

III. BAKERIAN LECTURE.—*The Rate of Explosion in Gases.*

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Received July 8, 1892,—Read January 19, 1893.

[PLATE 1.]

CAP. I.—INTRODUCTION.

THE experiments described in this memoir were undertaken with two objects : in the first place, to obtain information concerning the course of chemical change pursued by reacting gases ; and, secondly, to examine the nature of the “ explosion-wave ” in gaseous mixtures discovered by M. BERTHELOT.

The idea of using the rate of explosion as a means of determining the course of a chemical reaction occurred to me in 1877, when investigating the influence of steam on the union of carbonic oxide and oxygen. If steam acts as a carrier of oxygen to the carbonic oxide by a series of alternate reductions and oxidations, an increase in the amount of steam present, beyond that required to initiate the reaction, should be accompanied by an increase in the rate of combination up to a certain limit. Attempts were therefore made to detect such an increase by measuring the velocity of the flame in a tube.* But while the difference in the rate of explosion between the nearly dry and the moist gases was well marked, the attempts to directly measure the rate of the explosion of the moist gases failed, owing to the great rapidity of the flame. In the spring of 1881 I attempted to measure the rate of explosion of carbonic oxide and oxygen with varying quantities of steam by photographing on a moving plate the flashes at the beginning and end of a closed tube 20 feet long. The two flashes appeared to be *simultaneous* to the eye, but no record of the rate was obtained, for the apparatus was broken to pieces by the violence of the explosion. Shortly after this attempt was made the first of the brilliant series of papers by MM. BERTHELOT and VIEILLE, and by MM. MALLARD and LE CHATELIER, was read before the French Academy of Sciences. The work of these French chemists has opened a new era in the theory of explosions.

* ‘ Phil. Trans., ’ 1884, Pt. II., p. 635.

Thirty-five years ago BUNSEN* described a method of measuring the rapidity of the flame in gas explosions. Passing a mixture of explosive gases through an orifice at the end of a tube and igniting the gases as they issued into the air, he determined the rate at which the gases must be driven through the tube to prevent the flame passing back through the opening. By this method he found that the rate of propagation of the ignition of hydrogen and oxygen was 34 metres per second, while the rate of ignition of carbonic oxide and oxygen was less than 1 metre per second. BUNSEN *applied these results to the rate of explosion of gases in closed vessels*: his results were accepted without cavil for four and twenty years.

By 1880 facts began to accumulate which seemed inconsistent with BUNSEN's conclusions. For instance, between 1876-80 I had several times observed that the flame produced by igniting a mixture of moist carbonic oxide and oxygen travelled in a long eudiometer too quickly to be followed by the eye. Again, Mr. A. V. HARCOURT,† in his investigation of an explosion of coal-gas and air, which happened in a large gas main near the Tottenham Court Road in 1880, was led to the conclusion that the flame travelled at a rate exceeding 100 yards per second. In the winter of 1880-1 I was startled by the rapid increase of velocity and violence as a flame of carbon bisulphide with nitric oxide travelled down a long glass vessel.

In July, 1881, two papers appeared in the 'Comptes Rendus,' one by M. BERTHELOT, the other by MM. MALLARD and LE CHATELIER. Both papers announced the discovery of the enormous velocity of explosion of gaseous mixtures. Other papers quickly followed by the same authors. M. BERTHELOT made the important discovery that the rate of explosion rapidly increases from its point of origin until it reaches a maximum which remains constant, however long the column of gases may be. Each mixture of gases has a definite maximum velocity of explosion. The rate of explosion thus forms a new physico-chemical constant, having important theoretical and practical bearings. The name "L'Onde Explosive" is given by BERTHELOT to the flame when propagated through an explosive mixture of gases at the maximum velocity.

While BERTHELOT, associated with VIEILLE, was measuring the rate of the "explosion-wave" for various mixtures of gases, MALLARD and LE CHATELIER continued the study of the preliminary phenomena of explosion which precede the formation of the "wave." They showed by photographing on a revolving cylinder:—(1) that when a mixture such as nitric oxide and carbon bisulphide is ignited at the open end of a tube, the flame travels a certain distance (depending on the diameter and length of the tube) at a uniform velocity; (2) that at a certain point in the tube vibrations are set up, which alter the character of the flame, and that these vibrations become more intense, the flame swinging backwards and forwards with oscillations of increasing amplitude; and (3) that the flame either goes out altogether, or the rest of the gas detonates with extreme velocity. Again, when a mixture of gases was fired

* 'Gasometrische Methoden,' 1857.

† Report to the Board of Trade.

near the closed end of the tube, they found the velocity of the flame regularly increased, as far as their instruments were able to record the rapidly increasing pace.

Mixtures of coal-gas with air, and of fire-damp with air, show phenomena of the first and second kind. Ignited at the open end of a tube these mixtures burn at a uniform rate for a certain distance, and then the flame begins to vibrate. The vibrations acquire greater or less velocity according to the nature of the mixture and the conditions of the experiment; but the third *régime* of uniform maximum velocity is not set up. In narrow tubes the explosion soon dies out.

CAP. II.—BERTHELOT'S EXPERIMENTS.

BERTHELOT'S experiments were made partly with a tube of lead, and partly with a tube of thick caoutchouc, usually 5 mm. in internal diameter. The rate of explosion was determined by making the flame break two strips of thin tin stretched across the tube, each carrying a current. The interval between the interruption of the two circuits was measured by a Le Boulengé chronograph. The gases were fired by an electric spark near one of the interrupters. To ensure the fracture of the strips of tin a grain of fulminate was placed in a fold of the metal. The tube was 40 metres long, and was supported on a wooden screen in horizontal layers.

The following are the chief conclusions reached by BERTHELOT concerning the propagation of the explosion-wave in gases:—

(1) The propagation is uniform. Measurements made in tubes of 20, 30, and 40 metres length show the same velocity for the same mixture.

(2) The velocity is independent of the material of the tube: the explosion travels at the same rate in tubes of lead as in tubes of caoutchouc.

(3) The velocity is independent of the diameter of the tube above a small limit: the explosion travels at the same rate in a tube of 5 mm. diameter as in a tube of 15 mm. diameter.

(4) The velocity is independent of the pressure: the explosion travels at the same rate when the gas is under a pressure of 560 mm. as it does under a pressure of 1580 mm.

(5) The velocity of the explosion equals, or approximates closely to, the mean velocity of translation of the molecules at the moment of combination, on the supposition that they retain all the heat developed in the reaction. The rates of explosion of some twenty different mixtures agree with the theoretical rate calculated by the formula of CLAUSIUS:—

$$\theta = 29.354 \sqrt{\frac{T}{d}},$$

where T is the absolute temperature reached in the explosion, and *d* the density of the products of combustion referred to air.

In the following tables the rates of explosion of simple mixtures as measured by BERTHELOT are compared with the theoretical velocity of the products of combustion calculated from CLAUSIUS' formula. The temperature T is calculated on the supposition (1) that the gases are heated *at constant pressure*, and (2) that the specific heat of a compound gas is the sum of the specific heats of its constituents.

TABLE I.—BERTHELOT'S Experiments. Combustible Gases with Oxygen.

Gases.	Velocity in metres per second.	
	Calculated.	Found.
Hydrogen	2831	2810
Carbonic oxide	1940	1690
Marsh gas	2427	2287
Ethane	2483	2363
Ethylene	2517	2210
Acetylene	2660	2482
Cyanogen	2490	2195

TABLE II.—Combustible Gases with Nitrous Oxide.

Gases.	Velocity in metres per second.	
	Calculated.	Found.
Hydrogen	2250	2284
Carbonic oxide	1897	1106
Cyanogen	2198	2036

BERTHELOT observes that the formula does not apply to mixtures of carbonic oxide

either with oxygen or with nitrous oxide. *It is to be noticed that BERTHELOT worked with dry gases.*

TABLE III. — Mixtures of Combustible Gases with Oxygen.

Gases.	Velocity in metres per second.	
	Calculated.	Found.
Hydrogen and carbonic oxide. (1) $\text{H}_2 + \text{CO} + \text{O}_2$ (2) $3\text{H}_2 + 2\text{CO} + \text{O}_2$	2236 2321	2008 2170
Ethylene and hydrogen. (1) $\text{C}_2\text{H}_4 + \text{H}_2 + \text{O}_2$ (2) $\text{C}_2\text{H}_4 + 2\text{H}_2 + \text{O}_2$	2551 2588	2417 2579
Ethane and hydrogen. $\text{C}_2\text{H}_6 + \text{H}_2 + \text{O}_2$	2522	2250

With mixtures of hydrogen and carbonic oxide the formula is found to hold good. BERTHELOT explains this by saying that “the hydrogen communicates to the carbonic oxide a law of detonation analogous to its own.”

The general concordance between the observed velocities and the calculated rate of translation of the molecules shows, according to BERTHELOT, that dissociation plays but a small part in these phenomena, perhaps because of the high pressure developed : a result which is confirmed by the fact that the velocities are found to be independent of the pressure.

A comparison is next made between the rates of explosion of “isomeric mixtures,” *i.e.*, mixtures of different gases which yield the same products of combustion. For instance, the rate of explosion of marsh gas and oxygen is compared with the rate of explosion of a mixture of ethylene, hydrogen, and oxygen yielding identical products ; the object being to eliminate the influence of the individual gases burnt. The same conclusions are drawn.

TABLE IV.—Combustible Gases with Oxygen and Nitrogen.

Gases.	Velocity in metres per second.	
	Calculated.	Found.
$\text{H}_2 + \text{O} + \text{N}_2$ $\text{H}_2 + \text{O} + \text{N}_4$ (Air)	1935 1820	2121 1439
$\text{CO} + \text{O} + \text{N}_2$ $\text{CO} + \text{O} + \text{N}_4$	1661 1236	1000 ? { Detonation not propagated
$\text{CH}_4 + \text{O}_4 + \text{N}_4$ $\text{CH}_4 + \text{O}_4 + \text{N}_8$ $\text{CH}_4 + \text{O}_4 + \text{N}_{15}$ (Air)	2002 1744 1450	1858 1151 { Detonation not propagated
$\text{C}_2\text{N}_2 + \text{O}_4 + \text{N}_2$ $\text{C}_2\text{N}_2 + \text{O}_4 + \text{N}_4$ $\text{C}_2\text{N}_2 + \text{O}_4 + \text{N}_8$	2334 2152 1920	2044 1203 { Detonation not propagated

When the explosive gases are mixed with an inert gas, nitrogen, which takes no part in the reaction, the same law holds good—except when the nitrogen is added in excess. Before the gases are diluted sufficiently to stop the explosion, there is found a marked falling off in the velocity. The formula gives the theoretically highest rate the explosion can attain—a maximum reached in few cases only, but approached in a large number.

Berthelot's Conclusions.

These results show, according to BERTHELOT, that the velocity of the explosion-wave constitutes, for each inflammable mixture, a true specific constant. The wave is propagated by the impact of the products of combustion of one layer upon the unburnt gases in the next layer, and so on to the end of the tube at the rate of movement of the products of combustion themselves. In a word, the mean velocity of translation of the gaseous molecules retaining the total *vis viva* which corresponds to the heat developed in the reaction *may be regarded as a limit representing the maximum rate of propagation of the explosion-wave* ('*Sur la Force des Matières Explosives*,' 1, p. 159).

If this theory is true, it accounts not only for the extreme rapidity of explosion of gaseous mixtures, and gives us the means of calculating the maximum velocity

obtainable with any mixture of gases, but it also affords us information on the specific heats of gases at very high temperatures, and it explains the phenomena of *detonation* whether of gases or of solid or liquid explosives.

CAP. III.—REPETITION OF BERTHELOT'S EXPERIMENTS.

§ 1. *Objects in View.*

A consideration of BERTHELOT'S results, published in the 'Annales de Chimie' * in 1883, led me to think it would be useful to repeat and extend these experiments. The close coincidence between the rates of explosion of hydrogen, both with oxygen and with nitrous oxide, and the calculated velocities of the products of combustion showed that the formula held good for gases which could readily be prepared in a pure state ; and, again, the great discordance between the found and calculated rates for carbonic oxide, both with oxygen and nitrous oxide, was what I should have expected from my own experiments on the part taken by steam in the oxidation of carbonic oxide. On the other hand, BERTHELOT'S contention that the gases are heated at constant pressure appeared improbable, and his results obtained with the addition of an inert gas seemed to vary capriciously. The chief objects I had in view in continuing these experiments were :—

(1) To determine as accurately as possible the rate of the explosion-wave for some simple mixtures under varying conditions, *e.g.*, diameter of tube, initial pressure, initial temperature.

(2) To measure the rate of the explosion-wave in carbonic oxide and oxygen with different quantities of steam.

(3) To compare the effect of inert gases and of excess of one or other of the reacting gases on the rate of explosion.

§ 2. *Methods and Apparatus used.*

The mixtures of hydrogen, carbonic oxide, and marsh gas with oxygen were prepared in a graduated 5-foot iron gas-holder over water ; the mixtures containing ethylene, acetylene, cyanogen, and nitrous oxide were prepared in a 1-foot iron holder over mercury ; the mixtures of hydrogen and chlorine were passed directly from the generating and purifying apparatus into the explosion tube.

The gases were driven from the holders through drying vessels into the explosion tube by placing weights upon the holders. When all air-traps were avoided in the drying tubes and connections, very little diffusion was found to occur in driving out the air by the explosive mixture. One "Drechsel" washing bottle and three towers packed with pumice, all containing boiled oil of vitriol, were usually employed as drying vessels. When the explosive mixture contained either ethylene or acetylene

* 'Ann. Chim. et Phys.,' [V.] vol. 28 ; also 'Sur la force des Matières Explosives,' vol. 1., chap. 7.

the gas was driven from the mercury holder through one washing bottle containing strong aqueous potash and through two towers packed with lumps of caustic potash. The cyanogen mixtures were passed direct from the mercury holder into the explosion tube, the gases having been dried in preparation.

The explosion tube was, in most of the experiments, a leaden pipe, 100 metres long and 9 mm. in diameter. With some of the more violent explosives—*e.g.*, cyanogen and acetylene, a leaden tube of 6.5 mm. was used; and in the chlorine experiments straight wrought-iron pipes lined with glass were employed.

The leaden tube was, in most cases, coiled on a drum, 2 feet in diameter, which was immersed in an iron vessel containing water. By heating the water and pumping dry air through the tube, the apparatus could be quickly dried after an explosion in which water was formed. For determinations of the rate of explosion of gases at 100° C. this arrangement was also suitable. Two inconveniences arose from this disposition of the pipe: (1) the difficulty of determining its exact length, and (2) the uncertainty whether the explosion-wave was propagated along the axis of the coiled pipe, or whether it followed a shorter path nearer to the inside wall.

It was found impossible to coil a small leaden pipe without lengthening it appreciably; the outside of the tube was therefore measured after each coil was wound on the drum, and the length of the axis of the pipe calculated. After a series of experiments the coils were then unwound, by rolling the drum along a corridor, and the length was measured directly. The length so obtained did not vary more than an inch, or at most two, from that calculated on winding.

To determine whether the flame was propagated centrally, or whether it took a shorter cut, measurements of the rate of explosion of samples of oxygen and hydrogen from the same mixture were made alternately, in a leaden pipe 9 mm. in diameter (1) coiled on the drum, and (2) lying straight on the floor. The experiments were thrice repeated, and no appreciable difference in the rate could be detected; from which it may be concluded that in a pipe of this bore the wave-front travels quickest along the axis. Possibly in the experiments with tubes of a larger diameter the curvature may have slightly affected the results.

In the experiments made under reduced pressure, the tube was filled from the holder in the ordinary way. The steel stopcock* near the second bridge was closed, and the gas was then sucked from the tube by a powerful pump, maintaining a vacuum of about 26 inches of mercury. A gauge showed when the desired reduction of pressure was reached. The other stopcock was then closed, and the spark immediately passed. In the experiments made under increased pressure, the gases were driven into the tube from a strong reservoir, either by water or by mercury, according to the nature of the gaseous mixture. In all cases the gases were fired by an electric spark near one end

* These steel stopcocks, made for me by Mr. J. J. Hicks, of Hatton Garden, have stood many hundreds of explosions without leaking. The gun-metal stopcocks employed at first were indented by the explosions and soon leaked.

of the tube; about four feet from the firing point, the flame broke a piece of silver foil stretched across the tube, the moment of rupture being marked on a moving plate by an electro-magnetic style. On reaching the further end of the tube, the flame broke a second strip of silver, the moment of rupture being recorded by a second style. To eliminate errors due to retardation of the electro-magnets, a blank experiment was made immediately before firing the gases. The plate of the chronograph passed over two breaks, which could be adjusted so as to be broken by it at the same instant. In the preliminary experiment, the circuits of the two magnets were completed through these two breaks, and were thus broken simultaneously, the two styles registering their marks on the moving plate. The magnets, without their position being altered, were then connected with the silver bridges across the explosion tube, and the gases were fired by the moving plate striking one or other of the two breaks. The flame travelling down the tube broke the two silver bridges in turn, releasing the two styles, which again registered their marks on the moving plate. The two marks made by the first style gave the interval of time between the spark and the breaking of the first bridge, independently of the error of the electro-magnet; for both marks were equally affected by any error of retardation. In the same way, the two marks made by the second style gave the interval of time between the spark and the breaking of the second bridge, independently of the error of the electro-magnet. The difference between the intervals was the time taken by the flame to travel between the two bridges.

This method of cutting out the errors of the chronograph is only valid when the current flowing through the electro-magnets is constant. A small resistance coil was interposed in the preliminary experiment in each chronograph circuit, to match the resistance of the silver-bridge and connections used in the actual determination. The current was supplied by a storage cell (ELWELL and PARKER) to each electro-magnet, and the time between the preliminary and the final experiment was never more than one minute. In all the later portion of the work a confirmatory experiment was made after the gases were fired, the connections being made as in the preliminary. In most cases the styles passed absolutely over the preliminary marks—merely deepening the lines, thus showing that nothing had been displaced. In some cases the preliminary and confirmatory marks were just visibly separated; in these cases the mean position of the two was used to calculate the rate. In the few instances in which the confirmatory did not closely agree with the preliminary marks the experiment was rejected. In order further to eliminate errors of the instrument a second experiment was always made as soon as possible after the first, the connections of the chronograph being all reversed—the first style being connected with the second bridge, and *vice versa*. The mean result of the two experiments is taken as one determination.

The chief differences between my apparatus and that employed by BERTHELOT were the following :—

- a. The explosion tube was longer and wider.
- b. The interrupters or "bridges" were of silver foil, and no fulminate was used.
- c. A longer space was allowed between the firing spark and the first "bridge" where the record of the rate was begun. This was found essential in several cases, especially when the mixture was fired under reduced pressure, or in presence of inert gases, in which cases the explosion does not reach its maximum rate for some feet.

§ 3. *On the Constant Velocity of the Explosion Wave.*

Experiments on the rate of explosion of hydrogen and oxygen in a leaden tube, 55 metres long and 8 mm. in internal diameter, gave a mean rate of 2817 metres per second. In a tube of the same diameter and 100 metres long, the mean rate was 2821 metres; and in a tube 100 metres long and 13 mm. diameter the mean rate was 2819.

The general mean of these experiments—viz., 2819, is in close agreement with the mean result obtained by BERTHELOT in a shorter tube—viz., 2810.

The constancy of the rate of the explosion-wave, under ordinary conditions of temperature and pressure, was, therefore, fully confirmed.

In the course of this investigation I have made many measurements of the rate of explosion of hydrogen and oxygen under ordinary conditions. Some of these were made with more precautions than others, so that in arriving at the most probable value of the rate, I have given greater weight to some sets than to others. The sets, each of which consists of from eight to ten distinct measurements, are lettered in the following table A, B, C, etc., in the order in which they were made:—

TABLE V.—General Mean of $H_2 + O$ Rates.

Date.	Sets.	Mean.
1884, 1885	A + B + C	2819
1888	D	2822
1889	E + F + G	2824
1890	H	2818
		<hr/> 2821

The details of these experiments will be found in the Appendix.

§ 4. *The Influence of Pressure on the Velocity of the Explosion Wave.*

Preliminary experiments on the rate of explosion of hydrogen and oxygen under 500 mm. and 1000 mm. pressure having shown an appreciable difference, careful

measurements of the rate were made at pressures varying from 200 mm. to 1500 mm. at a temperature close to 10° C. In the experiments at low pressures it was, of course, essential that the firing tube should be absolutely gas-tight; the tube was therefore tested before each experiment. An important fact concerning the development of the explosion-wave was detected in these experiments. As the pressure was reduced the flame was found to travel a greater distance before its rate became constant; so that, although four feet start was allowed before the first measurement was taken, this distance was found insufficient. Accordingly a tube 20 feet long was interposed between the firing point and the first bridge, after it had been shown that the flame acquired its maximum velocity in this distance under the lowest pressure used. Electrolytic gas can be exploded under lower pressures than 200 mm., but the flame travels irregularly. At 100 mm. pressure the flame went out in the tube, and at 150 mm. the rates found were not constant.

TABLE VI.—Pressure Experiments. $H_2 + O$.

Pressure.	200 mm.	300 mm.	500 mm.	760 mm.	1100 mm.	1500 mm.
Mean rate . .	2627	2705	2775	2821	2856	2872

These figures show that the rate of explosion increases rapidly with increase of pressure from 200 mm.; that the rate of increase diminishes, and that the velocity becomes nearly constant at two atmospheres pressure. This effect of pressure on the rate is plainly seen when the results are expressed graphically (see Plate 1).

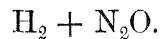
BERTHELOT's conclusion that the explosion-wave is independent of the initial pressure of the gases is, therefore, not strictly accurate. At lower pressures the rate falls off, but above a certain *crucial pressure*, which, in the case of hydrogen and oxygen, seems to be about two atmospheres, the velocity is independent of the pressure.

It will be observed that the mean rate of explosion of hydrogen and oxygen at 1500 mm. pressure is appreciably higher than BERTHELOT's θ —the calculated rate of translation of the steam molecules. But BERTHELOT, in his calculation, has not taken into account the fact that the gases are not at absolute zero to start with. Assuming that he worked at about 13° C., the theoretical rate would be 2900 metres per second.

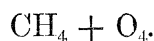
Analogous results were found in experiments with other mixtures under varying pressures. With hydrogen and nitrous oxide the rate is slower at 500 mm. than at 760 mm., but no increase is found on raising the pressure to 1000 mm. The crucial pressure is in this instance below the atmospheric pressure. The same was found to be the case with marsh gas, ethylene, acetylene, and cyanogen exploded with oxygen.

In the following table some of these results are shown :—

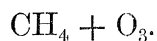
TABLE VII.—Pressure Experiments.



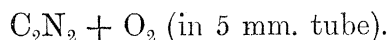
Pressure.	500 mm.	760 mm.	1000 mm.
Mean rate . .	2094	2307	2302



Pressure.	500 mm.	760 mm.	1000 mm.
Mean rate . .	2280	2322	2319



Pressure.	500 mm.	760 mm.	1000 mm.
Mean rate . .	2418	2470	2488



Pressure.	500 mm.	760 mm.	1000 mm.
Mean rate . .	2536	2677	2671

§ 5. *Influence of Temperature on the Velocity of the Explosion-Wave.*

BERTHELOT has published no experiments on the influence of initial temperature on the explosion-wave; but, if the wave is propagated in a manner analogous to a sound wave, it might be anticipated that an increase in the initial temperature of the gases would increase the velocity. The reverse effect is found in the explosion of hydrogen and oxygen. Experiments made at 10° C. and 100° C. showed a small, but distinct, lowering of the rate at the higher temperature. The experiments were made alternately at the high and low temperature, in order to eliminate the effect which might be produced by any mistake in the mixture or error in the chronograph. The comparative experiments made at 10° agreed with those previously obtained

under the same conditions, so that the results found at 100° must be accepted.* A similar lowering of the rate at 100° was found to occur at low and high pressures.

TABLE VIII.
TEMPERATURE Experiments. $\text{H}_2 + \text{O}$.

Temperature.	10°.	100°.
Mean rate . .	2821	2790

$\text{H}_2 + \text{O}$ at 100° C. at different pressures.

