for information and record
purposes, is not to be referenced
in any publication.

NATIONAL BUREAU OF STANDARDS REPORT

6588

INHIBITION OF FLAME REACTIONS:

A PRELIMINARY INVESTIGATION OF THE ROLE OF IONS AND ELECTRONS

by

E. C. Creitz

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

AUTHENTICATED
U.S. GOVERNMENT
INFORMATION
GPO

THE NATIONAL BUREAU OF STANDARDS

Functions and Activities

The functions of the National Bureau of Standards are set forth in the Act of Congress, March 3, 1901, as amended by Congress in Public Law 619, 1950. These include the development and maintenance of the national standards of measurement and the provision of means and methods for making measurements consistent with these standards; the determination of physical constants and properties of materials; the development of methods and instruments for testing materials, devices, and structures; advisory services to government agencies on scientific and technical problems; invention and development of devices to serve special needs of the Government; and the development of standard practices, codes, and specifications. The work includes basic and applied research, development, engineering, instrumentation, testing, evaluation, calibration services, and various consultation and information services. Research projects are also performed for other government agencies when the work relates to and supplements the basic program of the Bureau or when the Bureau's unique competence is required. The scope of activities is suggested by the listing of divisions and sections on the inside of the back cover.

Publications

The results of the Bureau's work take the form of either actual equipment and devices or published papers. These papers appear either in the Bureau's own series of publications or in the journals of professional and scientific societies. The Bureau itself publishes three periodicals available from the Government Printing Office: The Journal of Research, published in four separate sections, presents complete scientific and technical papers; the Technical News Bulletin presents summary and preliminary reports on work in progress; and Basic Radio Propagation Predictions provides data for determining the best frequencies to use for radio communications throughout the world. There are also five series of nonperiodical publications: Monographs, Applied Mathematics Series, Handbooks, Miscellaneous Publications, and Technical Notes.

Information on the Bureau's publications can be found in NBS Circular 460, Publications of the National Bureau of Standards ($1.25) and its Supplement ($1.50), available from the Superintendent of Documents, Government Printing Office, Washington 25, D.C.

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT		NBS REPORT
1002-11-10121	November 4, 1959	6588

INHIBITION OF FLAME REACTIONS:
A PRELIMINARY INVESTIGATION OF THE ROLE OF IONS AND ELECTRONS

by

E. C. Creitz

IMPORTANT NOTICE

NATIONAL BUREAU OF ST
Intended for use within the
to additional evaluation and
listing of this Report, either
the Office of the Director, N
however, by the Government
to reproduce additional copi

Approved for public release by the Director of the National Institute of Standards and Technology (NIST) on October 9, 2015.

rogress accounting documents
rmally published it is subjected
reproduction, or open-literature
sion is obtained in writing from
Such permission is not needed,
prepared if that agency wishes



U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

INHIBITION OF FLAME REACTIONS:

A PRELIMINARY INVESTIGSTION OF THE ROLE OF IONS AND ELECTRONS

E. C. Creitz

ABSTRACT

It is proposed that activation of oxygen molecules in flames proceeds by capture of electrons to form O_2^- ions and that inhibition may be accomplished by capture of electrons by substances other than oxygen molecules. The proposal is supported by evidence that the efficiency of an inhibitor is related to the cross section for capture of electrons of the inhibitor, that its efficiency is related to the oxygen concentration and is relatively independent of the nature of the (hydrocarbon) fuel, and, in the case of dry powder extinguishing agents, it is related to the ability to capture ions or electrons.

Experimental results are presented which indicate that both the average lifetimes of ions and their steady-state concentrations in uninhibited flames depend on the initial oxygen concentration.

---

1. INTRODUCTION

The modern physical concept of a gas involves particles of molecular dimensions and smaller, which are free to move in a random manner. Flame gases are in no way an exception to this concept. Gaseous particulate matter present in flames may be classified as electrically neutral, i.e., molecules or free radicals, or electrically charged, as ions and electrons.

