The Movements of Flame in Carbonic Oxide-Oxygen Explosions.

RECENT WORK AT SOUTH KENSINGTON.

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IF the highest reward a teacher can reach is to start a school which will carry on his lines of research, improving his technique, extending his data and enlarging his horizon, I may well claim that my lines have fallen on pleasant and fruitful places. This reflection is not a new one, for I have had many students who have extended and improved on my experiments, but it is brought vividly to mind by the appearance of a memoir by my old pupil and colleague, Prof. W. A. Bone, in conjunction with Dr. R. P. Fraser, on the photographic analysis of carbonic oxide explosion-flames (*Phil. Trans.*, A, 228; 1929).

It is more than fifty years ago since the observation was made (at Oxford) that an electric spark, which would fire 'knall-gas' (a mixture of two volumes of carbonic oxide with one volume of oxygen— $2\text{CO} + \text{O}_2$) in a moist eudiometer, failed to cause an explosion when the gases and vessel were dried. The experiment was tried because in repeating Bunsen's work on the division of oxygen between an excess of carbonic oxide and hydrogen, I had found that the steam readily oxidised carbonic oxide at flame temperatures leaving free hydrogen. The moisture present in Bunsen's experiments must have taken part in the change, and the amount of carbon dioxide formed depended not only on the relative affinity between carbonic oxide and oxygen, but also on the quantity of steam present.

Since carbonic oxide was oxidised apparently by water, and not directly by oxygen, an attempt was made to measure the rate of the knall-gas flame along a tube when different amounts of steam were present. I can well remember how I first tried to do this by photographing the explosion flame with a camera swung on a long pendulum in front of a coiled lead pipe with glass end-pieces which were brought vertically one above the other.

The camera, as it swung, broke a circuit and fired the gases at one end of the coil: the object was to record the two flashes at either end of the coil on the plate as it was moving with a known velocity. The passage of the flame appeared to be instantaneous, but the explosion was so violent that the glass-piece at the farther end was shattered and the camera put out of action. This was in 1881: just afterwards came the discovery of *l'onde explosive* by Berthelot, and the photographs of the 'uniform' and 'vibratory' movements by Le Chatelier. Some years later (in 1895) my students at Manchester and I made the first spinning-wheel camera to study explosion-flames—especially those of cyanogen. I remember how we were warned that the wheel would probably fly to bits, and that the film attached to the wheel would certainly break off. Neither of these things happened; and from this crude rotating-film has descended a line of machines which has now culminated in the

beautiful high-speed camera of Dr. Fraser's described in this memoir.

The most novel feature in this camera is the method of driving the rotating drum by contact between a small friction-wheel and the spherical surface of a phosphor-bronze driving-wheel attached to the motor. The friction-wheel is built up of two steel plates claspings a disc of compressed leather, the surface of which is machined at such an angle that only a narrow rim of it is actually touching the driving wheel. The latter (with its motor) is fastened to a turn-table which can be moved to make contact with the friction-wheel at any point in a line from the centre of the spherical surface to its outer edge. The gear ratio between the motor and the drum can thus be varied from one infinitely small up to a ratio of 4.5 to 1; and any constant speed between 30 r.p.m. and 16,000 r.p.m. can be maintained. With the larger of the two cameras now installed at South Kensington, a vertical film speed of 160 metres per second can be secured readily. Owing to the massiveness of the driving-wheel and the balance of the moving parts, very smooth running is attained, the vibration even at the highest speeds being remarkably small. The rate of the drum is measured by a Hasler high-speed counter which can be put in action at any moment, and works automatically. Having had the privilege of testing this driving gear recently, I was delighted with its steadiness over a wide range of speeds, and speaking from a long experience, could assure Messrs. Bone and Fraser (to borrow the words of Mr. Staple) that I "envied them the luxury of their own feelings on this occasion".

