydrogen.

In each case the explosion was made under a pressure of 1000 millims. of mercury.

TABLE XLII.

Reference No.	Before the explosion.			After the explosion.				Temperature.	a.
	Oxygen.	Carbonic oxide.	Hydrogen.	Carbonic oxide.	Carbonic acid.	Hydrogen.	Steam.	° C	
97	17·5	73·3	26·7	53·6	19·7	11·4	15·3	80	3·7
134	26·3	75·3	24·7	41·3	34·0	6·1	18·6	,,	3·7
135	27·2	75·7	24·4	39·8	35·9	5·8	18·6	,,	3·6
136	30·5	75·3	24·7	34·5	40·8	4·7	20·0	,,	3·6
137	38·6	75·3	24·7	20·6	54·7	2·3	22·4	,,	3·6

The increase in oxygen from 17·5 to 38·6 for 100 of the combustible gases produces only the slight change in the coefficient from 3·7 to 3·6.

According to HORSTMANN, this change in the quantity of oxygen should be accompanied by a fall in the coefficient from about 6 to 4·5.

With a mixture containing three times as much hydrogen as carbonic oxide a change in the quantity of oxygen added from 16 to 26 made no difference in the coefficient, when the mixtures were exploded at 100°, and above the critical pressure. The following table contains the results of these experiments.

Table XLIII.—Pressure = 1000 millims.

Reference No.	Before the explosion.			After the explosion.				α.
	Oxygen.	Carbonic oxide.	Hydrogen.	Carbonic oxide.	Carbonic acid.	Hydrogen.	Steam.	
104	15·8	24·5	75·5	21·2	3·3	47·0	28·5	4·0
103	17·3	24·0	76·0	20·4	3·6	44·4	31·6	4·0
139	25·9	24·5	75·5	17·9	6·6	30·4	45·1	4·0

With another portion of the third mixture, containing about 26 per cent. of oxygen, an explosion was made under 1000 millims. pressure at 80° C. The tension of the steam formed in the unimpeded reaction being 451 millims., and the maximum tension of aqueous vapour being only 355 millims. at 80°, it follows that condensation of steam should occur during the explosion at the lower temperature. The coefficient was found to be 4·2, a result which confirms the previous experiments made on condensation.

Table XLIV.—Pressure = 1000 millims.

Reference No.	Before the explosion.			After the explosion.				Temperature.	α.
	Oxygen.	Carbonic oxide.	Hydrogen.	Carbonic oxide.	Carbonic acid.	Hydrogen.	Steam.		
139	25·9	24·5	75·5	17·9	6·6	30·4	45·1	100°	4·0
138	,,	,,	,,	18·0	6·5	30·2	45·3	80	4·2

When a dry mixture of carbonic oxide and hydrogen is exploded with 12 to 15 per cent. of oxygen, at a pressure greater than the critical pressure, and at a temperature sufficiently high to prevent any condensation of steam, the coefficient α is found to be 4 when the hydrogen is equal to or greater than the carbonic oxide, but 3·7 when the carbonic oxide is three times the hydrogen. This difference I believe to be due to the fact that carbonic oxide and oxygen, under the conditions of these experiments, are incapable of direct combination, so that when the volume of hydrogen taken is less than double the volume of the oxygen, there is present during a part of the reaction an excess of oxygen chemically indifferent to the three other gases present—steam, carbonic oxide, and carbonic acid.

For instance, in the last three experiments of Table XL., where 17·5 parts of oxygen were exploded with 73·3 of carbonic oxide, and 26·7 of hydrogen, there was only sufficient hydrogen to burn at once 13·3 parts of oxygen; now, supposing the hydrogen to have been all burnt at once, then the other 4·2 parts of oxygen had to wait until the corresponding quantity of steam, formed at first, had been decomposed by the carbonic oxide. Of course the steam produced at first immediately began to react with the carbonic oxide, but owing to the deficiency of hydrogen, the rate of formation of steam was limited, during a considerable portion of the reaction, by the rate of formation of carbonic acid through the double decomposition of steam and carbonic oxide. The intensity of the reaction was thus diminished.

Now the presence of an inert gas, such as nitrogen, is found to affect the coefficient α in the same way. To a mixture containing about three times as much hydrogen as carbonic oxide and some 14 per cent. of oxygen, was added about two-thirds its volume of nitrogen. When this mixture was exploded under 1000 millims. pressure at 100° C., the coefficient was found to be 3·2. A similar mixture without the addition of nitrogen gave 4 for the coefficient under the same conditions.

TABLE XLV.—Pressure = 1000 millims.

Reference No.		Before the explosion.				After the explosion.				Temperature.	*a.*
		Oxygen.	Carbonic oxide.	Hydrogen	Nitrogen.	Carbonic oxide.	Carbonic acid.	Hydrogen.	Steam.	°C	
104	Mixture without nitrogen . . .	15·9	24·5	75·5	..	21·2	3·3	47·0	28·5	100	4.0
140	Mixture with nitrogen . . .	16·5	24·5	75·5	72·0	20·5	4·0	46·3	29·2	100	3·2

The diminution in intensity produced by the presence of the inert nitrogen favours the formation of carbonic acid in preference to steam in the explosion.

If the fall of the coefficient from 4 to 3·7 is due to the presence of inert oxygen during a portion of the reaction, it will follow that, so long as the oxygen employed is not more than half the hydrogen, the coefficient will remain normal whatever be the proportions of carbonic oxide and hydrogen present; but whenever the oxygen is more than half the hydrogen the coefficient will fall. The change of the coefficient will not be abrupt, but the chief gradient will occur at the point when the hydrogen is double the oxygen.

This explanation can therefore be readily tested experimentally. Two mixtures were made; one of carbonic oxide and oxygen, the other of hydrogen and oxygen—both containing the same percentage of oxygen. Varying proportions of these two mixtures were brought together in the eudiometer and exploded at a high temperature, and at a pressure greater than the critical pressure. It was found that when the hydrogen was more than double the oxygen, the coefficient was almost exactly 4; when the hydrogen was just double the oxygen, the coefficient was slightly lowered, and when the hydrogen was less than double the oxygen, the coefficient fell gradually from 4 to 3·6. In the following table the results of these experiments are tabulated, together with one or two previous experiments which fit into the series.

TABLE XLVI.—Temperature = 90°–100°. Pressure = 1000 millims.

Reference No.	Before the explosion.			After the explosion.				a.
	Oxygen.	Carbonic oxide.	Hydrogen.	Carbonic oxide.	Carbonic acid.	Hydrogen.	Steam.	
141	17·2	18·3	81·7	15·8	2·5	49·9	31·8	3·98
103	17·3	24·0	76·0	20·4	3·5	44·7	31·3	4·03
142	16·9	39·7	60·3	33·0	6·8	33·2	27·1	3·97
106	15·4	51·7	48·3	42·9	8·7	26·6	21·8	4·02
143	17·4	58·8	41·2	45·8	13·0	19·4	21·8	3·97
144	17·35	61·6	38·4	47·5	14·1	17·8	20·6	3·93
145	17·35	66·0	34·0	50·0	16·0	15·3	18·7	3·81
98	17·5	73·3	26·7	53·7	19·6	11·4	15·2	3·67
146	16·7	79·2	20·8	57·9	21·3	8·8	12·05	3·68
147	16·6	84·3	15·7	60·3	24·0	6·4	9·25	3·61

Again, similar experiments were made with a smaller proportion of oxygen; instead of 17·4 parts of oxygen 12·4 were taken. With 17·4 parts of oxygen, the percentage of hydrogen could not be reduced to 34 per cent. of the combustible gases without lowering the coefficient, but with only 12·4 parts of oxygen the lowering of the coefficient should only occur when the percentage of hydrogen is reduced to about 25 per cent.

