

### 9. *The Cathodic Combustion of Hydrogen and Carbonic Oxide.*

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THE substance of this communication was read in opening a discussion on combustion in electric discharges before the Society in November, 1932. Publication has been delayed pending completion of certain experimental work in progress at that time. The object is to summarise the main results and to draw therefrom the broad conclusions of a series of studies of gaseous combustion in electric discharges carried out by the author and his collaborators since 1925 (see references, p. 39).

Before combustion can be initiated in an inflammable mixture of gases, energy in some form must be furnished from an external source. If heat energy be so supplied, the "ignition temperature" marks the transition point between slow, non-self-propellant combustion and the self-propellant, pre-flame combustion which leads to flame propagation. In the case of electrical energy the term "least igniting energy or current" has a somewhat similar significance. When once set up, the self-propellant stage of combustion is propagated throughout the system independently of the nature of the source of ignition. On the other hand, slow combustion is intimately associated with, and determined by, the energy supply to the combustible system. It is natural, therefore, that the present state of knowledge of the nature and mechanism of gaseous combustion in flame is largely founded upon the study of the pre-ignition stage. In most such experimental inquiries, slow combustion has been brought about by heat, which has, however, certain outstanding disadvantages. For instance, it is difficult to determine the amount of energy expended in inducing and maintaining slow combustion.

Then, whilst flame propagation may be regarded as a homogeneous process, slow combustion supported by an external supply of heat occurs to a greater or lesser extent heterogeneously, *i.e.*, in contact with the reaction vessel, the surface of which may exert such disturbing effects as to obscure the issues. It is true that supposed examples of heat-induced slow combustion have been put forward as occurring homogeneously; but for the most part such claims do not appear to have been substantiated. Also, so far as the author is aware, explosion of a gaseous mixture effected by the transmission of heat through the walls of a containing vessel is always initiated heterogeneously, *i.e.*, at some point where gas and surface, whether solid or liquid, are in contact. Finally, the nature of the radiation emitted shows that the degree to which the component molecules are excited in flame is of a very different and much higher order than that obtaining under the thermal pre-flame conditions of heat-induced slow combustion.

A direct-current discharge between solid electrodes in a gas may take the form of either a low- or a high-tension arc, the essential difference between the two being in the temperature of the cathode. In the first case, the cathode is so hot that electron emission is mainly thermal and the cathode fall of potential is of the order of only 20 volts; in the second case, the cathode is cool, so that electron emission is due to ionic bombardment, and the cathode fall of potential is of the order of several hundred volts. Owing to the necessarily high cathode temperature, a low-tension arc is unsuitable for the experimental study of the slow combustion of gases; but a high-tension arc dissipating energy at a surprisingly high rate can be maintained in a sensitive explosive gaseous mixture without causing ignition (I).

In the high-tension discharge, three luminous zones are ordinarily distinguishable: (i) the cathode and negative glows sheathing the cathode and constituting the cathode zone, (ii) the anode glow, or spot, and finally (iii) the positive column between which and the cathode zone lies the Faraday dark space. The positive column can be wholly suppressed or varied in extent by a suitable choice of gap-width, gas pressure, or current. Reduction of the positive column of a high-tension arc, maintained in an explosive mixture such as, *e.g.*,  $2\text{H}_2 + \text{O}_2$ , by decreasing the distance between the electrodes, in no way affects either the anode or the cathode glow, but proportionately reduces the rate of combustion (I). Therefore some combustion occurs in the positive column. Once the positive column has been eliminated, a further reduction in gap-width merely encroaches on the Faraday dark space, but has no effect upon the rate of combustion (I, III). It follows that combustion must be limited to the luminous zones of the discharge.

The rate of combustion in a discharge from which the positive column is absent is directly proportional to the current and independent of the nature of the anode material, but is profoundly affected by that of the cathode (I, III). This remarkable effect cannot be due to a difference in the cathode-potential falls; *e.g.*, dry  $2\text{CO} + \text{O}_2$  burns more than three times as rapidly at a silver cathode ( $P.D. = 345$  volts) than at a copper cathode (355 volts) (III). It may therefore be concluded that, in the absence of a positive column, combustion is confined to the cathode zone. Such combustion may conveniently be termed "cathodic combustion."

