THE MECHANISM OF IGNITION BY ELECTRIC DISCHARGES

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The precise sequence of events by which a potentially explosive gaseous mixture is caused to ignite has for long been a matter of speculation and experiment, and has suffered several reinterpretations in the light of various theories. Of the two commonest modes of ignition, electrical and thermal, the former, being inherently the more complex, has received the less attention. Its very complexity, however, insofar as it places a greater number of controllable variables at the disposal of the investigator, gives it added utility as a means of probing the molecular processes involved. This paper is intended briefly to survey the development of the theory of electrical ignition of explosive gaseous mixtures, and to give an account of its present position.

The general characteristics of electrical ignition can be briefly summarized: (*1*) *Limits of inflammability.* All combustible gases in admixture with air or oxygen have the property in common that explosion will only occur within certain limits of composition. In all cases which have been examined, more electrical energy is necessary to bring about ignition of mixtures near the limits than in the middle zone of the region of inflammability. In this respect electrical ignition differs markedly from thermal ignition. (*2*) *Limiting igniting pressure.* A given gaseous mixture becomes increasingly more difficult to ignite as its pressure is reduced, and a greater dissipation of electrical energy becomes necessary to initiate explosion. Hence the incendivities of different sparks may be compared by determining the least pressures at which they will ignite a given mixture. Such limiting pressures have only relative significance; up to the present time no absolute lower pressure limit for electrical ignition has been established. (*3*) *Least igniting energy.* Alternatively, the relative ignitabilities of different gas mixtures may be compared by measuring the least sparks which will ignite them. The igniting spark may be characterized, for example, by its total energy.

A bibliography of published work is appended to this paper. Because of imperfect control of electrical factors, much of the earlier work on electrical ignition cannot be used as a sound basis for generalization; indeed, progress has to a large extent been conditioned by improved control and understanding of the electrical factors underlying the phenomena. The development of early ideas may be briefly outlined.

The alternative possibilities that ignition might be the result either of specifically electrical effects or of thermal effects due to the conversion of electrical energy to heat energy have been recognized from the time of the first systematic work on the subject. Coward and his collaborators (9, 8) determined the sensitivities of various gaseous mixtures by the method of limiting igniting pressures. Certain diluents (e.g., oxygen up to 70 per cent) were found to decrease the limiting (to certain arbitrary spark conditions) igniting pressures of hydrogen–oxygen mixtures, whilst others brought about an increase; a partial correlation appeared to exist between ignitability and thermal conductivity. Hence the view was taken that thermal factors were predominant, although it was necessary to make an exception in the case of carbon monoxide–oxygen mixtures, in which some specific activation of oxygen was suspected; the balance of evidence failed to decide whether thermal or electrical factors predominated. Similar phenomena have more recently received a different explanation based on chain propagation (44). It must, however, be pointed out in this connection that unless electrical factors are fully under control, data based on limiting igniting pressures may be misleading, since the electrical characteristics of a gaseous mixture can be, and often are, fundamentally altered by the addition of a diluent gas.

The first experiments in which systematic control of electrical conditions was aimed at were made by Thornton (45–50, 63, 51–55), using the method of least igniting energy or current. His work included studies of many different types of igniting agent, and led to the fundamentally important observation that a given amount of electrical energy can possess vastly different igniting powers when dissipated in different forms. For example, a capacity spark was found to be considerably more effective in igniting certain gases than a spark produced by breaking a circuit containing inductance, and the incendivity of the latter type of discharge increased as the voltage applied to the circuit increased. From the undoubted specificity of the discharge characteristics which Thornton's work revealed, he concluded (46) that ionization was the effective cause of ignition. More recently, however, in the light of the results to be described later, which led to the excitation theory of ignition, Thornton has recognized that ionization is not the only factor to be considered (18).

THE THERMAL THEORY OF ELECTRICAL IGNITION

The question was reopened by Morgan (29). It had long been known that a spark discharge produced by an oscillation transformer, i.e., a coil or magneto, was a complex phenomenon consisting in the main of two characteristically different parts. One such part is due to the discharge, on breakdown of the gap, of the energy stored in the distributed self-capacity of the secondary circuit, and is termed the "capacity component." The subsequent discharge of electromagnetic energy through the secondary circuit forms what is known as the "inductance component" of the discharge. Morgan found that if a magneto is shunted by a variable air condenser, the incendivity of the spark so produced towards a particular gaseous mixture increased with increasing capacity. He concluded that the igniting power of an induction coil or magneto spark is associated chiefly with the capacity component, and only secondarily with the inductance component which follows it. Meanwhile Wheeler (59) had independently postulated that the necessary condition for ignition was that sufficient energy should be introduced to maintain for a sufficient time a sufficient volume of a gaseous mixture at or above its ignition temperature. Although experiments, designed to show whether incendivity could be correlated with the thermal properties of the gaseous mixture concerned or with its speed of flame propagation, yielded negative results (59, 60), Wheeler found in the assumed general superiority of the capacity component in ignition a confirmation of a purely thermal view of electrical ignition phenomena, and jointly with Morgan and Taylor-Jones (43) put forward a thermal theory of ignition, ultimately depending on that assumption.

The theory was founded on analysis of the temperature distribution in a gas in the immediate neighborhood of various types of localized heat sources. Such analysis indicated that for a given amount of energy, an instantaneous point source was superior to a continued source and that a volume source was superior to a point source, and it was considered that these differences were sufficient to account for the marked effect which the precise mode of dissipation of a given amount of electrical energy had on its igniting power—as shown by the researches of Thornton and others—without reference to ionization or any other specific characteristic of the spark discharge.

The theory was put by Morgan in the form "the ignition of a gaseous mixture depends primarily . . . on the raising of a sufficient volume to a sufficient temperature (43)," with the corollary that "the heat energy required in the source to produce ignition is least when the heat is imparted instantaneously. When the rate of heat supply is less, a greater quantity of heat must be given to the gas before ignition can occur" (31). The theory was applied to various ignition phenomena (see Morgan (30, 31, 32, 34, 35), Morgan and Wheeler (36), Coward and Meiter (10), Taylor-Jones (42), and Holm (24)), nevertheless it embodied a principle which was inherently improbable. Taking the statement of the thermal theory as set forth above, it is not difficult to show that it implies the view that the igniting power of a given quantity of energy lies dormant until the energy is converted into heat and thus increases with increasing lack of availability of such source energy. For temperature, a statistical measure of the mean kinetic energy of the random translational motions of the molecules of a system, is a fundamental conception which loses in significance as the entropy falls below the maximum consistent with the energy of the system. As in the case of a single molecule, the term "temperature" is meaningless when applied to mass motion. And since, according to the thermal theory, ignition calls for the raising of the gas to a sufficient temperature, it is clear that this view suggests that in the case of a source of least igniting energy the entropy/energy ratio of the system must be at a maximum before ignition can be determined therein. Coward and Meiter (10), as a result of their experiments, appear indeed to have arrived at this conclusion, because they state that "nothing in the results of (their) experiments suggests the intervention of any electrical effect of the spark . . . other than the normal effect of the degradation of its electrical energy."