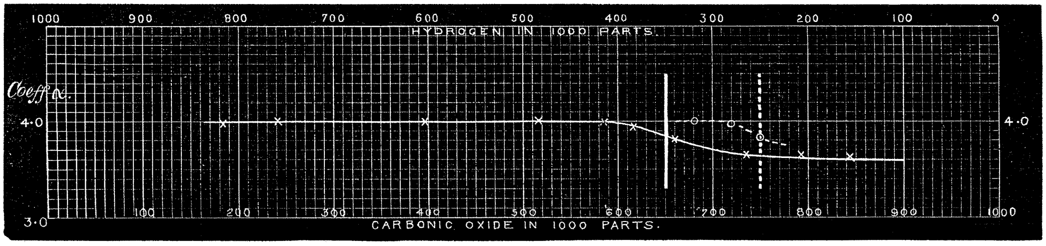
The experiments agreed perfectly with the theory.

With 32 per cent. of hydrogen the coefficient was normal, with 28 per cent. it was still nearly normal, with 24 per cent. it had fallen.

TABLE XLVII.—Temperature = 90°. Pressure = 1000 millims.

Reference No.	Before the explosion.			After the explosion.				a.
	Oxygen.	Carbonic oxide.	Hydrogen.	Carbonic oxide.	Carbonic acid.	Hydrogen.	Steam.	
148	12·45	67·9	32·1	56·9	11·0	18·2	13·9	3·96
149	12·45	72·0	28·0	59·6	12·4	15·5	12·5	3·91
150	12·45	76·1	23·9	62·1	14·0	12·9	11·0	3·77

The results of these two series of experiments are expressed graphically below. The abscissæ are parts of carbonic oxide in 1000 of the combustible gases, the ordinates are the coefficients found.



The continuous curve is drawn through the coefficients given by the mixtures with 17·4 parts of oxygen. The vertical line shows the point where the hydrogen is just twice the oxygen in the first series. The dotted curve is drawn through the coefficients given by the mixture with 12·4 parts of oxygen. The vertical line shows the point where the hydrogen is just twice the oxygen in the second series.

General conclusions.

1. BUNSEN'S original experiments on the incomplete combustion of carbonic oxide and hydrogen are vitiated by the presence of aqueous vapour in the eudiometer. Both HORSTMANN'S experiments and my own show that no alteration *per saltum* occurs in the ratio of the products of combustion.

2. A mixture of dry carbonic oxide and oxygen does not explode when an electric spark is passed through it. The union of carbonic oxide and oxygen is effected indirectly by steam. A mere trace of steam renders a mixture of oxygen and carbonic oxide explosive. The steam undergoes a series of alternate reductions and oxidations, acting as a carrier of oxygen to the carbonic oxide. With a very small quantity of steam the oxidation of carbonic oxide takes place slowly. As the quantity of steam is increased the rapidity of the explosion increases.

3. When a mixture of dry carbonic oxide and hydrogen is exploded with a quantity of oxygen insufficient for complete combustion, the ratio of the carbonic acid to steam formed, depends on the shape of the vessel and the pressure under which the gases are fired. By continually increasing the initial pressure a point is reached where no further increase in the pressure affects the products of the reaction. At and above this "critical pressure" the result is independent of the shape of the vessel. The larger the quantity of oxygen used the lower the "critical pressure" is found to be.

4. When dry mixtures of carbonic oxide and hydrogen in varying proportions are exploded above the "critical pressure" with oxygen insufficient for complete combustion, an equilibrium is established between two opposite chemical changes represented by the equations

$$(1)\ CO + H_2O = CO_2 + H_2$$
$$(2)\ CO_2 + H_2 = CO + H_2O$$

So that at the end of the reaction the product of the carbonic oxide and steam molecules is equal to the product of the carbonic acid and hydrogen molecules multiplied by a "coefficient of affinity." This result agrees with HORSTMANN'S conclusion; but HORSTMANN considers the coefficient to vary with the relative mass of oxygen taken.

5. A small difference in the initial temperature at which the gases are fired makes a considerable difference in the products of the reaction. This difference is due to the condensation of steam by the sides of the vessel during the explosion, and its consequent removal from the sphere of action during the chemical change. When the gases are exploded at a temperature sufficiently high to prevent any condensation of steam during the progress of the reaction, the coefficient is found to be constant whatever the quantity of oxygen used, provided that the hydrogen is more than double the oxygen.

6. The presence of an inert gas, such as nitrogen, by diminishing the intensity of the reaction favours the formation of carbonic acid in preference to steam. When the hydrogen is less than double the oxygen the excess of oxygen cannot react with any of the three other gases present—carbonic oxide, carbonic acid, and steam—but has to wait until an equal volume of steam is reduced to hydrogen by the carbonic oxide. The excess of inert oxygen has the same effect as the inert nitrogen in favouring the formation of carbonic acid.

The variations in the coefficient of affinity found by HORSTMANN with different quantities of oxygen are due partly to this cause, but chiefly to the varying amounts of steam condensed by the cold eudiometer during the reaction in different experiments.

7. As the general result of these experiments, it has been shown that when a mixture of carbonic oxide and hydrogen is exploded with insufficient oxygen for complete combustion, at a temperature at which no condensation of steam can take place during the reaction, and at a pressure greater than the critical pressure, an equilibrium between two opposite changes is established, which is independent of the quantity of oxygen taken, so long as this quantity is less than half the hydrogen. Within the limits marked out above, the law of mass is completely verified for the gaseous system composed of carbonic oxide, carbonic acid, hydrogen, and steam at a high temperature.

The experiments described in this paper were made partly in the laboratory of Christ Church, and partly in the laboratory of Balliol College, Oxford. I desire to express my sincere thanks to Mr. A. G. VERNON HARCOURT and to Mr. W. ESSON for their constant help and advice in all stages of the inquiry, and to the Government Grant Committee of the Royal Society for giving me the leisure and the appliances to complete this research.

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APPENDIX.

1. In the following tables the actual numbers obtained in each analysis are given—beginning with those summarised in Table VIII. of the paper—in which the pressure of the gases at explosion was observed. The first column gives the reference number. In the three next columns the percentage composition of the gas is given, as determined by mixture or analysis previous to each experiment. The next two columns give the pressure (P) and the temperature (T) of the gases just before the spark was passed. In the seventh and succeeding columns are given the volumes reduced to cubic centimetres at 0° C. and 760 millims. before the explosion (V_o), after the explosion (V_e), after absorption with potash (V_a), after addition of excess of oxygen (V'_o), after explosion (V'_e), and lastly after absorption with potash (V'_a).

