CXCVII.—*On the Dielectric Strengths of Some Explosive Mixtures containing Carbonic Oxide.*

By Bernard William Bradford and George Ingle Finch.

The electrical ignition of an explosive gaseous mixture is determined by the setting up of a certain definite concentration of ions at some point within the body of the gas (Finch and Cowen, *Proc. Roy. Soc.*, 1927, *A*, **116**, 539). Other conditions being equal, this is in its turn determined by the passage through the mixture of a definite current, termed the "least igniting current" (Thornton, *ibid.*, 1914, *A*, **90**, 272). If the source of electrical energy be an induction coil or magneto, the maximum current flows during the first half-cycle of the oscillatory, though frequently fully damped, capacity component. Campbell and Patterson (*Proc. Physical Soc.*, 1919, **31**, 177) have shown, and it has repeatedly been confirmed by others (see Morgan, "Electric Spark Ignition," Crosby Lockwood, 1922, pp. 19 *et seq.*), that, in these circumstances, it is the capacity and not the inductance component which causes ignition. *Ceteris paribus*, the maximum current passed by the capacity component, and likewise the energy associated therewith, are determined by the dielectric strength of the gaseous medium traversed by the discharge.

It is well known that intensive drying of a gas greatly increases its dielectric strength; and, although for some time we have been aware in these laboratories that the same statement applies also to explosive gaseous mixtures, no account of the effect, from this point of view, has been published.

At a meeting of the Society, held in London on the 19th December, 1929, Professor Smithells read a paper on "The Influence of Hydrogen and Water Vapour on the Ignition of Carbon Monoxide" (this vol., p. 185), and concluded from the results of experiments carried out by himself, in conjunction with Mr. H. Whitaker and Miss T. Holmes, that hydrogen was more effective than water vapour in conferring ignitability upon a mixture of carbonic oxide and oxygen in equivalent proportion. This conclusion was criticised at that meeting by one of us (G. I. F.) on the ground that the dielectric strengths of the two classes of mixture, $2CO + O_2(+$ water vapour) and $2CO + O_2(+$ hydrogen), must have differed considerably (*J. Soc. Chem. Ind.*, 1930, **49**, 12). In order, therefore, to substantiate this criticism by determining the effect of moisture upon the dielectric strengths of some explosive mixtures, containing, in the main, carbonic oxide and oxygen in their combining proportion, the following investigation was carried out. The mixture corresponding to $2CO + O_2$ will be referred to, for the sake of brevity, as " detonating gas."

EXPERIMENTAL.

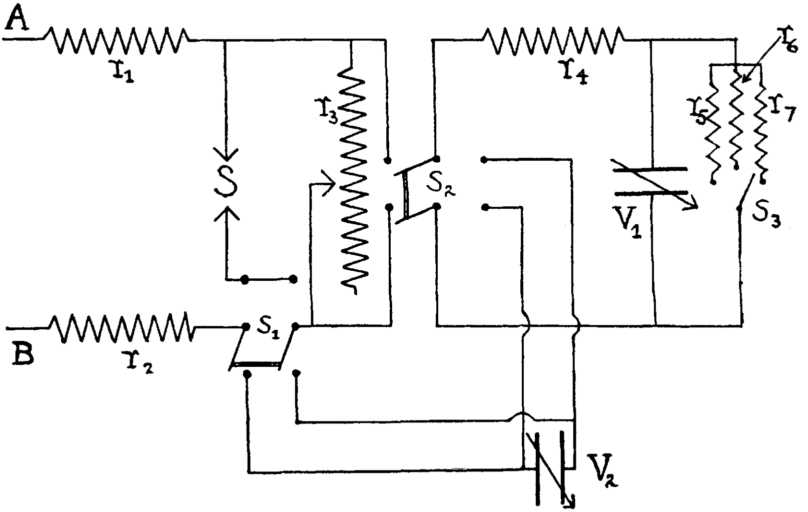
The dielectric strengths of the gaseous mixtures examined were determined in (i) three test-tube eudiometers, A, B, and C, sealed off by mercury and provided with fused-in platinum-wire (S.W.G. 28) electrodes, (ii) a test-tube, D, the open end of which was sealed off after filling the tube—the electrodes were similar to those described under (i)—and (iii) a pipette, also fitted with platinum-wire electrodes, through which a current of the gaseous mixture under examination could be passed.