Flame reactions must, of necessity, involve interactions between only these kinds of particles. In general, molecules serve only as sources of molecular fragments which possess characteristics of instability, under flame conditions, permitting them to react, chemically, one with another. Reactions between free radicals are probable in flames because free radicals need very little additional activation energy to prepare them for reaction. Free radicals are known to be present in flames.[1]* Reactions between ions bearing charges of opposite sign are even more probable. The presence of the charges is responsible for large, long-range forces and large effective collision diameters. These effects result in a probability for reaction between ions of opposite charge that may be several orders of magnitude larger than that for reactions between free radicals of the same concentration.

The work reported here is an attempt to deduce whether the inhibition of hydrocarbon flame reactions is through interference with free radical or ionic flame processes and to suggest a mechanism of inhibition based on the results of several experimental approaches.

2. The Mechanism in Normal Flames

Rosser, Inami and Wise [2] have observed that neither CH_3Br or CF_3Br inhibit the methane-nitrogen dioxide flame. The same is true of the CH_4-NO flame. There are two important consequences of these observations. The usually advanced theory that inhibition takes place through interference with H, OH and HO_2 chains [2,3] cannot be applicable in this case even though all of the chain-forming elements are presumably present. The equation given by Rosser et al. for the overall reaction between NO_2 and methane is:

$$CH_4 + 3\ NO_2 \longrightarrow CO + 2H_2O + 3NO$$

It should be noted that the decomposition of NO_2 is not complete, having stopped after the liberation of one oxygen atom per molecule. The freed oxygen atom, whether neutral or ionic, is thermodynamically very active, and one may infer, that since no inhibition is produced by CH_3Br or CF_3Br, inhibition is, in some way, related to the activation of oxygen atoms or molecules.

* Numbers in brackets refer to "References" at the end of the report.

The fact that interruption of hydrogen chain reactions is not important in the CH_4- NO_2 flame, casts some doubt on the applicability to hydrocarbon flames in general. This doubt is strengthened by the lack of any correlation between the hydrogen content of the fuel molecule and the efficiency of the inhibiting agent. For these reasons it seemed reasonable to study further the process of activation of oxygen in normal and inhibited flames.

Of the possible processes for the activation of oxygen, the most likely appears to be the capture of one electron per molecule to form the O_2^- ion. The ease with which this process takes place was demonstrated by Crain [4] who filled a microwave cavity resonator with various gases, subjected it to gamma radiations from an atomic reactor and from cobalt-60. By measurements of the resonant frequency he was able to calculate the concentration of electrons produced by ionization of the gases. Nitrogen and argon gave electron concentrations in order of $10^7/cm^3$. When air was used in the cavity, he was unable to detect any evidence of electrons even at radiation levels as high as 8×10^{11} gammas/cm^2. He attributed lack of electrons, when oxygen was present, to the capture by oxygen molecules.

Burch, Smith and Branscomb [5] have determined the energy required to detach an electron from the O_2^- ion as having a threshold of 0.15 ± 0.05 electron volts. The collision cross section at this electron energy is quite small, but increases gradually, reaching a maximum somewhat above 3 electron volts where the curve was stopped. Chanin, Phelps and Biondi [6] have extended the studies of attachment cross section to near thermal energies (0.04 ev) and have shown that it consists of two separate processes, two-body and three-body, having appreciable cross sections at this low value of electron energy. Thus, on the basis of energy and collision cross section, oxygen molecules are able to capture, with varying probabilities, electrons of almost any energy which may be encountered in flames. The electron affinity of the O_2^- ion determines whether it can retain its extra electron under flame conditions. For atoms, the electron affinity, radiative attachment coefficient, and photodetachment threshhold are identical. For molecules these three energy differences are usually not the same. Branscomb [7] gives a value of 0.9 electron volt for the electron affinity of O_2, derived from thermochemical data, as probably the most reliable value. Branscomb and Smith [8] give a value of 1.45 ± 0.15 electron volts for the photodetachment threshold of $O^-$and, since the atomic form is involved,

this is also the electron affinity. In the case of molecular oxygen, the energy acquired in the capture of an electron is either redistributed or lost, resulting in a more stable configuration which requires additional energy for removal of the electron over that acquired in the capture process.

