XL.—*The Effect of Catalysts on the Speed of Flame, Infra-red Emission, and Ionisation during the Combustion of Carbon Monoxide and Oxygen.*

By W. E. Garner and C. H. Johnson.

In previous papers (Garner and Johnson, *Phil. Mag.*, 1927, **3**, 97; Johnson, *ibid.*, 1928, **5**, 301) it was shown that the loss of radiant energy from explosions of carbon monoxide and oxygen, dried for 2 hours over commercial phosphoric oxide, is nearly 10% of the total chemical energy set free during the explosion. With 1·9% of water vapour present in the mixture, the fraction of the chemical energy emitted as radiation fell to one-quarter of the value for the dried gases.

The explosions were carried out in metal tubes, 1 inch in internal diameter; under these experimental conditions, the hot products of explosion are rapidly chilled by the walls of the bomb, and the radiation emitted comes very largely from the burning gases. The amount of thermal emission from the hot products of explosion is thereby very much reduced, and the conditions are thus suitable for the detection of chemiluminescence if this be present in the radiant energy from the burning layers.

The temperature in the zone of combustion depends very largely on the velocity of chemical change, which is much more rapid in the moist than in the dry gases (Dixon, *Phil. Trans.*, 1884, **175**, *A*, 617). Thus the temperatures attained and the thermal energy emitted should be higher for the moist than for the dry gases. Experiment shows, however, that the emission of radiation is the greater for the dry gases. It must therefore be concluded that the difference between the emissions for moist and dry gases cannot be due to thermal emission but must be accounted for as chemiluminescence.

There is an intimate relationship between the speed of flame and the emission of radiation, which cannot be expressed in an exact manner on account of lack of knowledge of the mechanism by which the flame is propagated. It is clear, however, that the additional loss of 7·5% of the total energy of the explosion which occurs in the dry gases will reduce materially the velocity of the flame. It would appear, therefore, that one of the causes of the reduction in speed of flame in mixtures of carbon monoxide and oxygen which occurs on drying lies in the increased loss of energy as radiation.

Hydrogen and hydrogen-containing substances act similarly to water in promoting an increased speed of flame and in reducing the emission of radiant energy. The effects of ethyl nitrate, ethyl iodide, and hydrogen are similar to those of water. The magnitude of the changes produced on the addition of 1% is of the same order for all of these substances. The radiation emitted at 2·8 and 4·4 μ is diminished to practically the same extent as the total radiation.

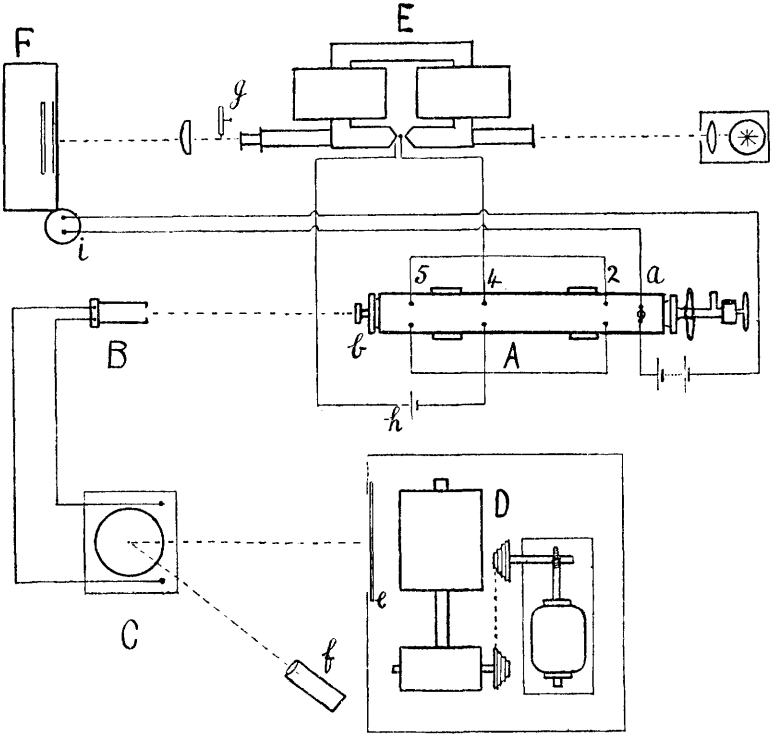
Other substances, such as carbon tetrachloride and nitrogen peroxide, have an opposite effect, decreasing the speed and increasing the emission of radiation. Their action is antagonistic to that of water, and it is highly probable that they reduce the concentration of this substance by interaction.

The extinction coefficients of the mixtures of carbon monoxide and oxygen, as measured in a column 10·7 cm. long, were not appreciably affected by the presence of the small quantities of the catalysts used. Thus the effects cannot be attributed to the absorption of radiation by the catalysts in front of the burning gases.

