CCCCI.—*The Ignition of Gases by an Explosion-Wave. Part I. Carbon Monoxide and Hydrogen Mixtures.*

By COLIN CAMPBELL and DONALD WHITLEY WOODHEAD.

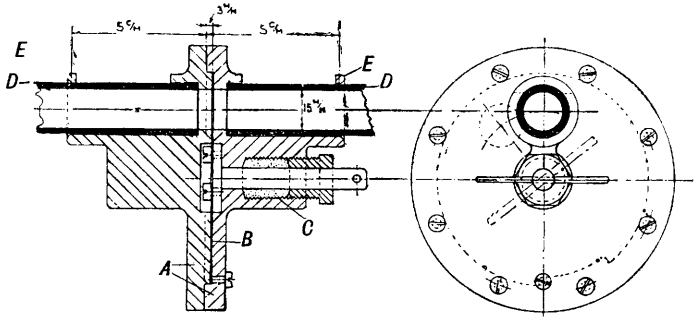
DIXON and WALLS (J., 1923, **123**, 1025), in measuring the velocity of detonation of carbon monoxide–oxygen mixtures, observed that the velocity, measured between two time-bridges in a long coiled tube, depended on the distance which the flame had travelled in the same mixture before it reached the first bridge. When the mixture $2CO + O_2$, saturated with water vapour at room temperature, was ignited by the explosion-wave set up in electrolytic gas, the first bridge being 10 cm. from the point at which the two mixtures were in contact, the velocity recorded was 1673 m./sec.; when a loop of tubing, 2·4 metres long,* filled with the carbon monoxide mixture, was inserted before the first bridge, the observed rate was 1708 m./sec. It was believed that the carbon monoxide mixture was not immediately detonated by the wave in the electrolytic gas and that the retarded flame, moving slowly for a short time, eventually recuperated and reached its full rate after travelling about 2·4 metres. The experiments were made with lead tubes (12·5 mm. in diameter), and no direct observations of the slow flame were possible. The experiments now described were made in glass tubes and photographic methods were adopted.

The apparatus consisted of a series of metal and glass tubes of uniform internal diameter (15 mm.) forming a continuous horizontal gallery through which flame passed in front of a drum-camera; one portion of the gallery contained the igniting mixture (usually electrolytic gas) and the other the carbon monoxide mixture to be ignited. Separation of the two mixtures up to the moment of firing was effected by a metal shutter. The igniting mixture was fired by a jump-spark, and the flame traversed first a lead tube 2·8 metres long and then a thick-walled glass tube 50 cm. long, these being cemented together; having now reached its full detonating rate, the flame passed through the shutter apparatus into another glass tube containing the second mixture. To the end of the last tube (the " experimental tube ") was fitted a filling-stopper which could be quickly detached. All the joints were made with cement and were rigid and internally smooth; irregularities which might give rise to accelerations or retardations of flame speed were avoided (see Campbell, J., 1922, **121**, 2483).

* The length given in the original paper was 1·4 metres; Prof. Dixon informs us that this was a clerical error.

The shutter apparatus (Fig. 1) consisted of two outer brass casings, *AA*, bolted together round a flanged edge and surrounding a circular brass plate, *B*, 1 mm. thick, which contained a circular aperture 15 mm. in diameter. The plate could be rotated to a limited extent about a horizontal axis by means of a handle which passed through a stuffing-box, *C*. In the *off* position, the plate formed a complete barrier between two glass tubes, *DD*, which were cemented into supporting sleeves, *EE*; in the *on* position, the aperture coincided with similar apertures in the outer casings. The plate was as thin as possible consistent with the strength required to allow the evacuation of one side of the gallery. Two vulcanite rings were recessed into the interior faces of the outer casings, concentrically with the apertures, and we were then able

FIG. 1.



Mechanical arrangement of the shutter.

to reduce the pressure on one side to 1 mm. Hg whilst the other side was at atmospheric pressure.

In carrying out an experiment the gallery was evacuated and then the respective mixtures were allowed to enter the two sections of the apparatus at equal rates until each was at atmospheric pressure; this process of evacuation and filling was twice rapidly repeated. In order to avoid any mass movement of gas on the opening of the shutter, the two portions of the gallery were put into communication for a moment with the outside air through long leading-tubes. The tap beyond the spark-gap was closed, the further end of the experimental tube opened, the shutter rotated to the *on* position, and the gases were fired; the time taken in the last three operations did not exceed 2 seconds and therefore diffusion at the point of contact of the two mixtures was very slight.

