23. *The Ignition of Some Explosive Mixtures by Modified Coil Discharges.*

By B. W. BRADFORD, G. I. FINCH, and (MISS) A. M. PRIOR.

IN a previous communication (Bradford, Finch, and Prior, J., 1933, 227) it was shown experimentally that the capacity component of a coil discharge plays a rôle in the ignition of certain explosive gaseous mixtures wholly subordinate to that of the inductance component, even though this be reduced to a practical minimum. It was also found that the igniting power of a coil discharge is not only a function of the total inductance component energy, but is also conditioned partly by the peak, and partly by the mean rates of dissipation of this energy to an extent varying with the nature of the gas mixture. The experiments to be described below were carried out with the object of defining more closely the discharge properties determining igniting power; they bring to a close this series of investigations on the electrical ignition of gases (*Proc. Roy. Soc.*, 1927, **116**, *A*, 529; J., 1930, 1540; *Proc. Roy. Soc.*, 1931, **134**, *A*, 343; *Proc. Physical Soc.*, 1931, **43**, 502; 1932, **44**, 190; *Nature*, 1932, **30**, 929; *Proc. Physical Soc.*, 1933, **45**, 288; J., 1933, 227).

EXPERIMENTAL.

In addition to the apparatus previously described (*loc. cit.*), a Mullard U.9. diode was incorporated in the one spark-gap lead on the gap side of earth, *i.e.*, one end of the valve filament was at earth potential. Provision was made for shunting the valve as and when required by an air-dielectric condenser of $23\mu\mu F$, a capacity which offered negligible impedance to oscillatory currents of frequencies of the order of 10^6 cycles and higher, but effectively blocked the inductance component oscillations ($n < 10^4$ cycles).

A pure tungsten filamented valve of suitable characteristics was not available, and since the U.9. filament was thoriated, the saturation current of the valve varied somewhat with the potential drop. By a suitable choice of filament temperature it was possible, as is shown both in the oscillograms and in the results of the ignition experiments, to reduce the capacity component to a negligible quantity and at the same time to exercise a wide measure of control of the inductance component. The various conditions employed in the experiments, of which an account follows below, together with the corresponding discharge modifications may be summarised as follows :

Circuit conditions.	Nature of discharge.	Typical current–time oscillogram.
A. Valve short-circuited.	Normal coil discharge.	J., 1933. p. 228, Fig. 3.
B. Valve shunted by condenser; filament fully heated.	Normal coil discharge.	As in A.
C. Valve without shunting condenser :		
(*a*) filament fully heated.	Negligible capacity component; inductance component unimpaired.	Fig. 1.
(*b*) filament under-run.	Negligible capacity component; normal (or nearly so) inductance component duration, but oscillations more or less damped out, according to extent of under-running.	Figs. 2—6.
D. Valve shunted by condenser; filament cold.	Normal capacity component; negligible inductance component.	Voltage–time trace only visible up to moment of breakdown of gap (*Proc. Physical Soc.*, 1933, **45**, 291, Fig. 2*a*).
E. Valve as in D but without condenser.	Negligible capacity and inductance component.	

Additional modification of the discharge could be effected in the shape of cut-off of part or whole of the inductance component by means of the special double contact-breaker mentioned in the previous paper (*loc. cit.*) to which reference should be made for further information regarding experimental conditions and procedure.

Results.—Series I. The explosive mixture consisted of $2CO + O_2$ with 5% added hydrogen, the whole dried by slow passage over a 30-cm. column of redistilled phosphoric oxide. The estimated normal capacity component was between 0·58 and 7·1 mJ, according to the least igniting pressure. Under the circuit conditions, C and E, the capacity component energy was virtually confined to that due to the discharge of the ignition vessel inter-electrode capacity on breakdown of the gap. By a simple estimate based upon the observed breakdown-potential and the geometry of the spark-gap and lay-out of its associated leads (undamped), the energy of the capacity component under circuit conditions C and E was found to be not greater than 1/20th of the corresponding normal capacity component energy.