CHARACTERISTICS OF GASEOUS COMBUSTION IN ELECTRIC DISCHARGES

About this time there came to light a set of facts relating to gaseous combustion in electric discharges which put the question of spark ignition in a new light, and enabled it to be divorced from the older standpoint of thermal ignition with which it had hitherto been linked. These facts will now be briefly reviewed.

A discharge between solid electrodes may take the form of either a low- or a high-tension arc, the essential difference being in the temperature of the cathode. The discharges employed in ignition are almost without exception of the high-tension type, and it has been shown by Finch and Cowen (14) that a high-tension arc dissipating energy at a surprisingly high rate can be maintained in an explosive gaseous mixture without causing ignition. In such a discharge, three luminous zones are ordinarily distinguishable: (*i*) the cathode and negative glows sheathing the cathode and constituting the cathode glow, (*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 $2H_2 + O_2$, 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 (14). 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 on the rate of combustion. 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 (14, 16). For example, dry $2CO + O_2$ burns more than three times more rapidly at a silver cathode than at a copper cathode. It has been shown that this remarkable effect cannot be due to a difference in the cathode potential falls of different metals; it may therefore be concluded that in the absence of a positive column, combustion is confined to the cathode zone.

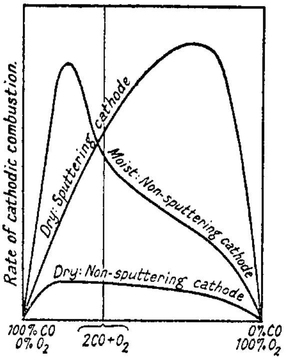


FIG. 1

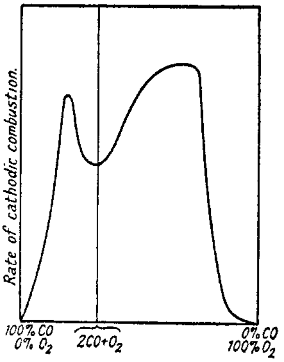


FIG. 2

FIG. 1. Showing the change in rate of cathodic combustion with composition in moist and dry carbon monoxide–oxygen mixtures at sputtering and non-sputtering cathodes.

FIG. 2. Showing the change in rate of cathodic combustion with composition in moist carbon monoxide–oxygen mixtures at a sputtering cathode.

In suitable conditions the cathode potential fall is independent of either the current or the gas pressure; thus the rate of combustion is directly related to the energy dissipated in the cathode zone. It has been established that the specific and very considerable influence which the nature of the cathode material exerts on the rate of cathodic combustion is not connected with the occurrence of heterogeneous combustion, as might at first sight be supposed, but that the effects are due to the influence of sputtered metal atoms, i.e., atoms of the cathode material torn from its surface and projected into the cathode zone under the influence of ionic bombardment.

Figures 1 to 4 summarize some of the results of a series of researches, for details of which reference must be made to the original papers (14, 15, 16, 19, 13). In these graphs the ordinates represent rates of cathodic combustion, expressed in terms of the ratio of the rate of combustion of the gas to the current carried by the discharge. Figures 1, 2, and 4 are drawn to the same scale.

Dry $2CO + O_2$ burns slowly at a tantalum or tungsten, i.e., non-sputtering, cathode (figure 1), but at a freely sputtering cathode such as silver or gold, the metal atoms projected into the cathode zone effect an approximately fivefold increase in the rate of combustion, and a rather similar acceleration is brought about by the addition of water vapor (see figure 1) (16). The accelerating effects of steam and of metal atoms are not, however, additive, for the presence of moisture slightly reduces the rate of combustion of a $2CO + O_2$ mixture at a sputtering cathode (19). Furthermore, the rôles played by steam and by metal atoms in overcoming the reluctance of carbon monoxide to burn cathodically must differ fundamentally, because steam is most active in promoting the combustion of mixtures rich in carbon monoxide, whereas the rate of combustion of carbon monoxide at a freely sputtering cathode attains a maximum when excess oxygen is present (figure 1) (19), whilst replacement of the excess of oxygen by helium or argon mainly results in a dilution effect. Finally, the independent modes of activity of steam and metal atoms in promoting the combustion of carbon monoxide–oxygen mixtures is established by the results recorded graphically in figure 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, one due to moisture when carbon monoxide is in excess, and the other due to sputtered metal atoms in oxygen-rich mixtures (19). Thus, steam and metal atoms do not interfere with each other to any material extent in promoting the cathodic combustion of carbon monoxide–oxygen mixtures.

From this and other cognate data it was concluded that the process of the combustion of carbon monoxide in different conditions may be represented as follows:

(*i*) Dry carbon monoxide–oxygen mixtures in the absence of metal atoms:
    (a) $2CO = CO_2 + C$, and
    (b) C is burnt by oxygen.
(*ii*) Dry carbon monoxide–oxygen mixtures in the presence of metal atoms:
    (a) Me + oxygen = MeO, an unstable metal oxide, and
    (b) $CO + MeO = CO_2 + Me$
(*iii*) Moist carbon monoxide–oxygen mixtures:

$$CO + H_2O = CO_2 + H_2$$

Carbon monoxide–oxygen–hydrogen mixtures containing not more than sufficient oxygen for complete combustion burn at either sputtering or non-sputtering cathodes in such a manner that carbon dioxide is more rapidly formed than is steam (figure 3); thus the carbon monoxide 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 moist or dry carbon monoxide–oxygen mixtures; carbon monoxide–oxygen–hydrogen 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 carbon monoxide–oxygen mixtures (figure 1). A close parallel exists, however, between the rates of cathodic combustion of carbon monoxide–oxygen–hydrogen and hydrogen–oxygen mixtures; in both, the rates of combustion at a non-sputtering cathode increase rapidly and in a similar manner with increasing combustible contents (19, 17, 13) (figure 4). Furthermore, within the limits hitherto examined, a partial substitution of carbon monoxide by an equivalent amount of hydrogen has little or no

