Summary and Conclusions

The speed of uniform movement of flame in mixtures of methane with air and with artificial "atmospheres" composed of 20.9% of oxygen, the remainder argon or helium, has been observed in tubes of various diameters, for upward, horizontal and downward propagation of flame. The results indicate that, in this case at least, the important factors which determine flame speeds are: (1) the heat developed in the flame and the heat capacities of burnt and unburnt mixture; (2) the rate of chemical reaction. The rate of transmission of energy from the flame, whether it be by conduction of heat or by some form of readily absorbed radiant energy, is so rapid that but little change in flame speed is observed when helium (of high thermal conductivity and low absorption for radiant energy) is replaced by argon (of low thermal conductivity and higher absorption for radiant energy), the inert gas being present to the extent of about three-fourths of the whole mixture.

Certain observations concerning the composition of the "maximum flame-speed mixtures" of methane in various "atmospheres" have led to the suggestion that the temperature coefficient of the rate of oxidation of methane is relatively small at flame temperatures.

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[CONTRIBUTION FROM THE BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, AND THE SAFETY IN MINES RESEARCH BOARD, BRITISH MINES DEPARTMENT]

CHEMICAL ACTION IN THE ELECTRIC SPARK DISCHARGE. THE IGNITION OF METHANE[1]

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Introduction

The nature and sequence of the chemical changes which occur during the ignition of an explosive gas mixture have received little investigation. It is known, however, that a stream of small, weak sparks from an induction coil will cause, not explosion, but a gradual combustion of an explosive mixture.[4]

Other aspects of spark ignition have received considerable attention in

[1] This is a joint report on one of a series of investigations to decrease accidents in mines, being conducted under the coöperation between the Bureau of Mines, United States Department of Commerce, and the Safety in Mines Research Board, British Mines Department. Published with the approval of the Director, United States Bureau of Mines.

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[4] An intimate study of the gradual reaction of electrolytic gas ($2H_2 + O_2$) at reduced pressures in the continuous discharge has recently been reported by G. I. Finch and L. G. Cowen [*Proc. Roy. Soc.*, **111A**, 257 (1926)].

the past. Thus, estimates have been made of the minimum amount of energy which, applied in some form of electric spark discharge, will just ignite an inflammable gas mixture.[5] The sensitiveness of various gas mixtures to ignition by the electric discharge has been compared by means of determinations of the limiting pressures of gas for ignition with a fixed sparking arrangement.[6] Measurements have been made of the relative amounts of energy required to ignite a series of inflammable mixtures, such as the range of methane-air mixtures between the limits of inflammability.[7]

Several years ago one of us initiated experiments to determine the amount of chemical reaction induced by a single electric spark[8] which was just not strong enough to ignite inflammable gas mixtures. In these attempts, Jacobs found that the contraction in electrolytic gas ($2H_2 + O_2$) was exceedingly small; later, Lund obtained some success with a mixture of carbon monoxide, oxygen and carbon dioxide.

We are now able to report the successful measurement of the amount of reaction in the path of single electric sparks passed through explosive mixtures of methane and air, when the sparks are just too weak to cause ignition; analyses of the products have been obtained which give an interesting and somewhat unexpected picture of the chemical changes involved. Methane-air mixtures were chosen for investigation on account of the practical importance of a knowledge of the conditions affecting the ignition of fire damp in collieries by means of electric or frictional sparks from tools and machines.

The amount of reaction in the path of a single spark which is passed through an explosive mixture without causing ignition is too small for direct measurement. We have, therefore, used means for producing a series of equal sparks at intervals of about one second, and have found that the gas mixtures used show sufficient change in composition after the passage of several thousand sparks, for the progress of the reaction to be measurable by a carefully conducted gas analysis.

In the beginning it was expected that the amount of reaction could be

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[5] (a) Thornton, *Phil. Mag.*, [6] **28**, 734 (1914); *Proc. Roy. Soc.*, **91A**, 17 (1914). (b) Paterson and Campbell, *Proc. Phys. Soc.*, **31**, 168 (1919). (c) Morgan, *Phil. Mag.*, **45**, 968 (1923); (d) "Electric Spark Ignition," Crosby, Lockwood and Son, London, **1922.** (e) Bone and others, *Proc. Roy. Soc.*, **110A**, 615, 634 (1926).

[6] Coward, Cooper and Jacobs, *J. Chem. Soc.*, **105**, 1069 (1914).