Circuit conditions.	Complete discharge.					Cut-off at end of first inductance component oscillation.				
	Least igniting pressure, mm.	Igniting power = 1000/(least igniting pressure).	Capacity component energy, mJ.	Inductance component.		Least igniting pressure, mm.	Igniting power = 1000/(least igniting pressure).	Capacity component energy, mJ.	Inductance component.	
				Energy. mJ.	Duration, m.-sec.				Energy. mJ.	Duration. m.-sec.
					Series I.					
A	92·5	10·8	0·62	29·8	3·66	149·0	6·7	1·6	5·11	0·38
B	108·0	9·3	0·84			150·5	6·65	1·6		
C (*a*)	111·0	9·0	0·89			152·0	6·6	1·7		
D	No ignition at 304·0	<3·3	6·7	—	—	No ignition at 350·0	<2·9	8·8	—	—
E	No ignition at 313·0	<3·2	7·1	—	—	No ignition at 350·0	<2·9	8·8	—	—
					Series II.					
A	89·5	11·2	0·58	23·8	2·67	101·0	9·9	0·73	4·65	0·36
B	90·5	11·1	0·59			114·5	8·7	0·95		
C (*a*)	92·0	10·8	0·61			119·0	8·4	1·0		
D	224	4·5	3·6	—	—	No ignition at 263	<3·8	5·0	—	—
E	No ignition at 250	<4·0	4·5	—	—	No ignition at 263	<3·8	5·0	—	—

Series II. The mixture of $CH_4 + 2O_2$ used in this series was dried as described in Series I above.

By cathode-ray oscillographic means, the upper limit of the duration of the capacity component has been found previously to be certainly less than 10 μ secs. (see Fig. 2, *loc. cit.*), but since the most prominent frequency of the normal capacity component in the coil lay-out employed was $1 \cdot 2 \times 10^7$ c./sec. (*loc. cit.*). the total distributed capacity being about 80 cm., this estimate further reduces to less than 1 μ sec., the extremely moderate damping factor of only 0·5 being assumed.

Series III—V. In these experiments the effect of variation in the inductance component peak current, discharge life, and the shape of the inductance component current–time relationship of the discharge upon the igniting power was studied. It may be recalled that since the discharge voltage has previously been shown experimentally to be constant during the life of the inductance component (*Proc. Physical Soc.*, *loc. cit.*) and since, as has now been shown, the effect of the capacity component is practically negligible in bringing about ignition, the current–time trace affords a measure of the effective discharge energy and of its rate of dissipation.

The results of these experiments are summarised in Fig. 7. The circuit and other experimental conditions were as follows :

Series.	Mixture.	Circuit conditions.	Peak current, mA.	Duration of discharge, m.-sec.
III (*a*)	$(2CO + O_2) + 5\% H_2$	A	96·3	Varied by cut-off between 0·47 and 6·0
III (*b*)	do.	A	128·0	Varied by cut-off between 0·40 and 6·25
III (*c*)	do.	C (*b*)	15·9—149·4	0·70—4·12
IV (*a*)	$2H_2 + O_2$	A	96·3	Varied by cut-off between 0·60 and 6·19
IV (*b*)	do.	A	128·0	Varied by cut-off between 0·38 and 6·27
IV (*c*)	do.	C (*b*)	70·4—127·2	0·72
V (*a*)	$CH_4 + 2O_2$	A	96·3	Varied by cut-off between 0·38 and 6·27
V (*b*)	do.	A	128·0	Varied by cut-off between 0·39 and 6·27
V (*c*)	do.	C (*b*)	70·4—127·2	0·72

FIG. 1.

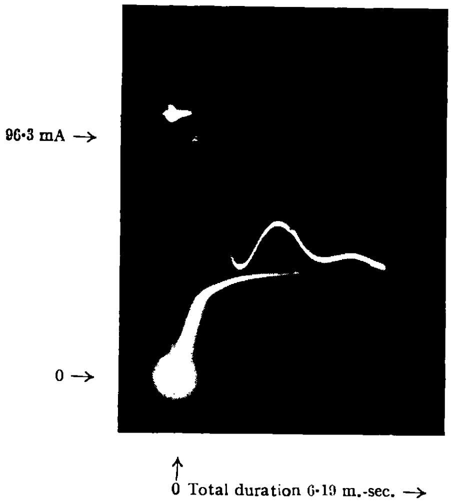


FIG. 2.

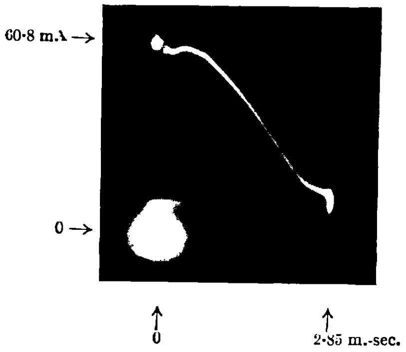


FIG. 3.

