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Ignition of Explosive Gas Mixtures by Electric Sparks. I. Minimum Ignition Energies and Quenching Distances of Mixtures of Methane, Oxygen, and Inert Gases

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It is difficult to explain the previous conflicting results from experiments on cooling the ozone because of lack of sufficient detail about the manner in which the experiments were performed and the spectrograms evaluated. It is perhaps significant that in those cases[1,3] where an increase in absorption was reported after cooling, high concentrations of ozone were used in the absorption cell. Absorption coefficients published by A. Vassy[18] for the visible bands using a 50 percent ozone-oxygen mixture in the path are approximately 30 percent higher than those of Colange, who used 4 percent ozone by volume. Colange determined the concentration of ozone in his work by chemical analyses, while A. Vassy based her determinations of concentration on the absorption in the ultraviolet bands using absorption coefficients determined by Ny and Choong,[19] who employed concentrations of ozone varying from 2–6 percent by volume (chemical analyses).

It should be remarked that the concentration of ozone in the atmosphere is greatly below that used in the experiments described here. Consequently, if there is a temperature effect which becomes apparent only at ozone concentrations considerably higher than we have employed in our work, then this effect would not render the visible bands unsuitable for determining atmospheric ozone.

[18] A. Vassy, Comptes Rendus **204**, 1413 (1937); *ibid.* **206**, 1638 (1938).

[19] Ny-Tsi-Ze and Choong-Shin-Piaw, Chinese J. Phys. **1**, 38 (1933).

CONCLUSIONS

Although the reduction of intensity of solar radiation by the ozone of the atmosphere is small in the visible region of the spectrum, modern photoelectric methods are quite capable of measuring such weak absorption. Moreover, in view of the broad and continuous character of the absorption in the visible ozone bands, the relative simplicity of photometry in the visible region compared with other regions of the spectrum, and the absence of any uncertainty from effects of temperature or pressure on the bands, it seems likely that they will find further application in the measurement of atmospheric ozone.

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Ignition of Explosive Gas Mixtures by Electric Sparks. I. Minimum Ignition Energies and Quenching Distances of Mixtures of Methane, Oxygen, and Inert Gases*

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An apparatus and experimental procedure is described for measuring capacitances and gap voltages of condensed electric spark circuits for sparks just powerful enough to ignite explosive gas mixtures. Mixtures of methane, oxygen, and inert gases are investigated. From the measured capacitances and gap voltages the minimum ignition energies are calculated. These energies are found to be independent of gap voltage. With increasing gap length they attain a minimum at critical distances which mark the farthest penetration of the flame-quenching effect of the electrode material. Above the quenching distances the energies remain constant over some range which is governed by mixture composition and pressure. Energies measured in this range may be regarded as absolute minimum energies, as defined in a subsequent paper. Data of such minimum energies and of quenching distances are presented for mixtures at room temperature and pressures ranging from 0.2 to 1 atmosphere.

CAPACITANCES and gap voltages of condensed electric spark circuits have been measured for sparks just powerful enough to ignite various explosive gas mixtures. From these data *minimum ignition energies* have been calculated. Data on the quenching of ignition

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between two plane-parallel plates are also presented. Quenching occurs below rather sharply defined plate distances, the *quenching distances*. The experiments were made with mixtures of methane, oxygen, and nitrogen. In some series, nitrogen was replaced by helium, argon, or carbon dioxide. All tests were made at room temperature (about 25°C).

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus differed from a previously described set-up[1] by a larger capacitance range and improved circuit connections which minimize resistance and corona losses. As shown in Fig. 1, the gases were admitted to a test bomb which was made of stainless steel and had an inside diameter of 5 inches. The spark electrodes were mounted in the center of the bomb. The gap length could be adjusted accurately by means of a built-in micrometer. For the determination of quenching distances plate-shaped electrodes were required. Metal plates were not suitable because sparks tended to occur erratically at the rim even though the center was slightly raised; therefore, electrodes with precisely mounted glass flanges were used, as shown in Fig. 1. The electrode tips were rounded to minimize corona discharge, and the glass was coated with a trace of paraffin wax to eliminate surface conduction. The electrodes were connected to a system of fixed and variable air condensers and a variable-range voltmeter which was periodically calibrated against corona-shielded high precision resistors and a high precision milliammeter. The aggregate capacitance was continuously variable between 3 and 5000 micromicrofarads. Its exact value was determined for any test condition by means of a Wien bridge which was periodically checked against a Leeds and Northrup precision standard air capacitor. Measurements of very small capacitances were corroborated by other well-known methods. High voltage was supplied *via* a protective resistor to the terminal *a*, whence it was gradually transferred to the electrode-