Pressure.	390 mm.	500 mm.	760 mm.	1000 mm.	1450 mm.
Mean rate . .	2697	2738	2790	2828	2842

When the rates at 100° and varying pressures are compared graphically with the rates found at 10° and varying pressures, it is seen that the two curves run parallel one with the other (see fig. 1 on Plate 1).

The explosion-rates of ethylene and oxygen at 10° C. and 100° C. were also compared. Samples of the same mixture were exploded alternately at the low and at the high temperature. Five concordant determinations at 10° C. gave a mean velocity of 2581 metres per second; four concordant determinations at 100° C. gave a mean velocity of 2538 metres per second. Similar experiments were made with cyanogen.

TABLE IX.
RATE of Explosion of Ethylene and Oxygen. $\text{C}_2\text{H}_4 + 2\text{O}_2$.

Temperature.	10° C.	100° C.
Mean rate . .	2581	2538

RATE of Explosion of Cyanogen and Oxygen. $\text{C}_2\text{N}_2 + \text{O}_2$.

Temperature.	10° C.	100° C.
Mean rate . .	2728	2711

* The expansion of the metal tube is taken into account in calculating the rates at 100° C.

The small differences in the rate of explosion of hydrogen and oxygen, and of ethylene and oxygen at 10° and at 100° show that the effect of ordinary atmospheric changes of temperature may be neglected.

§ 6. *Comparison of the Rate of Explosion of different Gaseous Mixtures with BERTHELOT'S results.*

The results obtained, under ordinary conditions of pressure and temperature, with hydrogen and oxygen, with hydrogen and nitrous oxide, and with marsh gas and oxygen, in exact proportions for complete combustion, were in close accordance with the mean results of BERTHELOT; for ethylene, acetylene, and cyanogen my numbers differed appreciably, but in no case differed by more than 7 per cent. from the rates observed by BERTHELOT. In the following table our measurements for the same mixtures are compared :—

TABLE X.—Mean Velocity of Explosion in Metres per Second.

	BERTHELOT.	DIXON.
Hydrogen and oxygen $H_2 + O$. .	2810	2821
Hydrogen and nitrous oxide $H_2 + N_2O$.	2284	2305
Marsh gas and oxygen $CH_4 + O_4$.	2287	2322
Ethylene and oxygen $C_2H_4 + O_6$.	2210	2364
Acetylene and oxygen $C_2H_2 + O_5$.	2482	2391
Cyanogen and oxygen $C_2N_2 + O_4$.	2195	2321

The general agreement between these measurements leaves, I think, no room for doubt about the substantial accuracy of the results.

CAP. IV.—THE INFLUENCE OF STEAM ON THE RATE OF EXPLOSION OF CARBONIC OXIDE AND OXYGEN.

The results already described show that the formula proposed by BERTHELOT expresses with a close degree of approximation the rates of explosion of several gaseous mixtures. The formula fails for the explosion of carbonic oxide with oxygen or with nitrous oxide. This was to be expected if, in the *detonation* of carbonic oxide in a long tube, the oxidation is effected indirectly by means of steam—as it is in the ordinary combustion of the gas. Measurements of the rate of explosion of carbonic oxide and oxygen in a long tube showed that the rate increased as steam was added to the

dry mixture, until a maximum velocity was attained when between 5 and 6 per cent. of steam was present.

The experiments were conducted in the following way :—In the “dry” experiments the coil of pipe was heated and a current of dry air drawn through it. The mixture of carbonic oxide and oxygen was passed into the dry coil through drying apparatus, consisting of two wash-bottles and three pumice towers containing boiled oil of vitriol, and then two long tubes packed with anhydrous phosphoric acid. The mixture under these conditions is called “well-dried”; it readily transmits the explosion. In the next experiments the phosphoric acid tubes were omitted; the mixture is called “dried.” For saturating the gases with steam the mixture was led through water in three small wash-bottles before entering the coil. The first wash-bottle was kept about 5° C., the second about 3° C., and the third exactly 1° above the temperature at which the mixture was to be exploded. The last bottle and the connections between it and the coil were kept entirely surrounded by water. The gas, on its passage through the wash-bottles, carried over steam, which was partly condensed in the cooler wash-bottles and in the coil. While the gas was being admitted to the coil the water jacket was kept about 5° above the final temperature required. When the tube was full the source of heat was removed, and the water in the jacket well stirred. When the exact temperature was reached the stop-cocks were closed and the gases fired. This arrangement ensured that the gases were *saturated* with moisture, and prevented any accumulation of liquid in the coil which might have retarded the explosion.

In the following table the *mean* results obtained with the dried and with the moistened gases are given :—

TABLE XI.—Rate of Explosion of Carbonic Oxide and Oxygen saturated with Steam at Different Temperatures.

Condition.	Per cent. of steam present.	Mean rate in metres per second.
Well dried	1264
Dried	1305
Saturated at 10° C.	1·2	1676
„ 20° C.	2·3	1703
„ 28° C.	3·7	1713
„ 35° C.	5·6	1738
„ 45° C.	9·5	1693
„ 55° C.	15·6	1666
„ 65° C.	24·9	1526
„ 75° C.	38·4	1266

The maximum rate was obtained when the mixture was saturated at 35° C.—*i.e.*, contained 5·6 per cent. of steam. Excess of steam slowly retards the rate. A few

experiments were made above and below the atmospheric pressure, which showed that the maximum rate always occurred when the same percentage of steam was present. Under 1100 mm. pressure the fastest rate was found when the mixture was saturated at 43° —*i.e.*, contained 5·6 per cent. of steam; and under 400 mm. pressure the fastest rate was found when the mixture was saturated at 25° —*i.e.*, contained 5·6 per cent. of steam. Increase of pressure increased, and diminution of pressure diminished, the rate of explosion of moist carbonic oxide and oxygen. Under 300 mm. pressure the explosion-wave was not propagated in the mixture of carbonic oxide and oxygen saturated at 10° C. In one experiment the flame reached the end of the tube, taking about 30 seconds to travel 100 metres. Under 400 mm. pressure the explosion-wave was propagated.

TABLE XII.—Rate of Explosion of Carbonic Oxide and Oxygen.

1. UNDER 1100 mm. pressure.

Condition.	Per cent. of steam present.	Mean rate in metres per second.
Saturated at 26° C.	2·3	1737
„ 43° C.	5·6	1782
„ 53° C.	9·5	1742

2. UNDER 400 mm. pressure.

Condition.	Per cent. of steam present.	Mean rate in metres per second.
Saturated at 10° C.	2·3	1576
„ 25° C.	5·6	1616
„ 33° C.	9·5	1570

These results are shown graphically by curves on fig. 2, Plate 1, in which the ordinates are the rates of explosion, and the abscissæ the percentages of steam present in the mixture.

These curves show the very marked increase of the rate of explosion on adding 1 or 2 per cent. of steam to the dried gases. Now the addition of steam to other dry gaseous mixtures, such as hydrogen and oxygen, ethylene and oxygen, cyanogen and oxygen, has been found to *lower* the rate of explosion. I think these results, therefore, are strong evidence that *at the extreme temperatures of the explosion-wave, as well as in ordinary combustion, carbonic oxide is oxidised by the steam, and not directly by the oxygen.*

CAP. V.—THE MODE OF BURNING OF GASEOUS CARBON.

§ 1. The fact that carbonic oxide is not acted on directly by oxygen, even in the explosion-wave, points to the possibility that the carbon in gaseous hydrocarbons, and in other volatile carbon compounds, is not oxidised directly to carbonic acid when these gases are burnt with an excess of oxygen. When cyanogen, for instance, is exploded with oxygen, the carbon may burn in one or in two stages. Each atom may either combine directly with two atoms of oxygen to form carbonic acid, or each atom may combine first with a single atom of oxygen to form carbonic oxide, which afterwards combines with a second atom of oxygen to form carbonic acid. If the oxidation is effected in *two* stages, the chemical change first occurring, viz., the oxidation of the carbon to carbonic oxide, must take place in the presence of an excess of oxygen. Will this excess of oxygen influence the velocity with which the *initiation* of the chemical change is propagated, *i.e.*, the rate of explosion? The interest of tracing the *course* of any chemical change, and the scientific importance of this particular reaction, led me to study the influence of the presence of an excess of oxygen, and of an inert gas, on the rate of explosion of gaseous mixtures—with a view to obtain evidence on their mode of burning.

§ 2. *The Retardation of the Wave caused by Inert Gases.*

When electrolytic gas is mixed with oxygen, nitrogen, or steam, the explosion-wave is retarded, the oxygen having most effect, the steam least. For instance, the addition of one volume of steam to three volumes of electrolytic hydrogen and oxygen reduced the rate of explosion to 2494 metres per second in experiments made at 65° C. At the same temperature the addition of one volume of nitrogen to three of electrolytic gas reduced the rate to 2402 metres per second. According to BERTHELOT'S formula a retardation of this order was to be expected—the greater specific heat of the steam being more than counterbalanced by the greater density of the nitrogen. Experiments made with hydrogen and oxygen at ordinary temperatures, with successive additions of oxygen and of nitrogen respectively, showed that, so long as the explosion-wave was propagated in both cases, the retarding influence of nitrogen was less than that of an equal volume of oxygen. Three volumes of electrolytic gas can be exploded with five volumes of nitrogen, but with seven volumes of nitrogen the explosion is not propagated through a long tube; whereas three volumes of electrolytic gas can still be exploded when mixed with eight of oxygen. But so long as the volume of nitrogen added is not sufficient to stop the explosion, the addition of this inert gas, incapable of taking part in the chemical change, produces less effect than the addition of oxygen, one of the reacting substances.

Some experiments published by BERTHELOT in 1885* seem to be at variance with this statement. When electrolytic gas, largely diluted with oxygen, was exploded in a bomb, the flame traversed the bomb more quickly than when an equal volume of nitrogen was used as a diluent. But the rate measured in this case was not that of the explosion-wave; it was the mean rate of the flame from the point of inflammation to a point about 250 mm. distant. On the other hand, with a smaller volume of diluent gas, BERTHELOT found the rate of explosion to be less retarded by nitrogen than by oxygen:—

Time taken by flame to travel 250 mm.		
$\text{H}_2 + \text{O}$	2·14	thousandths of a second.
$\text{H}_2 + \text{O} + 3\text{O}_2$	16·04	„ „
$\text{H}_2 + \text{O} + 3\text{N}_2$	24·45	„ „
$\text{H}_2 + \text{O} + \text{O}_2$	8·16	„ „
$\text{H}_2 + \text{O} + \text{N}_2$	6·87	„ „

I have found that the explosion-wave is sooner initiated when electrolytic gas is largely diluted with oxygen than when it is diluted with the same volume of nitrogen; a fact which explains the apparent anomaly in BERTHELOT's experiments.

On repeating my measurements of the rate of explosion of electrolytic gas with large volumes of diluent gases, some discrepancies were found, which could not at first be explained. A tube of larger diameter (13 mm.) was then substituted for the smaller tube (9 mm.). The results were more regular. It was then discovered that the explosion frequently died out near the end of the smaller tube, whilst transmitting a sound-wave sufficiently powerful to break the silver foil composing the "second bridge." A record was thus obtained on the chronograph plate, indicating a smaller velocity than the true rate of explosion. By inserting a glass tube just before the second bridge, and watching for the flame, the observers made sure that the explosion-wave reached the end of the pipe. A second precaution, which must also be observed in experiments on largely diluted gases, is to make sure that the explosion-wave has been set up before the flame reaches the first bridge. M. BERTHELOT does not state the free run he allowed his flame before beginning the measurements; but, from an inspection of the figure of his apparatus ('*Sur la Force des Matières Explosives*,' vol. 1, p. 138) it would appear that a few inches only were allowed between the firing spark and his first "interrupter." No doubt, the use of a grain of fulminate in the interrupter hastened the establishment of the explosion-wave in his experiments, but I think it possible that in some of his measurements he began to record the rate before the wave was started, and so obtained a rate below the true one. In all my later experiments on diluted gases, some pure electrolytic gas was passed into the long firing piece, just before the explosion, so as to fill it for a length of two or three feet.

* '*Ann. Chim. Phys.*' [VI.], vol. 4, p. 44.

The explosion-wave, rapidly started in this mixture, was communicated to the dilute mixture beyond, without break of continuity, before the first bridge was reached.

A comparison between the few experiments made by BERTHELOT with diluted mixtures and the similar ones made by me will, I think, show the need of these precautions. To three volumes of electrolytic gas BERTHELOT added two volumes of nitrogen: the rate of explosion was found to be 2121 metres per second. To three volumes of electrolytic gas he added four volumes of nitrogen: the rate of explosion was only 1439 metres per second. By interpolation* I find from my own experiments with one, three, and five volumes of nitrogen (added to three volumes of electrolytic gas) the rates 2200 and 1930, for the explosion of electrolytic gas with two volumes and four volumes of nitrogen respectively. The first agrees fairly with BERTHELOT's number, the second is far higher than his. I imagine in the second case the interrupter was broken before the explosion-wave was established in his experiment. Similarly, in two experiments with cyanogen, BERTHELOT found a rapid falling off of the rate which I did not observe. On firing a mixture of cyanogen with twice its volume of oxygen and one volume of nitrogen, he found the rate to be 2044 metres; on adding another volume of nitrogen the rate fell to 1203 metres. By interpolation I find from my experiments 2125 and 1960 as the rates of these two mixtures. The first agrees fairly well with, the second is far higher than, BERTHELOT's number.

The *mean* results obtained in a number of experiments on the retarding effect of oxygen and nitrogen are given in the following table:—

TABLE XIII.—Electrolytic Gas with excess (1) of Oxygen and (2) of Nitrogen.

(1.)

Mixture.	2 vols. hydrogen } 1 vol. oxygen. $H_2 + O$	With addition of 1 vol. oxygen. $H_2 + O + O$	With addition of 3 vols. oxygen. $H_2 + O + O_3$	With addition of 5 vols. oxygen. $H_2 + O + O_5$	With addition of 7 vols. oxygen. $H_2 + O + O_7$
Mean rate . .	2821	2328	1927	1707	1281

(2.)

Mixture.	2 vols. hydrogen } 1 vol. oxygen. $H_2 + O$	With addition of 1 vol. nitrogen. $H_2 + O + N$	With addition of 3 vols. nitrogen. $H_2 + O + N_3$	With addition of 5 vols. nitrogen. $H_2 + O + N_5$	With addition of 7 vols. nitrogen. $H_2 + O + N_7$
Mean rate . .	2821	2426	2055	1822	—

These results are shown graphically in fig. 3, Plate 1, where the ordinates are volumes of nitrogen (or oxygen) added to three volumes of electrolytic gas, and the abscissæ are the rates of explosion of the mixtures in metres per second.

* See fig. 3, Plate 1.

These curves plainly show that the retardation of the explosion-wave depends upon the density of the gas added as well as upon its volume—a result in accordance with BERTHELOT'S theory.

I think it a fair inference from these facts to conclude, when the addition of a gas to an explosive mixture retards the rate of explosion by an amount which depends upon its volume and density, that such added gas is inert as far as the propagation of the wave is concerned, and that any change which it may undergo takes place after the wave-front has passed by—in other words, is a *secondary* change.

§ 3. *Oxygen Inert to Carbonic Oxide in Explosion of Carbon Compounds.*

This principle can be applied to determine whether, in the combustion of gaseous carbon, the oxidation to carbonic acid is effected in one or two stages. If, for instance, the carbon is first burnt to carbonic oxide, which subsequently is burnt to carbonic acid, the rate of the explosion-wave should correspond with the carbonic oxide reaction retarded by an excess of oxygen; whereas, if the carbon burns to carbonic acid directly, in one stage, then the rate of the explosion-wave should correspond with the complete and unretarded reaction.

Now, if we adopt BERTHELOT'S theory as a working hypothesis, we can calculate the theoretical rates of explosion of marsh gas, ethylene, or cyanogen: (1) on the supposition that, with sufficient oxygen, the carbon burns directly to carbonic acid, and (2) on the supposition that the carbon burns first to carbonic oxide, and the further oxidation is a subsequent or secondary reaction. On the first supposition, if 100 represents the rate of explosion of these three gases with oxygen only sufficient to burn them to carbonic oxide, the addition of the oxygen required to burn the gases to carbonic acid should *increase* the rate of explosion:—

	Marsh gas.	Ethylene.	Cyanogen.
Calculated rate of explosion when burnt to CO_2	104	103	107

Whereas, if these gases really burn first to carbonic oxide, and the extra oxygen is inert in propagating the explosion-wave, then the addition of this inert oxygen would *diminish* the rate of explosion:—

	Marsh gas.	Ethylene.	Cyanogen.
Calculated rate of explosion when burnt to CO with inert oxygen present	92	88	87

The experiments show that if 100 be taken as the rate of explosion when the

oxygen is only sufficient to burn the carbon to carbonic oxide, the following are the rates found when oxygen is added sufficient to burn the carbon to carbonic acid :—

	Marsh gas.	Ethylene.	Cyanogen.
Rates found	94	92	84

The results are, therefore, in favour of the view that, in the explosion of these gases, the carbon is first burnt to carbonic oxide.*

But stronger evidence on this point is obtained by comparing the explosion rates of these gases (1) when fired with oxygen sufficient to burn the carbon in them to carbonic acid, and (2) when nitrogen is substituted for the oxygen in excess of that required to burn the carbon to carbonic oxide. We have seen that oxygen, added to electrolytic gas, hinders the explosion more than nitrogen. In precisely the same way oxygen, added to a mixture of equal volumes of cyanogen and oxygen, hinders the explosion more than the same volume of nitrogen. The conclusion we must come to is, that the oxygen, added to the mixture expressed by the formula $C_2N_2 + O_2$, is as inert (so far as the propagation of the explosion-wave is concerned) as oxygen added to the mixture expressed by the formula $H_2 + O$. The same phenomena occur in the explosion of marsh gas, ethylene, and acetylene.

The following tables contain the results of my last experiments on this subject. The rates come out on the whole somewhat higher than in my earlier experiments. This is mainly due to the later explosions having been made in a tube of larger diameter—9 mm. instead of 5 mm.

TABLE XIV.—The Rate of Explosion of Cyanogen (1) with Oxygen, and (2) with Oxygen and Nitrogen.

(1.)

Mixture.	1 vol. cyanogen } 1 vol. oxygen } $C_2N_2 + O_2$	With addition of 1 vol. oxygen. $C_2N_2 + 2O_2$	With addition of 2 vols. oxygen. $C_2N_2 + 3O_2$
Mean rate . .	2728	2321	2110

* [It might be urged that, with defect of oxygen, the reactions really are—

1. $CH_4 + O_3 = CO_2 + H_2O + H_2$
2. $C_2H_4 + O_4 = 2CO_2 + 2H_2$
3. $C_2N_2 + O_2 = CO_2 + C + N_2$

If this were true, and 100 represented the observed rates of explosion in each case, then on adding oxygen sufficient for complete combustion, the rates should be 101, 99, and 107 respectively.—Jan., 1893.]

(2.)

Mixture.	1 vol. cyanogen } 1 vol. oxygen. } $C_2N_2 + O_2$	With addition of 1 vol. nitrogen. $C_2N_2 + O_2 + N_2$	With addition of 2 vols. nitrogen. $C_2N_2 + O_2 + 2N_2$
Mean rate . .	2728	2398	2165

Cyanogen will explode when mixed with four times its volume of oxygen. When three volumes of nitrogen are added to one volume of cyanogen and one of oxygen, the mixture will not explode, but burns at the mouth of the tube. So long, however, as the nitrogen does not prevent the explosion, its addition to the mixture has less retarding effect than the addition of an equal volume of oxygen.

TABLE XV.—The Rate of Explosion of Marsh Gas (1) with Oxygen and (2) with Oxygen and Nitrogen.

(1.)

Mixture.	2 vols. methane } 3 vols. oxygen } $CH_4 + O_3$	With addition of 1 vol. oxygen. $CH_4 + O_4$	With addition of 3 vols. oxygen. $CH_4 + O_6$	With addition of 5 vols. oxygen. $CH_4 + O_8$
Mean rate . .	2470	2322	2146	1963

(2.)

Mixture.	2 vols. methane } 3 vols. oxygen } $CH_4 + O_3$	With addition of 1 vol. nitrogen. $CH_4 + O_3 + N$	With addition of 3 vols. nitrogen. $CH_4 + O_3 + N_3$	With addition of 5 vols. nitrogen. $CH_4 + O_3 + N_5$
Mean rate . .	2470	2349	2154	1880 (goes out sometimes)

The addition of one and of three volumes of nitrogen to the mixture of marsh gas and oxygen ($CH_4 + O_3$) is found to retard the rate less than the addition of the same volumes of oxygen. When, however, five volumes of nitrogen are added, the retardation is greater than with oxygen: this mixture is near the limit of explosion, and once or twice the flame died out before reaching the end of the tube.*

* Many attempts were made to explode mixtures of marsh gas and air in a tube. A vigorous explosion, initiated by firing electrolytic gas down the first few feet of the tube, soon dies out in the mixtures of marsh gas and air. In a metal tube 1 inch in diameter the flame travelled a considerable distance, but in a slow and irregular way. Similar results were obtained with mixtures of coal-gas and air. On the other hand, mixtures of ethylene and air explode readily down a narrow tube.

TABLE XVI.—The Rate of Explosion of Ethylene (1) with Oxygen, and (2) with Oxygen and Nitrogen.

(1.)

Mixture.	1 vol. ethylene 2 vols. oxygen $C_2H_4 + 2O_2$	With addition of 1 vol. oxygen. $C_2H_4 + 3O_2$	With addition of 2 vols. oxygen. $C_2H_4 + 4O_2$	With addition of 4 vols. oxygen. $C_2H_4 + 6O_2$	With addition of 6 vols. oxygen. $C_2H_4 + 8O_2$	With addition of 8 vols. oxygen. $C_2H_4 + 10O_2$
Mean rate .	2581	2368	2247	2118	1980	1856

(2.)

Mixture.	1 vol. ethylene 2 vols. oxygen $C_2H_4 + 2O_2$	With addition of 1 vol. nitrogen. $C_2H_4 + 2O_2 + N_2$	With addition of 2 vols. nitrogen. $C_2H_4 + 2O_2 + 2N_2$	With addition of 4 vols. nitrogen. $C_2H_4 + 2O_2 + 4N_2$	With addition of 6 vols. nitrogen. $C_2H_4 + 2O_2 + 6N_2$	With addition of 8 vols. nitrogen. $C_2H_4 + 2O_2 + 8N_2$
Mean rate .	2581	2413	2211	2024	1878	1734

In the case of ethylene, the retarding action of oxygen, which is greater than that of nitrogen for the first volume added to the mixture ($\text{C}_2\text{H}_4 + 2\text{O}_2$), becomes less and less as a large excess of oxygen is added; so that the rate of explosion of ethylene and air would be considerably increased by the substitution of oxygen for the nitrogen of the air. With a large excess of oxygen the *secondary* reaction, whereby carbonic acid is formed, influences the result, for the conditions are eminently favourable for the interaction of the carbonic oxide, steam, and oxygen.

TABLE XVII.—The Rate of Explosion of Acetylene (1) with Oxygen, and (2) with Oxygen and Nitrogen.*

(1.)

Mixture.	2 vols. acetylene } 3 vols. oxygen } $\text{C}_2\text{H}_2 + \text{O}_3$	With addition of 2 vols. oxygen. $\text{C}_2\text{H}_2 + \text{O}_5$
Mean rate . .	2716	2391

(2.)

Mixture.	2 vols. acetylene } 3 vols. oxygen } $\text{C}_2\text{H}_2 + \text{O}_3$	With addition of 2 vols. nitrogen. $\text{C}_2\text{H}_2 + \text{O}_3 + \text{N}_2$
Mean rate . .	2716	2414

These experiments show that in all the cases examined, viz., the combustion of cyanogen, marsh gas, ethylene, and acetylene, the substitution of nitrogen for the oxygen required to burn the carbon from carbonic oxide to carbonic acid *increases* the velocity of the explosion. *These facts seem only consistent with the view that the carbon burns directly to carbonic oxide, and the formation of carbonic acid is an after-occurrence.*

§ 4. BERTHELOT'S *Experiments bearing on the mode of Combustion of Carbon.*

M. BERTHELOT found that the pressures produced in the explosion of cyanogen were greater for the *incomplete* than for the *complete* combustions.†

* No doubt with a large excess of oxygen the explosion of acetylene would be less retarded than with a large excess of nitrogen, as in the case of ethylene. Owing to the expense of preparing the acetylene, experiments with a large excess of oxygen were not made.

