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SOME FACTORS INFLUENCING THE IGNITION OF CARBON MONOXIDE AND OXYGEN

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In a recent article² Professor W. A. Bone has shown that combination can take place between carbon monoxide and oxygen when dried over phosphorus pentoxide for six months, provided sufficient energy is added to the explosive mixture. The condensed discharges used by Professor Bone to ignite the dry mixture were of the order of magnitude of the hot sparks used by Millikan and Bowen in their experiments on stripped atoms, and were amply sufficient to dissociate the gas in the path of the spark into atoms stripped of their valence electrons.

The heavy condensed discharges necessary for the ignition of the dry gas raised the question as to the mechanism involved. The ignition in the absence of water might result from some higher stage of ionization, or it might be that the ignition is independent of any given stage of ionization but is dependent on the introduction of a given amount of energy in a definite volume of gas. The present research was, therefore, undertaken to test this point, as well as to determine the effect of various impurities on the energy of ignition.

The apparatus consisted of an explosion chamber with platinum electrodes placed at right angles to one another. The vertical electrode was placed on a strip of flexible platinum from which was suspended a piece of iron enclosed in glass; it was thus possible to vary the spark gap by means of an external electro-magnet.

The condensed discharge was obtained from twelve 1500-volt 1-mf. condensers which could be placed in parallel and charged to any required potential by means of a high voltage d. c. generator placed across a suitable potentiometer.

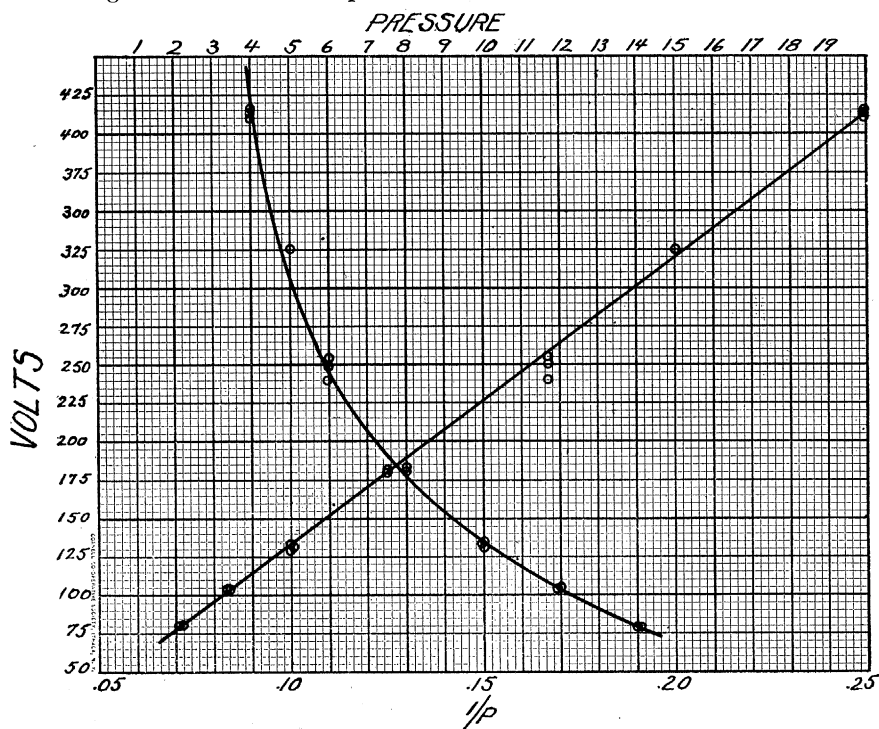
The explosion chamber was connected through a ground glass stopcock to a reservoir train where an explosive mixture of carbon monoxide and oxygen could be generated and stored up either over water or sulfuric acid. Another gas train was provided so that the vapor of any liquid could be introduced at any given pressure up to the vapor pressure of the liquid. The pressures were read by means of mercury manometers. A Hyvac pump was used for evacuation.

All stopcocks were lubricated with high vacuum stopcock grease, as it was shown by experiment to have no detectable effect on the ignition of the gases in question.

