417. *The Combination of Hydrogen and Oxygen in Direct-current Discharges.*

By E. M. Guénault and R. V. Wheeler.

Finch and Cowan (*Proc. Roy. Soc.*, 1926, **111**, *A*, 257) studied the combustion of electrolytic gas in a steady direct-current discharge under conditions which, they considered, eliminated, as far as possible, " any chemical combination, including that due to heat, other than that caused by the ionisation of the gas," and concluded that combustion was, in fact, determined primarily by the ionisation of the gaseous medium through which the current passed. As a result of later work (*e.g.*, Finch and Mahler, *ibid.*, 1931, **133**, *A*, 173), preference was given to the view that " the cathodic combustion of H_2–O_2 mixtures is primarily determined by prior excitation of both constituents." From spectroscopic evidence, such as that adduced by Finch and Thompson (*ibid.*, 1930, **129**, *A*, 314), there seems little doubt but that the discharge causes electronic excitation of gaseous molecules in its path such as to make them more ready to combine than they otherwise would be.

We have carried out similar experiments, with substantially the same results, and, in addition, have measured temperatures in the path of the discharge. The temperature was found to vary systematically with the experimental conditions. Moreover, in comparative experiments in which nitrogen, argon, or helium was used as a diluent, the relative rates of combination of hydrogen and oxygen varied, not according to the effect each diluent gas would have on the degree of ionisation, but with the temperature produced in the mixture by the discharge.

We conclude that the combination of hydrogen and oxygen in the direct-current discharge is not primarily determined by its ionising effect; the ability of the discharge to cause chemical reaction in electrolytic gas by electronic excitation of the molecules may be materially assisted by its thermal effect.

EXPERIMENTAL.

Combustion Chamber.—The combustion chamber (Fig. 1) was a glass vessel, of about 550 c.c. capacity, comprising two portions which could be joined together at broad ground flanges, F. The upper portion was fitted with a three-way tap, T, for evacuation and the admission of gases, and two tubulures to receive electrodes. To the lower portion, in which a glass dish, D, containing concentrated sulphuric acid was placed, a mercury manometer, G, was sealed.

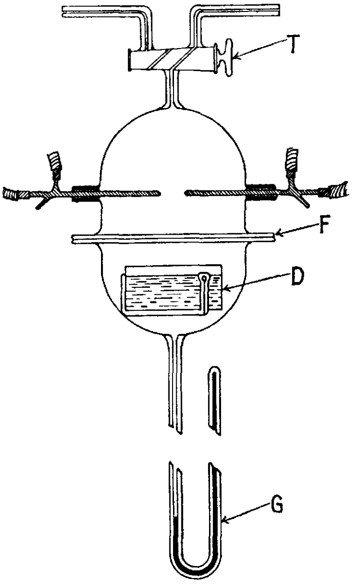
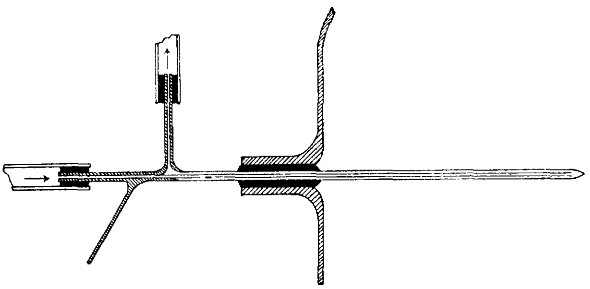


FIG. 1.

FIG. 2.



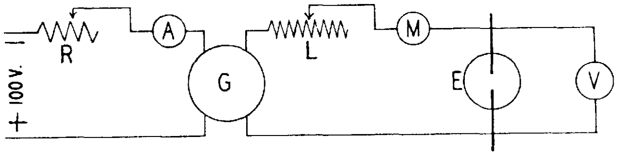
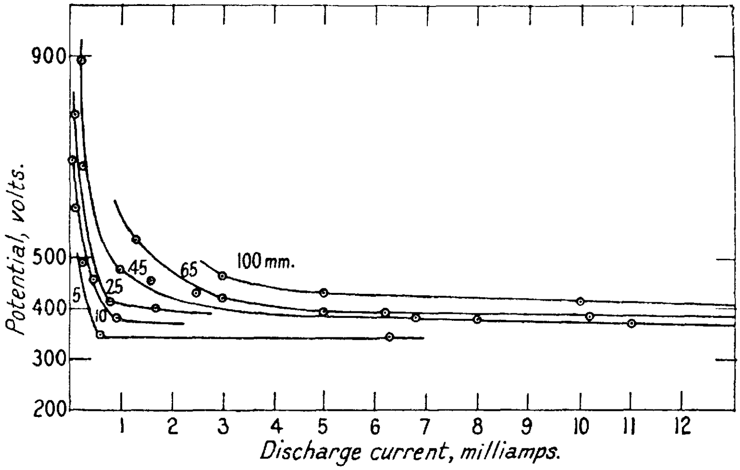


FIG. 3.