† 'Ann. Chim. et Phys.' [VI.], vol. 4, p. 38.

Mixtures.	Pressures.
$\{ \text{C}_2\text{N}_2 + \text{O}_2 \quad . \quad . \quad . \quad . \quad .$	25·11 atmospheres.
$\{ \text{C}_2\text{N}_2 + 2\text{O}_2 \quad . \quad . \quad . \quad . \quad .$	20·96 „
$\{ \text{C}_2\text{N}_2 + 2\text{N}_2\text{O} \quad . \quad . \quad . \quad . \quad .$	26·02 „
$\{ \text{C}_2\text{N}_2 + 4\text{N}_2\text{O} \quad . \quad . \quad . \quad . \quad .$	22·66 „
$\{ \text{C}_2\text{N}_2 + 2\text{NO} \quad . \quad . \quad . \quad . \quad .$	23·34 „
$\{ \text{C}_2\text{N}_2 + 4\text{NO} \quad . \quad . \quad . \quad . \quad .$	16·92 „

It is difficult to reconcile these numbers with the received view as to the burning of carbon; they are readily explained on the hypothesis that carbon burns in two stages.

BERTHELOT has also made some observations of the initial rate of explosion of cyanogen when burnt to carbonic oxide and when burnt to carbonic acid. The time taken by the flame in travelling a distance of about 130 mm. from the point of inflammation was *less* for the incomplete than for the complete combustion; a result which agrees with my measurements of the rate of the explosion-wave in the two cases. When a mixture of carbonic oxide, oxygen and nitrogen, having a composition corresponding to the first stage of the combustion of cyanogen, was fired in the same apparatus, the rate of the flame was found by BERTHELOT to be far slower than in the complete combustion of cyanogen:—

	Time taken by flame to travel 130 mm.
$\text{C}_2\text{N}_2 + \text{O}_2 \quad . \quad . \quad . \quad . \quad .$	1·05 thousandths of a sec.
$\text{C}_2\text{N}_2 + 2\text{O}_2 \quad . \quad . \quad . \quad . \quad .$	1·55 „ „
$2\text{CO} + \text{O}_2 + \text{N}_2 \quad . \quad . \quad .$	17·78 „ „

M. BERTHELOT adds:—“D’après ces nombres, il ne paraît pas que la combustion totale du cyanogène s’effectue en deux temps, en formant d’abord en totalité de l’oxyde de carbone qui brûlerait ensuite; car la combustion totale est beaucoup plus rapide que la somme de ces deux effets séparés.”*

On first reading this passage I understood M. BERTHELOT to mean that in the complete combustion of cyanogen there was no intermediate formation of carbonic oxide. But I am led to think that this interpretation cannot be correct for two reasons. First, because the conditions of temperature and pressure are so entirely different in the two cases compared, that no argument drawn from one can be applied to the other. In one case, a reaction is initiated in a mixture of carbonic oxide, oxygen, and nitrogen at the atmospheric temperature and pressure; in the other, the same gases are at an enormously high temperature and pressure when the reaction begins. Secondly, because M. BERTHELOT, in the same paper, has drawn from analogous facts an argument in an exactly opposite sense. Having determined the initial rate of explosion of hydrogen and oxygen, and of carbonic oxide and oxygen

* ‘Ann. Chim. et Phys.,’ [VI.] vol. 4, p. 43.

in a bomb, he found the rate of explosion of the mixture of the two to be less than the mean of the two separately :—

	Time.
$\text{H}_2 + \text{O}$	1·04
$\text{CO} + \text{O}$	12·86
$\text{H}_2 + \text{CO} + \text{O}_2$	3·88

“La vitesse de combustion n’est, dans aucun cas, la moyenne de celle des composants mélangés. Mais les deux gaz paraissent tendre à brûler séparément, chacun avec sa vitesse propre.”

The meaning of the passage quoted, concerning the combustion of cyanogen, would therefore appear to be: “In the complete combustion of cyanogen there are not two flames propagated from the point of inflammation with different velocities—the quicker due to the burning of cyanogen to carbonic oxide, the slower to the burning of carbonic oxide to carbonic acid.” With this literal interpretation of the passage I entirely agree: there are not two flames or two explosions, but the burning of each molecule takes places in two stages, the second stage prolonging the duration of the flame due to the first.

§ 5. *Other Experiments on the burning of Carbon.*

It is usually assumed that carbon, in all its states, burns to carbonic acid, and then the excess of carbon, if it is present, reduces the carbonic acid, first formed, to carbonic oxide. This view, no doubt, originated from the observation that solid carbon burns in oxygen, without apparent flame, to form carbonic acid; and that carbonic acid is readily reduced to carbonic oxide when passed over heated carbon. The experiments, however, of Mr. BRERETON BAKER (‘Phil. Trans.’ 1888) show that purified charcoal may be heated to redness in a current of dry oxygen without visible combustion taking place, but with the formation of carbonic oxide—although the oxygen is in large excess. It would appear, from Mr. BAKER’s observations, that carbonic oxide is the first product of the action of oxygen on solid carbon at a high temperature; the formation of carbonic acid being a secondary change due to the interaction of carbonic oxide, steam and oxygen. Both solid and gaseous carbon, therefore, appear to undergo oxidation in two stages; the second stage being facilitated by the presence of steam.

The evidence, above described, led me, two years ago, to hazard an explanation of the appearance of a cyanogen flame burning in air. The crimson inner zone might be due to the primary reaction—the burning of the cyanogen to carbonic oxide and nitrogen, with the limited air supply that reaches it; the blue outer zone might be due to the burning of the carbonic oxide (formed in the crimson zone), as it meets with a plentiful supply of air outside. A few experiments I made showed the presence

of carbonic oxide in abundance on the edge of the crimson zone; but I have left the further investigation of the structure of the cyanogen flame to Professor A. SMITHELLS, who has devised a most ingenious method of separating the outer and inner cones of flame, formed when a mixture of a combustible gas and air is burnt in a Bunsen burner. His experiments show that the cyanogen is completely destroyed in the inner red flame, and carbonic oxide is the main product of its oxidation there. This carbonic oxide burns above, on reaching the air, with its well-known blue flame* ('Chem. Soc. Journ.,' 1892, vol. 1, p. 215).

CAP. VI.—THE REACTIONS OF CARBONIC OXIDE IN THE FLAME.

If it be true that in a flame gaseous carbon burns to carbonic oxide, and that carbonic oxide reacts with steam (if present) to a limited extent, and is completely oxidised in presence of steam and oxygen, two questions arise: (1) What happens to the carbonic oxide first formed in the combustion of hydrocarbons or cyanogen with excess of oxygen? and (2) How do these secondary reactions affect the rate of explosion? In the case of cyanogen we should expect, if the gases are fairly dry, that the formation of carbonic acid would be comparatively slow, since no steam is formed in the reaction. We find, in accordance with this expectation, that so long as the mixtures will explode, successive additions of oxygen retard the rate more than the additions of nitrogen—just as in the case of electrolytic gas. This means that in the cyanogen explosion the excess of oxygen and carbonic oxide are as inert towards each other (as far as the propagation of the wave is concerned) as the excess of oxygen and steam are in the explosion of electrolytic gas. On the other hand, the carbonic oxide formed in the explosion of hydrocarbons, with excess of oxygen, meets with the steam also formed in the flame. This is the condition necessary for its most rapid oxidation. We should expect, therefore, to find in the explosions of hydrocarbons that the retarding action of large quantities of oxygen is partly counteracted by this secondary reaction, for the oxygen in presence of the steam is not inert towards the carbonic oxide. As a matter of fact, we find that the first additions of oxygen to the hydrocarbon mixtures retard more than nitrogen, but as the additions are continued the oxygen has less and less retarding influence compared with the nitrogen.

When carbonic oxide, which has the same density as nitrogen, is added to electrolytic gas, the retarding effect on the explosion is very nearly the same as when an equal volume of nitrogen is added:—

* The greenish-grey tint, observable in the outer flame, may be due to some oxide of nitrogen formed in the inner flame. A little peroxide of nitrogen gives a similar tint to an ordinary Bunsen gas flame; and peroxide of nitrogen is formed when cyanogen is burnt under certain conditions (*vide* 'Chem. Soc. Journ.,' 1886, vol. 1, p. 390).

TABLE XVIII.—Rate of Explosion of Electrolytic Gas (1) with Nitrogen, and (2) with Carbonic Oxide. (K.)

(1.)

Mixture.	2 vols. hydrogen and 1 vol. oxygen. } $H_2 + O$	With addition of 1 vol. nitrogen. $H_2 + O + N$	With addition of 3 vols. nitrogen. $H_2 + O + N_3$
Mean rate .	2821	2426	2055

(2.)

Mixture.	2 vols. hydrogen and 1 vol. oxygen. } $H_2 + O$	With addition of 1 vol. carbonic oxide. $H_2 + O + K$	With addition of 3 vols. carbonic oxide. $H_2 + O + K_3$
Mean rate .	2821	2455	2080

It is true that carbonic acid and free hydrogen are found in the tube after the explosion; but these are due to a *secondary* reaction, which need not necessarily affect the rate; in other words, the carbonic acid may be formed in the heated gases after the wave-front has passed by.

This similarity in the retarding action of carbonic oxide and nitrogen can be explained in two ways. First, the carbonic oxide may be for the most part unaffected in the initial change occurring in the wave-front, and be, consequently, as inert as an equal volume of nitrogen. Secondly, the carbonic oxide—inert towards the hydrogen and oxygen—may react with the steam produced both in the wave-front and behind it. The reaction between the steam and carbonic oxide *in the wave-front* would slightly quicken the explosion by developing heat. The experiments show that nitrogen retards the wave to an extent just appreciably greater than carbonic oxide.

To test the correctness of these views concerning the *rôle* played by carbonic oxide in the flame, an experiment was tried with electrolytic gas diluted (1) with oxygen and nitrogen, and (2) with oxygen and carbonic oxide. We have seen that electrolytic gas, when diluted with carbonic oxide, explodes at nearly the same rate as when diluted with nitrogen. Now, if the views expressed above are correct, we may replace some of the diluent nitrogen by oxygen, and thereby make the explosion slower; but if the diluent carbonic oxide is partly replaced by oxygen, the explosion should be considerably faster. The rates found in the two cases agree with this prediction:—

TABLE XIX.

(1.)

Mixture.	2 vols. hydrogen 1 vol. oxygen $H_2 + O$ }	With addition of 3 vols. nitrogen. $H_2 + O + N_3$	With addition of 2 vols. nitrogen and 1 vol. oxygen. $H_2 + O + O + N_2$
Mean rate.	2821	2055	2003

(2.)

Mixture.	2 vols. hydrogen 1 vol. oxygen $H_2 + O$ }	With addition of 3 vols. carbonic oxide. $H_2 + O + K_3$	With addition of 2 vols. carb. ox. and 1 vol. oxygen. $H_2 + O + O + K_2$
Mean rate . .	2821	2080	2143

A study of these several tables brings us to the conclusion that secondary reactions, whereby carbonic oxide is oxidised in the flame, may affect the velocity of the wave to a smaller extent when the explosion is rapid, to a greater extent when the explosion is slow.

CAP. VII.—EXAMINATION OF BERTHELOT'S THEORY.

The measurements of the rate of explosion of the various gaseous mixtures described in Cap. V. permitted an extended comparison between the theoretical velocities calculated by BERTHELOT'S formula (θ) and the actual rates (ν). This comparison is made in the following tables for electrolytic gas, diluted with oxygen and with nitrogen; for cyanogen burning to carbonic oxide, and when this mixture is diluted with nitrogen; for marsh gas, ethylene, and acetylene, all burning to carbonic oxide and steam, and for the same gases diluted with nitrogen. In calculating θ , I made a correction for the gases being at the ordinary temperature (13°C.) before explosion, and not at absolute zero; the theoretical velocities are, therefore, rather higher than those given by BERTHELOT. This correction raises the theoretical velocity of explosion of electrolytic gas from 2831 metres per second (BERTHELOT) to 2900.

TABLE XX.—Electrolytic Gas with excess of Oxygen added.

Mixture.	2 vols. hydrogen } 1 vol. oxygen. } $H_2 + O$	With addition of 1 vol. oxygen. $H_2 + O + O$	With addition of 3 vols. oxygen. $H_2 + O + O_3$	With addition of 5 vols. oxygen. $H_2 + O + O_5$
Theory, θ . .	2900	2252	1730	1476
Found, ν . .	2821	2328	1927	1707

TABLE XXI.—Electrolytic Gas with excess of Nitrogen added.

Mixture.	$H_2 + O$	$H_2 + O + N$	$H_2 + O + N_3$	$H_2 + O + N_5$
Theory, θ . .	2900	2321	1814	1558
Found, ν . .	2821	2426	2055	1822

These measurements show that BERTHELOT'S formula, which gives a calculated rate 3 per cent. too high for pure electrolytic gas, also gives a calculated rate which is found to be 16 and 17 per cent. *too low* for the same gas when largely diluted with oxygen and with nitrogen respectively.

Again, in the explosion of cyanogen to carbonic oxide with its own volume of oxygen, and also when the same mixture is diluted with nitrogen, the theoretical rates calculated by BERTHELOT'S formula are far too low :—

TABLE XXII.—Cyanogen and Oxygen with excess of Nitrogen added.

Mixture.	1 vol. cyanogen } 1 vol. oxygen. } $C_2N_2 + O_2$	With addition of 1 vol. nitrogen. $C_2N_2 + O_2 + N_2$	With addition of 2 vols. nitrogen. $C_2N_2 + O_2 + 2N_2$
Theory, θ . .	2361	2083	1877
Found, ν . .	2728	2397	2166

The observed rates of explosion are 15 per cent. higher than the calculated rates. Similar differences are found between the observed and the calculated rates when the cyanogen mixture is diluted with oxygen.

When marsh gas and ethylene are exploded with oxygen sufficient to burn them

to carbonic oxide and steam, the observed rates are higher than those given by the formula. Again, when these mixtures are diluted with nitrogen the rates come out higher than the formula predicts.

TABLE XXIII.—Marsh Gas and Oxygen with excess of Nitrogen added.

Mixture.	2 vols. methane } 3 vols. oxygen. } $\text{CH}_4 + \text{O}_3$	With addition of 1 vol. nitrogen. $\text{CH}_4 + \text{O}_3 + \text{N}$	With addition of 3 vols. nitrogen. $\text{CH}_4 + \text{O}_3 + \text{N}_3$
Theory, θ . .	2387	2211	1958
Found, ν . .	2470	2349	2154

For pure marsh gas and oxygen, the calculated velocity is $3\frac{1}{2}$ per cent. too low ; when 3 volumes of nitrogen are added, the calculated velocity is 10 per cent. too low. The mixture cannot be detonated with a large excess of nitrogen.

TABLE XXIV.—Ethylene and Oxygen with excess of Nitrogen added.

Mixture.	$C_2H_4 + 2O_2$	$C_2H_4 + 2O_2 + N_2$	$C_2H_4 + 2O_2 + 2N_2$	$C_2H_4 + 2O_2 + 2N_2$	$C_2H_4 + 2O_2 + 6N_2$	$C_2H_4 + 2O_2 + 8N_2$
Theory, θ .	2487	2234	2050	1796	1624	1498
Found, ν .	2581	2413	2211	2024	1878	1734

The divergence between the calculated and observed rates varies with the dilution from 4 per cent. to 16 per cent. The calculated velocities are all too low. In the following table are given the rates of explosion of acetylene burning to carbonic oxide and steam, alone, and with successive additions of nitrogen.

TABLE XXV.—Acetylene and Oxygen with excess of Nitrogen added.

Mixture.	$\left. \begin{array}{l} 2 \text{ vols. acetylene } \\ 3 \text{ vols. oxygen. } \end{array} \right\} \\ C_2H_2 + O_3 $	$C_2H_2 + O_3 + N_2$	$C_2H_2 + O_3 + 3N_2$	$C_2H_2 + O_3 + 4N_2$	$C_2H_2 + O_3 + 5N_2$	$C_2H_2 + O_3 + 6N_2$
Theory, θ .	2749	2397	1983	1848	1739	1650
Found, ν .	2716	2414	2209	2116	2019	1908

Here, as in the case of electrolytic gas, the rate for the pure mixture is in close agreement with the calculated velocity. Taken by itself, this experiment (not tried by BERTHELOT) would have offered strong confirmation of the correctness of the theory. But as successive additions of nitrogen are made to the mixture, the calculated velocities fall *below* the observed rates, until, with a large excess of nitrogen, the calculated rate is 16 per cent. too low.

The gradual divergence between the observed and the calculated rates of explosion for different gaseous mixtures, as successive quantities of nitrogen were added to the pure explosive gas, led me to try the effect of diluting electrolytic gas with hydrogen. According to BERTHELOT'S formula a slight increase in the rate should occur; actually a very marked increase in the rate was observed.

TABLE XXVI.—Rate of Explosion of Electrolytic Gas with excess of Hydrogen added.

Mixture.	2 vols. hydrogen } 1 vol. oxygen. $H_2 + O$	With addition of 2 vols. hydrogen. $H_2 + O + H_2$	With addition of 4 vols. hydrogen. $H_2 + O + H_4$	With addition of 6 vols. hydrogen. $H_2 + O + H_6$
Theory, θ . .	2900	3055	3061	3028
Found, ν . .	2821	3268	3527	3532

To compare with this series of experiments, and with those given in Table XXI., a mixture of hydrogen and nitrous oxide was exploded (1) by itself, (2) with excess of hydrogen, and (3) with excess of nitrogen. A similar divergence between the calculated and observed rates was found both when the mixture was diluted with hydrogen, and when it was diluted with nitrogen.

TABLE XXVII.—Rate of Explosion of Hydrogen and Nitrous Oxide, with excess of (1) Hydrogen, (2) Nitrogen.

(1.)

Mixture.	2 vols. hydrogen 2 vols. nitrous oxide. $H_2 + N_2O$	With addition of 2 vols. hydrogen. $H_2 + N_2O + H_2$	With addition of 4 vols. hydrogen. $H_2 + N_2O + H_4$	With addition of 5 vols. hydrogen. $H_2 + N_2O + H_5$
Theory, θ . .	2319	2374	2396	2400
Found, ν . .	2305	2545	2705	2732

(2.)

Mixture.	$H_2 + N_2O$	With addition of 2 vols. nitrogen. $H_2 + N_2O + N_2$	With addition of 3 vols. nitrogen. $H_2 + N_2O + N_3$
Theory, θ . .	2319	1912	1782
Found, ν . .	2305	1991	1880

NOW M. BERTHELOT especially insists that the formula gives a *maximum* velocity which may be reached, but not surpassed, by the actual explosion-wave. If, then, the rates of explosion of the diluted mixtures had fallen below the calculated rates, such divergence might be explained on the supposition that the diluent gases interfere with the normal propagation of the wave, an explanation which is indeed advanced by BERTHELOT to account for the falling off in the rate of certain diluted mixtures observed by him. But since the theory assumes that the explosion-wave travels at the rate of the gaseous molecules themselves while they still retain all the heat developed by the reaction, the presence of inert molecules could not possibly *increase* this rate of motion.*

Since the amount and regularity of the divergence between the found and calculated rates precluded the idea of experimental error being its sole cause, I was driven to conclude either that the hypothesis was incorrect, or that the formulas used failed to express the hypothesis with exactness.

M. BERTHELOT'S theory is that the explosion does not travel with the velocity of *sound* in the heated gases, but with a velocity equal to the mean rate of translation of the molecules produced in the explosion.

Let us examine the mode in which BERTHELOT calculates the theoretical velocity, *i.e.*, the mean rate of translation of the products of combustion at the temperature of the explosion. In CLAUSIUS' formula

$$\nu = 29.354 \sqrt{\frac{T}{d}}$$

M. BERTHELOT calculates the absolute temperature of the explosion by dividing the quantity of heat developed in the complete reaction by the specific heat of the products of combustion *taken at constant pressure*. He argues that each layer of gas, in transmitting the explosion, is heated under constant pressure. I cannot follow his reasoning.

"The combustion," he says, "in propagating itself from layer to layer, is preceded by the compression of the gaseous layer which it is about to transform.

* It will be shown in the sequel that BERTHELOT'S formula fails to express the rates of explosion of some undiluted explosive mixtures, viz., hydrogen and chlorine, ammonia and nitrous oxide.

. . . The combustion of each layer produces both heat and at the same time the work necessary to compress the following layer—that is to say, the layer loses on this score just as much heat as it gained by its own compression. The whole proceeds, as far as the elevation of temperature is concerned, precisely as if we had operated under constant pressure.” On the facts of the case there is no dispute. The gas is exploded in a closed vessel. Each layer is compressed before being fired; after firing it compresses the layer beyond it. Now, as regards this preliminary compression, each layer, in turn, expends the same energy as was previously communicated to it, and, therefore, it does no work of its own. But a gas heated under conditions where it does no work is raised to the same temperature as it would be had its volume remained constant. M. BERTHELOT admits that it would appear at first sight as if the gases were heated at constant volume; he adds that the concordance of the calculated with the observed numbers supports his explanation of the phenomena.

Again, the fact that each layer is fired by compression involves the preliminary heating of that layer, and this heating must be added to the heat developed by its burning. The temperature of the burning layer must, therefore, be greater than that obtained by dividing the heat developed in the chemical change by the specific heat of the products of combustion.

When a sound-wave alone is transmitted through a gas its velocity shows that each layer of gas forming the wave-front is heated by compression, and there is no reason why this should not happen when the compression is accompanied by a chemical change.

To what extent is each layer heated before combustion? MM. MALLARD and LE CHATELIER* state that the explosion-wave will be propagated when each layer is brought by compression to its own temperature of inflammation. For hydrogen and oxygen, they find this temperature to be about 550°C ., and calculate that a pressure of 30 atmospheres must be exerted upon the gas to raise it to this point. This temperature may be regarded as the *lowest limit* of the preliminary heating of each layer before combustion. But having regard to the fact that the individual molecules of hydrogen and oxygen in a yet unburnt layer may, in the interval of time between their meetings, be heated above the point at which they combine with each other, we cannot affirm that this limit of temperature may not be greatly surpassed in the explosion.

If we regard the transmission of the explosion to be due to the collisions of the molecules, and assume that molecules which are chemically inactive towards each other act as elastic bodies when they come into collision, and that molecules which combine chemically lose energy of translation and gain energy of vibration, then it must happen that unburnt molecules come into collision with burnt molecules and take up their energy in the form of motion. For instance, in the explosion of hydrogen and chlorine, the energy of the hydrogen chloride formed will be communicated by

* ‘Recherches sur la combustion des Mélanges Gazeux Explosifs,’ p. 88-91.

collision to molecules of hydrogen and chlorine; * these *heated* molecules, moving forwards, will meet *unheated* molecules moving backwards, when combination will occur between those of opposite kind. Heated hydrogen will thus combine with cool chlorine, and heated chlorine with cool hydrogen. The heat of combustion is thus communicated to a molecule of hydrogen or chlorine which *shares it* with a molecule of the opposite kind; each hydrogen chloride molecule formed in turn will therefore have, on the average, a temperature corresponding to the heat of chemical combination *plus* half the heat of a molecule previously formed. According to this view the temperature reached by each successive layer would increase until it was *double* that due to the chemical change alone. The temperature of the explosion would then remain constant, and the wave would advance at a uniform rate as long as it met the same mixture of gases.