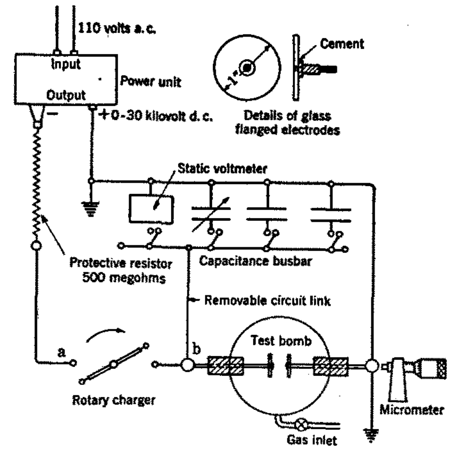

FIG. 1. Scheme of apparatus.

capacitor system by means of a rotary charger. In this device, small metal spheres mounted on hard rubber alternately touched terminals *a* and *b*, thus transferring charge at a rate governed by the speed of rotation while the spark circuit remained effectively isolated from the power source with regard to both capacitance and voltage ripple. After the bomb had been filled with an explosive mixture of accurately determined composition and pressure, the electrode and capacitor system was slowly charged, and the voltage V at which the spark occurred was observed. If the mixture did not ignite the capacitance was increased, until by trial and error the critical capacitance C for ignition was found. At capacitances below about 50 micromicrofarads it became necessary to disconnect the voltmeter from the circuit and to charge the

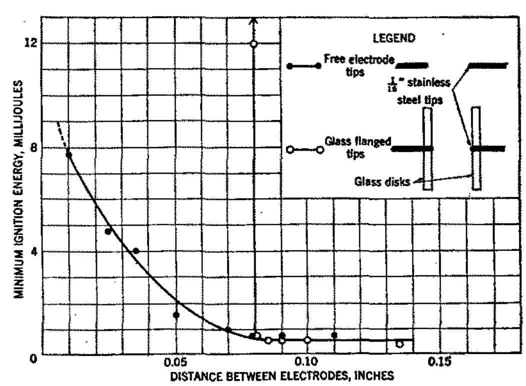

FIG. 2. Minimum ignition energies for free and glass-flanged electrode tips as function of electrode distance. Stoichiometric mixture of natural gas (about 83 percent CH_4+17 percent C_2H_6) and air at one atmosphere pressure.

ives Division, and Chief, Explosives Division, respectively, Central Experiment Station, Bureau of Mines, Pittsburgh, Pennsylvania.

[1] P. G. Guest, Apparatus for determining minimum ignition energies for electric-spark ignition. U. S. Bureau of Mines Report of Investigations 3753 (1944).

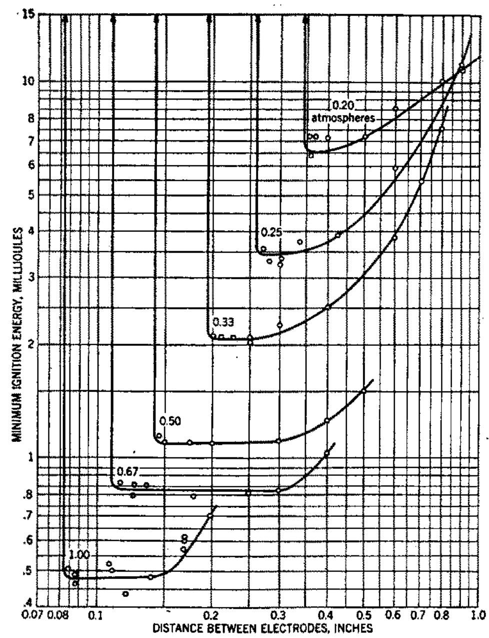

FIG. 3. Minimum ignition energies for glass-flanged electrode tips as functions of electrode distance and pressure. Stoichiometric mixture of methane and air.

electrode-capacitor system from a large capacitor which was accurately maintained at the breakdown voltage of the spark gap. The breakdown voltage was determined independently with the voltmeter in the circuit for conditions of gas mixture and electrodes identical with those of the ignition test, and the rotary charger was sometimes replaced by a Micarta rod connecting the terminal b with the terminal of the charge reservoir. This rod permitted slow leakage of electricity without increasing the effective capacitance of the spark circuit. At very low capacitances the electrode-capacitor system consisted solely of the electrode tip connected to a suitably long metal rod which below about 6 micromicrofarads was so short that it did not extend through the insulating gland to the outside of the bomb. The Micarta rod connection solved the difficulty of making contact with the outside charge source.

TABLE I. Results showing the minimum spark ignition energy to be independent of gap voltage.