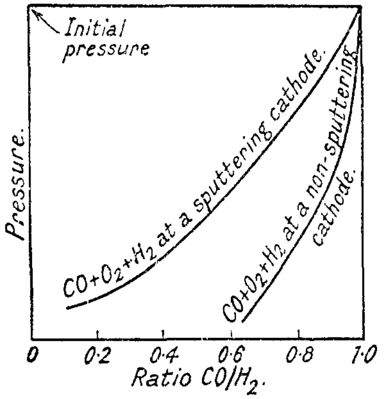


FIG. 3

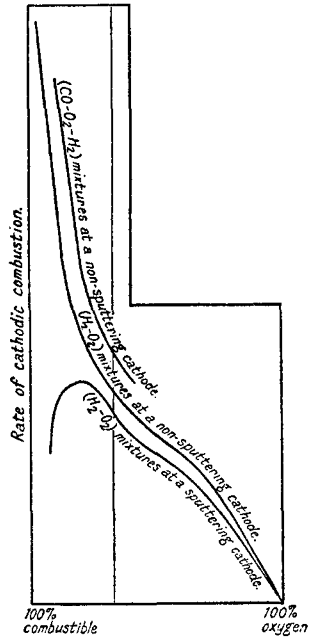


FIG. 4

FIG. 3. Preferential combustion of carbon monoxide in a carbon monoxide–oxygen–hydrogen mixture

FIG. 4. Cathodic combustion of hydrogen–oxygen and carbon monoxide–oxygen–hydrogen mixtures. Rate of combustion to same scale as in figures 1 and 2.

effect on the rate of combustion of carbon monoxide–oxygen–hydrogen mixtures. In view of these facts, it is difficult to resist the conclusion that, during the combustion of carbon monoxide–oxygen–hydrogen 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 carbon monoxide, 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 carbon monoxide burns when undergoing such preferential combustion is much higher than that observed in the case of dry carbon monoxide–oxygen mixtures, it follows that carbon monoxide is burnt far more readily by the product or products of the combustion of hydrogen than by oxygen.

Moreover, the extent to which carbon monoxide burns preferentially in carbon monoxide–oxygen–hydrogen mixtures is far greater when combustion proceeds at a sputtering cathode than otherwise (figure 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 (19). These facts strongly suggest (*i*) that carbon monoxide 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 to the burning mixture, and (*ii*) that 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 carbon monoxide is burnt preferentially, but are also responsible for the reduction in the rate of combustion in carbon monoxide–oxygen–hydrogen mixtures observed at a sputtering cathode. This view is further supported by the fact that hydrogen–oxygen and carbon monoxide–oxygen–hydrogen 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 of the mixture (19, 17).

In addition to steam, the chief oxidation products of hydrogen known to be formed within the cathode zone maintained in either steam or hydrogen–oxygen mixtures are hydroxyl, and possibly hydrogen peroxide, which has been detected, though only in small amounts, in the products issuing from the discharge (19, 17). Hydrogen, however, is present in profusion (22).

It is improbable for several reasons that hydrogen peroxide plays any material rôle, and the facts strongly suggest that it is OH which, like steam, is so active in burning carbon monoxide, and that metal atoms neither decompose OH, nor do they prevent its formation from steam, but that sputtered metal in some manner inhibits the formation of OH as a direct intermediate product of the cathodic combustion of hydrogen to steam. Thus the combustion of carbon monoxide–oxygen–hydrogen mixtures at non-sputtering cathodes may be represented as follows:

(a) H_2 burns *via* OH to H_2O,
(b) $CO + OH = CO_2 + H$, and
(c) $CO + H_2O = CO_2 + H_2$

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 (figure 4) (17). 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 threefold 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 mechanism of the combustion of carbon monoxide–oxygen–hydrogen 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 OH is freely formed as an intermediate product, it may be concluded that OH in some manner powerfully promotes the combustion of hydrogen.

The fact that the rates of combustion of hydrogen–oxygen and of carbon monoxide–oxygen–hydrogen mixtures at a non-sputtering cathode increase rapidly and in a similar manner with increasing combustible contents (figure 4) suggests that the short life of oxygen in the suitably excited state for combustion with hydrogen is due to deactivation by collision with oxygen in some form or other, but not with hydrogen or carbon monoxide. 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 afterglow and rich in ozone undergoing decomposition (12); 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 promotor of combustion such as OH. It is well known, however, that steam dissociates to a measurable extent at comparatively low temperatures of the order of 800°C. 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 steam molecules, whereby hydroxyl and molecular hydrogen are formed. Herein lies a probable explanation of the striking fact, discovered by Smithells, Whitaker, and Holmes (40) that the ignitability of a $2CO + O_2 + H_2$ mixture by a spark is greatly increased 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 OH 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.

Concluding the summarized combustion mechanisms so far established: (*i*) hydrogen–oxygen mixtures in the absence of metal atoms: when the mixture is rigidly dried the initial step is (a) $H_2 + O_2 = 2OH$, but (b) $2H_2O = 2OH + H_2$ when moisture is present; whereupon OH in some manner acts as a powerful promotor in the succeeding stages of combustion. (*ii*) Hydrogen–oxygen mixtures in the presence of metal atoms: $Me + \text{oxygen} = MeO$, and $H_2 + MeO = H_2O + Me$.

These results provided clear evidence that the cathode zone of a high-tension discharge is a region in which gas molecules are excited to states of specific excitation which determine their subsequent reactivity, and that the gas in the path of the discharge is not merely heated by passage of the current.

IGNITION BY HIGH-TENSION, DIRECT-CURRENT DISCHARGES

At a given gas pressure, a high-tension, direct-current discharge can be maintained in an explosive gaseous mixture up to a limiting current; above this current the mixture explodes. The transition from steady combustion to ignition was the subject of a separate investigation (14); in the case of $2H_2 + O_2$ mixtures it was shown, *inter alia*, that: (*i*) Ignition occurs without lag immediately on attainment of a certain limiting current. (*ii*) A hyperbolic relationship exists between the gas pressure and the igniting current over a considerable range of conditions. (*iii*) A decrease in gap width, which results in a broadening out of the bright positive glow, increases the value of the igniting current.