[7] (a) Sastry, *ibid.*, **109**, 523 (1916). (b) Wheeler, *ibid.*, **117**, 903 (1920); (c) **125**, 1858 (1924); (d) **127**, 14 (1925). (e) Morgan and Wheeler, *ibid.*, **119**, 239 (1921).

[8] The term "*single* spark" as used in this communication implies the whole discharge which occurs at a gap in the secondary circuit of an induction coil when the primary is broken, or at a gap in leads from a condenser which is slowly charged to the break-down voltage of the gap. The spark is usually complex with a small but appreciable duration, in these circumstances. See a paragraph later entitled, "A Photographic Analysis of the Sparks Used."

measured by the pressure or volume change of those mixtures which contained more than enough oxygen for complete combustion of the methane, but much carbon monoxide and some hydrogen were always found in the products. Hence, the amount of reaction in the spark had to be deduced from analyses of the gases and, therefore, for moderate accuracy, it was necessary to pass enough sparks to reduce the methane content of the mixture by about 1%—from, say, 8.5 to 7.5%. It follows that the amount of combustion recorded per spark is merely an average of that which occurs in a series of mixtures of varying composition. It might be preferable, from some points of view, to refer each result to a mixture whose composition was the mean of those of the initial and final mixtures, but the advantage would be small, and complete accuracy of statement would not be attained thereby, so it is preferred to relate the experimental results to the composition of the original mixture.

Experimental Part

Two ignition vessels were used, both of glass with electrodes of bluntly pointed platinum wire. The first (Fig. 1) had fixed electrodes 0.52 mm. apart. The second (Fig. 2) had one of the electrodes attached to an accurate screw-thread in order that the gap length might be changed as required without alteration in the shape of the electrodes; the other electrode was fixed in position. The vessels held about 23 and 38 cc. of gas, respectively. A small tube to contain soda lime was attached to each ignition vessel by a ground-glass joint.

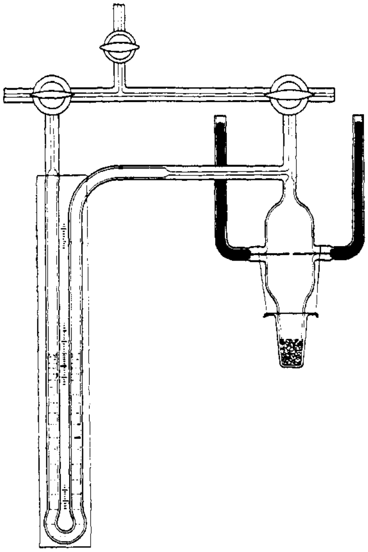

Fig. 1.

The total volume of each vessel was determined up to the various graduation points on the attached manometer gage. The amount of methane consumed was calculated from the volume and analysis of the original gas and of the products of reaction. The analyses were conducted over mercury in the Bone and Wheeler apparatus,[9] with an accuracy of about 0.02%. The high-tension igniting current for sparking was supplied by short, stout, insulated wires; for the ignition vessel (Fig. 1) the connection was made through mercury in side tubes arranged to enable the sparking vessel to be immersed in a water-bath, so that its exact temperature could be observed.

[9] Grice and Payman, *Fuel*, 3, 236 (1924).

For induction coil sparks, a 15cm. coil was used with a motor-driven mechanical break for the primary similar to that used by Wheeler.[10] The current through the primary was regulated by resistances so that the spark from the secondary terminals should be of igniting strength or otherwise. For condenser sparks a large air condenser of variable capacity (up to 0.0006 microfarad) was constructed with aluminum plates 11 mm. apart. This was charged from the same induction coil through a Kenotron two-electrode tube at such a rate that the condenser discharged once a second through the gap in the ignition vessel. The position of the movable plates in the condenser was regulated to provide a spark which, passing at the sparking voltage of the gap, would have sufficient energy for ignition or otherwise, as required. The electrical arrangements for induction coil and condenser sparks are indicated diagrammatically in Figs. 3 and 4, respectively.