The photographs were taken on films attached to a drum, of 1 metre circumference and 45 mm. edge, which was rotated at

about 40 revolutions per second. The speed of the wheel was calculated with an accuracy of 1—2% by timing the making of an electrical circuit in a mechanism attached to the drum spindle; the calculations of the flame speeds from measurements of the photographs were of the same order of accuracy.

The wall of the experimental tube was about 3 mm. thick, and the length of the longest obtainable was 140 cm.; such a tube was not usually shattered when a detonation-wave passed through it, but was invariably broken when a detonation-wave was actually initiated in it. In some experiments a very long experimental tube was required; this was formed by placing two tubes end to end and cementing them together in a glass or metal sleeve; the junction was made as smooth as possible internally and the velocities of flames passing through it did not appear to suffer any change. Since slow flames are readily affected by slight obstructions in their path (*vide infra*), single tubes were used whenever possible In order to follow the progress of the flame in a long tube, different portions of the gallery were photographed in successive experiments made under similar conditions.

The carbon monoxide was prepared by the action of hot concentrated sulphuric acid on formic acid; after being washed with caustic potash, the gas had a purity of 98·5%, the remainder being nitrogen. No hydrogen was ever found. Oxygen was either obtained from a cylinder, in which case it contained a small amount of nitrogen, or prepared by heating potassium permanganate; no differences in the results of the experiments were detected. The mixtures were analysed in a modified form of the Bone–Wheeler apparatus and were stored over water at temperatures ranging from 15° to 18°; the amount of water vapour was therefore between 1·6 and 2·0%.

Initial Experiments.

It was shown by two experiments with electrolytic gas that the construction of the shutter and the method of filling the gallery had no effect on the velocity of a flame passing through the apparatus; in the first, the shutter was kept open and the whole of the gallery swept out by the mixture, whilst in the second each side was evacuated and filled separately with the same gas. There was no change in flame velocity in either experiment. When the igniting side of the gallery was filled with electrolytic gas and the other side with the mixture $2H_2 + 3O_2$, the velocity of the flame fell uniformly from that of the igniting gas (rate of explosion-wave, 2820 m./sec.) to that of the ignited mixture (2090 m./sec.) over the first 10 cm. from the junction. Similar results were obtained when the mixture $2H_2 + 5O_2$ (1810 m./sec.) was fired by electro-

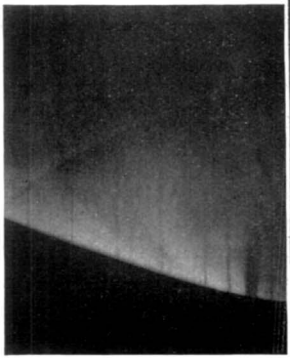


FIG. 2.

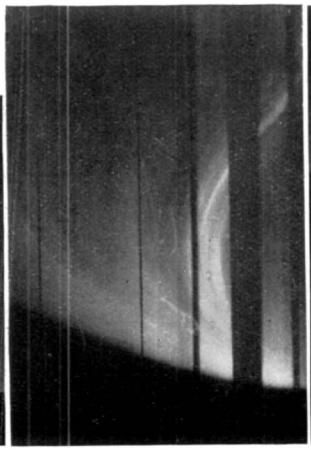


FIG. 3.

FIG. 4.

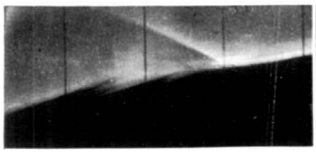
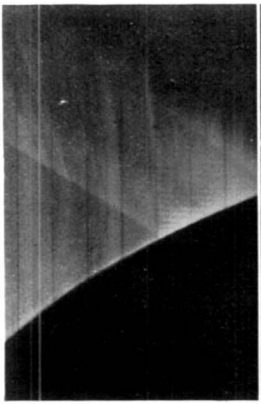


FIG. 6.



