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SEMI-ANNUAL REPORT JULY 1947

Contract NOrd-7920

Task PRN-3

DEPARTMENT OF CHEMISTRY
PRINCETON UNIVERSITY

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SEMI-ANNUAL REPORT - JULY, 1947

Contract NOrd-7920, Task PRN-3
Department of Chemistry,
Princeton University
Princeton, N.J.

This Task was formally assigned to Princeton University as an Associated Contractor of the Applied Physics Laboratory, Johns Hopkins University, by letter dated June 19, 1945, from A. F. Hussey, Jr., Rear Admiral U.S.N. Chief of Bureau of Ordnance; E. N. Parker, Captain, U.S. N., by direction, in the following terms-

"Research and development work is to be carried on in connection with rocket launched, jet-propelled, guided, anti-aircraft missiles related to Task F (Bumblebee) assigned to the Applied Physics Laboratory, The Johns Hopkins University, by the Bureau of Ordnance, with special emphasis on combustion of fuels and fundamental research of chemical principles governing the operation of such devices. This work shall include experimentation and testing of such fuels and principles, and design and fabrication of supplementary equipment used in carrying out this work. It shall also include cooperation through consultation and otherwise, as may be practicable, with other agencies concerned with the development or use of devices and techniques related to this Task PRN-3."

The above has been supplemented by Problem Statement PRN-3-A as follows-

PRN-3-A - Combustion Principles

By the assignment of this problem under the scope of Task PRN-3 of Contract NOrd-7920, Princeton University is directed to do the following work in accordance with the provisions of said contract:

Conduct basic research on physico-chemical principles involved in the combustion of fuels, including specifically the following:

A. Flame Propagation.

Make experimental and theoretical studies of flame speeds for laminar flow to a bunsen cone as a function of composition, pressure, temperature, flow velocity, tube diameter, and Reynold's number; study the relation to calculated equilibrium atom and radical concentrations; make use of spectroscopic, photographic and sampling techniques; study the transition from laminar to turbulent flow, especially at low pressures.

B. Reaction Kinetics.

Make experimental and theoretical studies of the kinetics of oxidation reactions, including the oxidation of diborane, hydrazine, and related substances; study the spontaneous ignition of fuels using addition agents.

Beginning April 1, 1947, the expenses of this project have been divided equally between Contract NOrd-7920, Task PRN-3, and Contract N6-ori-105, Task III, Phase 2. (Letters: Office of Naval Research 17 January, 1947, File EXOS:ONR:251, Serial No. 9707; and Bureau of Ordnance 14 February, 1947, File: NOrd-7920, Re9d-AKC/gep). From January 1, 1947, to June 30, 1947, the amount charged to Contract NOrd-7920, Task PRN-3, was $13, 701.21.

Authorization to treat the subject matter as unclassified has also been received (Letter: Bureau of Ordnance, 21 April, 1947, File NOrd-7920-Re9d-AKC/gep).

SUMMARY OF TECHNICAL PAPERS

Experimental work undertaken in the past six months is partially summarized in six Technical Papers, copies of which are appended.

Two of these papers (nos. 26 and 30) deal with methods of flame detection and flame speed measurement in glass tubes without the use of internal probes or electrodes which might interfere with the flame itself. In one application the loading characteristics of a high-frequency oscillator tank coil are altered as the flame passes - due presumably to increased eddy current losses in the ionized gas. In the other case, two narrow aluminum bands around the explosion tube are connected through a high resistance to a source of e.m.f. Passage of the flame alters the resistance of the circuit producing a voltage pulse which triggers an electronic timing circuit.

The broadening of low-pressure ignition limits of n-butane in air or oxygen as temperature is raised reveals some interesting results (Paper No. 28). With oxygen the only effect is to halve the lean limit between 25° and 300° C. The low-pressure limit remains fixed at about 25 mm. (Spark ignition is one inch glass tube; downward propagation). With air, on the other hand, the lean limit is only moderately reduced, but the lower pressure limit falls from about 100 to 50 mms.

In the field of spontaneously ignitable compounds, it is found that boron tri-ethyl ignites in oxygen at pressures of the order of 1 mm. without a measureable induction period. (Paper No. 27) There is an inverse relationship between pressure and vessel diameter. A spray of boron tri-ethyl directed at a stream of oxygen from a tank also ignites. Further, introduction of a butane-oxygen mixture to a bulb containing a few mms. pressure of boron tri-ethyl leads to explosion. All of the above refers to room temperature.

Experiments on the interaction of atomic hydrogen (from Wood's discharge tube) with molecular oxygen at low pressures have led to interesting results (Paper No. 31). If the product is condensed at liquid nitrogen temperature (77° K.) a considerable amount of hydrogen peroxide is recovered. However, condensation at solid carbon dioxide temperature (194° K.) gives no peroxide and very little water. It seems fairly evident that the reaction is occurring mainly on the walls of the cold trap - perhaps by adsorption of hydrogen atoms on a liquid oxygen layer.

A significant outgrowth from the work of this project has been a theory of the bunsen-type flame, due largely to the work of a graduate student, Mr. C. Tanford, who has been a National Research Council Pre-doctoral Fellow for the past year. It is assumed that flame propagation depends on the back-diffusion into unburnt gas of atoms and radicals from the flame front. These atoms and radicals are assumed to be at thermodynamic equilibrium concentrations at the calculated flame temperature. Simultaneous calculations of concentrations and temperature are made by successive approximations. The atom and radical concentrations are then compared with the observed burning velocities. Assuming there is no net loss of atoms and radicals during reaction, it turns out that as a first approximation one may write -

$$V = \left(\frac{k\ C\ \text{ave.}\ c_o\ D}{Q}\right)^{1/2}$$

where

V = the linear burning velocity in cms. per sec.;

k = a velocity constant;

C ave. = average concentration of reactant;

C_o = atom or radical concentration at equilibrium in the flame front;

Q = concentration of combustible;

D = coefficient of diffusion.

Thus, if C ave. and Q may be approximately equated -

$$V = k'\ c_o^{1/2}$$

where k' is a constant characteristic of the reaction. The velocity, v, should then vary roughly as the square-root of the atom and radical concentration in the flame front. This relation is found to apply. Further, since c_o should decrease roughly as the square-root of the pressure whereas D should increase linearly as pressure is decreased, the burning velocity should first increase as pressure is decreased (roughly as the fourth-root). This is also found, though at lower pressures the velocity passes through a maximum.

In connection with the above, burning velocities of butadiene with "air" in which the nitrogen is replaced by helium have been compared with ordinary air (Paper No. 29). The difference (nearly 4 to 1) is due mainly to the fact that atom concentrations in the flame front are greatly increased. This in turn follows from the fact that the lower heat capacity of helium leads to a higher temperature (about 300° C.) and hence more dissociation. In addition, the diffusion coefficients in helium air are increased.

It would thus appear that at least a start had been made in accounting for some of the special properties of flames.

CURRENT PROBLEMS

Activities being carried on at the present time include the following: -

1. Low-pressure flames using a Bunsen-type burner of relatively large orifice;
2. Kinetics of oxidation of hydrazine, diborane, and aluminum borohydride
3. Spectroscopic verification of NO, NH, and CN radicals in Bunsen-type flames;
4. Evaluation of leak-detector type mass spectograph;
5. Calculation relating to flame speeds.

(Signed) Robert N. Pease

Robert N. Pease
Professor of Chemistry
Princeton University

THE HIGH FREQUENCY OSCILLATOR AS A FLAME DETECTOR

By

Hartwell F. Calcote

(Transmitted by Robert N. Pease)

Department of Chemistry, Princeton University

Contract NOrd-7920, Task PRN-3

Technical Paper No. 26

March 25, 1947

SUMMARY

A new method of detecting ionization in flames utilizing the loading characteristics of a high frequency oscillator is described for use in the measurement of flame speeds. As the flame passes through an oscillator tank coil which is constructed around a combustion tube, the absorption of energy due to ion formation and increased eddy-current losses in the gas causes an increase in the plate current of the oscillator which is used to trigger an electronic chronoscope. Two distinct advantages of the method are: (1) direct measurement of flame speeds can be made without the introduction of electrodes or screen wires into the tube, and (2) the point in the tube at which the measurement is made can be varied at will.

INTRODUCTION

Various methods of detection have been described for use in the measurement of flame speeds in addition to the photographic method of Mallard and Le Chatelier(1). These have been necessary in some cases where the luminosity of the flame is extremely low, and in others as a matter of convenience to avoid the development of film. All of them, however, have the disadvantage that something must be placed inside the tube which may distort the flow of flame gases and thus enhance the flame surface area. This is undesirable since the surface area plays a large part in determining flame speeds(2). In the case of very weak flames, metal probes may actually extinguish the flame by cooling.

In both the spark method(1)(3) and in the flame conductivity method(4)(5) it is necessary to have electrodes in the tube. In the method of melting screen wires(6) it is not only necessary to have a thin wire stretched across the inside of the tube but it is also necessary that after each measurement the screen wires be replaced.

The method described below, which takes advantage of the fact that an increase in ionization within a coil will absorb energy from, or lower the Q*, of the coil, does not have any of these disadvantages. The coil can be wound around the glass tube through which the flame is propagated, and the additional advantage is obtained that the coil can be simply moved from one point on the tube to another so that measurements are not confined to one region of the tube. Of course in the measurement of flame speeds two such oscillators are used to trigger a chronoscope "on" and then "off".

Similar applications of loading tank coils to detect ionization have recently been made in the field of electrolytic solutions. Bradhurst(8) used a Hartley oscillator with the tank coil wound around a sector of glass tube in a "decant" line. Oscillations were obtained when oil passed through the line.

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* The Q or "quality factor" of a coil or circuit is defined as the ratio of the energy stored to that dissipated in each cycle of the oscillation(7). Since the energy stored is proportional to the reactance and the energy dissipated is proportional to the resistance: $Q=X/R$, where X is the reactance of the circuit, and R is the equivalent resistance.

coil but stopped when a conducting acid entered. Jensen and Parrack(9) used a tuned plate-tuned grid oscillator with the tank coil of the oscillator wound around a titrating flask. Conductomeric titrations were run using the change in plate current due to loading as a measure of the change in conductivity of the solution.

CIRCUIT CONSIDERATIONS

Since this application of an oscillator depends on the loading of the circuit, i.e. on an increase in the dissipation of energy in the tank coil, it is important that (1) the normal circuit losses be negligible and (2) that the circuit be sensitive to any change in the Q of the tank coil. Both requirements demand a high Q circuit. In addition the second requirement suggests that the inductance, L, in the tank circuit should be large compared to the capacity, C.

High frequencies are necessary because eddy-current losses are proportional to the square of the frequency. Assuming the same type of argument for eddy-current losses in a conducting flame as in an iron core transformer(10), the power loss is $P_e = KB_m^2 f^2/R$ where, K is a constant containing the dimensions of the volume in which the losses occur, B_m is the maximum value of the flux density, f is the frequency, and R is the resistance of the flame. However as the frequency is increased, the effective Q of the coil is decreased due to the skin effect so that it is necessary to obtain a balance between the two effects.

The above considerations might be fulfilled by almost any type of oscillator having one or more tuned circuits. However in addition to changing the efficiency of oscillation, examination of the complete equation for the frequency of an LCR circuit:

$$f_{osc} = \frac{1}{2\pi}\sqrt{\frac{1}{LC} - \frac{R^2}{4L^2}}$$

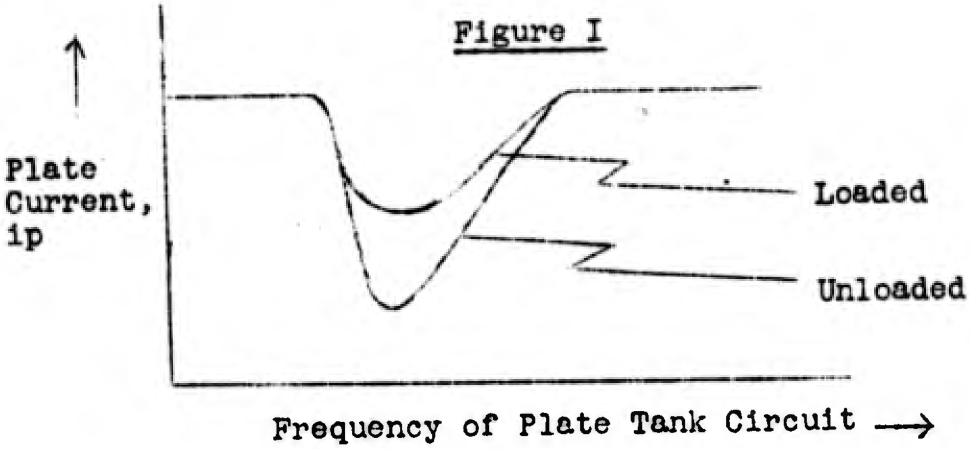
or for a tuned plate oscillator:(11)

$$f_{osc} = \frac{1}{2\pi\sqrt{LC}}\sqrt{\frac{R + R_p}{R_p}}$$

shows that the frequency is also dependent upon the resistance in the circuit. R_p is the tube resistance and the other symbols have their usual meaning. These equations although applying only to the special cases where the resistance is in series show that some advantage might also be taken of the change in frequency due to a change in the effective resistance of the coil. This can be done by using an oscillator with more than one tuned circuit, such as a tuned plate-tuned grid oscillator.

Figure I for a tuned plate-tuned grid oscillator shows that any change of loading or frequency variation in the plate tank circuit will produce a change in plate current.

Figure I



DESCRIPTION OF OSCILLATOR

The particular oscillator used was a tuned plate-tuned grid oscillator, with the plate tank coil consisting of three turns of bare No. 12 copper wire wound close-spaced around the combustion tube (28 mm. pyrex). In order to obtain the maximum L/C ratio no additional capacity was placed in parallel with this coil, the stray capacity and plate to cathode capacity of the tube being utilized. When a 6J5 triode was used, this gave a resonant frequency of approximately 65 megacycles; and with a 955 acorn tube the resonant frequency was 100 megacycles. The frequencies were measured by the Lecher wire method.