By the two explosions and absorptions a complete analysis of the mixture is made. The second part of the operation not only serves to control the whole, but gives a second independent value for the amount of hydrogen and carbonic oxide burnt in the first explosion. By subtracting the quantity of hydrogen burnt in the second explosion from the quantity of hydrogen originally measured, a number is obtained which should be identical with the quantity of steam formed in the first explosion—if no experimental error occurred. In the column under "*h* found" is given the quantity of hydrogen burnt in the first explosion as directly determined by the contraction and absorption; in the column under "*h* calculated" is given the quantity of hydrogen burnt in the first explosion as calculated from the quantity originally measured and that found in the second explosion. The mean between these two numbers is taken as the correct quantity of hydrogen burnt in the first explosion.

Exactly in the same way the mean between the found and the calculated quantity of carbonic oxide burnt is taken as the correct quantity.

From the numbers given the entire analysis may be calculated out in the following way:—

No. 1. COMPOSITION of mixture.

Carbonic oxide	67·10
Hydrogen	21·91
Oxygen	11·09
	100·00

VOLUMES reduced to 0° C. and 760 millims.

	Cub. centims.
Volume of mixture taken	8·25
,, after explosion	6·50
,, ,, absorption	5·51
,, ,, addition of oxygen . . .	16·14
,, ,, explosion	12·40
,, ,, absorption	7·83

First contraction $=1·74=c$ First absorption $=·99=k$
Second ,, $=3·74=c'$ Second ,, $=4·57=k'$

By first explosion and absorption:—

Oxygen $=\frac{1}{3}(c+k)=·908$, Hydrogen $=\frac{2}{3}\left(c-\frac{k}{2}\right)=·83$, Carbonic oxide $=·99$

By second explosion and absorption:—

Hydrogen $=\frac{2}{3}\left(c'-\frac{k'}{2}\right)=·97$, Carbonic oxide $=4·57$

Total hydrogen $=1·80$, Total carbonic oxide $=5·56$

COMPOSITION of mixture by analysis.

CO . . .	5·56	67·39
H_2 . . .	1·80	21·82
O_2 . . .	·91	11·01
	8·27	100·22

Then by calculation from the original mixture, 8·25 cub. centims. contain 5·54 cub. centims. carbonic oxide and 1·81 cub. centims. hydrogen.

5·54	1·81
4·57	·97
·97 k calculated	·84 h calculated
·99 k found	·83 h found
·98 mean k	·835 mean h

$$\frac{k}{h} = \frac{\cdot 98}{\cdot 835} = 1\cdot 17$$

I.

Reference No.	Oxygen.	Carbonic oxide.	Hydrogen.	P.	T.	V_o.	V_e.	V_a.	V'_o.	V'_e.	V'_a.	h found.	h calculated.	$\frac{k}{h}$
				millims.	°C.									
1	11·09	67·10	21·91	210	10·5	8·25	6·50	5·51	16·14	12·40	7·83	·83	·84	1·17
2	,,	,,	,,	,,	9·7	11·26	8·87	7·53	17·065	12·087	5·940	1·150	1·195	1·17
3	,,	,,	,,	,,	11·1	12·82	10·10	8·58	21·33	15·51	8·47	1·31	1·28	1·19
4	,,	,,	,,	,,	10·5	16·61	13·10	11·11	21·51	14·04	4·97	1·67	1·68	1·21
5	,,	,,	,,	,,	11·1	17·04	13·41	11·34	21·25	13·63	4·32	1·73	1·74	1·21
6	,,	,,	,,	,,	10·3	23·61	18·66	15·79	28·88	18·22	5·34	2·35	2·36	1·24
7	,,	,,	,,	,,	10·3	31·25	24·71	20·81	35·60	21·54	4·78	3·06	3·06	1·32
8	,,	,,	,,	200	8·5	12·52	9·95	8·37	18·51	12·82	6·02	1·19	1·21	1·33
9	16·88	49·60	33·52	250	10·5	9·89	6·02	4·86	11·40	7·85	4·08	2·19	2·19	·52
10	,,	,,	,,	,,	10·1	10·61	6·45	5·22	14·40	10·58	6·57	2·36	2·35	·53
11	,,	,,	,,	,,	9·0	10·70	6·53	5·28	16·14	12·29	8·23	2·36	2·37	·53
12	,,	,,	,,	,,	10·5	11·19	6·84	5·55	15·30	11·28	7·02	2·47	2·49	·52
13	,,	,,	,,	,,	9·6	35·43	21·75	17·59	38·52	25·85	12·63	7·73	7·84	·55
14	,,	,,	,,	,,	10·5	38·54	23·66	19·11	36·99	22·93	8·38	8·40	8·40	·54
15	,,	,,	,,	,,	9·5	36·83	22·59	18·21	32·96	19·53	5·62	8·03	8·03	·545
16	19·70	41·02	39·28	250	9·0	37·42	19·445	15·325	31·594	19·834	8·656	10·61	10·59	·39
17	,,	,,	,,	,,	7·4	32·52	16·89	13·33	25·20	15·04	5·25	9·23	9·25	·385
18	,,	,,	,,	,,	7·9	11·026	5·724	4·512	17·406	13·974	10·661	3·131	3·146	·385
19	,,	,,	,,	,,	6·7	11·264	5·836	4·599	16·960	13·440	10·060	3·206	3·204	·39
20	19·70	41·02	39·28	100	8·6	7·99	4·19	3·26	15·26	12·73	10·41	2·22	2·22	·426
21	,,	,,	,,	,,	9·8	15·64	8·34	6·44	23·90	18·78	14·29	4·23	4·22	·453
22	12·86	61·64	25·50	75	6·5	6·033	4·580	3·712	13·990	11·272	8·412	·679	·679	1·27
23	,,	,,	,,	100	5·6	8·370	6·321	5·145	15·963	12·224	8·240	·974	·969	1·21
24	,,	,,	,,	125	6·4	10·33	7·69	6·34	19·65	15·18	10·14	1·310	1·333	1·01
25	,,	,,	,,	150	6·5	12·47	9·21	7·65	20·440	15·090	8·976	1·65	1·65	·95
26	,,	,,	,,	200	5·8	18·80	13·83	11·53	29·09	21·07	11·84	2·55	2·514	·92
27	,,	,,	,,	300	6·9	24·68	18·06	15·14	34·35	23·96	11·66	3·44	3·46	·85
28	,,	,,	,,	425	7·0	34·523	25·177	21·189	38·090	23·630	6·350	4·90	4·922	·81
29	,,	,,	,,	600	6·4	49·069	35·826	30·165	49·530	28·880	4·340	6·942	6·920	·82