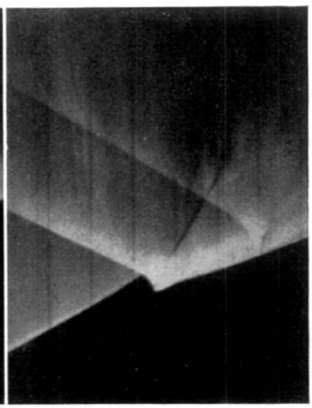
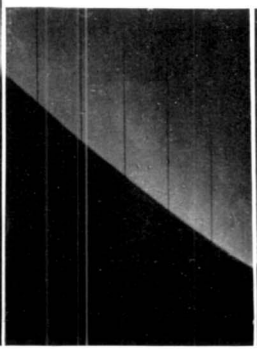


FIG. 7.

FIG. 8.



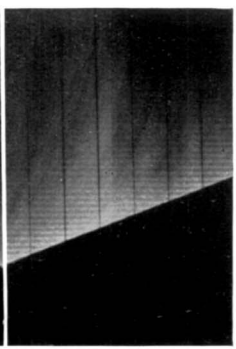


FIG. 9.

FIG. 10.

FIG. 11.

[*To face p.* 3012.]

lytic gas, and when $2H_2 + 3O_2$ was fired by $6H_2 + O_2$ (3530 m./sec.). Fig. 2, which is a photograph of the last experiment, shows the gradual change in velocity as the flame passed through the shutter from one mixture to the other. (The broad vertical band in the photograph denotes the position of the shutter.) When the second portion of the gallery contained air or nitrogen (Fig. 3) the electrolytic flame was projected into the inert gas and still affected the photographic film when it had travelled 40 cm. past the shutter; the flame front was not well defined and showed a rapid fall in velocity. This photograph shows the forward movement of the burning gas, then a period of rest followed by a swinging back (compare Dixon, *Phil. Trans.*, 1903, **200**, 315). In one experiment, when a small amount of air was allowed to remain at the shutter between the two explosive mixtures, the flame appeared to hesitate for a brief period and then to proceed at its full rate in the second mixture. Whether a flame could be projected through a considerable length of air or inert gas and ignite a mixture beyond it is a matter under investigation (compare Lean and Dixon, *Manc. Lit. Phil. Soc.*, 1891, **5**, 16).

The Ignition of $2CO + O_2$ *by Electrolytic Gas (moist gases).*

The flame travelled in the electrolytic gas at the rate of 2820 m./sec., but soon after it entered the carbon monoxide mixture its velocity fell rapidly until, at the point 30 cm. (*i.e.*, 30 cm. past the shutter), it was of the order of 800 m./sec. Acceleration then took place until a velocity of about 1250 m./sec. was reached at 140 cm. Fig. 4 is a typical photograph and shows the flame (moving from right to left) from 10 cm. before to 60 cm. after the shutter. When the longer experimental tube was used, a second smaller retardation was found to occur near 150 cm., and this was followed by acceleration and the setting up of the explosive-wave. In three experiments, detonation occurred at very nearly the same point, *viz.*, 260, 260, and 270 cm., respectively. The details of a number of experiments are recorded in Table I, the mean rates over each length of 10 cm. of experimental tube being given. Curve I, Fig. 5, represents the average velocities of flame (calculated from the rates in Table I) throughout an experimental tube 3·2 metres long; it was obtained by plotting flame speed against distance along the tube. The flame speed falls rapidly from that in the electrolytic gas (2820 m./sec.) to a minimum value of 760 m./sec. over the first 50 cm. of carbon monoxide mixture; an ensuing acceleration is checked at 130 cm. when the flame has attained a speed of 1250 m./sec.; the velocity falls to 1050 m./sec. at 165 cm., and from that point to 280 cm. it cannot be represented by a con-

Table I.

Flame speeds (metres per second) in wet $2CO + O_2$.