The coil was mounted directly to the circuit to avoid any unnecessary losses in the lead from the coil to the oscillator. The circuit (Figure 2) was constructed on a piece of Lucite 8 x 11 cm. and a steel rod connected perpendicular to the plane of the Lucite. The rod was then mounted by means of a regular clamp holder to a long steel rod running parallel to the Pyrex combustion tube. This arrangement permitted the measurement of flame speeds over any section of the combustion tube by merely moving the coil and oscillator along the tube.

Tuning of the oscillator was achieved by placing a vacuum tube voltmeter across R_1 and tuning C_1 for a maximum voltage i.e. a minimum current. C_2, which controls the feedback, is then adjusted until the circuit goes out of oscillation easily when either C_1 is varied or when one holds his hand in the vicinity of L_2.

The circuit values are not critical although maximum sensitivity will be obtained when R_1 is as large as feasible. In order to obtain a high Q for the overall circuit, C_1 should be large compared to L_1, and R_2 should be large(7). The value of R_2 is usually limited by the fact that when it becomes excessively large the time constant of R_2C_2 will cause the grid bias to build up until the tube blocks i.e. is "cut-off". The circuit then ceases to oscillate until the condenser C_2 has discharged sufficiently to permit the tube to again conduct and oscillations to take place. The cycle is then repeated giving bursts of oscillations, a phenomena which is commonly called motorboating. In most oscillators this cannot be tolerated. However in this application motorboating at a frequency sufficiently high so that it does not pass appreciably by the choke coil, to give a trigger pulse to the chronoscope, is not objectional. In fact it has been found to increase the sensitivity considerably.

With a B^+ voltage supply of 400 volts the D.C. voltage at the point "output pulse" is 35 volts and a voltage pulse of approximately 4 volts is obtained. When motorboating is allowed the D.C. voltage is 80 volts and the pulse voltage is approximately 15 volts.

The flame speed was measured in a stoichiometric n-butane + air mixture at 200 mm. Hg. pressure. Other pressures and compositions gave equally satisfactory results.

SUGGESTED APPLICATION

It is suggested that in addition to the use described herein this type of flame detector might be used in industry as a combustion protection control i.e. as a safety measure to indicate when a flame goes out. At present the indicators used include such things as:(12) (1) flame conductivity measurements, (2) photocells, and (3) the utilization of the flame rectification principle. The high frequency oscillator detector should prove a much simpler and cheaper piece of equipment than those already in use.

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LEGEND TO FIGURE 2

T - 955 Acorn tube

C_1,C_2 - 25 mmf. tuning condensers, Cardwell ZR-25-AS

C_3,C_4 - 500 mmf. midget mica condensers

L_1 - Three turns No. 12 copper wire, 1/2 inch in diameter and 3/4 inches long.

L_2 - Three turns No. 12 copper wire wound close spaced around the reaction tube.

L_3 - 2.5 mh. R. F. choke

R_1 - 1 megohm resistance

R_2 - 0.5 megohm resistance

The filament and plate voltages were obtained from an electronically regulated power supply.

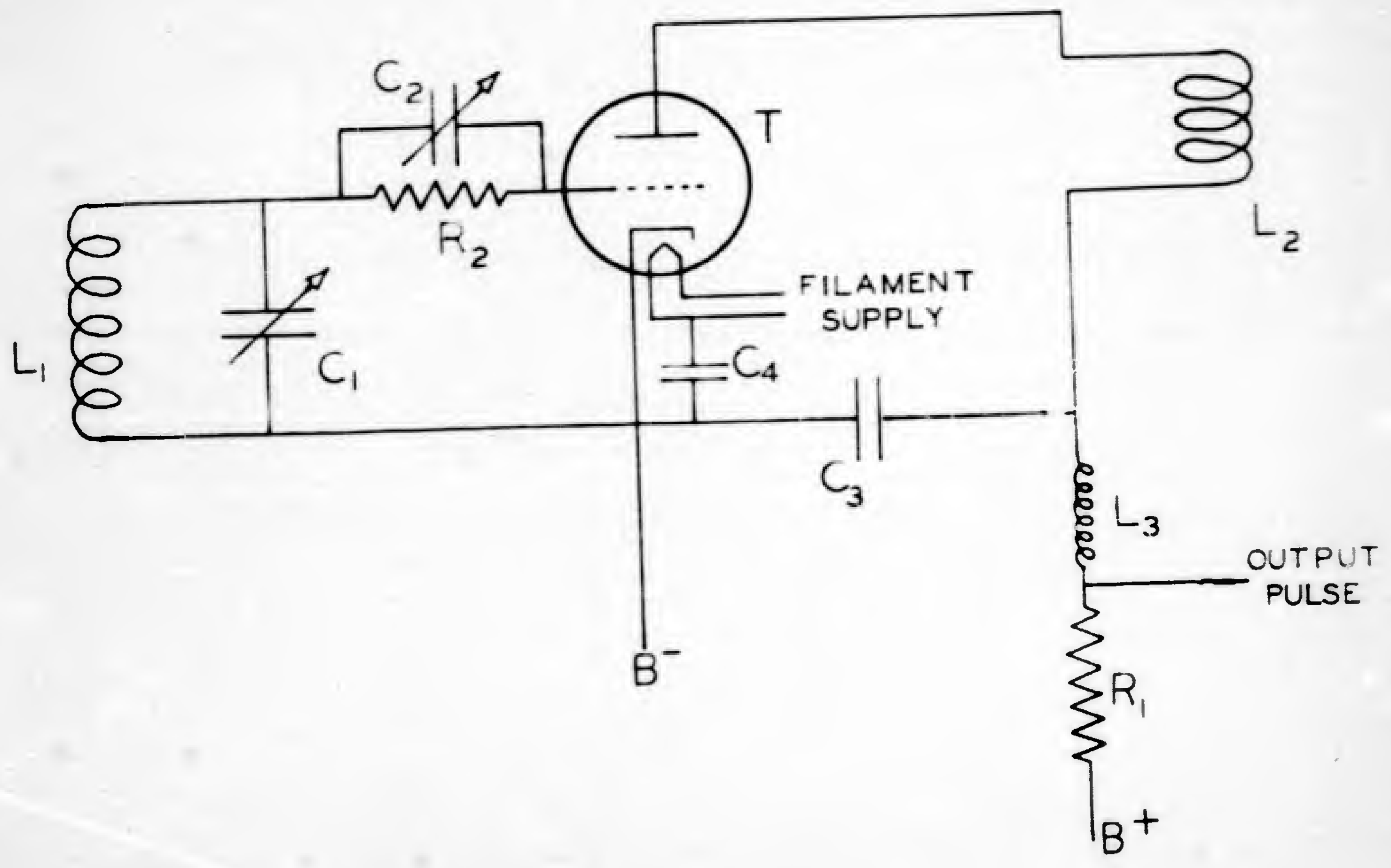

FIG. 2 OSCILLATOR CIRCUIT

EFFECT OF VESSEL SIZE AND SURFACE COATING ON THE COMBUSTION OF BORON TRIETHYL

By Richard S. Brokaw And Elmer J. Badin

(Transmitted by Robert N. Pease)

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Contract NOrd-7920, Task PRN-3

Technical Paper No. 27

March 25, 1947

SUMMARY

The effects of the diameter of the explosion vessel and of surface coatings on the spontaneous combustion of boron triethyl and oxygen has been studied. In general, decreasing the bulb diameter raises the explosion limit; bulbs self-coated with reaction products raise the limit. Good agreement with collision theory for variation of total pressure and diameter of reaction bulb has been obtained. In addition the effect on the explosion limit of various other surfaces has been determined.

INTRODUCTION

Studies of the spontaneous combustion of zinc dimethyl-oxygen, nickel carbonyl-oxygen and aluminum borohydride-oxygen have previously been reported(1). All such combustions have been carried out in spherical pyrex bulbs and have been characterized by formation of solid reaction products. Formation of solid reaction products or "mists" suspended in the gaseous mixture would undoubtedly be expected to have an effect on the combustion characteristics. As a first step in evaluating the effect of surface coatings and vessel size, the combustion of boron triethyl has been studied under various conditions. The effects of flask size and various surface treatments on the combustion limits of boron triethyl-oxygen mixtures at 0°C. are reported here.

APPARATUS AND METHOD

The apparatus used is shown in Figure I. The $B(C_2H_5)_3$ was contained in bulb A. Bulbs B and B' were used for gas storage, the gases being admitted through stopcocks C and C'. Air from the room was admitted through a charcoal-calcium chloride dryer D. Reaction bulbs, E, were spherical flasks of volumes close to 50, 150, 200, 500 and 1000 cc. corresponding to calculated inside diameters of 4.6, 6.6, 7.4, 9.8 and 12.7 cm. respectively and were fitted with 10-30 ST joints. Oxygen was stored before reaction in the reservoir X. Both the reaction bulb E and the storage reservoir X were thermostatted. The connecting tubing between them was 6 mm. diameter, to permit rapid introduction and mixing of reacting gases. Pressures were measured on a direct reading manometer M and with a McLeod gauge F, designed to read pressures over a range of 0.0-15.0 mm.

Reaction bulbs were cleaned by treatment with boiling concentrated nitric acid followed by six rinses with distilled water. Drying was carried out over-night in an oven at 135°C., followed by blowing the flasks with dried air. Coatings were applied after this standard cleaning procedure, but coated bulbs were dried before use.

Bulbs were attached to the apparatus and evacuated to a pressure of about 10^{-4} mm., and $B(C_2H_5)_3$ vapor admitted to the reaction bulb to the desired pressure. The reaction bulb was then closed off by its stopcock. Oxygen was admitted to the reservoir X in an amount sufficient to give the desired final pressure when the connecting stopcock was opened and the gases allowed to mix. Experiments were carried out in a darkened room in order to make observation of faint flashes. Flashes occurred immediately on opening the stopcock, without measurable induction period.

Since all the limits observed were below 11 mm. total pressure, accurate measurements of the pressure of $B(C_2H_5)_3$ (always less than 0.6 mm. at the limit) were necessary. While it is realized that the accuracy of McLeod gauge readings are subject to gas law deviations, particularly great with gases below their critical temperatures, it was felt that at the low pressures studied these deviations were of lesser significance. Also, the McLeod gauge permitted readings to less than ± 0.01 mm. in the pressure range of 0.00-1.00 mm., yielding pressure readings which were precise relative to one another, if not on an absolute basis. It was felt that the greater precision obtained using this system of metering was justifiable.

In the combustion experiments reported here the manner of addition of the reactant was of importance. In each case the oxygen was admitted rapidly to the boron triethyl vapor. It was noticed that if the addition of oxygen was slow, a slow burning or sustained "diffusion flame" resulted. This was true especially at pressures considerably above ($\sim$ 150 mm.) the explosion limits and at high concentrations of $B(C_2H_5)_3$ ($\sim$ 0.20 mole fraction).

Boron triethyl was prepared from the Grignard reagent and boron trichloride-etherate. It was purified by several distillations. As a final purification step 125 g. was fractionated in a helium atmosphere through a 20 plate column. A middle fraction of 20 g. (b. p. 95.0°C.) was used for all experiments.

RESULTS AND DISCUSSION

In a previous study of the combustion of zinc dimethyl(1) it was observed that below the explosion limit a slow and measurable oxidation of the metal alkyl occurred. An increase in pressure led to an increase in the rate of the slow oxidation finally going over into explosion. No such slow oxidation has been observed in terms of pressure-change or appearance of a mist with boron triethyl below the limit for periods as long as 1000 seconds. It appeared that reaction occurred instantaneously or not at all, that is, there was no evidence of a measurable induction period.

Initially a considerable amount of work was carried out at the reactant temperature of 25°C. In order to magnify any changes produced on the limits by varying the scale of operations the temperature was lowered to 0°C. In Table I data are given for the explosion limits of a 5% (0.05 mole fraction) mixture of boron triethyl in oxygen at 0° initial reactant temperature with varying bulb sizes and using clean "dry" pyrex surfaces and surfaces self-coated with reaction products. In the latter case the limit was approached from above; that is, successive runs were made in the same bulb with decreasing total pressure until the limit was reached. In this way some degree of uniformity in the coating produced was achieved.

In Table I the product pd (where p = total pressure, d = diameter of reaction bulb) has been calculated. From kinetic theory as shown by Smoluchowski(2) the number of collisions suffered by a molecule in travelling a distance ΔX is

$$z = \frac{3\pi \Delta X^2}{4 \lambda^2} \qquad (1)$$

where λ is the mean free path of the molecule. Assuming that destruction of chain carriers occurs at the walls, the maximum displacement ΔX will be proportional to the diameter d of the bulb. In addition it may be assumed that λ will be inversely proportional to the total pressure at low pressures. Therefore (1) will reduce to

$$z = (\text{constant})\ P^2 d^2 \qquad (2)$$

Since a critical value of describes the explosion limit, one would expect the product pd to be constant at the limit. The values calculated in Table I show this to be a reasonably good approximation. These points have been plotted (Figure II) and can be seen to fall on the curve calculated for an average pd value in each case.

The same relationship has been shown to be true for various other combustions. N. Semenova(3) obtained pd values for the lower limit of hydrogen-oxygen combustion which checked to within 2.5% in vessels where d was greater than 15 mm. Values were 25% low for a vessel of 6 mm. diameter. Earlier, Hinshelwood and Moelwyn-Hughes(4) studied the same

TABLE I

EXPLOSION LIMITS OF $B(C_2H_5)_3$ IN OXYGEN

(0.05 mole fraction boron triethyl in oxygen.)
(Temperature 0°C.)