My conception may perhaps be illustrated by an analogy, although an imperfect one. Imagine a kilogram of water at 0° falling *in vacuo* through 425 metres into a vessel filled with an equal mass of water at 0° : its motion is stopped, but an equal mass of water is displaced. Imagine that the heat developed (which would raise the fallen water to 1°) be divided equally between the water which fell and that which was displaced. The displaced kilogram of water, now at $.5^{\circ}$, falls into a similar vessel 425 metres below, where it divides its heat with, and displaces, a third kilogram of water, and so on. By successive divisions of heat, the temperature of the *falling* water will approach 1° , beyond which it cannot rise. But if the heat developed were not divided, and remained in the fallen water, the *falling* water would be always at 0° , and the *fallen* water at 1° . The latter case is the analogue of the condition imagined by M. BERTHELOT, where the heat of the burnt layer is not imparted to the unburnt layer next it; the former case is the analogue of the condition which I imagine holds in the propagation of the explosion-wave.

Again, M. BERTHELOT considers the velocity of the wave to be solely governed by the mean rate of translation of the *products* of combustion. If, however, we accept the hypothesis that the explosion is propagated by molecular collisions, we have just seen that the movement of the products of combustion is communicated to the unburnt molecules in front. It will, therefore, follow that the rate of the advancing explosion will depend not only on the rate of translation of the products of combustion, but also on the rate of translation of the heated *but yet uncombined molecules*. If the burnt molecules communicate their rise of temperature without loss to the molecules in front, no difference in the mean rate of motion will be caused by this transference so long as the burnt and the unburnt gases are of the same average density. But if a change in density is produced by the combustion, the average velocity of the molecules in the burnt layer will differ from the average velocity of

* [I make the assumption that a very thin layer of gas (comparable in thickness with the mean free path of the molecules) may be raised by collisions to *nearly* the same temperature as the highly heated layer next it.—Jan., 1893.]

the molecules in the heated but yet unburnt layer, and this difference must be taken into account. Lastly, there is a correction to be applied for changes of density in the explosion which in part counteracts the foregoing correction. In the oxidation of hydrogen and of carbonic oxide there is a contraction from three volumes to two; in the burning of cyanogen to carbonic oxide there is an expansion of two volumes to three.* If each layer of the reacting gases is heated at constant volume, a change in the number of molecules must affect the temperature reached.

If the number of molecules is increased by the chemical change the temperature from which the velocity of the wave is calculated will be higher than that directly deduced from calorimetric observations; and *vice versa*. In allowing for this change we may suppose that the new formed molecules have been suddenly compressed or expanded, without loss of heat, into the volume previously occupied by the initial molecules, in which case the temperature would be altered according to RANKINE'S formula

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

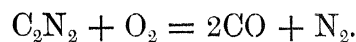
where T_1 and T_2 are the absolute temperatures, V_1 and V_2 the volumes before and after the reaction, and γ the ratio of the specific heats at constant pressure and at constant volume.

CAP. VIII.—COMPARISON OF THE RATE OF EXPLOSION TO THAT OF A SOUND-WAVE.

The criticisms which I have ventured to make on BERTHELOT'S method of calculating the mean rate of translation of the gaseous molecules concerned in the propagation of the explosion-wave, tend to show that the rate so calculated must be too small. But in attempting to apply corrections suggested by these criticisms, one is beset with difficulties. As an approximation I assume (1) that the explosion-wave is carried forward by the movements of molecules of density intermediate between that of the products of combustion and that of the unburnt gas; (2) that the temperature of the gas propagating the wave is double that due to the chemical reaction alone; (3) that the temperature is increased when the chemical volume of the products is larger, and is diminished when the chemical volume of the products is smaller than that of the initial gases; (4) that the gases are heated at constant volume, and their specific heats remain constant at high temperatures. On calculating the mean rate of translation of the molecules on these assumptions one arrives at numbers greatly in excess of any of the observed rates of explosion; but some of the observed rates agree with *the velocity of sound* in a gas of the temperature and density so calculated. For instance, when one volume of cyanogen is exploded with an equal

* M. BERTHELOT rightly takes this change into account in interpreting BUNSEN'S experiments on the temperature produced in explosions. 'Ann. Chim. et Phys.,' [V.], vol. 12, p. 302.

volume of oxygen, two volumes of carbonic oxide are formed, and one volume of nitrogen :—



Taking the quantity of heat evolved as 126,100 calories, and the specific heat at constant volume of the products of combustion as $4.8 \times 3 = 14.4$, the temperature produced by the chemical change is 8694°C . If the gases were initially at 13° , or 286° degrees above absolute zero, the chemical reaction will raise the temperature to 8980° . But, since three molecules are formed where two previously existed, the temperature is further raised by the heat developed in compressing three volumes to two. This will raise the temperature to $10,595^\circ$. At *double* this temperature the mean rate of translation of a molecule of the mean density of the burnt and unburnt gases would be 3892 metres per second. If the formula for the velocity of sound under ordinary conditions held good in the explosion, the velocity of the sound wave would be 2670 metres per second—a rate which is about 2 per cent. less than the observed velocity of the explosion-wave. Now, the theoretical velocity of sound is calculated on the assumption that the disturbance is very small; if the displacements are large the velocity of sound should be higher. Direct measurements of the velocity of sound-waves of great intensity have confirmed this anticipation. Under ordinary conditions the rate of the sound-wave is to the mean rate of the molecules as $.688 : 1$. If we take the ratio in an explosion as $.7 : 1$ the velocity of the sound-wave agrees with the observed rate of explosion in this particular case.

We may now compare the rate of the sound-wave so calculated with the velocity of explosion of cyanogen with oxygen (1) in presence of excess of oxygen, (2) in presence of excess of nitrogen; (3) of cyanogen with nitrous oxide alone, and (4) in presence of excess of nitrogen; and lastly (5) of cyanogen with nitric oxide.

Taking the data furnished by BERTHELOT's experiments, we have, for the quantities of heat evolved, the expansion on explosion, the specific heat of the products, and for the mean density of the burnt and unburnt gases :—

TABLE XXVIII.—Explosion of Cyanogen with Oxygen.

Explosive gases.	Inert gases.	Heat developed.	Expansion.	Specific heat of products.	Mean density.
$C_2N_2 + O_2$	126,100 Cals.	2 : 3	4.8×3	1.213
" . .	O_2	"	3 : 4	4.8×4	1.172
" . .	$2O_2$	"	4 : 5	4.8×5	1.154
" . .	$3O_2$	"	5 : 6	4.8×6	1.144
EXPLOSION of Cyanogen with Oxygen and Nitrogen.					
$C_2N_2 + O_2$. .	N_2	126,100 Cals.	3 : 4	4.8×4	1.132
" . .	$2N_2$	"	4 : 5	4.8×5	1.092
EXPLOSION of Cyanogen with Nitrous Oxide and Nitrogen.					
$C_2N_2 + 2N_2O$.	..	167,300 Cals.	3 : 5	4.8×5	1.294
" .	N_2	"	4 : 6	4.8×6	1.213
" .	$2N_2$	"	5 : 7	4.8×7	1.165
EXPLOSION of Cyanogen with Nitric Oxide.					
$C_2N_2 + 2NO$.	..	169,300 Cals.	3 : 4	4.8×4	1.132

TABLE XXIX.—The Rate of Explosion of Cyanogen Mixtures compared with the calculated Velocity of Sound (Σ).

1. CYANOGEN with Oxygen.

Mixture . . .	$C_2N_2 + O_2$.	$C_2N_2 + 2O_2$.	$C_2N_2 + 3O_2$.
Mean rate . .	2728	2321	2110
Σ	2725	2310	2066

2. CYANOGEN with Oxygen and Nitrogen.

Mixture . . .	$C_2N_2 + O_2$.	$C_2N_2 + O_2 + N_2$.	$C_2N_2 + O_2 + 2N_2$.
Mean rate . .	2728	2397	2163
Σ	2725	2397	2166

3. CYANOGEN with Nitrous Oxide and Nitrogen.

Mixture.	$C_2N_2 + 2N_2O$	$C_2N_2 + 2N_2O + N_2$	$C_2N_2 + 2N_2O + 2N_2$
Mean rate .	2454	2283	2098
Σ	2416	2237	2093

4. CYANOGEN with Nitric Oxide.

Mixture.	$C_2N_2 + 2NO$
Mean rate	2760
Σ	2763

This comparison shows that the formula, which makes the velocity of sound in cyanogen burning to carbonic oxide equal to the observed rate of explosion, also gives for the velocity of sound in the same gases diluted with oxygen or nitrogen numbers closely concordant with the observed rates of explosion. The same formula holds for the explosion of cyanogen with nitrous oxide and when this mixture is diluted with nitrogen. Lastly, by firing a cartridge of fulminate in a steel cylinder filled with a mixture of cyanogen and nitric oxide I succeeded in propagating the explosion from the cylinder through a long leaden tube filled with the gases. The rate of explosion so obtained agreed exactly with the calculated sound-wave. I believe this was the first time that a mixture of cyanogen and nitric oxide had been exploded in a tube. BERTHELOT, who fired this mixture in a bomb, states that the *wave* is not propagated in these gases. I found that neither a strong spark, nor an initial explosion of hydrogen and nitric oxide, would set up the explosion-wave in cyanogen and nitric oxide. The details of these experiments are given in the Appendix.

The formula that I have given was thus found to agree with all the cyanogen explosions. It is therefore, at all events, an empirical expression which can be applied to calculate the rates of explosion of cyanogen burning to carbonic oxide and nitrogen under a fairly wide range of conditions. It was accordingly a matter of considerable interest to apply the formula to the rates found when electrolytic gas was exploded by itself and when diluted with hydrogen, oxygen, and nitrogen. In the following table the rates for electrolytic gas with excess of hydrogen and of oxygen are compared with the numbers calculated from BERTHELOT's formula (θ), and with the sound wave (Σ) calculated as before. In calculating Σ the *contraction* which occurs on the union of hydrogen and oxygen is taken into account, but not the existence (which is possible) of free *atoms* of oxygen :—

TABLE XXX.

Explosive gases.	Inert gases.	Heat developed.	Contraction.	Specific heat of products.	Mean density.
$H_2 + O$	—	59,000 Cals.	3 : 2	4.8×1.5	.520
$H_2 + O$	H_6	„	9 : 8	4.8×4.5	.1964
$H_2 + O$	O_5	„	8 : 7	4.8×4	.910
$H_2 + O$	N_5	„	8 : 7	4.8×4	.8302

THE Rate of Explosion of Electrolytic Gas with excess of Hydrogen and with excess of Oxygen compared with Calculated Velocities.

Mixture.	$H_8 + O$	$H_6 + O$	$H_4 + O$	$H_2 + O$	$H_2 + O_2$	$H_2 + O_4$	$H_2 + O_6$
BERTHELOT'S θ .	3028	3061	3055	2900	2252	1730	1476
Rate of explosion . .	3532	3527	3268	2821	2328	1927	1707
Σ	3516	3571	3585	3416	2650	2024	1718

A glance at this table reveals the fact that the sound-wave calculated by my formula does not agree in velocity with the explosion-wave of pure electrolytic gas ; but as the electrolytic gas is more and more diluted with hydrogen or with oxygen, the observed and calculated velocities come nearer together, until, not far from the two limits of regular explosion, they are in close agreement. Conversely we have seen that BERTHELOT'S formula gives the correct rate for pure electrolytic gas, but diverges more and more from the observed rates as the gas is diluted. Where BERTHELOT'S " θ " fails to represent the facts, the " Σ " I have calculated does so ; and *vice versa*.

I advance the following hypothesis to account for this divergence. *At the high temperature of the explosion-wave the combination of hydrogen and oxygen is not complete ; or, in other words, steam is partly dissociated under these conditions.* The temperature of the wave front is therefore less than that calculated. As more and more inert gases are added to electrolytic gas, the temperature of the explosion is lowered by the division of the heat between the diluent gases ; more and more of the explosive gases are thus able to combine. As the gases are diluted, therefore, the temperature of the wave front comes nearer and nearer to that calculated.

A comparison of the sound-wave, Σ , with the rates of explosion of electrolytic gas diluted with nitrogen, and of hydrogen with nitrous oxide and nitrogen, brings out

similar divergences which admit of the same explanation. It is to be noted in the case of hydrogen and nitrous oxide that no alteration of volume occurs in the chemical change; no correction in temperature need, therefore, be made in calculating the sound-wave, and the question of the density of the molecules concerned does not arise.

TABLE XXXI.—The Rate of Explosion of Electrolytic Gas with excess of Nitrogen compared with Calculated Velocities.

Mixture.	$H_2 + O$	$H_2 + O + N$	$H_2 + O + N_3$	$H_2 + O + N_5$
BERTHELOT'S θ . . .	2900	2321	1814	1558
Rate of explosion . .	2821	2426	2055	1822
Σ	3416	2731	2122	1813

TABLE XXXII.—The Rate of Explosion of Hydrogen and Nitrous Oxide, with excess of Hydrogen, and of Nitrogen, compared with Calculated Velocities.

Mixture.	$H_7 + N_2O$	$H_6 + N_2O$	$H_4 + N_2O$	$H_2 + N_2O$	$H_2 + N_2O + N_2$	$H_2 + N_2O + N_3$
BERTHELOT'S θ . . .	2400	2396	2374	2319	1912	1782
Rate of explosion . .	2732	2705	2545	2305	1991	1880
Σ	2776	2781	2765	2706	2227	2067

When electrolytic gas is diluted with excess of nitrogen, the observed rate of explosion closely agrees with the calculated sound-wave. With hydrogen and nitrous oxide the temperature cannot be diminished to the same extent by dilution. When three volumes of hydrogen, or two volumes of nitrogen, are added to the mixture consisting of one volume of hydrogen and one of nitrous oxide, the explosion-wave is not propagated with regularity; consequently the temperature cannot be brought down by dilution below the dissociation-point of steam. As the mixture is diluted the rate of explosion approaches Σ , but agreement is not reached at the limits of dilution at which the explosion-wave will still travel.

The rates of explosion of mixtures of ammonia with oxygen and with nitrous oxide were also determined. The gases were mixed in an iron holder standing over mercury. The rate of explosion of ammonia and oxygen is faster than the velocity calculated by

BERTHELOT's formula, but falls far below the velocity of sound " Σ ." On the other hand, the rate of explosion of ammonia and nitrous oxide is close to the calculated sound-wave and is far above " θ ."

TABLE XXXIII.

	Explosive gases.	Heat developed.	Expansion.	Specific heat of products.	Mean density.
1.	$4\text{NH}_3 + 3\text{O}_2$	305,200	7 : 8	4.8×11	.761
2.	$2\text{NH}_3 + 3\text{N}_2\text{O}$	193,800	5 : 7	4.8×8.5	.987

(1.)

Mixture.	$4\text{NH}_3 + 3\text{O}_2$.
BERTHELOT'S θ . . .	2300
Rate of explosion . .	2390
Σ	2665

(2.)

Mixture.	$2\text{NH}_3 + 3\text{N}_2\text{O}$.
BERTHELOT'S θ . . .	1953
Rate of explosion . .	2200
Σ	2223

Mixtures of oxygen with the hydrocarbons ethylene and acetylene will explode when largely diluted with nitrogen. For instance, the explosion-wave is propagated in a mixture of one volume of ethylene with two of oxygen and eight of nitrogen. The temperature reached in the explosion is comparable with that produced when three volumes of electrolytic gas are fired with five volumes of nitrogen. It is found both with ethylene and acetylene that the rate of explosion exactly agrees with the calculated velocity of the sound-wave when the mixtures are largely diluted with nitrogen, but not when the gases are exploded without dilution :—

TABLE XXXIV.

Explosive gases.	Inert gases.	Heat developed.	Expansion.	Specific heat of products. 4.8×5	Mean density.
$C_2H_4 + O_4$	—	185,000	3 : 4		.930
$C_2H_4 + O_4$	$8N_2$	185,000	11 : 12	4.8×13	.954

Rate of Explosion of Ethylene and Oxygen with excess of Nitrogen compared with Calculated Velocities.

Mixture.	$C_2H_4 + 2O_2$	$C_2H_4 + 2O_2 + N_2$	$C_2H_4 + 2O_2 + 2N_2$	$C_2H_4 + 2O_2 + 4N_4$	$C_2H_4 + 2O_2 + 6N_3$	$C_2H_4 + 2O_2 + 8N_2$
BERTHELOT'S θ . .	2487	2234	2050	1796	1624	1498
Rate of explosion .	2581	2413	2211	2024	1878	1734
Σ	2856	2575	2367	2073	1873	1727

TABLE XXXV.

Explosive gases. $C_2H_2 + O_3$	Inert gases. —	Heat developed. 171,700	Expansion. 5 : 6	Specific heat of products, 4.8×3.5	Mean density. .9406
$C_2H_2 + O_3$	$6N_2$	„	17 : 18	4.8×9.5	.9594

Rate of Explosion of Acetylene and Oxygen with excess of Nitrogen compared with Calculated Velocities.

Mixture.	$C_2H_2 + O_3$	$C_2H_2 + O_3 + N_2$	$C_2H_2 + O_3 + N_6$	$C_2H_2 + O_3 + N_8$	$C_2H_2 + O_3 + N_{10}$	$C_2H_2 + O_3 + N_{12}$
BERTHELOT'S θ . . .	2749	2397	1983	1848	1739	1650
Rate of Explosion . . .	2716	2414	2209	2116	2019	1908
Σ	3187	2784	2303	2144	2016	1910

Since steam is known to be partially dissociated under atmospheric pressure at the temperature of the oxy-hydrogen flame, it does not seem improbable that dissociation would also occur at the higher pressures and higher temperatures of the explosion-wave. The researches of MM. BERTHELOT and VIEILLE, and those of MM. MALLARD and LE CHATELIER, on the pressures registered in an explosion of gases, have led these investigators to the conclusion that the specific heat of steam rapidly rises with the temperature. The deficiency of "available" pressure, which BUNSEN first observed in the explosion of gases and attributed to incomplete combustion, they consider to be due to an increase of specific heat. Such an increase in the specific heat of steam with rise of temperature would explain the divergence between the observed and calculated rates of explosion of hydrogen with oxygen, and with nitrous oxide. And conversely, it appears to me that the results of the French experimenters would be equally well explained by the temporary dissociation of steam in their explosions.

One fact appears, at first sight, to be opposed to the hypothesis of incomplete combustion. The addition of oxygen, one of the products of the dissociation of steam, retards the explosion of electrolytic gas more than the addition of an equal volume of nitrogen—an inert gas. WURTZ found, in the case of phosphoric chloride, that the amount of dissociation was greater when the chloride was volatilised in air—an inert gas, than when it was volatilised in the presence of the lower chloride—one of the products of its decomposition. Arguing from this observation, one might have expected that excess of oxygen would tend to hinder dissociation, and therefore, if the combustion were really incomplete, that the rate should be faster when oxygen was used as a diluent instead of nitrogen. But the condition of equilibrium under which WURTZ determined the vapour density of phosphoric chloride is not the condition of the wave-front of an explosion. If we imagine in the wave-front a molecule A dashing against a molecule B with such extreme velocity that the compound AB is not formed, the two molecules may be supposed to rebound, exchanging energies, and the motion of B may be communicated to the molecules in front continuing the explosion. This is a case where dissociation of AB occurs in the wave-front. Now if a number of B molecules are present in excess, A will shortly combine with one of them, behind the wave-front, and the dissociation will not be permanent. On the other hand, if there are a number of inert molecules C present, dissociation may occur as before in the wave-front, but the uncombined molecules may be prevented from combining behind the wave by the inert molecules present. The propagation of the wave does not depend on what occurs after it has passed; the rate of the wave will therefore be independent of the permanency of the dissociation occurring in it.

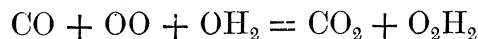
That the combustion of pure electrolytic gas is not *wholly* complete in the explosion-wave has been proved by collecting the residue and exploding it.* In the propagation

* "Incompleteness of Combustion in Gaseous Explosions," by H. B. DIXON and H. W. SMITH. 'Manchester Memoirs' [IV.], vol. 2. 1888.

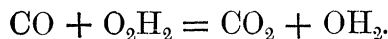
of the wave the cooling due to expansion is so rapid that some molecules of hydrogen and oxygen, which are unburnt in the wave-front, have not time to combine before they are cooled below the temperature of combination. In a leaden tube, 9 mm. in diameter and 100 metres long, about 1 per cent. of electrolytic gas was found uncombined after the explosion. That this incompleteness of combustion was not due to the cooling effect of the walls was shown by making comparative experiments in tubes 4 mm. and 19 mm. in diameter. Nearly the same percentage of unburnt residue was found in all the tubes, and also when the gases were detonated in an iron bomb 100 mm. in diameter. We have, therefore, positive evidence that in the explosion-wave the combustion of electrolytic gas is incomplete; it seems, therefore, not unreasonable to assume that in the wave-front—*i.e.*, at the highest temperature—a considerable proportion of hydrogen and oxygen is uncombined, and the propagation of the wave is retarded accordingly.

The residual gases, left after the explosion of electrolytic gas, were examined for peroxide of hydrogen; the water condensed on the tube was also washed out and examined. In neither case could peroxide of hydrogen be detected. If the view were correct that hydrogen and oxygen first form peroxide on explosion, it would seem likely that, in the rapid cooling, some of the peroxide would remain undecomposed, and be found in the residue.

In the explosion of carbonic oxide and oxygen a similar residue of unburnt gas is found—indicating the dissociation of carbonic acid at the temperature of the wave. No trace of peroxide of hydrogen could be detected in the tube. These observations give no support to the view put forward by MORITZ TRAUBE* that steam promotes the oxidation of carbonic oxide by dividing with it the molecules of oxygen:—



and that the peroxide so formed is again reduced to steam by more carbonic oxide:—



CAP. IX.—THE EXPLOSION OF HYDROGEN AND CHLORINE.

The coincidences and the divergences found between the calculated and observed rates of explosion, as described above, made it important to examine a reaction in which no steam should be formed, and, if possible, one in which no alteration in volume should be produced. The simplest case fulfilling these conditions is the explosion of hydrogen and chlorine; a reaction which has the further advantage of forming, as the product of explosion, a gas which approximates to a perfect gas. So

* 'Ber. Dent. Chem. Ges.,' vol. 18, p. 1890. (See 'Chem. Soc. Journ.,' 1886, vol. 1, p. 94.)

far as I know the rate of explosion of hydrogen and chlorine had never been measured.

Before devising apparatus to carry out the experiments, it was necessary to determine whether the action between hydrogen and chlorine was a direct one, or whether it was influenced by the presence of other gases, *e.g.*, steam.* Electrolytic hydrogen and chlorine were accordingly sealed up in glass vessels with anhydrous phosphoric acid, and were kept in the dark for several weeks. The dried gases were found to be far less sensitive to the action of *light* than when a trace of aqueous vapour was present, a result in accordance with PRINGSHEIM'S† observations. But on the passage of an induction spark by means of platinum-iridium wires the dried gases exploded violently.

Since these experiments left it doubtful whether the presence of steam influenced the rate of explosion of hydrogen and chlorine, a preliminary series of measurements were made with the dry and moist gases.‡ The explosion-vessel consisted of two long glass tubes§ (34 and 30 feet) cemented together. The ends were provided with steel flanges so that they could be rapidly joined to two smaller tubes which carried the silver bridges. The explosion tube was hung to the wall of a long, darkened corridor.

The gas passed directly from the electrolytic cell through washing tubes into the long explosion tube—driving out the air before it: at the further end it passed through an “analyser,” which served to determine the composition of the mixture issuing from the tube. When the long tube was completely filled with hydrogen and chlorine, the two smaller tubes carrying the bridges were fastened to its two ends by the steel flanges. These smaller tubes had previously been filled with hydrogen and oxygen. The electric connections were then made to the chronograph, and the gases fired by the passage of a spark through the hydrogen and oxygen in one of the smaller tubes. The flame travelling down this tube, which was about 4 feet long, broke the silver bridge at the end of it, and communicated the explosion to the hydrogen and chlorine. On reaching the end of the glass tube, the flame broke the silver bridge carried by the second smaller tube. In the few seconds that elapsed between the joining on of the small tubes and the firing of the mixture but little diffusion of the gases was possible; and the silver bridges, being coated with paraffin, were hardly acted on by the chlorine. By this arrangement the electrolytic hydrogen and chlorine were kept from contact with metals or india-rubber, and

* “On the Combination of Hydrogen and Chlorine, alone, and in Presence of other Gases.” By H. B. DIXON and J. A. HARKER. ‘*Manch. Memoirs*’ [IV.], vol. 3, p. 118.