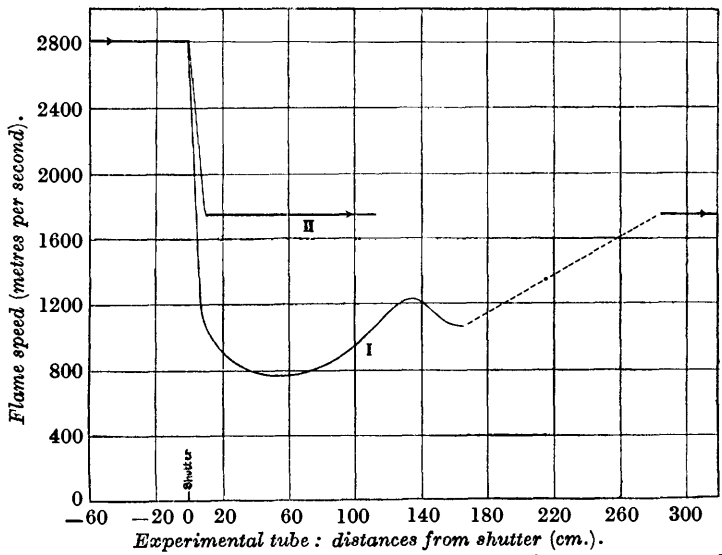
Expt. No.	Distance from shutter (cm.). 5.	15.	25.	35.	45.	55.	65.	75.	85.	95.
234	1560	1000	840	810	780	760			e	
235	1680	1030	870	860	760	760			e	
256			860	770	810	810	810		810	e
257			860	850	790	790	790	790	790	e
193		890	800	800	800	800	800	e		
194				780	780	780	780	e		
195				840	840	840	840	e		
199		920	840	780	760	780	780	e		

Expt. No.	Distance from shutter (cm.). 85.	95.	105.	115.	125.	135.	145.	155.	165.	175.	185.
278	940	940	1100	1200	1270	1270	1100	1030		e	
279	830	880	960	1060	1280	1330	1290	1140		e	
280		900	930	1000	1200	1200	1200	1110	e at 259		
281				1110	1100	1100	1100	1060	1060	1100	1170e
282					1180	1270	1180	1080	1080	1080	1140e

Expt. No.	Distance from shutter (cm.). 215.	225.	235.	245.	255.	265.	275.	285.	295.
298		1360	S		D		e		
299	1080	1270	1400		e				
300		1360	1360	S		D	e		
314			1370	S			D	2000	e

e, end of tube. S, serrated edge. D, detonation.

Fig. 5.



Experimental tube : distances from shutter (cm.).

Curve I : *The velocity of flame in* $2CO + O_2$ (*saturated with water vapour at* 15°) *when ignited by detonated electrolytic gas.*

Curve II ; *The velocity of flame when* 1% *of the* CO *had been replaced by* H_2.

tinuous curve because of a peculiar variability. This period immediately preceding detonation is of interest in that one or more separate regions of inflammation appear in the unburnt gases in front of the retarded flame proper; the serrated appearance of the flame edge in Fig. 6 was caused by such discontinuous inflammation, three secondary flames appearing within 15 cm. of the point where the explosion-wave was set up. The point of initiation of the wave is indicated by the usual characteristics, *viz.*, an abrupt increase in illumination intensity and the production of a retonation-wave.

If we calculate from the rates given by Dixon and Walls the average velocity of their retarded flame from the point of ignition by the electrolytic gas to a point 2·4 metres along the tube, where detonation was presumed to occur, a value of 1070 m./sec. is obtained. The curve in Fig. 5 gives a value not very different from this, although in the present experiments, which, it should be noted, have been made with straight tubes, detonation did not occur until the flame had travelled about 2·7 metres.

The retarded flame was accelerated more quickly when a small obstruction was placed in the gallery: Fig. 7 was obtained when 1 g. of sand was deposited evenly along 10 cm. of the tube at 130—140 cm. from the shutter, *i.e.*, at the middle of the photograph; the velocity of the flame at 150 cm. was 1500 m./sec., whereas in a similar experiment without sand the rate at the same point was 1130 m./sec. This observation agrees with that of Laffitte (*Compt. rend.*, 1923, **176**, 1392) who found that the distance traversed by the flame in a mixture of oxygen and carbon disulphide vapour before the setting up of the explosion-wave depended upon the condition of the interior of the tube, the distance being shorter when the interior was not perfectly smooth. In Fig. 7, although there was no sharp increase in velocity when the flame reached the sanded portion of the experimental tube, yet there appeared to be a definite and abrupt increase in the rate of reaction as indicated by the relative intensities of illumination. Fig. 8 shows the result of placing in the tube at the points 145 and 165 cm. two hollow cork cylinders (10 mm. internal diameter); the rate immediately before the first obstruction was 1160 m./sec. but increased to 1850 m./sec. within the next 10 cm. It will be observed that the rapid flame had a separate point of initiation at the obstruction previous to the arrival of the slow flame, and it is assumed that the gas was ignited adiabatically by a pressure-wave which had preceded the retarded flame (compare Dixon and Bradshaw, *Proc. Roy. Soc.*, 1907, **79**, 238). The rapid flame did not suffer any marked change in velocity on encountering the second obstruction;

the cork cylinders were ejected from the experimental tube at about 380 m./sec., this value being calculated from the inclination of the dark line in the photograph.