	Gap voltage,* kilovolt	Minimum ignition energy, millijoule
8.7 percent natural gas** in air at 1 atmosphere	6.1	0.5
	9.9	0.5
0.5 atmosphere	8.6	1.7
	10.2	1.7
0.33 atmosphere	5.4	2.4
	7.5	2.4
0.25 atmosphere	4.5	4.0
	6.8	4.2
8.5 percent methane in air at 0.33 atmosphere	14.2	2.6
	20.0	2.6

* The distance between the electrodes was held constant for each pair of runs.
** Approximately 83 percent CH_4, and 17 percent C_2H_6.

Sparking occurred after a statistical time lag which was often inconveniently long. Inasmuch as breakdown is initiated by extraneous ions in the gap, it was generally possible to reduce the lag substantially by placing radium capsules of various strengths into the bomb. This also caused a slow leakage of electricity from the charged electrode before breakdown, and hence the gap voltage dropped below the voltage of the charge reservoir to a value governed by the rates of charge transfer from the reservoir and leakage from the electrode. This was potentially troublesome when the voltmeter was disconnected, and hence the gap voltage was not directly observable; generally, however, it was found possible to adjust the rates of charging and ionization so that the voltage drop became inappreciable.

The product $(1/2)CV^2$ may be termed the minimum ignition energy. It represents energy expended in the spark gap where it is available for the ignition process, and also outside losses of Joule heat, Hertzian waves, and dielectric hysteresis. However, hysteresis losses have been substantially eliminated by the use of air condensers, and electromagnetic wave losses from a circuit of this type are small. Since the d.c. resistance of the metallic part of the circuit was less than 0.1 ohm it is felt that, despite a possible skin effect caused by discharge oscillations, the metallic resistance to the flow of current was much smaller than the effective resistance of the gap during the discharge, and that therefore the external heat loss was negligible. To test this point, various non-inductive resistances were introduced in the circuit in place of the removable circuit link, Fig. 1, and the minimum energy required for the ignition of near-stoichiometric methane-air mixtures was determined. No effect of the additional resistance was noted up to 30 ohms.

EFFECT OF INDUCTANCE

A number of tests in which the circuit link (Fig. 1) was replaced by a helix of heavy wire failed to show any effect of moderate changes of inductance and oscillatory frequency on the minimum ignition energy.

EFFECT OF ELECTRODE VOLTAGE

It was possible to increase the breakdown voltage between the electrodes considerably by applying an overvoltage, either taking advantage of the breakdown time lag or by charging the condensers and connecting them with the electrode circuit by a fast-acting switch in place of the removable circuit link. In the latter procedure there is a possible energy loss caused by a spark in the switch. However, while this has not been determined quantitatively it is believed to be small because of the statistical lag of the igniting spark which permits the closing of the switch before the full current flows. As shown by the data in Table I, the minimum ignition energy was found to be essentially independent of overvoltage; that is, as the gap voltage was increased the capacitance had to be correspondingly decreased.

It appears relevant to note[2] that in spark discharges only a very small fraction of the energy goes into the production of ions. By far the largest part goes into the production of atoms, free radicals, and thermal motion in general.

EFFECT OF ELECTRODE DISTANCE

Figure 2 shows a typical example of the effect of electrode distance on the minimum ignition energy. Two electrode systems are compared, one with free and the other with glass-flanged tips. Above a critical distance, which in this instance is 0.08 inch, the data with the two electrode systems practically coincide; below this distance the minimum ignition energy increases abruptly with plate electrodes and gradually with point electrodes. This distance marks the farthest penetration of the flame-quenching

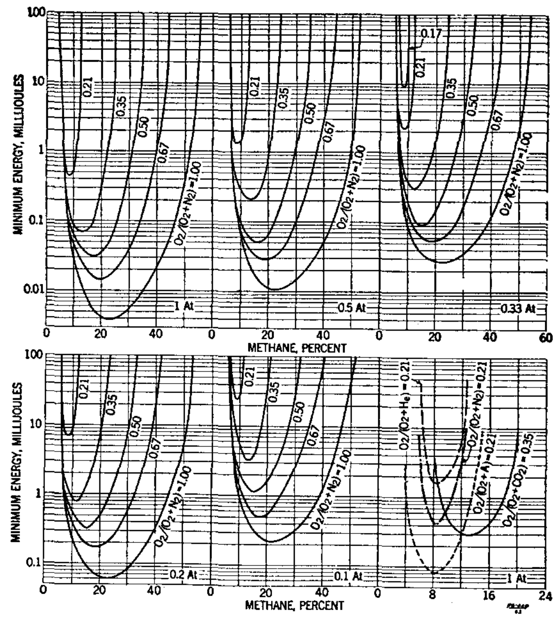

FIG. 4. Minimum spark ignition energies in millijoules of mixtures of methane, oxygen, and inert gases at one atmosphere and lower pressure. Curves correspond to constant ratios of oxygen and inert gas. $\frac{1}{16}$-in. diameter rounded electrodes cemented flush into perforated glass or quartz disks.

effect of the solid electrode material and is analogous to the critical diameter of a tube below which flame will not propagate through the tube.

