37. *The Correlation of Flame Movement and Ionisation Current during Explosions.*

By WILLIAM A. KIRKBY.

IONISATION phenomena during explosions of mixtures of carbon monoxide and oxygen in closed cylinders have been studied by Garner and Johnson (J., 1928, 280) and Garner and Roffey (J., 1929, 1123), who obtained current–time curves for the gases during the explosions and correlated them with the emission of infra-red radiation and the speed of flame. The extinction of steady infra-red radiation was found to coincide almost exactly with that of flame. Garner and Johnson therefore suggested that the so-called " afterglow " of such explosions is not " after-burning " but is due to the recombination of ions formed by the absorption of ultra-violet radiation by the hot gases behind the flame front.

In a previous communication (J., 1931, 847), it was shown that, in certain vibratory

explosions of methane and air, there was a correspondence between the frequency of striations in the luminous gases behind the flame front and that of fluctuations in current–time curves representing the electrical conductivity of the gases; and it was concluded that each luminous band, corresponding with a forward movement of the vibrating flame, represented a recombination of ions. In continuation of this work, explosions of mixtures of carbon monoxide and oxygen ($2CO + O_2$) have been studied by using (*a*) a cylindrical explosion vessel of glass, so that direct correlation of the movement of flame and the development of an ionisation current could be obtained; and (*b*) a cylinder of phosphor-bronze, of comparable dimensions, similar to Garner's explosion vessel.

The results, in general, support Garner's suggestion that the " after-glow " can be ascribed, at least in part, to recombination of ions. Such ions, however, need not have

Fig. 1.
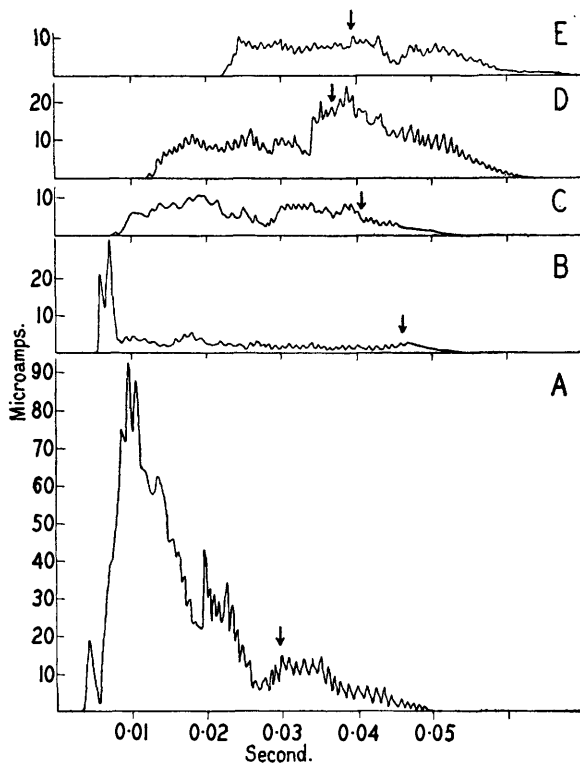
been formed exclusively, or even principally, by the absorption of ultra-violet radiation. To some extent, at least, they may have been produced as an immediate result of chemical reaction at high temperature. The visible radiation may also be accounted for, in part, by the return of electrons to their normal orbits in molecules of carbon dioxide, which have sustained excitation but not ionisation, by the chemical reactions and by the subsequent rise in temperature. For want of data, it is impossible at present to assess the relative importance of the two factors, the recombination of ions and molecular excitation, in the production of the after-glow.

Typical results are reproduced on Plates I and II, in Figs. 1 and 2, and in the tables. Records of ionisation currents were obtained (A, B, C, D, E) in turn, at each of five pairs of pointed platinum electrodes spaced at equal distances along the cylinders. Parallel sets of records were obtained, in both cylinders, with " moist " and " dried " mixtures of composition $2CO + O_2$. On each flame-photograph on Plates I and II, a diagram representing the explosion vessel has been drawn, and a broken line indicates the position of

the electrodes at which the synchronised ionisation-current curve, reproduced under each photograph, was obtained.