Experiments with Drier Gases.

Dixon and Walls (*loc. cit.*) accepted the efficiency of their drying train when they failed to obtain complete detonation of the dried carbon monoxide mixture after ignition with electrolytic gas, but they did not determine how far, if at all, flame travelled. We have attempted to follow the progress of the flame in carbon monoxide mixtures from which most of the water vapour had been removed. Even if the mixed gases had been completely dried it would have been very difficult to ensure the dryness of the large internal area of the gallery and filling apparatus; no attempt was made, therefore, to secure the degree of dryness attained on long exposure to phosphorus pentoxide. The gallery was dried by passing a stream of warm dry air through it for several hours and then exhausting it for some time by means of a " Hyvac " rotary oil-pump; in this way we were able to reduce the air pressure to less than 1 mm. Hg.

The gaseous mixtures were dried by one of two methods: Method A was to pass the mixture slowly in succession through sulphuric acid, caustic potash, calcium chloride, and a glass worm cooled to — 80° into a reservoir containing dry mercury; in a sample of this gas the vapour pressure of the water was less than 0·4 mm. In method B, the gas was passed slowly in very small bubbles through sulphuric acid, through caustic potash and calcium chloride direct to the explosion gallery, the filling operation taking 8 minutes. The flame speeds obtained in these experiments are given in Table II.

TABLE II.

Flame speeds (metres per second) in dried $2CO + O_2$.

Expt. No.	Drying method.	Distance from shutter (cm.). 175.	185.	195.	205.	215.	225.	235.	245.
315	B	1040	980	910	880	850	S		
316	B	1090	1030	950	910	860	860	950	1060
317	B	1020	990	900	880	860	900	930	1090
318	B	1000	910	880	860	880	970	1060	1180

Tube 275 cm. long in each experiment.

Expt. No.	Drying method.	Distance from shutter (cm.). 235.	245.	255.	265.	275.	285.	295.	305.
302	A	S	1640		D e				
303	A			S	e				
304	A			2040	2040	e			
305	A			1990	1990	e			
319	B	860	940	1140	1400	1600	1700	1750	1750e

When method A was used and the experimental tube consisted of two jointed sections, the mixture had detonated before the point 240 cm. (Expts. 304 and 305) or was giving the serrated edge, which, in the "wet" experiments, preceded detonation (Expts. 302 and 303). The measured velocity of detonation in Expts. 304 and 305 is higher than that given by Dixon and Walls for this mixture; in both experiments, the luminous particles behind the wave front appear to be moving towards the open end considerably faster than is usual, and it would seem that the temporary abnormally high rate was due to the increased translational motion of the medium in which the wave was travelling.

When method B was employed for drying, lower velocities were recorded and in no case had detonation occurred at 240 cm. In Expt. 319 the flame had travelled 305 cm. after its initiation and had attained a velocity of about 1750 m./sec., apparently without having reached its full rate. Sometimes the serrated flame edge was more distinct than usual; in Fig. 9 a secondary flame originated at a point 15 cm. in advance of the retarded flame and moved as a whole towards the end of the tube. This movement confirms the previous suggestion that the gaseous medium had a marked translational velocity in front of the advancing flame. Moreover, the motion may be greater than is immediately apparent, since the inner face of this single secondary flame is itself serrated, a number of distinct tongues of flame being formed before there is coalescence with the primary inflammation. At the point of coalescence a rapid rise in the rate of reaction is indicated by increased luminosity and this brighter zone travelled backwards into the burning gases in the form of a wave and, apparently, in much the same way as a wave of retonation.

