XLVII.—*The Combustion of Complex Gaseous Mixtures. Part III. The Inflammation of Mixtures of Carbon Monoxide and Hydrogen with Air in a Closed Vessel.*

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In Part II of this research (J., 1923, **123**, 1251) reference was made to preliminary experiments on the inflammation of mixtures of carbon monoxide and hydrogen with air, ignited at the centre of a spherical vessel, and some of the results were quoted to show that the " law of speeds " * would apply to the spread of flame in complex gaseous mixtures ignited under such conditions. In the present paper further series of experiments of a like nature are described.

Few measurements by earlier investigators are available of the magnitude and rate of development of pressure when mixtures of carbon monoxide or hydrogen with air are inflamed in closed vessels. Langen's experiments with these gases (" Mitteilungen über Forschungsarbeiten aus dem Gebiete des Ingenieurwesens," **8**, 1903) were chiefly with mixtures with pure oxygen, and he was only concerned with measuring the maximum pressures. The rate of development of pressure, under the same conditions of experiment, was examined by Nägel (*ibid.*, **54**, 1908) for hydrogen, but he chose only mixtures containing excess of oxygen. Both Langen and Nägel used a spherical vessel of 34 litres capacity, and ignited their mixtures by an electric spark passed at the centre. Bone and Haward (*Proc. Roy. Soc.*, 1922, **100**, 67) and Bone,

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* " Given two or more mixtures of air or oxygen with different individual gases, in each of which the speed of propagation of flame is the same, all combinations of the mixtures, of the same type, propagate flame at the same speed, under the same conditions of experiment " (J., 1922, **121**, 365).

Newitt, and Townend (J., 1923, **123**, 2008) have made measurements of the pressures produced and their rate of development with hydrogen–air and carbon monoxide–air mixtures at various initial pressures up to 50 atm.   Their explosion-vessel was spherical, and their source of ignition, a heated platinum wire, was near the wall.   Under these conditions, part of the flame is in contact with the wall of the vessel whilst the remainder is travelling through the mixture, so that heat is lost by conduction before the maximum pressure is attained;   on the other hand, with central ignition, except when the speed of the flame is very slow, the flame does not reach the boundary of the vessel until the whole of the mixture has been inflamed, *i.e.*, until the instant of maximum pressure.

Crowe and Newey (*Phil. Mag.*, 1925, **49**, 1112) have carried out experiments with mixtures of carbon monoxide and air ignited centrally in a sphere of 40·6 cm. diameter.   They have, however, disregarded the effect of water vapour on the rate of combustion of carbon monoxide, and their results are consequently difficult to interpret.   Fenning (*Phil. Trans.*, 1926, *A*, **225**, 331) ignited mixtures of carbon monoxide and air, hydrogen and air, and blends of the two mixtures, at the centre of a cylindrical explosion-vessel, 20 cm. long and 18 cm. in diameter, at an initial pressure of 5·2 atm. and an initial temperature of 50°.   He also studied the effect of water vapour on the rate of explosion of carbon monoxide.