With this fine instrument the authors have followed in detail the spread of the flame in carbonic oxide knall-gas, both when moist and when submitted to various stages of drying up to the desiccation produced by contact with purified phosphorus pentoxide during eight months.

SPREAD OF FLAME IN CARBONIC OXIDE KNALL-GAS.

The first photographs in the memoir bring out very clearly the difference in the burning of the moist and dried gases. Fig. 1 (with a moist $2\text{CO} + \text{O}_2$ mixture) shows how the flame starts rapidly with an accelerating motion for the first 5 cm. from the powerful discharge spark; it then slackens and proceeds at a nearly uniform rate to the ends of the tube. At this moment there is a sudden increase of luminosity, which spreads backwards towards the centre of the tube. The region immediately round the sparking wires is at first more luminous than the flame fronts, forming a bright vertical streak on the film. It is probable, as the authors say, that the combustion is more rapid near the spark than elsewhere, and this is borne out by the fact that this narrow zone loses

its light and remains *dark* when the central region becomes luminous again—an indication that this layer of gas is completely burnt. Analysis of the residual gas showed that after the flame died out the combustion was complete throughout.

On the other hand, when the ignition occurs

movement, a dark patch spreads from the centre of the tube and occupies a central zone 10 cm. long by the time the outward movement of the flame ceases. At this moment, some 120 milli-seconds after the spark, the dark patch contracts, and a bright flame nearly fills the central region of the

FIG. 1.

FIG. 2.

FIG. 3.

(Fig. 2) in a moderately dried gas (6 hours' contact with phosphorus pentoxide), the flames start slowly, but with an increasing speed, until, about 6 cm. along the tube, they are retarded and proceed at a slow uniform pace nearly, but not quite, to the ends of the tube. During this slow uniform

tube, leaving (as in the moist gas) only a narrow dark streak. The luminous flame persists in this semi-dried gas six times as long as in the moist, and about 1 per cent of the gas was left unburnt.

With stronger drying the flames last longer (Fig. 3), and where the first retardations occur, after 3 cm. run, actually stop for a considerable time, and then proceed outwards until a second

¹ The illustrations are from *Phil. Trans.*, A, 228, by courtesy of the Royal Society and Prof. W. A. Bone.

stationary period ensues. Each stoppage is accompanied by the development of a dark central zone; the flames finally reach the ends of the tube when the usual re-luminence spreads backwards. In this slow flame, although it had spread completely through the tube, more than 10 per cent of the gas remained unburnt. It is to be noticed that while the rapid flame in the moist knall-gas is traversed by marked bands, similar to the 'reflection' waves in my old photographs, there are no such bands visible in the flames of the dried gases.

In similar experiments made in a longer tube (60 cm. long) the same general phenomena were recorded; but in the moist mixture the initial period was marked by vibrations, and in the well-dried mixtures the 'halts' became temporary 'retreats', and the flames appeared to be drawn back and extinguished before they reached the ends.

In these experiments on long-dried mixtures, a large proportion of the gas remained unburnt. It was such a desiccated knall-gas that I saw tested in Prof. Bone's laboratory. It resisted ignition by many powerful sparks; but when at last the electric discharge sufficed for inflammation, the flame could be easily followed by the eye until it halted, remained stationary, and went out about half-way along the tube. The colour of the flame appeared to me different from that in the moist gas—the front of the flame being a pinkish orange. This colour was perhaps more marked when long-dried knall-gas was exploded in glass bulbs.

I may add that, more recently, I have witnessed similar experiments elsewhere—the conditions of dryness and purity being equally assured. The knall-gas showed the same resistance to powerful sparks, but when ignition took place the flame travelled with a slow motion to the ends of the tube.