During the explosions in the glass cylinder (Plates I and II), an ionisation current, rising immediately to a peak value, was recorded at No. 1 pair of electrodes (see A, Plates I and II), nearest to the point of ignition which was at one end of the cylinder, as soon as the flame arrived there and considerably before the " arrest " in its movement consequent on its touching the wall of the cylinder (see Ellis and Wheeler, J., 1928, 3215). That the maximum ionisation is recorded when the flame is at this position in the cylinder, is to be attributed to the pressure prevailing then being much lower than at any subsequent stage of the explosion. The " arrest " of the flame in each explosion of the " dried " gases occurred almost exactly at the position of No. 2 pair of electrodes (see, in particular, B, Plate II). The conductivity there measured was considerably less, the temperature of the gases within the flame having been immediately reduced. During the later stages of the explosion, the conductivity just within the flame front gradually increased (Plate II, C, D, E).

At each pair of electrodes successively, after the flame-front had passed it, the conductivity recorded varied in a manner directly dependent on the variations in the rate

FIG. 2.
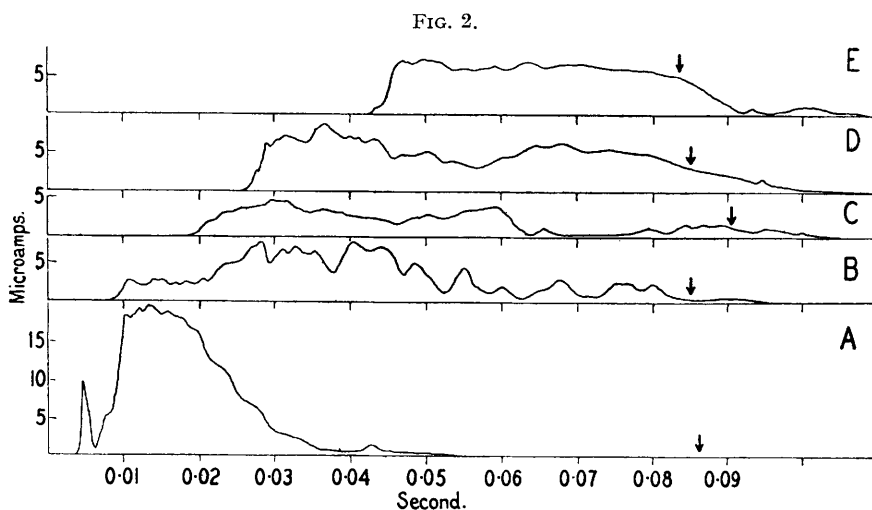
of combustion and consequent rise in temperature, as indicated by the speed of the flame at different stages of the explosion. For example, at the moment of maximum temperature, when the flame had just reached the far end of the cylinder, an increase in conductivity was recorded at each pair of electrodes.

From the synchronised records of movement of flame and development of ionisation current, it can be seen that the ionisation persists for a period which approximately corresponds, at any of the positions along the cylinder, with the duration of the " after-glow " at that position as recorded photographically. Although with the moist mixtures the degree of ionisation is greater than with the " dried," yet neither the ionisation current nor the after-glow persists as long. This is due, partly to the fact that in the moist mixtures, the flame speed being greater, the period of explosion is shorter, and consequently ionised gases are present for a shorter time; and partly to a more rapid recombination of ions in explosions of the moist mixtures, by reason of the steeper pressure gradient consequent on the more rapid movement of flame.

[Giese (*Ann. Physik*, 1882, **17**, 529) showed that, not only does the flame itself possess electrical conductivity, but the gases ascending from a stationary flame remain in a conducting state for some time after the flame has ceased to exist. The conductivity of these gases was regarded by Giese as a specific property of the products of combustion, which are in an abnormal condition, and in time assume the properties of ordinary gases. Turpin

("Studies in the Physical and Chemical Laboratories of Owens College," Vol. I, 1893, p. 283) attempted to measure the duration of electrical conductivity in explosions of hydrogen and oxygen mixtures in a tube.]