The mechanism of ignition of the explosive mixture of gas at a constant

pressure was shown to be independent of any particular stage of ionization produced in the spark by placing inductance in the discharge circuit. A small inductance capable of cutting the peak current density to about one-tenth its normal value as well as a large inductance which reduced the current density much farther had no appreciable effect on the ignition point of the gas over that obtained with a similar resistance in the circuit but without the inductance. This was true for both the moist gas and the gas dried by sulfuric acid at 14 cm. pressure.

The ignition at constant pressure was shown to be dependent on the



energy of the spark in which the voltage for ignition was determined for different condenser capacities. The energy of the spark is given by $E = \frac{1}{2}CV^2$.

The results obtained are listed in table 1.

CAPACITY	VOLTAGE	ENERGY $\times 10^6$ JOULES
12 mf.	290	504,000
11	310	528,000
9	344	532,000
6	437	570,000
3	616	570,000
2	785	617,000

It will be seen that the energy necessary to ignite a given pressure of gas varies but little for different voltages, increasing slightly for increasing voltage. This slight increase in energy is readily accounted for by the greater distance the spark jumps at the higher voltages, thus distributing the energy over a slightly larger volume.

The effect of the pressure of the explosive mixture on the voltage necessary for ignition is shown by the accompanying curve.

In these experiments the capacity was kept constant at 11 mf. The experiment was performed with moist gas.

It will be seen that the pressure-voltage curve is a hyperbola where $V = k/P$, where P is the pressure of the explosive mixture.

From these data it will be seen that while the ignition at any one pressure is determined by the energy of the spark and not by the voltage, the ignition points at various pressures are related not as the energy ($\frac{1}{2}CV^2$) but as the voltage (V).

The effect of water vapor on the energy of ignition is shown by the following data.

TABLE 2

PARTIAL PRESSURE	IGNITION VOLTAGE
0.4 mm.	262
1.0	182
1.6	120
2.0	101
4.0	71
6.0	60
10.0	54
20.0	46

In these experiments the pressure of the explosive mixture dried by sulphuric acid was maintained at 14 cm. and the pressure of the water vapor added varied.

The combustion of the explosive mixture dried by sulphuric acid seldom went to over 10% completion; likewise the flame lacked sufficient energy to propagate itself throughout the entire explosion chamber. Only the most minute quantities of water vapor were necessary to cause the reaction to go to completion. Long-continued exhaustion followed by many explosions in the reaction chamber was necessary to remove the water vapor sufficient for incomplete combustion.

Unfortunately adsorption on the walls of the explosion chamber made it impossible to determine accurately the pressure of a vapor such as water to 0.1 mm. The per cent experimental error is, therefore, high for the very low pressures.

The impurities other than water which were added to the explosive gas may be divided into two general classes, those which are inert in the explosion except in that they absorb energy, thus increasing the ignition

potential, and those which in themselves are oxidized in the explosion and thus lower the ignition potential.

In the following table are listed the various impurities which, when added in appreciable quantities, increase the energy of ignition. In the table are given the partial pressures for the different gases which, when added to 14 cm. of explosive mixture (2 cm. water and 12 cm. $2\text{CO} + \text{O}_2$), increase the voltage of ignition from 100 volts to 400 volts, or increase the energy of ignition 16-fold.

TABLE 3

GAS	PARTIAL PRESSURE	GAS	PARTIAL PRESSURE
Argon	26 cm.	Alcohol	3.8
Nitrogen	20	Isopropyl nitrite	0.7
Carbon dioxide	9.4	Ether	0.66
Chloroform	4.2		

It will be noted that the effect of the added impurity on raising the voltage of ignition increases with the increasing complexity of the molecule added. Unfortunately, the energy going into dissociation and the specific heat of the gas under ignition conditions cannot be told accurately. Rough calculations, however, indicate that the ability of a gas to raise the ignition voltage depends directly on the amount of energy that it absorbs.

The second class of impurities which ignite during the explosion affect the voltage of ignition in a manner identical to that of water, i.e., greatly reduce the ignition voltage, and cause the oxidation to go to completion when present even in traces. In order that these results might be obtained it was essential to add oxygen sufficient to burn completely the ignitable impurity.

The pure explosive mixture dried by sulphuric acid ignited from between 375 and 400 volts for an 11 mf. condenser capacity, varying somewhat from time to time. In the following table are listed the partial pressures of ignitable impurity which when added to 14 cm. of explosive mixture reduced the energy of ignition to 200 volts, to 100 volts and to 50 volts.