The changes in the emission of radiant energy occur in the region of the carbon dioxide maxima at 2·8 and 4·4 μ. We are thus dealing with an effect in which the molecules of carbon dioxide are concerned, and not those associated with the formation of some peculiarly active decomposition product of the catalysts employed.

These facts were established in a series of preliminary experiments and were confirmed later by more accurate measurements

FIG. 1.



with a new experimental arrangement by which the emission of radiation, the ionisation, and the speed of flame could be measured simultaneously.

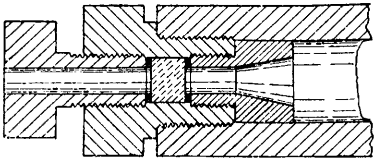
EXPERIMENTAL.

The disposition of the apparatus is shown in Fig. 1. The gases were fired in a cylindrical explosion vessel A of the same dimensions as that described previously. The ignition was brought about at *a* by the fusion of very thin iron wire, 1·5 mm. long, stretched between the insulated terminals of a firing plug. A 12-volt battery was used as a source of current. The bomb carried in addition five pairs of insulated electrodes (only three are shown in the figure), which were placed between the firing plug and the fluorite window (*b*, Figs. 1 and 2). These were used in connexion with the measurement of speeds of flame.

In Fig. 3 a section is given showing the detailed construction of the electrodes. They carried stout platinum wires penetrating 0·4 cm. into the interior of the bomb, the tips of the wires of each pair being separated by 1·5 mm.

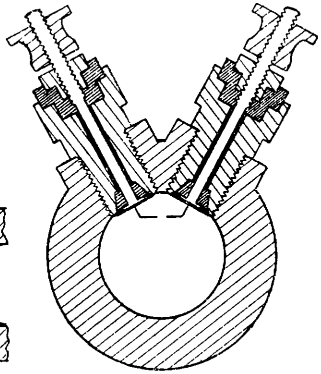
The bomb was clamped in a rigid iron framework in alinement with a sensitive, quick-acting, linear thermopile, B, mounted separately on a stand. The distance separating the fluorite window of the bomb and the thermopile was 34 cm., and in this position the thermopile could not "see" the walls of the bomb. Both the bomb and the thermopile were fastened through their stands to the bench. The thermopile slit was maintained at 0·5 mm. throughout the experiments.

FIG. 2.



Section across fluorite window.

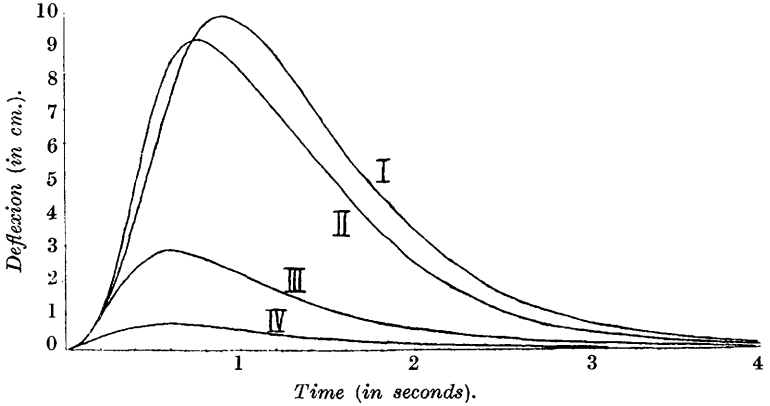
FIG. 3.



The thermopile was used in conjunction with a Downing galvanometer, C, which was enclosed in a shield of Mu-metal. The galvanometer was supported upon a slate slab resting on a 3-inch thickness of brown paper on the top of a brick column going down into the concrete foundations of the building, and this proved very effective in eliminating vibrational disturbances. A light mica damping vane attached to the suspension and a device for regulating the damping enabled the galvanometer to be critically damped when taking records. The sensitivity of the galvanometer was checked before every experiment by noting the deflexion produced when a small current from a standard cell passed through the coils of the instrument.

A photographic record was obtained of the galvanometer deflexion by projecting a bright vertical line of light from a small filament lamp, *f*, upon the galvanometer mirror. This passed by reflexion to the adjustable horizontal slit of an improvised camera, D, placed about 40 cm. from the galvanometer and directly in front of it. Immediately behind the camera slit was a long cylindrical lens, *e*, which brought the line of light to a point focus upon a drum carrying Wellington and Ward " Negative Paper." Deflexions up to about 12 cm. could be recorded on the drum. A time marker, placed between the lamp and the galvanometer mirror (not shown in Fig. 1), was operated by the electrically driven tuning fork, which operated another time marker, *g*, used with the Einthoven galvanometer E. From the curves recorded on the revolving drum, the amounts of radiation falling on the thermopile could be calculated.

FIG. 4.