Bulb Diameter* d (cm.)	Total Pressure at Limit, p (mm.)	$[B(C_2H_5)_3]$ (mm.)	$[O_2]$ (mm.)	p x d
Clean "dry" pyrex surface:				
4.56	7.5	0.375	7.1	34
6.56	4.3	0.215	4.1	28
7.38	4.1	0.205	3.9	30
9.82	3.1	0.155	2.9	30
12.66	2.1	0.105	2.0	27
Surface self-coated with reaction products:				
4.56	10.7	0.535	10.2	49
6.56	9.0	0.45	8.5	59
7.38	7.3	0.365	6.9	54
9.82	4.7	0.235	4.5	46
12.66	3.6	0.18	3.4	46

* Calculated from the volumes of the near-spherical bulbs.

reaction with considerably less consistent results. N. Semenoff(s) has investigated the reaction between phosphorus and oxygen. In his experiments the partial pressure of phosphorus was held constant, and it was shown that $P_{O_2}d^2$ should be a constant. His results were in agreement with this. In Dalton and Hinshelwood's(s) work on the reaction between phosphine and oxygen pd varied between 3.1 and 3.9 for surfaces coated with reaction products, while somewhat lower values were obtained with a phosphoric acid coated surface.

From Table I and Figure II it can be seen that the general effect of the reaction product coating was to raise the explosion limit. Another significant difference was that produced on the nature of the visible "flash" produced. This difference is shown for a given diameter bulb in Table II. A decrease in pressure for a clean surface led to a transition from brilliant flashes to dull flashes visible only in a darkened room. Also an occasional anomaly was noted as shown in Table II. The same experiments with "dirty" surfaces completely eliminated this region of "cool" flames leading to a sharp transition to no reaction. It thus seems that the surface of a clean "dry" bulb can possibly catalyze the "cool" flame formation. The function of the reaction products in raising the limit seems to be essentially elimination of this region of barely visible flashes. It also definitely lowers the region of bright green flashes.

A variety of additional surface treatments was carried out. These are shown in Table III. In each case clean bulbs were coated with the material and dried in an oven at 135°. A series of clean bulbs treated in the manner shown was used in locating the limit. As can be seen no strikingly significant differences from the limit produced with a clean pyrex surface were noted.

The initial work (bulb diameter 6.56 cm.) at 25° has led to the qualitative conclusion that a sort of upper limit may exist for the bright green flash observed. Thus, for a constant composition of 5% (0.05 mole fraction) boron triethyl in oxygen the bright green flash was observed from about 10 mm. to 100 mm. total pressure. At pressures above 120 mm. the flashes observed were definitely less brilliant. It was also noted that when the ratio of boron

TABLE II

NATURE OF FLASHES OF BORON TRIETHYL WITH OXYGEN

(0.05 mole fraction of boron triethyl in oxygen.)
(Temperature 0°C. 6.56 cm. bulbs)

Total Pressure (mm.)	Nature of Flash
Clean "dry" pyrex surface:	
19.3	Bright Green
17.6	" "
16.5	" "
15.0	" "
13.6	" "
13.4	" "
12.6	Dull Green
12.0	Faint Bluegreen
11.9	Bright Green
9.2	Bluegreen
8.0	"
6.3	"
4.8	Faint Bluegreen
4.4	" "
4.4	" "
4.2	No Reaction
4.0	" "
Surface self-coated with reaction products:	
13.6	Bright Green
13.6	" "
12.8	" "
10.4	" "
9.4	" "
9.2	" "
9.2	" "
9.0	" "
9.0	No Reaction
9.0	" "
8.8	" "
8.2	" "
6.9	" "
5.8	" "

TABLE III

EFFECT OF SURFACE TREATMENT ON EXPLOSION LIMITS OF BORON TRIETHYL IN OXYGEN

(0.05 mole fraction $B(C_2H_5)_3$ in O_2.)

(Reactant temperature 0°C. 6.56 cm. diam. bulbs.)

Type of Surface	Total Pressure at Limit (mm.)	p x d
Clean "dry" pyrex surface: (oven dried at 135°C.)	4.3	28
Baked pyrex surface: (dried with flame under vacuum)	5.1	33
Surface self-coated with reaction products.	9.0	59
H_3BO_3 (rinsed with saturated solution and oven dried at 135°C.)	4.9	32
Parraffin (rinsed with 1% sol'n in n-pentane and oven dried at 135°C.)	5.0	33
HCl (rinsed with concentrated HCl and oven dried at 135°C.)	5.1	33
KCl (rinsed with 5% solution and oven dried at 135°C.)	4.1	27
KOH (rinsed with 1% solution and oven dried at 135°C.)	4.8	31

triethyl to oxygen was increased at a given total pressure, the brilliance of the flashes diminished. Apparently an increase in boron triethyl concentration has a quenching effect on the radiation.

It may be added that the brilliance of the flash understandably increased with vessel diameter.

Though no detailed determinations of limits at other than 5 volume % were made, explosions were observed over a range from 5-60% boron triethyl at low pressures. It may be added that stoichiometric butane-oxygen mixtures were ignited by small concentrations of boron triethyl. A stoichiometric mixture of n-butane in oxygen (0.133 mole fraction n-C_4H_{10} in O_2) with varying amounts of $B(C_2H_5)_3$ was exploded at a total pressure of 100 mm. The data contained in Table IV show that a very definite explosion resulted with only about 3% $B(C_2H_5)_3$. Moreover, all the experiments shown in Table IV resulted in a neglible pressure change except the 3% experiment which had a large negative pressure change.

TABLE IV

EXPLOSION OF STOICHIOMETRIC n-BUTANE-OXYGEN MIXTURES WITH $B(C_2H_5)_3$

(Total pressure 100 mm., Temperature 20°)

Pressure $B(C_2H_5)_3$ (mm.)	Pressure C_4H_{10}-O_2 Mixture (mm.)	Nature of Explosion
10	90	Very faint flash
5	95	Faint flash
3	97	Very bright explosive flash
1	99	No reaction

ADDENDUM

Below the explosion limit no visible reaction between boron triethyl and oxygen was apparent. It seems very likely, however, that a reaction of boron triethyl with oxygen (possibly an instantaneous one) does occur. A series of experiments was carried out at low temperatures and pressures to determine the products formed with oxygen. Boron triethyl vapor was metered into a 500 ml. reaction bulb at 20°C., the vapor was then condensed out at -79°C. (carbon dioxide-acetone bath) and an excess of oxygen added slowly. A small amount of oxygen absorption occurred at -79°C. The temperature was then raised to 20° during which time additional oxygen absorption occurred. The mixture was allowed to stand at 20° until a constant pressure (no additional oxygen absorption) resulted. The resulting product was an oily liquid, stable in air at room temperature. For two experiments carried out in this manner analyses were

(1) 9.15 % H, 42.16% C.

(2) 9.74 % H, 45.84% C.

The average value was 9.45% H, 44.00% C. which compares with calculated values of 9.34% H, 44.5% C. for the compound $B(C_2H_5)_3.2\ O_2$. From the pressure data for oxygen consumption enough oxygen was absorbed in both experiments to give an average value corresponding to $B(C_2H_5)_3.1.7\ O_2$. This figure was uncorrected for the vapor pressure of the compound formed. A value of only 10 mm. for the vapor pressure would raise the value to 1.9 or 2.0 O_2.

The same addition compound was titrated for peroxides using the sodium thiosulfate-iodide method. In three experiments in which boron triethyl was reacted with oxygen as above, potassium iodide solution was added to the frozen addition compound, and the mixture allowed to warm to room temperature. The iodine, which was only slowly liberated, was titrated with sodium thiosulfate (starch indicator). The results corresponded to 1.04-1.09 equivalents I per mole $B(C_2H_5)_3$.

The oxygen addition compound would not decolorise $KMnO_4$ after solution in 2% H_2SO_4. On the other hand, when the experiment was repeated without addition of oxygen, there was a reaction with acid permanganate solution. The end-point was not sharp, but about 2.2-2.45 equivalents $KMnO_4$ reacted per mole of $B(C_2H_5)_3$.

There is, therefore, evidence of the formation of an oxygenated intermediate, but its nature is not yet clear.

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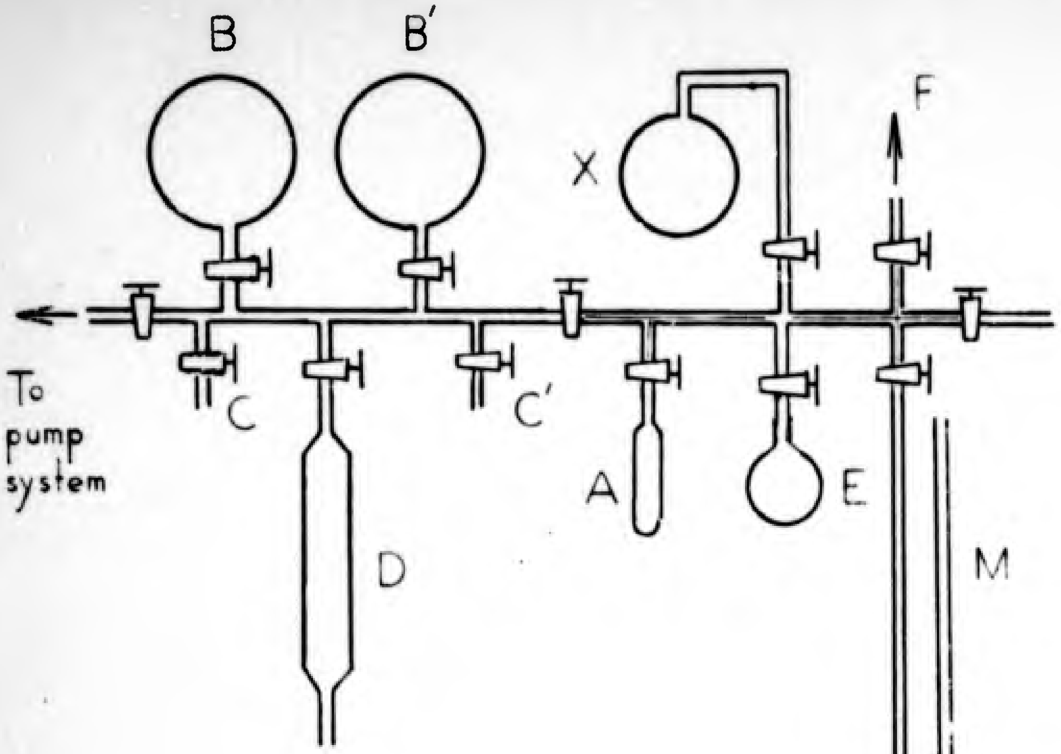
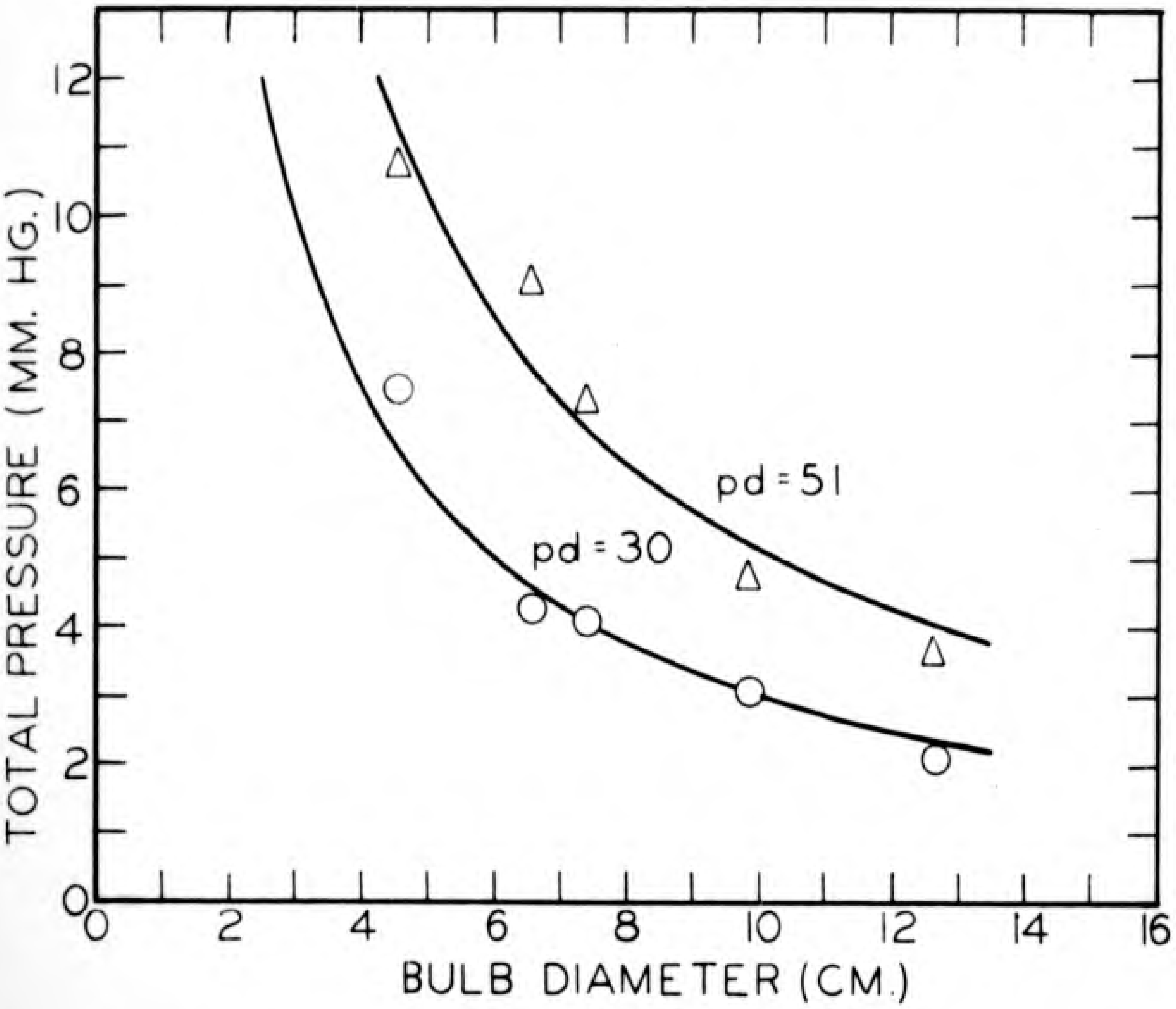


FIGURE I APPARATUS



△ Surface self-coated with reaction products.