I. (continued.)

Reference No.	Oxygen.	Carbonic oxide.	Hydrogen	P.	T.	V_o.	V_e.	V_a.	V'_o.	V'_e.	V'_a.	h found.	h calculated.	$\frac{k}{h}$
				millims.	°C.									
30	12·29	63·31	24·40	75	15·7	6·024	4·666	3·815	12·824	10·047	7·060	·622	·614	1·36
31	"	"	"	"	16·6	5·479	4·276	3·466	10·651	8·104	5·396	·532	·542	1·46
32	"	"	"	"	15·0	5·834	4·516	3·673	13·255	10·582	7·744	·598	·588	1·43
33	"	"	"	"	14·3	6·645	5·158	4·206	15·489	12·442	9·160	·674	·684	1·38
34	"	"	"	"	14·0	6·511	5·083	4·126	12·292	9·290	6·082	·634	·657	1·45
35	"	"	"	"	13·2	6·997	5·411	4·414	12·468	9·283	5·841	·725	·731	1·36
36	"	"	"	"	14·2	6·207	4·800	3·920	15·000	12·156	9·084	·645	·643	1·35
37	"	"	"	"	14·5	5·753	4·430	3·602	15·908	13·271	10·438	·606	·590	1·37
38	"	"	"	100	14·4	9·124	7·071	5·765	16·118	11·926	7·442	·933	·926	1·40
39	"	"	"	"	13·3	9·082	7·044	5·725	18·565	14·441	10·012	·919	·942	1·42
40	"	"	"	"	14·8	9·497	7·357	5·998	20·951	16·615	11·956	·974	·979	1·39
41	"	"	"	125	19·9	10·214	7·795	6·437	21·767	17·211	12·137	1·160	1·146	1·19
42	"	"	"	"	14·9	10·311	7·874	6·513	17·430	12·835	7·654	1·171	1·180	1·15
43	"	"	"	150	15·1	12·575	9·537	7·949	20·249	14·710	8·356	1·496	1·493	1·07
44	"	"	"	175	15·2	15·538	11·738	9·811	21·077	14·269	6·405	1·891	1·874	1·035
45	"	"	"	200	15·1	15·45	11·63	9·75	27·84	21·15	13·29	1·92	1·93	·99
46	"	"	"	250	15·0	20·502	15·360	12·920	26·650	17·836	7·327	2·610	2·63	·94
47	"	"	"	300	11·7	27·74	20·77	17·51	37·53	25·61	11·36	3·56	3·57	·92
48	"	"	"	400	15·3	33·00	24·68	20·80	39·61	25·42	8·43	4·25	4·25	·915
49	"	"	"	700	14·9	59·95	44·83	37·85	..	..	..	7·75	..	·90
50	"	"	"	1000	15·7	83·47	62·39	52·66	..	..	..	10·81	..	·90
51	18·99	58·47	22·54	75	18·8	6·100	4·026	2·615	10·359	8·572	6·399	·912	·908	1·54
52	"	"	"	100	18·2	9·080	5·920	3·906	11·445	8·876	5·568	1·435	1·437	1·40
53	"	"	"	125	16·2	10·193	6·562	4·377	15·889	13·110	9·339	1·682	1·701	1·29
54	"	"	"	200	12·6	17·108	10·894	7·349	22·946	18·420	11·965	2·961	2·990	1·19
55	"	"	"	400	13·7	38·61	24·68	16·82	37·86	27·44	12·82	6·67	6·632	1·19
56	"	"	"	500	8·8	45·511	28·927	19·566	33·597	21·479	4·337	7·936	7·892	1·19
57	12·29	63·31	24·40	400	13·0	16·89	12·59	10·63	22·66	15·45	6·79	2·21	2·20	·905
58	"	"	"	"	9·5	17·730	13·228	11·205	21·528	13·922	4·759	2·327	2·310	·88
59	"	"	"	1000	10·4	17·665	13·161	11·148	20·479	12·916	3·847	2·332	2·291	·89
60	"	"	"	"	12·9	16·803	12·563	10·610	22·475	15·262	6·656	2·176	2·160	·92
61	8·06	66·28	25·66	125	11·3	11·992	10·065	9·116	17·037	10·378	3·426	·963	·955	1·02
62	"	"	"	150	11·2	13·020	10·950	9·883	20·488	13·265	5·769	1·023	1·023	1·08
63	"	"	"	175	11·2	16·562	13·932	12·532	24·638	15·463	5·913	1·287	1·316	1·09
64	"	"	"	200	12·5	17·262	14·531	13·074	26·236	16·673	6·722	1·334	1·371	1·09
65	"	"	"	250	7·8	21·757	18·357	16·527	28·152	15·999	3·393	1·657	1·682	1·09
66	"	"	"	300	8·6	25·468	21·424	19·320	31·982	17·816	3·004	1·995	2·027	1·04
67	"	"	"	400	14·5	32·85	27·59	24·97	46·73	28·34	9·27	2·63	2·53	1·03
68	"	"	"	600	12·4	48·700	40·780	36·820	..	..	..	3·960	..	1·00
69	"	"	"	1000	10·0	84·369	70·512	63·699	..	..	..	6·966	..	·98
70	"	"	"	"	8·0	10·342	8·642	7·869	16·421	10·708	4·643	·876	·866	·90
71	"	"	"	"	8·4	15·004	12·526	11·379	23·632	15·374	6·595	1·270	1·270	·91

2. The experiments 72 to 150 are given in detail in the following table. The last column contains the coefficient found by dividing the product of the carbonic oxide and steam molecules by the product of the carbonic acid and hydrogen molecules. The values of h and h' in this column are the *means* between the found and calculated values for the hydrogen burnt in the first and second explosion respectively; and the values of and k and k' are the *means* between the found and calculated values for the carbonic oxide burnt in the two explosions. The other columns are exactly similar to those in the previous table.

Experiment 72 is here given in full :—

COMPOSITION of mixture.

Carbonic oxide	73·19
Hydrogen	14·36
Oxygen	12·45
	100·00

VOLUMES reduced to 0° C. and 760 millims.

	Cub. centims.
Volume of mixture taken	22·075
,, after explosion	17·503
,, ,, absorption	13·836
,, ,, addition of oxygen . . .	28·055
,, ,, explosion	19·829
,, ,, absorption	7·357

First contraction $=4{\cdot}572=c$ First absorption $=3{\cdot}667=k$

Second ,, $=8{\cdot}226=c'$ Second ,, $=12{\cdot}472=k'$

$$0=\tfrac{1}{3}(c+k)=2{\cdot}746 \qquad h=\tfrac{2}{3}\left\{c-\frac{k}{2}\right\}=1{\cdot}826$$

$$h'=\tfrac{2}{3}\left\{c'-\frac{k'}{2}\right\}=1{\cdot}327$$

Total hydrogen $=3{\cdot}153$ Total carbonic oxide $=16{\cdot}139$

COMPOSITION of mixture by analysis.

CO . . .	16·139	73·12
H_2 . . .	3·153	14·28
O_2 . . .	2·746	12·44
	22·038	99·84

By calculation from original mixture 22·075 cub. centims. contain 16·159 cub. centims. carbonic oxide and 3·169 cub. centims. hydrogen :—

16·159				3·169			
12·472				1·327			
3·687	calculated	16·159		1·842	calculated *h*	3·169	
3·667	found	3·677		1·826	found *h*	1·834	
3·677	mean *k*	12·482	mean *k′*	1·834	mean *h*	1·335	mean *h′*

$$\frac{k'\times h}{k\times h'}=\frac{12{\cdot}482\times 1{\cdot}834}{3{\cdot}677\times 1{\cdot}335}=4{\cdot}67.$$

II.