The areas below these curves are proportional to the quantities of radiation received. By comparing the areas obtained from experiments on gaseous explosions with the area of a " control curve," obtained by allowing a known amount of radiation to fall instantaneously upon the thermopile, the radiation received by the thermopile can be expressed in absolute units. The method of obtaining the control curve has been described previously. Typical radiation records are shown in Fig. 4; the ordinates of the experimental curves have been measured and re-plotted to the same time axis, so that they are directly comparable. Curve I was obtained with standard dry mixture in the presence of carbon tetrachloride. Curve II is a well-dried mixture; III is the record taken with wet gas; IV is the control curve.

Measurement of Flame Speeds.—A new method for the measurement of flame speeds was devised which involved the use of an

Einthoven galvanometer, E (Fig. 1), period $\frac{1}{350}$ second. The principle of the method is as follows: Each pair of the insulated electrodes in the bomb is connected in parallel with one another and in series with the string (movable part) of the galvanometer and a source of potential, *h*. Prior to explosion the gases in the bomb offer an infinite resistance and no current passes round the circuit; on exploding the gas mixture, the flame travels along the bomb, and as it passes each pair of electrodes it renders the gases conducting, thus causing a momentary deflexion of the fibre. These deflexions are recorded upon the falling plate of the Einthoven camera, F. The time of fall of the plate is automatically marked in twenty-fifths of a second, so that, the distances between the pairs of electrodes being known, direct measurements from the plates of the times between successive deflexions enable one to calculate mean flame speeds in the successive sections of the bomb. In practice, the method proved trustworthy only for the slowest flames, chiefly owing to the smallness of the bomb and the slow rate of fall of the plate. With a long bomb and a fast-moving drum in place of the falling-plate camera, this method would give highly accurate results, but in any arrangement a definite limit of usefulness is imposed by the period of the galvanometer, which may be comparable with the time taken by the explosion to traverse the distance between successive pairs of electrodes, in which case the fibre is set oscillating. The potential applied to the pairs of electrodes was either 2 or 4 volts according to the nature of the explosive mixture. In the very fast explosions, where considerable ionisation occurred, the galvanometer was shunted with a resistance equal to that of the fibre.

General.—It was found possible to co-ordinate the actions of both galvanometers, one recording radiation and the other speeds, so that simultaneous records were obtained of these properties in every explosion. By means of a simple device at *i*, it was arranged that the mechanism controlling the falling plate of the Einthoven camera automatically fired the bomb. In order to correlate completely the two photographic records, pieces of iron wire, similar to that used in firing the gas mixture, were affixed, one above the drum camera and another in front of the lens of the falling-plate camera, both connected in parallel with the firing plug. (These are not shown in the figure.) The wire above the drum was enclosed in a small black box with a slit so that the light emitted when the wire fused caused a sharp image of the slit to be registered upon the sensitised paper. By this means it was possible to determine if there was any appreciable lag between the moment of ignition of the gases in the bomb and the initial reception of heat by the thermopile. In very few cases was a lag indicated, generally with dried gas mixture, and then only of the order of 0·01 sec. The fusing of the wire placed in front of the Einthoven camera removed its shadow from the plate.

Results.

Measurements of the total infra-red radiation and the speed of flame were made on a standard mixture of carbon monoxide and oxygen to which small quantities of catalysts had been added. The speeds were not determined with a high order of accuracy but are sufficiently exact to bring out the main points at issue. The data are collected in Tables I to VI. The emission of infra-red radiation decreases as the speed of flame increases, and *vice versa.*

In order to arrive at the values for the radiation received by the thermopile, the areas of the curves were measured and their equivalent calorific values calculated by comparison with the area of the control curve. These are expressed in calories, but any arbitrary scale would do equally well for the purposes of the present discussion. The speeds are the means of the velocity of propagation between electrodes 2 and 4, and 4 and 5 (see Fig. 1). Usually the velocity was uniform in these two sections of the bomb.

Dried Gas.—The standard mixture consisted of 2 vols. of carbon monoxide and 1 vol. of oxygen, dried for two hours over 130 cm. of commercial phosphoric anhydride before admission to the dried bomb. Thus the drying was more complete than in the previous work. It was very necessary to dry the bomb to the same extent before each experiment. Only about one in every three mixtures, prepared as above, could be fired by the fusion of iron wire, and there was a greater variation between the individual results than was observed previously, owing, presumably, to the difficulty in drying the walls of the bomb to the same extent each time. The results of five explosions are in Table I.

TABLE I.

Dried gas.

Explosion No.	1.	2.	3.	4.	5.	Mean.
Radiation (cal. × 10^6)	5·79	5·72	6·28	5·68	6·55	6·00
Speed (cm./sec.)	94	108	79	130	89	100

Positive Catalysts.—1. *Water vapour.* The effect of addition of water on the radiation and speed is very marked. The radiation is reduced to 27% of the value for the standard mixture by the presence of 1·95% of water, whilst the speed increases more than ten-fold. Very small percentages of water vapour have a very great effect upon the amount of radiant energy emitted, as was shown by removing two of the four tubes of phosphoric oxide, and by drying for 1 instead of 2 hours. The ratio of the emission from dry to that from wet gas fell from 3·5 : 1 to 2·5 : 1. In explosion 3 (Table II), the bomb was saturated with water vapour at 17·1°. This, therefore, corresponds to "wet gas" mixture. The water vapour in Nos. 1 and 2 was introduced into the evacuated bomb from water or ice maintained at a constant temperature.