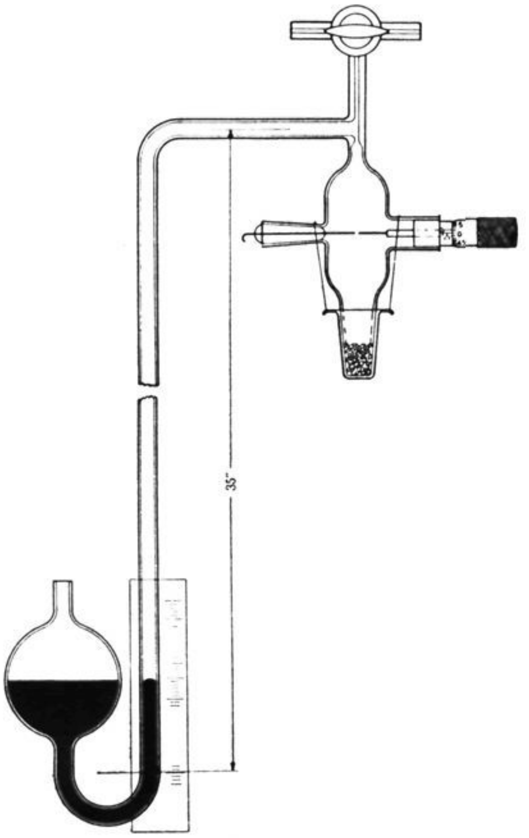

Fig. 2.

Preliminary Experiments

The fundamental experimental requisite was the production of a succession of thousands of sparks, each just incapable of igniting the explosive mixture in its path. This proved easier of attainment with the induction-coil sparks than with the condenser sparks, for in the latter case there was observed, as the test progressed, a tendency to build up a higher sparking voltage at the gap; the result was a spark of increased igniting power. Much greater regularity was obtained by adopting a suggestion to introduce a source of ionization, made by J. D. Morgan, who had experienced

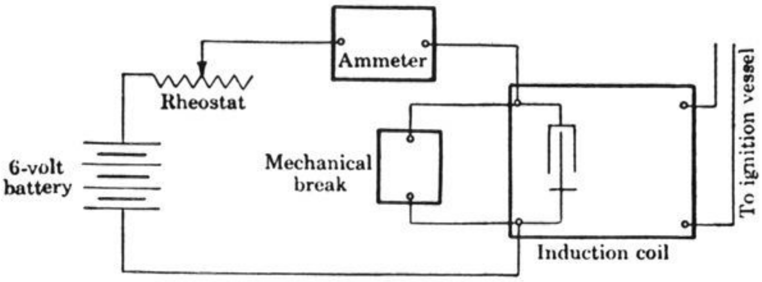

Fig. 3.

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[10] Wheeler, *J. Chem. Soc.*, **111**, 130 (1917).

the same trouble. A few fragments of a preparation which contained four parts per million of radium bromide (kindly supplied by Dr. S. C. Lind) were placed on the electrode wires at some distance from the gap. In consequence of the improvement observed with condenser sparks, the same procedure was adopted in experiments with induction-coil sparks.

The induction-coil sparks are thought to have been regular in character for the following reasons. (1) The appearance of the spark did not appreciably alter during the passage of many thousands in one test of 30,000, in another of 23,000, and so on. (2) The contraction in the gas was regular within the limits of accuracy of the measurements. Thus, when 30,000 sparks were passed in an explosive mixture, the contractions observed, per spark, for successive periods of 5000 sparks, were 39, 36, 37, 34, 37 and 36 thousandths of a cubic millimeter. (3) The regularity observed in (2) above might be deceptive, for the average contraction obtained during each 5000 sparks might have smoothed out the irregularities of individual sparks. It was repeatedly found, however, that when the minimum primary current to ignite a mixture by one of the first two or three sparks was determined, a current 0.05 amp. less would never produce ignition however many sparks were passed. Hence, no spark was obtained when the smaller current used was abnormally strong, at any rate to a significant amount. (4) Photographic analysis of the sparks on a rotating film gave regular and reproducible results.

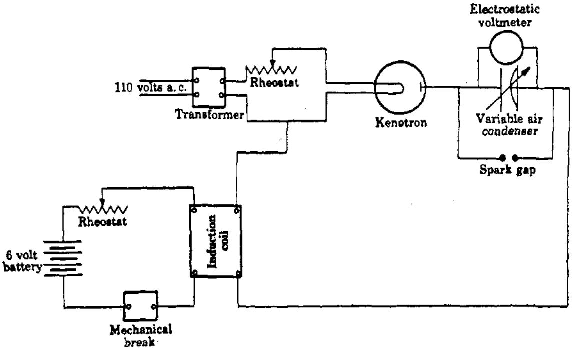

Fig. 4.

At times, irregularities in the spark effects were observed. On these occasions a redetermination of the igniting current showed an anomalous result, similar to those experienced by Sastry[7a] and by Wheeler.[7b] The irregularity was corrected by a careful cleaning of the gap and vessel, and normal igniting currents were then observed.

