38. *The Correlation of Ionisation and Radiation in Carbon Monoxide–Oxygen Explosions.*

By William A. Kirkby.

The author has already demonstrated (J., 1931, 878) an apparent connexion between the recombination of ions formed during explosion and the after-glow which may succeed the passage of flame in closed vessels. Photographic records of explosions in a sphere indicated that the after-glow was most intense slightly after the time that the ionisation was at a maximum; and that, following this maximum, the duration of the fading after-glow corresponded closely to that of the diminishing ionisation. It has now been found, however, that there is no other simple relationship. The decay of ionisation is essentially different in character from the decay of the after-glow, for it follows the law of recombination of ions, and consequently the decay of the after-glow cannot wholly be attributed to ionic recombination.

In this study, use has been made of photoelectric cells. The visible and the near infra-red radiation have been recorded separately, and measurements have been made of their variation of intensity with time.

Experimental.

The explosion vessel was a glass sphere, 9 cm. in diameter, as used in previous work (*loc. cit.*). Following the method originally adopted by Wilson ("Electrical Properties of Flame," p. 57, 1912) for measuring the ionisation in flames, the explosion sphere was fitted with two stout wires of platinum, diametrically opposed, which served as conductivity electrodes across a gap of 1 cm. at the centre. The mixture was ignited by a single secondary discharge from an induction coil, across a 2-mm. spark-gap formed at the centre of the sphere by two platinum wires. In each experiment the primary current of the induction coil at break was 5 amps. The passage of the flame through the sphere, as seen through a horizontal slit 3 mm. wide on its equator, was photographed on a revolving drum. The peripheral speed of the drum was obtained by photographically recording, simultaneously with the experiment, the spark of the mercury contact-breaker of an electrically-maintained tuning fork of 100 frequency.

The radiation from an explosion passed through a circular window, 2 cm. in diameter (the remainder of the outside of the sphere, except the equatorial window for the flame photograph, being painted black), and was then focused on the cathode of the photoelectric cell by a quartz lens.

For measurement of the visible radiation, a G.E.C. cell, KMV6, was used; this is a vacuum cell with a potassium cathode, its limits of sensitivity being at 0·4 μ and 0·78 μ, with a maximum at 0·6 μ. A Wratten No. 64 Minus Red (light) Filter, with limits of transmission at 0·27 μ and 0·63 μ, was used to cut out the near infra-red. Thus the visible radiation received by the cell extended from 0·4 μ to 0·63 μ. For measurement of the near infra-red radiation over a small range, an Oxford Instrument Company's vacuum cell, X11, was employed. This has maximum sensitivity at 0·85 μ with an upper limit at 1·2 μ. Radiation below 0·74 μ was cut out by a Wratten No. 87 infra-red filter. Thus the range of infra-red radiation measured by this cell extended from 0·74 μ to 1·2 μ and did not include the important bands at 2·72 μ and 4·4 μ (due to water and carbon dioxide molecules respectively); but, even so, these experiments showed certain differences of a minor character between the infra-red and the visible radiation.

The photoelectric current set up by the radiation was amplified and recorded on a Cambridge Duddell oscillograph by means of the circuit shown on the right-hand side of Fig. 1. The photoelectric current from the cell, P, was proportional to the intensity of the light received by it from the explosion in the sphere, A. The battery, B_2, supplied a potential of 50 volts to the anode of the cell. The current passed through a high resistance, R_2, producing a change in the potential of the grid of an Osram PX4 valve, V_2, and therefore a change in the anode current which passed through the oscillograph, OSC. The value of the resistance R_2 was usually a few megohms. A potential of 100 volts was applied to the anode of the valve by the battery H_2. The valve-filament and grid-bias batteries, F_2 and C_2, were 4 volts and 17 volts respectively. The circuit was mounted within a copper box which, in turn, was inside and insulated from a second box, thus screening from electromagnetic fields the photo-cell and its connexions to the grid of the valve through the high resistance.

FIG. 1.