For the experiments now described, new apparatus was constructed, the general arrangement of which is shown in Fig. 1. The principal new feature was a manometer of the Petavel type, designed to obtain as accurate a measure as possible of the rate of development of pressure with explosions that varied considerably in this respect.   The gauge consisted essentially of a steel piston 5 cm. in diameter, screwed into the free end of a tubular steel spring, S.   The other end of the spring was attached rigidly to a brass casing, C, which screwed on to the explosion-vessel.   When assembled, the face of the manometer piston was flush with the inner wall of the explosion-vessel.   Any movement of the piston caused a compression of the spring, which was transmitted, by a steel connecting-rod, R, to a small concave mirror, M, of stainless steel.   One end of the connecting-rod was screwed into the piston, whilst the mirror rested in a slot in the other end and was held in position by taut stays of piano-wire, W.   Considerable difficulty had been experienced with a previous example of this type of manometer, used in our preliminary experiments, in arranging that it should be equally sensitive in registering explosions of very slow and very rapid development.   In the present example, the clearance between the piston and a brass bush which is screwed
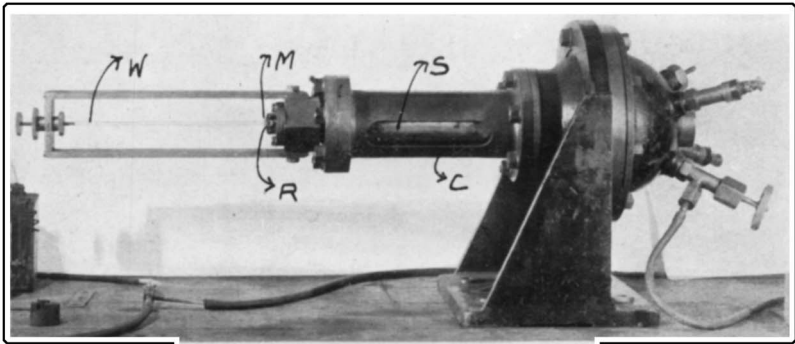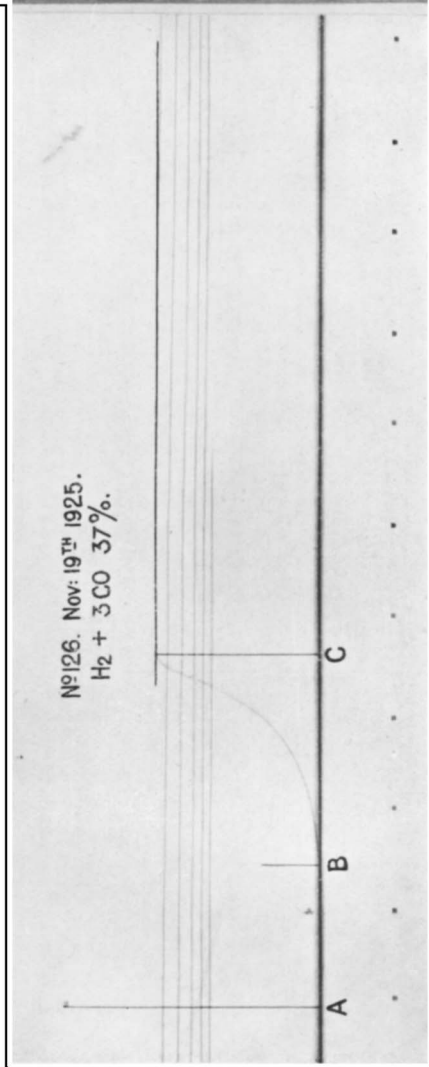
Fig. 1.

Fig. 2.

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H₂ + 3CO 37%.

into the wall of the bomb was exceedingly small, and, unless the piston was frequently removed and carefully cleaned, there was a danger that a film of moisture would form on its periphery. This would cause a frictional force resisting the free movement of the piston. Strict attention has been paid to this point throughout our experiments.

The explosion-vessel was a spherical bomb of 4 litres capacity, fitted with a valve and firing electrodes, similar to that used in earlier work (J., 1918, **113**, 854). A rubber washer between the spring of the manometer and a seating in the wall of the bomb made a gas-tight joint.

A rise in pressure within the explosion-vessel of 1 atm. caused a movement of the piston of 0·0012 mm. This movement was magnified by an optical lever. A beam of light, reflected from the mirror, was focussed on the surface of a strip of sensitised paper carried by a revolving drum. The source of illumination of the mirror was a carbon arc-lamp. The moment of ignition of the mixture was recorded on the sensitised paper by focussing on it, through a telescope, the spark from a gap in series with the spark-gap at the centre of the explosion-vessel. This latter was between pointed electrodes of copper, 3 mm. apart. The spark used to cause ignition was, throughout the experiments, the secondary discharge from a 6-inch induction-coil, using a current of 10 amps. through the primary circuit, the trembler being locked. The rate of revolution of the camera drum was recorded by photographing on it the sparks produced at the mercury contact of an electrically driven tuning-fork, of 100 frequency. A typical record (reduced in size to nearly one-half for reproduction) is shown in Fig. 2. On this record, A is the time of ignition; B, the time of first appearance of pressure; and C, the time of attainment of maximum pressure. The record of the tuning-fork, marking 1/100ths of a second, appears at the bottom of the chart. The speed of revolution of the recording drum was varied according to the rapidity of the explosion. With the most rapid explosions, those of mixtures of hydrogen and air, it was such that a time-interval of 0·01 sec. measured 4·5 cm. on the chart.