The various gaps were set by eye, and then measured electrically in terms of breakdown voltage in air of known moisture content, pressure, and temperature. Full details of the methods employed for cleaning these vessels, for purifying and drying mercury, for purifying phosphoric oxide, and for preparing and checking the composition of the " detonating gas " have been given elsewhere (Bone and others, *Proc. Roy. Soc.*, 1925, *A*, **127**, 2464; Finch and Cowen, *loc. cit.*; Finch and Hodge, *ibid.*, 1929, **124**, 306; Finch and Fraser, J., 1922, **121**, 122). The pressures employed in the dielectric-strength determinations were furnished by a high-tension direct-current generator capable of exerting up to 5000 volts on full load (100 milliamps.). Ripple and other irregularities were removed by means of the smoothing circuit fully described by Finch and Cowen (*Proc. Roy. Soc.*, 1926, *A*, **111**, 257, and *loc. cit.*).

The smoothed output was fed into the circuit shown in Fig. 1; s_1 and s_2 were double-pole, double-throw switches, s_3 was a triple-stud switch, V_1 a Kelvin multicellular electrostatic voltmeter (30—120 volts), and V_2 an electrostatic voltmeter (1200—2800 volts). Both instruments were referred to a Weston normal cell, an N.P.L. calibrated standard ohm, and a Ferranti 1-megohm potentiometer, wire-wound in steps of 100,000 ohms. The values of r_1, r_2, r_3, r_4, r_5, r_6, and r_7 were respectively 2·5, 2·5 megohms (tap water); 0 to above 50 megohms, continuously variable (distilled water); 45 megohms (alcohol–xylene); $\frac{1}{2}$, 1, and 2 megohms (sputtered silver on quartz rod in a vacuum). S was the gap, the breakdown voltage of which was to be measured. The smoothed generator output was fed to A and B. The lay-out of the circuit was such as to reduce the interelectrodic capacity to a practical minimum.

Procedure.—The electrodes of the test-tube containing the gaseous mixture of which the dielectric strength was to be determined were connected into the circuit at S, s_1 and s_2 being thrown over into such positions that S was out of, but V_2 in, circuit. The system V_1, including the potentiometer, r_4 and r_5, r_6 or r_7, was then calibrated over the desired range against V_2, whereupon s_1 and s_2 were thrown over to the opposite terminal pairs, thus placing S in, but V_2 out of, the circuit. By varying r_3 and the speed of the generator, any desired pressure up to 5000 volts could then be applied to S. On completion of a dielectric-strength determination, s_1 and s_2 were reversed and V_1, together with the potentiometer associated therewith, was recalibrated. The importance of taking due account of lag phenomena (Campbell, *Phil. Mag.*, 1921, 41; Townsend, "Electricity in Gases," Oxford, 1915; Peek, "Dielectric Phenomena," McGraw-Hill, 2nd edtn.; Morgan, *loc. cit.*) was recognised, and all experiments were therefore carried out in daylight, the pressure being raised in each determination by 10-volt steps at 10-second intervals until breakdown occurred. It will be appreciated that the rate of dissipation of energy ensuing upon breakdown was such that ignition never occurred, even in the case of the most sensitive mixtures examined (see Finch and Cowen, *loc. cit.*; Finch and Hodge, *Proc. Roy. Soc.*, 1929, *A*, **124**, 303; 1929, **125**, 532). In all experiments, with the exception of those carried out with the sealed-off tube, D, the pressure of the tube contents was 760 ± 2·5 mm.

FIG. 1.