† ‘*Annalen der Physik*,’ N.F., vol. 32, p. 421, 1887.

‡ ‘*Manch. Memoirs*’ [IV.], vol. 4, p. 3. (The numbers given in this paper were afterwards found to be affected by a constant error.)

§ These glass tubes were made for me by MESSRS. MOLINEAUX and WEBB, of Manchester. They were unannealed, but stood the shock of many explosions.

from all liquids but water, and, in the "dry" experiments, oil of vitriol saturated with chlorine. The drying apparatus consisted of a "Winkler" worm, a series of bulbs, and a large U-tube packed with pumice, all filled with boiled oil of vitriol.

The following table gives the mean of each pair of experiments with the dry and with the moist gases saturated at 14°.

TABLE XXXVI.—Rate of Explosion of Hydrogen and Chlorine.

Dry.	Moist.
1748 1745 1737 1748 1750	1724 1707 1730
Mean 1745	Mean 1720

It appeared, therefore, that the explosion, once started, travelled at a slightly faster rate in the dry than in the wet gases, the steam appearing to act merely as a diluent.

These experiments, together with the analysis of the mixture which issued from the end of the explosion tube, showed that it was possible to fill a long tube directly from the electrolytic cell with hydrogen and chlorine in equal volumes, and that the mixture *detonated* in a glass tube of 10 mm. diameter. To prove the constancy of the rate of explosion, and at the same time to have a longer interval of time to measure, it was necessary to obtain a longer explosion tube. The difficulty of joining up long pieces of unannealed glass-tubing led me to try the glass-lined wrought-iron tubing manufactured by Messrs. RYLANDS, at Barnsley. Having found that this tubing answered the purpose, I made an explosion tube 40 yards long, and $\frac{1}{2}$ -inch diameter, by joining together a number of six-foot lengths. The junctions were made by fitting an asbestos washer on to the ends of each tube, and screwing them together with a nut. The tube was supported at intervals by wooden brackets fastened to the wall of a long corridor. The explosion tube so put together was perfectly gas-tight; it was unaffected by the chlorine passed into it during the experiments, and it stood the shock of many explosions without leaking. This tube was filled, as before, direct from the electrolytic cell of aqueous hydrochloric acid. The cell and drying vessels were all of glass with ground glass joints. Two short tubes charged with hydrogen and oxygen were used, as before, to carry the silver bridges. They were joined to the long tube immediately before the explosion. The mean rate of explosion of dry hydrogen and chlorine in this tube was found to be 1723 metres per second—as the result of three pairs of experiments:—

TABLE XXXVII.—Rate of Explosion of Hydrogen and Chlorine. 2nd Series.

	1718
	1727
	1725
	<hr/>
Mean	1723

If the preliminary series of experiments with the dry gases is regarded as of equal value with *one* of these pairs, the mean rate of explosion is found to be 1729 metres per second.

The heat of combination of hydrogen and chlorine was found by FAVRE and SILBERMANN to be 23,780 calories ; by J. THOMSEN it was found to be 22,000 calories. BERTHELOT gives one determination 22,100 calories. The mean of these numbers is 22,630 calories. Taking THOMSEN's number for the heat of combination, the mean rate of translation of the products of combustion according to BERTHELOT's formula (corrected to 13° C.) is found to be 1551 metres per second ; taking the mean number 22,630 calories for the heat of combination, BERTHELOT's formula gives 1571 metres for the mean rate. The rate of explosion of hydrogen and chlorine under ordinary conditions is, therefore, considerably faster than the rate given by BERTHELOT's formula. The velocity of the sound-wave (Σ) calculated by my formula is 1805 or 1830, according as the lower or higher heat of combination is taken. The rate of the explosion thus falls appreciably below the calculated velocity of the sound-wave. Since BERTHELOT contends that his formula gives the maximum velocity of explosion, his hypothesis fails in the case of the explosion of hydrogen and chlorine. On the other hand, two questions arise : (1) Does dissociation occur in the explosion ? (2) On diluting the mixture will the rate of explosion approach the velocity of the sound-wave ?

When the hydrochloric acid gas, produced by the explosion in the long tube, was driven out by a stream of hydrogen through a washing apparatus containing potassium iodide, a quantity of iodide was liberated, showing the presence of free chlorine in the products of combustion. And when the gases were driven out by a stream of carbonic acid through a washing apparatus containing caustic soda, free hydrogen was found to be present also. Even after passing the current for many hours the gases coming from the electrolytic cell, and issuing from the further end of the explosion tube, were always found to contain a slight excess (amounting to between .2 and .5 per cent.) of hydrogen. The presence of free chlorine in the vessel after the explosion was thus a proof of dissociation occurring in the explosion, and the determination of this free chlorine by the liberation of iodine afforded a ready means of measuring the volume of gases left unburnt. About 1 per cent. of the combustible gases were found uncombined.

On diluting the electrolytic gas with hydrogen the rate of explosion was found to increase, and to approximate to the calculated velocity of the sound-wave. The mixtures were made by bringing the electrolytic gas from the cell, and the hydrogen from a holder, into a sulphuric acid wash-bottle through two tubes of the same size dipping side by side beneath the liquid. By regulating the flow of hydrogen the bubbles of each gas could be kept passing at an equal rate. In this way a mixture containing three volumes of hydrogen to one volume of chlorine was passed into the explosion tube. The correctness of the mixture was checked by collecting and analysing a sample of the gas escaping from the end of the tube. By passing the hydrogen at half the rate a mixture containing approximately two volumes of hydrogen to one of chlorine was obtained. While the addition of diluent hydrogen to the electrolytic gas makes little difference in the calculated rates, the observed velocities of explosion increased appreciably. On the assumption that the heat of combination of hydrogen and chlorine is 22,630 calories, the calculated and observed velocities are as follow :—

TABLE XXXVIII.—Rate of Explosion of Hydrogen and Chlorine with addition of Hydrogen.

Mixture.	$H_2 + Cl_2$	$H_4 + Cl_2$	$H_6 + Cl_2$
BERTHELOT'S θ	1571	1581	1589
Rate of explosion	1729	1849	1855
Σ	1830	1832	1832

These experiments show that in the explosion of hydrogen and chlorine as in the explosion of hydrogen and oxygen, in equivalent proportions, the rate falls below the calculated velocity of the sound-wave, but on diluting the gases the calculated and observed velocities come together. This divergence at the highest temperature may be explained either by the dissociation of the hydrochloric acid or by a rise in its specific heat.* As I have shown, we have direct evidence of *some* dissociation. On the other hand, the physical properties of hydrochloric acid more nearly resemble those of carbonic oxide and the elementary gases than those of steam or carbonic acid; we should expect, therefore, that the specific heat of hydrochloric acid should remain as constant as that of carbonic oxide at high temperatures.

* MM. MALLARD and LE CHATELIER conclude from their experiments that some dissociation occurs when equal volumes of hydrogen and chlorine are exploded. When excess of hydrogen is added they find no dissociation.

The fact that the rate of explosion of hydrogen and chlorine exceeds the calculated velocity of the sound-wave, as calculated from THOMSEN'S Heat of Combination (22,000 cal.), is possibly due to the behaviour of the unburnt chlorine in the wave-front. The rates agree fairly with the sound-wave calculated from the *mean* heat of combination, which I have given in the table.

CAP. X.—THE INSTANTANEOUS PRESSURES PRODUCED IN THE EXPLOSION-WAVE.

There is, lastly, one important phenomenon in the propagation of explosions in gases which I have not touched on—the pressure produced in the reacting gases. BUNSEN was the first who attempted to measure this pressure. In his well-known work* he describes the explosion of mixtures of hydrogen and of carbonic oxide with oxygen in a strong vessel closed with a loaded lid. When the pressure produced in the vessel exceeded the pressure on the lid, the latter was raised in the manner of a safety valve, and some of the heated gas escaped; when the pressure was less than that on the lid, no gas escaped and but little noise was heard.

By successive trials he thus found the pressure produced by the explosion of carbonic oxide and oxygen to be about 10 atmospheres, and the pressure produced by the explosion of hydrogen and oxygen to be about 9.5 atmospheres. The comparison of these pressures with the numbers calculated from the heat of combination and the specific heats of the products led BUNSEN to the conclusion that, at the highest temperature reached in the explosion, only one-third of the gases entered into combination. BERTHELOT and VIEILLE, working in a manner essentially the same, only replacing BUNSEN'S loaded lid by a light piston moving against a spring, found the pressures produced in the explosion of carbonic oxide and hydrogen to be 10.1 and 9.8 atmospheres respectively. BERTHELOT rightly calls these pressures "*effective pressures*."† On the other hand, MALLARD and LE CHATELIER, using the more delicate indicator of DEPREZ, found pressures produced in the explosion of hydrogen and oxygen, of far greater amount, but lasting an exceedingly short time. These fugitive pressures of great intensity were only obtained with mixtures which burnt very rapidly:—‡

"Cette pression très fugitive est d'autant plus grande que la vitesse de propagation est plus considérable. Elle peut devenir énorme avec l'onde explosive. C'est à ces pressions, si instantanées qu'elles soient, que sont dus les surprenants effets des substances explosives telles que la nitroglycérine. Ce sont précisément ces pressions passagères, sans relation directe avec le phénomène que nous voulions mesurer, qu'enregistrait notre appareil."

On substituting for the DEPREZ indicator a less sensitive Bourdon manometer,

* 'Gasometrische Methoden,' 1857.

† 'Ann. Chim. et Phys.' [vi.] 4, p. 14, 1885.

‡ 'Combustions des Mélanges gazeux,' p. 123.

LE CHATELIER found "effective pressures" in agreement with those obtained by BUNSEN and by BERTHELOT, *i.e.*, about 10 atmospheres.

It is evident from these experiments that sudden pressures are produced in the explosion-wave greater than those shown by the experiments of BUNSEN and of BERTHELOT. If the explosion is propagated by compression after the manner of a sound-wave enormously high temperatures must be produced in the wave, as I have already shown, and correspondingly high pressures must also exist. This aspect of the matter has been well stated by MALLARD and LE CHATELIER :—

"A gas, increasing in volume by combustion, exerts a certain pressure on the unburnt gas next to it : it is possible to conceive that this pressure may be raised sufficiently high to bring the neighbouring layer to the temperature of ignition. The possibility of the propagation of the inflammation by the propagation of the pressure can thus be understood.

"Take for example the explosive mixture of hydrogen and oxygen. According to our experiments it inflames at 555° , and the pressure exerted after the combustion in a closed vessel is 10 atmospheres. An infinitely thin layer inflamed by heating, reaches this pressure at the greatest, and cannot exert any higher pressure on the uninflamed layer next to it.

"A compression of 10 atmospheres evolves a quantity of heat which can readily be calculated by thermo-dynamics : it is not sufficient to produce an elevation of temperature equal to that inflammation. To obtain this temperature a compression of 30 atmospheres would be needed. It would appear, then, that the explosion-wave could not be initiated under these conditions.

"Suppose, however, that the inflammation of the first layer is not brought about by heating, but by a suitable pressure, *i.e.*, one of not less than thirty atmospheres, which may readily be produced by the detonation of a little fulminate. After the combustion the pressure of the inflamed layer will be multiplied by ten, or at least will be far higher than the initial pressure of thirty atmospheres, and will be able, consequently, to exert on the next layer a pressure sufficient to inflame it. This will continue then to propagate itself from layer to layer by the same mechanism."— ('Combustion des Mélanges Gazeux,' p. 88.)

The sudden state of pressure produced in each layer of burning gas ceases as suddenly as it is caused, by the expansion of the gas which compresses the unburnt layer in front ; the high temperature of the burnt layer, therefore, rapidly falls by the transformation of heat into work. MALLARD and LE CHATELIER have shown by photographs of the flame that, in the explosion-wave, the luminosity of each layer does not last longer than one thousandth part of a second ; while in the *régime* of ordinary combustion each layer remains luminous more than ten times as long. I can fully confirm these statements. By photographing the explosion-wave of hydrogen and oxygen on a fixed and on a rapidly moving plate at the same time, I have found that

the interval during which the gas remains bright enough to effect a sensitive isochromatic plate cannot be more than *one five-thousandth of a second*.

The problem of measuring the pressure in a thin layer of gas, lasting for so small a fraction of a second, is one of the greatest difficulty. I believe the method tried by MALLARD and LE CHATELIER for explosions of carbon bisulphide and oxygen is probably the best that has yet been devised. This depends on the principle that if a pressure is produced in a glass vessel greater than the glass can stand, the vessel will be broken, although the pressure may endure for a very small interval of time. If the vessel is broken by the explosion, I believe that there must have been a pressure produced in the layer of gas next the glass *at least* equal to that which would break the vessel when gradually applied. By compressing gas in the vessel by means of a pump, it can be shown that the vessel is able to withstand a certain pressure. The vessel can then be connected with a long tube, the whole filled with an explosive mixture, and the explosion-wave set up in the tube. If the vessel is fractured, a pressure was exerted on its walls greater than the pressure applied by the pump.

To test this method, I have carried out a few preliminary experiments. Out of a piece of strong combustion tubing I made twelve short tubes, carefully sealed at one end, and slightly opened at the other. These tubes were then firmly attached to a metal piece by a collar and nut working against india-rubber rings—care being taken that the glass did not come anywhere into contact with the metal, but only with the rubber rings. The metal piece could be attached either to the pump or to a leaden firing tube. The twelve tubes were first tested with compressed air, which was slowly forced into the tube while an observer read the manometer. One tube (it was rather unevenly sealed) broke down between nineteen and twenty atmospheres. A second broke at twenty-three atmospheres. The other ten stood a pressure of twenty-five atmospheres for two minutes. These tubes were then in turn attached to one end of a firing-tube about twenty feet long. On filling the whole with a mixture of carbonic oxide and oxygen, and passing a spark through the gases at the other end of the tube, the explosion-wave was propagated through the leaden pipe into the glass vessel. All ten tubes were blown into small fragments by the explosion. Four stronger green glass tubes were tested by compressed air at fifty atmospheres. All these tubes stood the explosion of carbonic oxide and oxygen, and hydrogen and oxygen. Two of these green tubes were blown to pieces by the explosion of equal volumes of cyanogen and oxygen, a third was fractured by compressed air at seventy-eight atmospheres. These experiments confirm LE CHATELIER's results with the DEPREZ indicator, showing that very high pressures are produced for the moment in the explosion-wave; they do not, of course, *measure* the pressures, they only indicate a lower limit.

The quiet burning of carbonic oxide and oxygen, when this mixture is lighted at the open end at a short tube, such as a test-tube, is in striking contrast to the violence of the explosion when the "wave" is set up in the same gases. As a lecture experiment a test-tube full of the mixture may be ignited by a taper, when the quiet

passage of the blue flame down to the tube can be followed by the eye; the tube is then refilled and screwed on to the end of a few feet of leaden pipe filled with the mixture. The test-tube is surrounded by metal gauze and a thick glass cylinder. On applying a flame to the open end of the pipe, or passing a spark near the extremity, a loud report is heard, and the test-tube is reduced to powder.* The explosion-wave in a glass tube produces a brilliant flash of orange light.

Professor A. SCHUSTER† has drawn my attention to a memoir, by RIEMANN, on the propagation of intense disturbances in gases, and has suggested a mode of calculating the momentary pressures produced in the explosion-wave from its known velocity of propagation, and the density of the unburnt gas. On the assumption that RIEMANN'S theory holds for an explosion, I have calculated, from the observed rates of the wave and the densities of the unburnt gas, the pressures existing in the wave in the explosion of different gaseous mixtures. In parallel columns I have given the "effective" pressures as registered in the apparatus used by BERTHELOT for the same mixtures. The pressures calculated for the wave are rather more than four times larger than these effective pressures. In the third column I have given the calculated pressures divided by 4.2.

The pressure in the wave is given by the equation

$$\pi = \frac{\nu^2 \rho}{100}$$

where π is the pressure in atmospheres, ν the rate in metres per second, and ρ is the weight in grammes of 1 c.c. of the unburnt gas.

* Professor DEWAR has noticed the great violence with which carbonic oxide and oxygen explode under certain conditions. He says: "Sometimes the explosions were so violent as to break the plate closing the end of the tube, though this had resisted the explosions of the hydrogen mixture; while at the other times the wave of explosion passed slowly along the tube." 'Roy. Soc. Proc.,' April 3, 1884. Probably owing to differences in the nature of the electric sparks, the "explosion-wave" was sometimes set up in his tube and sometimes not.

† See note at end of cap.

TABLE XXXIX.—Pressures in the Explosion-wave calculated from RIEMANN'S Theory.

Explosive Mixture.	Calculated Pressure. Π	$\frac{\Pi}{4.2}$	Effective Pressure measured by BERTHELOT.
$C_2N_2 + O_2$	135.2	32.2	25.11
$C_2N_2 + 2NO$	123.0	29.3	23.34
$C_2N_2 + 2N_2O$	121.6	28.9	26.02
$C_2N_2 + 2O_2$	90.1	21.5	20.96
$C_2N_2 + O_2 + 2N_2$	71.0	16.9	15.25
$C_2H_4 + O_3$	81.5	17.9	16.13
$C_2H_4 + O_3$	94.3		
$C_2H_4 + O_4$	88.4		
$C_2H_4 + O_6$	75.2		
$CH_4 + O_4$	62.2	14.8	16.34
$C_2H_2 + O_3$	110.0		
$C_2H_2 + O_3$	94.5		
$C_2H_2 + O_3 + N_{12}$	45.3		
$H_2 + O$	28.8	6.9	7.05
$H_2 + O$	41.3	9.8	9.8
$H_2 + O + N_5$	31.6	7.5	7.41
$H_2 + N_2O$	52.9	12.6	13.6
$CO + O$	35.7	8.5	10.1
$H + Cl$	46.9	11.2	By LE CHATELIER. 10.0

It is to be noticed that these calculated pressures are in substantial agreement with my experiments on the fracturing of glass tubes by the explosion of carbonic oxide and of cyanogen with oxygen; and also that the minimum pressures calculated for the diluted electrolytic gas are close to 30 atmospheres—the pressure required to fire electrolytic gas by the heat of compression.

NOTE BY PROFESSOR ARTHUR SCHUSTER, F.R.S.

In 1859 RIEMANN* deduced an equation for the propagation of abrupt variations in the density and pressure of a gas, on the supposition that such an abrupt variation could be propagated without change of type. Lord RAYLEIGH† criticising this investigation, draws attention to the fact that a steady wave

* 'Göttingen Abhandlungen,' vol. 8 (1860).

† RAYLEIGH, 'Sound,' vol. 2, p. 41.

is only possible for a particular relation between the pressure and density of the gas, which is different from the one actually holding. In the case of the explosion-waves it seems possible, however, that the temperature, pressure, and density of the gas should so adjust themselves as to make RIEMANN'S equations applicable. In fact, they must do so if the front of the wave keeps its type, which it probably does when the velocity has become constant.

If ρ_0 and ρ are the densities of the gas in the undisturbed state, and at some point in the wave respectively, then, referring the motion to a system of coordinates moving forward with the velocity V of the wave, we have the condition of steady motion

$$\rho u = \rho_0 V$$

where u is the velocity at the point at which the density is ρ ;
also

$$\frac{dp}{dx} = -\rho u \cdot \frac{du}{dx}.$$

As ρu is a constant quantity we may integrate the latter equation and obtain

$$p - p_0 = -\rho u (u - u_0) = \frac{\rho_0}{\rho} V^2 (\rho - \rho_0),$$

which gives for the velocity of the wave propagation

$$V = \sqrt{\frac{(p - p_0)}{(\rho - \rho_0)} \cdot \frac{\rho}{\rho_0}}.$$

This equation gives a relation between the density ρ at any point of the wave and the pressure p at that point, the pressure and density in the initial state being p_0 and ρ_0 . The equation can be simplified if ρ is large compared to ρ_0 for

$$\frac{\rho}{\rho_0 (\rho - \rho_0)} = \frac{1}{\rho_0} \left(1 - \rho_0/\rho \right)$$

so that we may write

$$V = \sqrt{\frac{p - p_0}{\rho_0}} \cdot \sqrt{\frac{1}{1 - \rho_0/\rho}}$$

Putting, for the sake of argument, $\rho = 10\rho_0$, the second square root in the above expression becomes 1.05, so that as a first approximation it may be put equal to one. Writing P for the *excess* of pressure over the atmospheric pressure, the equation now takes the simple form

$$V = \sqrt{\frac{P}{\rho_0}}.$$

In this expression the value of P has to be written in dynes per square centimetre, and the velocity would be given in centimetres. For more convenient numerical calculation we may adopt provisionally the suggestion of GUILLAUME that a pressure of 75 cms. of mercury under the normal conditions should be called an *atmosphere*. The atmosphere then would be exactly one megadyne per square centimetre, and if P is given in atmospheres, the equation becomes

$$V = 1000 \sqrt{\frac{P}{\rho_0}},$$

or if V is expressed in metres per second,

$$V = 10 \sqrt{\frac{P}{\rho_0}}.$$

The excess of pressure in the waves, therefore, will be, as far as the equations hold,

$$P = \frac{V^2 \rho_0}{100}.$$

If the factor

$$\sqrt{\frac{\rho}{\rho - \rho_0}}$$

be retained, the calculated pressure P would be rather smaller than that given; thus if the maximum density of the wave is only double that of the undisturbed state, the calculated value of P would have to be reduced in the ratio of 1.4 to 1.

In order to test the equation

$$V = \sqrt{\frac{P}{\rho_0}}$$

I have applied it to compare the rates of explosions in the mixtures $H_2 + O$, $H_2 + O + N_5$, $H_2 + O_6$. In these three cases the explosive mixture $H_2 + O$ is diluted with the same volume of inert gases, and according to the equation the rates should be inversely as the square roots of the densities of unburnt gases, for the pressure P may be expected to be the same in all three cases. The rates found by Professor DIXON are 3532; 1822; 1707. Assuming 3532 to be right, I calculate for the other two combinations 1806 and 1711, which so far confirms the equation. But I am doubtful whether this means much, as the same result could be deduced from arguments relating merely to the dimensions of the quantities involved.

I have not discussed the question whether a steady wave is really possible, but assuming it to be steady I believe that the equation

$$V = \sqrt{\frac{p - p_0}{\rho - \rho_0} \cdot \frac{\rho}{\rho_0}}$$

holds. In the strict sense of the word I do not think the explosion-wave can be steady, because if the motion is, as assumed, linear, compression must precede the explosion, and Lord RAYLEIGH's objection would hold for the front part of the wave in which no combination takes place.

But it seems possible to me that the motion may not strictly be a linear one, and that yet taking the average velocities over a cross-section of the tube the ordinary equations would apply. It seems probable that jets of hot gases are projected bodily forward from that part of the wave in which the combination takes place, and that these jets, which would correspond to the spray of a breaking wave, really fire the mixture.

CAP. XI.—SOME DIFFICULTIES IN THE "WAVE" THEORY.

§ 1. In calculating a theoretical velocity for the rate of the explosion-wave in gases, I am aware that I have passed over many difficulties which demand consideration. For some of the problems raised here we have, I believe, no data which might enable us to solve them. RIEMANN's theory of the propagation of an intense disturbance in a gas requires, in order to calculate the velocity of propagation, a knowledge of the highest pressure reached in the wave. But concerning the pressures produced for extremely short periods in the explosion-wave, we have less exact knowledge than of the velocities, and possibly the rates of explosion may be used to calculate the pressures produced.