Each gas mixture was prepared in a 20-litre glass gas-holder and analysed before use. In each experiment, the bomb was exhausted of air to within a few mm. of mercury, filled with the mixture to be experimented with, re-exhausted, and refilled. The results, both for maximum pressures attained and for rates of development of these pressures, have been checked by explosions of similar mixtures in a bomb of the same dimensions fitted with a different type of manometer. Details of these check experiments, together

with the records of pressures, will be given in a later communication. The present paper deals only with the rate of development of pressure.

The main object of the present series of experiments has been to test the application of the law of speeds to the rate of development of pressure when complex gaseous mixtures are ignited in a closed vessel. With this object in view, a series of mixtures has been used of air with hydrogen and carbon monoxide, both individually and also jointly in the proportions corresponding to $3H_2 + CO$, $H_2 + CO$, and $H_2 + 3CO$. Since these experiments also throw light on the effect of water vapour on the combustion of carbon monoxide, a further series of experiments has been made with mixtures of carbon monoxide and air saturated with water vapour at different temperatures. Unless otherwise stated, the mixtures were initially at atmospheric pressure.

Rate of Development of Pressure.

The values obtained for the rate of development of pressure on explosion of the various mixtures, all saturated with water vapour at 15°, are given in Table I, in which the percentage given in col. 1 relates to the inflammable gas shown at the head of each sub-section.

TABLE I.

The Rate of Development of Pressure.   Hydrogen, Carbon Monoxide, and Mixtures of the Two with Air.   (Saturated with water vapour at 15° and atmospheric pressure.)

| Inflam- mable gas, %.	Time between ignition and first appearance of pressure (sec.).	Time between ignition and maximum pressure t (sec.).	$1/t$.	Mean speed of flame (cm./sec.).
		(a) Hydrogen.		
10·2	0·070	0·166	6·0	58
15·1	0·019	0·038	26·3	260
19·4	0·009	0·019	52·6	510
24·5	0·005	0·011	90·9	880
28·9	0·003	0·008	125	1220
34·1	0·003	0·007	143	1390
37·2	0·003	0·007	143	1390
39·3	0·003	0·007	143	1390
44·4	0·003	0·008	125	1220
45·8	0·004	0·008	125	1220
49·0	0·005	0·010	100	970
54·0	0·005	0·011	90·9	880
56·2	0·006	0·013	76·9	750
57·2	0·006	0·015	66·9	650
62·3	0·009	0·020	50·0	440
66·1	0·018	0·033	30·3	290

TABLE I (continued).

Inflam-mable gas, %.	Time between ignition and first appearance of pressure (sec.).	Time between ignition and maximum pressure t (sec.).	$1/t$.	Mean speed of flame (cm./sec.).
		(b) $3H_2 + CO$.		
14·4	0·036	0·072	13·9	130
20·0	0·012	0·026	38·5	370
24·0	0·007	0·016	62·5	610
29·2	0·006	0·011	90·9	880
37·7	0·004	0·009	111	1080
43·7	0·004	0·009	111	1080
51·0	0·006	0·013	76·9	750
56·5	0·007	0·016	62·5	610
64·6	0·020	0·041	24·4	240
		(c) $H_2 + CO$.		
15·8	0·037	0·095	10·5	100
18·0	0·024	0·078	12·8	120
24·0	0·009	0·026	38·5	370
28·9	0·006	0·017	58·8	570
33·3	0·005	0·013	76·9	750
38·9	0·005	0·012	83·3	810
43·4	0·004	0·012	83·3	810
56·1	0·006	0·017	58·8	570
60·8	0·017	0·030	33·3	320
		(d) $H_2 + 3CO$.		
15·9	0·056	0·017	5·9	58
21·0	0·023	0·062	16·1	160
26·8	0·012	0·032	31·1	300
30·0	0·009	0·025	40·9	390
37·0	0·007	0·018	55·6	540
39·3	0·007	0·017	58·8	570
46·3	0·007	0·017	58·8	570
49·1	0·007	0·018	55·6	540
57·6	0·012	0·029	34·5	340
60·7	0·019	0·045	22·2	220
		(e) Carbon Monoxide.		
21·6	0·050	0·159	6·3	60
23·5	0·050	0·144	16·9	65
28·0	0·029	0·087	11·5	110
31·1	0·026	0·067	14·9	145
36·6	0·027	0·065	15·4	150
39·4	0·027	0·071	14·2	135
44·9	0·025	0·065	15·4	150
49·6	0·023	0·065	15·4	150
54·7	0·032	0·078	12·8	125

Time–pressure curves, reproduced from the records, for each of the maximum-speed mixtures [i.e., those mixtures of inflammable gas and air (or oxygen) in which the proportions of inflammable gas are such that the speed of flame in the mixture, under given experimental conditions, is the fastest obtainable] are shown in Fig. 3 plotted on the same time-scale to enable direct comparison to be made. The curves form a continuous series, of the same

general character, from the slow carbon monoxide–air explosion to the comparatively rapid hydrogen–air explosion.