Electrodes.—Each electrode, shown in detail in Fig. 2, was a tube of platinum–iridium alloy, 2 mm. in diameter, sealed at one end, which was pointed. An inner tube passed centrally to the tip, so that a stream of cold water could be forced through it. This cooling water was drawn from a high-pressure water-supply through coils of stout rubber tubing of sufficient length to ensure that any leakage current to earth would be negligible. The electrodes were set with Chatterton compound in the tubulures of the combustion chamber so as to leave a discharge gap of 6·8 mm.

Electric Circuit.—Power was supplied from D.C. mains at 100 volts through a rotary generator, G, Fig. 3, capable of developing up to 1,500 volts. The output could be controlled by a variable resistance, R, in series with the " exciting " circuit of the generator, which was connected to the electrodes, E, through a milliammeter, M, and a variable non-inductive liquid resistance, L, consisting of 20 water-cooled tubes containing a mixture of glycerol and a solution of copper sulphate in water, any number of which could be included in the circuit in parallel. Each tube had a resistance of about 2 megohms and could pass up to 1 milliamp. Across the electrodes an electrostatic voltmeter, V, was connected. The voltage applied to the circuit could thus be varied by altering the exciting current through the generator, and the current passing in the discharge could be further controlled by the variable liquid resistance.

Fig. 4.



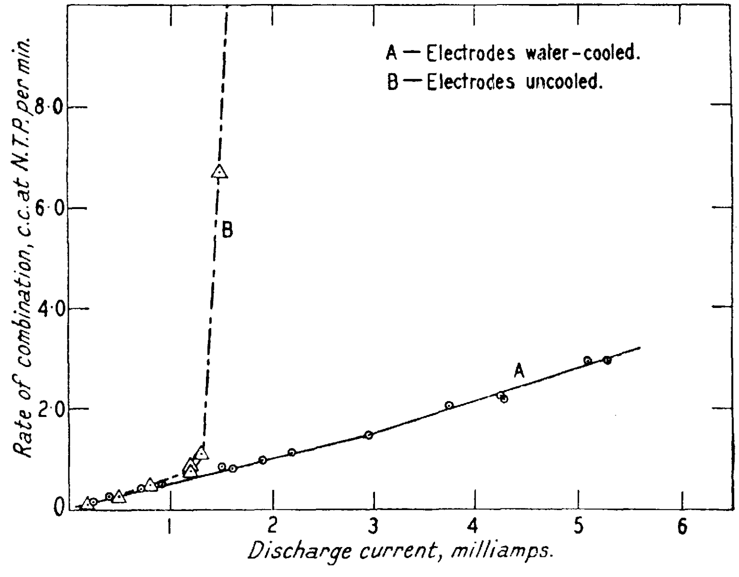
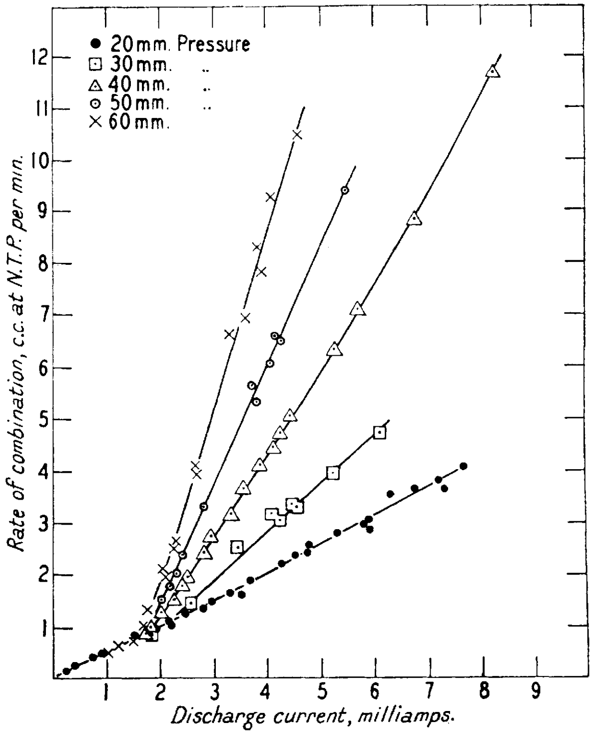


Fig. 5.