Reference No.	Oxygen.	Carbonic oxide.	Hydrogen.	P.	T.	V_o.	V_e.	V_a.	V'_o.	V'_e.	V'_a.	h found.	h calculated.	$\frac{k'h}{kh'}$
				millims.	°C.									
72	12·45	73·19	14·36	1000	15·6	22·075	17·503	13·836	28·055	19·829	7·357	1·826	1·843	4·67
73	12·44	67·76	19·80	,,	14·6	26·406	20·198	16·501	29·847	19·306	5·178	2·906	2·911	4·76
74	12·40	58·12	29·48	,,	13·4	16·842	12·207	10·556	22·259	14·578	6·476	2·540	2·545	5·11
75	12·38	45·96	41·66	,,	13·6	17·057	11·763	10·716	18·880	9·609	2·658	3·180	3·176	5·13
76	12·36	35·60	52·04	,,	15·2	19·116	12·797	12·026	24·917	12·957	6·907	3·956	3·990	5·26
77	12·33	26·42	61·25	,,	15·2	22·284	14·612	14·035	30·214	14·505	9·209	4·922	4·942	5·14
78	12·30	11·80	75·90	,,	14·6	19·911	12·767	12·563	23·790	7·050	4·890	4·695	4·671	4·90
79	15·03	71·76	13·21	1000	13·4	21·411	16·265	11·677	22·693	15·893	5·171	1·901	1·869	4·68
80	14·98	67·85	17·18	,,	13·4	15·347	11·259	8·387	21·933	16·854	9·402	1·768	1·735	5·09
81	15·00	66·77	18·23	,,	12·6	21·410	15·610	11·717	27·370	20·170	9·800	2·569	2·559	5·09
82	14·98	58·55	26·47	,,	13·6	15·070	10·306	8·257	20·119	14·498	7·788	2·493	2·478	5·36
83	15·01	39·08	45·91	,,	13·0	11·445	7·018	6·310	14·132	8·412	4·734	2·715	2·667	5·22
84	15·01	30·55	54·44	,,	13·2	15·080	8·948	8·287	19·298	10·827	6·901	3·868	3·872	5·23
85	14·99	13·48	71·53	,,	13·7	18·222	10·283	9·988	23·725	10·917	8·764	5·194	5·214	4·80
86	13·81	63·10	23·09	1000	6·7	11·125	8·008	6·495	17·648	13·412	7·909	1·574	1·579	5·77
87	,,	,,	,,	,,	8·9	10·070	7·241	5·882	15·617	11·784	6·790	1·433	1·434	5·91
88	,,	,,	,,	,,	8·8	11·197	7·044	4·460	13·536	10·810	6·852	1·907	1·917	5·82
89	,,	,,	,,	,,	8·0	13·527	8·510	5·408	13·884	10·585	5·821	2·311	2·306	5·82
90	14·08	60·80	25·12	1000	3	15·320	10·760	8·762	22·147	16·297	9·066	2·373	2·359	5·69
91	,,	,,	,,	,,	19	12·999	9·209	7·473	20·807	15·791	9·687	1·948	1·956	5·15
92	,,	,,	,,	,,	20	15·063	10·681	8·638	22·925	17·085	10·030	2·240	2·242	4·94
93	,,	,,	,,	,,	40	13·903	9·874	7·930	21·385	16·007	9·590	2·038	2·047	4·57
94	,,	,,	,,	,,	60	10·640	7·635	6·060	16·558	12·351	7·490	1·480	1·489	3·83
95	14·73	62·50	22·77	1000	−10	11·127	7·763	6·170	22·010	18·130	12·800	1·712	1·724	7·03
96	,,	,,	,,	,,	60	14·322	10·304	7·963	22·434	17·096	10·524	1·898	1·893	3·87
97	,,	,,	,,	,,	80	12·782	9·231	7·100	16·353	11·593	5·756	1·657	1·683	3·68
98	,,	,,	,,	,,	100	17·348	12·529	9·647	21·508	15·014	7·078	2·252	2·269	3·67
99	15·02	52·40	22·58	,,	120	19·706	14·207	10·852	24·429	17·133	8·143	2·548	2·582	3·66
100	14·78	20·44	64·78	1000	0	15·122	8·779	8·435	21·536	11·642	8·888	4·114	4·119	5·86
101	,,	,,	,,	,,	70	19·920	11·685	11·105	24·746	11·665	8·171	5·300	5·340	4·19
102	,,	,,	,,	,,	80	15·560	9·137	8·656	17·571	7·350	4·622	4·121	4·173	4·03
103	,,	,,	,,	,,	100	17·816	10·455	9·914	19·244	7·684	4·616	4·737	4·859	3·98
104	13·71	21·12	65·17	,,	125	17·274	10·671	10·204	19·706	7·616	4·449	4·246	4·252	4·05
105	13·42	44·72	41·86	1000	70	12·503	8·397	7·422	19·508	12·975	8·337	2·412	2·425	4·12
106	,,	,,	,,	,,	80	15·060	10·214	9·061	19·779	11·763	6·156	2·846	2·829	4·02
107	,,	,,	,,	,,	120	13·462	9·112	8·084	18·286	11·171	6·186	2·557	2·553	4·01
108	15·02	62·40	22·58	400	40	7·943	5·685	4·356	11·760	8·872	5·223	1·062	1·084	4·11
109	,,	,,	,,	,,	50	9·270	6·679	5·117	13·047	9·616	5·408	1·207	1·209	3·67
110	,,	,,	,,	,,	100	8·281	5·961	4·565	13·776	10·738	6·981	1·081	1·097	3·74
111	15·02	62·40	22·58	100	16	7·379	5·362	4·089	12·371	9·574	6·217	·920	·940	3·39
112	,,	,,	,,	,,	30	8·362	6·139	4·620	12·241	9·031	5·305	·976	·989	2·67
113	,,	,,	,,	,,	60	6·611	4·844	3·627	9·754	7·241	4·299	·772	·798	2·70
114	,,	,,	,,	,,	100	6·248	4·565	3·442	8·576	6·184	3·406	·732	·742	2·67
115	13·42	44·72	41·86	150	80	6·937	4·764	4·165	11·456	7·730	5·190	1·249	1·267	3·32
116	,,	,,	,,	200	,,	7·661	5·198	4·556	11·477	7·429	4·628	1·428	1·442	3·55
117	,,	,,	,,	300	,,	10·385	7·058	6·252	16·003	10·510	6·662	1·949	1·968	3·93
118	,,	,,	,,	400	,,	11·358	7·647	6·755	15·353	9·417	5·238	2·177	2·190	3·97
119	13·71	21·12	65·17	100	100	6·942	4·391	4·125	14·100	9·118	7·876	1·612	1·617	2·76
120	,,	,,	,,	300	,,	9·988	6·206	5·910	14·713	7·702	5·863	2·423	2·448	3·85
121	7·83	44·47	47·70	400	90	13·192	10·632	10·072	15·455	5·640	·356	1·520	1·510	2·94
122	,,	,,	,,	800	,,	14·815	11·940	11·340	30·297	19·280	13·268	1·717	1·725	3·28
123	,,	,,	,,	1000	,,	10·991	8·788	8·346	16·773	8·668	4·247	1·321	1·312	3·28
124	,,	,,	,,	1500	,,	13·330	10·678	10·130	17·580	7·798	2·398	1·585	1·637	3·39
125	,,	,,	,,	2000	,,	17·167	13·807	13·152	25·171	12·434	5·459	2·022	2·022	3·48