Strictly speaking, the measure of the " rate of development of pressure " should be the increment of pressure per unit of time. Since, however, this is continuously changing from one instant to the next, it is usual to regard the rate of development as the rate at which the maximum pressure is reached. For convenience, the time between the moment of ignition and that of attainment of maximum pressure (time of explosion, t) is actually measured, but the rate of development of pressure is given by the reciprocal of this time, $1/t$.

FIG. 3.

Time.– Seconds . (Time 0 = time of ignition).
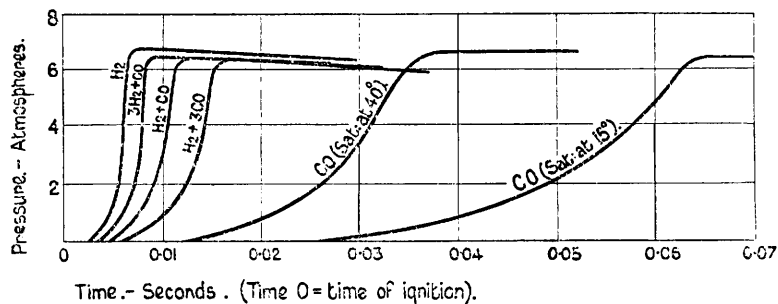
When ignition takes place at the centre of a spherical vessel, the moment of attainment of maximum pressure synchronises with the moment at which the flame reaches the walls.* Hence the

* Unless the speed of the flame is very slow. This was proved by Wheeler (J., 1918, **113**, 840) for mixtures of methane and air containing 7—11% of methane, by recording the time of fusion of screen wires (tinned copper wire of 0·025 mm. diameter) carrying an electric current and stretched near the wall of the explosion-vessel at a measured distance from the spark-gap. A similar method has been used in the present research, using mixtures of carbon monoxide and air, with the following results :

CO (%).	Time from ignition to maximum pressure (sec.).	Time taken for flame to reach wall of explosion-vessel (sec.).
(a) Mixtures dried by calcium chloride.		
30·5	0·129	0·128
33·1	0·122	0·121
40·0	0·115	0·113
45·8	0·121	0·119
(b) Mixtures saturated with water vapour at 15°.		
23·5	0·144	0·142
28·0	0·087	0·082
49·6	0·065	0·066

The times correspond within the limits of error of measurement of the speeds of the flames by the screen-wire method.

mean speed of the flame during its passage from the centre to the sides gives a direct measure of the " rate of development of pressure " as defined in the previous paragraph. This mean speed is r/t, where r is the radius of the sphere, which was 9·73 cm. in the present experiments. The equivalent value was used by Nägel (*loc. cit.*) for recording his results.

In Fig. 4, the rates of development of pressure are plotted against the compositions of the mixtures with air of H_2, $3H_2 + CO$, $H_2 + CO$, $H_2 + 3CO$, and CO. The dependence of the rate of development of pressure on the speed of the flame will be apparent if Fig. 4 be compared with Fig. 5, which records the speeds of propagation of flame during the uniform movement in a horizontal glass tube 2·5 cm. in diameter, the speeds being plotted against the compositions of the same series of mixtures as has been used in the present research. The mean speed of the flame in the sphere is about $2\frac{1}{2}$ times as great as that of the uniform movement in the glass tube.

FIG. 4.