The cathodic potential fall is independent of either the current or the gas pressure provided, as was throughout the case in the experiments on cathodic combustion now to be considered, the cathode glow be "normal," *i.e.*, free to expand or contract over the electrode surface; thus, since the rate of combustion is directly proportional to the current, it is also similarly related to the rate of energy dissipation within the cathode zone. Also, it is well known that within the range of conditions under consideration, the spectral distribution of energy is determined solely by the nature of the medium in which the discharge is maintained. Thus, from the point of view of the experimental study of gaseous combustion in general, the fact that the rate of cathodic combustion is directly proportional to the discharge current, itself easily measured and controlled, is of the highest importance.

The remarkable effect which the nature of the cathode material can and does exert upon the rate of cathodic combustion might at first sight suggest that such combustion is heterogeneous, *i.e.*, occurs either in part or wholly upon the surface of the cathode.

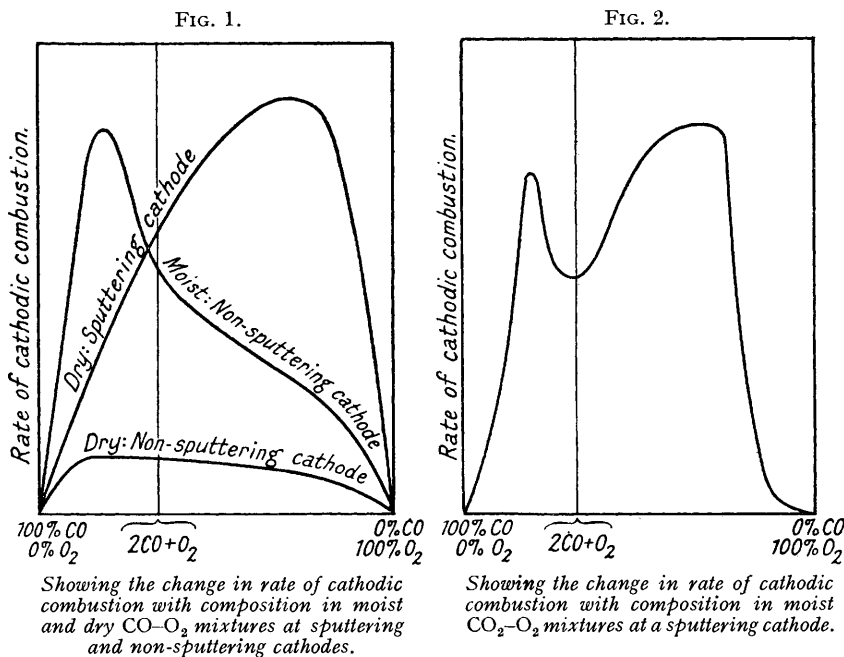
Such a view is, however, at once negated by the following facts: The area of the electrode surface enveloped by the cathode glow increases with either increasing current or decreasing gas pressure (I), but the rate of cathodic combustion of a given gaseous mixture is directly proportional to the current and, in the case of hydrogen-oxygen or carbon monoxide-oxygen mixtures in their combining proportions, is also practically independent of the pressure (I, III). On the other hand, with certain mixtures an increase in pressure may result in either an increase or a decrease in the rate of combustion, depending in the main upon the nature of their composition (VI, VII, VIII). Thus the rate of cathodic combustion is in no way determined by the area of electrode surface enclosed by the cathode glow. Finally, a change in pressure by itself affects, not only the extent of cathode area enveloped by the cathode glow, but also the thickness of the glow (I) without, however, necessarily affecting the rate of combustion (I, III). In view of these facts, it seems reasonable to conclude that cathodic combustion does not take place, even in part, at the immediate surface of the electrode, but is confined to the cathode zone. These considerations, in conjunction with the fact that the cathode material can and does greatly affect the rate of combustion, strongly suggest that the specific effect of the nature of the cathode material must be due to something projected away from the electrode surface into the cathode zone, where alone its influence is felt.