Ignition of an 8.3–8.5% Methane-Air Mixture

Of all mixtures of methane and air, the most readily ignited by electric sparks are those which contain between 8 and 9% of methane; they differ inappreciably in the amount of energy required for ignition by a given type of spark.[7] An 8.49% methane-air mixture, in the vessel of Fig. 1, was ignited when the current in the primary of the induction coil was 1.45 amp.; when the current was reduced to 1.40 amp.,[11] 5500 sparks were passed at intervals of one second without causing general inflammation. The volume of the gas changed from 23.57 to 23.37 cc , and its methane content from 8.49 to 7.38%. Hence the volume of methane consumed (at the mean temperature and pressure of the experiment, 23° and 752 mm.) was 0.276 cc., or 0.050 cu. mm., per spark. This amount of methane was present originally in a volume of mixture equal to 0.59 cu. mm. which is, therefore, the average amount of mixture inflamed per spark.

When the spark strength was reduced by changing the current in the primary of the coil from 1.40 to 1.20 amp., the average amount of mixture inflamed per spark became 0.39 cu. mm.

The variable-gap apparatus (Fig. 2) gave the following results, with sparks from the same induction coil with the same mechanical break for the primary current. For an 8.29% methane-air mixture, gap = 0.52 mm. (as before), the igniting current was 1.30 amp. (less than before, presumably due to some difference in the electrodes) and at 1.25 amp., the average amount of mixture inflamed was 0.53 and 0.52 cu. mm., in duplicate experiments. The agreement with the result obtained in the first apparatus is as good as could be expected. When, in the same apparatus, the gap was increased to 1.00 mm., the igniting current was only 0.90 amp.; at 0.85 amp. the average amount of mixture inflamed was 0.45 and 0.41 cu. mm., in duplicate experiments. Hence, the large increase in gap and consequent decrease in spark energy required for ignition have brought about a decrease, but not so great, in the amount of mixture which has to be ignited to produce general inflammation. This is ascribed mainly to the smaller cooling effect of the electrodes when the spark is longer.

Ignition of Other Methane-Air Mixtures

Table I contains the results of experiments with mixtures of methane and air containing less methane (6.22%) or more (11.18%) than is present in the most easily ignited mixtures (8–9%). The experiments were conducted in the apparatus shown in Fig. 1. The spark gap was 0.52 mm.; the experiments were conducted at laboratory temperatures and pressures.

The bold-face figures in Table I represent, for three mixtures, the amount which, when inflamed by the spark, is nearly sufficient to start a self-propagating flame. It is clear that as the composition of the mixture is altered from that of the most readily ignited mixture, the amount which

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[11] A closer approach between the current in the primary used for the experiment and the "igniting" current was not possible, for at intermediate values of the current, ignition was observed after the passage of some dozens or hundreds of sparks, the number being greater as the current was decreased.

has to be ignited in order to start a flame increases rapidly, much more rapidly, in fact, than the rate of decrease of the thermal energy of the reaction per unit volume.

TABLE I

IGNITION TESTS OF EXPLOSIVE METHANE-AIR MIXTURES

Compn. of methane-air mixture; CH_4, %	6.22				6.33	8.49		11.18		
Igniting current in primary, amp.	2.40				..	1.45		2.80		
Current in primary used for expt., amp.	2.35	2.35	1.50	1.50	1.50	1.40	1.20	2.75	2.00	1.50
Mixture burnt per spark, cu. mm.	**1.40**	**1.50**	0.72	0.81	0.77	**0.59**	0.39	**1.01**	0.53	0.21
Ratio $\frac{\text{Mixture burnt}}{\text{current}}$	0.60	0.64	.48	.54	.51	.42	.325	0.37	.265	.14
Ratio $\frac{\text{Mixture burnt}}{\text{Square of current}}$	.25	.27	.32	.36	.34	.30	.27	.13	.13	.09

Table I contains several additional examples of the reproducibility of results. It also shows that for each of the mixtures, the amount of reaction per spark increased regularly with the strength of primary current used, and at a greater rate than simple proportionality. No sudden jump was ever observed near to, but rather just below the igniting current. The amount of reaction ("mixture burnt") for any one mixture appears to be more nearly proportional to the square of the current, a result which would be expected if the energy of the discharge is proportional to the square of the current.[7d] In this respect the results for the 6.22% methane mixtures are least definite.