Combustible gas. Per cent in air.
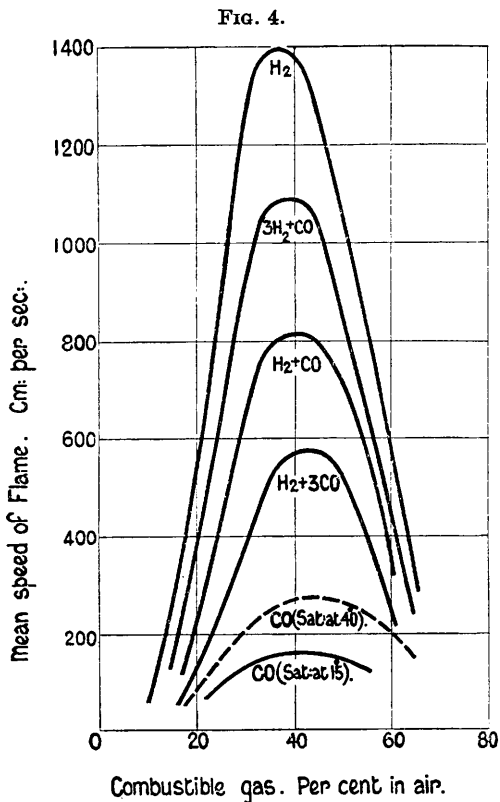
Application of the Law of Speeds.

To simplify the application of the law of speeds to the results recorded in Table I, those obtained with mixtures of carbon monoxide and air are not used in the first calculations, but are reserved until the effect of water vapour on the rate of development of pressure in carbon monoxide–air mixtures has been discussed. Instead of using hydrogen and carbon monoxide, therefore, as the two " standard " gases, hydrogen and the mixture

($H_2 + 3CO$) are used.   Two vols. of hydrogen mixed with 1 vol. of ($H_2 + 3CO$) will yield a mixture of composition $3H_2 + CO$, whilst 1 vol. of hydrogen mixed with 2 vols. of ($H_2 + 3CO$) will yield a mixture of composition $H_2 + CO$.

The results of the calculations are shown in Fig. 6.   In preparing this diagram, the times of explosion were first plotted against the compositions of the mixtures used as " standard." These curves are shown as continuous lines.   From these curves, the " theoretical curves " for the mixtures $3H_2 + CO$ and $H_2 + CO$ were calculated by means 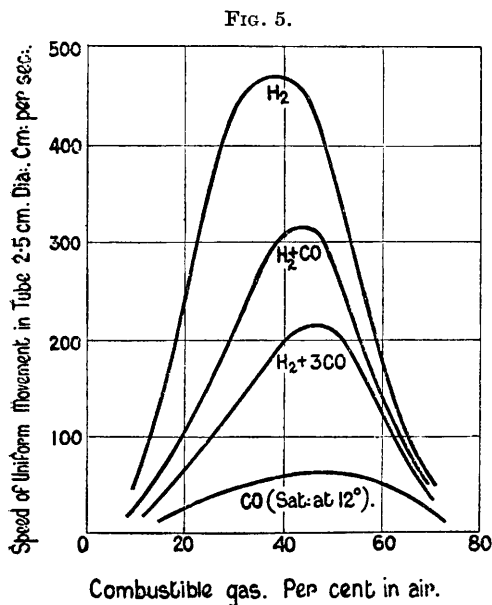of the law of speeds and are shown in the diagram in broken line. The values found experimentally were added to the diagram later.   They show satisfactory agreement between observed and calculated values.   Only the lower portions of the curves are shown in the diagram, since inclusion of all values found would have necessitated an excessive lengthening of the time scale.

FIG. 5.

Combustible gas. Per cent in air.

The Effect of Water Vapour on the Combustion of Carbon Monoxide.

In Part II of this series of papers (*loc. cit.*, p. 1252) it was shown that the speed of the uniform movement of flame in mixtures of carbon monoxide and air varied with the proportion of water vapour present. Some doubt, therefore, existed as to the correct value to use for the speed of flame in mixtures of carbon monoxide and air when attempting to calculate, by means of the law of speeds, the speed of flame in complex mixtures containing carbon monoxide, unless the degree of saturation of the complex mixture by water vapour was known.   It was shown, however, that when hydrogen, or an inflammable gas containing hydrogen, was present in the complex mixture in more than quite a small proportion, the speed of flame became independent of the concentration of water vapour,

so that the speed of flame in such a complex mixture could be used as a basis from which an " effective " speed of flame in the mixtures of carbon monoxide and air could be calculated, and the value thus obtained could be used for further calculations. An alternative method for determining the " effective " speed of flame in a given mixture of carbon monoxide and air was described, this speed being the maximum obtainable with that mixture with the concentration of water vapour that had the optimum effect.