At the same time it is to be observed that the duration of after-glow and persistence of ionisation after the flame period are less in moist than in dried mixtures. Other experiments (to be communicated later) have been carried out in a sphere, and comparative measurements made, of the intensity and amount of radiation in the visible region, which were found to be less in moist mixtures (and in those containing small amounts of hydrogen) than in dried mixtures. It has been suggested by Garner and his co-workers (J., 1929, 1123; 1931, 641) that the average duration of life of the activated carbon dioxide molecules is decreased on addition of water vapour, and the internal energy of the molecules is removed by collision, less energy being emitted as radiation. In dried gases, these activated molecules are very stable towards collisions, but can lose their energy by emission of radiation, *i.e.*, $CO_2' \longrightarrow CO_2 + h\nu$, or by resonance to other molecules of carbon dioxide, *i.e.*, $CO_2' + CO_2 \longrightarrow CO_2 + CO_2'$.

The photographs of explosions of " moist " mixtures of carbon monoxide and oxygen show that the flame vibrates with a frequency which increases as the explosion proceeds. Just prior to completion of the explosion (for the last 6 cm. of the cylinder) the frequency remains constant, and is about 1220. This is also the frequency of the fluctuations in the corresponding ionisation current–time curves and of the luminescent bands in the gases behind the flame front. These striations are found to be compression waves, as was shown previously in the case of methane–air explosions (J., 1931, 847), and each corresponds to a trough in the fluctuations of the ionisation current–time curves.


Fig. 3.

With " dried " mixtures the flame speed is much slower than with " moist " mixtures, there is no vibratory movement of flame, and there are no small fluctuations of constant frequency in the ionisation current–time curves as in the " moist " mixtures.

The explosions in the phosphor-bronze were slower than in the glass cylinder. The mean speeds of the flame were 920 cm./sec. for the " moist " mixtures and 390 cm./sec. for the " dried," the corresponding values in the glass cylinder being 1,750 and 640 cm./sec. In consequence, the degree of ionisation was less during the explosions in the former cylinder, though the general character of the ionisation current curves (Figs. 1 and 2) was the same for corresponding explosions.

EXPERIMENTAL.

Series I. Explosions in a Glass Cylinder.—The cylinder was 34·5 cm. long and of 2·5 cm. internal diameter, and the ends were closed by metal plates, rubber washers making gas-tight joints. An ignition plug, which could be used for ignition by either a spark or a hot wire, was fitted centrally in one end-plate, and there was a tap for evacuating the vessel in the other. The cylinder was painted dead black save for a horizontal slit throughout its length, 3 mm. wide, through which flame could be photographed. The electrodes projected 0·5 cm. within the cylinder so that there was a gap of 1·5 mm. at each pair.

A Cambridge oscillograph of the Duddell type, with a periodicity of 2000—2500, was used for recording the ionisation currents. The electrical circuit used is shown in Fig. 3. A potential of 100 volts applied to the electrodes in the cylinder, A, was supplied by the battery, B. The current through the ionised gases between the electrodes passed through the resistance, R, which was varied between 50,000 ohms and 1 megohm, according to the particular pair of electrodes in the circuit, so as to obtain the maximum deflexion on the oscillograph OSC, which was included in the anode circuit (100 volts supplied by the battery, H) of an Osram PX4
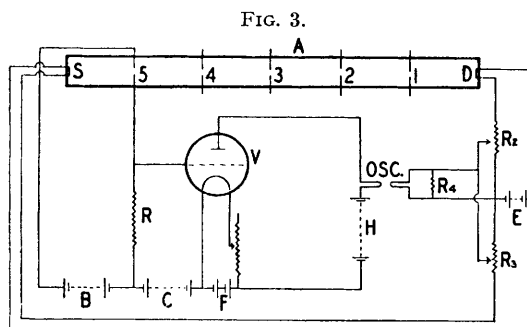
valve, V. The fall in potential due to the passage of the ionisation current through the resistance, R, was applied to the grid of the valve. C and F represent the grid-bias (17 volts) and filament (4 volts) batteries. The principle of this circuit is that described by Teegan (*Nature*, 1929, **124**, 91).

(Fig. 3 also indicates circuits used in Series II, with the phosphor-bronze cylinder, for recording the moment of ignition and the time of explosion, for which purpose a second element of the oscillograph was used. A 24-volt battery, E, supplied current for an ignition wire, D, and a screen wire, S.)