A dry  $2\text{CO} + \text{O}_2$  mixture burns approximately five times faster at a silver, gold, platinum, or palladium cathode than at one consisting of either tantalum or tungsten (III). It will at once be recognised that this order also divides these metals into two classes, according to whether they are good or indifferent cathodic sputterers. Further examples of these two groups of metals have been examined, and without exception it has been found that dry carbon monoxide-oxygen mixtures always burn more readily at a freely sputtering cathode than at a poor sputterer (III, VI). We may, therefore, conclude that the specific effect of the nature of the cathode material is due to the presence within the cathode zone of metal particles emanating from the cathode. There is evidence to show that such metal is projected into the cathode zone, not in the form of aggregates, but as discrete atoms. Thus, (i) the spectrum of the cathode glow in  $2\text{CO} + \text{O}_2$  burning at silver exhibits the line spectrum of this metal (V); (ii) an electron beam traversing a jet of magnesium, aluminium, or zinc vapour is randomly scattered (XI); (iii) the crystal structure of a film formed by the condensation of aluminium vapour is profoundly affected by the nature of the substrate (XI), which could hardly be the case if appreciable aggregation of atoms had taken place prior to deposition; (iv) finally, the crystal size of platinum films formed by cathodic sputtering decreases with increasing rate of sputtering, until practically all sign of organised crystal structure is lost (XII, XIII). In the light of these facts, it may be concluded that the specific effect of the nature of the cathode material upon the rate of cathodic combustion is due to the presence within the cathode zone of atoms of the metal of which the electrode consists, and that cathodic combustion is a purely homogeneous process, all reactions occurring in the gaseous phase.

Dry  $2\text{CO} + \text{O}_2$  burns slowly at a tantalum or tungsten, *i.e.*, non-sputtering, cathode (Fig. 1); but at a freely sputtered cathode, such as gold or silver, the metal atoms projected into the cathode zone effect an approximately five-fold (Fig. 1) increase in the rate of combustion of the dry mixture (III), and a similar remarkable acceleration (Fig. 1) is brought about by the addition of water vapour (IV). The accelerating effects of steam and metal atoms are, however, not additive, for the presence of moisture slightly reduces the rate of combustion of a  $2\text{CO} + \text{O}_2$  mixture at a sputtering cathode (IV). Furthermore, the rôles played by steam and metal atoms in overcoming the reluctance of carbonic oxide to burn cathodically must differ fundamentally, because steam is most active in accelerating the combustion of mixtures rich in carbonic oxide, whereas the rate of combustion of carbonic oxide at a freely sputtering cathode attains a maximum when excess oxygen is present (VI, VII) (Fig. 1), whilst replacement of the excess of oxygen by helium or argon mainly results in a dilution effect (VI). Finally, the independent modes of activity of steam and metal atoms in promoting the combustion of carbonic oxide-oxygen mixtures is established by the results recorded graphically in Fig. 2; when both steam and metal particles are present, the curve showing the relation between rate of cathodic

combustion and mixture composition exhibits two characteristic maxima, the one due to moisture where carbonic oxide is in excess, and the other due to sputtered metal in oxygen-rich mixtures (VI, VII). Thus, steam and metal atoms do not interfere to any pronounced extent with each other in promoting the cathodic combustion of carbonic oxide-oxygen mixtures.

From these facts and considerations, the following general conclusions relating to the cathodic combustion of carbonic oxide may be drawn: (i) Carbonic oxide has great difficulty in combining directly with oxygen; (ii) metal atoms overcome the reluctance of carbonic oxide to burn by acting in some manner with oxygen and rendering it suitable for easy interaction with carbonic oxide; finally, (iii) steam or some product of its decomposition by the discharge promotes the combustion by reacting with carbonic oxide. These general conclusions can now be examined more closely in the light of the further experimentally established facts set forth below.



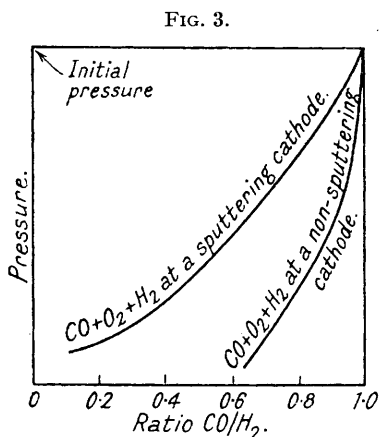
Note.—Figs. 1, 2, and 4 are to the same scale.

Dry, arced carbonic oxide exhibits the phenomenon of after-glow, and oxygen does so likewise (X). Oxygen in the state of after-glow contains ozone in abundance (X). In spite of the high levels of excitation which the colours of the after-glows indicate, and in spite of the fact that the glowing oxygen contains ozone, no combustion occurs on mixing such streams of carbonic oxide and oxygen (X).