The same argument applies to the rate of development of pressure in complex mixtures of inflammable gases, containing carbon monoxide, ignited centrally in a spherical vessel. We have tested it experimentally, using a " maximum-speed mixture " of carbon monoxide and air, containing 48% of carbon monoxide, the amount of water vapour present being varied by varying the saturation-temperature. The explosion-vessel was installed within a heat-insulated wooden box, which also contained electric heater lamps. The pressure-gauge mirror and a portion of the gauge itself protruded from the enclosure.

Fig. 6.

The charge density was kept constant in these experiments, the bomb being filled at 15° and closed before being heated to the desired temperature. Sufficient water to ensure saturation at the experimental temperature was introduced into the bomb before filling it with the explosive mixture. The results are shown in Table II.

Time—pressure curves are reproduced in Fig. 7.

It will be seen that the rate of development of pressure tended towards a maximum when 6—7% of water vapour was present.
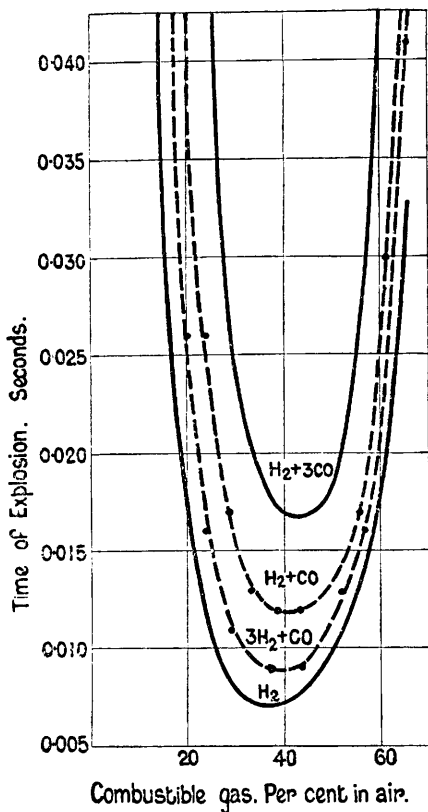
TABLE II.

The Influence of Water Vapour on the Rate of Development of Pressure in a Mixture of Carbon Monoxide and Air.   (48% CO.)

Saturation temp.	Water vapour (% by vol.).	Time between ignition and first appearance of pressure (sec.).	Time between ignition and maximum pressure (sec.).
15°	1·7	0·025	0·065
25	2·9	0·020	0·053
35	4·8	0·017	0·043
40	6·2	0·012	0·038
45	7·9	0·014	0·037
50	9·7	0·014	0·038
55	12·0	0·015	0·037
65	17·3	0·015	0·037

This is rather more than is required to develop the maximum speed during the uniform movement of flame, when the explosive mixture is initially at atmospheric pressure.

FIG. 7.

Time.- Seconds .   (Time 0 = time of ignition).
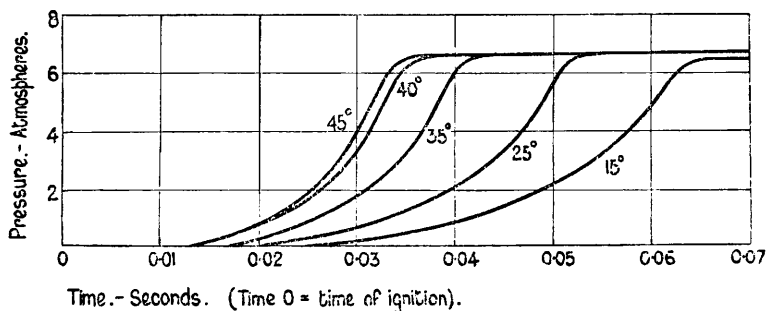
Pressure development.   Mixtures of carbon monoxide and air saturated with water vapour at different temperatures.

The value so obtained, 0·037 sec., for the " effective " time of explosion in the maximum-speed mixture of carbon monoxide and air, was now used as the standard, together with the corresponding value for the maximum-speed mixture of hydrogen and air, to calculate the times of explosion for the three mixtures $3H_2 + CO$, $H_2 + CO$, and $H_2 + 3CO$.   The results are recorded, and compared with the experimentally determined values, in Table III.

TABLE III.