The cylinder was supported horizontally and the mixtures were ignited either by an electric spark or by an iron wire, 0·1014 mm. in diameter and 3—4 mm. long, fixed 0·5 cm. from the end of the cylinder and heated by current from a 24-volt battery. It was found that the latter method (as used by Garner and Johnson) did not always allow a direct record of the time of ignition, which is essential for correlation of the flame and oscillograph records, to be obtained by the oscillograph. Ignition might occur either before the wire fused, at the moment of fusion, or by the combustion of the ends of the wire after fusion. With spark ignition (which could be accurately recorded), and also with wire ignition in those experiments in the glass tube in which flame photographs showed that ignition and fusion of the wire occurred simultaneously, the first indication of an ionisation current was obtained at the instant that flame arrived at the electrodes used for its measurement. This fact was utilised, together with data regarding the speed of flame, to gauge the time of ignition when the hot wire was used.

Carbon monoxide was prepared by the action of sulphuric acid on formic acid, and oxygen from potassium permanganate and hydrogen peroxide. The gases were purified by passage through a series of wash-bottles containing water and dilute aqueous sodium hydroxide. The mixtures ($2CO + O_2$) were stored in glass gas-holders over water if they were to be used " moist," and in long tubes in contact with phosphoric oxide if they were to be used " dried." For filling of the explosion vessel, the " moist " mixtures were caused to bubble slowly through water in a wash-bottle; nevertheless, they could not be regarded as completely saturated with water vapour at the temperature of experiment.

Results.—(a) " *Moist* " $2CO + O_2$ *at* 18°. Measurements from the records (Plate I) are given in the following table. The values for the ionisation current in this and the other tables are not those of saturation current, and no deductions can be made from them as to the amount of ionisation. Under the particular conditions of the experiments, the ionisation currents given are those recorded when the flame is at each electrode in turn, *i.e.*, they are the values of the first maximum of each of the five current–time curves in each series of experiments. The electrodes for the measurement of ionisation currents are numbered as in Fig. 3, No. 1 being nearest to the point of ignition.

Explosions of $2CO + O_2$, " *moist* " *at* 18°.

Expt. No.	Time of explosion, sec.	Electrode No.	Ionisation current, amp. × 10⁻⁶.	Duration of ionisation current, sec.
1	0·021	1	68·0	0·035
2	0·022	2	58·4	0·036
3	0·020	3	10·6	0·021
4	0·022	4	11·2	0·025
5	0·018	5	13·6	0·033

The explosions were vibratory, the frequency of the vibrations being 1220.

(b) " *Dried* " $2CO + O_2$. Measurements from the records (Plate II) are given below :