Method of Experiment.—Electrolytic gas was prepared by the electrolysis of a solution of repeatedly recrystallised barium hydroxide, dried by passage through concentrated sulphuric acid, and stored in glass gas-holders over mercury. Since the experiments necessitated the introduction of the electrolytic gas whilst an electric discharge was passing, a guard tube containing granulated copper was interposed between the storage holder and the combustion chamber. The latter, assembled with the dish of concentrated sulphuric acid in position, was swept out with electrolytic gas and evacuated. The discharge was started and, when it had become steady, the current was adjusted to a predetermined value. Electrolytic gas was then slowly admitted to the required pressure, and any necessary minor adjustment of the discharge was made. Readings were then taken at frequent intervals of the manometer, milliammeter, and voltmeter. As combustion in the discharge proceeded, the water vapour formed was absorbed by the sulphuric acid, so the rate of combination could be calculated from the rate of fall of pressure.

Character of the Discharge.—The glow discharge used had a negative voltage–current characteristic. Curves relating the drop in potential to the current when the discharge passed in argon at different pressures are shown in Fig. 4, and indicate a steep fall in the *P.D.* to a fairly steady value on passing from the lower to the higher currents; under the conditions during which the steep fall occurred (which were outside the range used for the combustion experiments) the discharge was striated. Under the experimental conditions, the discharge appeared to consist of a small but brilliant "anode spot," from which a faint brush-like glow extended, a dark interelectrode space, and a blue glow enveloping the tip of the cathode like a sheath 1—2 mm. thick. On closer examination, the cathode zone was seen to consist of a thin bright layer (the cathode glow proper), a thin dark layer (the Crookes dark space), and the outer blue glow.

Fig. 6.



Catalytic Action of the Electrodes.—Early experiments had shown that hydrogen and oxygen at a pressure of 20—100 mm. could combine at a measurable rate on the surface of a heated platinum wire at a temperature of 170°, and that the rate of combination increased exponentially with increase in temperature of the wire. At 300° combination was so rapid as to heat the wire to glowing point, so that the mixture exploded. It was therefore necessary to test the efficacy of the water-cooling of the electrodes. Parallel tests were made, with the electrodes cooled and uncooled, with dried electrolytic gas at 20 mm. pressure and with a number of different values for the discharge current. The results are shown as curves in Fig. 5. With the electrodes water-cooled, the curve relating rate of combination with discharge current is nearly a straight line, the ratio C (c.c. at N.T.P. per min.) to i (milliamps.) being 0·51 over the first part of the curve and rising to 0·62 when the current exceeded 3 milliamps. When the electrodes were not water-cooled, a discharge current greater than about 0·75 milliamp. heated the electrodes so much that catalytic combustion on their surfaces became appreciable. With discharge currents greater than about 1·3 milliamps., the catalytic combustion, which was almost entirely at the cathode, masked that in the discharge itself.

Rate of Combustion of Electrolytic Gas at Different Pressures.—With the electrodes water-cooled, so as to eliminate their catalytic action, the ratio C/i was determined with the electrolytic gas at pressures from 20 to 60 mm. The results are recorded in Fig. 6. The curves are similar to those obtained by Finch and Cowan. The rate of combination was independent of pressure when the discharge current was less than about 1·5 milliamps.

Temperature Effects in the Discharge.—An exploration of relative temperature changes in the gases through which the discharge was passed was made in two ways.

(*a*) A thermocouple was made of copper and constantan wires, each of 36 S.W.G., and enclosed in a thin sheath of glass of diameter 1 mm. With this thermocouple, variations in heating effect in different zones of the discharge with a current of 5 milliamps., passed in argon at 25 mm. pressure, were made (Table I). The room temperature was 18°.

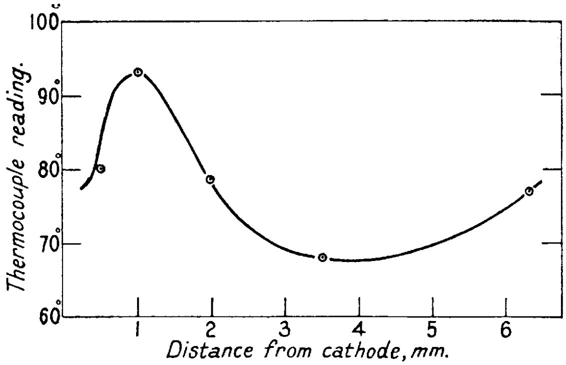
TABLE I.

Temperature Measurements in Discharge in Argon.