TABLE 4

VAPOR	200V	PARTIAL PRESSURE 100 V	50 V
Water	1.0 mm.	2.0 mm.	20.0 mm.
Hydrogen	0.4	1.2	12.0
Alcohol	0.6	1.8	10.0
Ether	0.2	1.0	6.0
Carbon disulphide	3.2	9.0	18.0

It will be noted that a vapor, such as alcohol or ether, either raises or lowers the ignition voltage depending on the amount of oxygen present. For instance, pure ether vapor, when added to the moist explosive mixture at 14 cm. pressure, lowered the ignition point up to a concentration of 0.7%,

beyond which the ignition voltage rose rapidly. When, however, sufficient oxygen was added to burn the ether a pressure-voltage curve similar to that given for water was obtained.

The partial pressure-voltage curve for the added carbon disulphide was a hyperbola giving $V = k/p$, where p refers to the pressure of the added disulphide. This curve was identical in form to the pressure-voltage curve obtained in the ignition of the $2\text{CO} + \text{O}_2$ mixture where P referred to the total pressure. From this relationship it may be concluded that the voltage necessary to ignite a constant volume of explosive mixture in the presence of carbon disulphide is inversely proportional to the number of molecules of disulphide present.

The partial pressure-voltage curve for water, hydrogen, alcohol and ether were distinctly different from that for carbon disulphide in that the point of inflection beyond which additional vapor had but little effect on lowering the voltage was much sharper. While the per cent experimental error was necessarily very large in measuring the lowest pressures of the added vapor, the curves were nevertheless fairly well expressed by an equation of the form $V = k/pe^{\beta p}$, where p refers again to the partial pressure. It is interesting to note that the value of β came out to be 0.10 in every instance.

The fact that the partial pressure-voltage curves for hydrogen, alcohol and ether gave values of β practically identical to that obtained for water, combined with the fact that these gases acted as positive catalysts only when in the presence of sufficient oxygen for complete combustion, suggests that their positive catalytic properties are derived largely, if not entirely, from their ability to furnish water in the explosive gas. If this contention is correct then it follows that, since these vapors are more efficient in lowering the ignition voltage than is water, the water produced from the burning vapor (new-born water) is a more potent catalyst for the oxidation of carbon monoxide than is ordinary water.

The catalytic properties of carbon disulphide may be explained in a similar manner. Sulphur dioxide in small quantities showed itself to be a very weak positive catalyst; however, it is very possible that the "new-born" sulphur dioxide from the oxidized carbon disulphide possesses stronger catalytic properties.

It might be suggested that the combustible vapors lower the ignition voltage for the explosive mixture by raising the temperature as a result of their own combustion. Such a simple picture hardly seems probable, however, since the energy derived from the oxidation of the vapor is extremely small compared with the energy of the igniting hot spark discharge,

A further series of experiments was performed in the hopes of throwing light upon this point. The conditions were maintained identical to those in which the data in table 4 were obtained except that the carbon mon-

oxide of the explosive mixture was replaced by nitrogen. Comparative data are given in table 5.

VAPOR	TABLE 5		
	800 V	PARTIAL PRESSURE 200 V	100 V
Hydrogen	4.0 mm.	11.0 mm.	18.5 mm.
Alcohol	6.0	20.0	
Ether	4.4	8.0	20.0
Carbon disulfide	2.4	23.0	

A comparison of the data in tables 4 and 5 reveals the fact that the amount of vapor necessary to bring about the ignition of the carbon monoxide-oxygen explosive mixture is many times less than an amount which can undergo ignition in the absence of the carbon monoxide. From this it is possible to draw the very interesting conclusion that two explosive gases in an explosive mixture may ignite more readily than will either gas separately under similar conditions.

The pressure-voltage curves for the vapors listed above were all hyperbolas similar to that obtained from the ignition of the pure carbon monoxide and oxygen. Thus the ignition voltage will be seen to be inversely proportional to the pressure, hence the number of molecules in the path of the spark. In this respect it will be seen that the present curves differ materially from the partial pressure-voltage curves obtained when these vapors were added to the carbon monoxide-oxygen explosive mixture. It, therefore, seems very improbable that the lowering of the ignition voltage of the latter by the presence of these vapors can be due to the energy liberated by their ignition.

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² Bone, *Proc. Roy. Soc.*, **110**, 615 (1926).