When pure dry carbonic oxide circulates through the cathode zone, carbon dioxide is formed and carbon is deposited in equivalent amount, mainly on the cathode (VI). The 'CO' band, but not the Swan spectrum, is emitted (V). It may therefore be concluded that under these conditions auto-oxidation occurs as follows:  $\text{CO} + \text{CO} = \text{CO}_2 + \text{C}$ . The rate of such auto-oxidation is about three times less than that of the combustion of dry  $2\text{CO} + \text{O}_2$  at a non-sputtering cathode (VI). No carbon deposition is to be observed on the cathode enveloped by the cathode zone during the combustion of carbonic oxide-oxygen mixtures containing not less than about 10% of the latter (VI). Thus it would appear that carbon formed by the auto-oxidation of carbonic oxide is burnt too rapidly by oxygen to permit of its escape from the cathode zone and subsequent deposition upon the cathode in any except carbonic oxide-oxygen mixtures greatly deficient in oxygen. We may therefore conclude that the mechanism of the cathodic combustion of carbonic

oxide with oxygen in the absence of sputtered metal atoms consists, at least in part, of the auto-oxidation of carbonic oxide and the subsequent combustion of the carbon thus set free. So far the study of the cathodic combustion of carbonic oxide has afforded no proof of the possibility or otherwise of the direct oxidation of carbonic oxide by oxygen. This does not warrant, however, the assumption that any such direct union is impossible; the evidence on this point must be regarded as neutral, in so far as concerns cathodic combustion.

Thin films of an oxide of platinum exhibiting little or no crystal structure can be formed by cathodic sputtering in oxygen under suitable conditions of pressure and current. Films sputtered under similar conditions, but in oxygen-free hydrogen, nitrogen, or argon, however, consist mainly of relatively large crystals of platinum (XII). Thus, platinum atoms are chemically active in that they readily combine with oxygen to form an oxide which exhibits little tendency to aggregate, whereas platinum atoms by themselves tend to group into crystals. The platinum oxide films are more or less readily reduced by hydrogen at room temperature (XII, XIII), and carbonic oxide exerts a similar but far



Showing that carbonic oxide disappears more rapidly than does hydrogen as cathodic combustion proceeds in a CO + O<sub>2</sub> + H<sub>2</sub> mixture.

more sluggish action (XII). Such films are almost instantaneously reduced by a cool stream of dry, arced hydrogen or carbonic oxide (X). The reduction is accompanied by a pronounced, sometimes even remarkable, increase in crystal size (XII, XIII). In view of these results and of the fact that sputtered metal atoms are most active as promoters of cathodic combustion when oxygen is in excess (VI), it seems reasonable to conclude that the metal acts by forming oxides or unstable metal atom-oxygen complexes which are readily reduced by suitably excited carbonic oxide.