Above the quenching distance the minimum ignition energy is remarkably constant over a considerable range, if the pressure of the gas

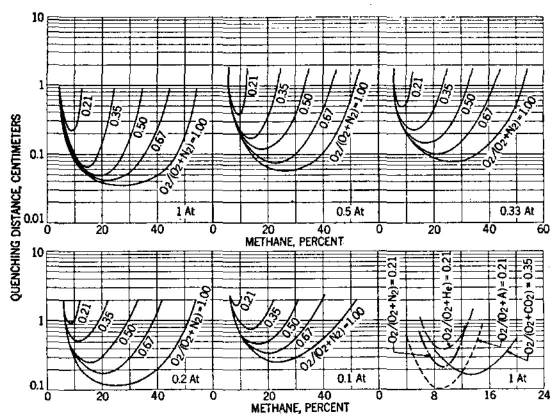

FIG. 5. Quenching distances between parallel plates for mixtures of methane, oxygen, and inert gases at one atmosphere and lower pressures. Curves correspond to constant ratios of oxygen and inert gas. $\frac{1}{16}$-in. diameter rounded electrodes cemented flush into perforated glass or quartz disks.

[2] E. L. E. Wheatcroft, *Gaseous Electrical Conductors* (Oxford University Press, New York, 1938), p. 144.

mixture is not too low. This is illustrated in Fig. 3 by a family of curves for stoichiometric mixtures of methane and air at various pressures. It appears that toward smaller distances even the data for low pressures would fall on a horizontal line if the quenching effect of the electrodes could be eliminated.

In a following paper of this series the existence of an absolute minimum ignition energy of sparks is demonstrated from theoretical considerations. This energy is the sole ignition condition if both the duration of the discharge and the volume over which the spark energy is distributed remain below some fairly well defined critical limits. If either limit is exceeded the ignition energy increases. It is easily demonstrated that in the experiments reported here the duration of the spark remains always well below the critical limit. Hence, if the horizontal part of the curves in Fig. 3 is taken to represent the absolute minimum ignition energy, the subsequent rise of the energy curves at larger electrode distances is attributable to the distribution of the spark energy over a volume exceeding a critical sphere in cubic or linear dimensions. It is obvious that as the spark electrodes are pulled apart this should become the case. It appears rather remarkable that there should be such large horizontal sections of the ignition-energy curves as have actually been found. This suggests that most of the spark energy is transferred to the gas over a fairly small fraction of the spark length. This appears to be consistent with present knowledge of the sparking mechanism.[3] At the beginning of the discharge a steep potential gradient is formed near the cathode. At the end of this gradient there exists a zone of high concentration of positive ions and high energy electrons, within which the rate of energy transfer to the gas is larger than elsewhere along the spark path.

If, as suggested by the latter considerations, the flame origin is always closer to the cathode than to the anode, then in the case of a point electrode facing a plate electrode within the quenching distance the ignition energy should be larger when the plate is the cathode than when it is the anode. This has been confirmed by experiments in which one of the electrodes was a small sphere and the other a plate.

It was found that at high gap voltage, particularly at combinations of large electrode distances and high pressures, ignition occurred statistically after a number of sparks had passed. The cause for this randomness may have been the gas motion caused by corona leakage from the electrode tips. The leakage itself was not considered to be an appreciable source of error since, as mentioned above, it was compensated by the charging rate. However, sufficiently strong gusts of "electric wind" may blow the incipient flame against the opposite electrode and thus quench it. This may be expected to occur at random with increasing probability as the variables favoring corona discharge are increased.

EFFECT OF MIXTURE COMPOSITION AND PRESSURE

The energy values corresponding to the horizontal part of the curves of minimum ignition energy *versus* electrode distance are functions only of the variables of the gas mixtures and may be regarded as absolute minimum values. Figure 4 shows families of curves of such minimum energies for various mixture compositions and pressures. Figure 5 shows corresponding families of curves for quenching distances. The limits of the U-shaped curves correspond to the limits of inflammability. A profound effect of inert gas dilution is noted. For example, near stoichiometric composition the minimum ignition energy is found to be approximately 100 times larger for air than for oxygen.

Similar families of curves are being determined for other gases, and a detailed study of the electrical characteristics of sparks and spark gaps is planned.

[3] See reference 2, p. 139.