Course of Chemical Reaction in the Path of the Spark in Methane-Air and Methane-Oxygen Mixtures

Carbon dioxide and water vapor were efficiently absorbed by the soda lime in the ignition vessel. The mixture in the vessel, after sparking, was removed and analyzed and its composition was calculated back to the same figure for nitrogen as that for the mixture before sparking. This procedure was justified because in special experiments for the purpose, no oxides of

TABLE II

CHEMICAL CHANGES PRODUCED BY THE PASSAGE OF WEAK SPARKS IN EXPLOSIVE MIXTURES OF METHANE AND AIR

Original mixture, CH_4, %	6.22	6.22	8.49	11.18
CH_4 burnt	2.12	2.26	1.23	2.80
CO formed	1.25	1.26	0.74	1.99
CO_2 formed (calcd.)	0.87	1.00	.49	0.81
H_2 formed	.21	0.36	.49	1.46
H_2O formed (calcd.)	4.03	4.16	1.97	4.14
O_2 consumed (calcd.)	3.51	3.71	1.85	3.88
(found)	3.58	3.90	1.94	3.92
Ratio, CO_2/CH_4 burnt	41	44	40	29
Ratio, H_2O ($\times$ $^1/_2$)/CH_4 burnt	95	92	80	74

nitrogen were detectable after similar sparking. Table II gives the results corresponding with experiments already quoted.

The "calculated" figures of this Table were obtained as follows. The carbon dioxide (all of which had been absorbed by soda lime during the experiment) was equal to the difference between the volume of methane burnt and the volume of carbon monoxide found by analysis; the water (likewise absorbed) was equal to the difference between twice the volume of methane burnt and the volume of hydrogen found by analysis; the oxygen consumed was equal to the sum of the oxygen contents of the carbon monoxide, carbon dioxide and water. The agreement between the oxygen consumed, as calculated and as found by analysis, must be regarded as highly satisfactory, for the errors of analysis are accumulated in the calculated figure for oxygen. In view of this agreement, the writers are satisfied that the analyses represent substantially the entire products of the reaction. All methane-air mixtures which contain less than 9.46% of methane have an excess of oxygen above that required for complete oxidation of the methane; hence, it was almost certain that products of incomplete combustion of methane would be found for the 11.18% mixture. It was surprising, however, to find so much carbon monoxide and hydrogen in the products from the mixtures containing an excess of oxygen. The carbon monoxide exceeded the carbon dioxide in each experiment, while the water greatly exceeded the hydrogen. The interpretation suggested is as follows. According to the current theory of hydrocarbon oxidation,[12] the first reaction of combustion is $CH_4 + O_2 \longrightarrow (CH_2O + H_2O \longrightarrow)$ $CO + H_2 + H_2O$. Even in the presence of excess of oxygen, the greater part of the carbon monoxide and a small part of the hydrogen escape from the hot zone and are cooled without change. As hydrogen has the greater rate of diffusion it would tend to cool more rapidly and hence escape in greater proportion than carbon monoxide; as this is the reverse of what is observed, it appears that hydrogen is much more readily oxidized in the circumstances of the experiment.

From this it appears reasonable to conclude that when a methane-air flame is started by a spark discharge, it is propagated from the neighborhood of the spark by means of the heat of the reaction $CH_4 + O_2 \longrightarrow CO + H_2 + H_2O$ (vapor) + 65,000 cal., assisted by the heat of the reaction $H_2 + {}^1/_2O_2 \longrightarrow H_2O$ (vapor) + 58,000 cal., but not materially helped by the final combustion of carbon monoxide, even when an excess of air is present. If this is so, then, as the propagation of flame in a homogeneous mixture is merely a case of repeated ignitions of gas, layer after layer, it may be concluded that the methane flame has a definite (though small) thickness, whose first lamina includes chiefly the formation of carbon monoxide and water; the last, chiefly of carbon dioxide.

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[12] Bone, *Brit. Assoc. Advancement Sci. Repts.*, **85**, 376 (1915).

It appeared desirable to discover whether incomplete combustion would be observed when similar amounts of methane were sparked in the presence of oxygen instead of air. When a 6.26% methane-oxygen mixture was used, it was found that a less intense spark was necessary for ignition than that required by the corresponding mixture in air, 6.22% (the difference is immaterial), and less methane was burned. A greater proportion of the carbon oxidized was burnt completely to carbon dioxide, but there still remained some unburnt carbon monoxide and hydrogen even in the presence of this great excess of oxygen. Table III gives the details.