II. (continued).

Reference No.	Oxygen.	Carbonic oxide.	Hydrogen.	P.	T.	V_o.	V_e.	V_a.	V'_o.	V'_e.	V'_a.	h found.	h calculated.	$\frac{k'h}{kh'}$
				millims.	°C.									
126	9·24	48·33	42·42	400	90	15·311	11·924	11·062	21·223	11·200	4·645	1·971	1·998	3·38
127	"	"	"	1500	"	16·630	12·889	11·995	21·223	10·390	3·246	2·196	2·214	3·63
128	"	"	"	1750	"	17·010	13·177	12·286	24·894	13·804	6·479	2·258	2·264	3·74
129	"	"	"	2000	"	22·667	17·543	16·391	29·567	14·747	4·966	3·032	2·996	3·84
130	10·35	41·89	47·76	400	90	17·914	13·250	12·334	28·801	16·905	10·297	2·804	2·829	3·57
131	"	"	"	600	"	14·591	10·785	10 079	22·548	12·886	7·495	2·302	2·325	3·76
132	"	"	"	800	"	12·680	9·343	8·742	18·014	9·627	4·931	2·024	2·030	3·90
133	"	"	"	1000	"	18·828	13·874	12·981	23·073	10·622	3·637	3·005	3·021	3·93
134	21·18	59·37	19·45	1000	90	19·652	12·712	7·432	19·707	15·087	8·667	2·867	2·883	3·69
135	21·19	59·63	19·18	"	"	17·840	11·442	6·424	14·555	10·585	5·013	2·593	2·632	3·59
136	23·26	57·80	18·94	"	"	17·807	10·945	5·379	15·210	11·930	7·224	2·719	2·755	3·64
137	27·75	54·42	17·83	"	"	16·757	9·404	2·805	10·238	8·574	6·087	2·702	2·708	3·62
138	20·67	19·42	59·91	1000	80	17·163	7·501	6·607	15·664	8·302	5·841	6·143	6·195	4·16
139	"	"	"	"	100	16·777	7·340	6·486	17·944	10·676	8·281	5·998	6·016	4·05
140	N_2 38·2 O_2 8·77	12·98	40·04	1000	80	17·346	13·143	12·776	21·350	14·020	12·134	2·680	2·687	3·25
141	14·66	15·64	69·70	1000	90	22·615	13·177	12·677	24·165	8·642	5·580	6·125	6·133	3·98
142	14·33	34·03	51·64	"	"	19·661	12·291	11·148	23·335	12·204	6·648	4·532	4·584	3·97
143	14·63	50·19	35·13	"	"	15·056	10·047	8·381	18·260	11·609	5·725	2·784	2·816	3·97
144	14·70	52·56	32·74	"	"	23·372	15·787	12·990	26·522	16·467	6·997	4·124	4·106	3·93
145	14·79	56·29	29·02	"	"	18·578	12·880	10·328	21·633	14·054	6·121	2·948	2·983	3·81
146	14·33	67·83	17·84	"	"	21·868	16.501	12·506	20·879	12·981	2·148	2·246	2·247	3·68
147	14·33	72·23	13·44	"	"	20·951	16·282	11·973	21·908	14·740	3·918	1·676	1·645	3·61
148	11·07	60·35	28·58	1000	80	20·600	15·769	13·760	28·151	17·927	7·503	2·551	2·547	3·96
149	11·06	64·02	24·92	"	"	20·885	16·243	13·942	23·825	13·978	2·900	2·328	2·331	3·91
150	11·06	67·69	21·25	"	"	18·417	14·581	12·297	22·754	14·488	4·316	1·796	1·794	3·77

Note on the preceding Paper.

By W. ESSON, *M.A., F.R.S., Fellow of Merton College, Oxford.*

IN January, 1882, Mr. DIXON sent to me the results of the experiments recorded on p. 659 of the preceding memoir, and asked me to discover if I could the relation between the quantities of the gases at the beginning and end of the explosion. The facts already discovered by Mr. DIXON (1) that the union of carbonic oxide and oxygen does not take place except in the presence of steam, and (2) that carbonic oxide is oxidized by steam at a high temperature, led me to conjecture that the first effect of the explosion was to combine all the oxygen present with the proper amount of hydrogen to form steam. An action was then set up between the steam and carbonic oxide resulting in the formation of hydrogen and carbonic acid, and simultaneously a reverse action took place between the hydrogen and carbonic acid resulting in the formation of steam and carbonic oxide. Finally an equilibrium was established between the action and reverse action when the amount of each per unit of time was equal to that of the other.

In a paper by Mr. HARCOURT and myself, communicated to the Royal Society in November, 1865 (Transactions, Vol. 156, p. 217), it is shown that the amount of action per unit of time between two substances is proportional to the quantity of each substance. In the course of a hitherto unpublished investigation on the reaction of hydrogen iodide and peroxide a case of equilibrium occurred in November, 1865, precisely analogous to the present case, and admitting of the same explanation. The two cases are represented by the following chemical equations

$$\left.\begin{array}{r} H_2O_2+2HI=2H_2O+I_2 \\ 2H_2O+I_2=H_2O_2+2HI \end{array}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$\left.\begin{array}{r} H_2O+CO=H_2+CO_2 \\ H_2+CO_2=H_2O+CO \end{array}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

If in general A_1, B_1, A_2, B_2 are substances reacting according to the chemical equation

$$A_1+B_1=A_2+B_2,$$
$$A_2+B_2=A_1+B_1,$$

and if a_1, a_2, b_1, b_2 are the quantities of A_1, A_2, B_1, B_2 respectively in an unit of volume, the amount of the first action per unit of time is $\alpha a_1 b_1$, and the amount of the second action per unit of time is $\beta a_2 b_2$, so that when equilibrium is established $\alpha a_1 b_1=\beta a_2 b_2$.

In the present case, if H_2O, CO, H_2, CO_2 represent the quantities per unit of volume of steam, carbonic oxide, hydrogen, and carbonic acid respectively, the ratio of $H_2O\times CO$ to $H_2\times CO_2$ is a ratio independent of the quantities of substance taking part in the reaction, and depending only upon the conditions of temperature, pressure, &c. In the experiments which Mr. DIXON submitted to me this constant is 5, and on p. 660 the numbers calculated on this hypothesis are compared with those actually found.