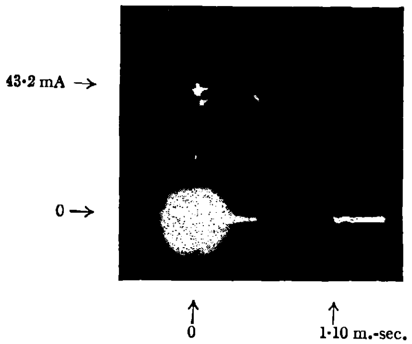


FIG. 4.

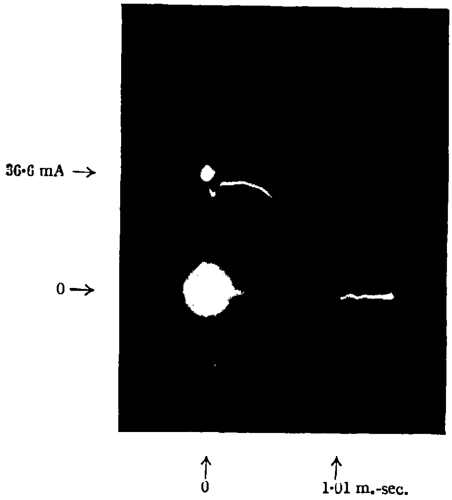


FIG. 5.

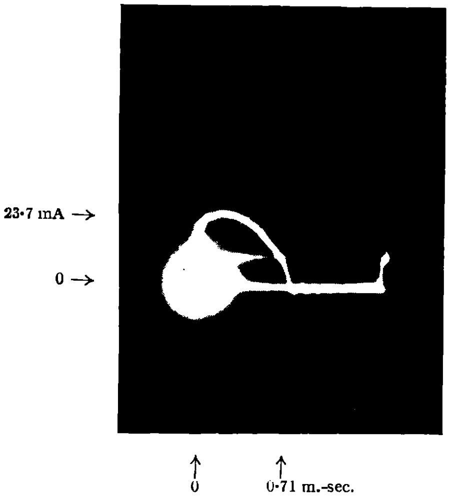
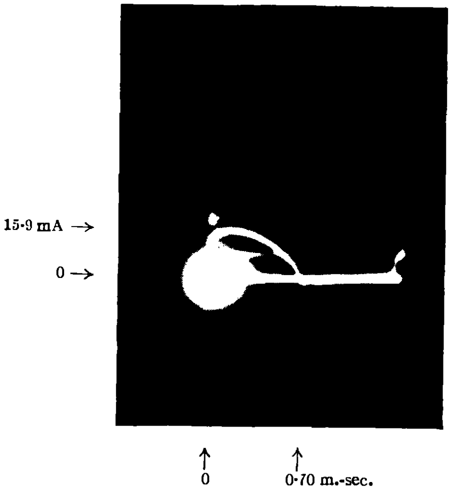


FIG. 6.

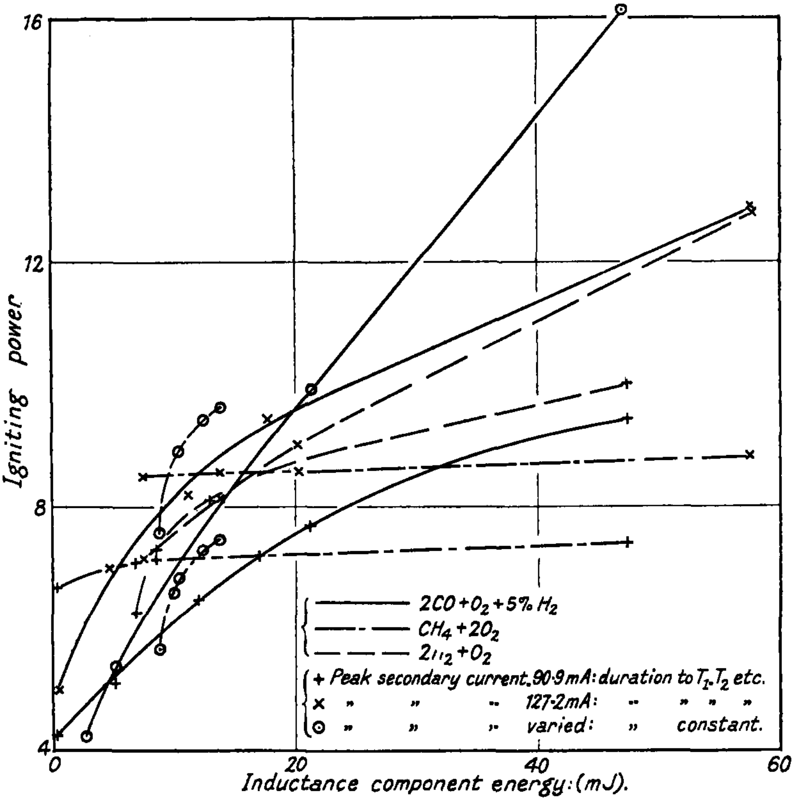


Ordinates = current; abscissæ = time.