○ Clean "dry" pyrex surface.

FIGURE 11 VARIATION OF EXPLOSION LIMIT WITH BULB DIAMETER FOR THE COMBUSTION OF BORON TRIETHYL.

EFFECT OF TEMPERATURE ON THE LOW-PRESSURE IGNITION LIMITS OF n-BUTANE IN AIR AND OXYGEN

By

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Department of Chemistry, Princeton University

Princeton, N. J.

Contract NOrd-7920 Task PRN-3

Technical Paper No. 28

July 1, 1947

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Summary

Spark ignition limits for n-butane in air and oxygen have been determined at 25°, 100°, 200° and 300° for downward propagation in a 25 mm. glass tube. The lean limits at 760 mm. are nearly the same in air and oxygen, and are somewhat broadened at higher temperatures. (2.5 to 1.7% C_4H_{10} between 25° and 300° C.). The rich limit in air is moderately increased (6.2 to 7.6% C_4H_{10}), whereas that in oxygen remains nearly constant at about 40% C_4H_{10}. Pressure minima occur near stoichiometric composition in each case. That for air is lowered from 82 to 46 mm. (25° to 300°C.) while that for oxygen is nearly constant at 26 to 29 mm.

Introduction

In Technical Paper No. 5 of this series, data on the ignition of n-butane as a function of pressure at room temperature were presented. In view of the fact that the entering air in a ram-jet is at an elevated temperature, it was of interest to investigate the temperature effect. Results are here reported for ignition in both air and oxygen at 25°, 100°, 200° and 300°C.

Apparatus and Method

The apparatus and method were essentially the same as previously reported. The gases were pre-mixed and introduced into a 25 mm. I.D. Pyrex tube placed vertically with a spark gap at the upper end (downward propagation). Ignition limits were fixed within about 3 mms.

The ignition tube was contained in a somewhat larger tube around which nichrome wire was wound, leaving spaces to permit observation of explosion. This was in turn jacketed by a still larger tube to minimize temperature variation. Mercury thermometers in contact with the outer wall of the explosion tube served for temperature determination.

A two-liquid manometer (toluene-mercury) was used in preparing mixtures in the lower pressure range.

Table I

Pressure Limits for Combustion of n-Butane-Air

(Downward Propagation, Spark Ignition)

Temperature (°C.)	Volume % n-Butane	Pressure Limit (mm. Hg.)
25°	2.2	760
	2.7	120
	3.3	100
	4.0	82
	4.6	85
	5.2	116
	5.4	121
	5.8	304
	6.2	760
100°	2.1	763
	2.4	145
	2.6	122
	3.0	86
	3.7	64
	4.3	65
	5.4	191
	6.8	763

Temp. (°C.)	Volume % n-Butane	Pressure Limit (mm. Hg.)
200°	1.7	757
	2.1	187
	2.6	77
	2.8	66
	3.5	53
	4.0	51
	5.0	62
	5.6	105
	5.9	131
	6.4	206
	7.4	757
300°	1.7	752
	2.0	325
	2.2	75
	2.6	58
	3.2	54
	3.7	49
	4.5	46
	5.1	53
	5.7	84
	6.2	108
	6.4	91
	6.7	94
	7.0	124
	7.0	152
	7.2	229
	7.6	758

Table II

Pressure Limits for Combustion of n-Butane-Oxygen

(Downward Propagation, Spark Ignition)

Temp. (°C.)	Volume % n-Butane	Pressure Limit (mm. Hg.)
25°	2.8	755
	3.8	128
	4.8	56
	5.7	47
	8.1	31
	12.5	27
	16.2	28
	19.9	33
	24.6	35
	28.1	87
	30.4	106
	33.0	68
	35.4	164
	37.5	300
	40.1	758
100°	1.9	748
	2.8	79
	3.0	64
	4.1	49
	6.8	28
	8.2	26
	13.1	24
	15.3	26
	19.8	30
	24.8	32
	29.7	81
	30.0	80
	32.4	70
	34.3	77
	38.1	238
	41.3	756

Temp. (° C.)	Volume % n-Butane	Pressure Limit (mm.Hg)
200°	1.7	757
	2.0	438
	2.5	55
	3.5	39
	4.6	34
	6.2	29
	7.3	28
	9.3	26
	15.1	26
	23.0	32
	27.4	56
	29.6	68
	33.5	56
	37.2	67
	39.6	275
	41.3	758
300°	1.7	763
	2.0	137
	2.2	113
	2.8	55
	5.0	31
	8.3	29
	13.9	27
	14.3	31
	15.1	29
	19.9	31
	25.0	38
	29.4	45
	32.4	65
	35.1	62
	36.3	53
	37.6	97

Results

Experimental data are presented in Figures I (air) and II (oxygen) and Tables I and II. In each case it was found that the low-pressure limit came near stoichiometric composition (3.1% in air and 13.3% in oxygen). For the air mixtures, this low-prêssure limit was 82 mm. at 25°C. dropping to 46 mms. at 300°C.; whereas for the oxygen mixtures, it remained fairly constant at 26 to 29 mms. The lean limits for air and oxygen mixtures were very similar, both dropping from about 2.5% butane at 25°C. to 1.7% at 300°C. The rich limit for air mixtures was raised from 6.2 to 7.6% (25° to 300°C.), while for oxygen mixtures it was nearly constant at 40 to 41%.

It thus appears that apart from the considerable drop in the low-pressure minimum for near-stoichiometric air mixtures there is relatively little effect of temperature on the ignition limits of n-butane in the 25°-300° range. This is the more remarkable since at 300° and above, the thermal reaction becomes appreciable - a fact which prevents measurements at still higher temperatures. Evidently the critical quantities determining spark sensitivity are not very responsive to temperature change, and are not very directly related to the factors which determine the onset of the normal thermal reaction.

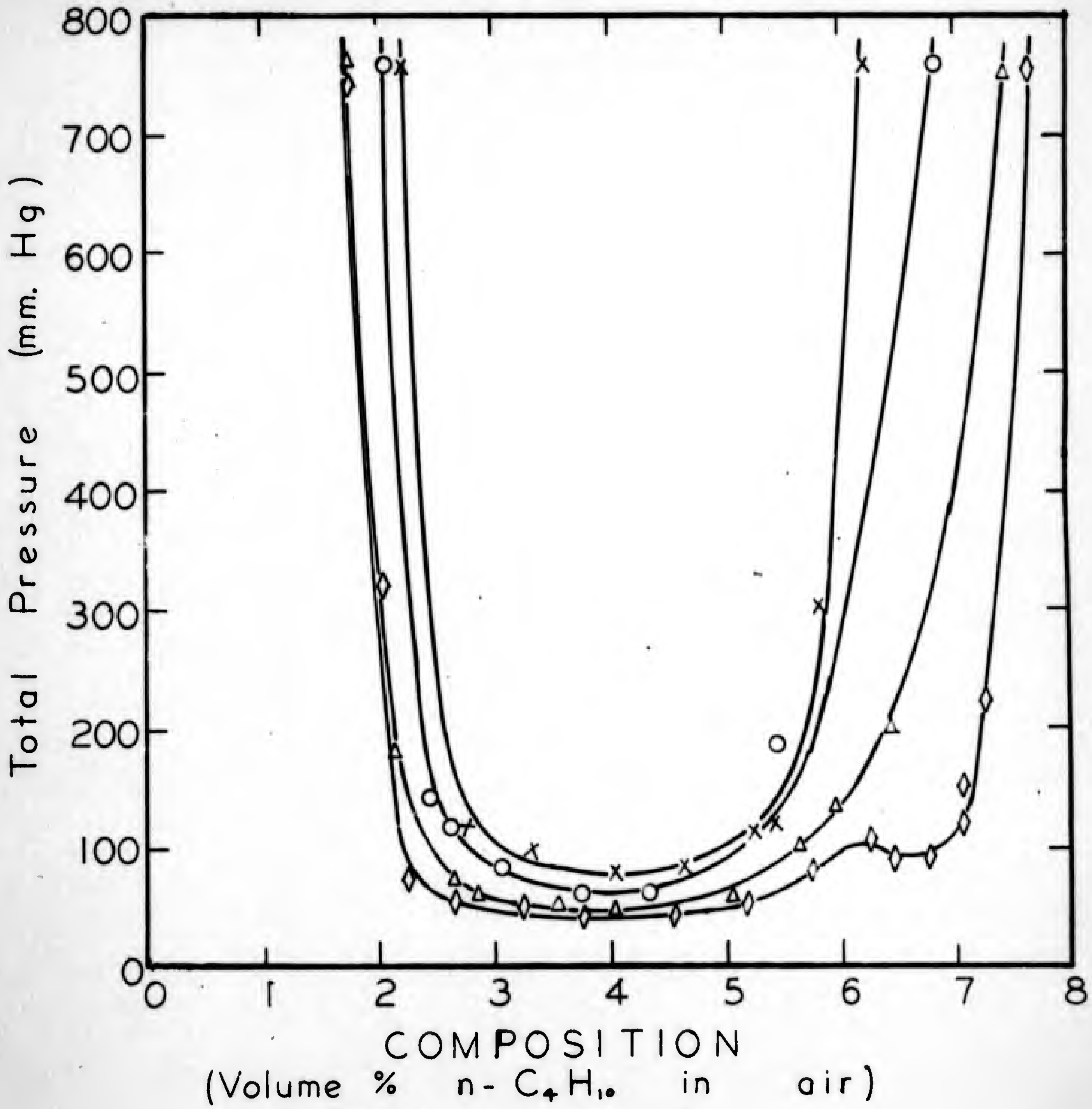

FIGURE 1 PRESSURE LIMITS FOR COMBUSTION OF N-BUTANE IN AIR (Downward Propagation)

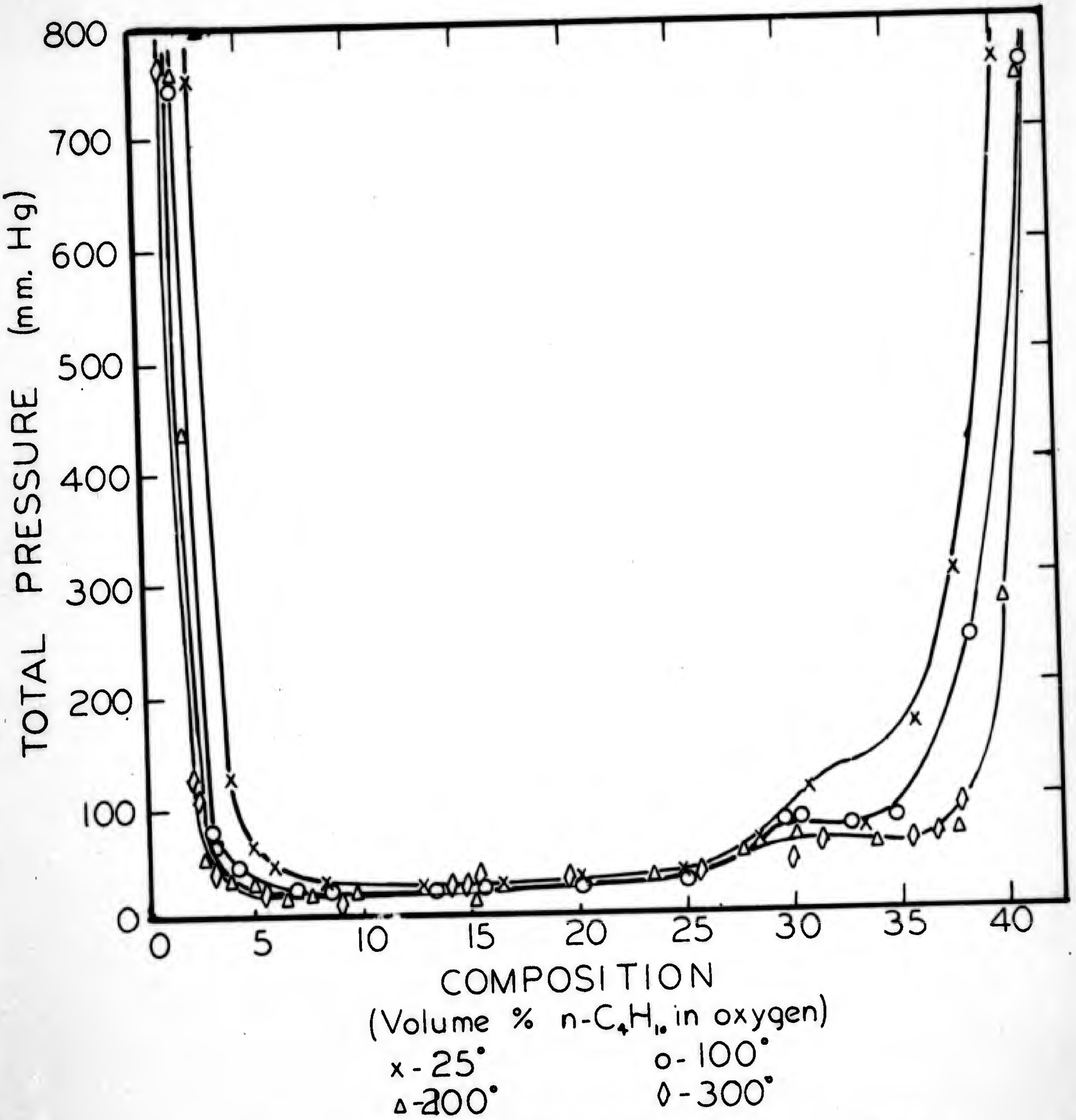

FIGURE 11 PRESSURE LIMITS FOR COMBUSTION OF N-BUTANE IN OXYGEN

(Downward Propagation)

Princeton University
Chemistry Department
July 1, 1947
APL-CF No. _____
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BURNING VELOCITIES OF NITROGEN-OXYGEN-BUTADIENE-1,3 AND HELIUM-OXYGEN-BUTADIENE-1,3 AT REDUCED PRESSURES

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Contract NOrd-7920, Task PRN-3

Technical Paper No.29

July 1, 1947

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SUMMARY

Burning velocities of nitrogen-oxygen-butadiene-1,3 and helium-oxygen-butadiene-1,3 have been measured at atmospheric and reduced pressures. At atmospheric pressure the ratio of 3.7:1 for the maximum burning velocities was obtained for helium compared to nitrogen as the inert gas. Reduction of pressure caused an increase then a decrease in burning velocity for helium-oxygen-butadiene-1,3. The maximum value of the burning velocity occurred at 300 mm. pressure.

