

CXXVI.—*Ionisation in Gaseous Explosions.*

By WILLIAM ANTHONY KIRKBY.

DURING the past few years increasing attention has been paid to the rôle of ionisation during gaseous explosions. Apart from experiments to determine the possible effect of electric and magnetic fields on the development of flame, measurements have been made of the amount of ionisation produced during explosions. Latterly, a more detailed study of ionisation phenomena during gaseous explosions has been undertaken by Garner and Saunders and their co-workers, who have attempted to measure the instantaneous values of the ionisation, and to relate them to other phenomena of explosions, such as the speed of flame and the emission of infra-red radiation. The results of their experiments have led them to conclude that the ionisation is mainly thermal in character (*Trans. Faraday Soc.*, 1926, **22**, 281, 324; 1927, **23**, 242, 248, 256; *J.*, 1929, 1123).

The method adopted by these authors for measuring the ionisation occurring during an explosion was to allow the flame to travel (in either a spherical or a cylindrical vessel) between two metallic electrodes maintained at different electrical potentials. Measurements of the current produced as the gases were rendered conducting were made with an Einthoven string galvanometer, having a sensitivity of  $10^{-8}$  amp. and a period of vibration of its fibre of  $1/350$ -sec.

From the details given in Garner and Saunders' papers as to the manner of using the galvanometer, and from a study of some of the time-current curves reproduced, it is doubtful whether much significance can be attached to conclusions therefrom as to the character of the chemical reactions or the mode of propagation of the explosions. In their second paper quoted above, these authors have reproduced typical photographs of curves obtained by them, and in five out of the six curves it is evident that free vibrations of the galvanometer were recorded, due to the absence of the requisite conditions for critical damping. In Fig. 2 of their paper (*loc. cit.*, p. 327) a time-current curve is given to indicate the general character of the records obtained. This exhibits similar free vibrations of the galvanometer and shows that a deflexion was obtained greater than that given by a steady direct current. Any rapid variations in the current could not, therefore, be truly recorded. The authors state that the sensitivity of their galvanometer varied as much as 50% during the course of a week or two. This, coupled with the fact that the sensitivity was kept at a constant value by adjustment of the tension on the fibre (with consequent alteration in its natural period), makes it almost impossible to draw conclusions from the character of the time-current curves obtained.

In order to study the relationship between ionisation and the propagation of flame, further experiments similar to those by Garner and Saunders have been carried out, but a more accurately recording galvanometer circuit has been used, as described in Section I of "Experimental."

*The Relation between Ionisation and After-burning.*—Ellis and Wheeler (J., 1927, 310) have described the re-illumination which occurs, in closed vessels, following the passage of a flame through explosive gaseous mixtures. This intense luminescence, which originates in the neighbourhood of the point of ignition, they attribute to "the completion of the combustion, under increased pressure, of molecules of combustible gas that escaped being burnt whilst the flame was travelling." A consideration of the relative actinic effects of the flames and of this "after-burning" led them to suggest that different forms of radiation were being emitted, although there appears to be no evidence that the chemical reactions during after-burning differ in character from those during the propagation of flame. They have also noted that the after-burning gas is stationary and homogeneous whilst the flame surface is moving quickly across the photographic field and is only a thin film. They do not ignore the contributions to the luminosity which must necessarily be made under changing pressure and temperature respectively by changes in the equilibria (i)  $2\text{CO} + \text{O}_2 \rightleftharpoons 2\text{CO}_2$  and (ii)  $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO}$  (in mixtures in which this must occur). Their contention in all cases is the same, *viz.*, that the luminosity observed is due, wholly or partially, to continued chemical action.

As a result of experiments on the ionisation accompanying explosions of mixtures of carbon monoxide and oxygen, Garner and Johnson (J., 1928, 280) suggested that the luminescence attributed by Ellis and Wheeler to "after-burning" is due to the neutralisation of ions produced during the passage of the flame. Their conclusions are based on the observed persistence of ionisation, after the passage of the flame, at the end of a cylinder opposite to that at which ignition took place.