It is of interest to compare the above results of experiments on the ignition of well-dried carbon monoxide–oxygen mixtures with those of previous workers. Dixon (*Phil. Trans.*, 1893, **184**, 97) gave 1264 m./sec. as the rate of explosion of the well-dried mixture $2CO + O_2$; Girvan (*Proc. Chem. Soc.*, 1903, 236) has shown that, when the theoretical carbon monoxide–oxygen mixture had been cooled to $-50°$, the pressure of aqueous vapour being 0·05 mm., powerful sparks could initiate an "explosion" which travelled slowly down a tube. Wartenburg and Sieg (*Ber.*, 1920, **53**, 2192) found that, although a partial water pressure of at least 0·5 mm. was needed to promote an explosion, a flame might be initiated in gases which had been cooled to $-80°$ when the tube was heated strongly at one point. The length of time of exposure to a low temperature affects considerably the degree of dryness of the mixture, for Coehn and Tramm (*Ber.*, 1921, **54**, 1148) have shown

that a mixture dried by short exposure to the temperature of solid carbon dioxide and alcohol will inflame and burn quietly, although it will not "explode"; with a longer exposure to the low temperature a flame will not spread from the spark. It is, therefore, evident that an extremely small amount of water vapour is sufficient to promote slow burning. Payman and Wheeler (J., 1923, **123**, 1251) state that, although only a trace of moisture is needed to enable the propagation of flame to take place, about 6% is required to give the flame its complete freedom. Bone, Fraser, and Newitt (*Proc. Roy. Soc.*, 1926, **110**, 640) believe that "whilst the presence of water vapour is undoubtedly helpful, it is not essential to the ignition and explosive combination of carbon monoxide and oxygen mixtures, but that, on the contrary, these gases can, and under high pressures do, combine directly."

In all the experiments quoted, the inflammation of the carbon monoxide mixture was effected by a spark, whereas in the present experiments ignition was by the detonation-wave of electrolytic gas; the results in the two cases are, however, in general agreement. When the carbon monoxide had a partial aqueous vapour pressure of 16 mm. (above 2% of moisture), the rate of explosion soon after ignition was between 700 and 800 m./sec., *i.e.*, about half the theoretical rate. Acceleration to detonation occurred at a considerable distance along the tube. Reduction of the pressure of aqueous vapour to 1 mm. or less had little effect upon either the extent of the retardation or the rate of acceleration of the slow flame. A further reduction in the moisture content had the effect of causing the flame to travel slowly over a greater distance; the flame, however, was never extinguished with the most complete drying we were able to effect.

The Addition of Hydrogen to $2CO + O_2$ (*moist and dried gases*).

A series of experiments has been carried out in which definite amounts of hydrogen, together with the equivalent amounts of oxygen, were added to carbon monoxide–oxygen mixtures, some of which were saturated at the ordinary temperatures with water vapour, whilst others were dried by method A (*vide supra*). The results of these experiments are detailed in Table III. In experiments with both wet and dried gases when the amount of hydrogen in the mixture did not exceed 0·7% the flame speed fell considerably, but when there was above 1·8% of hydrogen no fall occurred. Between these extremes the results were not consistent; even when the same mixture was used, the gases and the tube being dried by the same method, two results agreed but differed from a

TABLE III.

The effect of the addition of hydrogen to $2CO + O_2$.

Expt. No.	Length of tube.	% H_2.	Dried.	Wet.
293	135 cm.	0·6	Fall.	
294	135	0·6	,,	
295	135	0·6	,,	
296	135	0·6		Fall.
334	105	0·7		,,
259	98	0·7	Fall.	
291	135	0·9	,,	
292	135	0·9	No fall.	
232	88	1·1		No fall.
236	88	1·1		,,
262	98	1·2	Fall.	
332	60	1·2		No fall.
333	60	1·2		,,
288	143	1·3	No fall.	
289	135	1·3	Fall.	
290	135	1·3	No fall.	
245	166	1·5	Fall.	
246	160	1·5	,,	
286	143	1·8	No fall.	
287	143	2·3	,,	
233	88	2·5		No fall.
335	105	2·5		,,
336	105	2·5		,,
237	86	3·4		,,
231	88	4·2		,,
229	100	9·0		,,