INTRODUCTION

The characteristics of nitrogen-oxygen-butadiene-1,3 flames and helium-oxygen-butadiene-1,3 flames have been studied at reduced pressures with especial regard to burning velocities. It has been previously shown that the burning velocity of a hydrocarbon-air flame increased with decreasing pressure in the range studied.[1] A similar study has been made here with helium substituted for nitrogen. It was anticipated that this substitution, due to large differences in the thermal conductivities, heat capacities and diffusion coefficients of nitrogen and helium, would lead to broader limits and larger burning velocities than those found when air was used as oxidant.

APPARATUS AND METHOD

The metering system and low pressure apparatus used were those described previously[1]. In each case flows were adjusted to the desired rate at atmospheric pressure and then throttled down to the low pressure. A 10.55 mm. I.D. quartz burner was used for the low pressure measurements. Two cathetometers, one mounted for measuring vertical distances and one mounted for measuring horizontal distances, were used for measuring the dead space, flame cone height and cone base diameter. A second "projection method" was used for determining the flame dimensions. In this method a light-tight box fitted with a transparent screen at the end was mounted directly behind the flame. An 80 mm. diameter, 100 mm. focus double convex lens was mounted in the box so that the flame was just outside the focus. In this way an inverted real image of the stationary flame was cast on the screen and traced on a thin piece of paper. A beam of light was used to obtain a projection of the burner tube of known outside dimension. By using an enlargement factor it was possible to determine all the flame dimensions including the dead space. The method was essentially that used by Garsyth, Forsyth and Townend[3].

Three methods were used for determining the cone areas:-

(1) Calculation using base diameter and flame height on the basis of an ideal cone from the cathetometer measurements.

(2) Calculation as in (1) with measurements taken from the projected image instead of the cathetometer measurements.

(3) Calculation from the projected image by obtaining the lateral areas of frustums into which the projected image was divided.

Burning velocities were calculated using[3]

$$S = V/A$$

where

S = burning velocity in cm. per sec.
V = volume feed rate of flow in $cm.^3$ per sec. at the operating pressure.
A = flame cone area in $cm.^2$ calculated from $\pi r(r^2 + h^2)^{1/2}$

Data for areas and burning velocities (V/A in cm. per sec.) calculated by the above three methods are collected in Table II. In each case burning velocities were based on the outer cone areas. At the lower pressures the reaction zone appears to become thicker. If burning velocities had been based on the inner cone border or an intermediate border, somewhat larger burning velocities would have resulted.

To determine burning velocities at atmospheric pressure a 6.66 mm. I.D. mantled (25 mm. I.D. mantle) quartz burner was used.

Butadiene-1,3 was obtained from the Matheson Company. Helium-oxygen mixtures were obtained from the American Oxygen Company. By gas analyses the helium-oxygen mixture contained about 21% oxygen (average of several tank mixtures).

RESULTS AND DISCUSSION

In Table I and Figure I data are shown for burning velocities of helium-oxygen-butadiene-1,3 and nitrogen-oxygen-butadiene-1,3 for a 6.66 mm. burner. From these data it can be seen that the ratio of the maximum value for helium as compared with nitrogen is 3.7:1 corresponding to values of 163 and 43.9 cm./sec. There is, thus, a striking increase produced in the burning velocity when helium is substituted for nitrogen.

Data at reduced pressures (a 10.55 mm. diameter burner was used so that lower pressures might be attained) are shown in Table II. The variation of burning velocity with pressure has been plotted from values obtained from graphs of the data in Tables I and II for the composition 3.68 vol.% and 300% butadiene-1,3. For helium-oxygen this correlation indicates an increase in burning velocity with decrease in pressure down to 300 mm. Below this pressure the burning velocity of helium-oxygen-butadiene-1,3 mixtures decreases.

Higher burning velocities in "helium air" have been observed in methane combustion by Coward and Jones[4]. As they point out, the lower heat capacity of helium results in a higher flame temperature. This is borne out by the calculated values given in Table III.

The concentrations of H, O, and OH have also been calculated from the thermodynamic data and are included in Table III. It will be noted that the increase in equilibrium H-atom concentration at either pressure on substituting helium for nitrogen roughly parallels the increase in burning velocity. Assuming that the controlling factor is the back-diffusion of H-atoms from the flame front into unburned gas, an approximate solution indicates that the burning velocities should be given by

$$u = A(c_0D)^{1/2}$$

where

A = a coefficient depending on mixture composition;
c_0 = equilibrium H-atom concentration at flame temperature;
D = coefficient of diffusion for H-atoms into unburned gas.

This equation is roughly obeyed (Table IV) when account is taken of the somewhat greater diffusibility into "helium air". The higher flame velocities at lower pressures follow from the increase in diffusion coefficients (greater mean free path).

Table I

BURNING VELOCITIES OF NITROGEN-OXYGEN-BUTADIENE-1,3 AND HELIUM-OXYGEN-BUTADIENE-1,3 AT ATMOSPHERIC PRESSURE

(6.66 mm. I.D. quartz mantled burner)

Oxidant Rate (l/min.)*	C_4H_6-1,3 Rate (l/min.)*	Vol.% C_4H_6-1,3	Flame base diam. (mm.)	Flame height (mm.)	Burning Velocity (cm./sec.)
Helium-oxygen:					
12.9	0.35	2.86	lower limit		
	0.39	3.18	6.80	14.7	126.
	0.47	3.81	6.70	12.8	148.
	0.55	4.02	6.70	12.5	153.
	0.62	4.96	6.70	11.7	163.
	0.72	5.70	6.70	11.8	161.
	0.78	6.16	6.70	12.3	157.
	0.83	6.51	6.70	13.4	146.
	0.91	7.10	6.80	14.8	138.
	0.99	7.79	upper limit		
Nitrogen-oxygen:					
4.00	0.121	2.93	lower limit		
	0.139	3.36	7.6	14.85	37.9
	0.151	3.64	7.4	13.80	41.9
	0.163	3.92	7.2	13.55	43.9
	0.171	4.10	7.2	13.50	44.3
	0.187	4.48	7.4	14.50	40.3
	0.200	4.76	7.6	16.15	35.4
	0.216	5.13	7.8	18.70	29.9
	0.277	5.38	upper limit		

* Rates at 25°, 760 mm. pressure.
Stoichiometric mixture - 3.68 vol.% C_4H_6.

TABLE II. BURNING VELOCITIES OF BUTADIENE-1,3 IN NITROGEN-OXYGEN AND HELIUM-OXYGEN AT REDUCED PRESSURES

(10.55 mm. quartz burner)

Pressure (mm.Hg.)	FLOW RATES* Oxidant	FLOW RATES* C_4H_6-1,3	Volume % C_4H_6-1,3	CONE AREAS (cm^2) (1)	CONE AREAS (cm^2) (2)	CONE AREAS (cm^2) (3)	BURNING VELOCITIES (cm/sec.) (1)	BURNING VELOCITIES (cm/sec.) (2)	BURNING VELOCITIES (cm/sec.) (3)
Helium-Oxygen:									
180	14.0	0.40	2.79	2.09	1.43	1.98	115	168	121
180	14.0	0.61	4.16	1.67	1.49	1.54	146	163	158
180	14.0	0.74	5.04	1.97	1.63	2.02	125	151	122
180	14.0	0.83	5.62	2.67	2.41	2.87	92.3	102	86.1
300	14.0	0.39	2.69	1.72	1.64	1.65	139	146	146
300	14.0	0.47	3.28	1.32	1.48	1.50	183	163	161
300	14.0	0.60	4.09	1.35	1.51	1.44	180	161	169
300	14.0	0.73	4.92	1.97	1.85	1.56	125	133	157
450	14.0	0.36	2.50	1.95	1.89	2.11	123	127	115
450	14.0	0.41	2.85	1.63	1.63	1.68	147	147	142
450	14.0	0.86	5.76	2.12	2.06	2.10	117	120	118
450	14.0	0.96	6.41	3.15	2.92	3.04	79.1	85.4	81.9
Nitrogen-Oxygen:									
300	14.0	0.50	3.43	4.34	4.38	4.11	55.7	55.0	58.8
300	14.0	0.54	3.68	4.31	4.07	4.23	56.2	59.7	57.3
300	14.0	0.66	4.47	5.15	5.06	5.09	47.4	48.3	48.0
450	14.0	0.53	3.63	4.88	4.98	5.04	49.6	48.6	48.2
450	14.0	0.61	4.19	6.79	4.80	4.92		50.8	53.7

See notes on next page.

(Footnotes from Table II)

* All flow rates are given at the pressure indicated in liters per minute.

(1) The height and diameter at the base of the flame determined by cathetometer and the area determined by

$$A = \pi r(r^2 + h^2)^{1/2}$$

(2) Dimensions determined by projection and area calculated as in (1).

(3) Dimensions determined by projection, area calculated by dividing the flame outline into frustums of cones and making a summation of the surface area using 1/2 (sum of the perimeters) (slant height) to determine the area of each frustum.

Table III

CALCULATED RADICAL CONCENTRATIONS FOR BUTADIENE-1,3 FLAMES IN HELIUM-OXYGEN AND NITROGEN-OXYGEN

(Stoichiometric composition: 3.68% butadiene-1,3)

Inert Gas	Total Pressure (atm.)	Burning velocity (expt.) (cm/sec.)	Calculated equilibrium Flame Temperature (°K)	Radical Concentrations (atm.)		
				H	O	OH
N_2	1	43.	2380.	0.00088	0.00086	0.0039
He	1	143.	2660.	0.00430	0.00470	0.0115
N_2	1/2	53.	2350.	0.00057	0.00057	0.00233
He	1/2	179.	2600.	0.00264	0.00273	0.00600

Table IV

COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED BURNING VELOCITY RATIOS

	$\frac{He}{N_2}$ expt.	$\frac{He}{N_2}$ cal.	$\frac{1 \text{ atm.}}{1/2 \text{ atm.}}$ expt.	$\frac{1 \text{ atm.}}{1/2 \text{ atm}}$ cal.
Total pressure, 1 atm.	3.3	3.2	----	------
Total pressure, 1/2 atm.	3.4	3.1	----	------
Inert gas, N_2	---	----	0.81	0.88
Inert gas, He	---	----	0.80	0.90

* * *

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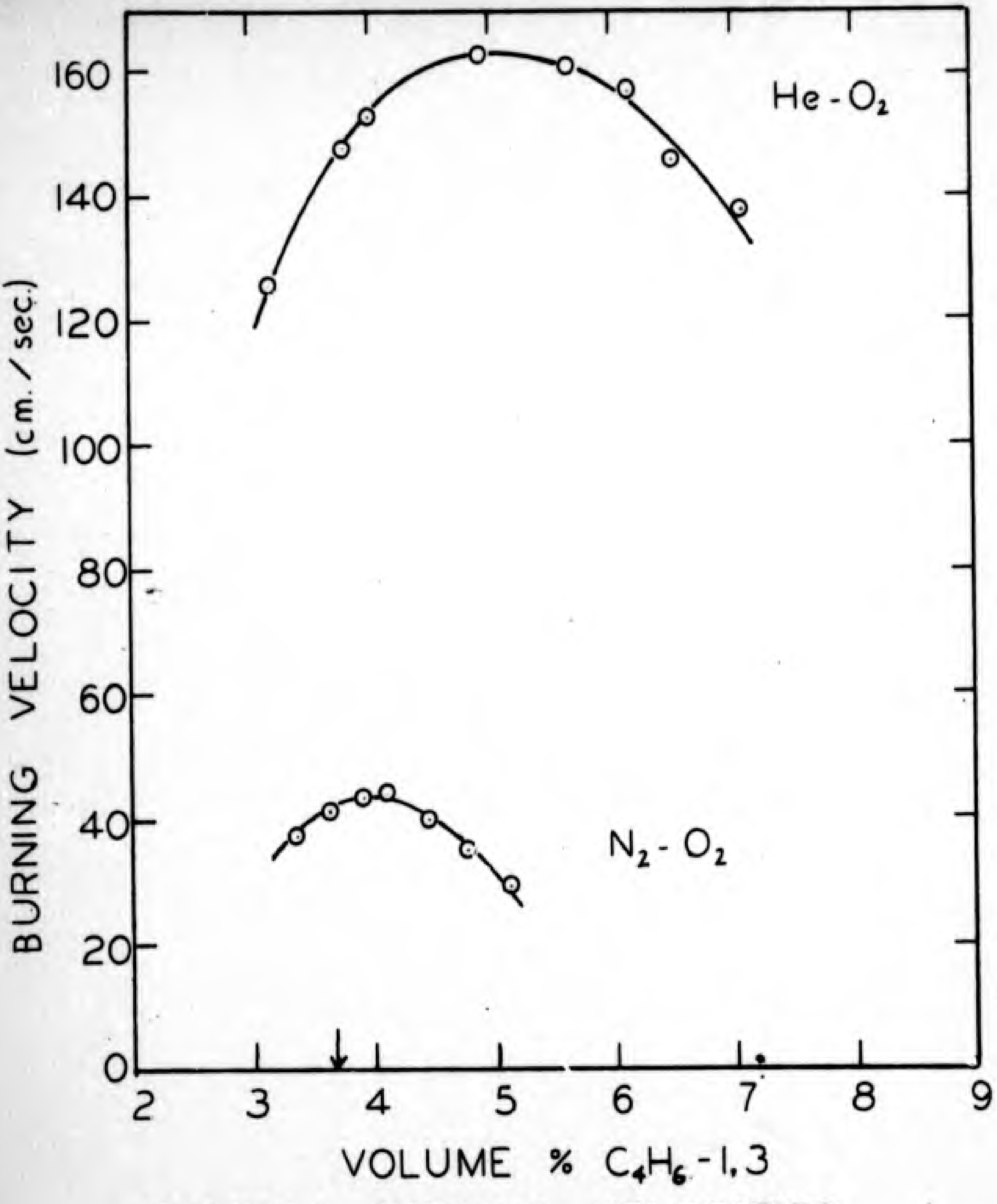