	Temperature indicated.	
Position of thermocouple.	Electrodes cooled.	Electrodes uncooled.
In line of discharge : (i) 0·5 mm. from cathode ...	80°	95°
(ii) 1·0 ,, ,, ...	93	—
(iii) 2·0 ,, ,, ...	79	—
(iv) 3·5 ,, ,, ...	68	—
(v) 6·3 ,, ,, ...	77	108
Above centre of discharge, 9 mm.	61	—
,, ,, ,, 20 ,, ...	58	—
Below ,, ,, 15 ,, ...	28	—

A graph of the measurements in the line of discharge is shown in Fig. 7, from which it is evident that the discharge heats the gas in its path; the heating effect is greatest in the glow near each electrode, and the water-cooled electrodes absorb heat. The values in Table I show also that convection currents are produced. For comparison, a typical curve for the distribution of fall of potential across the gap is shown in Fig. 8. At the anode the fall is small (about 20 volts) but steep; across the inter-electrode space it is gradual; whilst most of the fall (about 380 volts) occurs near the cathode. The energy liberated in the discharge is thus greatest near the electrodes; most is released in the cathode glow, but since this occupies a volume greater than that of the anode glow the concentration of energy may not be much greater at the cathode than at the anode. The maximum rise in temperature in the cathode zone was nearly 1½ times that in the inter-electrode space.

FIG. 7.

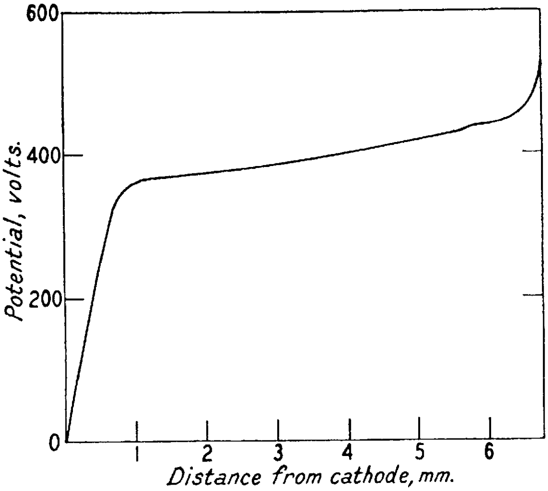


(*b*) The temperature gradients in the discharge were also explored with mercury thermometers. These indicated temperatures about 50° higher than did the thermocouples, no doubt because heat was lost by conduction through the leads of the latter. Two thermometers were used, of lengths 43 and 35 mm. and diameters 3·5 and 2 mm. respectively. The temperature readings were nearly the same with each under similar conditions, those of the smaller being but a few degrees the higher.

At the centre of the discharge in argon, the temperature reading increased with the discharge current when the pressure was constant, and increased with the pressure of the argon when the discharge current was constant. On plotting the rise in temperature against the discharge current for different pressures of the argon, the curves obtained were not regular; but smooth curves of the type $kt^x = Vi$ were obtained if the power liberated were plotted against the temperature, the value of x being about 2. A similar quadratic relation was obtained between the rise in temperature and the pressure of the gas, the power liberated being maintained constant. Thus for a given rise in temperature the value *Vip* was almost constant.

In Fig. 9, values of *Vip* are plotted against the rise in temperature, *t*, and form a fairly smooth curve. In Fig. 10, values of $\log_{10}$ *Vip* are plotted against $\log_{10} t$. For small values of *t* (when the discharge was striated) the points are scattered. For higher values of *t* the points lie closely on a straight line of the type $\log Vip = a \log t + \log C$; hence the relation for the rise in temperature is of the form $t = k'(Vip)^{1/a}$. The value of *a* is about 2, giving the relation $t = k'(Vip)^{\frac{1}{2}}$. The form of this relation, which is empirical, cannot indicate the separate effect of variation in the three factors involved, for they are inter-related; for example, even though it should be possible to express the relation in terms of *V* and *p* only (for equations could be obtained for the voltage current characteristic curves of the discharge passing at different values of *p*), it could not be assumed that variation in the value of *i* was of no moment.

Fig. 8.



Temperature Effects during Combustion in the Discharge.—Similar explorations of the temperature gradients were made when the discharge was passing in electrolytic gas. Similar curves relating *t* with $(Vip)^{\frac{1}{2}}$ were obtained. During the course of these measurements, temperatures as high as 270° were recorded in the inter-electrode space, with presumably considerably higher temperatures in the electrode glows. There were thus differences of temperature depending in a systematic manner on the pressure of the gas and the current in the discharge.

Fig. 9.