TABLE II.

Dried gas + water.

Explosion No.	% Water.	Radiant energy (cal. × 10^6).	Speed (cm./sec.).
—	0·00	6·00	100
1	0·23	2·76	780
2	0·44	2·39	900
3	1·95	1·63	>1000

2. *Other positive catalysts.* A number of hydrogen-containing substances were added in order to compare their action with that of water. The vapours were in all cases introduced into the thoroughly dried bomb, and the explosive mixture was added subsequently, leaving time for thorough mixing. The vapours were strongly absorbed by the walls of the bomb, so that the percentages given in Tables III—VI are maximum values. Ethyl nitrate, ethyl iodide, ethyl bromide, and chloroform behave like water, increasing the speed and diminishing the radiant energy. They act as positive catalysts by virtue of the hydrogen they contain. In a number of experiments the speeds could not be read accurately from the records on account of overlapping of the deflexions. Nevertheless, even for the fastest explosions the order of magnitude of the velocity could be derived.

TABLE III.

Dried gas + hydrogen-containing substances.

Expl. No.	Catalyst.	% Added.	Radiant energy (cal. × 10^6).	Speed (cm./sec.).
—	—	0·00	6·00	100
1	$C_2H_5NO_3$	0·28	2·30	930
2	,,	0·46	2·20	>930
3	,,	0·89	1·56	2500 ?
1	C_2H_5I	0·18	2·16	>800
2	,,	0·32	1·67	1100
	C_2H_5Br	0·69	1·90	1100
	$CHCl_3$	0·47	2·30	560 ?

Negative Catalysts.—The effect of carbon tetrachloride upon the radiation intensity is not so marked as in the preliminary experiments, doubtless owing to the more thorough drying of the standard mixture.

TABLE IV.

Dried gas + carbon tetrachloride.

Expl. No.	% Added.	Radiant energy (cal. × 10⁶).	Speed (cm./sec.).
—	0·00	6·00	100
1	0·35	6·34	79
2	0·72	6·60	44
3	1·05	6·84	63
4	1·42	6·47	55
5	1·14	6·49	81
6	1·01	6·97	57
Mean	—	6·62	63

TABLE V.

Dried gas + nitrogen peroxide.

Expl. No.	% Added.	Radiant energy (cal. × 10⁶).	Speed (cm./sec.).
—	0·00	6·00	100
1	1·09	5·10	110
2	1·63	4·67	133
3	?	4·78	169
4	From walls.	4·91	128
5	,, ,,	4·25	?

Nitrogen peroxide. Nitrogen peroxide behaves as a feebly positive catalyst in the mixture dried as above, but as a negative catalyst in an imperfectly dried mixture. In the earlier experiments, this vapour functioned as a negative catalyst.

TABLE VI.

Partially dried gas + nitrogen peroxide.

% Added.	Radiant energy (cal. × 10^{-6}).	Speed (cm./sec.).
0·0	3·94	375
<1·0	5·20	85 (approx.)

General Conclusions.—The relationship between the speed of propagation and the radiant energy has been shown to hold good, within the error of experiment, for all cases examined. The emission intensity varies inversely with the speed of flame.

The behaviour of carbon tetrachloride and nitrogen peroxide is worthy of special consideration. Both substances can directly counter the action of water molecules, as has been demonstrated by addition of the vapours to partially dried gas mixture.

Carbon tetrachloride. Chemical interaction at high temperatures between this vapour and the small amount of water present scarcely seems a sufficient explanation for the effect, since the products must obviously contain hydrogen and it is known that even hydrogen chloride (Dixon) and chloroform (Table III) behave as positive catalysts for the reaction. Nothing is known, however, regarding the relative efficiencies of the various hydrogen-containing catalysts.

It is scarcely conceivable that the energy absorbed from the system during the breakdown of the carbon tetrachloride and, possibly, subsequent formation of oxides of chlorine, is of sufficient magnitude to reduce the flame temperature materially. Calculation shows that if all the carbon tetrachloride is decomposed, the energy involved amounts to much less than 1% of the heat of combustion of the carbon monoxide. Even if this explanation were admissible in accounting for the slow rate of reaction, it would not explain the increased emission of infra-red radiation.

Nitrogen peroxide. The anomalous catalytic behaviour of this substance towards partly dried and thoroughly dried gas mixtures is readily understood if it is assumed that in the former case reaction occurs between the vapour and the water molecules, accompanied, maybe, by adsorption of the resulting complex on the walls of the bomb. The net result is the substitution of a small amount of a feeble positive catalyst (nitrogen peroxide) for a smaller amount of an exceedingly powerful positive catalyst (water). This also explains why, in the preliminary experiments, nitrogen peroxide was found to be a less powerful negative catalyst than carbon tetrachloride.