The calculation of the steam and carbonic acid ultimately remaining after the explosion of given quantities of hydrogen, carbonic oxide, and oxygen is effected in the following way:—

Let a, b, c be the original quantities of hydrogen (H_2), carbonic oxide (CO), and oxygen (O_2) respectively, and x the ultimate quantity of steam, then the ultimate quantities of carbonic oxide (CO), hydrogen (H_2), and carbonic acid (CO_2) are respectively $b-2c+x$, $a-x$, $2c-x$, hence if $H_2O \times CO : H_2 \times CO_2 = \mu$

$$x(b-2c+x)=\mu(a-x)(2c-x)$$

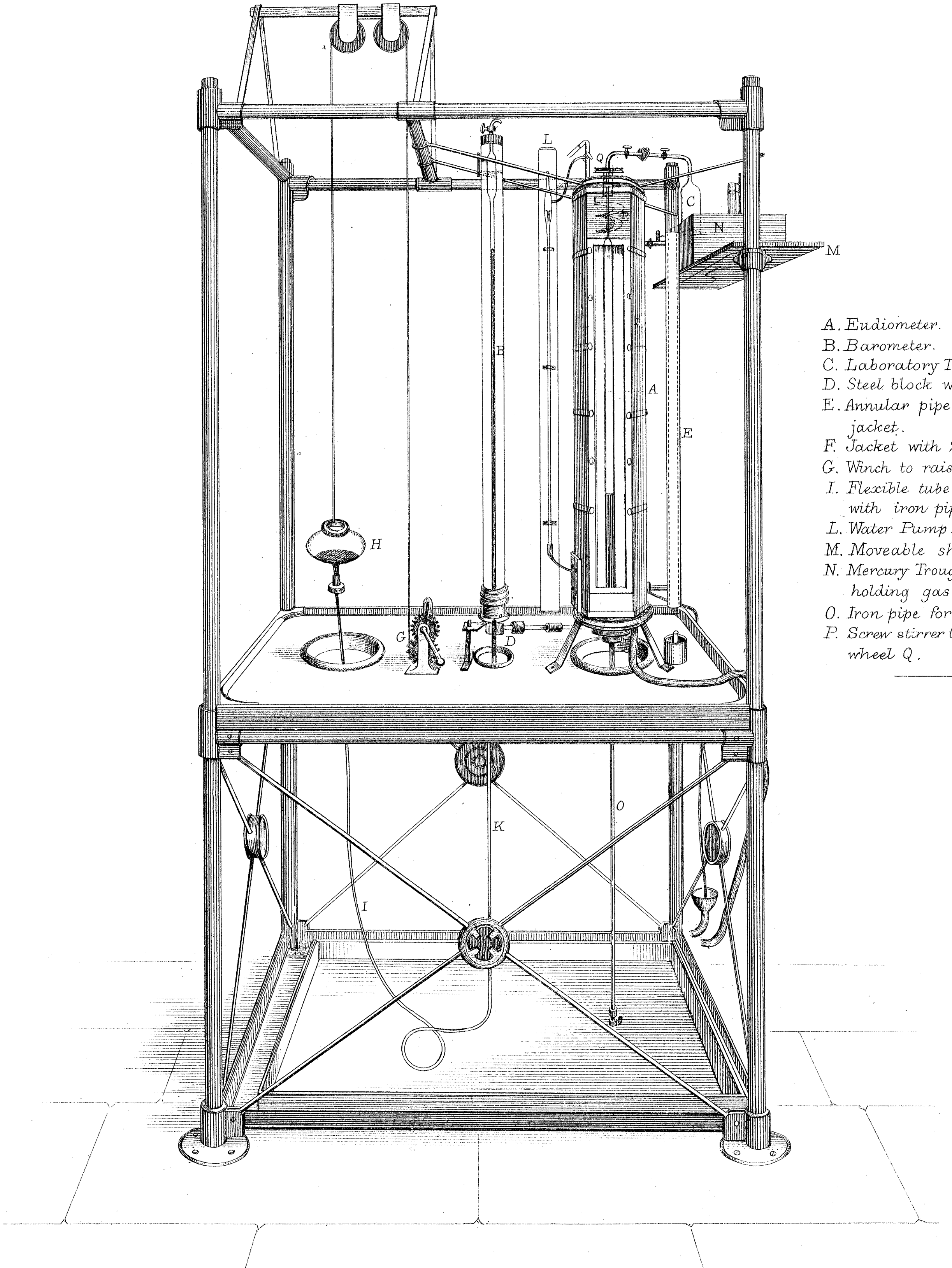
or

$$(\mu-1)x^2-\{\mu(a+2c)+b-2c\}x+2\mu ac=0,$$

the lesser root x_1 of this quadratic is the amount of steam, and $2c-x_1$ is the amount of carbonic acid after the explosion. In the experiments recorded on p. 659 $a+b=100$, $c=14{\cdot}2$, $\mu=5$, and a has values varying from 16·4 to 86·54. The quadratic in the case of the experiment in which $a=86{\cdot}54$ is

$$4x^2-558{\cdot}16x+12115{\cdot}6=0$$

the lesser root of which is 26·89.



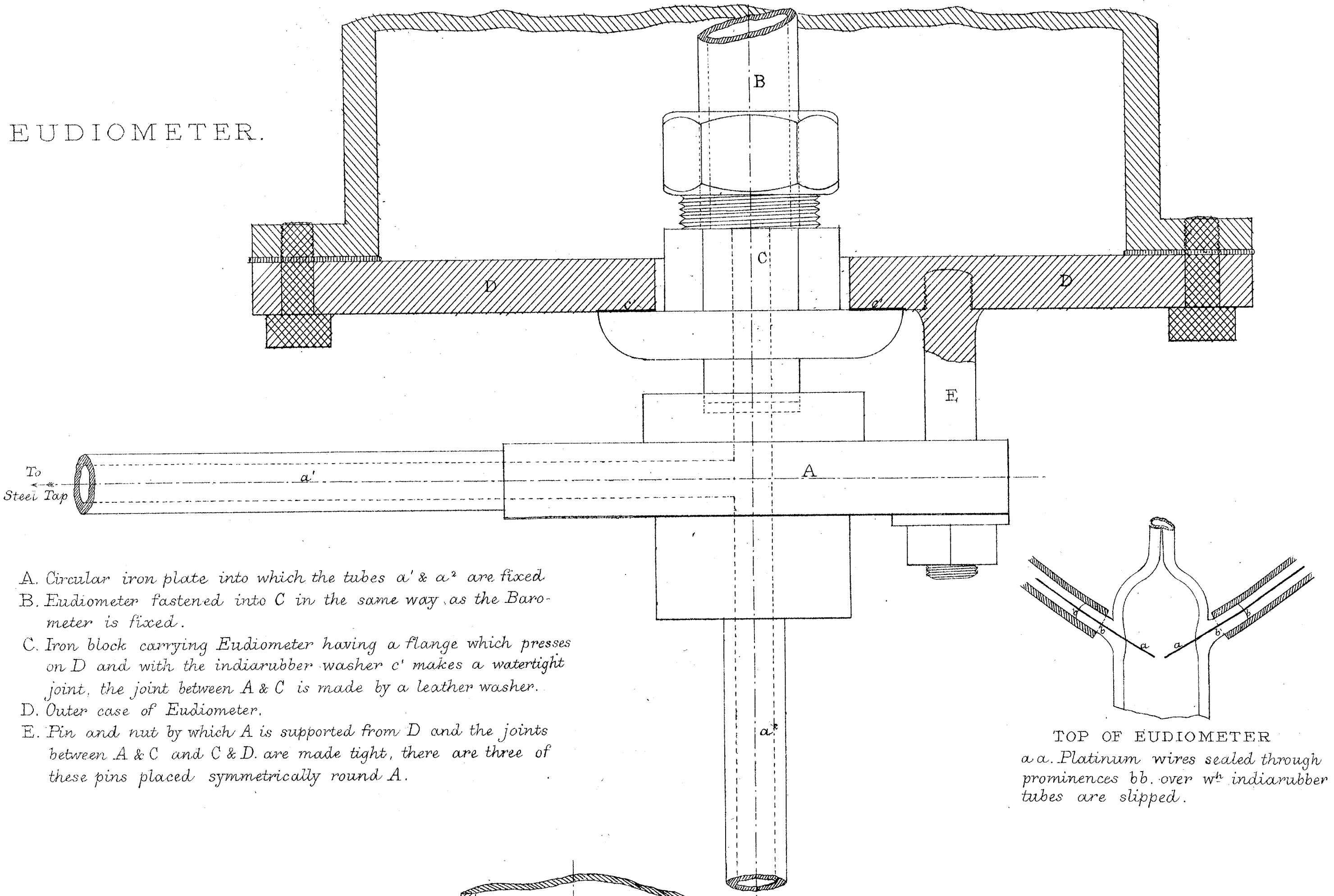
A. *Eudiometer.*
B. *Barometer.*
C. *Laboratory Tube*
D. *Steel block with 3 way tap.*
E. *Annular pipe for heating liquid in jacket.*
F. *Jacket with 2 plate glass windows.*
G. *Winch to raise Mercury Reservoir H.*
I. *Flexible tube connecting Reservoir with iron pipe K.*
L. *Water Pump.*
M. *Moveable shelf to support Trough N.*
N. *Mercury Trough with side shelf for holding gas-cylinders.*
O. *Iron pipe for emptying Eudiometer.*
P. *Screw stirrer turned by a cord round the wheel Q.*