By means of the galvanometer circuit herein described, direct correlation was obtained of the progress of flame through an explosive mixture of gases (as recorded photographically) with the ionisation which occurs; and evidence was obtained that after-burning was closely connected with recombination of ions formed during the primary reactions.

#### EXPERIMENTAL.

I. *Method.*—As the flame travelled between two platinum electrodes fixed in the explosion vessel and maintained at a given

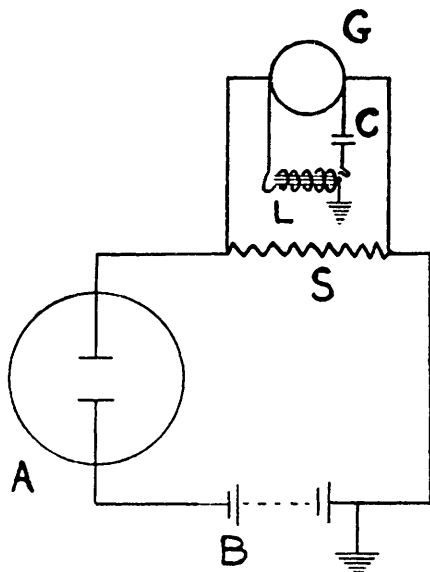
potential difference, which could be varied according to the characteristics of the explosive mixture, the ionisation current was measured by means of an Einthoven string galvanometer. This was fitted with a silvered glass fibre, having a resistance of 3600 ohms, with which the conductivity electrodes were connected in series. The deflexion of the galvanometer was recorded on a revolving drum camera carrying Lumière sensitised paper on which was photographed simultaneously the passage of the flame through the explosion vessel as seen through a horizontal slit.

In order to analyse the rapid ionisation phenomena as accurately as possible, it was essential (i) that the period of the galvanometer should be as small as possible and (ii) that critical damping should be obtained without adding to the moving system. On using the galvanometer with the string at a fairly high degree of tension (natural frequency 400), it was found to "overshoot" considerably. The utility of the galvanometer is not determined by its current sensitivity, but by its sensitivity at a certain, arbitrarily fixed but constant, time of deflexion. In order to secure the two essential conditions, a resonant shunt circuit was introduced (see Butterworth, Wood, and Lakey, *J. Sci. Instr.*, 1926, 4, 8). The fundamental requirement is that the resonant frequency of the electrical oscillation in the shunt is the same as that of the free mechanical oscillation of the galvanometer string. Such a shunt merely increases the mechanical damping without affecting in any way the sensitivity. By this means a small amount of extra damping is provided, which, in conjunction with the mechanical damping of the string which is already considerable, ensures a dead-beat condition for a suddenly applied current.

The electrical circuit is shown in Fig. 1. The voltage applied to the electrodes in the spherical explosion-vessel, A, was supplied by the battery, B, the positive pole of which was earthed. The current through the ionised gas between the electrodes passed through the shunt, S, to the galvanometer, G. The resonant shunt circuit, connected in parallel with the galvanometer, consisted of a choke, L, with an iron core, and a condenser, C, in series. The approximate value of the inductance of the choke being known, the value of the condenser required could be calculated. The condenser value was finally adjusted by experiment. When the resonant shunt circuit was being adjusted to give a critically damped record, a current of known value was "tapped" into the galvanometer (shunted) through a circuit having an *E.M.F.* of the same order as that used during an experiment and a resistance of the same amount as the effective resistance (about 2 megohms) of the gas space between the conductivity electrodes.

The galvanometer was calibrated frequently, usually just before each experiment, with the aid of a standard voltmeter. For the experiments described below, a deflexion of 1 cm. was produced by a current of  $3.9 \times 10^{-6}$  amp. During early experiments it was found that the apparent sensitivity of the galvanometer varied as much as 40% during the course of a few days, although re-determinations of the resistance of the galvanometer string showed that no alteration had occurred in its value. The variation was subsequently traced to a thermoelectric effect consequent upon the junction of dissimilar metals in the calibration system. The use of brass wire

FIG. 1.



throughout eliminated this apparent variation in sensitivity. It was found necessary to have all the leads to the galvanometer in earthed metal casings to shield it from the effect of the alternating current used for the lighting circuit of the laboratory.