Inflammable gas	H_2.	$3H_2+CO$.	H_2+CO.	H_2+3CO.	CO.
Time of explosion (calc.) (sec.)	—	0·009	0·012	0·018	—
„ „ (obs.) „	0·007	0·009	0·012	0·017	0·037

The close agreement between the observed and calculated values affords decisive proof of the assumption that the " effective speed "

of combustion of carbon monoxide is developed when a sufficient quantity of hydrogen is mixed with it, just as it is when a sufficiency of water vapour is present.

We pointed out, in our previous paper, that the results obtained by Bone and Haward (*loc. cit.*) for the rate of development of pressure in explosions of mixtures of carbon monoxide and hydrogen with air—results which the authors deemed to require an abnormal explanation—could be explained by the law of speeds. Bone, Newitt, and Townend (*loc. cit.*) have not accepted our explanation, regarding as " wholly fanciful " the assumption with regard to the " effective speed " of combustion of carbon monoxide which we have now proved to be correct, and have recorded the results of experiments intended to disprove it. Briefly, they have found that in certain explosions of the mixture $2CO + O_2 + 4N_2$, fired at an initial pressure of 50 atm., and at an initial temperature of 17—23·1°, what they term " the time in seconds taken for the attainment of maximum pressure " did not vary much whether the mixture were " dry," " undried," " moist," or " wet." Thus, they say : " There is practically no difference between the ' dry ' and either the ' moist ' or the ' wet ' series; for in all these cases it amounted as nearly as may be to 0·18 second. In the ' undried ' series (that is, when the water vapour present would probably not much exceed 1 in 2000) the time was somewhat shorter, namely, 0·13 to 0·15 second. It therefore seems clear that the presence of a very much smaller amount of water vapour sufficed to produce the optimum combustion conditions in our said experiments than was found necessary either by H. B. Dixon for the fastest propagation of detonation through $2CO + O_2$ mixtures at ordinary pressures, or by Payman and Wheeler for the fastest inflammation of carbon monoxide–air mixtures also at atmospheric pressure."

Apparently, the assumption is made that the amount of water vapour required to produce the optimum combustion conditions in their experiments was attained with the " undried " mixtures and had been passed with the " moist " and the " wet." Assuming that in the " wet " experiments the gases were saturated at the initial temperature and pressure (23·1° and 50 atm.), there could have been no more than 0·06% of water vapour present. In view of the fact that, under similar conditions of combustion, the concentration of water vapour found to be most effective lies between 6 and 7%, the speed of flame in a given mixture of carbon monoxide and air being then nearly four times as great as when the mixture is roughly dried, it is not surprising that Bone, Newitt, and Townend noticed very little difference between their series of experiments.

On the other hand, the smallest proportion of hydrogen in the mixture used by Bone and Haward was 1·2% (in the mixture $1/12H_2 + 23/12CO + O_2 + 4N_2$), or 20 times as much as the greatest proportion of water vapour in the mixtures used by Bone, Newitt, and Townend, whose experiments, therefore, yield no information regarding the relative influence of water vapour and hydrogen upon the explosion of carbon monoxide–air mixtures at high pressures. It may here be pointed out that although the times given by these authors are recorded as the times taken for " the attainment of maximum pressure," they are actually the times that elapsed between (a) the first indication of a rise above the initial pressure and (b) the attainment of the maximum, for they did not determine the time of ignition. There is no evidence that the interval that elapsed between ignition and the first appearance of pressure was negligible in their experiments or was the same in every one of the series. There is ample evidence that, in the explosion of mixtures initially at atmospheric pressure, this interval is of considerable importance.

Confirmation of our results is given by the work of Fenning (loc. cit.), who measured the time taken from the moment of ignition to the moment of attainment of maximum pressure in explosions (at an initial pressure of 5·2 atm. and an initial temperature of 50°) with a series of mixtures similar to those used by Bone and Haward. In discussing the results of his experiments, Fenning comments on the marked effect of a small proportion of hydrogen on the rapidity of explosion of a carbon monoxide–air mixture. The effect could have been calculated from the law of speeds in the following manner : Under the conditions of Fenning's experiments, the shortest time of explosion of the mixture $2CO + O_2 + 3\cdot8N_2$, viz., 0·0901 sec., was obtained when the mixture was completely saturated with water vapour, when it contained 2·38% by volume. The time of explosion with a " comparatively dry " mixture of the same composition (containing less than 0·05% of water vapour) was 0·2693 sec. The time of explosion of a mixture $2H_2 + O_2 + 3\cdot8N_2$ was 0·0074 sec. From these values, the times of explosion for blends of the hydrogen–air and carbon monoxide–air mixtures can be calculated by the law of speeds, using alternatively the value for the " comparatively dry " and the " saturated " carbon monoxide–air mixture. The calculations are shown graphically in Fig. 8, in which the times of explosion are plotted against the compositions of the blends, the upper and lower curves being obtained when the values for the times of explosion in the dry and saturated carbon monoxide–air mixtures, respectively, are used. It is clear that the times of explosion of the blends used by Fenning