DISCUSSION.

The results set forth for Series I and II afford striking evidence of the relative inefficiency of the capacity component, *i.e.*, a high-frequency condensed discharge, in the ignition of an explosive gaseous mixture, as compared with the inductance component, the discharge of which consists of damped oscillations of relatively low frequency and amplitude, superimposed upon a unidirectional flow suffering linear decay of only moderate slope. Thus, for example, a capacity component of approximately 0·6 mJ exhibited an igniting power certainly less, and possibly much less, than half that of a similar amount of energy dissipated by a truncated inductance component in igniting a $(2CO + O_2) + 5\%$ H_2 mixture; and a similar result was obtained in the case of $CH_4 + 2O_2$. These results not only bring out clearly 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 these experiments and therefore also in normal coil ignition practice.

FIG. 7.



The results incorporated in Fig. 7 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 the mean rate 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 in 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 discharge duration. With a damped and partially cut-off inductance component (as in Figs. 2—6) dissipating, *e.g.*, 10 mJ, the order of decreasing sensitivity to ignition of the mixtures examined was $2H_2 + O_2$, $(2CO + O_2) + 5\% H_2$, $CH_4 + 2O_2$; 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 Figs. 3—7, previous paper, *loc. cit.*) resulted in an inversion of this order (see Fig. 7), thus confirming the fact already brought out, to the effect 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 contents remaining otherwise unchanged.

To sum up: The effectiveness as a source of ignition of a unidirectional discharge, consisting of a train of more or less damped oscillations superimposed upon a decaying component, with a life of between 0·3 and 6·27 m.-sec. and of given total energy is determined in the manner outlined above either by the peak or by the mean rate of energy dissipation according to the nature of the explosive mixture. It has also been shown experimentally that a partially cut-off inductance component can and does act more efficiently as a source of ignition than a capacity component dissipating nearly twice the energy. Finally, it has been shown experimentally (*Proc. Roy. Soc.*, 1931, **134**, 343) that the ignition of mixtures of carbonic oxide and air in their combining proportions by high-frequency oscillatory discharges is determined by the discharge frequency to such an extent that a reduction in either the total energy associated with the discharge or its peak rate of dissipation is more than outweighed by a suitable decrease in frequency and corresponding increase in the life of the discharge. For instance, a high-frequency spark dissipating 2·30 J, the discharge frequency being 570 k.c./sec., was found to be less effective than a spark of 1·43 J and 340 k.c./sec.

The above results are in direct conflict with the thermal theory of ignition, because they show that the discharge duration can and does determine the igniting power of a spark to a greater extent than either the total energy associated with the discharge or its maximum rate of dissipation. The thermal theory, however, suggests that "the ignition of a gaseous mixture depends primarily . . . on the heating of a sufficient volume to a sufficient temperature" (Taylor-Jones, Morgan, and Wheeler, *Phil. Mag.*, 1922, **43**, 359), which leads to the corollary that "the heat energy required in the source for ignition is least when the heat is imparted instantaneously" (Morgan, *Phil. Mag.*, 1931, **11**, 158); from which it follows that the igniting power of discharges dissipating equal energy amounts should increase with increasing rate of dissipation of such energy, but never with increasing discharge duration. Under the conditions of our experiments, however, this has now been shown to be contrary to fact.

Taking the statement of the thermal theory as set forth above, it is not difficult to show that this theory 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. Thus, temperature, a statistical measure of the mean kinetic energy of the random translatory 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 (*J. Amer. Chem. Soc.*, 1927, **49**, 396) 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." It would seem difficult to reconcile this view with well-known facts such as, *e.g.*, those relating to the photo-ignition of hydrogen–chlorine mixtures and the adiabatic compression ignition of hydrogen–oxygen mixtures (Dixon and Crofts; Bone and Townend, " Flame and Combustion in Gases," 1927, p. 75).

The facts relating to the ignition of gases, so far as they are now known, can, however, be reasonably explained on lines previously suggested (*Proc. Roy. Soc.*, 1931, **134**, 350), according to which, 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.

Imperial College, London, S.W. 7.

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