By this method it has been found possible to record maximum values for the ionisation currents during explosions, and any sudden variations in the current, with a high degree of accuracy.

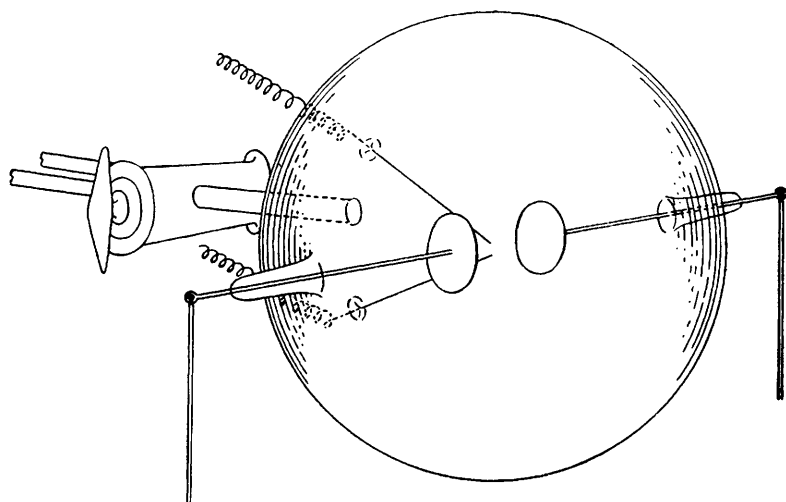
II. *Relation between Ionisation and After-burning.*—The explosion vessel (Fig. 2) was a glass sphere, 9 cm. in diameter, fitted with platinum electrodes forming a 2-mm. spark gap at the centre. Two platinum discs, 1.5 cm. in diameter, were fixed 2 cm. apart at the centre of the sphere diametrically opposite each other. These were used as the conductivity electrodes. With this arrangement,

explosion was completed before any cooling could occur by contact of the flame with the walls of the vessel, whilst the flame spread outwards from the spark and the re-illumination centred itself round the point of ignition, both symmetrically with respect to the conductivity electrodes.

In carrying out an experiment, the sphere was twice alternately evacuated and filled with the required mixture, prepared beforehand and stored in a gas holder over water. Ignition was effected by a single secondary discharge from an induction coil.

The deflexion of the galvanometer was recorded on a revolving drum camera on which was photographed simultaneously the

FIG. 2.



passage of the flame through the sphere, as seen through a horizontal slit, 3 mm. wide, on its equator. The speed of revolution of the drum camera was obtained by means of an electrically maintained tuning fork of 50 frequency.

On Plate I are shown photographic records of the flame as it travels through the sphere, together with time-current curves as recorded by the galvanometer. The mixture for each experiment was  $\text{CO} + 2\text{O}_2$ , saturated with water vapour at  $18^\circ$ , initially at atmospheric pressure. The potential applied to the electrodes was (A) 38.8 and (B) 29 volts. The time taken for the flame to reach the walls of the sphere was (A) 0.0184 sec. and (B) 0.019 sec., and the maximum value of the current was (A)  $6.5 \times 10^{-6}$  amp. and (B)  $5.3 \times 10^{-6}$  amp. (The last pair of values have no absolute significance.) It will be seen that the current is first recorded when