should lie on a curve intermediate between the two calculated curves. That they do so is shown in the diagram by the insertion of his experimental values (*loc. cit.*, p. 351) as points.

To emphasise the importance of the presence of water vapour on the rate of development of pressure on explosion of mixtures of carbon monoxide and air, three series of experiments have been carried out, each covering a full range of mixtures between the limits of inflammability, with different concentrations of water vapour in each series. For the first series, the mixtures were roughly

FIG. 8.
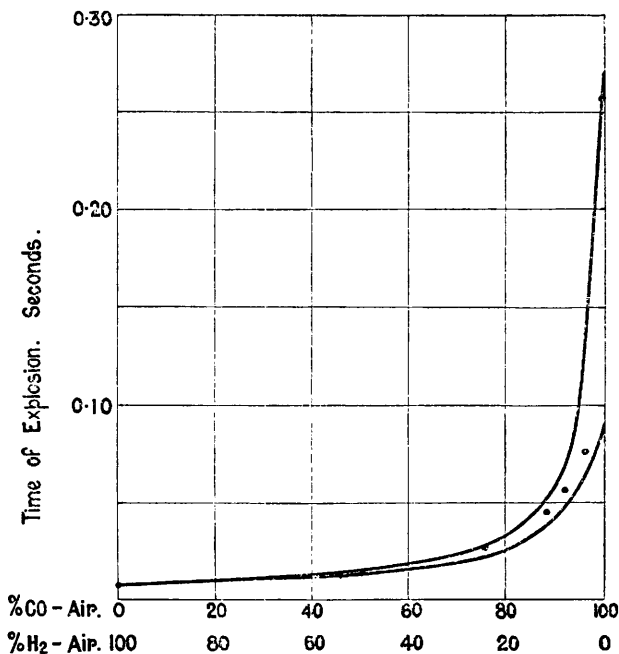
dried by passing them through calcium chloride tubes. For the second, they were saturated with water vapour at 15°, the results being recorded in Table I. For the third, they were saturated with water vapour at 40°, this being the temperature at which the optimum effect is produced. The values for the mean speeds of flame obtained in the last series of experiments may be taken as the " effective " values for the rate of development of pressure in carbon monoxide–air mixtures. They have been plotted as a broken line in Fig. 4. The results of the first and third series of experiments are recorded in Table IV.

TABLE IV.

The Rate of Development of Pressure.   Mixtures of Carbon Monoxide and Air.

Carbon monoxide, %.	Time between ignition and first appearance of pressure (sec.).	Time between ignition and maximum pressure, t (sec.).	$1/t$.	Mean speed of flame (cm./sec.).
(a) Mixtures dried by calcium chloride.				
19·4	0·105	0·337	3·0	30
24·9	0·054	0·150	6·7	65
30·5	0·048	0·129	7·7	75
33·1	0·050	0·122	8·2	80
40·0	0·042	0·115	8·7	85
45·8	0·046	0·121	8·3	80
49·6	0·048	0·136	7·3	70
(b) Mixtures saturated with water vapour at 40°.				
18·4	0·063	0·218	4·6	40
21·8	0·038	0·096	10·4	100
23·7	0·035	0·080	12·5	120
24·1	0·030	0·076	13·2	130
26·7	0·027	0·058	17·2	170
31·0	0·018	0·047	21·3	210
34·5	0·014	0·041	24·4	240
38·3	0·014	0·038	26·3	260
46·1	0·014	0·037	27·0	270
48·3	0·013	0·038	26·3	260
53·3	0·015	0·040	25·0	250
59·1	0·017	0·045	22·0	220
64·3	0·023	0·062	16·1	160