On kinetic grounds, the concentration of ions, or of molecules or atoms excited to any particular state, is also approximately a hyperbolic function of gas pressure for conditions such as those under consideration, in which the potential drop across the discharge is constant. It follows, therefore, that in the conditions of these experiments, ignition was determined by the attainment of a certain definite concentration of suitably excited molecules or atoms.

THE FUNCTION OF IONS

Ions, however, could not be excluded on the evidence so far available, although analyses of the rates of cathodic combustion of hydrogen and of carbon monoxide indicated that combustion was probably determined by excitation of the reactant molecules to states falling short of complete ionization. In the case of carbon monoxide a direct proof of this was furnished by a spectrographic examination (22). Spectrograms of the positive column and cathode zones of discharges at both sputtering and non-sputtering electrodes in carbon monoxide and in the mixture $2CO + O_2$ revealed the presence of carbon monoxide bands, but no evidence of ionized carbon monoxide. Carbon monoxide molecules in the discharge were therefore excited, but not ionized; hence it was clear, at least in the case of carbon monoxide, that combustion was determined by excitation falling short of ionization.

EXCITATION THEORY OF ELECTRICAL IGNITION

From this and much other cognate evidence it became increasingly clear that the necessary prerequisite for the ignition of an explosive gaseous mixture was the setting up of a *sufficient concentration of suitably activated molecules,* and abundant indications existed that ignition by an electrical discharge depended on this specific activation and not on the fully degenerate activation associated with thermal energy, as postulated by the thermal theory of ignition. The two theories conflicted directly, and a crucial test between them was therefore devised (23). The experimental method employed is shown in figure 5.

Mixtures of carbon monoxide and air in their equivalent proportions were ignited by means of condensed discharges of known oscillation frequency, and the igniting powers of the sparks were determined in terms of minimum igniting pressures, conditions being so arranged that the effect of frequency on igniting power could be studied independently of (*i*) the total amount of energy dissipated or (*ii*) its rate of dissipation either during the first half-cycle or during the complete discharge.

The condenser was charged through a diode and discharged at a constant initial voltage of 8300 volts through a circuit containing a variable inductance but otherwise of negligible impedance. Hemispherical aluminum electrodes were used for the spark gap, this metal being chosen because of its low cathode potential fall and freedom from sputtering. A subsidiary spark gap discharging in a lagged chamber fitted with a thermo-

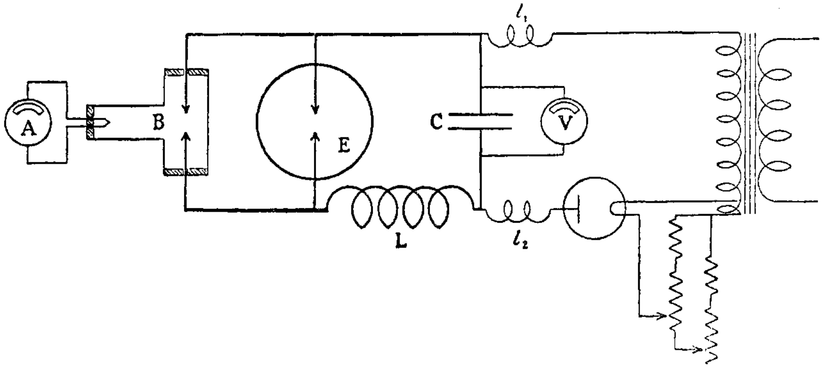


FIG. 5. Diagram of a condenser discharge circuit for ignition experiments (Finch and Thompson)

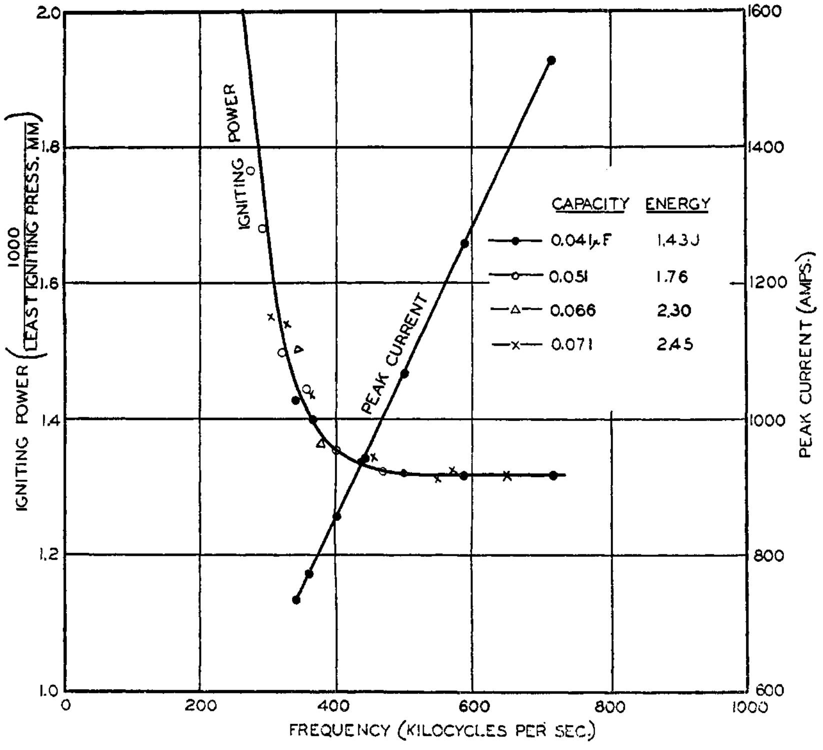


FIG. 6. Effect of frequency of discharge on its igniting power and on peak current. The peak current is for a capacity of 0.041μF; other capacities gave similar curves.

couple furnished a means of comparing the relative energies of different sparks. Experiments were carried out over a range of frequencies for a number of different capacities. The results are summarized in figure 6.