FIGURE I BURNING VELOCITIES OF BUTADIENE - 1,3

(6.66 mm. I.D. quartz mantled burner)

(atmospheric pressure)

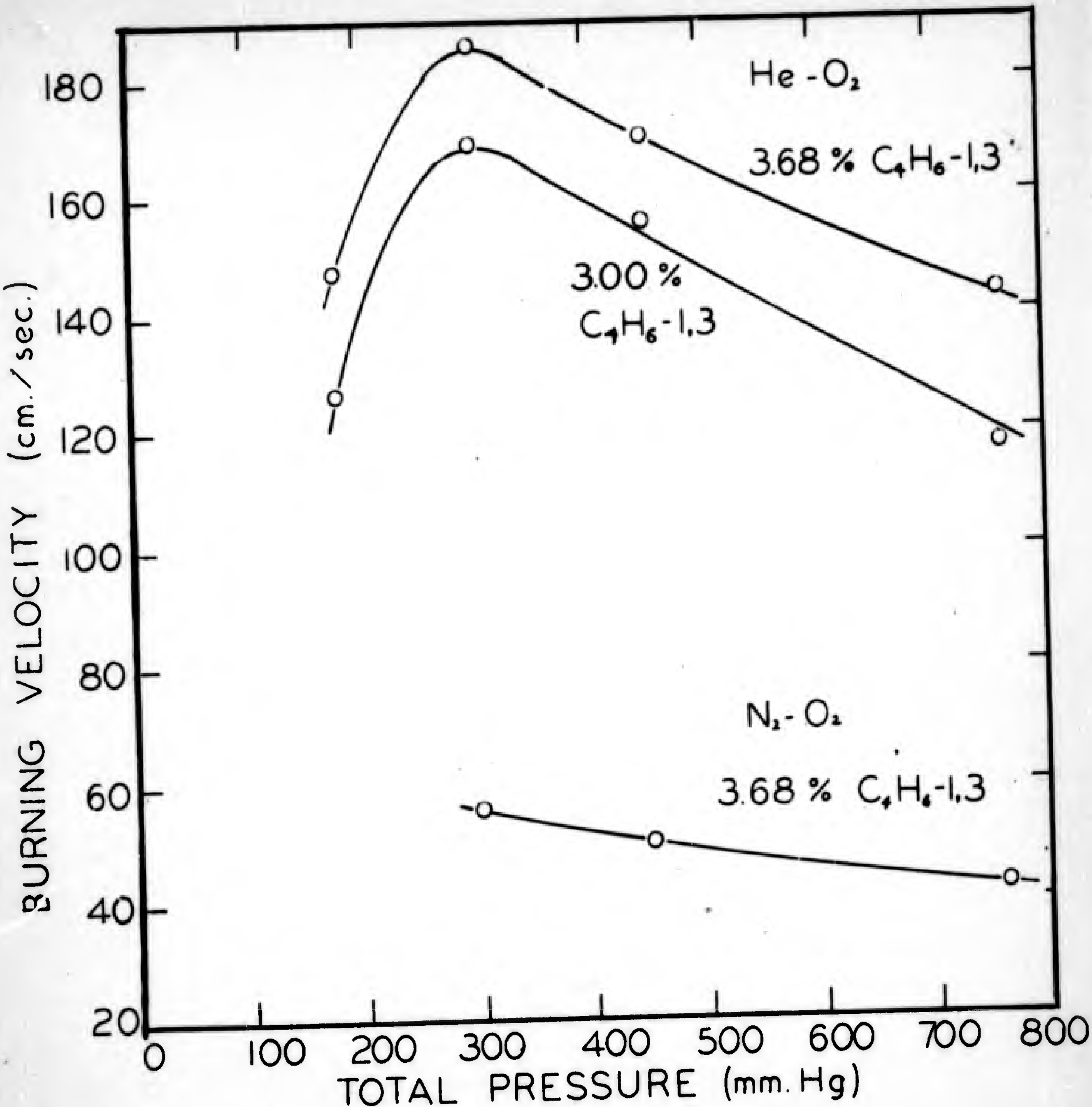

FIGURE 11 VARIATION OF BURNING VELOCITY OF BUTADIENE-1,3 WITH PRESSURE

(cathetometer measurements)

(points at 760 mm., 6.66 mm. burner; other values using 10.55 mm. burner)

IONIZATION FLAME DETECTOR

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Combustion Research

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Technical Paper No. 30

July 1, 1947

SUMMARY

An extremely simple method of detecting ionization in flames utilizing the flame conductivity without the introduction of probes into the flame is described for use in the measurement of flame speeds. The apparatus consists of two pieces of aluminum foil around the outside of a glass combustion tube, a large resistance, and a source of D.C. voltage. The small currents caused to flow in the flame between the exterior aluminum electrodes produces a flow of current through the resistance. The voltage pulse thus created is used to trigger an electronic chronoscope. Two distinct advantages of the method are: (1) its extreme simplicity, and (2) the direct measurement of flame speeds without the introduction of electrodes or screen wires into the combustion tube.

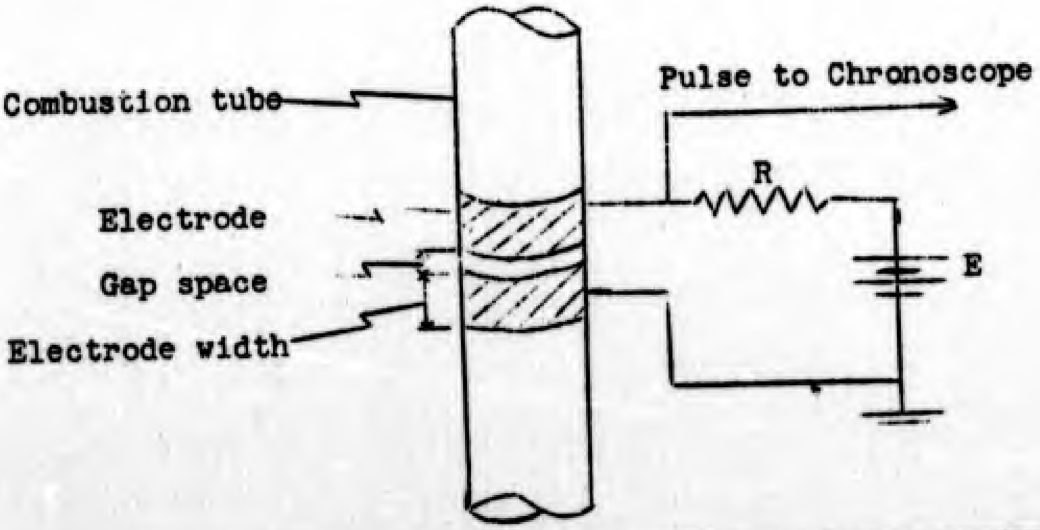
INTRODUCTION

In a recent paper (1) describing the high frequency oscillator as a flame detector the disadvantages of the various electrical methods of flame detection were reviewed and a new method presented which avoided particularly the necessity for introducing probes or other devices into the combustion tube. The method described below has, in addition to this advantage, the advantage of its extreme simplicity. It consists of only two pieces of metal foil, a high resistance, and a source of D.C. potential.

DESCRIPTION OF METHOD

The experimental arrangement used is shown in Fig. I.

Fig. I



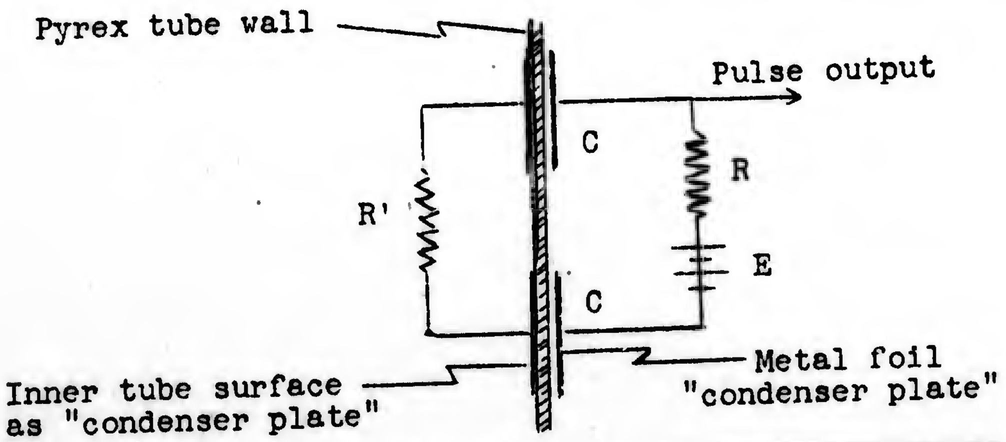
The electrodes were aluminum foil 5/1000 inch thick and 0.7 to 5.6 cm. wide wrapped around the outside of the combustion tube. The resistance R was either 7 or 10 megohms, and the source of D.C. voltage was a variable regulated rectifier power supply. For the measurement of flame speeds two such devices were used to trigger an electronic chronoscope.(2) "on" and then "off".

DESCRIPTION OF CIRCUIT OPERATION

The detector does not act due to a change in the capacity between the electrodes as one might at first assume. An analysis of the circuit shows that a decrease in capacity due to ion formation would produce a positive pulse. The pulse actually obtained is negative as seen on a cathode ray oscilloscope screen and as deduced by its ability to trigger the electronic chronoscope previously described.(2)

This detector may be assumed to operate due to the momentary migration of charged particles (ions and electrons) in the electric field between the electrodes. The equivalent electrical circuit would be as shown in fig. II.

Fig. II



The two condensers are formed by the two metal electrodes and (3) the glass surface inside the tube opposite each electrode. The resistance R' represents the resistance between the two inner glass surface "condenser plates". With no flame in the detector R' will be determined by the surface resistance of the glass and will be very large. The presence of ions in the flame will reduce this resistance when the flame passes through the detector so that a very small current ($\sim 10^{-8}$ amperes) will flow in the circuit producing a voltage drop of the proper sign across R.

OBSERVATION OF OUTPUT PULSE

In order to characterize the new flame detector it was necessary to determine the size of the output voltage pulse. This was done by photographing the pulse on a cathode ray oscilloscope screen and in some cases by visual observation of the pulse on the oscilloscope screen. Since the pulse was taken from across a 10 megohm resistance and the C.R.O. input is only 1 megohm it was necessary to use some type of impedance matching device. For this purpose a cathode follower circuit employing a 6J5 triode was constructed.

The photographs of the transients were obtained with a standard type three inch oscilloscope (Dumont 164-E) and a Leica camera having an f 2.5 lens.* This was accomplished by blocking out the stationary light trace on the oscilloscope

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*The writer wishes to express his appreciation to Mr. R. S. Brokaw for the use of his camera.

screen with a narrow strip of black paper. The camera lens was shielded from light by a blackened glass tube between the C.R.O. screen and the camera, so that operations could be carried out in daylight. The camera lens was opened prior to the transient to be recorded and closed after the phenomena had taken place.

CHARACTERIZATION OF DETECTOR

A few preliminary observations of the effect of varying various parameters on the size and type of pulse obtained from the detector are presented below.

The effect of varying the electrode width and the gap space is shown in table I. The output voltage increases with increasing electrode width and decreases with increasing gap width, possibly going through a maximum.

TABLE I

3.13% n-Butane in Air at 200 mm pressure

E = 700 volts R = 10 megohms

Electrode Width cm.	Gap Space cm.	Peak Pulse Voltage
0.7	0.1	2.0
1.9	0.1	3.8
5.6	0.1	4.5
5.6	0.2	4.8
5.6	0.5	3.3

The effect of the power supply voltage is demonstrated in table II. An increase in power supply voltage causes an increase in the output pulse voltage.

TABLE II

3.13% n-Butane in Air at 200 mm pressure

R = 7 megohms, Electrode width = 1.0 cm., Gap space = 0.1 cm

Voltage Across Detector	350	600	700
Peak Pulse Voltage	0.42	1.4	1.5

A comparison of this flame detector with the high frequency oscillator detector is presented in table III. Although the new detector has the advantage of simplicity, it is less sensitive than the oscillator detector.