The question, indeed, may be raised whether the propagation of the ignition is due

to a forward movement *en masse* of the burning molecules, or to the advance of a comparatively few molecules with extreme rapidity. In the latter case the explosion-wave might be propagated with a velocity far higher than the *average* velocity of the molecules of burning gas. I think the available evidence precludes the idea that the ignition can be propagated by a few molecules moving with velocities far above the mean. For, if this were the case, the presence of a diluent gas ought not to hinder the advance of the wave in the manner it is found to do. The heat evolved on the formation of a compound molecule is the same whether inert molecules are in the neighbourhood or not, and for the moment the temperature of the compound is the same. If, therefore, the ignition could be propagated by the advance of individual molecules, we might expect the explosion to be propagated at the same, or nearly the same, rate in the presence of an inert gas. My experiments have, however, conclusively shown that an inert gas retards the wave by an amount which depends upon its volume and density. It would seem to follow that each layer is heated as a whole and that the advance of the wave depends upon the average motion of the molecules. Two other facts appear to support this view. It is well known that small electric sparks may be sent through explosive mixtures of gases, *e.g.*, through electrolytic gas, without causing explosion. Yet the temperature in the spark must be extremely high, and combination occurs in the path of the spark. It would seem that the number of molecules heated by each spark was not sufficient to communicate ignition to the rest. Again, when a sound-wave is started in a mixture of gases, its rate of propagation depends upon the mean density of the gaseous mixture; there is no selective propagation of the wave by one of the constituents of the mixture.* This fact, of which I could find no experimental demonstration for gases of widely different density, has been verified, at my request, by Mr. F. J. SMITH in the MILLARD Laboratory, at Trinity College, Oxford. According to Mr. SMITH's careful experiments, sound is propagated at the same rate in ammonia gas (density 8.5) as in a mixture of equal volumes of hydrogen and oxygen of the same mean density as ammonia.

On the other hand, it may be that the wave does not advance perfectly regularly, but *breaks*, like a water-wave is broken by the quicker movement of the crest. In breaking, jets of heated gas may be projected in front of the wave into the unburnt gas beyond—such jets becoming the centres of fresh disturbances which coalesce to

* FARADAY thought that gases of very different density would not mix perfectly. "As the atmosphere is now constituted, there exists a permanency of sonorous pitch; any tone being once generated remains the same tone until it dies away. . . . If, however, the atmosphere had been composed of two gases, each having widely different specific gravities, there would have been a difference. No permanency of tone could then have been depended upon—the pitch of every original note would have been continually varying as its transmission might be propagated by the vibrations of ever-varying mixtures of the two gases of dissimilar specific gravities." FARADAY'S Lectures, SCOFFERN, 1853.

re-form a wave. If the jets were produced in sufficient number their average effect would be uniform.

§ 2. *The Specific Heat of Gases at High Temperatures.*

In calculating the theoretical velocity of the explosion-wave, I have assumed that the specific heats of the simple gases do not rise with increase of temperature. On the other hand, I have assumed that the specific heats of gases formed from their elements with a condensation of volume—such as steam, nitrous oxide, ethylene, etc.—are equal at a high temperature to the sum of the specific heats of their elements. Thus, I have taken the specific heat of steam at constant volume to be 7·2 instead of 6·5, as given by determinations at low temperatures. In making these assumptions, I have followed the example of BERTHELOT in his investigations on the explosion-wave. But in his later work on the specific heat of the gaseous elements at very high temperatures, BERTHELOT comes to the conclusion that these specific heats rise so rapidly with an increase of temperature that they are doubled between 1600° and 4400° C.* He arrives at this result by exploding cyanogen to carbonic oxide in a bomb, and observing the pressures registered by a piston moving against a spring when the cyanogen is burnt by oxygen alone, and when nitrogen is added or oxides of nitrogen are used instead of oxygen.

TABLE XL.—BERTHELOT'S Experiments on the Specific Heats of Simple Gases.

Mixture.	Pressure developed.	Temperature.	Specific heat of N ₂ or CO.
	At	°	
C ₂ N ₂ + O ₂	25·11	4394	9·60
C ₂ N ₂ + O ₂ + 1½N ₂ .	20·67	4024	8·39
C ₂ N ₂ + O ₂ + 2N ₂ . .	15·26	3191	7·93
C ₂ N ₂ + O ₂ + ½N ₂ . .	11·78	2810	6·67
C ₂ N ₂ + 2NO	23·34	4309	9·85
C ₂ N ₂ + 2N ₂ O	26·02	3993	8·43

These values of the specific heats depend upon the accuracy with which the maximum pressure developed in the explosion is registered by the moving piston. Now the more rapidly the combustion takes place, the more nearly does the pressure exerted resemble a blow. I have found that a short column of mercury in a pressure-gauge suffers a far greater movement under the influence of a slow explosion than it does under the influence of a rapid explosion, although the quantity of heat evolved and the specific heats of the products were nearly the same in the two cases. No doubt this gauge was less sensitive to sudden pressures than the instrument used by M. BERTHELOT; but the experiment warns us that the pressures registered by a

* 'Ann. Chim. et Phys.' (VI.), vol. 4, p. 66. 1885.

moving piston may fall below the true value, and the more rapid the explosion the greater this error may be. That the pressures registered, and, therefore, the specific heats deduced from them, vary with the instruments employed appears from a comparison of the numbers obtained by M. BERTHELOT, and those of MM. MALLARD and LE CHATELIER in the explosion of cyanogen. According to BERTHELOT's experiments, the specific heat of nitrogen and carbonic oxide is $6\cdot2$ at 2500° ; according to MM. MALLARD and LE CHATELIER, it is $7\cdot2$ at this temperature. Again the latter have determined the specific heat of the simple gases by adding measured volumes of hydrogen, oxygen, and nitrogen to electrolytic gas, and measuring the pressures produced on explosion. From the seven experiments* made at temperatures near 2000° (calculated), they obtain, as a mean, the number $5\cdot6$ for the specific heat of the elementary gases at this temperature; in a former paper they gave the value $7\cdot5$ as the specific heat at this temperature. Neither of these values agrees with the $7\cdot2$ deduced from their cyanogen experiment at 2500° . The great difficulties attending determinations of this nature, in spite of the skill and patience with which the French chemists have attacked the problem, still leave it an open question whether the specific heats of the simple gases increase with the temperature.

§ 3. The observations I have made on the effect of changes of initial pressure and temperature on the rate of explosion in gases are not such as might have been expected from the theory of ordinary sound-waves. There appears to be for each mixture a *crucial pressure*, above which variations of pressure do not affect the rate of explosion. Below this point the rates fall with diminution of pressure. In the case of electrolytic gas an increase of pressure from one to two atmospheres increases the rate of explosion from 2821 to 2872 metres per second. When the electrolytic gas is largely diluted, an increase in pressure from one to two atmospheres has less effect. The following rates were found at one and two atmospheres for electrolytic gas diluted with oxygen, nitrogen, and hydrogen respectively :—

TABLE XLI.

(1.) MIXTURE $H_2 + O_6$.

Pressure	1 At.	2 At.
Rate of explosion . . .	1696.	1718

* 'Combustion des Mélanges Gazeux,' p 259.

(2.) MIXTURE $\text{H}_2 + \text{O} + \text{N}_5$.

Pressure	1 At.	2 At.
Rate of explosion . . .	1815	1830

(3.) MIXTURE $\text{H}_8 + \text{O}$.

Pressure	1 At.	2 At.
Rate of explosion . . .	3532	3538

No doubt the numbers obtained point to a slight increase in the rate on doubling the pressure, but the differences are so small as to be confounded with the experimental error. I have not, therefore, given the higher rates as the true rates of the explosion, but have taken the mean of the two in each case.

The difference in the effect of pressure on electrolytic gas when pure, and when diluted, may be due to one of two causes. In the case of the pure gas increase of pressure may check dissociation, and thus increase the rate of explosion; whereas the diluted gas does not dissociate, and is consequently unaffected by changes of pressure. Or, more probably, since the diluted gas suffers less contraction in the chemical change, its crucial pressure is lower than that of the pure gas, and the change from one to two atmospheres being wholly, or in large part, *above* the crucial pressure, the effect on the rate is nil or very slight. In all the mixtures I have tried the rate of the explosion-wave is diminished by a sufficient reduction of pressure, even when the products of combustion are carbonic oxide and nitrogen alone. Changes of pressure appear, therefore, to affect the rate apart from any dissociation; and consequently may influence the rate of explosion of electrolytic gas independently of any effect on dissociation. Why changes of pressure affect the rate of explosion has yet received no satisfactory explanation.

As the initial pressure of a gaseous mixture is reduced, it is found that the flame travels further from the ignition-point before its rate becomes constant; it requires a longer run to attain its maximum velocity. By sufficiently reducing the pressure it is possible to stop the explosion of gases altogether; but the flame is still propagated slowly at pressures below that at which the explosion-wave dies out. For instance, with electrolytic gas, the explosion-wave is propagated at 200 mm. pressure, but not at 150 mm. At 200 mm. pressure the flame travels about 2 metres before attaining its maximum rate. According to my experiments* the flame is still propagated in

* 'Phil. Trans.,' 1884, p. 634.

electrolytic gas at 75 mm., but not at 70 mm., when an induction spark is passed through the mixture. LOTHAR MEYER and SEUBERT* found that a spark from a RUHMKORFF's coil caused partial ignition of electrolytic gas at 70 mm., and complete combustion at 72 mm., the exact pressure under which the gases unite varying with the strength of the spark.

It is conceivable, on the "breaking-wave" hypothesis, that the projected jets of heated gas do not under reduced pressure initiate their own explosion-waves so rapidly as under higher pressure.

Similarly with regard to changes of initial temperature, I do not know why a rise of temperature should diminish the rate of explosion. The limited range in which it is possible to conduct the experiments, and the small differences found within this range, do not permit of a curve being drawn which might indicate the general effect of changes of temperature upon the rate. In the case of electrolytic gas the effect of heating was found to lower the rate both at low and at high pressures. Experiments made at atmospheric pressure with ethylene, burning to carbonic oxide and steam, at 10° and 100°, showed a lowering of the rate rather greater than that of electrolytic gas; while similar experiments made with cyanogen, burning to carbonic oxide and nitrogen, showed a smaller difference—hardly, perhaps, to be distinguished from the experimental error.

§ 3. *The Rate of Explosion of Hydrocarbons with insufficient Oxygen.*

The explosion of hydrocarbons with insufficient oxygen has been studied by DALTON, J. DAVY, KERSTEN, and E. VON MEYER. In the 'New System of Chemical Philosophy,' Part II., p. 442 (1810), DALTON thus describes the explosion of equal volumes of ethylene and oxygen:—

"If 100 measures of oxygen be put to 100 of olefiant gas, and electrified, an explosion ensues, not very violent; but instead of a diminution, as usual, there is a great increase of gas; instead of 200 measures, there will be found about 360; some traces of carbonic acid are commonly observed, which disappear on passing two or three times through lime water; there will then remain perhaps 350 measures of a permanent gas, which is all combustible, yielding by an additional dose of oxygen, carbonic acid, and water, the same as if entirely burnt in the first instance. What, therefore, is this new gas in the intermediate state? The answer is clear. It is carbonic oxide and hydrogen mixed together, an equal number of atoms of each."

DALTON found that marsh gas could not be exploded with less than its own volume of oxygen, in which case half the hydrogen formed water and the other half was liberated:—

"If 100 measures of carburetted hydrogen be mixed with 100 measures of oxygen (the least that can be used with effect), and a spark passed through the mixture,

* 'Chem. Soc. Journ.,' 1884, vol. 1. p. 587.

there is an explosion without any material change of volume: after passing a few times through lime water, it is reduced a little, manifesting signs of carbonic acid. This residue is found to possess the characters of a mixture of equal volumes of carbonic oxide and hydrogen."

JOHN DAVY,* in 1832, described some experiments on the explosion of ethylene with insufficient oxygen, in which the volume was nearly doubled after detonation.

In 1861 KERSTEN† opposed the view, which he stated was common at that time, that in the combustion of hydrocarbons the hydrogen burns before the carbon. He describes experiments on the explosion of ethylene and of marsh gas with electrolytic gas, and with air. His conclusion is "that before a portion of hydrogen is burnt, all the carbon is burnt to carbonic oxide, and that then the excess of oxygen divides itself between the carbonic oxide and hydrogen."

In 1874, ERNST VON MEYER‡ (who does not refer to the previous work on the subject) showed that equal volumes of ethylene and oxygen formed carbonic oxide and hydrogen when exploded in an eudiometer. Acetylene, diluted with hydrogen to diminish the force of the explosion, behaved in the same way.

On the other hand, in many of the text-books of the present day the doctrine is taught that in the combustion of hydrocarbons the hydrogen burns before the carbon.§ BERTHELOT comes to the same conclusion from observations of the rate of explosion of ethylene mixed with hydrogen, and that of other hydrocarbons rich in hydrogen. Measuring the rate of explosion from the point of ignition through a space some 130 mm. long, BERTHELOT found that a mixture of hydrogen and ethylene burnt at a rate which was quicker than the mean of the rates of hydrogen and of ethylene when exploded with oxygen in the same apparatus:

Mixture.	Time taken by flame to travel 130 mm.	
$C_2H_4 + O_6$	2·86 thousandths of second	} 1·95 mean.
$H_2 + O$	1·04 ,, ,,	
$C_2H_4 + H_2 + O_7$	1·37 ,, ,,	

He concludes from these experiments that the hydrogen burns before the ethylene in the mixture. It must again be pointed out that these velocities refer to the

* 'Edin. Journal of Science,' New Ser., vol. 6, p. 50.

† 'Journ. Prakt. Chem.,' vol. 84, p. 303.

‡ 'Journ. Prakt. Chem.' [II.], vol. 10, p. 308.

§ FARADAY, lecturing at the Royal Institution, said:—"The volatile matter raised by combustion from the tallow of a candle is a vapour composed of carbon and hydrogen; and our experiment teaches us that the forces which hold these elements together are so nicely balanced that the hydrogen is made to combine first, the carbon afterwards" ('Lectures at Royal Institution,' p. 280, J. SCOFFERN, 1853).

For a lucid discussion of this question, as far as it affects the liberation of carbon in hydrocarbon flames, see Professor A. SMITHELLS "On the Structure of Luminous Flames" ('Journ. Chem. Soc.,' 1892, vol. 1, p. 217).

irregular period of vibration, and that everything depends on the quickness with which the explosion-wave is developed. Again, BERTHELOT compares the rate of explosion of hydrocarbons with that of hydrogen in the same apparatus :—

Gas.	Time.
Acetylene	1·94
Ethylene	2·86
Ethane	·83
Marsh Gas	1·24
Hydrogen	1·04

“ The rate of combustion of gases rich in hydrogen is very close to that of hydrogen. This seems to indicate that the hydrogen burns before the carbon, even in total combustions.”

I do not think this conclusion is justified by the figures ; nor do I see how the second argument can be reconciled with the first.

I have made experiments on the rate of the explosion-wave in ethylene and in acetylene mixed with their own volume of oxygen. In both cases the main reaction is the formation of carbonic oxide and hydrogen ; but the rates found are not so near the calculated velocities as I have found in other cases. The explosions being made in a gas-tight tube surrounded with water, the increase in pressure gave the expansion due to the chemical changes. With ethylene and oxygen the volume was almost doubled ; with acetylene and oxygen the volume was increased by one-half. In the following table I have given the observed rates of explosion for ethylene and acetylene, with an equal volume of oxygen, compared with the rate calculated by BERTHELOT's formula and with the sound-wave Σ :—

TABLE XLII.—Rates of Explosion of Ethylene and Acetylene with an equal volume of Oxygen.

1. $C_2H_4 + O_2 = 2CO + 2H_2$ ($Q = 67,000$ cals.)
2. $C_2H_2 + O_2 = 2CO + H_2$ ($Q = 112,700$ cals.)

Mixture.	$C_2H_4 + O_2$	$C_2H_2 + O_2$
BERTHELOT'S θ . . .	2134	2733
Rate of explosion . .	2507	2961
Σ	2330	3084

The rate of explosion of ethylene and an equal volume of oxygen was found to be MDCCCXCIII.—A.

2505 metres per second as the mean of four double determinations. The rate of the sound-wave " Σ ," calculated on the hypothesis that the mixture burns directly to carbonic oxide and hydrogen, is 2330. The calculated velocity is, therefore, about 7 per cent. too low. This is the only instance I have yet found where the observed rate is largely in excess of the calculated sound-wave. On the other hand, the rate of explosion of acetylene and an equal volume of oxygen was found to be 2961 metres per second as the mean of four double determinations. The rate of the sound-wave, calculated on the hypothesis that the mixture burns directly to carbonic oxide and hydrogen, is 3084. The calculated velocity is, therefore, about 4 per cent. too high. This difference between the explosion of ethylene and acetylene, with an equal volume of oxygen, is somewhat striking; it seems to point to some different mode of decomposition in the two cases.

As stated by DALTON, a mixture of marsh gas with half its volume of oxygen will not explode; but a mixture of equal volumes of marsh gas and oxygen explodes. I have determined the rate of explosion of this mixture, and find the velocity is $2\frac{1}{2}$ per cent. faster than the sound-wave calculated for the reaction—



TABLE XLIII.—Rate of Explosion of Marsh Gas with an equal volume of Oxygen.

Mixture.	$\text{CH}_4 + \text{O}_2$.
BERTHELOT'S θ	2184
Rate of explosion . .	2528
Σ	2466

At the temperature produced in this reaction the steam must be partly dissociated—lowering the rate. The observed velocity, therefore, is undoubtedly too high to reconcile with the calculated sound-wave. Marsh gas must, therefore, be classed with ethylene as giving exceptionally high rates.

At this point a difficulty must be pointed out which I have hitherto avoided. I have endeavoured to show that the explosion-wave is in part propagated by the movements of the yet unburnt molecules. The question arises—Are these unburnt molecules ever broken up by impact before they are burnt? In the case of an endothermic compound, such as cyanogen or acetylene, is the propagation of the flame partly due to the explosive decomposition of the compound, previous to the combustion of its constituents? If so, the unburnt gas would be diminished in density, and one might expect to find the explosion of endothermic compounds travelling at

velocities greater than those calculated for sound in the undecomposed gas. But this is exactly the reverse of what is observed. The formula, which gives the correct velocity for explosions of cyanogen, gives numbers which are rather too high for acetylene (also a strongly endothermic compound), and too low for ethylene and for marsh gas (an exothermic compound). It would appear as if ethylene and marsh gas were unstable bodies, and acetylene and cyanogen were stable bodies, in the particular condition of the explosion-wave. Let me recall the words used by Professor OSTWALD in his address last year at Halle, to the sections of Physics and Chemistry, when speaking on a cognate subject—the spectra of gases at high temperatures:—

“It is held as an undoubted dogma that at the highest temperatures, as, for example, in the electric arc, all compounds must be dissociated into their elements. This view is certainly not justified. What we do know about the stability of compounds is, on the contrary, that all compounds which are formed with absorption of heat become *more stable* with rising temperature, and the reverse. Because the majority of the compounds known to us are formed from the elements with evolution of heat, and correspondingly become more unstable with rising temperature, the conclusion has been drawn that this is in general the case. But if we reflect that cyanogen and acetylene, two compounds formed with great absorption of energy, are readily formed in quantity, at the highest temperatures, in the blast furnace and in the arc light, we become conscious that spectra occurring at high temperatures may belong to compounds which have a fleeting existence confined to those temperatures only.”*

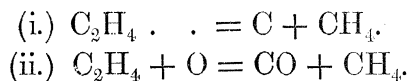
We know, then, that cyanogen and acetylene are formed from their elements at the highest temperature; but BERTHELOT has shown that these gases are decomposed by the shock of a fulminate detonator.† Is it possible that there is an essential difference between the two acts—that molecules of acetylene, charged by highly heated molecules, do not break up, but that they are decomposed when they are dashed against cold molecules, or the cold walls of the containing vessel? I have found that the decomposition of acetylene by a fulminate is confined to the neighbourhood of the detonator. When a charge of fulminate is fired in a steel bomb filled with acetylene, the decomposition of the acetylene is not propagated along a tube attached to the bomb and filled with the gas. The flame of the detonator is “carried on” for some little distance, but *no explosion-wave is set up in the acetylene*. Similar results were found with carbon bisulphide vapour, though in this case the decomposition is propagated to a greater distance from the detonator. These experiments show that “the decomposition by shock of acetylene and carbon bisulphide is not propagated like the explosion-wave at a constant velocity as far as the gas extends, but the decomposition set up by the fulminate dies out at a distance from the detonator, depending on the

* See ‘Nature,’ April 21, 1892.

† ‘La Force des Matières Explosives,’ vol. 1, p. 109. See also THORPE, ‘Journ. Chem. Soc.,’ 1889, p. 220.

nature of the gas, and also probably on the intensity of the initial shock and the cooling power of the walls.”*

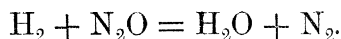
On the other hand, there is some evidence of the breaking up of ethylene in the explosion-wave. When ethylene is exploded with an equal volume of oxygen some carbon is deposited, and an appreciable quantity of marsh gas is found in the products of combustion. It is difficult to account for this formation of marsh gas except by the decomposition of the ethylene, either directly or by partial oxidation:—



When ethylene is exploded with less than its own volume of oxygen, the proportion of marsh gas found in the residue increases as the volume of oxygen is diminished.† This points to the formation of marsh gas as an intermediate product in the explosion of ethylene.

Again, it is a matter of frequent observation in the analysis of coal gas, when the residue of marsh gas, hydrogen, and carbonic oxide is exploded in an eudiometer, with a large excess of oxygen, that carbon is deposited towards the bottom of the tube. When, however, the mixture is sufficiently diluted with air, the marsh gas is completely burnt. This fact is easily explained on the assumption that in the explosion-wave (which is set up in marsh gas with oxygen but not with air) the marsh gas is more or less decomposed in the wave-front, and some of the liberated carbon escapes combustion by cooling.‡

I do not forget that the question raised concerning the breaking up of yet unburnt compounds in the explosion-wave, may also be asked concerning the elementary molecules. What happens, for instance, to the molecules of oxygen in the wave? When a molecule of oxygen reacts with a molecule of hydrogen, is an oxygen atom liberated, and, if so, how far does its existence influence the rate? It was with the object of obtaining some answer to these questions that experiments were made on the rate of explosion of hydrogen with nitrous oxide, in which reaction it is possible that no free atoms are liberated:—



So far as the experiments go, I cannot trace the influence of liberated atoms of oxygen.

* DIXON and HARKER, “On the Decomposition by Shock of Endothermic Compounds.” ‘Manchester Memoirs’ [IV.], vol. 5, 1892.

† LEAN and BONE, “The Behaviour of Ethylene on Explosion with less than its own Volume of Oxygen.” ‘Chem. Soc. Journ.’, 1892.

‡ Results which might be explained on the same hypothesis—viz., the decomposition of unburnt compounds in the wave-front, are afforded by the explosion of ammonia with nitrous oxide, and of chlorine with hydrogen. In both cases the rate is somewhat higher than might be expected.

§ 4. *Conclusion.*

The difficulties I have touched on show how far we are from a complete theory of explosions.

The tentative formula which I have proposed must be taken for nothing more than a "working hypothesis." It has been found so far *parallel to the truth* that it may be useful to suggest further experiments on the nature of explosions. As BERTHELOT'S formula helped me to interpret the reactions of gaseous carbon, and suggested experiments which led me to modify the hypothesis I was using; so I will venture to hope that this modified hypothesis may in turn lead other workers to a truer knowledge of explosions.

In concluding, I wish to thank three former pupils of mine, who have rendered me devoted service in the conduct of these experiments—Mr. J. E. MARSH, of Balliol College, Oxford, and Messrs. H. W. SMITH and J. A. HARKER, of Owens College, Manchester.

GENERAL CONCLUSIONS.

1. BERTHELOT'S measurements of the rates of explosion of a number of gaseous mixtures have been confirmed. The rate of the explosion-wave for each mixture is constant. It is independent of the diameter of the tube above a certain limit.

2. The rate is not absolutely independent of the initial temperature and pressure of the gases. With rise of temperature the rate falls; with rise of pressure the rate increases; but above a certain *crucial pressure* variations in pressure appear to have no effect.

3. In the explosion of carbonic oxide and oxygen in a long tube the presence of steam has a marked influence on the rate. From measurements of the rate of explosion with different quantities of steam the conclusion is drawn that at the high temperature of the explosion-wave, as well as in ordinary combustion, the oxidation of the carbonic oxide is effected by the interaction of the steam.

4. Inert gases are found to retard the explosion-wave according to their volume and density. Within wide limits an excess of one of the combustible gases has the same retarding effect as an inert gas (of the same volume and density) which can take no part in the reaction.