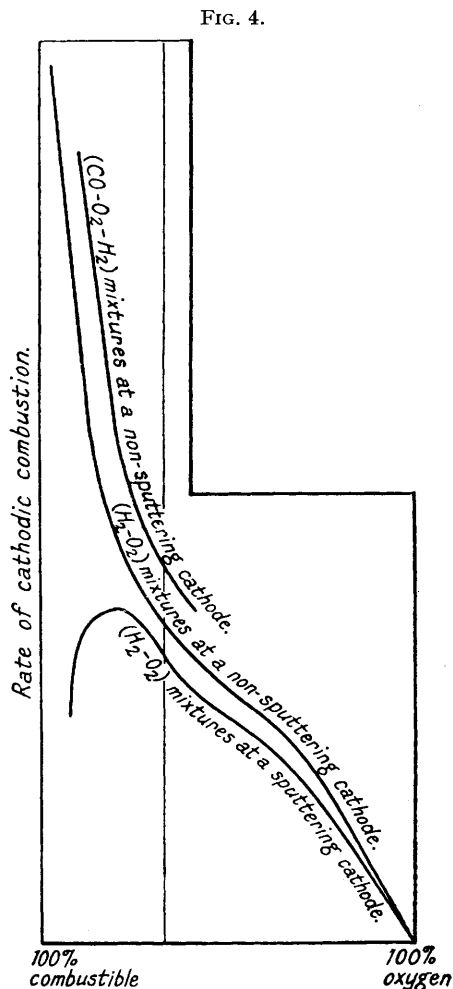
Carbonic oxide-oxygen-hydrogen mixtures containing not more than sufficient oxygen for complete combustion burn at either non-sputtering or sputtering cathodes in such a manner that carbon dioxide is more rapidly formed than is steam (VII) (Fig. 3); thus, the carbonic oxide appears to burn more rapidly than does the hydrogen. The rates of cathodic combustion occurring in such mixtures at non-sputtering cathodes have, however, little or nothing in common with those observed in the case of either dry or moist carbonic oxide-oxygen mixtures; CO-O<sub>2</sub>-H<sub>2</sub> mixtures burn, in general, not only much faster, but the manner in which the rate of combustion varies with increasing combustible contents also bears no resemblance to that observed in the case of dry or moist CO-O<sub>2</sub> mixtures (VI, VII) (Fig. 1). A close parallel exists, however, between the rates of cathodic combustion of CO-O<sub>2</sub>-H<sub>2</sub> and H<sub>2</sub>-O<sub>2</sub> mixtures; in both, the rates of combustion at a non-sputtering cathode increase rapidly and in a similar manner with increasing combustible contents (VII, VIII, IX) (Fig. 4). Furthermore, within the limits hitherto examined, a partial substitution of carbonic oxide by an equivalent amount of hydrogen has little or no effect upon the rate of combustion of CO-O<sub>2</sub>-H<sub>2</sub> mixtures. In view of these facts, it is difficult to resist the conclusion that, during the combustion of CO-O<sub>2</sub>-H<sub>2</sub> mixtures at a sputtering cathode, the hydrogen burns first and at a rate which in effect determines that of the mixture as a whole, and that the apparent preferential combustion, *i.e.*, the more rapid disappearance of carbonic oxide, is due to oxidation by some product, or products, of the combustion of hydrogen which is thereby returned to the mixture; and, further, since the rate at which carbonic oxide burns when undergoing such preferential combustion is much higher than that observed in the case of dry carbonic oxide-oxygen mixtures, it follows that carbonic oxide is burnt far more readily by the product, or products, of the combustion of hydrogen than by oxygen.

The extent to which carbonic oxide burns preferentially in CO-O<sub>2</sub>-H<sub>2</sub> mixtures is far greater when combustion proceeds at a sputtering cathode than otherwise (Fig. 3), although

the total rate of combustion is greatly reduced, in some cases by as much as three times, by the presence of metal atoms (VII). These facts strongly suggest that (i) carbonic oxide is burnt by at least two oxidation products of hydrogen, one of which is more highly oxygenated than the other, and thus, on reduction, leads to the return of less hydrogen, and that (ii) metal atoms either prevent the formation of, or decompose, the oxygen-rich hydrogen combustion product, and in this manner not only increase the extent to which the carbonic oxide is burnt preferentially, but are also responsible for the reduction in the rate of combustion observed at a sputtering cathode. This view is further supported by the fact that  $H_2-O_2$  and  $CO-O_2-H_2$  mixtures containing combustible in sufficient excess all burn at a sputtering cathode at a practically similar rate, which is, within wide limits, independent of the composition (VII, VIII). Thus the conclusion may be drawn that the dominating mechanism in the combustion of  $CO-O_2-H_2$  mixtures at either sputtering or non-sputtering cathodes is that of the combustion of hydrogen, in the sense that in such mixtures the oxidation of carbonic oxide is effected by oxidation products of hydrogen and is thus determined mainly by the prior combustion of hydrogen.

In addition to steam, the only oxidation products of hydrogen known to be formed within the cathode zone maintained in either steam or electrolytic gas are hydroxyl and, possibly, hydrogen peroxide, which has been detected, though only in small amounts, in the products issuing from the discharge (VI, VII, VIII). Hydroxyl, however, is present in profusion (V). It is well known that finely divided metals are capable of decomposing hydrogen peroxide, sometimes even explosively. Nevertheless, it is improbable that hydrogen peroxide plays any material rôle in the cathodic combustion of  $CO-O_2-H_2$  mixtures, because moist  $CO-O_2$  mixtures deficient in oxygen burn at rates which are not only practically independent of the presence, or otherwise, of metal atoms, but are also much higher than the rates of combustion at a sputtering cathode of similar mixtures in which the steam has been replaced by an equivalent amount of hydrogen (VI and VII); and it can hardly be supposed that hydrogen peroxide is more liable to decomposition by metal atoms when produced directly from hydrogen than when formed in any other manner. These facts do, however, strongly suggest that the oxygen-rich combustion product of hydrogen which is so active in burning carbonic oxide is hydroxyl, and that metal atoms neither decompose hydroxyl nor do they prevent its formation from steam; but that sputtered metal in some manner inhibits the formation of hydroxyl as a direct intermediate product of the cathodic combustion of hydrogen to steam.