Analysis of the Total-radiation Records.

The total-radiation curves give no direct information regarding the rates at which the energy is emitted from the bomb, since the galvanometer deflexion is determined by factors other than the emission of heat—notably by the inertia of the suspension and the various forces controlling its movements. A method of analysing galvanometer records (deflexion–time curves) has been developed by Hartree and Hill (*Proc. Roy. Soc.*, 1921, *A*, **99**, 172; *J. Sci. Inst.*, 1923, 267), by means of which the elimination of thermopile and galvanometer constants is possible. First, it is necessary to obtain a standard curve or " control curve " by recording the galvanometer deflexion when a known amount of energy is directed instantaneously upon the thermopile. It is assumed that when a certain quantity of heat falls suddenly on the thermopile, there is obtained a curve of definite shape with ordinates proportional to the amount of heat received. The underlying idea is the analysis of the experimental curve into a set of curves of the same shape as the control curve but of different magnitudes, their starting point as regards time being determined by trial. The effect is thus to divide what is in reality a continuous emission of heat from an explosion, into a succession of discrete impulses of energy, given out at definite small intervals of time. The closer the intervals are together, the more nearly does the derived rate of emission correspond to the actual rate.

The control curve is obtained by radiating to the thermopile a known amount of heat over a time short enough to be considered instantaneous in comparison with the duration of an explosion, the thermopile and galvanometer being used under precisely the same conditions (as regards sensitivity, slit width, etc.) as when recording radiation from the explosions. The control curve is time-marked so that the ordinates (deflexions) can be measured every twenty-fifth of a second. This series of ordinates, then, corresponds to the reception by the thermopile of an arbitrary unit of heat; multiples and sub-multiples of these ordinates are tabulated, corresponding to multiples and sub-multiples of this arbitrary energy unit. This is the "Control Table." The explosion curve is measured up in the same way, and its ordinates are written in a horizontal column at the top of a large sheet of paper. From inspection of the first two or three of these it is seen that they agree more or less with the numbers in the control table corresponding to heat, say, x units at time 0; these numbers in the control table are then subtracted throughout from the tabulated ordinates of the experimental curve, and a note made, x units at time 0. The first two or three remainders are then seen to correspond to heat, say, y units at time 0·04 second (this being the interval chosen), and the numbers for y units in the control table are therefore shifted along to 0·04 second, and subtracted throughout, leaving a second series of remainders. The process is continued until the remainders become zero, or practically so.

The space required prohibits the reproduction of the operations by which the analysis is carried out; this was performed upon average curves obtained by measuring the ordinates of all the experimental curves and taking means at corresponding times after the instant of ignition.

TABLE VII.

Rates of emission of radiant energy.

Time from ignition (in $\frac{1}{25}$-sec. periods)	0	1	2	3	4	5	6	7
				Heat units.				
Wet gas	1·25	1·25	1·56	—				
Partially dried gas ...	1·25	1·5	2·0	2·25	1·9	1·9		
Dried gas	1·25	1·5	1·5	1·75	1·5	1·75	1·5	1·5
Dried gas + CCl_4	1·25	1·25	1·5	1·25	1·25	1·0	1·0	1·0

Time from ignition (in $\frac{1}{25}$-sec. periods)	8	9	10	11	12	13	14	15
				Heat units.				
Wet gas								
Partially dried gas ...								
Dried gas	1·25							
Dried gas + CCl_4	0·75	0·75	0·75	0·75	0·75	0·75	1·0	—

Each horizontal series in Table VII represents a succession of discrete impulses of heat given to the thermopile at intervals of 0·04 sec.; time 0 corresponds to the instant of ignition. The thermopile receives practically the same quantity of radiant energy from each section of the bomb (see *Phil. Mag.*, 1928, **5**, 301), so that with a uniform flame movement an almost steady rate of emission would be recorded, provided that the bulk of the energy is received from the wave front and not from the hot products of combustion. The above table indicates that these conditions hold fairly well. Absorption by the cold gases diminishes the amount of radiation received from the initial stages of combustion, and retardation of the flame as it approaches the fluorite window reduces the quantity radiated per 0·04 sec. in the slower-moving flames.

Except for small residues, the radiation ceases abruptly at times dependent upon the nature of the catalyst present. These residues of heat, which are emitted some time after the steady radiation has ceased, probably have considerable theoretical interest and are therefore recorded in Table VIII.

TABLE VIII.

Heat residues.

	Dried gas + CCl_4.		Dried gas.			Partially dried gas.	Wet gas.
Time from ignition (secs.)	1·1	2·7	0·8	0·9	1·1	1·4	—
Heat units	0·75	0·75	0·5	0·5	0·25	0·5	—
Total residue	1·5		1·25			0·5	—
% of total radiation ...	9·1		8·5			4·4	—

The duration of this residual radiation cannot be measured accurately without considerable refinements in the experimental technique (notably in the accuracy of time-marking the records) and without increasing enormously the labour of analysis. The time values tabulated above have therefore very little significance except as rough indications of the times over which the after-radiation was appreciable.