5. Measurements of the rate of explosion can be employed for determining the course of some chemical changes.

In the explosion of a volatile carbon-compound with oxygen, the gaseous carbon burns first to carbonic oxide, and afterwards, if oxygen is present in excess, the carbonic oxide first formed burns to carbonic acid.

6. The theory proposed by BERTHELOT—that in the explosion-wave the flame travels at the mean velocity of the products of combustion—although in agreement with the rates observed in a certain number of cases, does not account for the velocities found in other gaseous mixtures.

7. It seems probable that in the explosion-wave—

- (1) The gases are heated at *constant volume*, and not at *constant pressure*;
- (2) Each layer of gas is raised in temperature *before* being burnt;
- (3) The wave is propagated not only by the movements of the burnt molecules, but also by those of the heated but yet unburnt molecules;
- (4) When the permanent volume of the gases is changed in the chemical reaction an alteration of temperature is thereby caused which affects the velocity of the wave.

8. In a gas, of the mean density and temperature calculated on these assumptions, a sound-wave would travel at a velocity which nearly agrees with the observed rate of explosion in those cases where the products of combustion are perfect gases.

9. With mixtures in which steam is formed, the rate of explosion falls below the calculated rate of the sound-wave. But when such mixtures are largely diluted with an inert gas, the calculated and found velocities coincide. It seems reasonable to suppose that at the higher temperatures the lowering of the rate of explosion is brought about by the dissociation of the steam, or by an increase in its specific heat, or by both these causes.

10. The propagation of the explosion-wave in gases must be accompanied by a very high pressure lasting for a very short time. The experiments of MM. MALLARD and LE CHATELIER, as well as my own, show the presence of these fugitive pressures. It is possible that data for calculating the pressures produced may be derived from a knowledge of the densities of the unburnt gases and of their rates of explosion.

APPENDIX.

Received July 22, 1892.

Part I.—*The Preparation of the Gases.*

Hydrogen.—The hydrogen used in most of the experiments was prepared by the action of pure dilute sulphuric acid on re-distilled zinc, free from arsenic. The gas was washed with potash and silver nitrate solutions, and was then passed through a scrubbing tower and a series of bulbs filled with a strong solution of alkaline permanganate. The gas so prepared had only the faintest odour.

For a few experiments the gas was prepared by the electrolysis of pure dilute sulphuric acid with platinum electrodes.

Marsh Gas.—The marsh gas was prepared by GLADSTONE and TRIBE's method,* in which pure methyl iodide is decomposed by the zinc-copper couple in presence of absolute alcohol. The "scrubber," packed with the zinc-copper couple, was kept moistened by alcohol dropping from a tap-funnel, and the gas was further washed

* 'Chem. Soc. Journ.,' 1884, p. 1.

with strong alcoholic potash and finally with oil of vitriol. The generating flask (of 2 litres capacity) was kept at 30° C.

An analysis of the gas by explosion with air in McLEOD's gas apparatus showed 99.3 per cent. of marsh gas.

Ethylene.—The ethylene was prepared by the method given by ERLÉNMEYER and BUNTE. 25 grms. of absolute alcohol are mixed with 150 grms. of pure sulphuric acid, and the mixture is heated in a large flask, on a sand bath, to 160°–170° C. A mixture of one part alcohol and two parts sulphuric acid is then slowly added by a tap-funnel. Great difficulty was experienced in getting rid of all acid gases from the ethylene. The gas was passed (1) through two wash-bottles containing oil of vitriol, (2) through a tower packed with pieces of solid potash, (3) through two wash-bottles containing strong potash solution, (4) through a second tower packed with pieces of solid potash. The large quantity of air contained in the flask and washing apparatus rendered it difficult to obtain the gas quite free from air. The gas was analysed and found to be free from sulphurous acid, but it contained small quantities of nitrogen. Allowance was made for the presence of this diluent gas in making up the mixtures of ethylene with oxygen, &c. The percentage impurity in the ethylene could be reduced to 1 per cent.; no other gas used in these experiments presented the same difficulty in making pure.

Acetylene.—The acetylene was prepared by the action of strong alcoholic potash or ethylene dibromide. The potash was dissolved in amyl alcohol. The gas evolved from the boiling solution was passed through a second flask containing boiling potash solution, and then into an ammoniacal solution of cuprous chloride. The precipitated cuprous acetylide was washed with dilute ammonia solution and kept till required under this solution. On warming the red precipitate with strong hydrochloric acid to 50° C. a regular stream of acetylene was given off. It was washed with water, dried with caustic potash, and collected over mercury. Analysis showed that the gas was pure.

Ammonia.—The ammonia was distilled from a strong aqueous solution, was dried by caustic potash, and was collected over mercury.

Carbonic Oxide.—This gas was prepared by gently warming formic acid with pure sulphuric acid diluted with an equal volume of water. It was washed with potash solution.

Cyanogen.—Re-crystallised mercuric cyanide was powdered and carefully heated to drive off moisture. The dry powder was introduced into a steel retort with a long neck. After a considerable quantity of cyanogen had been allowed to escape, the gas was collected directly in a mercury holder. The retort was raised to dull redness in a fireclay furnace, heated by gas.

Oxygen.—The oxygen was prepared by heating powdered chlorate of potash in a hard glass flask. It was washed by a solution of caustic potash.

Nitrous Oxide.—This gas was prepared by heating pure ammonium nitrate in a

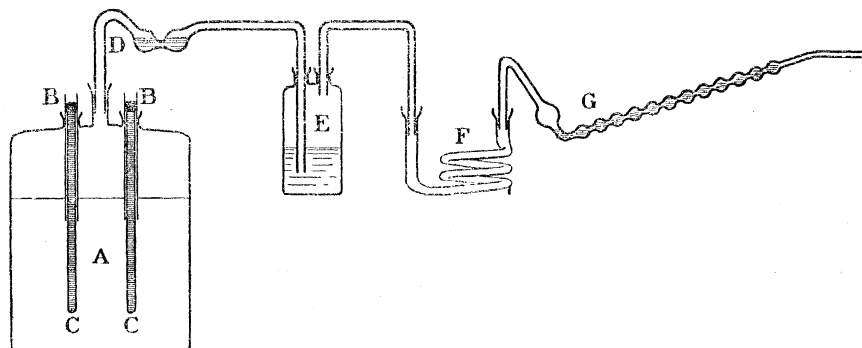
hard glass flask. It was washed with a solution of ferrous sulphate, dried by sulphuric acid, and collected over mercury.

Nitric Oxide.—The nitric oxide was made by mixing eight parts of crystallised ferrous sulphate with one part of crystallised nitre, and pouring on to this mixture sulphuric acid diluted with three volumes of water. If the acid is warm the action starts at once, afterwards the flask is gently warmed.

Nitrogen.—The nitrogen was prepared by VERNON HARCOURT'S method, in which a mixture of air and ammonia is passed through a heated tube containing copper and copper oxide. The nitrogen issuing from the tube was washed with sulphuric acid.

Chlorine.—The chlorine employed in determining the rates of explosion of hydrogen and chlorine was prepared by the electrolysis of aqueous hydrochloric acid, and was passed, mixed with hydrogen, into the explosion-tube without standing in a holder. The gas was washed first with water, and then with sulphuric acid, and was dried in a glass worm and a series of bulbs filled with sulphuric acid. The electrolytic cell was made entirely of glass, and the washing bottles and drying vessels were all fitted together with ground glass joints with cups.

Fig. 1.



Apparatus for preparing chlorine and hydrogen.

The electrolytic vessel A was made with three tubulures, into which ground glass tubes were fitted. Two of these, BB, passed into the vessel, and dipped about an inch below the level of the acid. Through these tubes passed the gas-carbon electrodes CC, the small annular space between the rods and tubes being made tight with paraffin. A little mercury poured on top of the carbon rods served to connect them with the battery wires. Into the third tubulure was ground a gas delivery tube D, containing washing bulbs filled with water, and passing through a tubulure in the sulphuric acid wash-bottle E. From E the gas passed through the worm F and through the bulbs G to a long flexible glass tube leading into the explosion-tube.

For mixtures containing an excess of hydrogen, the wash-bottle E was replaced by a vessel fitted with three tubulures similar in shape to A. Two of the tubulures were fitted with tubes of the same size dipping beneath the acid, the third tubulure serving

for the exit tube. The electrolytic gas entered through one tube, while hydrogen was driven from a holder through the other.

At the further end of the explosion tube the gases passed through (1) a wash bottle; (2) a long graduated tube fitted with taps at either end; (3) a thin glass bulb; (4) a tower filled with lime and powdered charcoal. The thin bulb could be readily detached and submitted to a "magnesium flash." The graduated tube served to analyse the gas. It was connected with a movable reservoir from which a solution of caustic potash could be introduced into the tube. The volume of chlorine present could thus be readily estimated, the residual hydrogen being measured under atmospheric pressure by bringing the level of the liquid in the tube and reservoir to the same height.

The current for the electrolysis was given by 7 secondary cells (ELWELL and PARKER), E.M.F. 13-15 volts; current 4-6 amperes. The preliminary saturation occupied many hours. It was found best to leave a small current (about $\frac{1}{2}$ ampere) passing through the cell for two days before making an experiment. When the liquids were all saturated it took about four hours to fill the explosion tube. An analysis of the issuing gas at the end of that time gave—

Chlorine	49.82
Hydrogen	50.18

In another experiment an analysis at the end of $4\frac{1}{2}$ hours gave—

Chlorine	49.90
Hydrogen	50.10

Part II.—*Arrangement of the Firing Tubes.*

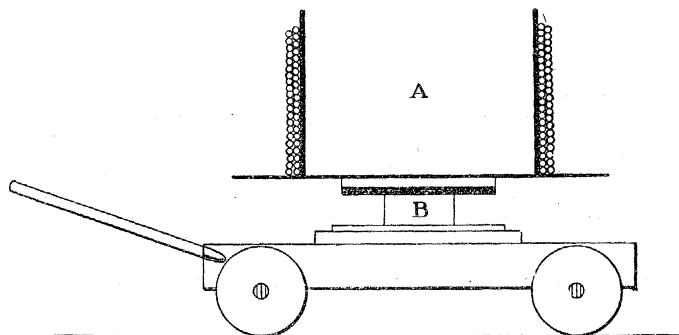
The leaden pipes used for the explosion tubes were 5, $6\frac{1}{2}$, 9, and 13 mm. in internal diameter. The pipe was wound on a galvanised iron drum about 2 feet in diameter, provided with a flange at the bottom.

In order to wind the pipe it was first laid straight along a corridor. The drum A was attached to a turntable B fixed to a low trolley, which was pushed forward as the pipe was wound on the revolving drum.

The drum with the pipe wound on it was placed in an iron water-bath, which could be heated by a large ring burner. The ends of the pipe passed out through two openings near the top of the bath. To each end of the explosion tube was soldered a short steel tube, ending in a cap with a polished steel face 30 mm. in diameter, perforated in the centre by a hole 10 mm. in diameter. The steel face of each cap is pressed by a clamp against a similar steel face, as in REGNAULT'S gas apparatus, from which these joints are taken. One end of the explosion tube is thus joined to the

“firing piece,” the other end to a shorter tube, called the “end piece,” carrying the second “bridge.”

Fig. 2.

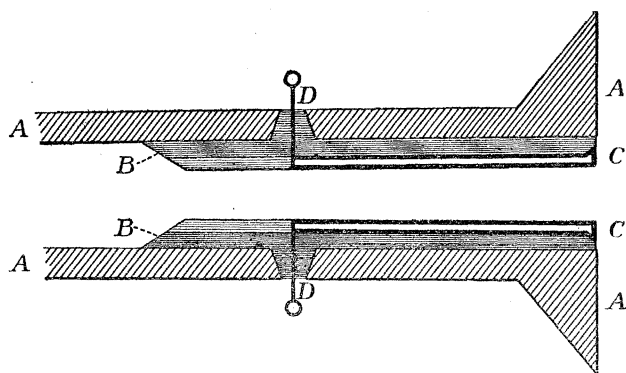


Section of drum mounted on turntable, and trolley for winding the explosion tube.

The caps which carried the bridges to be broken by the flame were constructed in the following way :—

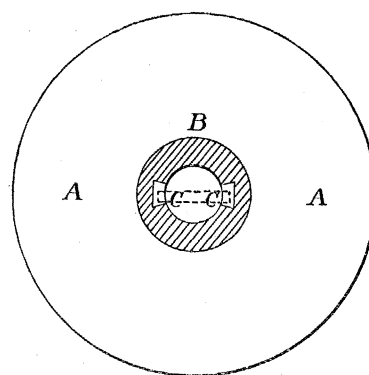
The steel tube AA was pierced at a distance of 30 mm. from the face by two conical holes opposite each other. The interior of the tube was lined with a cylinder of vulcanite, which also filled the conical holes. Two thick platinum wires, DD, passed through the holes, and were soldered to two pieces of silver, CC, embedded in the vulcanite, and thus insulated from the steel tube. The silver pieces were broadened out at the face end into two small plates, on to which the narrow strip of silver foil forming the bridge was soldered. The silver plates were brought not quite flush with the polished steel face, so that there was no danger of breaking the bridge when clamping up the two caps.

Fig. 3.



Section of bridge-piece.

Fig. 4.

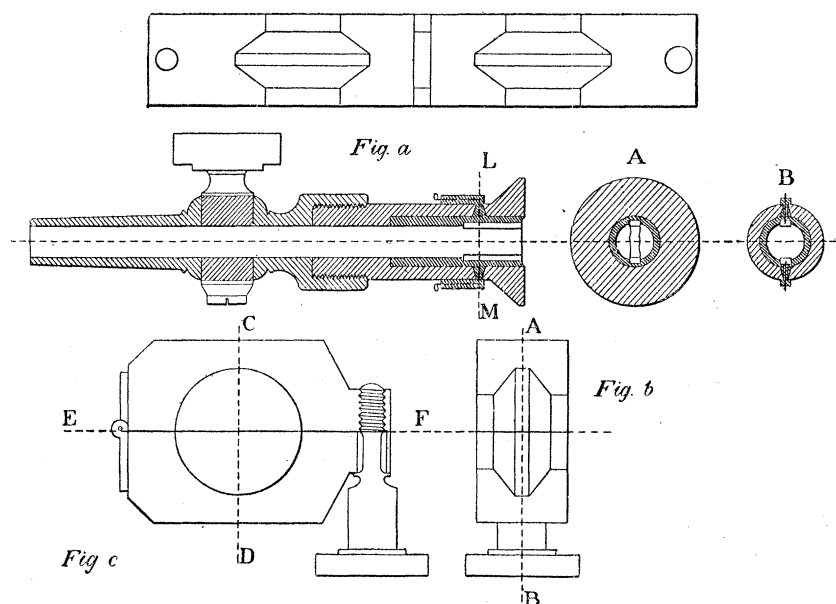


Front view.

For the experiments with chlorine and hydrogen a glass tube was fixed inside the vulcanite so as to protect it from the action of the chlorine. The silver bridge, after being soldered to the silver plates, was warmed and coated with a layer of paraffin as a protection from the chlorine.

The apparatus being arranged as shown in fig. 7, the explosive mixture from the holder was driven through the washing vessel A, partly filled with boiled oil of vitriol, and through the two drying towers B, B, packed with pieces of asbestos saturated with boiled oil of vitriol. The gas then passed through a short length of black rubber tubing to the end piece C carrying the second bridge. From the end piece the mixture passed into the explosion tube coiled on a drum standing in the large iron water-bath D. A second clamp united the explosion tube to the firing piece E, carrying the first bridge at one end, and the firing wires *f, f*, sealed through

Fig. 5.

Fig. d

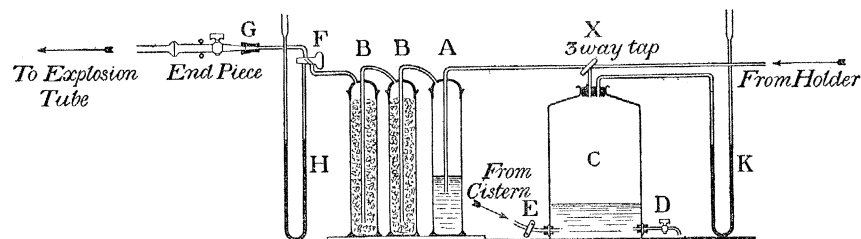
Shows the construction of a second pair of bridge pieces and clamps used during the last two years.

a stout glass tube, and a tap G at the other. The taps were made of hardened steel. After leaving the firing piece the gas passed by a glass tube M to a three-way tap H, by which it could be sent either to the testing tube I or by the pipe K to the window. In many of the experiments a sulphuric acid wash-bottle L was joined to the tube at M, and connected with a holder containing electrolytic gas. Before starting the experiment the air was displaced from the vessel L by a stream of electrolytic gas. When the explosion tube and firing piece were full of the explosive mixture, the tap H was shut, and a few bubbles of electrolytic gas were driven into the firing piece so as to fill about one-third of its length. This insured the explosion-wave being set up in the firing piece before the flame reached the first bridge, and was a convenient mode of firing mixtures—such as those containing cyanogen—which do not readily ignite.

For experiments under increased pressure the arrangement shown in fig. 6 was

adopted. The strong glass cylinder C, filled with water from a high cistern through the tube E, or (when necessary) with mercury from a second movable cylinder, was filled with the mixture from the holder by allowing the liquid to run out at the tap D. After the cylinder was filled, the three-way tap X was turned so as to send the gas from the holder through the drying vessels A, B, B, and through the three-way tap F, into the explosion tube. When the explosion tube was full, the tap X was turned so as to put

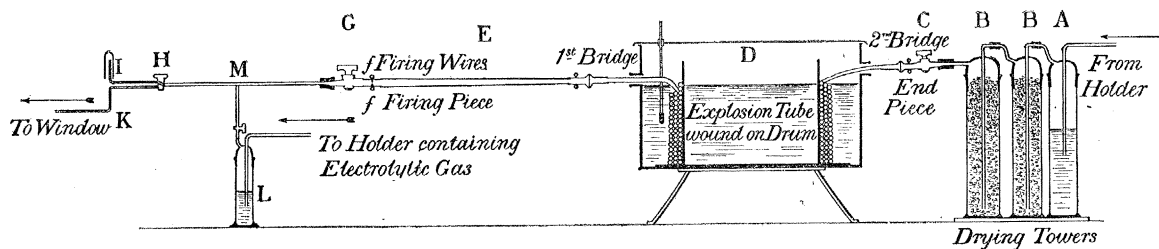
Fig. 6.



it in communication with the cylinder C. The tap at the further end of the explosion tube being closed, water or mercury was admitted to C, forcing the gas into the explosion tube through the drying vessels. When the manometer K showed the desired pressure had been reached, the taps were closed and the connections made with the chronograph and firing wires. Just before firing, the taps were opened to the manometer K and the pressure in the explosion tube was read off. The taps were then shut and the mixture fired.

For experiments under reduced pressure the explosion tube was filled in the usual way. The gas was then sucked from the apparatus by a pump attached to the tube K (Fig. 7), a manometer sealed in at M (in place of the wash bottle L) giving the pressure in the explosion tube.

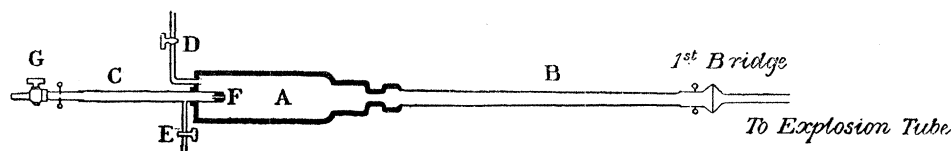
Fig. 7.



For firing the mixture of cyanogen with nitric oxide the following arrangement was adopted. The firing piece B was firmly screwed to a stout steel cylinder A. Through the other end of this cylinder a tube C was screwed so as to project 2 inches into the cylinder. Into the end of this tube a copper detonator holding fulminate of mercury was attached, by a caoutchouc stopper with a large hole, the open end of the detonator pointing inwards. The explosive mixture passed from the explosion tube through the firing piece and cylinder, escaping at the tube D which was also screwed

into the base of the cylinder. The tube C was then filled with electrolytic gas through the tap G, the air escaping at E. On firing the gas in C by the firing wires the explosion travelled to F, and there set off the detonator in the middle of the cyanogen mixture. The explosion thus started was propagated through the tube B, into the explosion tube which it traversed to the end.

Fig. 8.



Part III.—*Chronographic Apparatus.*

The arrangement of the chronograph and electrical connections are shown in fig. 9. The chronograph, made by Messrs. ELLIOT, consisted of a heavy pendulum carrying a smoked glass plate. The electro-magnetic styli used were made by PFEIL, of Berlin, and by Mr. F. J. SMITH,* of Trinity College, Oxford, to whom I am greatly indebted for several of these instruments. In most of the experiments recorded in this paper, one of PFEIL's instruments and one of Mr. SMITH's were employed. These two were chosen out of several, for the great constancy of their latent period, and for the sharpness of their action. The styli were attached to an upright bar on a heavy iron stand, with three pointed feet. The bar could be tilted back on two feet and exactly replaced.

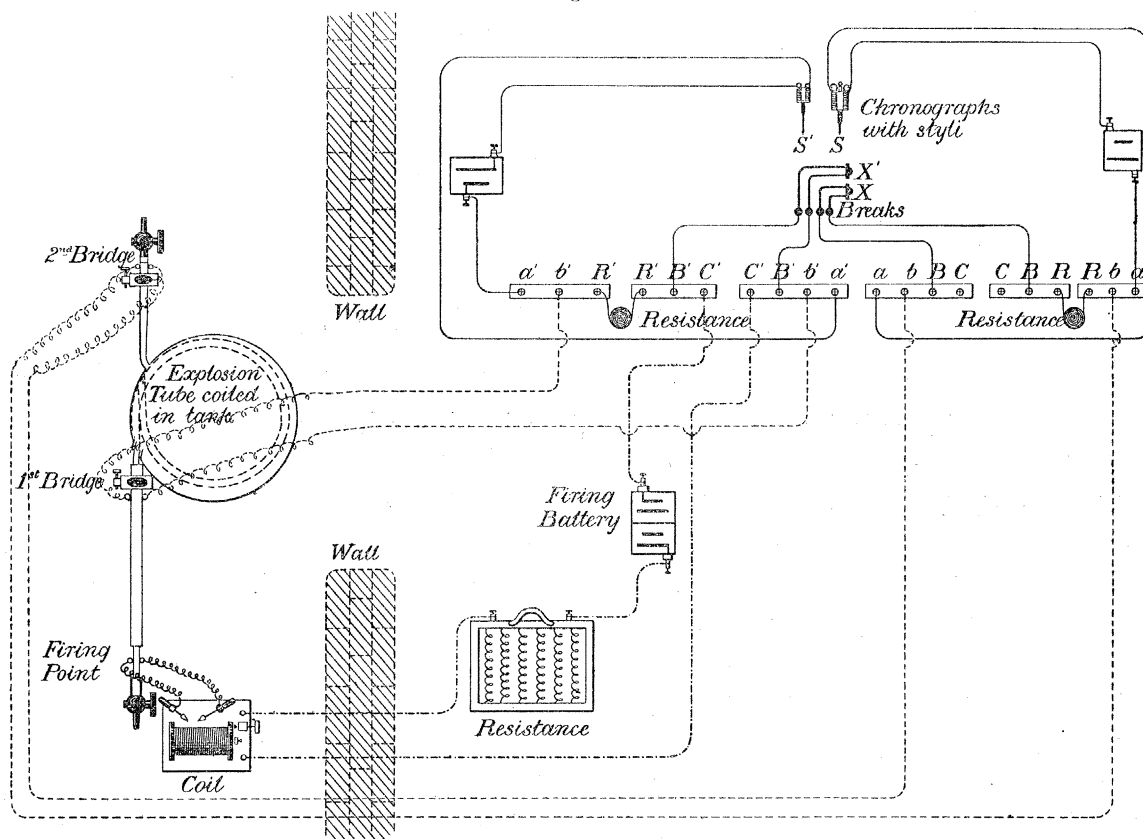
At the lowest point of its swing the pendulum acted on two breaks, X and X', which by a rack and pinion could be brought exactly in a line. By bringing the pendulum slowly against the uprights the position of the two breaks could be adjusted so that they were broken at the same instant.