A view can now be put forward, according to which carbonic oxide can be and is burnt during the cathodic combustion of  $CO-O_2-H_2$  mixtures both by steam and by hydroxyl. Thus, according to this view, the rate of combustion in moist  $CO-O_2$  mixtures deficient in oxygen is independent of the nature of the cathode material, because metal



Showing the rates of combustion with composition in various mixtures burning at sputtering and non-sputtering cathodes (to scale with Figs. 1 and 2).

atoms do not impede the formation of hydroxyl as a result of the decomposition of steam by the discharge. In the case of  $\text{CO-O}_2\text{-H}_2$  mixtures, however, since metal atoms inhibit the formation of hydroxyl from hydrogen, the carbonic oxide is burnt in the main by steam, with the result that the extent to which carbonic oxide burns preferentially in such mixtures is much greater at a sputtering than at a non-sputtering cathode. Finally, it is in the absence of metal atoms that the rate of burning of  $\text{CO-O}_2\text{-H}_2$  mixtures containing excess combustible attains a maximum and the extent of preferential carbonic oxide combustion a minimum, because the oxidation of hydrogen *via* the hydroxyl stage is unhindered, with the result that, not only steam, but also hydroxyl is available to take part in burning the carbonic oxide. The view that carbonic oxide can be and is burnt by two products of the combustion of hydrogen is further supported by the fact that the position of the cathodic water-gas equilibrium is determined mainly by the gas pressure (IX), which suggests that in the one direction equilibrium is approached by two simultaneous reactions, one of which is favoured by an increase in pressure whilst the other is retarded.

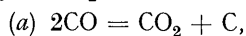
Oxygen-rich hydrogen-oxygen mixtures burn at relatively low rates at either a sputtering or a non-sputtering cathode. In the case of mixtures containing excess hydrogen, however, and burning at a non-sputtering cathode, combustion increases at a remarkable rate with increasing hydrogen concentration, an effect which is almost wholly suppressed by the presence of metal atoms (VIII) (Fig. 4). In the first place, these facts strongly suggest that both hydrogen and oxygen must be suitably excited before they can combine, and that the life of oxygen in the excited state is short, whilst that of the hydrogen is long. Further, the more than three-fold reduction in the rate of cathodic combustion which can be and is effected by the presence of sputtered metal atoms can be reasonably explained, in accordance with the view of the mechanism of the combustion of  $\text{CO-O}_2\text{-H}_2$  mixtures put forward above, as follows. Hydroxyl is an intermediate product in the normal combustion of hydrogen to steam. Metal atoms form with oxygen easily reduced oxides or unstable complexes which burn hydrogen to steam directly and thus suppress the intermediate formation of hydroxyl. Finally, since the rate of combustion of a hydrogen-rich hydrogen-oxygen mixture is much greater in the absence than otherwise of metal atoms, *i.e.*, when hydroxyl is freely formed as an intermediate product, it may be concluded that hydroxyl in some manner powerfully promotes the combustion of hydrogen.