LATE I

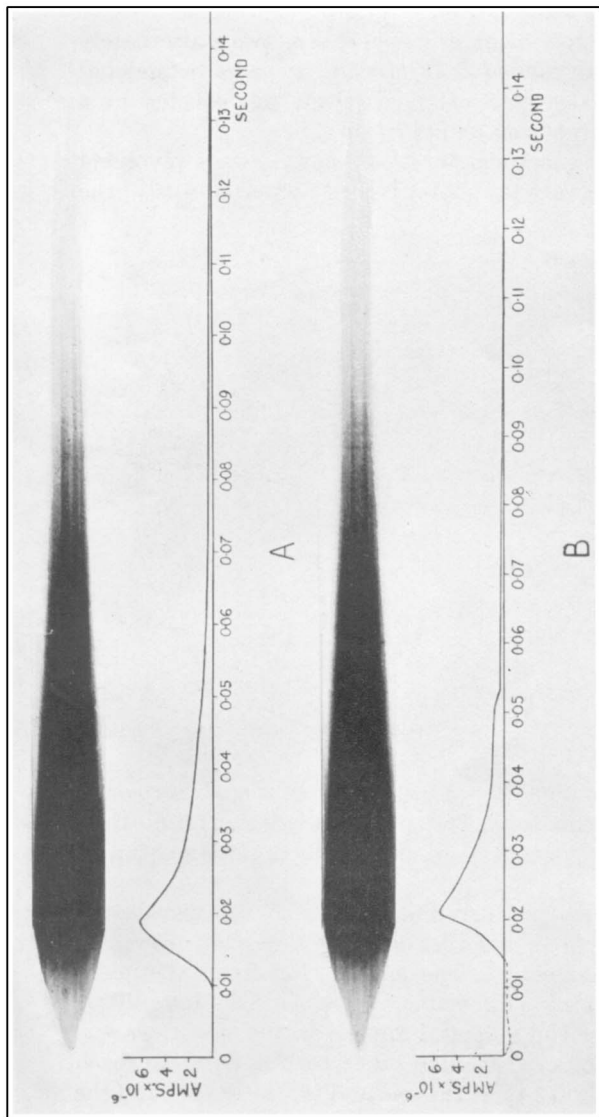
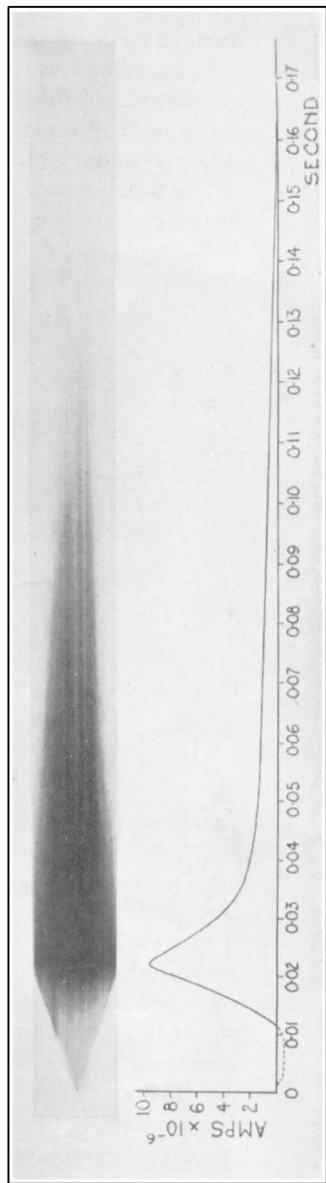


PLATE II



the diameter of the flame is about two-thirds that of the sphere. It then rises rapidly to a maximum at the moment when the flame has arrived at the walls of the sphere. In record (B) a small current, shown in broken line, was indicated in reverse direction to that of the battery circuit in series with the electrodes. This was probably due to the *E.M.F.* of the flame itself.

On comparing these time-current records with that given by Saunders and Sato (*Trans. Faraday Soc.*, 1927, **23**, 252) as characteristic of explosions of carbon monoxide and oxygen, roughly dried by phosphoric oxide, it will be seen that in the present experiments no fluctuations of the current are obtained as in their record. Saunders and Sato state that explosions of moist mixtures of carbon monoxide and oxygen sometimes gave similar fluctuating records. The asymmetrical point of ignition (a few mm. from the walls) in their spherical explosion vessel renders difficult the interpretation of their record, for cooling of the flame under such conditions occurs, by the contact of part of its surface with the wall of the sphere, before the completion of the explosion.