In the preliminary experiment the wires were arranged as shown in the figure, except that the wires to the firing battery were detached at C'C', and the wires from bb, b'b' to the two bridges were not connected. The stylus S was put in circuit through a resistance RR, and the break X; the stylus S' was put in circuit through a resistance R'R' and the break X'. On letting the pendulum fall the two styli were released, and registered their marks on the moving plate. The resistances RR and R'R' were now removed, the firing battery and coil put into circuit at C'C', the wires from bb and b'b' attached to the two bridges, and the wires from the coil attached to the firing piece. The pendulum, being again let fall, broke the primary circuit of the coil on striking X', causing a spark to pass between the platinum wires in the firing piece. The flame travelling down the tube broke both bridges in turn, and the styli connected with them registered their marks on the moving plate. The

* 'Phil. Mag.,' 1890, p. 377.

connections were immediately adjusted as in the preliminary experiment, and the pendulum was again let fall. If the "confirmatory" marks passed directly over the "preliminary" it was a proof that nothing had been displaced during the experiment.*

Fig. 9.



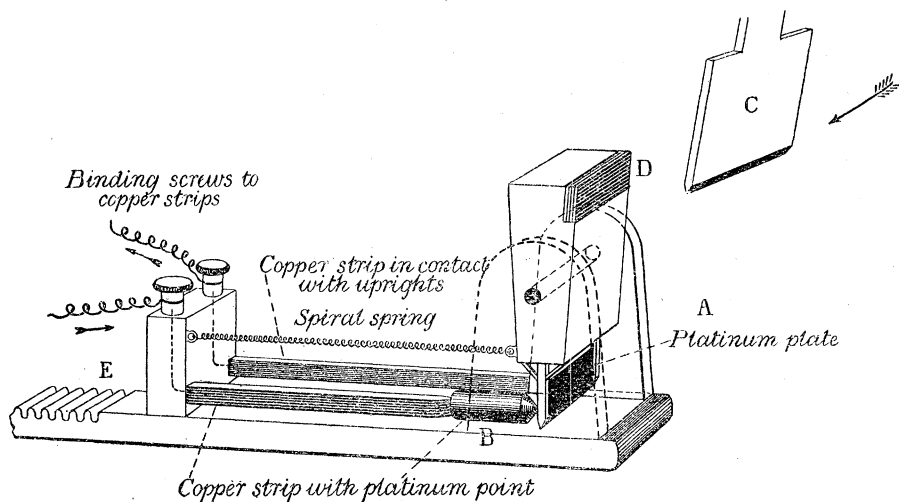
In the companion experiment, which was made as soon as possible after the first, the wires from the break X were removed from BB to B'B', and the wires from X' from B'B' to BB. X was now the firing break. Any difference between the two breaks which might affect the moment of firing was thus eliminated by taking the mean of the pair of experiments.

The breaks were constructed as shown in fig. 10. The contact was made between a platinum plate A and a platinum point B joined to a copper strip. The platinum plate was fastened to a piece of ebonite turning on a horizontal axis; a spiral spring pressed the plate against the platinum point until the arm C of the pendulum struck

* Mr. F. J. SMITH has pointed out that the difference in the latencies of two electro-magnetic styli may be eliminated by making two experiments, and reversing the connections for the second experiment. I think my plan of making a "preliminary experiment" (without firing the gases) is quicker. In both cases it is assumed that the latencies remain constant during the experiment: the quicker the operation the more likely is this condition to be attained.

the copper plate D attached to the ebonite. The whole piece could be moved to the right or left by a pinion working in the rack E.

Fig. 10.



Side view of one of the breaks.

The tuning fork was by KOENIG. It gave 100 complete vibrations per second at 15° C. Its temperature correction was determined by Mr. R. H. M. BOSANQUET in the Laboratory of St. John's College, Oxford. By measuring the length of the wave traced by the tuning fork on the plate at different heights, a table of wave-lengths was constructed, giving the value of $\frac{1}{100}$ second at different heights on the plate, and for different lengths of swing. After measuring the distance between two marks of a stylus and the height of the tracing on the plate, a reference to the table gave the value of the distance in time. But, to make sure that the pendulum was moving at the same rate as when the table was constructed, a tuning fork trace was taken after each experiment—everything being in the same state except that the tuning fork was substituted for the electro-magnetic styli. From the length of the observed trace, compared with that given in the table, a correction could readily be applied to the table readings. A small correction was also made, when necessary, for the effect of temperature on the tuning fork.

The distance between the marks of the styli was measured by cutting the rising trace 2 mm. above the datum line with a pointed style, and drawing a perpendicular line through the points of intersection, as shown in fig. 11. At *a* the upper stylus began to rise in the preliminary experiment, and the lower stylus at *b*. In the explosion the lower stylus was released by the breaking of the first bridge, and began to rise at *b'*; the upper stylus was released by the breaking of the second bridge, and began to rise at *a'*. The distances between the lines AA' and between the lines BB' being measured, as well as the position of *aa'* and *bb'* on the plate, the value of BB'

(corrected for position) is subtracted from AA', the remainder giving the time of explosion.

I take one example from my note-book of the actual measurements obtained in a pair of experiments :—

	mm.
A.—Distance between “firing” and “second bridge” marks	= 70·5
Distance between “firing” and “first bridge” marks .	= 4·7
Distance between first and second bridge marks . . .	= 65·8

At this point on the plate and for this length of swing the distance, which is equal to $\frac{1}{100}$ second, is 24·62 mm. Length of tube between bridges, 75·35 metres.

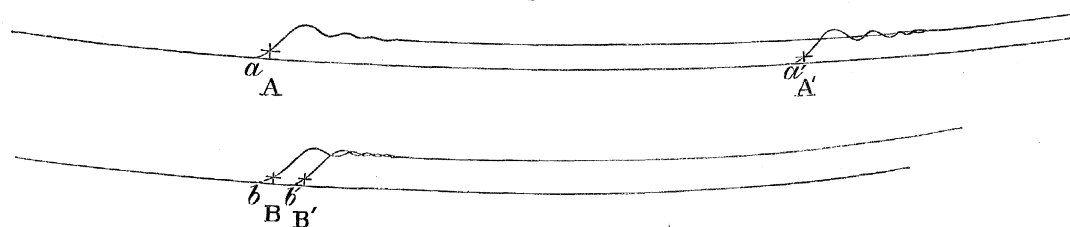
Rate of explosion = 2820 metres per second.

B. (with connections reversed)—	mm.
Distance between “firing” and “second bridge” marks	= 68·6
Distance between “firing” and “first bridge” marks .	= 2·4
Distance between first and second bridge marks . . .	= 66·2

At this point on the plate and for this length of swing, the distance, which is equal to $\frac{1}{100}$ second, is 24·70 mm.

Rate of explosion = 2811 metres per second.
Mean rate = 2815 „ „

Fig. 11.



Traces made by electro-magnetic styli on the moving plate.

Part IV.—*The Rates of Explosion as Measured.*

(1.) HYDROGEN and Oxygen under Ordinary Temperature and Pressure.

The rate of explosion of the mixture $H_2 + O$ was measured in a tube 9 mm. in diameter and 55 metres long.

Rates Found.

SERIES A.
Metres per sec. 2804 2812 2835
Mean 2817

In a tube of same diameter and 100 metres long :—

SERIES B.
2822 2847 2795
2821

In a tube 13 mm. diameter and 100 metres long :—

SERIES C.
2805 2840 2831 2800
2819

In 1888-90 these experiments were repeated. The numbers which follow are all the means of pairs of measurements with the connections of the chronograph reversed :—

SERIES D.
2818 2820 2831 2828
2824

SERIES E.	SERIES F.	SERIES G.
In 9 mm. tube.	In $6\frac{1}{2}$ mm. tube.	In $6\frac{1}{2}$ mm. tube.
2852 2814 2825 2825 2830	2795 2781 2814 2807	2827 2840 2803 2836
2828	2799	2826

Most of the experiments given in these three series, E, F, and G, were *control* experiments interpolated in other series to check the working of the whole apparatus.

In the following series the mixture was fired alternately in a straight tube and in the same tube coiled on a drum. Each number is the mean of a pair of measurements with connections reversed :—

SERIES H.
9 mm. tube 100 metres long.
2828 straight 2829 coiled 2820 straight 2812 coiled 2818 straight
2821

(2.) HYDROGEN and Oxygen under Varying Pressure.

1. At 10° C.				
200 mm.	300 mm.	500 mm.	1100 mm.	1500 mm.
2636 2619 2626	2716 2693 2680 2713 2723	2784 2764 2777	2869 2850 2864 2844 2852 2845	2869 2871 2873 2883 2861 2873
2627	2705	2775	2856	2872

2. At 100° C.				
390 mm.	500 mm.	760 mm.	1000 mm.	1450 mm.
2704 2689	2730 2746	2784 2793 2799 2796 2789 2800 2782 2774	2833 2825 2824 2832	2831 2837 2849 2849
2697	2738	2790	2828	2842

(3.) HYDROGEN and Oxygen in Different Proportions, under Ordinary Temperature and Pressure.

In 13 mm. tube.	In 9 mm. tube.				In 13 mm. tube.
H ₈ +O.	H ₆ +O.	H ₄ +O.	H ₂ +O ₂ .	H ₂ +O ₄ .	H ₂ +O ₆ .
3547 3518 3537 3526	3517 3526 3538 3527	3265 3281 3261 3266	2315 2331 2344 2322	1945 1905 1943 1914	1703 1728 1708 1691
3532	3527	3268	2328	1927	1707

(4.) HYDROGEN and Oxygen in Different Proportions under 1500 mm.

$H_8 + O$	$H_2 + O_6$
3534 3542	1723 1713
3538	1718

(5.) HYDROGEN and Oxygen Diluted with Nitrogen.

At 760 mm. and 10° .		
In 9 mm. tube.		In 13 mm. tube.
$H_2 + O + N$	$H_2 + O + N_3$	$H_2 + O + N_5$
2429 2408 2443 2425	2065 2045 2065 2063 2035	1822 1805 1809 1824
2426	2055	1815

Under 1500 mm. and 10° .
$H_2 + O + N_5$
1821 1838
1830

MARSH Gas and Oxygen in Varying Proportions.

At 760 mm. and 10°.				
$\text{CH}_4 + \text{O}_2$	$\text{CH}_4 + \text{O}_3$	$\text{CH}_4 + \text{O}_4$	$\text{CH}_4 + \text{O}_6$	$\text{CH}_4 + \text{O}_8$
2531 2510 2552 2520	2479 2469 2463	2322 2318 2326	2147 2145	1954 1972
2528	2470	2322	2146	1963

MARSH Gas and Oxygen diluted with Nitrogen.

At 760 mm. and 10°.		
$\text{CH}_4 + \text{O}_3 + \text{N}$	$\text{CH}_4 + \text{O}_3 + \text{N}_3$	$\text{CH}_4 + \text{O}_3 + \text{N}_5$
2349 2364 2348 2334	2146 2162 2155	1872 1888
2349	2154	1880

MARSH Gas and Oxygen under Varying Pressures.

$\text{CH}_4 + \text{O}_3$		$\text{CH}_4 + \text{O}_4$	
500 mm.	1000 mm.	500 mm.	1000 mm.
2414 2422	2480 2496	2273 2287	2324 2314
2413	2488	2280	2319

ETHYLENE and Oxygen in Different Proportions.

At 760 mm. and 10° C.						
$C_2H_4 + O_2$	$C_2H_4 + 2O_2$	$C_2H_4 + 3O_2$	$C_2H_4 + 4O_2$	$C_2H_4 + 6O_2$	$C_2H_4 + 8O_2$	$C_2H_4 + 10O_2$
2516 2527 2472 2515	2606 2578 2562 2571 2586	2364 2359 2380 2369	2239 2255	2131 2105	1974 1986	1852 1860
2507	2581	2368	2247	2118	1980	1856

ETHYLENE and Oxygen Diluted with Nitrogen.

$C_2H_4 + 2O_2 + N_2$	$C_2H_4 + 2O_2 + 2N_2$	$C_2H_4 + 2O_2 + 4N_2$	$C_2H_4 + 2O_2 + 6N_2$	$C_2H_4 + 2O_2 + 8N_2$
2430 2401 2408	2202 2220	2009 2039	1881 1874	1737 1731
2413	2211	2024	1878	1734

ETHYLENE and Oxygen.

At 760 mm. and 100° C.
$C_2H_4 + 2O_2$
2541 2532 2532 2548
2538

ACETYLENE and Oxygen in Different Proportions.

At 760 mm. and 10° C.		
$C_2H_2 + O_2$	$C_2H_2 + O_3$	$C_2H_2 + O_5$
2961 2950 2971	2698 2747 2691 2703 2722 2733	2389 2399 2382
2961	2716	2391

ACETYLENE and Oxygen Diluted with Nitrogen.

$C_2H_2 + O_3 + N_2$	$C_2H_2 + O_3 + N_6$	$C_2H_2 + O_3 + N_8$	$C_2H_2 + O_3 + N_{10}$	$C_2H_2 + O_3 + N_{12}$
2410 2418 2415	2197 2221	2110 2122	2028 2009	1903 1913
2414	2209	2116	2019	1908

ACETYLENE and Oxygen under Varying Pressures.

At 500 mm.
2685 2693
2689

CYANOGEN and Oxygen in Varying Proportions.

At 760 mm. and 10°.		
$C_2N_2 + O_2$	$C_2N_2 + 2O_2$	$C_2N_2 + 3O_2$
2714 2742 2727	2319 2318 2326	2108 2112
2728	2321	2110

CYANOGEN and Oxygen Diluted with Nitrogen.

$C_2N_2 + O_2 + N_2$	$C_2N_2 + O_2 + 2N_2$
2394 2401	2156 2175
2398	2166

CYANOGEN and Oxygen under Varying Pressures.

In 5 mm. tube. 10° C.		
$C_2N_2 + O_2$		
At 500 mm.	At 760 mm.	At 1000 mm.
2533 2539	2663 2686	2667 2675
2536	2677	2671

At 760 mm. and 100° C.
In 9 mm. tube.
2697 2725
2711

CYANOGEN and Nitrous Oxide.

In 9 mm. tube.		
$C_2N_2 + 2N_2O$	$C_2N_2 + 2N_2O + N_2$	$C_2N_2 + 2N_2O + 2N_2$
2451 2458	2273 2292	2101 2095
2454	2283	2098

CYANOGEN and Nitric Oxide.

In 9 mm. tube. (Fired with fulminate detonator.)
$C_2N_2 + 2NO$
2766 2740 2773
2760

HYDROGEN and Nitrous Oxide in Varying Proportions.

At 760 mm. and 10° C.			
In 13 mm. tube.	In 9 mm. tube.		
$H_7 + N_2O$	$H_6 + N_2O$	$H_4 + N_2O$	$H_2 + N_2O$
2728 2737	2700 2711	2552 2538	2307 2302
2732	2705	2545	2305

HYDROGEN and Nitrous Oxide Diluted with Nitrogen.

In 9 mm. tube.	In 13 mm. tube.	
$H_2 + N_2O + N_2$	$H_2 + N_2O + N_3$	$H_2 + N_2O + N_4$
2001 1980	1886 1875	1650 1416 went out ditto
1991	1880	irregular

HYDROGEN with Nitrous Oxide under Varying Pressures.

$\text{H}_2 + \text{N}_2\text{O}$	
At 500 mm.	At 1000 mm.
2089 2098	2306 2298
2094	2302

AMMONIA and Oxygen.

At 760 mm. and 10°C .
$4\text{NH}_3 + 3\text{O}_2$
2381 2399
2390

AMMONIA and Nitrous Oxide.

$2\text{NH}_3 + 3\text{N}_2\text{O}$
2199 2202
2200

CARBONIC Oxide and Oxygen with Varying Proportions of Steam.

CO + O at 760 mm.				
Well dried.	Dried.	Saturated at 10°.	Saturated at 20°.	Saturated at 28°.
1267 1262	1289 1297 1320 1316	1670 1673 1679 1674 1687 1675	1710 1704 1685 1718 1700 1701	1711 1726 1702
1264	1305	1676	1703	1713

CO + O at 760 mm.				
Saturated at 35°.	Saturated at 45°.	Saturated at 55°.	Saturated at 65°.	Saturated at 75°.
1741 1731 1726 1750 1742	1700 1681 1697	1673 1650 1674	1519 1534	1260 1272
1738	1693	1666	1526	1266

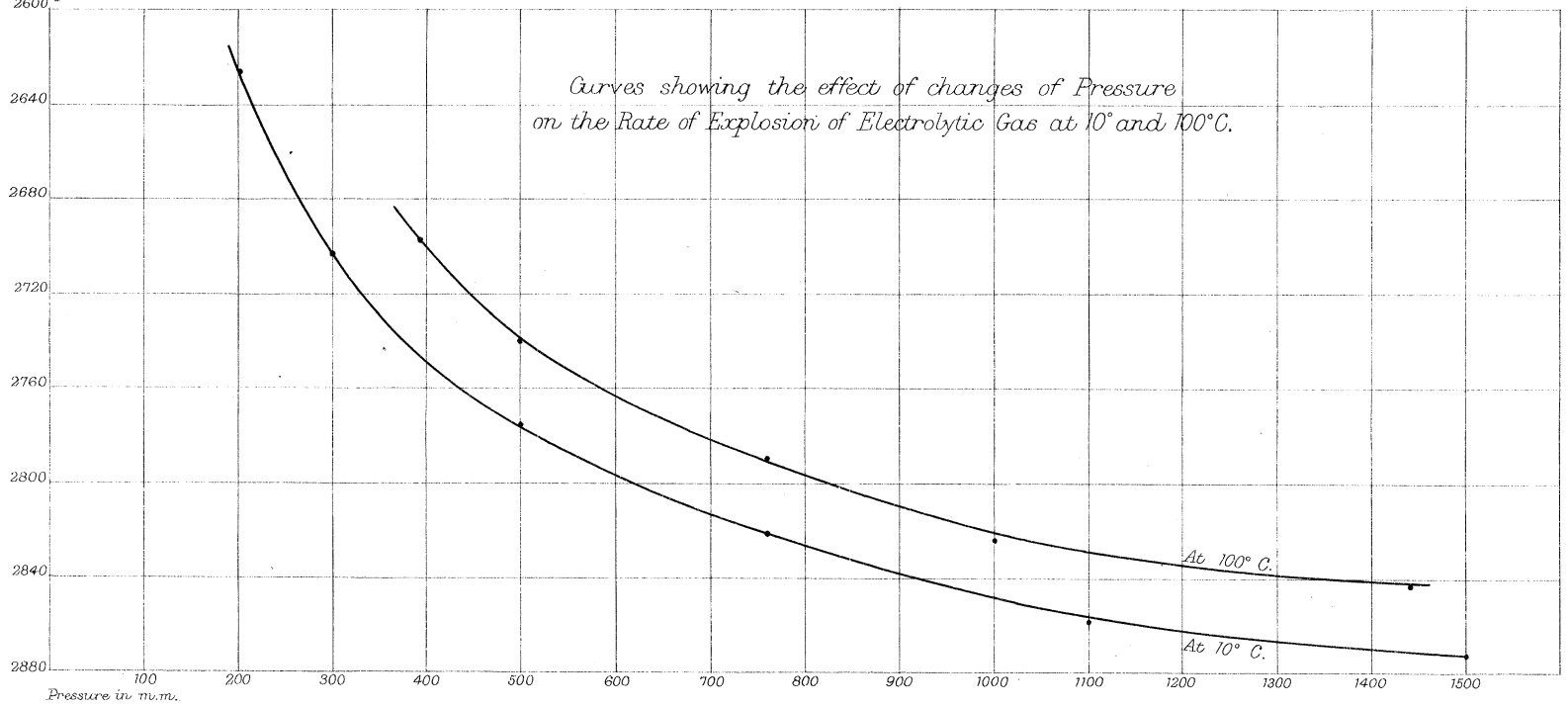
At 400 mm.		
Saturated at 10°.	Saturated at 25°.	Saturated at 33°.
1573 1582 1574	1607 1617 1625	1580 1568 1562
1576	1616	1570

At 1100 mm.		
Saturated at 26°.	Saturated at 43°.	Saturated at 53°.
1747 1737 1728	1767 1799 1779	1730 1751 1745
1737	1782	1742

HYDROGEN and Oxygen Diluted with Carbonic Oxide [$K = 1$ vol. CO_2].

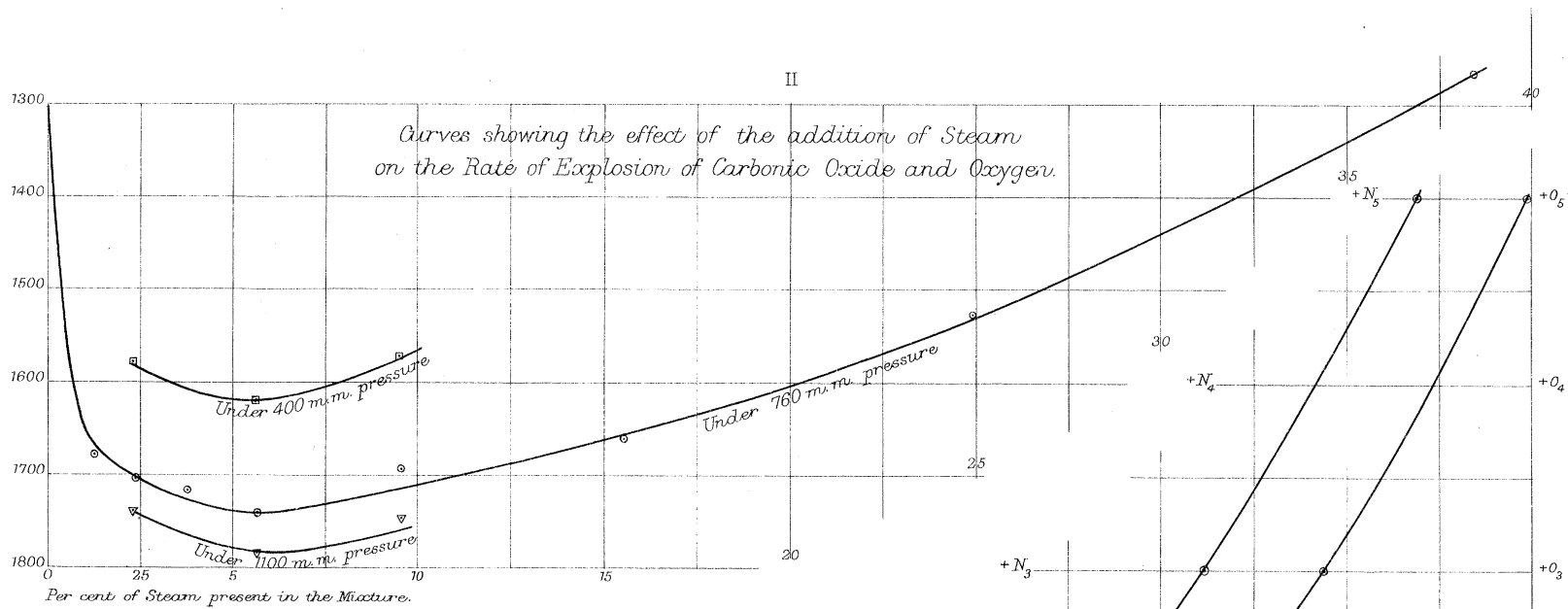
$\text{H}_2 + \text{O} + \text{K}_2$	$\text{H}_2 + \text{O} + \text{K}_3$	$\text{H}_2 + \text{O}_2 + \text{N}_2$	$\text{H}_2 + \text{O}_2 + \text{K}_3$
2467 2446 2458 2448	2086 2070 2084	1993 2014	2144 2142
2455	2080	2003	2143

Curves showing the effect of changes of Pressure
on the Rate of Explosion of Electrolytic Gas at 10° and 100°C.



II

Curves showing the effect of the addition of Steam
on the Rate of Explosion of Carbonic Oxide and Oxygen.



III

Curves showing the effect of the addition of Nitrogen and Oxygen
on the Rate of Explosion of Electrolytic Gas.