It will be seen that for each value of the capacity the igniting power of the discharge increased with decreasing frequency, in spite of the fact that the energy dissipated by the discharge decreased with decreasing frequency. Furthermore, it will be observed that the frequency of the discharge exerted a considerably greater effect on its igniting power than did its total energy. It is not difficult to see also that the igniting power of the spark was not determined by the value of the peak current. The experiments showed that the igniting power of a spark due to the discharge of a condenser through an inductive circuit is determined by the natural frequency of the circuit to such an extent that a suitable decrease in frequency may completely outweigh the effect of any possible reduction in igniting power due to either a decreased amount or rate of energy dissipation, or both, by either the first half-oscillation of a spark or by the entire discharge. According to the thermal theory, however, "ignition depends on the heating of a sufficient volume of the gas by conduction to a sufficient temperature" (34), which also implies that "the heat energy required in the source to produce ignition is least when the heat is imparted instantaneously. When the rate of heat supply is less, a greater quantity of heat must be given to the gas before ignition can occur" (31). Hence it is clear that the conflict between the thermal theory and the facts set forth herein is complete. The mechanism of electric spark ignition, therefore, and indeed of ignition as a whole, cannot be adequately explained in terms of any purely thermal theory. On the other hand, the excitation hypothesis is consistent with, and capable of, explaining these facts. For, according to this view, ignition being primarily determined by the setting up of a sufficient concentration of suitably activated molecules, the imparting of energy to the molecules in such a manner as to bring about either an insufficient or excessive degree of activation is wasteful from the point of view of causing ignition. Now it is well known that the greater the frequency of a condensed discharge, the higher is the level to which the molecules are thereby activated. Thus the high-frequency spark is in general a rich source of ionization, whereas the low-frequency arc spectrum reveals mainly the presence of neutral atoms or molecules, and it may be concluded that in the present case a reduction in frequency resulted in an increase in the ratio between energy usefully expended in the production of suitably activated molecules and that otherwise dissipated.

IGNITION BY THE COIL DISCHARGE

There remained for solution the problem of the mechanism of ignition by a coil discharge, which is the case of practical importance. A systematic study of the phenomenon called for an investigation of the respective rôles played by the two components of the coil discharge, and it was desirable to be able to modify or suppress one without materially affecting the other. Means of achieving this emerged from a consideration of the theory of the ignition coil based on a cathode-ray oscillographic study of the discharge.

CHARACTERISTICS OF THE IGNITION COIL DISCHARGE

Neglecting the secondary resistance, the general coil circuit equations may be written:

$$L_1 \mathrm{d}i_1/\mathrm{d}t + L_{12}\mathrm{d}i_2/\mathrm{d}t + R_1 i_1 + e_1 = 0$$

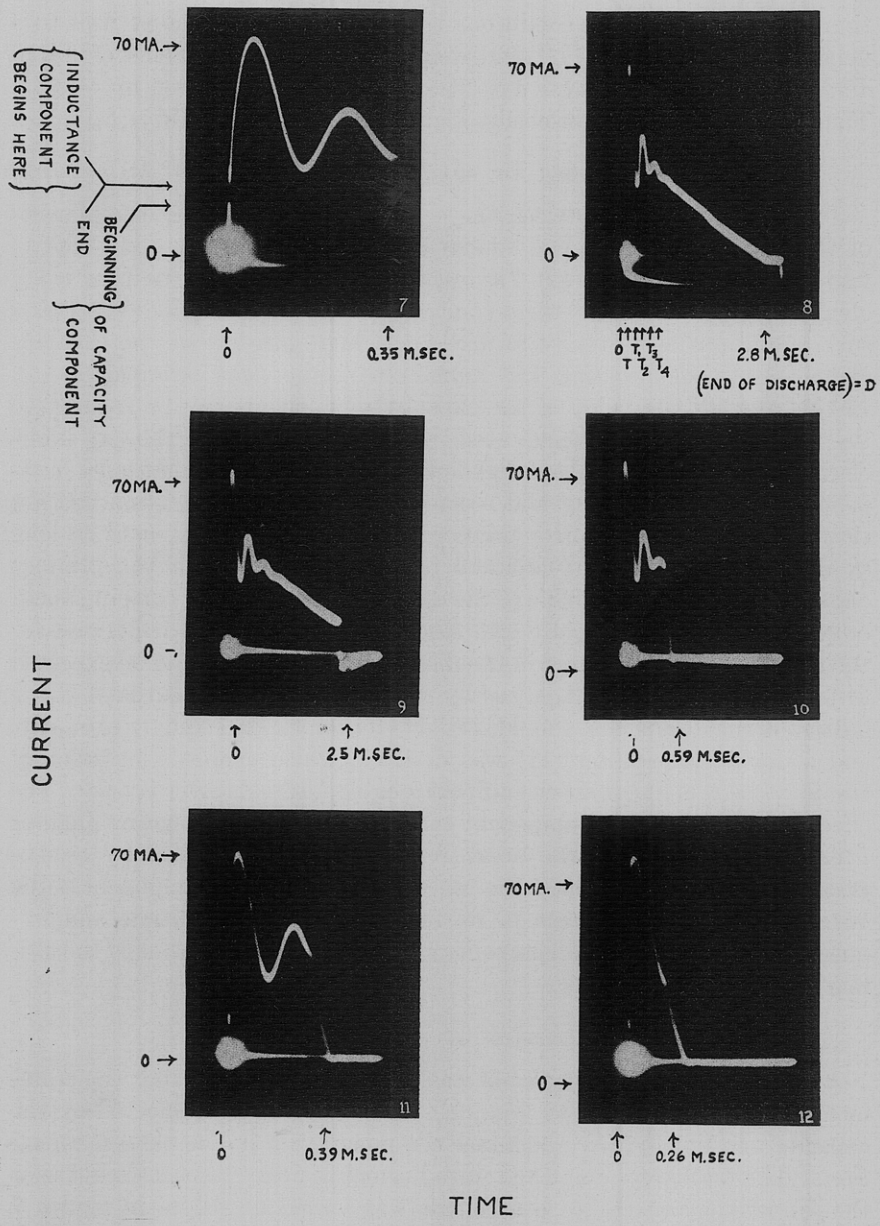
and

$$L_2 \mathrm{d}i_2/\mathrm{d}t + L_{21}\mathrm{d}i_1/\mathrm{d}t + e_2 = 0$$

where L_1, L_2 and C_1, C_2 are the primary and secondary inductances and capacities respectively, R_1 is the primary resistance, i_1 and i_2 are the primary and secondary currents, e_1 and e_2 are the potential differences across the condensers, L_{12} and L_{21} are the coefficients of mutual induction of the secondary on the primary and of the primary on the secondary, respectively, and t is the time. Taylor-Jones (41) has solved these equations for two special cases, i.e., (*i*) open-circuited secondary and (*ii*) secondary closed by an ohmic resistance, neither of which, however, is of much interest from the point of view of ignition, because, in the normal circumstances of its use, the coil is required to furnish a spark across a short fixed gap, the breakdown potential of which is much smaller than the maximum voltage which the coil is capable of exerting. The above equations can, however, be solved for the case of practical interest, provided the voltage-current characteristic of the spark be known.