TABLE III

EXPERIMENT WITH A 6.26% METHANE-OXYGEN MIXTURE

Compn. of CH_4-O_2 mixture, CH_4, %	6.26	CO_2 formed (calcd.)	0.77
Igniting current in primary, amp.	1.30	H_2 formed	0.25
Current in primary used for expt., amp.	1.25	H_2O formed (calcd.)	2.29
Mixture burnt per spark, cu. mm.	0.98	Ratio, CO_2/CH_4 burnt, %	61
CH_4 burnt	1.27	Ratio, H_2O ($\times$ 1/2)/CH_4 burnt, %	90
CO formed[a]	0.50		

[a] To avoid the possible formation of carbon monoxide from alkaline pyrogallol during the analysis, the mixture was treated with chromous chloride solution to remove nearly all of the oxygen, then with alkaline pyrogallol to remove any residual trace of oxygen.

Effects of Sparking Some Non-Inflammable Mixtures Containing Methane

When sparks are passed through a mixture of methane and air which contains a sufficient excess of the one or the other, no self-propagating flame can be obtained, but a "flare" may be observed around the spark. The volume of the flare, which may be considerable, is greater as the composition of the mixture approaches more nearly the dilution limits of inflammability, and greater for stronger sparks. Such mixtures become inflammable in that region to which the spark contributes sufficient heat.

It is interesting to compare the amount and character of combustion in these mixtures, non-inflammable *per se*, when tested with sparks comparable in strength with those which will ignite inflammable mixtures. For the experiments, sparks from an induction coil with 1.50 amp. in the primary were passed in the vessel of Fig. 1 between electrodes 0.52 mm. apart. Table IV gives the results.

TABLE IV

IGNITION TESTS OF NON-EXPLOSIVE AND EXPLOSIVE MIXTURES COMPARED

Compn. of mixture, CH_4, %	3.12	6.22	8.49	11.18	16.47	51.6	100
Mixture consumed per spark, cu. mm.	0.55	0.77	0.59[a]	0.22	0.43	0.37	0.14
CH_4 consumed, cu. mm.	.017	.048	.050	.025	.072	.19	.14

[a] At 1.40 amp. in primary circuit of coil.

The figures prove that the reaction in the path of sparks passed through mixtures which do not propagate flame at laboratory temperatures is of the same order of magnitude as the reaction in explosive mixtures. In the case of pure methane and of the mixture of methane and air in nearly equal volumes, notable amounts of acetylene were found, 0.05 and 0.015 cu. mm. per spark, respectively, together with free carbon as well as hydrogen.

Quantitatively, the results show a maximum of reaction in the explosive mixtures with a gradual drop on each side, except that there is an apparently anomalous figure for the 11.18% mixture. (A fracture of the apparatus, due to imperfect annealing around one electrode, made it impossible to check this odd result.) A spark passed through pure methane will decompose about one-fourth of the volume it will inflame, without the subsequent spread of flame therefrom, in explosive mixtures. This conclusion suggested a more direct experimental comparison, as follows. Two mixtures were made, each containing 8.29% of methane, the first with air, the second with pure nitrogen. When submitted to a series of equal sparks in the same vessel, the first gave 0.53 and 0.52 cu. mm. of mixture burnt per spark, and the second gave 0.13 cu. mm. of mixture, the methane of which was decomposed into carbon, hydrogen and acetylene. The spark passing in an explosive mixture is therefore able to bring about the direct dissociation of only about one-fourth as many methane molecules as it causes to burn. Therefore, at the temperature of the electric spark, oxidation occurs more readily than methane dissociation; this observation is paralleled by low-temperature results.

A Photographic Analysis of the Sparks Used

Information about the nature of the induction-coil sparks used for ignition experiments was obtained by photographing them on highly sensitive paper (Lumière) on a rapidly rotating drum. The results proved that even the short and weak sparks used were composite in character, as observed previously for stronger discharges.[13] A single, unresolvable discharge was obtained only when the primary current was so weak (0.50 amp.) that the secondary discharge was just capable of jumping the gap. Stronger primary currents gave a spark from the secondary which appeared on the photographic record as a succession of flashes, or oscillations, of diminishing frequency. As a rule the first flash appeared to be somewhat brighter than those succeeding (an observation which was possible because the quartz lens used was not optically corrected); with an occasional exception the flashes after the first were of equal intensity. Table V summarizes the observations.

The slide-wire resistance used to control the primary current for these observations, as well as for the ignition experiments, was not wound to

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[13] Jones, "Theory of the Induction Coil," Sir Isaac Pitman and Sons, London, **1921**.