Experimental Results.—24 Hours after the filling with a mixture corresponding in composition to $2CO + O_2 + 0{\cdot}017\%H_2O$ (85·6%

H_2SO_4 at 17·2°; see Landolt–Börnstein, "Tabellen," pp. 426, 427), the breakdown voltage across the electrodes of the tube, A, was found to be 1890 ± 5 volts. A repeat determination 24 hours later gave a similar value. Tube A was then emptied, rinsed out with distilled water, dried in a current of hot dry air, and filled with dry redistilled mercury, which was thereupon displaced by a dry mixture of the composition $2CO + O_2 + 0{\cdot}017\% H_2$. Two pellets of compressed phosphoric oxide, each weighing about 0·5 g., were then introduced into the tube. After 10 days the breakdown voltage was found to be 2300 ± 10 volts. Tube A was then accidentally destroyed. Similarly, the following results, set forth in the order in which the experiments were carried out, were obtained with the tube, B :

Gaseous mixture.	Breakdown voltage.
$2CO + O_2 + 0{\cdot}043\%\ H_2O$	2300 ± 10 volts
$2CO + O_2 + 0{\cdot}043\%\ H_2$, dried for 10 days	2850 ± 15 ,,
$2CO + O_2 + 0{\cdot}043\%\ H_2O$	2350 ± 10 ,,

The effect of progressive degrees of drying upon the dielectric strength of "detonating gas," free from hydrogen, was studied in the tube, C, with the following results :

Aqueous condition of mixture.	Breakdown voltage.
0·043% H_2O	2150 ± 5 volts
½ hour's drying over P_2O_5	2900 ± 20 ,,
1 day's ,, ,,	2500 ± 10 ,,
2 days' ,, ,,	3000 ± 20 ,,
4 ,, ,, ,,	3200 ± 20 ,,
5 ,, ,, ,,	3250 ± 20 ,,
6 ,, ,, ,,	3300 ± 20 ,,
7 ,, ,, ,,	3700 ± 25 ,,
8 ,, ,, ,,	3700 ± 25 ,,
9 ,, ,, ,,	3600 ± 25 ,,
10 ,, ,, ,,	3500 ± 25 ,,
0·043% H_2O	2300 ± 5 ,,

The effect of intensive drying upon the dielectric strength of "detonating gas" was studied in the tube, D, which was prepared and filled for this purpose in the following manner : After being cleaned, the tube was sealed on to one arm of a T-piece, the second branch of which carried a small bulb containing purified phosphoric oxide. The whole was evacuated by means of a "Hyvac" pump through the third arm, which was also in communication with a filling apparatus and drying train. The evacuated tube was heated to just below the softening point of the glass for ½ hour, and the electrodes were bombarded for 5 minutes, whereupon phosphoric oxide was distilled into the tube until its walls were thickly covered with a layer extending to within about 1 cm. of the electrodes. Gentle heating sufficed to free the sealing-off capillary from the oxide. "Detonating gas" was then slowly introduced to a pressure of 760 mm., and the tube sealed off. Breakdown voltages were now determined, with the following results :

Time after sealing off	½ hour	1 day	2 days	4 days	5 days
Breakdown voltage	3150	3300	3400	4000	4250

The breakdown voltage of this tube containing $2CO + O_2 + 0{\cdot}043\%$ H_2O had previously been found to be 2950 volts.

In a final series of experiments, a stream of " detonating gas " was passed through a train of washers containing aqueous sulphuric acid of known vapour tension, followed by a pipette of about 5 c.c. capacity and fitted with platinum wire electrodes. The pipette, in turn, delivered into a washer filled with sulphuric acid of similar concentration to that contained in the first washers. The gas flow was interrupted prior to each determination of the breakdown voltage, which was thus carried out on the stagnant gas. The results obtained were as follows :

Partial pressure of H_2O, mm.	0·0	0·29	3·9	8·4	13·8
Breakdown voltage	2640	2040	2340	2725	2730

Discussion.

The experimental results set forth above establish the following facts : (i) Drying with phosphoric oxide increases the dielectric strength of " detonating gas," (ii) small additions of hydrogen reduce, but do not inhibit, this effect, and (iii) successive small additions of water vapour to " detonating gas," previously dried over concentrated sulphuric acid, at first reduce and then increase its dielectric strength.