This part of the South Kensington research is concluded with a very suggestive experiment. Two similar tubes were filled with the knall-gas from the same holder: one tube was plain and the other furnished with wires sealed in half-way between the central firing-point and the two ends. After prolonged drying each tube was fired centrally, the second tube having the supplementary wires attached to the two poles respectively of a Wimshurst machine. The flames in both tubes are seen to start slowly. In the plain tube the flame halted twice, then *receded* and went out: in the second, the flames travelled at unequal rates, which, on the flames approaching the charged wires, were greatly accelerated. On the arrival of the flames near the ends of the tube, their brightness is suddenly increased, and this luminosity extends backwards until it nearly fills the tube except for the central dark zone. It was evident that the resistance to combination offered by the dryness of the gases could be overcome by the electrostatic field, and apparently this 'relief' was more easily given by one pole than the other.

I have seen other effects of the electric field on the propagation of the carbonic oxide flame obtained in Prof. Bone's laboratory since this memoir was read: I can only say, without anticipating the explanation, that the problem presented by the

burning of this gas has become one of the most interesting in physical chemistry.

THE EFFECT OF DIFFERENT SPARK DISCHARGES.

In part 2 of their memoir the authors study the effect on the flame of different modes of ignition of the moist knall-gas. There is little difference

FIG. 4.

between the spread of the flame when the ignition is made by heating a platinum wire to redness or by suddenly fusing a fine wire. In each case there appeared to be some little delay before ignition; the flame then started with its usual acceleration and slowed down to a nearly uniform speed after a run of 7 cm. When the same mixture was fired by

a high tension magneto-spark there was a measurable delay, but the spread of the flame followed much the same course.

The same kind of records was obtained when the moist gas was fired by the discharge from a condenser (charged up to 1000 volts) of increasing capacity, beginning with one of 0.001 mf. and passing on to 0.05, 0.5, and 3.75 mf., and then up to 8, 12, and 18 mf. With the lowest spark energy there appeared to be some delay in ignition; in the other cases the flame started immediately.

With the very powerful discharge sparks employed, oscillations were set up which had a visible effect on the flame from the start, and persisted so long as the flame was luminous—showing the well-known criss-cross patterns. There was also near the electrodes the very brilliant core of flame which burnt itself out rapidly and became a dark space. However fired, the spreading flame in the moist gases only became bright on reaching the ends of the tube.

While some photographs given in the memoir appear to show that, when the ignition is started close to one end of the tube, the flames exhibit a

FIG. 5.

mean speed and a set of oscillations nearly identical, although a heavy discharge is used in one tube and a light spark in the other; yet the beautiful photo-

graph (Fig. 4) shows that, when the knall-gas is lighted simultaneously at one end by a heavy discharge and at the other by a light spark, the flames start unsymmetrically—that from the heavy discharge travelling the faster. This last photograph strikingly illustrates the oscillations of the two flames and of the column of unburnt gas between them: when the flames at last meet, the striæ, which until that moment were moving away from the flame fronts, immediately became motionless and appear as vertical streaks.

Finally, by an ingenious device, the authors have studied the effect of shock-

FIG. 6.

waves catching up the accelerating flame, and of the accelerated flame overtaking shock-waves that have passed through it previously. They have shown how such shock-waves may impose a succession of 'uniform movements' on the flame, and how these accelerated flames may start a measurable distance ahead of the visible flame. When first confronted with such pre-ignitions, I attributed the appearance to halation on the photographic film; but the later work by Dr. Campbell at Manchester has long convinced me that the explosion wave may start under the influence of an invisible shock-wave ahead of the visible flame.

I agree, then, with the authors on their interpretation of the interesting photograph (Fig. 5). It is interesting not only because it shows the detonation starting at a point in front of the visible flame and

throwing back a well-marked retonation wave, but also because it shows the peculiar banded structure (discovered by Dr. Campbell and his colleagues) not only in the explosion wave, but also in the region before the detonation is set up. Fig. 6 gives an excellent illustration of the banded flame of the explosion wave, which, the authors agree, must be attributed to the rotation of the head of the flame round the inner surface of the tube as it advances with a helical motion—the explanation suggested and then demonstrated by Messrs. Campbell, Woodhead, and Finch. How this rotation is checked when the flame comes in contact with an electrified surface is only hinted at in the present memoir, but already the Fraser camera has brought other mysteries to light. It is a fine weapon—and in capable hands.