TABLE V

PHOTOGRAPHIC ANALYSIS OF SINGLE SPARKS FROM AN INDUCTION COIL WITH GAP OF 0.52 MM.

Primary current, amp.	Number of oscillations	Duration of spark, seconds
0.50	1	Very small
1.20	8 or 9	0.0007 to 0.0008
1.40	35 to 40	.0021
1.50	35 to 40	.0023
2.00	Not countable	.0041
2.35	Not countable	.0059
2.75	Not countable	.0081

avoid inductance. The use of a non-inductive resistance did not affect the nature of the discharge, as recorded photographically, nor did it affect the minimum igniting current, nor was the amount of methane burnt altered.

Some Observations with Different Types of Sparks

Although the object of this research was not to compare the igniting characteristics of various types of sparks, it was thought necessary to make observations with condenser sparks, in which the energy of the discharge is liberated more nearly instantaneously than in the case of induction-coil sparks. The large air condenser was used for the purpose, and photographic analysis failed to resolve the discharge obtained from it. If the duration of the spark had been so much as 0.00003 second, the means adopted would have shown that it was so; the condenser spark used was therefore much more nearly "instantaneous" than the induction-coil spark.

When the movable plates of the condenser were set so that on discharging through a gap, the spark just failed to ignite the mixture, the results were as follows.

Spark gap, mm.	Mixture, CH_4, %	Mixture burnt per spark, cm. mm.
0.52	8.47	0.84; 0.91
1.00	8.47	0.90

These figures are sensibly higher than those obtained in parallel experiments with the induction-coil spark—namely, about 0.5 cu. mm. In view of the great differences between the two types of spark, as revealed photographically, it is perhaps surprising that the amounts of gas burnt do not differ much more.

The comparison of effects obtained with the two types of spark was confirmed by the use of an intermediate type made by using the air condenser in parallel with the spark gap, when the induction coil was used as in the first set of experiments, the break of the primary current producing the spark at the secondary gap. The spark was of somewhat greater igniting power, as a primary current of 1.25 (instead of 1.40) amp. was the greatest that could be used without causing general inflammation. The amount of gas burnt by this spark had an intermediate value, 0.74 cu. mm., and there were only five flashes registered photographically for each spark.

It is curious that when the spark is concentrated in a smaller number of flashes, the amount of mixture which has to burn to initiate general inflammation is somewhat larger.

A Correlation of "Ignition-Volume" Data with the Energy Required for Ignition

M. Fourier[14] showed that if a quantity of heat, Q calories, is supplied instantaneously at a point in a medium of thermometric conductivity k and thermal capacity per unit volume c, then the temperature θ of any point r cm. away at a time t seconds later is

$$\theta = \frac{Q\, e^{-r^2/4kt}}{8\, c(\pi k t)^{3/2}} \qquad (1)$$

The maximum temperature, $\theta_{\text{max.}, r}$, attainable at the point r cm. from the source of heat occurs when $d\theta/dt = 0$. This occurs after an interval of time

$$t = r^2/6k \qquad (2)$$

Substituting for t in Equation 1, we have

$$\theta_{\text{max.}, r} = \frac{\sqrt{6}\, Q\, e^{-3/2}}{c\pi^{1/2}\,(4\pi r^3/3)} \qquad (3)$$

Putting $4\pi r^3/3 = V$, the volume of the sphere which is at or above the temperature θ, and assuming that $c = 0.00032$, we have

$$V = 964\, Q/\theta_{\text{max.}, r} \qquad (4)$$

This equation gives a means of correlating the present observations of the volume of gas raised to the temperature at which it burns, with that temperature, and with the energy of the spark which will just ignite an explosive mixture of methane and air, as determined by J. D. Morgan.[5c] His experiments showed that the energy Q of an air-condenser spark just strong enough to ignite an 8.8% methane-air mixture was 0.0009 cal. for a 1.00mm. gap. The volume V calculated from these figures with the aid of Equation 4 for several temperatures, together with the corresponding time interval[15] (after the passage of the spark) at which this occurs, is given in Table VI.

The calculated volumes of gas may be compared with the minimum volume of gas which, in the present experiments, had to be ignited to ensure general inflammation. This was about 0.9 cu. mm. for a con-

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[14] Fourier, "Théorie de la Chaleur," par. 385.

[15] Calculated from Equation 2, assuming that the thermal conductivity is 7×10^{-5} and therefore that $k = 7/32$.