In what follows we propose to show that, in the light of the foregoing results, the conclusion drawn by Smithells, Whitaker, and Holmes (*loc. cit.*), *viz.*, that " hydrogen was more effective than water vapour in conferring ignitability " on " detonating gas," is a *non sequitur.*

These investigators employed two eudiometers, fitted with geometrically similar platinum-wire spark gaps and filled with " detonating gas " to which were added respectively small amounts of hydrogen or of water vapour in equivalent proportion. The contents of the eudiometer containing the hydrogen were kept in contact with purified phosphoric oxide. After stated periods of drying, none of which was less than 10 days, an induction-coil discharge was passed through the two gaps in series. It was found that the dried mixture containing hydrogen exploded, but not the moist " detonating gas," and from this and similar results the conclusion already quoted was drawn. We have now shown, however, that the dielectric strengths of the individual media surrounding the two spark gaps in their experiments must have differed considerably. It follows that the separate amounts of energy dissipated in the two gaps must also have differed in such a manner that more energy was expended in the dried "detonating gas" containing hydrogen than in the moist mixture. It has been previously pointed out that, in estimating the effect of this difference in dielectric strengths upon the relative distribution of energy between the two gaps, we are only concerned with the energy associated with the capacity component of the coil discharge. It would only be in exceptional circumstances, which do not arise in this case, that the energy associated with the inductive component would also have to be taken into account.

At first sight it might appear that, for the purpose of evaluating in precise terms the effect of a difference in the dielectric strengths of the two media upon the distribution of energy between two spark gaps in series, it would suffice to consider the circuit as consisting of two gaps in series connected to a condenser charged to the sum of the breakdown voltages. This is not the case, however, because the investigators in question did not take adequate steps to keep down the interelectrodic capacities.

The eudiometers employed by Smithells and his co-workers were water-jacketed, separate jackets being used. The leads to the electrodes were taken through vertical glass or rubber tubes, filled with mercury, and partly immersed in the water of the jackets. From the diagram of their apparatus (*loc. cit.*, p. 190), the following approximate dimensions may be assumed in respect of each electrode: Length of immersed tubing containing mercury, 5 cm.; internal diameter of tubing, 0·5 cm.; wall thickness of tubing, 0·1 cm.; also, the dielectric constant of the tube material would be 3 (rubber) or 6 (glass). Hence, since the water-jackets contained tap-water, the interelectrodic capacity of each electrode pair must have been approximately 11·1 (rubber) or 22 cm. (glass). Taylor-Jones ("The Theory of the Induction Coil," Pitman, 1921, p. 130) found the secondary self-capacity of a slab-wound 18″ induction coil to be 48 cm. Smithells and his co-workers probably employed a 2—4″ coil, the secondary self-capacity of which, even if layer-built, must have been of the same order as, though probably less than, the individual interelectrodic capacities of their two electrode systems. That being so, and, further, in view of the secondary self-inductance and the damping due to the *H.F.* resistance of the secondary circuit and the tap-water columns contained in the tubes connecting the water-jackets with a common supply and drain, it may be considered that the circuit at the moment of breakdown of the two gaps consisted of two separate circuits in the electrical sense, each comprising an electrode pair shunted by a condenser (the interelectrodic capacity) charged to the breakdown voltage of the particular gap. Therefore, since in the experiments under consideration the gap widths were geometrically equal, the energies stored in the interelectrodic capacities and dissipated on breakdown in the two gaps were in the ratio of the squares of the respective dielectric strengths of the gaseous mixtures within which the gaps were individually situated. We have, however, shown experimentally, as set forth above, that the dielectric strength of moist " detonating gas " is greatly increased by 10 days' drying after substitution of an equivalent amount of hydrogen for the moisture. Thus, the gap in the tube, B, filled with $2CO + O_2 + 0{\cdot}043\% \ H_2O$ broke down at 2300 to 2350 volts, whereas, under similar conditions, but with an equivalent amount of hydrogen substituted for the water vapour and dried during 10 days over phosphoric oxide, the breakdown voltage was 2850 volts. The compositions of these mixtures correspond closely to those employed by Smithells and his co-workers in their experiments Nos. 5 and 6. Thus the ratio of the energies dissipated in their undried and dried mixtures respectively was as 53 or 56 is to (at least) 81, *i.e.*, between at least 1·45 and 1·53 times as much useful igniting energy was dissipated in the dry as in the moist mixture. Therefore, the fact that, in those authors' experiments, the dry mixture containing hydrogen exploded, but not the moist "detonating gas," did not justify their conclusion that " hydrogen was more effective than water vapour in conferring ignitability."

It should not be inferred from the above that we disagree with this conclusion *per se*. Bone and his co-workers and others have, as pointed out by Smithells (*loc. cit.*, pp. 185—187), proved its validity.

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