third (Expts. 288—290). We can only believe that the ignition of mixtures which contain about 1% of hydrogen is largely affected by a very small difference in moisture content. In all the experiments with hydrogen, one of two results was always obtained: (i) the flame velocity was considerably decreased, usually to about 800 m./sec., or (ii) the flame velocity was high and became constant at about 1750 m./sec. soon after entering the carbon monoxide portion. Curve II (Fig. 5) illustrates the latter result. The slow flame in the mixture containing 0·9% of hydrogen is shown in Fig. 10, and the rapid flame (the explosion-wave) in the mixture containing 1·3% in Fig. 11.* When the slow flame was photographed further along the experimental tube, acceleration was seen to have taken place, and it appears to be certain that in these experiments (as in those without hydrogen) detonation would have ultimately occurred. The flames in several experiments were photographed at 135 cm. and the highest velocity recorded there was 1230 m./sec.

Continuous propagation of the explosion-wave immediately on ignition was given in a dried carbon monoxide mixture which

* The burning gases behind the wave front in Fig. 11 show marked horizontal bands; a discussion of this appearance will be given in a later communication.

contained 0·9% of hydrogen, but the damping down of the wave occurred in a mixture free from hydrogen but containing 2% of water vapour; hydrogen is thus more efficient than water vapour in allowing the explosion-wave to develop in the carbon monoxide–oxygen mixtures under these special conditions of ignition.

The explanation advanced by Dixon and Walls (*loc. cit.*, p. 1031) of the temporary damping down of the explosion-wave is based on the assumption that carbon dioxide is largely dissociated at the high temperature produced by the burning electrolytic gas; under those conditions, "the oxidation of the carbon monoxide might be too slow to maintain the explosion-wave." Their results led to the suggestion that as carbon monoxide was gradually replaced by more hydrogen in the mixed gases, the discontinuity would grow less and finally disappear. We have been unable to detect any gradual change in the appearance of the discontinuity; a very small change in the hydrogen content of a mixture changes the character of the ignition completely and we find it difficult to believe that the temperatures in the two instances where the amounts of hydrogen differ by, say, 0·2% can be sufficiently different to affect the degree of dissociation to any considerable extent. Since the behaviour of the carbon monoxide mixtures appears to depend upon the pressure and temperature conditions in the wave-front of the igniting mixture, experiments with various igniting mixtures are being carried out.

It has been suggested (Crussard, *Bull. Soc. Ind. Min.*, 1907, **6**, 257) that the explosion-wave consists of a shock-wave accompanied and sustained by a chemical reaction in the form of flame and that the normal propagation of the wave depends upon the mutual assistance provided by these two factors. It would appear that when carbon monoxide–oxygen mixtures are ignited by electrolytic gas, the concussion component from the primary mixture becomes separated from the inflammation; the latter becomes very much reduced in speed and the shock-wave travels away in front, also at a falling speed, since it is unsustained. The retarded flame then accelerates in the same way as when such a mixture is ignited from a spark, and eventually overtakes the retarded shock-wave, the second smaller check to the flame probably occurring at this point; the initiation of separate flames in front of the retarded flame appears to be caused by a mechanical wave which was preceding the latter at a short distance.

Summary.

An apparatus has been described by which a flame is photographed as it travels from one explosive gaseous mixture into another.

When the igniting and the ignited gases are mixtures of hydrogen and oxygen in different proportions, the flame travels in both mixtures at the normal explosion-wave rates, the velocity in the second mixture becoming adjusted within a few centimetres. When carbon monoxide–oxygen mixtures are ignited by electrolytic gas, the flame velocity falls rapidly to less than half the normal rate and detonation is re-established only after the flame has travelled several metres. A fairly complete drying of the carbon monoxide does not appear to decrease the flame speed below a certain limit although it lengthens the period before detonation. The addition of more than 1% of hydrogen to the carbon monoxide mixture allows the flame to proceed immediately at its full rate. A flame just previous to the setting up of the explosion-wave in these mixtures tends to show marked discontinuities.

In conclusion, we wish to express our indebtedness to the Chemical Society for grants towards the cost of photographic materials and to the Brunner–Mond Research Fund for apparatus. We desire to thank Mr. A. G. Hartley, M.Sc., for considerable help in the experimental portion of the paper, and Professor Dixon for his kindly interest and criticism.

THE UNIVERSITY, MANCHESTER. [*Received, August 23rd,* 1926.]