TABLE VI

VOLUMES OF GAS ATTAINING VARIOUS TEMPERATURES AND THE TIMES REQUIRED

$\theta_{\max., r}$, °C.	Volume, cu. mm.	Corresponding time of attainment of $\theta_{\max., r}$, sec. $\times 10^3$
700	1.24	3.4
1000	0.87	2.7
1200	.72	2.4
1500	.58	2.0

denser spark passed through a mixture similar to that used by Morgan. The figure is close to that which would be expected, for although methane will ignite at 700° or thereabouts, there is a "time lag" of several seconds in its ignition at that temperature; at 800° the lag is less than one second, and a few hundred degrees higher the lag is presumably of the order of a thousandth of a second. It is demonstrated experimentally, therefore, that the volume of gas burnt in the spark (or the volume which has to be ignited to ensure general inflammation) is approximately the same as the volume raised to such a temperature that it will burn during the time this temperature is maintained.

For shorter sparks (0.52 mm.) calculated and observed figures are still of the same order, but not so close; this is accounted for by a much greater fraction of the spark energy being absorbed by the spark-gap wires.

The calculations depend on a number of assumptions. For instance, it is assumed that the whole energy of the discharge appears in the spark gap and that it is communicated to the gas as from a point source midway between the electrodes; furthermore, that the electrodes do not absorb energy from the thermal effects of the spark. None of these is true, but as a basis for an indication of the order of magnitude of the thermal effects in the gas, they may serve for want of anything more accurate. Actually, the volume of gas heated by the discharge to the temperatures indicated in the table must be smaller than has been calculated; on the other hand, when some gas has been burnt by the spark, an additional (but probably small) amount must be burnt by the heat of combustion of that portion which has already burnt.

While, therefore, a close comparison of the results with the calculated volumes of heated gases is not justifiable, it may reasonably be concluded that there is satisfactory agreement between the order of the results and those calculated from thermal data, and that this is evidence which supports the so-called "thermal theory" of ignition of gases by the electric discharge, which declares that "the requisite for a source of heat to initiate flame in a gaseous mixture is that sufficient energy shall be introduced to maintain for a sufficient length of time a sufficient volume of the mixture at or above its ignition temperature.[7b,16] Nothing in the results of the

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[16] Compare also Morgan, *Phil. Mag.*, **49**, 323 (1925).

present experiments suggests the intervention of any electric effect of the spark as "*fons et origo*" of ignition, other than the thermal effect of the degradation of its electric energy.

Similar calculations of the temperature distribution may be made when the duration of the spark discharge is as observed in induction-coil sparks. The necessary formulas are given by Jones, Morgan and Wheeler,[17] who were the first to suggest the application of Fourier's formulas to spark ignition. The results are again of the same order as those observed experimentally.

Summary and Conclusions

A spark from an induction coil will start the general inflammation of the most readily ignited mixtures of methane and air (8 to 9% of methane) when it is of sufficient strength to inflame just over 0.5 cu. mm. of the mixture, at ordinary temperatures and pressures, when discharged between bluntly pointed platinum electrodes 0.5 mm. apart. When, in otherwise similar circumstances, the electrodes are 1 mm. apart, a little less than 0.5 cu. mm. of gas has to be inflamed to induce general inflammation of the same mixtures. The difference, in the two cases, is ascribed mainly to the smaller cooling effect of the electrodes in the latter case.

The induction-coil spark, produced by a quick break in the primary circuit, was composed of a succession of flashes, the total duration of which was several thousandths of a second. The spark from an air condenser, composed of but one flash, had to inflame about 0.9 cu. mm. of the same mixture in order to induce general inflammation.

When the methane content of the mixture was but 6.2%, about 1.5 cu. mm. had to be inflamed by the induction-coil spark, when 11.2%, about 1.0 cu. mm., to produce general inflammation from a 0.5mm. gap.

When the spark is not quite strong enough to produce general inflammation, the products of its action contain much carbon monoxide and some hydrogen, even when there is an excess of oxygen in the mixture. These products of incomplete combustion are still found in notable amounts when mixtures of methane and considerable excess of oxygen are submitted to sparks which are just incapable of producing general inflammation.

The observed volumes of gas which have to be ignited in order to start a general inflammation are shown to be in approximate agreement with the known facts concerning the energy of the igniting spark, the thermal conductivity and the ignition temperature of the mixture; hence, the electric spark acts mainly, perhaps entirely, as a source of thermal energy in igniting a gas mixture.

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[17] Jones, Morgan and Wheeler, *Phil. Mag.*, **43**, 359 (1922).