Cathode-ray oscillographic analysis (20, 5) of a typical ignition coil discharge led to the following results. Upon breaking the primary circuit the discharge voltage rises in a manner determined by the coil constants and spark gap conductance to the breakdown potential of the gap, and then falls with extreme rapidity to a value at which it remains sensibly constant throughout the remaining life of the discharge. The corresponding current–time trace is shown completely in figure 8: the initial part of the current–time trace is best understood from figure 7, which was taken with a suitable air-dielectric capacity shunting the spark-gap. The gap in the trace near the origin corresponds to the discharge of the capacity component; the trace is invisible here because both the frequency and the amplitude of the discharge are exceedingly high. For a certain ignition coil assembly, for example, the frequency was of the order of $10^7\sim$, and the peak value of the current was calculated to be about 30 amp.

The spark potential is virtually constant and independent of the current during the life of the discharge; therefore no current flows in the secondary self-capacity during the discharge, and $L_{12} = L_{21}$. Hence it may be shown



FIGS. 7–12. Oscillograph records of induction coil spark discharges. FIG. 7, taken with a suitable air-dielectric capacity shunting the spark gap; FIG. 8, complete discharge; FIG. 9, late cut-off of discharge; FIG. 10, cut-off at T_3; FIG. 11, cut-off at T_2; FIG. 12, cut-off at T_1.

that in normal sparking conditions the inductance component rises to a maximum value of $2i_0e^{-a\pi/2\omega}$ and executes damped oscillations of initial amplitude ni_0 about a linear axis, the slope of which is given by $-e_2/L_2$. The total duration of the discharge is given by Mi_0/e_2, where $M = L_{12} = L_{21}$.

CONTROL OF SPARK COMPONENTS

Thus the difference between the capacity and inductance components of the discharge is clear and fundamental; their separation and control was carried out as follows: *The capacity component* can be practically eliminated by including in the secondary circuit a suitable diode run under such conditions as virtually to arrest the high currents of the capacity component whilst passing the inductance component unimpaired (5). In this manner the value of the capacity component may be reduced to the negligible quantity represented by the charging up of the gap inter-electrodic capacity to the breakdown potential. *The inductance component:* Since the primary and secondary circuits in an ignition coil are closely coupled, the effective primary inductance must be small as long as the secondary is short-circuited by a spark. Hence if the primary circuit is closed during the life of the discharge, the primary current should build up exceedingly rapidly and since the energy would otherwise for the most part have appeared in the discharge, the latter would be expected to terminate abruptly. Analysis by means of the theory outlined above indicated that the spark should, in fact, terminate exceedingly abruptly, and a double interrupter (11) was designed which enabled the primary circuit to be remade at short and controllable intervals after break. The effect on the inductance component can be seen in the oscillograms (figures 7 to 12). Variation of the break–remake period, controlled by oscillographic observation, enabled the life of the inductance component to be varied from practically zero to its full value. The amplitude and frequency of the inductance component were controllable through the primary current and capacity.

COIL IGNITION OF STAGNANT GASES

A series of critical experiments was planned to find whether the statement of Morgan and others (*loc. cit.*) that coil ignition is effected by the capacity and not by the inductance component is a justifiable generalization. The discharges employed were normal in every respect except that the life of the inductance component was varied as shown in figures 7 to 12. Table 1 shows a typical series of results with the explosive mixture $2CO + O_2 + 5\%H_2$ (4). It was immediately clear that the igniting power of the spark decreased with progressive suppression of the inductance component, and when the least possible amount of inductance component energy was allowed to pass, the mixture failed to ignite at the highest pressure which could be employed without danger of shattering the explosion vessel. It may be emphasized that the capacity component was not reduced by progressive suppression of the inductance component, but must have increased for the igniting sparks; Paschen's law is known to hold with accuracy over the range of pressures employed, and the breakdown potential of the gap, and hence the energy of the capacity component, must therefore have increased with increasing gas pressure.

The same principle was shown to apply to ignition of the mixtures $2H_2 + O_2$ and $CH_4 + O_2$, but with the latter, cut-off of the inductance component had considerably less effect on the igniting power of the discharge. Thus, whilst a $2CO + O_2 + 5\%H_2$ mixture was relatively insensitive to ignition by the capacity component as compared with $CH_4 + 2O_2$, the position was reversed when the energy associated with the inductance component was increased to more than 10% of its maximum possible value.

TABLE 1

Relation of coil ignition to inductance component

CUT-OFF (SEE FIGURES 8 TO 12)	INDUCTANCE COMPONENT ENERGY	DURATION OF INDUCTANCE COMPONENT	IGNITING POWER = 1000/LEAST IGNITING PRESSURE	LEAST IGNITING PRESSURE
	m.J.	*m.sec.*	*mm.*	*mm.*
End of discharge	20.5	2.81	9.43	106
T_4	9.2	0.79	7.70	130
T_3	7.4	0.59	7.41	149
T_2	5.2	0.39	6.50	154
T_1	2.4	0.20	5.13	195
T	*ca.* 0.15	0.02	4.26	235

It was clear therefore that the interaction of the spark and combustible gas molecules was complex and specific, and a study of the effects of further separation of the induction coil variables was necessary. As a final step, therefore, an investigation was made of the igniting powers of spark discharges modified in such ways as were necessary to isolate, not only the effect of the capacity component, but also the effects of the peak currents and duration of the inductance component (5). The discharge circuit conditions employed are shown in table 2.

With a normal inductance component duration the results were as shown in table 3.