The residual radiation can hardly be thermal, since none is detected after explosions of wet gas mixture in which the highest temperatures are reached. If it is due to "after-burning," then considerable chemical combination must occur at low temperatures, which suggests the persistence of activated (or possibly ionised) molecules.

Evidence is submitted subsequently which points to a possible connexion between this residual radiation and the persistence of ions in the gases after explosion.

The Duration of Emission of Radiant Energy and the Duration of Flame.

It seemed of interest to attempt to correlate the duration of steady radiation with the duration of flame within the bomb.

The duration of radiation, exclusive of residues, can be computed directly from the above analyses. The duration of flame can be calculated from speed measurements—small inaccuracies are liable to be introduced here owing to the somewhat unsatisfactory method of recording the instant of ignition upon the plates. In three cases in which dried gas mixture was used, it was possible to measure the speed between the moment of ignition and terminal 5, and the mean speed thus calculated was 93 cm./sec. Reference to Table I shows the average speed for explosions in dried gas to be 100 cm./sec. Calculation of the duration of flame was therefore made, taking the value 96 cm./sec. For carbon tetrachloride explosions, the mean speed between firing plug and T_5 was 67 cm./sec., and between T_2 and T_5 63 cm./sec. (see Table IV). A value 65 cm./sec. was therefore taken in making the calculation. Owing to the method by which the analyses of the total radiation curves were effected it must be emphasised that the figures in both columns of Table IX are derived from averaged data from corresponding records, and are therefore comparable.

TABLE IX.

Description.	Duration of steady radiation (sec.).	Duration of flame (sec.).
Dried gas	0·34 ± 0·02	0·36 ± 0·02
Dried gas + CCl_4	0·54 ,,	0·54 ,,
Partially dried gas	0·22 ,,	0·16 ,,
Wet gas	0·10 ,,	0·03 ,,

The table shows that, within the limits of accuracy of the analysis, the abrupt fall in the emission of radiation coincides with the extinction of flame in explosions of standard mixture with and without carbon tetrachloride. The bulk of the radiant energy, therefore, has its origin in the wave front where chemical change is proceeding, and not in the hot products of reaction. This is also supported by the aforementioned fact that the energy is emitted at an approximately uniform rate as the flame travels along the bomb (see Table VII). Had emission occurred to any important extent behind the wave, it would have been much less in the first than in the last twenty-fifth of a second. The small diameter of the bomb is responsible for rapid cooling of the gases and very probably for the sudden extinction of the radiant energy when the flame reaches the window.

When water is present the radiation outlasts the period of inflammation; in this case the flame temperature is higher, so that a considerable proportion of radiant energy may be of thermal origin.

Ionisation Phenomena accompanying Explosions of Carbon Monoxide and Oxygen. After-burning.

The speed records give comparative measurements of the maximum conductivity produced at the separate terminals and of its duration. It was not feasible to introduce the elaborations (guard-rings, etc.) necessary for a thoroughly trustworthy examination of ionisation, owing to the danger of screening off portions of the bomb from the thermopile and thus materially reducing the amount of radiant energy received upon it. Typical records are given in Figs. 5 and 7. The deflexions obtained are proportional to the electric current produced when the wave passes the platinum-point electrodes 2, 4, and 5.

The maximum deflexions obtained at electrode 2 for a number of explosive mixtures are recorded in the Table X under the heading of maximum conductivity, together with the speeds of flame and the persistence of ionisation at electrode 5.

The conductivity between platinum-point electrodes is dependent upon a large number of factors, *e.g.*, the rate of establishment of the ionisation equilibria, the nature of the elementary substances present, and the velocity of chemical change. It is not surprising, therefore, to find that the type of deflexions obtained for explosions in which various hydrogen-containing catalysts are present are similar to one another and different from that of the dried gases without catalyst. It is evident from Table X (*a*) that hydrogen-containing substances greatly increase the conductivity and decrease the duration of ionisation.

TABLE X.

Ionisation and speed of flame.