TABLE III

R = 10 megohms, E = 700 volts, 3.13% n-Butane in Air

Pressure mm. Hg	Peak Pulse Voltage Oscillator Detector	Peak Pulse Voltage Present Detector
150	9.0	---
200	8.0	4.5
300	8.5	---
500	10.0	4.3

In an oxygen mixture at a considerably lower pressure the output pulse is much larger than in the air mixtures above.

A mixture of 15.5% n-Butane in oxygen at 42 mm of Hg pressure, with the detector described in table II (E = 600 volts), gave a voltage pulse of 18 volts.

The flame speeds in the air mixtures were of the order of 60 cm/sec. and the pulse width at the base approximately 40 milliseconds. The pulses came to a point and were symmetrical. Several times, particularly at higher pressures, two pulses were observed. In the oxygen mixture the flame speed was approximately 9,000 cm./sec. and the electrical disturbance was actually a group of very sharp pulses over a period of approximately 40 milliseconds.

In some cases the flame appeared to show a slight vibration as it passed the new detector. This was never observed with the oscillator detector. Nevertheless, the flame speeds measured by the two methods agree within the experimental error (less than 2%).

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THE REACTION BETWEEN ATOMIC HYDROGEN AND MOLECULAR OXYGEN

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SUMMARY

Atomic hydrogen from a Wood's hydrogen discharge tube has been reacted with molecular oxygen at low temperatures and pressures. With an excess of hydrogen at liquid nitrogen temperature a good yield of hydrogen peroxide was obtained, but at "dry ice" temperature the yield is zero. It is concluded that at the low pressures involved (about 0.2 mms.) the reaction takes place largely on the surface.

INTRODUCTION

The reaction between atomic hydrogen and molecular oxygen has been studied as being of basic interest for combustion mechanisms. Data for this study are contained in this paper with atomic hydrogen produced by electrical discharge.

APPARATUS AND METHOD

The apparatus used is diagrammed in Figure I. The discharge tube G was constructed of 20 mm. O.D. pyrex glass and was coated with phosphoric acid down to point x. Two hollow cylindrical electrodes F and F' (length 20 cm., diameter 27 mm.) made of thin aluminum sheet with sealed in tungsten leads were used for supplying the potential necessary to dissociate the hydrogen. The leads were connected to a transformer which at atmospheric pressure would supply a voltage of ~25,000 volts (frequency 150 sec^{-1}). The total length of the discharge tube was approximately 2.5 meters.

Hydrogen was supplied through throttling stopcocks C and C' from the electrolyzer E. The U-tube electrolyzer was fitted with two platinum electrodes of large area. The electrolysis liquid was a 10% solution of H_3PO_4 and H_2SO_4. By varying the current any desired rate of hydrogen could be obtained. The hydrogen was introduced without drying.

Oxygen was introduced through a flowmeter system consisting of a variable-head water column N, flowmeter M and static manometer L. By varying the height of the water column a constant flow of oxygen could be obtained. The flowmeter M was of the capillary type calibrated by mercury displacement for the range 0 to 40 cc./min. at S.T.P. Oxygen was passed into the apparatus through stopcocks D and D' which were throttled down so as to maintain a zero reading on the static manometer L. Water was used as the liquid in both manometer L and flowmeter M.

In carrying out an experiment the entire apparatus was evacuated to 10^{-4} or 10^{-5} mm. (McLeod gauge 2). Hydrogen was then introduced by opening C and C' sufficient to maintain the liquid level in E constant. From the quantity of electricity used the amount of hydrogen could be calculated. The partial pressure of H_2 was read on McLeod gauge 1 (calibrated for the range 0-1.00 mm.). Oxygen was then introduced by opening D and D' and the total pressure read. The reaction tube A and trap B were then immersed in baths of the required temperature and the discharge turned on. At the end of an experiment trap A was disconnected, 25 ml. of 2% sulfuric acid added and the peroxide formed titrated with standardized N/10 potassium permanganate. In each case a sharp end point was obtained. The amount of peroxide adherring to the tubes X was washed off and also titrated. The major portion of peroxide formed was condensed on the walls of trap A. On warming to room temperature it appeared in the form of slightly viscous droplets. In determining the amount of water produced the trap was first weighed and then titrated; water was determined by difference.

The concentric reaction tubes leading into trap A were made of 17.5 mm. O.D. and 8.0 mm. O.D. tubing respectively. Traps A and B were connected by about 80 cm. of untreated 17 mm. O.D. pyrex tubing.

A helium-oxygen mixture containing 23% oxygen (quantitative absorption in Oxsorbent) was obtained from the American Oxygen Co. Calibration of flow rates for the helium-oxygen mixture was carried out as for oxygen.

RESULTS AND DISCUSSION

Data are contained in Table I for peroxide and water formation from the reaction of atomic hydrogen with oxygen at various temperatures.

TABLE I

VARIATION OF H_2O_2 AND H_2O PRODUCED WITH TEMPERATURE

Time, 1200 sec. Total pressure 0.27 mm.
H_2 - 20.9 cc./min. STP pressure 0.24 mm.
O_2 - 2.55 cc./min. STP

Trap A (main reaction trap)					Trap B (80 cm. from A.)				
Temp. °C.	H_2O_2 formed		H_2O formed		Temp. °C.	H_2O_2 formed		H_2O formed	
	millimoles	per cent*	millimoles	per cent*		millimoles	per cent*	millimoles	per cen
20	0	0	0	0	-196	0	0	0.18	4
-79	0	0	1.06	23	-196	0	0	0	0
-196	0.765	33.5	0.82	18	-196	0	0	0	0

* % yield on basis of oxygen introduced.

Table I shows the following:

(a) When atomic hydrogen and oxygen react at 20° and the products are condensed at -196° no peroxide and a small amount of water only are formed.

(b) At -79° reaction temperature no peroxide is formed but an appreciable amount of water results.

(c) At -196° reaction temperature most of the oxygen is converted to peroxide. Some water is also formed.

If the initial step for peroxide formation were

$$H + O_2 \rightarrow HO_2 \qquad (1)$$

occurring in the gas phase, one would expect formation of H_2O_2 even at -79° or higher. Since this does not occur, reaction (1) is apparently not involved. Geib and Harteck[1] have previously shown that the amount of peroxide formed gradually decreases to zero at -80° as the temperature is raised. Geib[2] has proposed the mechanism

$$W + H \rightleftharpoons WH \qquad (2)$$

$$(WH + H \rightleftharpoons W + H_2) \qquad (2')$$

$$WH + O_2 \longrightarrow Who_2 \qquad (3)$$

$$WHO_2 + H \longrightarrow W + H_2O_2 \qquad (4)$$

with the assumption that the activation energy for H_2O_2 formation is about zero.

Analogous results have been reported by Rodebush, Keizer, McKee and Quagliano [3] for the products of a discharge in water vapor. However, the results differ in that an appreciable amount of water is formed at -79° in the experiments here. Both Geib [2] and Rodebush, Keizer, McKee and Quagliano [3] conclude that the reactions are heterogeneous. For water formation Geib [2] has proposed a homogeneous three body collision mechanism:

$$H + O_2 + H_2 \dashrightarrow H_2O + OH \qquad (5)$$

$$H + O_2 + M \longrightarrow HO_2 + M \qquad (6)$$

$$HO_2 + H_2 \longrightarrow H_2O + OH \qquad (7)$$

Since some water is formed at the higher temperatures this would seem to apply.

TABLE II: REACTION OF ATOMIC HYDROGEN WITH MOLECULAR OXYGEN (Reaction temp., -196° C.)

Time (sec.)	Hydrogen introduced			Oxygen introduced		Total press. (mm.)	Ratio (milli-moles)	H_2O_2 formed		
	cc/min. STP	milli-moles	Partial press. (mm.)	cc/min. STP	milli-moles		O_2:H_2 introduced	milli-moles	%[1] yield	Average rate (milli-moles/sec)
Variation of O_2:H_2 ratio:										
1200	20.9	18.7	0.24	0	0	0.24	0	0.057	---	0.05×10^{-3}
1200	20.9	18.7	0.24	1.00	0.89	0.24	0.848	0.048	95.2	0.71×10^{-3}
1200	20.9	18.7	0.24	1.30	1.16	0.25	0.062	0.763	66.1	0.64×10^{-3}
1200	20.9	18.7	0.24	2.55	2.28	0.27	0.122	0.765	33.5	0.64×10^{-3}
1200	20.9	18.7	0.24	5.81	5.18	0.33	0.279	0.920	17.8	0.77×10^{-3}
1200	20.9	18.7	0.24	11.7	10.4	0.39	0.562	0.473	4.6	0.39×10^{-3}
1200	20.9	18.7	0.24	20.9	18.7	0.55	1.00	0.189	1.0	0.16×10^{-3}
Variation of reaction time:										
300	20.9	4.67	0.24	2.55	0.57	0.27	0.122	0.208	36.5	0.69×10^{-3}
600	20.9	9.35	0.24	2.55	1.14	0.27	0.122	0.393	34.5	0.65×10^{-3}
1200	20.9	18.7	0.24	2.55	2.28	0.27	0.122	0.765	33.5	0.64×10^{-3}
1800	20.9	28.1	0.24	2.55	3.42	0.27	0.122	1.14	33.3	0.63×10^{-3}
2400	20.9	37.4	0.24	2.55	4.55	0.27	0.122	1.52	33.4	0.63×10^{-3}
Variation of H_2 rate:										
1200	10.4	9.3	0.14	2.55	2.28	0.18	0.245	0.535	23.5	0.45×10^{-3}
1200	13.9	12.4	0.17	2.55	2.28	0.21	0.184	0.640	28.1	0.53×10^{-3}
1200	20.9	18.7	0.24	2.55	2.28	0.27	0.122	0.765	33.5	0.64×10^{-3}
1200	27.9	24.9	0.30	2.55	2.28	0.32	0.092	0.785	34.4	0.65×10^{-3}

(1) Yield calculated on basis of oxygen introduced.

In the first set of data in Table II and in Figure II conversions to H_2O_2 of amounts from 1.0 to 95.2 percent of the oxygen introduced are shown. The presence of an increased amount of oxygen in the gas phase leads to greatly reduced peroxide formation.

The greatly decreased yield with additional oxygen is probably due to deactivation of hydrogen atoms by recombination in the vapor phase.

$$H + H + O_2 \qquad H_2 + O_2, \ (E_a = 0) \tag{8}$$

With excess oxygen this can occur to a much greater extent, leading to a decrease in the H-atom concentration. In addition, back-diffusion of the oxygen would also lead to a smaller H-atom concentration at the point of mixing of the gases. In the first four experiments of Table II the rate of formation of H_2O_2 remains substantially constant at 0.64 - 0.77 millimoles per second for a wide range of oxygen concentration, indicating that, in this region, the rate of peroxide formation is independent of the oxygen concentration. With a further increase in the amount of oxygen the rates and yields drop greatly, indicating that some reaction such as (5) occurs. The amount of H_2O_2 formed was practically linear with time as shown in Figure III, although there was a slight decrease in both rate and yield (Table II) as the time increased.

Data in Table III show that peroxide formation is accompanied with water formation.

TABLE III

WATER AND PEROXIDE FORMATION

(Time, 1800 sec.; Reaction temperature, -196 °C.; H_2 - 20.9 cc./min. STP, partial pressure 0.24 mm.)

Total press. (mm.)	Oxygen introduced		Ratio millimoles $O_2:H_2$ introduced	H_2O_2 formed		H_2O formed	
	cc./min. STP	millimoles		millimoles	%[1]	millimoles[2]	%[1]
0.24	1.00	1.34	0.048	1.08	81.	0.67	~20.
0.27	2.55	3.41	0.122	1.13	33.	1.22	18.
0.39	11.7	15.7	0.562	0.604	3.9	0.61	1.9
0.55	20.9	28.1	1.00	0.189	0.7	0.70	1.2

(1) Yield calculated on basis of oxygen introduced.
(2) Accuracy ± 0.15 millimoles.

In no case, except at very low ratios of $O_2:H_2$ introduced, is all the oxygen accounted for indicating considerable escape of unchanged molecular oxygen.

A set of experiments has been carried out in which a portion of the oxygen introduced has been replaced by an inert non-condensible gas, helium. These results are collected in Table IV.

TABLE IV

EFFECT OF HELIUM ON H_2O_2 FORMATION

(Reaction temperature -196°C.)
(H_2 - 20.9 cc./min. STP, partial press. 0.24 mm.
Time - 1200 sec.)

Oxidant cc/min. STP	millimoles O_2	He	Total press. (mm.)	Ratio moles $O_2:H_2$ introduced	H_2O_2 formed milli-moles	%[1] yield	Average rate millimoles/sec. x 10^4
2.55	2.28	0	0.27	0.12	0.765	33.5	6.4
2.55	0.52	1.76	0.27	0.028	0.485	92.5	4.0
5.81	5.18	0	0.33	0.28	0.920	17.8	7.7
5.81	1.19	3.99	0.33	0.072	0.905	76.1	7.5
11.7	10.4	0	0.39	0.56	0.473	4.6	3.9
11.7	2.40	8.05	0.39	0.13	0.560	23.3	4.7
20.9	18.7	0	0.55	1.00	0.189	1.0	1.6
20.9	4.30	14.4	0.55	0.23	0.204	4.8	1.7

Excluding the first set of data in which practically all the oxygen present in the helium mixture has been consumed, it is seen that for each of the other cases the rate of peroxide formation is substantially constant but that in each case, with helium present, the percentage of peroxide calculated on the basis of oxygen is on the average 4.7 times as great. Substitution of helium for oxygen thus allows a greater relative concentration of oxygen to react.

The explanation for this is probably that substitution of a portion of the oxygen by helium minimizes reaction (8) so that

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(1) Yield calculated on basis of oxygen introduced.

a greater concentration of H-atoms can react. The greatly increased ability of H-atoms to diffuse through helium would also tend to account for the observed results.