Comparing the results for circuit conditions B and C(a) in the mixture $2CO + O_2 + 5\%H_2$ it will be seen that elimination of the capacity component of the discharge had an exceedingly small effect on its igniting

TABLE 2

Discharge circuit conditions employed

CIRCUIT CONDITIONS	NATURE OF DISCHARGE	CURRENT-TIME OSCILLOGRAM
A. Unmodified	Normal coil discharge	Figure 8
B. Diode in series with gap shunted by condenser and filament fully heated	Normal coil discharge	As in A
C. Diode without shunting condenser:		
(a) filament fully heated	Negligible capacity component; inductance component unimpaired	Figure 14
(b) filament underrun	Negligible capacity component; normal (or nearly so) inductance component duration, but oscillations more or less damped out, according to extent of underrunning	Figures 15 to 19
D. Diode shunted by condenser; filament cold	Normal capacity component; negligible inductance component	
E. Diode as in D but without condenser		

TABLE 3

Results with a normal inductance component duration

CIRCUIT CONDITIONS	LEAST IGNITING PRESSURE	IGNITING POWER	CAPACITY COMPONENT ENERGY	INDUCTANCE COMPONENT	
				Energy	Duration
Mixture $2CO + O_2 + 5\%H_2$					
	mm.		*m.J.*	*m.J.*	*m.sec.*
A	92.5	10.8	0.62	29.8	3.66
B	108.0	9.3	0.84		
C(a)	111.0	9.0	0.89		
D	No ignition at 304.0	3.3	6.7		
E	No ignition at 313.0	3.2	7.1		
Mixture $CH_4 + O_2$					
A	89.5	11.2	0.58	23.8	2.67
B	90.5	11.1	0.59		
C(a)	92.0	10.8	0.61		
D	224	4.5	3.6		
E	No ignition at 250	4.0	4.5		

power, and the mixture $CH_4 + O_2$ gave a similar result. The capacity component alone (circuit condition D) failed to ignite a $2CO + O_2 + 5\%H_2$ mixture at the highest pressure which could be safely employed; in $CH_4 + O_2$ ignition could be brought about by its sole agency, but at a greatly increased pressure.

The effect was even more striking when the inductance component energy was reduced by cutting off to a value nearer the capacity component energy. For example, with an inductance component duration of 0.38 m.sec. (i.e., a duration nearly half that shown in figure 19) inductance component energy (without associated capacity component) amounting to 5.11 mJ. ignited a $2CO + O_2 + 5\%H_2$ mixture at 152 mm., while capacity component energy of 8.8 mJ., without any succeeding inductance component energy, failed to ignite at a pressure of 350 mm.; the behavior

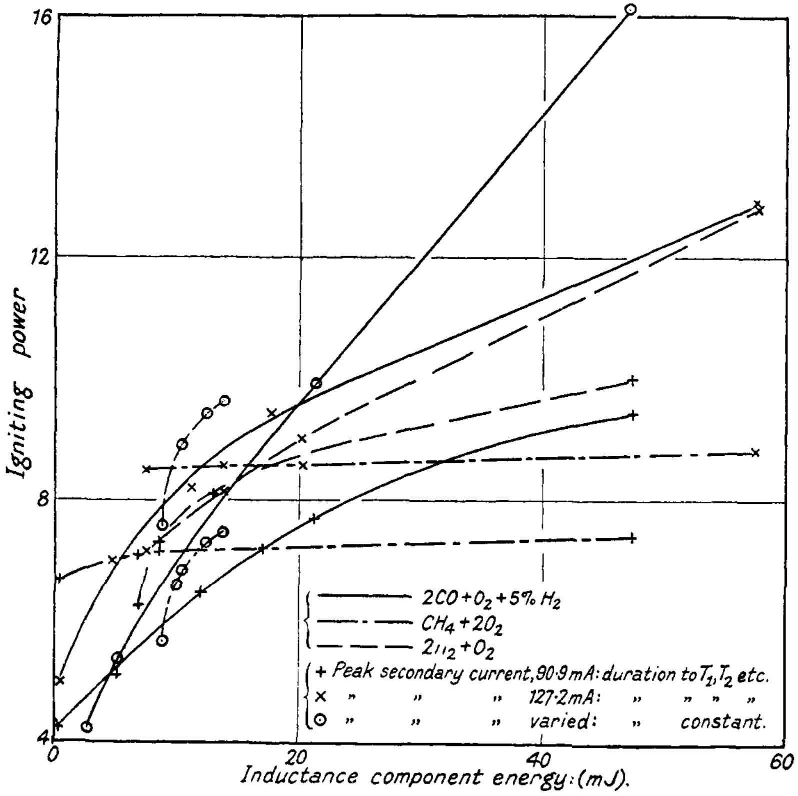
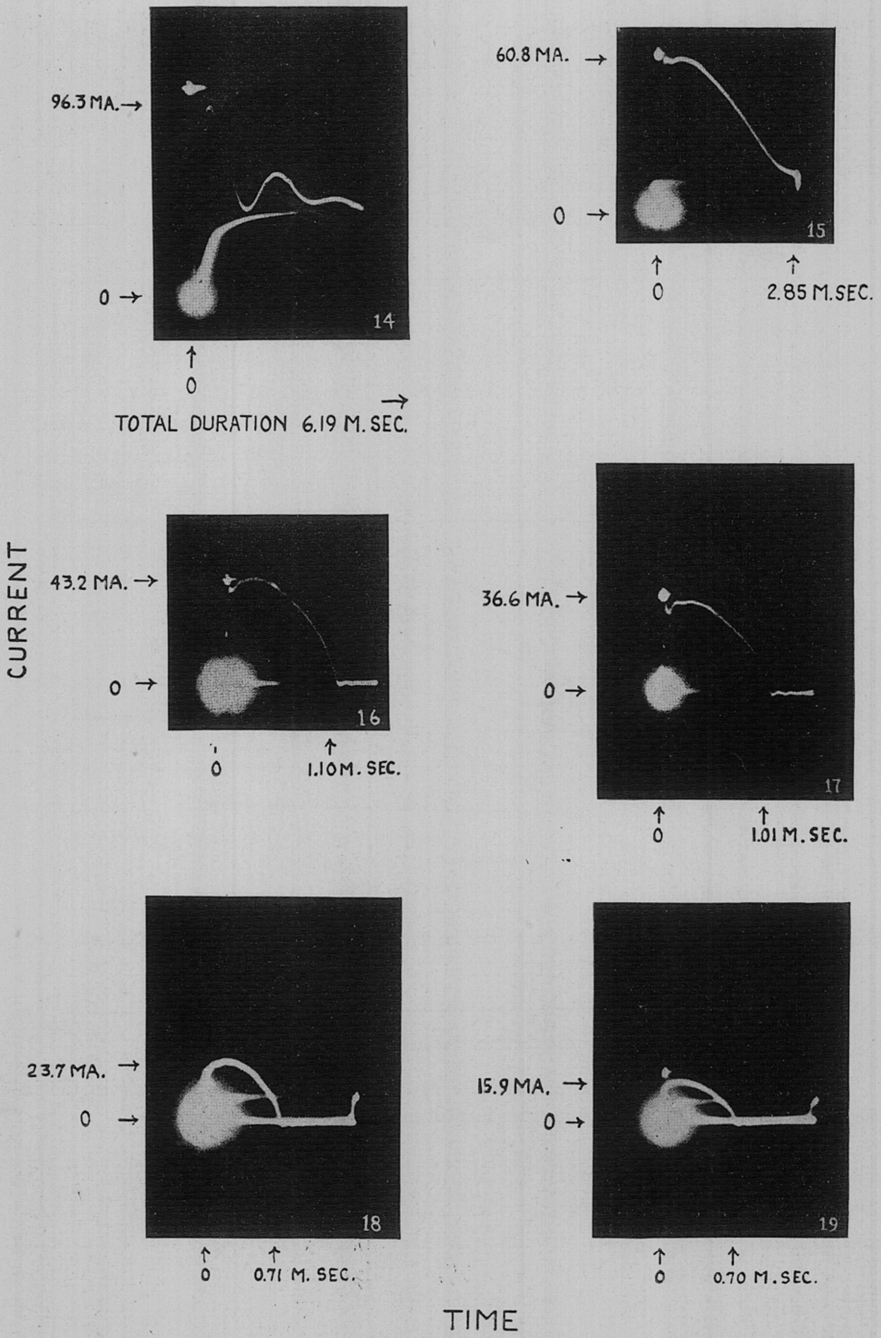