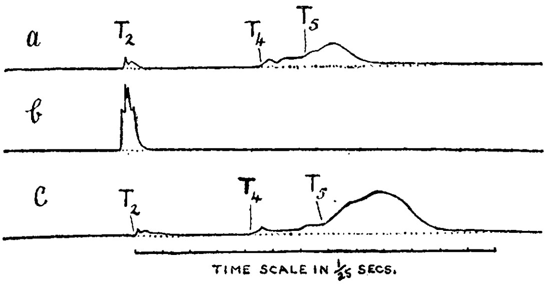
% Catalyst.	Speed of flame (cm./sec.).	Maximum conductivity (arbitrary units).	Persistence of ionisation at T_5 (sec.).
—	100	1·0	3·25 × 0·04
(*a*) Addition of hydrogen-containing substances.			
0·23 H_2O	780	8·5	0·8 × 0·04
0·44 ,,	900	17·0	0·6 ,,
1·95 ,,	>1000	30·0	0·4 ,,
0·28 $C_2H_5NO_3$	930	7·0	0·9 ,,
0·46 ,,	>930	11·0	0·7 ,,
0·89 ,,	2500	28·0	0·4 ,,
0·32 C_2H_5I	1100	$>12·0$	1·0 ,,
0·69 C_2H_5Br	1100	$>10·0$	0·9 ,,
0·47 $CHCl_3$	560 ?	12	1·6 ,,
(*b*) Addition of carbon tetrachloride and nitrogen peroxide.			
CCl_4	63	1·7	5·6 × 0·04
NO_2	140	2—8	2·5 ,,

Addition of Negative Catalysts.—Anomalous results are obtained with carbon tetrachloride; in spite of the fact that it reduces the speed, the conductivity is somewhat increased, and the persistence of ionisation lengthened. Nitrogen peroxide behaves normally, increasing both speed and conductivity and diminishing the persistence. The conductivity results in the presence of nitrogen peroxide are, however, erratic.

The Persistence of Ionisation.

A striking feature about explosions of dried standard mixture and of mixtures containing carbon tetrachloride is the persistence of ionisation for some time after the passage of flame across the electrodes. The persistence is not often evident at the first pair of electrodes (nearest the firing plug), the galvanometer deflexion rising sharply to its maximum value and falling to zero level immediately afterwards. The persistence is appreciable at the fourth electrode and most marked at the fifth. Thus the magnitude of the deflexion increases as the wave advances along the tube. This effect is not accidental, due to differences in the setting of the electrodes. Moreover, the result is in agreement with that obtained by Malinowski (*J. Chim. physique*, 1924, **21**, 469), who previously observed the effect in slow-moving benzene–air mixtures. In Fig. 5 are reproduced some of the actual records in order to illustrate the various points at issue. Curve *a* shows a typical record obtained from a dried gas explosion, with 4 volts across the terminals; the three breaks are clearly marked and the persistence of ionisation in the neighbourhood of T_4 and T_5 is very striking. Curve *b* was taken in the presence of ethyl nitrate with a *P.D.* of 2 volts and with the galvanometer shunted. Owing to the high speed of explosion, only the break corresponding with T_2 can be clearly distinguished. Curve *c* is a record obtained with carbon tetrachloride in the bomb, and a *P.D.* of 4 volts; the extraordinarily

FIG. 5.



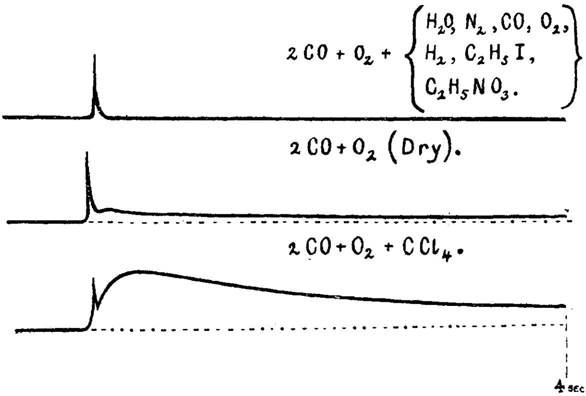
large deflexion, caused by an overlap of the effects at T_4 and T_5, and its long duration are obvious.

These results are in complete harmony with some unpublished experiments by Dr. S. W. Saunders, whose results are illustrated in Fig. 6, which is self-explanatory. In his work the electrode pair consisted of two platinum discs fitted with a guard ring, and the bomb was a spherical vessel of 2 litres capacity. The maximum deflexions are not directly comparable, since different voltages and galvanometer shunts were used in the three curves shown in Fig. 6.

Discussion.

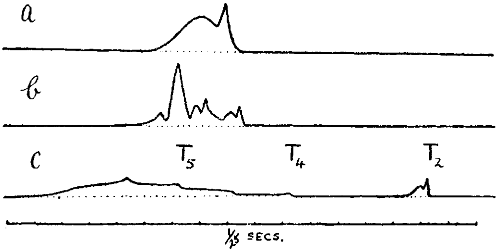
The ionisation results show that in the presence of hydrogen-containing substances the conductivity of the gases falls from its relatively high maximum value to zero within 0·02—0·03 sec. after the flame has reached an electrode. In explosions of dried gas mixture the ionisation at T_5 lasts for about 0·13 sec. after the passage of flame, and for 0·22 sec. in the presence of carbon tetrachloride. If this phenomenon were due primarily to "after-burning" (which Dixon and others claim to have found in dried mixtures of carbon monoxide and oxygen), it would surely have betrayed itself by appreciably prolonging the radiation of heat with respect to the duration of flame. The analyses of the radiation curves show, however, that the period of after-burning, if any, is too short to be detected with the experimental arrangement employed, and that the extinction of steady radiation practically coincides with the extinction of flame.