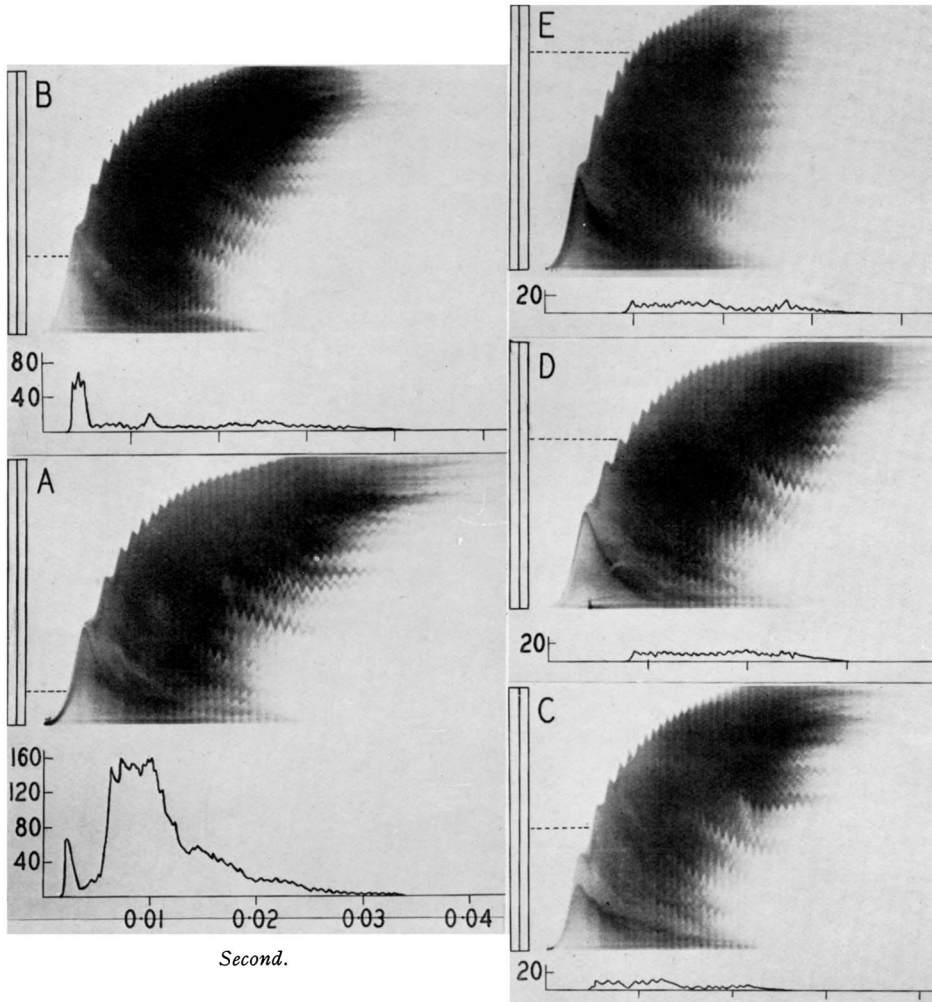*Explosions of* $2CO + O_2$ *dried over phosphoric oxide for 2 hours.*

6	0·055	1	9·3	0·038
7	0·056	2	3·5	0·055
8	0·056	3	2·4	0·065
9	0·058	4	6·9	0·085
10	0·053	5	7·7	0·065

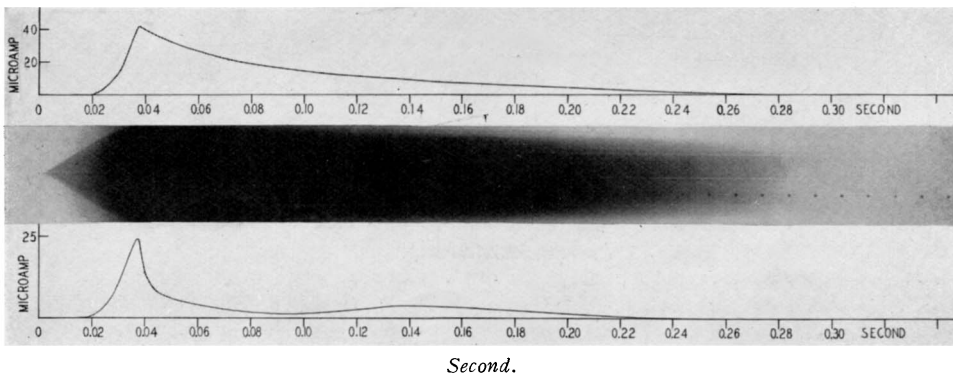The explosions were non-vibratory.