Molecular Spectra and Molecular Structure.

THE Faraday Society met at Bristol on Sept. 24 and 25 for one of its valuable discussions on subjects of interest to physicists and chemists. The subject for this discussion was molecular spectra and molecular structure, and the importance of the subject could be gauged from the number of distinguished workers who were attracted from Germany, Holland, Switzerland, America, India, and Japan, and from the fact that thirty-eight papers were presented for discussion. These papers covered the whole field of inquiry in molecular spectra and focused attention on some of the problems still outstanding. The discussion was particularly valuable as it brought together workers in the infra-red, visible, and ultra-violet regions and provided them with an opportunity of correlating their results with those recently obtained from a study of the Raman effect.

One of the most important questions to be discussed was that of notation, for the present lack of agreement causes much unnecessary difficulty in the reading of the prolific literature which is at present being published. R. S. Mulliken, F. Hund, and others have recently agreed upon a tentative scheme, which was presented by O. W. Richardson. The main object of this scheme is to devise a notation in as close harmony as possible with that already agreed upon for atomic spectra. The quantum numbers n and l are retained with meanings analogous to those used for atoms, and in addition a quantum number λ is introduced for the projection of l on the molecular axis. Small letters are used for individual electrons, and capital letters for the electron system as a whole. Thus, the resultant of the l values of individual electrons is denoted by L , and the resultant orbital angular momentum round the molecular axis by Λ . The individual electron spins are denoted by s , and the resultant by S , while the projection of S on the molecular axis is denoted by X . The quantum number of the sum total resultant angular momentum is denoted by J as in atoms. This consists of the electronic spin vector S and the resultant of orbital and rotation angular moments

(together denoted by K). When individual electrons are known to have a definite angular momentum round the molecular axis, they are described as $\sigma, \pi, \delta, \phi, \dots$ electrons according as $\lambda = 0, 1, 2, 3, \dots$, in analogy with the $s, p, d, f, \dots$ notation of atoms. For the molecule as a whole, the molecular states are denoted by $\Sigma, \Pi, \Delta, \Phi, \dots$ according as $\Lambda = 0, 1, 2, 3, \dots$, again in analogy with the $S, P, D, F, \dots$ terms of atoms. Multiplicities are denoted as in atomic spectra, as, for example, $^2\Sigma, ^4\Pi_{3/2}$.

There seemed to be general agreement among workers present at the discussion with regard to these main features, and criticism was directed mainly against other minor details. Those interested in polyatomic molecules urged, however, that the notation adopted for diatomic molecules should be capable of extension to more general cases.

One welcome feature of the discussion was that it led to a general stocktaking of the present position, and stimulated workers to review the advances made in the last few years. O. W. Richardson gave a summary of the results obtained for the hydrogen molecule, of which about forty different electronic levels are now known. W. E. Curtis gave an account of the present position with regard to the band spectrum of helium, the analysis of which is nearly complete in the visible and ultra-violet regions. This spectrum is particularly interesting, as it shows that the l vectors of the individual atoms gradually become uncoupled from the nuclear axis as the rotation of the molecule increases and tend to become coupled to the rotation axis. The transition from one case to the other gives rise to striking anomalies of structure and intensity.

Apart from hydrogen and helium, the band spectrum which has received most attention is carbon monoxide, and at present 16 band systems are known. A detailed account of these was given by R. C. Johnson, who directed attention to the recent discovery by Asundi of a quintet level $^5\Pi$ in this spectrum (the first quintet to be recorded in band spectra) and attributed the third positive carbon band system to a $^5\Sigma \rightarrow ^5\Pi$ transition. This