FIG. 6.



The long duration of ionisation can be interpreted on the assumption of an abnormally slow rate of recombination of the ions produced during combustion. It is natural to inquire whether this retarded neutralisation is in any way connected with the emission of "residual" infra-red radiation, mentioned previously, which the analyses disclosed. The two effects certainly run parallel to one another. They also call to mind the recent results of Ellis and Wheeler (J., 1927, 310), in which it was discovered that, immediately following the wave front in mixtures of carbon monoxide and oxygen, an intense visible luminescence set in, originating in the neighbourhood of the point of ignition. This is attributed by the authors to "after-burning," but it is conceivable that the secondary emission of visible radiation is due to the recombination of ions produced during the passage of flame, or to the return of electrons in excited molecules of carbon dioxide to their normal orbits. The small amounts of residual infra-red radiation, detected in our experiments and emitted after the flame has reached the window, and the emission of visible radiation may be complementary phenomena.

Fig. 7.



In this connexion it is desirable to relate an interesting experimental result obtained whilst carrying out some explosions in glass tubes. When a dried mixture containing a small quantity of carbon tetrachloride is exploded in a long glass tube, closed at the end remote from the point of ignition but open at the other, the flame sometimes separates into two portions—one, pale blue in colour, forming the wave front, and another, of conical shape, emitting an intense yellow luminescence and separated by a few mm. from the first—the whole having a length of about 5 cm. When no separation occurs, the two zones are readily distinguished in the flame.

It is impossible to trace the shape of the ionisation records for the fast explosions, but close examination of the numerous cases where the speed is moderate or slow reveals a rather striking phenomenon which suggests an explanation of the above phenomenon.

Fig. 7 *a* represents the general configuration of a deflexion at a single electrode. There are two maxima; the first, which is sharp, undoubtedly corresponds to the passage of flame over the electrode; the second, which is usually less well-defined and smoother, is of unknown origin. As an illustration, an actual record taken with a mixture containing a trace of water vapour is reproduced in Fig. 7 *b*, in which the double deflexions corresponding to T_2, T_4, and T_5 are clearly differentiated.

The form of some of the Einthoven records for explosions of dried gas mixture, and particularly in the presence of carbon tetrachloride or nitrogen peroxide, suggests the occurrence of simultaneous propagation of two waves within the bomb, travelling at approximately equal speeds. Fig. 7 *c* is an illustration of this type of record, in the presence of carbon tetrachloride; Figs. 5 (*a* and *c*) and 6 (Dr. Saunders) also illustrate it.

This effect may, however, be nothing more than a separation of the two maxima referred to above. Whatever the cause, there seems definite evidence for the existence of two " zones " of ionisation, which become more clearly differentiated the slower the combustion. Whether the flame actually divides into two portions within the bomb is a matter of conjecture; if such is the case, it is curious that the times for the duration of flame and radiation of heat are so nearly equal. The logical conclusion is that the infra-red emission from the second portion is very small.

The evidence for " after-burning " in explosions of carbon monoxide and oxygen rests chiefly upon the results of photographic examination. The interest attaching to the experiments described above is that a distinction is drawn between the combustion phase, with its attendant emission of infra-red energy, and another phase, the chief features of which are ionisation and an emission of visible radiation. The so-called " after-burning " may be nothing more than the registration of the latter upon a photographic plate.

Wheeler and Ellis (*loc. cit.*) have ascribed the after-glow to " after-burning," but it is conceivable, as already suggested, that it is merely a luminescence accompanying the neutralisation of ions.

It is impossible at present to do more than direct attention to the facts and to suggest an alternative explanation; further investigation must precede a detailed discussion of these curious phenomena.

Summary.

Measurements have been made of the rate of emission of radiation, the duration and magnitude of ionisation, and the speed of flame for carbon monoxide and oxygen mixtures to which a number of catalysts have been added.

Hydrogen-containing substances diminish the emission of infra-red radiation, and increase the speed of flame and the magnitude of ionisation in these explosions.

In an explosion of the dry gases, two maxima of ionisation are observed to move past the electrodes as the flame traverses the explosion vessel. These simulate the passage of two successive waves. The second maximum is frequently much larger than the first, especially when carbon tetrachloride is present. The persistence of the ionisation associated with the second maximum increases as the wave passes along the bomb. At the last electrode it persists for 0·1—0·2 sec. These phenomena do not appear to be due to reaction between carbon monoxide and oxygen, since the infra-red radiation emitted after the flame has reached the window of the bomb is small. It may be an effect due to the absorption of ultra-violet radiation by the hot gases behind the flame, with the production of ions which are relatively stable in the absence of water. The recombination of these ions may be the cause of the emission of visible radiation observed by Ellis and Wheeler to occur after the passage of the flame.

These phenomena disappear in the presence of hydrogen, the addition of which increases the rate of attainment of thermal equilibrium both in and behind the burning layers.

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