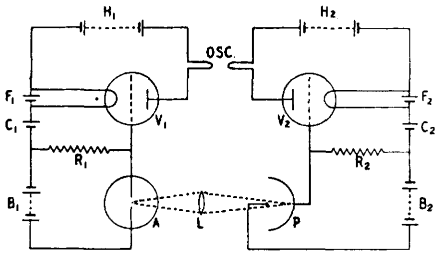
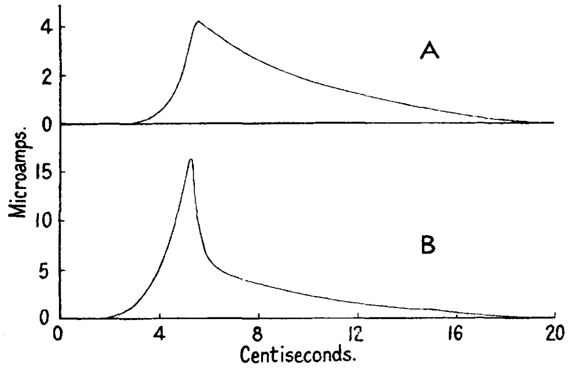


FIG. 2.



The method of measurement of the ionisation produced during explosions is described in detail in the preceding paper, but the circuit used to record the ionisation current for correlation with the photoelectric current is shown in Fig. 1. The ionisation current between the point electrodes in the explosion sphere, A, was amplified by a method similar to that used for the photoelectric current. The battery, B_1, supplied a potential of 100 volts to the conductivity electrodes, and the current passed through the high resistance, R_1 (a few megohms), thereby causing a potential fall proportional to the current, which was applied to the in-put of another Osram PX4 valve, V_1. The batteries, H_1 (100 volts), F_1 (4 volts), and C_1 (17 volts), were for the anode, filament, and grid bias respectively. The second vibrator of the oscillograph, OSC, was connected in the anode circuit of the valve to record the ionisation current.

As this investigation was the first of its kind, variation in experimental conditions was reduced to a minimum, and in all the experiments the gas mixture employed was $2CO + O_2$. The gases were prepared and stored as described in the preceding paper, and the degrees of dryness were also obtained as in those experiments.

Series I.

Synchronous Records of Ionisation and Visible Radiation.—Results typical of those obtained with " moist " and " dried " mixtures are shown below :

Expt. No.	Flame period (sec.).	Ionisation record.		Radiation record.			
		Time to max. current (sec.).	Max. current (10^{-6} amp.).	Time to max. current (sec.).	Max. current (10^{-6} amp.).	Energy received.*	
						Up to max.	After max.
1 Moist	0·008	0·009	45	0·0095	5·7	8	109
2 Dried	0·038	0·039	23	0·040	7·1	24	208

* Area under the curve; given in arbitrary units.

On Plate IA is shown a typical set of three records, simultaneously taken, of the explosion of a " dried " mixture. Above and below the photograph respectively are the photoelectric and the ionisation current–time curve. The only difference of any importance in the character of these records from those of a " moist " mixture is in the length of the flame period, which is much longer when a " dried " mixture is employed. Whether the mixture be " moist " or " dried," however, the after-glow always appears during the flame period, and first begins to be intense during the later stages of the explosion when pressure is rapidly increasing. It is seen from Plate IA that the maximum in the photoelectric current, which indicates the emission of maximum intensity of visible radiation, occurs at the end of the flame period; this, as the original photograph clearly shows, is also the most intense region of the after-glow as photographically recorded. From the results in the foregoing table, however, the maximum in the photoelectric current occurs very slightly after the time of maximum ionisation current; and from the records on Plate IA it is seen to correspond with the steepest portion of the ionisation current decay curve, immediately after its maximum. The maximum amount of ionisation occurs at the moment of maximum temperature, at the end of the flame period, when the flame is just arriving at the wall of the sphere. At this moment, because it is also the moment of maximum pressure, the ions formed during the explosion sustain the quickest rate of recombination, and the maximum intensity of radiation due to this source is then exhibited.

Series II.

Synchronous Records of Ionisation and Infra-red Radiation.—The following results are typical of those obtained with " moist " and " dried " mixtures :

Expt. No.	Flame period (sec.).	Ionisation record.		Radiation record.			
		Time to max. current (sec.).	Max. current (10^{-6} amp.).	Time to max. current (sec.).	Max. current (10^{-6} amp.).	Energy received.	
						Up to max.	After max.
3 Moist	0·008	0·009	54	0·012	1·2	4·0	30
4 Dried	—	0·036	24	0·039	1·0	5·5	29

The values in the above table for " maximum current " and " energy received," from the radiation record, are not comparable with similar values in the table of Series I, since the sensitivities of the two photoelectric cells were different.