With an electron affinity of 1.45 volts, it would appear that there is a small, but finite probability of a neutral oxygen atom capturing an electron in a flame to become an O^- ion. It seems more likely that NO_2 would be able to capture an electron and, in the process of redistribution of energy, liberate O^-. Fox [9] gives a value of 1.35 ± 0.05 ev for the onset of capture of electrons for NO_2 with a maximum cross section at 1.45 ev at room temperature. There seems to be no information available which would permit the estimation of the electron energy corresponding to the maximum at flame temperatures, but one would estimate that it might be less than at room temperature because of the instability of the molecule.

The above properties of oxygen along with Rosser's observations on the NO_2-CH_4 flame imply that the mechanism of normal flame propagation is, in part, the formation, from the fuel, of positive ions and electrons, followed by the capture of the electrons by oxygen molecules to form O_2^- ions, which, in turn, is followed by reactions between the positive and negative ions. It is probable that the first products of the ionic reactions will be unstable at flame temperatures and may decompose to give positive ions and electrons or O^- atoms which continue the reactions until stable products are formed. It is of interest to see how some known facts of hydrocarbon flame propagation substantiate this mechanism.

3. The Rate Controlling Process

If one assumes that the combination of positive and negative ions is rapid, the rate of ionic reactions in flames would appear to be controlled by one of two processes: the rate of production of electrons (and positive ions) or the rate of activation of O_2 molecules. Calculation of the maximum rate in terms of the activation of oxygen molecules is not consistent with the known facts with respect to flame velocity. The detonation velocity studies of Breton [10] show that the maximum reaction rate between propane and oxygen is attained at about 30% propane and 70% oxygen, which is considerably above the stoichiometric 16.7% propane. The continuous increase in reaction rate with fuel concentration suggests that below the limiting value of 30% fuel, the rate controlling factor is the rate of fuel supply.

Flame velocities for fuels in air are also known to increase as a function of the rate of fuel addition until some other effect becomes limiting. The results given in Table 1 show that the rate of reaction in lean flames at a constant rate of fuel supply is independent of the rate of oxygen supplied to the flame. An Egerton-Powling burner [11] was supplied with propane at very nearly the same rate for each determination shown in the table, while the oxygen and nitrogen were proportioned to give various concentrations of oxygen, all at very nearly the same total mixture velocity. Measurement of the flame velocity with this type of burner involves a measurement of the flame area, which was not done in this experiment. However, there was little apparent change in flame area with change in oxygen concentration so that the mixture velocity is, for practical purposes, equivalent to flame velocity. Column 4, therefore seems to show that the reaction rate is very nearly constant at a constant fuel supply rate, and is independent of oxygen concentration. One explanation of this might be that the decomposition of the fuel into positive ions and electrons is the rate-limiting reaction.

4. The Lifetime of Positive Ions as a Function of Oxygen Concentration

Deflection of a flame by a high potential electrostatic field is in such a direction that the flame follows the movement of the positive ions. At the instant of formation of the ion, the direction of the motion of the freed electron, with respect to the field, is completely random (unless the molecule, under the influence of the field, forms a dipole of sufficient strength to cause orientation prior to dissociation). A certain fraction of the electrons will have a component in the direction of the movement of the positive ions already present, immediately after being freed. After a time, depending on the field strength and its initial energy, such an electron will acquire a net motion opposite to that of the positive ions. In weak or moderate fields, this will take place only after the electron has made a number of collisions with molecules. If some of them are oxygen molecules, there is a good probability that the electrons will be absorbed to form oxygen ions. If the distance between O_2^- and the positive ions is not too great and the external field is not larger than that between the ions they will eventually react. If the applied field is so great that the electrons and positive ions are carried in opposite directions with sufficient energy, the flame will be extinguished [12]. Statistically, the net distance of

travel in the external field by a positive ion is determined by the field strength and the time it exists as an ion, i.e., the time interval between its formation and its destruction by reaction. On the average, this time is that required for an oxygen molecule to capture an electron, form a negative ion and make a reactive collision with a positive ion. For a given rate of positive ion production, the overall time interval should be reduced by any process which increases the number of oxygen ions. The proposed activation mechanism relates the ionic and molecular oxygen concentrations with the result that the amount of deflection of a flame should be inversely related to the oxygen concentration, provided the fuel concentration is held constant. Table 2 shows the results of measurements of this relationship.