It can not be decided with certainty whether the mechanism of the reaction is as outlined in steps (2), (2'), (3) and (4). However, peroxide formation by a heterogeneous reaction probably does occur. This does not immediately seem reconcilable with results obtained in the mercury sensitized-photochemical reaction. For this homogeneous reaction the mechanism proposed by Taylor and Marshall[4]

$$H + O_2 \longrightarrow HO_2$$

$$HO_2 + H_2 \longrightarrow H_2O_2 + H$$

$$H + H \longrightarrow H_2$$

has been shown to apply. However, no necessary discrepancy need exist. The hydrogen atom concentrations in experiments using the discharge as source are much higher*, hence recombination in the gas phase is favored. Also, the pressures are much lower favoring the wall as a third body, except with an increase in the oxygen concentration.

SUMMARY

(1) A study of the reaction between atomic hydrogen and oxygen has been carried out. Conversions of oxygen to hydrogen peroxide of from 1 to 95 percent, depending on the $O_2:H_2$ ratio, introduced have been obtained.

(2) The formation of hydrogen peroxide has been shown to be essentially linear with time with a slight decrease in yield and rate as the reaction progresses.

(3) Addition of helium increases the amount of oxygen converted to peroxide while maintaining the same rate of formation; the reaction, thus, is independent of the oxygen pressure.

(4) The reaction between hydrogen atoms produced by electrical discharge and molecular oxygen to form hydrogen peroxide is a heterogeneous one.

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*The H-atom concentration was unknown in these experiments. If one makes the rather improbable assumption,as pointed out by Bonhoeffer and Boehm[5],that all hydrogen found in the H_2O and H_2O_2 existed as atomic hydrogen,the concentration would be of the order of 8 percent of the total hydrogen pressure. In the mercury sensitized photochemical reaction this is of the order of $<<$ 8 percent.

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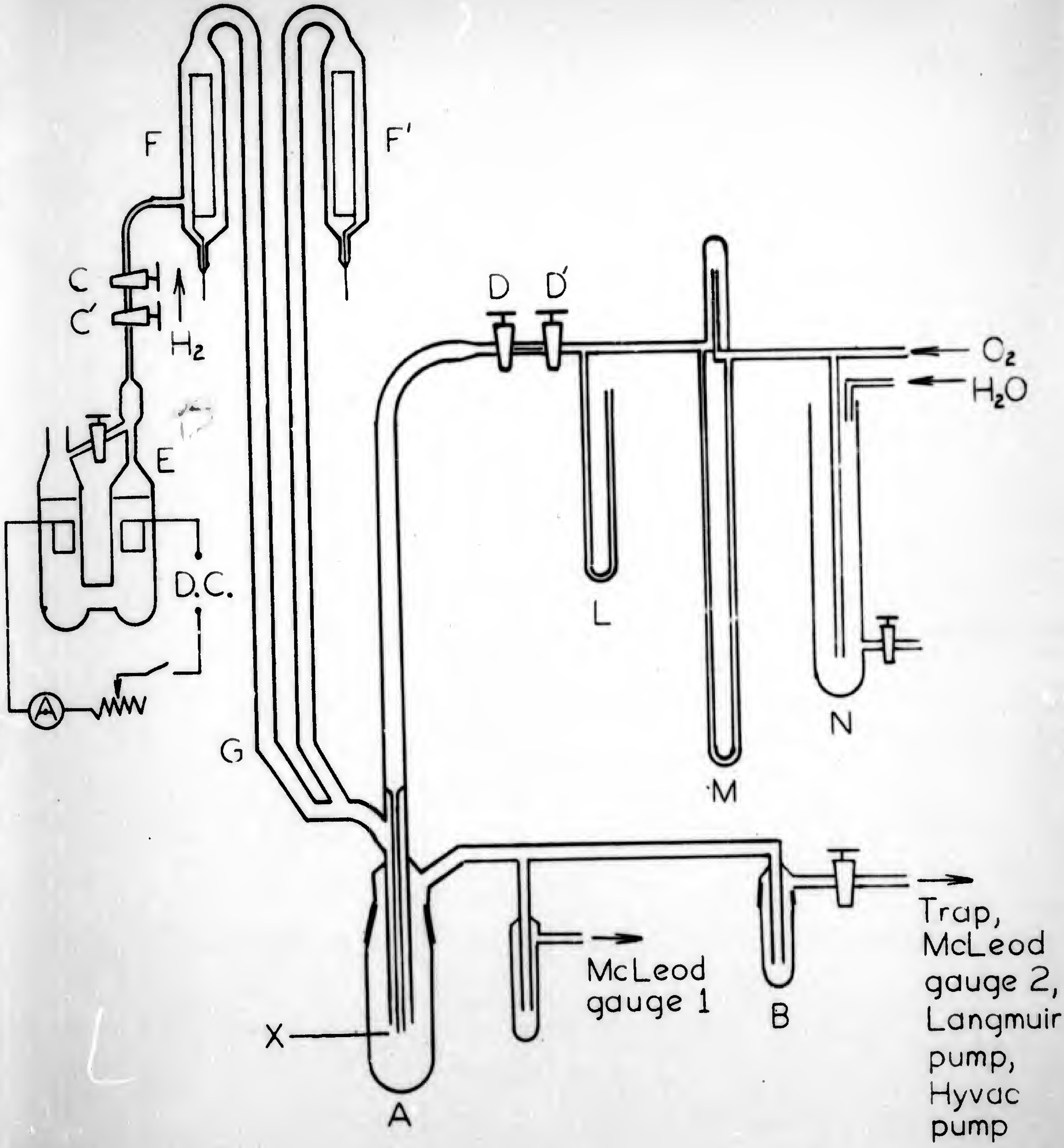

FIGURE I APPARATUS

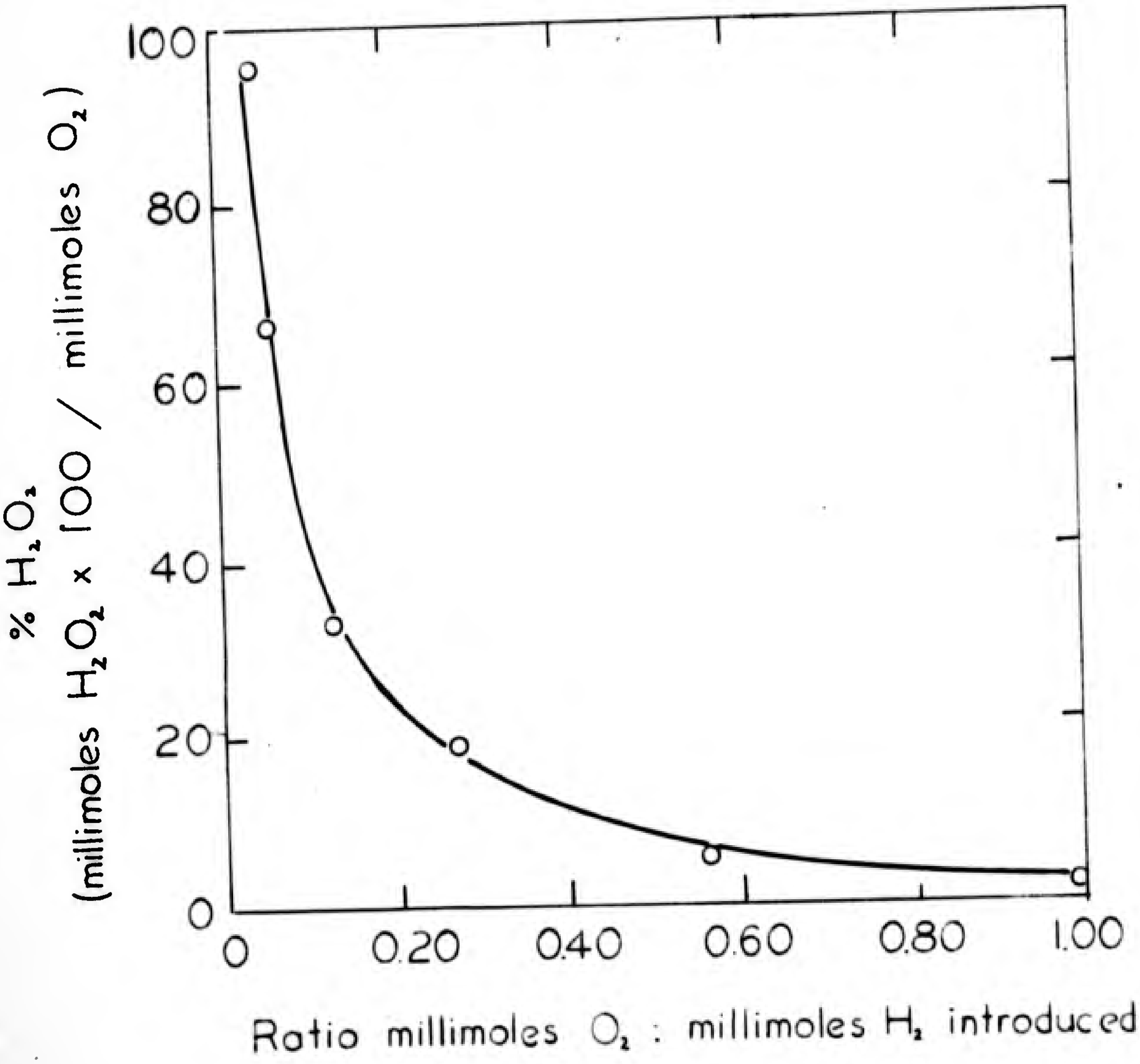

FIGURE II REACTION OF ATOMIC HYDROGEN WITH MOLECULAR OXYGEN. VARIATION OF H_2O_2 YIELD WITH REACTANT COMPOSITION
(Partial pressure H_2 0.24 mm., 20.9 c.c./min. H_2 at S. T. P., TEMPERATURE -196°C)

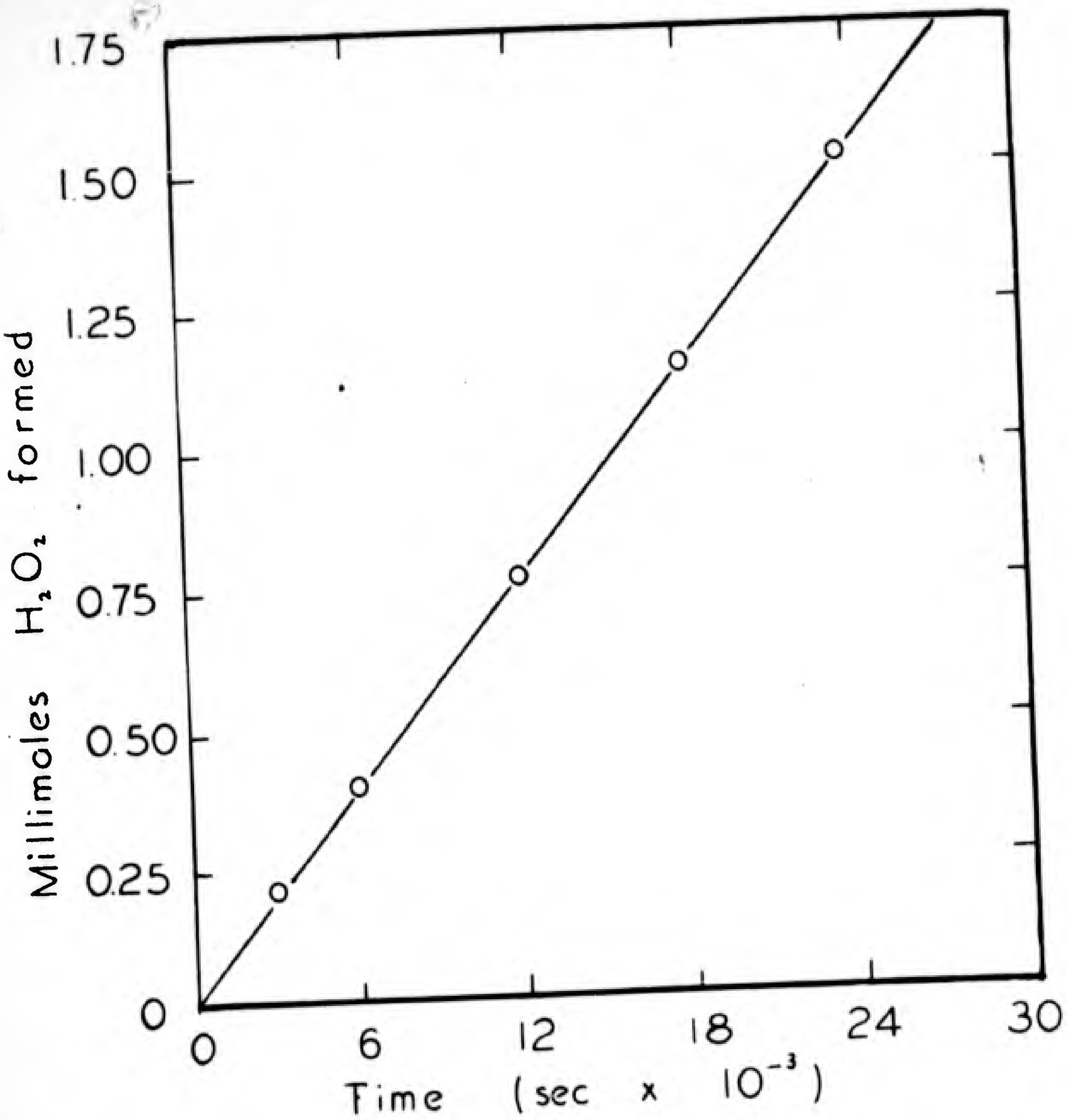

FIGURE III FORMATION OF H_2O_2 FROM ATOMIC HYDROGEN AND OXYGEN (partial pressure H_2, 0.24 mm.; temperature, -196 °C)