Series II. Explosions in a Phosphor-bronze Cylinder.—The internal dimensions of the cylinder were 35·2 cm. long and 2·5 cm. diameter. The screen-wire, S, for measuring the time of an explosion, was of tinned copper, 0·041 mm. in diameter, and carried an electric current (about 0·8 amp.) just insufficient to cause it to become visibly heated in air.
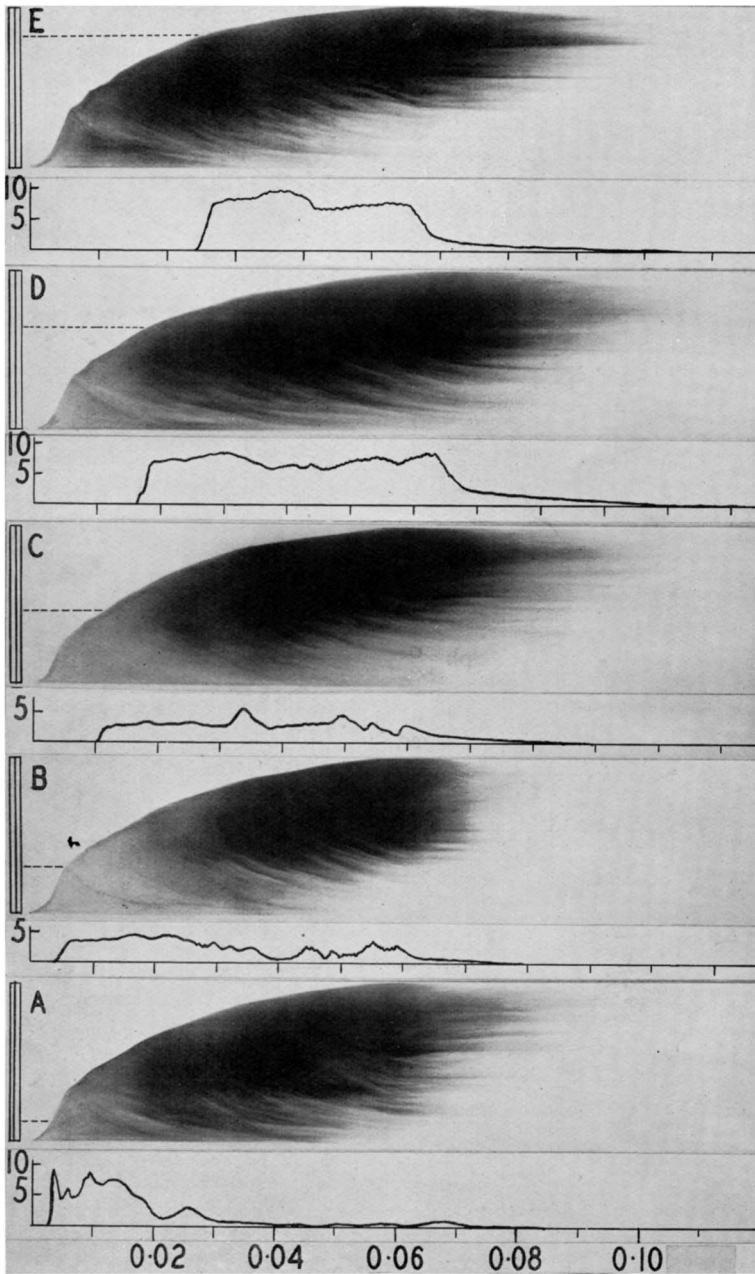
PLATE I.

80
40

160
120
80
40

0·01   0·02   0·03   0·04

Second.

20

20

20

Current, in microamp.

MICROAMP
40
20

0   0.02   0.04   0.06   0.08   0.10   0.12   0.14   0.16   0.18   0.20   0.22   0.24   0.26   0.28   0.30   SECOND

MICROAMP
25

0   0.02   0.04   0.06   0.08   0.10   0.12   0.14   0.16   0.18   0.20   0.22   0.24   0.26   0.28   0.30   SECOND

Second.
Current, in microamp.

PLATE II.

Second.
Current, in microamp.

Results.—(a) " *Moist* " $2CO + O_2$ *at* 17°. Measurements from the records (Fig. 1) are given in the following table. The arrow on each current–time record indicates the time of arrival of flame at the far end of the cylinder.

Explosions of $2CO + O_2$, " *moist* " *at* 17°.

11	0·030		1	19·0	0·035
12	0·046		2	21·0	0·050
13	0·041		3	6·0	0·045
14	0·037		4	5·0	0·053
15	0·039		5	10·1	0·050

The frequency of fluctuations in the ionisation currents during these explosions varied from 1000 to 1100 during the flame period, and thereafter was 900.

(b) " *Dried* " $2CO + O_2$. Measurements from the records (Fig. 2) are given below :

Explosions of $2CO + O_2$, *dried over phosphoric oxide for* 2 *hours.*

16	0·086		1	10·0	0·055
17	0·085		2	3·3	0·085
18	0·091		3	2·4	0·090
19	0·085		4	6·3	0·085
20	0·084		5	7·25	0·068

No regular fluctuations in the ionisation currents, indicative of vibratory explosions, were observed.