These data were obtained with an Egerton-Powling burner with a 15-mesh screen over the recessed section of the burner to provide a reasonably flat lower, negative electrode. The heat-radiating upper screen was used as the positive electrode and was adjusted so that the flat flame assumed a position 1 cm above the lower electrode when no voltage was applied. It was assumed, that because of the conductivity of the flame gases, the reaction zone of the flame is effectively the positive electrode. This is probably an acceptable assumption because the concentration of ions and electrons down-stream from the reaction zone is several orders of magnitude larger than it is up-stream in the unburned gases, so that the voltage drop is almost entirely across the space between the reaction zone and the lower screen. A constant potential of 500 volts was applied and the deflection measured by sighting across a scale attached to the outer side of the burner jacket. The displacement given in Table 2 for the lowest oxygen concentration is marked with "+" because portions of the flame were deflected downward to a definite flat surface 2.5 mm above the lower screen. This seems to correspond to a quenching distance and it is not known how much farther the flame would have been deflected in the absence of this effect. The movement of the reaction zone under the influence of the electric field changes the effective electrode spacing and, therefore the potential gradient, at constant applied potential. The fact that the potential gradient does not increase without limit is an indication of strong forces connected with the positioning of the flame in the burner.

In addition to clarifying somewhat the mechanism of deflection of flames in electrostatic fields, these results give further evidence that the rate of reaction in lean flames is controlled by the rate of formation of positive ions and electrons from the fuel, and give a qualitative explanation of the statement by Knewstubb and Sugden /13/ that ionization persists longer in rich than in lean flames.

5. The Relationship Between Electron and Oxygen Concentration

The presence of large concentrations of electrons and positive ions and low concentrations of negative atomic and molecular ions in normal flames [14] indicates that negative ions react as rapidly as they are formed. Since the rate of capture of electrons by oxygen molecules is proportional to the number of collisions occurring between the respective species, it is also proportional to their concentrations. In lean flames the rate of supply of electrons appears to be fixed by the rate of fuel supply as shown in Section 3, so that electron concentration should change as the oxygen concentration is varied. This is shown in Figure 1, which is a plot of some of the results shown in Table 1. These data were obtained on propane, supplied at very nearly the same rate for each determination, to an Egerton-Powling burner, equipped with a Langmuir probe [15] mounted axially thru the burner and extending into the reaction zone through the unburned fuel-air mixture. The heat-reflecting screen above the free-floating flame was used as the second electrode.

With this method one may obtain ion concentrations and, on the basis that the flame is a plasma, being neutral in the macroscopic sense, one may infer electron concentration is zero, or at least low [14]. The ordinate of Figure 1 is thus approximately equal to the electron, as well as the positive ion concentration. The disappearance of electrons as a linear function of oxygen concentration seems to provide direct evidence of the electron attachment process.

6. The Relationship Between Electron and Inhibitor

Conductivities of flames, measured with Langmuir probes, give ambiguous information on electron concentrations when negative ions are present. This is because there is no way of determining what fraction of the negative charges is carried by ions and what fraction is carried by electrons. When methyl bromide was added to a flame burning in the Egerton-Powling burner, even in very small quantities, the conductivity increased inordinately. There are two possible explanations of this effect. Since the flame was not perfectly stable, it was necessary to extend the probe a short distance beyond the reaction zone into the burned gases. It is probable that bromide ions formed in the reaction zone were carried into

the area above it where the concentration of negative charge carriers is normally low. This would have the effect of increasing the probe area. However, the increase in area seemed too small to account completely for the magnitude of the effect. It seems more likely that bromine ions are formed by electron attachment, but unlike oxygen ions, are unable to react with positive ions until the cooler parts of the flame are reached, persisting for longer times so that the total concentration of carriers of negative charges is increased. Because of their high electron affinity, halogen ions cannot readily take part in charge exchange reactions.

The increased lifetime of positive ions was demonstrated by adding CH_3Br to a mixture of propane and air which was burned in the Egerton-Powling burner. Propane was supplied at the same rate as for column 2 of Table 2, 267 cm^3/min, so that the rate of production of positive ions and electrons would be the same. The final concentration of oxygen was 20.5% as before, the CH_3Br concentration was 0.08%. Methyl bromide was supplied at a rate of 10 cm^3/min and the air adjusted to give a stable flame. The velocity of the final mixture indicated that the flame velocity had been reduced by 7.8% so that the rate of production of positive ions was correspondingly less. However, application of a 500 volt/cm electrostatic field produced a deflection of 6.5 mm, more than twice that of the former case. This increased deflection of the flame under the same conditions is taken as evidence of an increase in positive ion concentration and thus for the capture of electrons in the formation of Br^- ions.