FIG. 13. Relation of igniting power of spark discharges to the energy in the inductance component for various gas mixtures.



FIGS. 14–19. Oscillograph records of induction coil spark discharges

of methane was similar. These results not only bring out the relative inefficiency of a high-frequency oscillatory discharge as a source of ignition, but also enable the conclusion to be drawn that the igniting power of any subsequent inductance component is but little, if at all, enhanced by a preceding capacity component of dimensions similar to that met with in normal coil practice.

Variation of the inductance component energy, the peak current, and discharge life gave results which are summarized in figure 13. These again show clearly that the igniting power of the coil discharge is associated in the main with its inductance component, and, further, that not only the total energy of this component but also the peak and mean rates of dissipation of such energy influence the igniting power to extents which vary with the nature of the explosive mixture. For example, whilst in the case of all the mixtures an increase in either the peak rate of dissipation of energy or the total amount of energy resulted in an increase of igniting power, the influence of the total duration of the discharge varied according to the nature of the gas mixture. Thus, prolongation of the discharge beyond the second inductance component oscillation failed to effect any pronounced increase in the igniting power in the case of the methane mixture, whereas with $2H_2 + O_2$, and even more so in the case of $2CO + O_2 + 5\%H_2$, the igniting power of the discharge increased steadily with increasing duration. With a damped and partially cut-off inductance component (as in figures 15 to 19) dissipating, e.g., 10 mJ., the order of decreasing sensitivity to ignition of the mixtures was $2H_2 + O_2$, $2CO + O_2 + 5\%H_2$, $CH_4 + O_2$; on the other hand, dissipation of a similar amount of energy in the form of a normal undamped, but suitably cut-off inductance component (as in figures 7 to 12) resulted in an inversion of this order (see figure 13), thus confirming the fact already brought out that whilst methane was more particularly sensitive to the peak rate of energy dissipation, the ignition of the other mixtures could be brought about more efficiently by increasing the life of the discharge at the expense of the peak rate of energy dissipation, the total spark energy remaining otherwise unchanged.

SPARK IGNITION IN THE INTERNAL-COMBUSTION ENGINE

In the case of the experiments so far discussed, the ignition pressures were of the order of 0.1 to 0.2 atm., and the gas was both cool and stagnant. In the engine, however, the gas pressure at the moment of ignition is of the order of 10 atm., the gas is hot as a result of preheating and adiabatic compression, and is furthermore in a highly turbulent state. In order to bring out the practical bearing of the results obtained with stagnant gases, further experiments in which account was taken of these important changes in conditions were carried out with a standard four-cylinder petrol engine (18). For details, the original paper must be consulted; among the more important points established were the following: (*i*) Power output, efficiency, and speed were alike unaffected by cutting off the latter part of the inductance component, so that the total spark duration was reduced, in one case, for example, from 2.0 to 0.5 m.sec. (*ii*) Variation of peak secondary current in the inductance component was also without effect on the engine characteristics. (*iii*) When the duration of the discharge was reduced sufficiently, misfiring occurred, and it was proved that the misfires were due to the occasional failure of the spark to jump the plug points, and not to the failure of the spark to ignite the explosive mixture. In the engine cylinder the conditions are so far removed from the limits that the igniting power of any spark furnished by the coil is greater than the least igniting value, and even if the spark consists only of the capacity component of the discharge, ignition occurs without fail.

The results proved that the only part of the ignition coil discharge required for ignition of the explosive mixture in an internal-combustion engine is the capacity component, the discharge of which can be insured in spite of a relatively high plug conductance by the retention of only a short initial portion of the inductance component, and the discharge duration can be reduced to one-tenth and possibly much less, without affecting either the igniting properties of the spark or the performance of the engine.

CONCLUSION

The researches which have been outlined above enable the view that electrical ignition is attributable to purely thermal effects of the spark to be dismissed. For not only has a large body of evidence been accumulated which shows that an electrical discharge is a region in which gas molecules are activated directly to states in which they are capable of taking part in the process of combustion, but it has also been shown experimentally that electrical ignition does not possess the characteristics which a purely thermal process of ignition would require. The facts relating to the ignition of gases, so far as they are now known, are, however, consistent with the view that combination is determined by a prior excitation of the molecules to suitable energy levels; excitation falling short of, or exceeding, such levels leads in the main to waste of igniting energy. According to this quite general "excitation" view of ignition, temperature, as a measure of collision frequency, is only of secondary significance. Heat is but one of several forms of energy capable of giving rise to suitable excitation and, owing to the random element, by no means necessarily the most efficient.

The further definition of the precise mechanism by which an electrical discharge initiates an explosion in any particular gaseous mixture must depend on a full exploration of that system. Sufficient has been outlined above to show that the combustible gases which have so far been examined, i.e., carbon monoxide, hydrogen, and methane, differ characteristically in their response to discharges of various types. No attempt will be made here to explain the possible causes of the specific influence of the combustible gas; work shortly to be published on the cathodic combustion of methane bears on this point. As an indication of the lines along which many of the phenomena of ignition may be quantitatively expressed in terms of the rates at which activation and deactivation occur in various types of discharge, a paper by Mole (25) may be consulted.

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