The fact that the rates of combustion of  $\text{H}_2\text{-O}_2$  and of  $\text{CO-O}_2\text{-H}_2$  mixtures at a non-sputtering cathode increase rapidly and in a similar manner with increasing combustible contents (Fig. 4) suggests that the short life of oxygen in the suitably excited state for interaction with hydrogen is due to deactivation by collision with oxygen in some form or other, but not with hydrogen or carbonic oxide. Cool, arced moist hydrogen contains much atomic hydrogen but reacts most reluctantly, if at all, with similarly arced oxygen which is in a state of after-glow and rich in ozone undergoing decomposition (X); thus, the respective levels of excitation to which hydrogen and oxygen must be raised are high if they are to combine directly and without the intervention of any promoter of combustion such as hydroxyl. It is well known, however, that steam dissociates to a measurable extent at comparatively low temperatures of the order of  $800^\circ$ . It follows that the energy required to bring about the decomposition of steam is far less than that necessary in order to excite hydrogen and oxygen sufficiently for them to combine directly. For thermochemical reasons, the most probable initial step in the mechanism of the decomposition of steam consists in the interaction of two steam molecules, whereby hydroxyl and hydrogen are formed. Herein lies a probable explanation of the striking fact, discovered by Smithells, Whitaker, and Holmes (J., 1930, 185), that the ignitability of a  $2\text{CO} + \text{O}_2 + (\text{H}_2)$  mixture by an electric discharge is conditioned by a trace of steam. Thus, according to this view, a comparatively powerful discharge is required to ignite the rigidly dried mixture, because the initial formation of hydroxyl calls for the prior excitation of hydrogen and oxygen molecules to relatively high levels; in the case of the incompletely dried mixture, however, a much milder discharge suffices to produce hydroxyl by the decomposition of steam and thus to initiate combustion.

## SUMMARY.

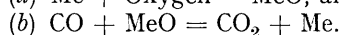
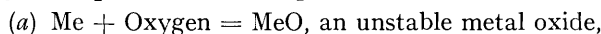
The results of a study of the cathodic combustion of hydrogen, carbonic oxide, and of their mixtures with moist and dry oxygen, are reviewed. It is concluded that the following reactions occur during the cathodic combustion.

(i) Dry CO-O<sub>2</sub> mixtures in the absence of metal atoms :

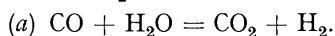


(b) C is burnt by oxygen.

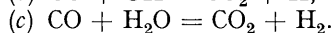
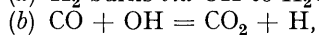
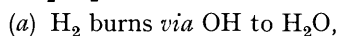
(ii) Dry CO-O<sub>2</sub> mixtures in the presence of metal atoms :



(iii) Moist CO-O<sub>2</sub> mixtures :

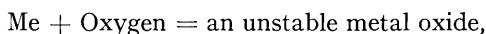


(iv) CO-O<sub>2</sub>-H<sub>2</sub> mixtures in the absence of metal atoms :



(v) H<sub>2</sub>-O<sub>2</sub> mixtures in the absence of metal atoms : When the mixture is rigidly dried the initial step is (a)  $\text{H}_2 + \text{O}_2 = 2\text{OH}$ , but (b)  $2\text{H}_2\text{O} = 2\text{OH} + \text{H}_2$  when moisture is present ; whereupon hydroxyl in some manner acts as a powerful promoter in the succeeding stages of combustion.

(vi) H<sub>2</sub>-O<sub>2</sub> mixtures in the presence of metal atoms :



It is not suggested that these views afford a complete explanation of the modes of combustion of hydrogen and carbonic oxide ; in view of the close parallel which can be drawn between the conditions of gaseous combustion in the cathode zone and in flame, however, it is submitted that the new facts brought to light by the study of cathodic combustion must be taken into account in any attempt to formulate a considered view of the mechanisms of the combustion of hydrogen and carbonic oxide, and of the rôle played therein by steam.

The author expresses his indebtedness to his collaborators whose names appear in the following list of references : I, Finch and Cowen, *Proc. Roy. Soc.*, 1926, **111**, A, 257 ; II, *idem*, *ibid.*, 1927, **116**, A, 529 ; III, Finch and Hodge, *ibid.*, 1929, **124**, A, 303 ; IV, *idem*, *ibid.*, 1929, **125**, A, 532 ; V, Finch and Thompson, *ibid.*, 1930, **129**, A, 314 ; VI, Finch and Patrick, *ibid.*, p. 656 ; VII, *idem*, *ibid.*, p. 672 ; VIII, Finch and Mahler, *ibid.*, 1931, **133**, A, 173 ; IX, Finch, Bradford, and Greenshields, *ibid.*, 1934, **143**, A, 482 ; X, Finch and Bradford, J., 1934, **360** ; XI, Finch and Quarrell, *Proc. Roy. Soc.*, 1933, **141**, A, 398 ; XII, Finch, Murison, Stuart, and Thomson, *ibid.*, p. 414 ; XIII, Finch and Ikin, *ibid.*, 1934, **145**, A, 551.