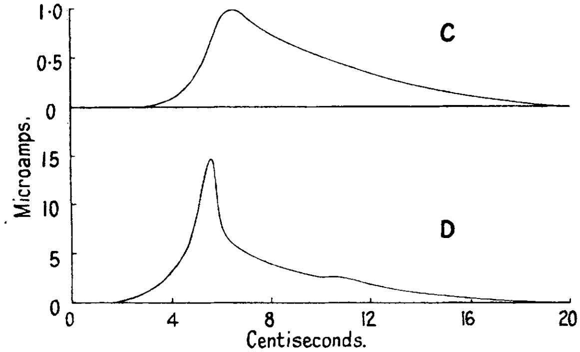
The maximum in the photoelectric current from the infra-red radiation (Fig. **3**, curve C) is blunt, whereas that for visible radiation was sharply pointed.

It is seen from the last table that the maximum in the photoelectric current occurs later (by 0·003 sec.) than the moment of the three coincident maxima of temperature, pressure, and ionisation current. There is a considerable increase in the infra-red emission during the period of most rapid ionic recombination, and these two phenomena may be connected. Garner and Johnson (J., **1928**, 296) suggested that in their experiments the residual infra-red radiation, which was emitted after the flame had passed entirely through the explosive mixture in the cylinder, and the emission of visible radiation may be complementary phenomena. The radiation emitted on recombination of ions will be absorbed by certain carbon dioxide molecules, bringing about a process analogous to that of " sensitised fluorescence " ; the absorbed radiation, undergoing degradation, will stimulate the vibrational energy of the molecules, with consequent emission in the near infra-red region.

The outstanding feature of the results, however, is neither the delayed incidence of the radiation maxima nor the difference in their shape, but the pronounced lack of similarity in the characters of both radiation curves as compared with the ionisation curve. The difference in character is fundamental, and yields proof that the after-glow in gaseous explosions is chiefly due to some cause other than the recombination of ions; though it remains true that the period during which this cause is operative is closely identified with the period of ionic recombination. Since the number of molecules formed during the chemical reaction which sustain excitation will be much larger than the number which simultaneously are ionised, the after-glow may be attributed to the return of the excited molecules to a normal state.

Two of the synchronous records of the explosion of a " dried " mixture are shown in Figs. 2 and 3. B and D are the ionisation curves, and the radiation curves are A (visible) and C (infra-red). They were obtained by photographically enlarging to several times their original size the oscillograph records of the amplified currents, and thence calculating and replotting, millisecond by millisecond, the actual currents entering the amplifiers. The rise of the curves from zero to their maxima calls for little comment now; the principal conclusion of this paper is founded upon the shape of the curves as they decay from their maxima, or just after, to zero.

FIG. 3.



The decay portions of some of these curves for a period of 30 millisecs. after maximum, the first ordinate being neglected, are expressible by (1) $C_{vr} = K_1 t^{0\cdot021} e^{-0\cdot022t}$, for visible radiation, where C is current in microamps., and t is time in millisecs. after maximum current, (2) $C_{ir} = K_2 e^{-0\cdot0202t}$ for the infra-red radiation, (3) $C_i = K_3 t^{-a}$, where the value of a is 0·38—0·40, for the ionisation current. The exponential factor in the first expression is dominant, and the decay of radiation in the two regions of the spectrum is essentially of the same character.

If the visible radiation were due to the recombination of ions, the intensity of the radiation would vary with the rate of recombination, and be proportional to the rate of change of current, which is given by $dC_i/dt = -aK_4 t^{-(a+1)}$. The expression for the decay of ionisation is of quite a different character from that for the decay of visible radiation.

Equations in ascending powers of t, obtained by a method based on the theory of differences, show that there can be no simple correlation of visible radiation with ionic recombination; *e.g.*, the decay of visible radiation may be written, $C_{vr} = 4\cdot22 - 0\cdot09t + 0\cdot001t^2$, whereas $C_i = 17\cdot36 - 3\cdot13t + 0\cdot40t^2 - 0\cdot03t^3 + 0\cdot001t^4$, and the rate of change of current during the decay period of ionisation is given by $-dC_i/dt = 3\cdot13 - 0\cdot8t + 0\cdot09t^2 - 0\cdot004t^3 + \ldots$.

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