Ellis and Wheeler (*loc. cit.*) have shown that the luminescence which they attribute to after-burning first begins to be intense when the unburnt mixture ahead of the flame-front can no longer move freely under the expansive force of the burning gases, and consequently combustion proceeds under a rapidly increasing pressure. In the present experiments it is only at this stage of the combustion that the ionic current becomes appreciable. At the same time it is to be observed that no deflexion of the galvanometer is recorded when the flame reaches the conductivity electrodes.\* The ionisation, therefore, appears to occur in the gases through which the flame has passed, *viz.*, those situated around the centre of the sphere. Moreover, the conductivity curve decays at the same rate as the intensity of the re-illumination of these gases diminishes, after the flame has completely filled the vessel, and becomes zero when the luminescence dies out 14 centiseecs. after ignition.

That the ionic current should be found to have its origin in the gases situated about the centre of the sphere is consistent with the observation first made by Hopkinson (*Proc. Roy. Soc.*, 1906, *A*, **77**, 387), that it is the gases so situated which represent the hottest zone in the explosion vessel. The recombination of ions in this zone may, then, partially account for the intense re-luminescence. The rate of recombination of ions, as shown by the slope of the conductivity curve, is most rapid during the first 0.5 centisecond after the expiration of the flame surface. The intensity of the lumin-

\* In other records small deflexions approximating to about one-twelfth of the maximum current have been recorded.

escence is greatest over the same period. Now, Saha (*Phil. Mag.*, 1920, **40**, 472, 808) has shown that the ionisation of a neutral atom can be treated as a reversible chemical reaction of which the equilibrium conditions can be fixed by the thermodynamic methods developed by Nernst and referred to by him as the "reaction isobar"; and, further, he has shown mathematically that the degree of ionisation of a gas can be expressed in terms of pressure, temperature, and the ionisation potential. High temperature and low pressure both favour ionisation. In explosions in a closed sphere, during the later stages, the temperature and pressure increase rapidly to a maximum. As the temperature of the gases at the centre of the vessel increases, the degree of ionisation increases also until, just before the completion of the explosion, the effect of the rapidly increasing pressure is manifested by a reduction in the rate of increase of ionisation. The recombination of ions thus effected is responsible for the point of inflexion of the time-current curve (Plate I) immediately before the maximum value is obtained.

Without prejudice to other possible causes, it appears probable that the re-illumination of the gases at the centre of the vessel is due, in part at least, to the recombination behind the flame-front of ions formed during the primary chemical reactions.

This work forms part of a research, under the general direction of Dr. R. V. Wheeler, that is being carried out for the Safety in Mines Research Board, to whom the thanks of the author are due for permission to publish the results.

*Addendum (March 24th, 1931).*

The time-current curve illustrated by Saunders and Sato (*loc. cit.*) refers more particularly to explosions of carbon monoxide and oxygen roughly dried by phosphoric oxide, whereas in my experiments the mixtures were saturated with water vapour at 18°. I have therefore carried out further experiments, using similar methods to those employed by Saunders and Sato for drying the gases.

The mixture of gases was passed at the rate of 4.5 l. per hour through three tubes in series, each 30 cm. long and filled with purified phosphoric oxide, into the evacuated explosion vessel. Thereafter, the procedure was as previously described. Records of one experiment are reproduced on Plate II. The mixture contained 38.5% of carbon monoxide and was initially at atmospheric pressure. The potential applied to the electrodes was 38 volts. It will be seen that the time-current record differs in no respect from those obtained during explosions of the moist gases.

In one experiment, a mixture of the same composition was allowed



to remain in contact with purified phosphoric oxide during 15 hours before being exploded. The maximum value for the ionisation current was less than with the more roughly dried mixtures, but the time-current curve was of the same character.

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