THE GAS ANALYSER.— Balliol College, Oxford.

W. H. Hill del.

West, Newman & C^o. sc.

EUDIOMETER.



A. Circular iron plate into which the tubes a' & a² are fixed.

B. Eudiometer fastened into C in the same way as the Barometer is fixed.

C. Iron block carrying Eudiometer having a flange which presses on D and with the indiarubber washer c' makes a watertight joint, the joint between A & C is made by a leather washer.

D. Outer case of Eudiometer.

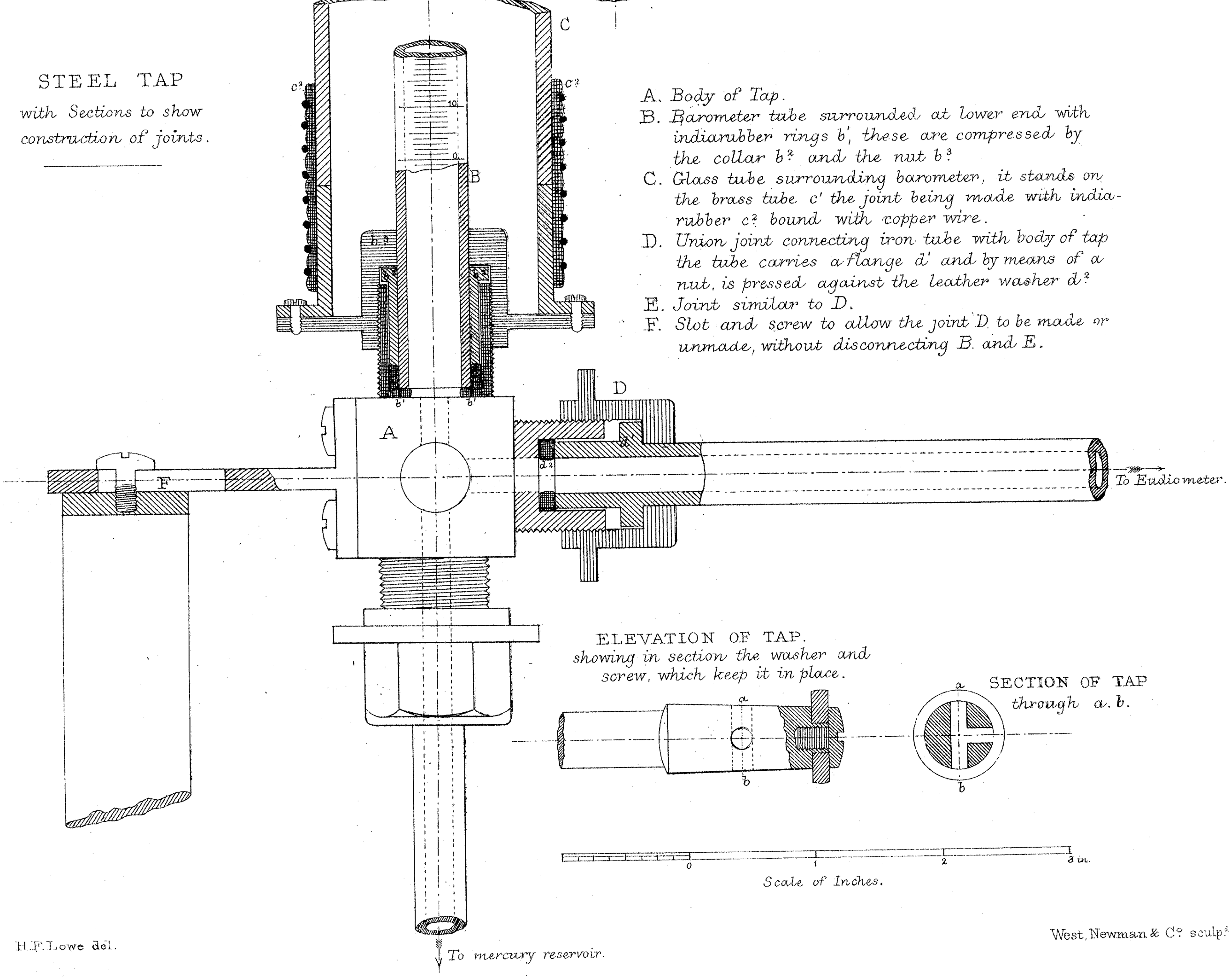
E. Pin and nut by which A is supported from D and the joints between A & C and C & D are made tight, there are three of these pins placed symmetrically round A.

TOP OF EUDIOMETER

a a. Platinum wires sealed through prominences b b. over wh. indiarubber tubes are slipped.

STEEL TAP

with Sections to show construction of joints.



A. Body of Tap.

B. Barometer tube surrounded at lower end with indiarubber rings b', these are compressed by the collar b² and the nut b³.

C. Glass tube surrounding barometer, it stands on the brass tube c' the joint being made with indiarubber c² bound with copper wire.

D. Union joint connecting iron tube with body of tap the tube carries a flange d' and by means of a nut, is pressed against the leather washer d².

E. Joint similar to D.

F. Slot and screw to allow the joint D to be made or unmade, without disconnecting B and E.

ELEVATION OF TAP.

showing in section the washer and screw, which keep it in place.

SECTION OF TAP

through a. b.

Scale of Inches.

H.F. Lowe del.

West, Newman & Co. sculp.