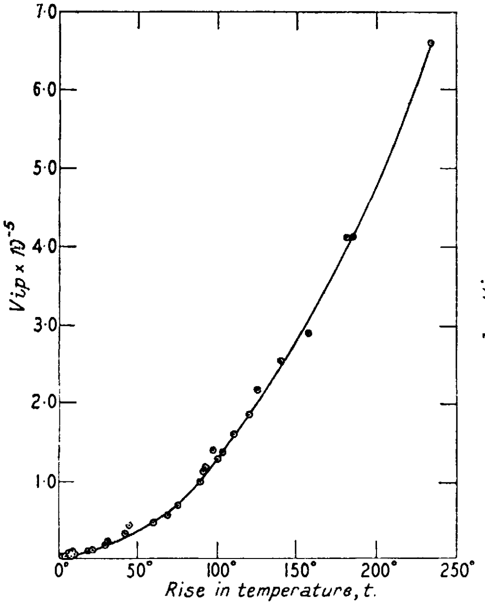
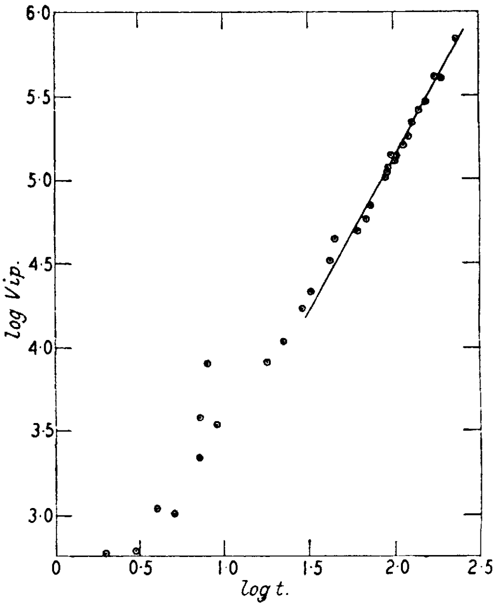


Fig. 10.



In order to obtain a better understanding of the heating effect of the discharge, a study was made under constant experimental conditions of the relative temperatures obtained with different gases in the combustion chamber; for, apart from variation in the amount of energy dissipated, the specific heat and viscosity of the gas should affect the rise of temperature. The results are recorded in Table II.

TABLE II.

Relative Temperature Effects of Discharge in Different Gases.

Gas.	Sp. ht. (cals. per g.-mol.).	Relative viscosity.	Relative rise in temp. (corrected for differences in fall of potential).
Argon	4·97	221	56°
Helium	4·97	197	14
Hydrogen	6·86	89	22
Oxygen	7·04	195	72
Nitrogen	6·93	171	78
Air	6·94	181	77
Carbon dioxide	8·79	146	134
$2H_2 + O_2$	—	—	60
$2H_2 + N_2$	—	—	59

For the monatomic and diatomic gases, considered separately, the relative heating effects were such as would be anticipated from their specific heats and viscosities, but, considered as a whole, the results in Table II suggest no relationship. The results for the mixtures $2H_2 + O_2$ and $2H_2 + N_2$ indicate that there is no increased heating effect in the discharge due to heat of combustion of reacting gases.

A mixture of electrolytic gas with nitrogen, argon, or helium as a diluent was prepared, such that, at the moment when observations of the rate of combination were started, its composition would be $2H_2 + O_2 + X$ at 40 mm. pressure (the partial pressure of $2H_2 + O_2$ being 30 mm.). The rate of combination was then determined, the discharge current being 5 milliamps. The results are recorded in Table III, the rate of combination of $2H_2 + O_2$ initially at 30 mm. pressure being given for comparison.

TABLE III.

Rate of Combination of $2H_2 + O_2 + X$.

Mixture.	Rate of combination, c.c. at *N.T.P.*/min.	Relative heating effect of X.
$2H_2 + O_2$ (at 30 mm.)	4·11	—
$2H_2 + O_2 + N_2$	4·67	78
$2H_2 + O_2 + A$	3·52	56
$2H_2 + O_2 + He$	3·07	14

Under the conditions of experiment, combustion occurred in the inter-electrode space as well as at the cathode. If combination occurred only between ionised molecules, it would be expected that helium, having a comparatively high ionisation potential (25 volts), would not become markedly ionised, and its presence therefore would not affect the rate of reaction; whilst nitrogen or argon, having ionisation potentials comparable with that of oxygen, would be ionised (any ionisation of the electrolytic gas being proportionately decreased) so that the presence of either should decrease the rate of reaction. Actually, the results show that the effect of the diluent gases was in accordance with the relative heating effects produced in them by the discharge.

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