Additional evidence for the capture of electrons by halogens is provided by the work of Sugden [16] who used microwave techniques. His method was insensitive to the presence of negative ions, measuring only the concentrations of electrons. However, because of the unfavorable lower limit for the detection of electrons, his measurements were made on flames salted with alkali metal ions from alkali halides. He reports that when additional halogen was added to such flames the electron concentration decreased. The effect was attributed to the formation of unionized salt or to the capture of electrons to form negative halogen ions. The latter seems more likely.

7. The Relationship Between Extinguishing Efficiency and Oxygen Concentration

For lean flames, in the absence of inhibition, the proposed mechanism and the results of Table 1, indicate that the overall rate controlling process is the rate of production of positive ions and electrons. In the case of fuel-rich mixtures, the burning rate depends on the rate at which active oxygen molecules can be supplied to the reaction zone and thus, depends on the rate of oxygen supply and the rate of oxygen activation. A diffusion flame, involving a gaseous fuel and having a high concentration of electrons, should be able to activate almost every oxygen molecule coming within range of the electron cloud in the flame, so that the overall rate controlling process is the rate of oxygen supply. If inhibition is produced by the proposed mechanism, the activation process must become rate controlling. This implies that inhibition should be related to the oxygen content of the oxygen-nitrogen mixture supplied to the flame. The addition of an amount of inhibitor sufficient to extinguish a diffusion flame should be counteracted by an increase in oxygen content.

The relationship between extinguishment efficiency of methyl bromide and oxygen content was determined using the simple jacketed burner shown in Figure 2. In order that diffusion effects remain as nearly constant as possible, flames were set to a constant height (2 cm) rather than to a constant volume rate of fuel supply. Mixtures of nitrogen, oxygen and methyl bromide were supplied to the annular space between the burner tube and jacket at rates producing linear velocities of the order of 7 cm per second which did not appreciably disturb the flames and were sufficient to remove combustion products and prevent back diffusion of air into the burner. The composition of the atmosphere surrounding the flames was produced by means of calibrated flow meters. In each measurement the methyl bromide content was slowly increased until extinguishment resulted. Since the precision was not high, a series of four determinations was averaged for each point on the curve.

Each of the fuel gases requires a certain concentration of oxygen in the O_2-N_2 mixture in order to maintain a flame in the absence of inhibitor. Since this concentration is a characteristic of the particular fuel, subtraction of this value from the total oxygen concentration permits comparison of the fuels on an equal basis. In Figure 3, the concentration of methyl bromide required to extinguish a diffusion flame is plotted against the oxygen concentration in excess of that required for the fuel alone for methane, ethane, propane, butane, isobutane and ethylene. The curves for the individual gases vary somewhat, as might be expected, and are subject to undetermined, but probably sizable, errors. Nevertheless, it appears that the amount of inhibitor required for extinction is more closely related to the oxygen content than to the kind of fuel, as required by the proposed mechanism.

It should be pointed out that the ratio of hydrogen to carbon for these gases ranges from 4.0 to 2.0, yet the efficiency of extinguishment is approximately the same. This seems to provide further evidence that the mechanism of inhibition does not involve chain reactions of the hydrogen atom. The above results correspond to the results of Rosser, et al[2] on ethyl alcohol inhibited by H Br.

The curvature of the relationship of Figure 3 is partially explained by the fact that methyl bromide itself is capable of supporting combustion over a limited range of oxygen concentrations. The total fuel consumed, therefore, is the sum of the hydrocarbon, supplied at a constant rate, and the methyl bromide, the concentration of which was varied. As the concentration of methyl bromide is increased, the amount of oxygen required is, therefore, increased. The closer to the point of combustion of methyl bromide, the less effective it is as an inhibitor. At some oxygen concentration it is capable of not only capturing electrons for the formation of Br^- but also of supplying them for the activation of O_2 molecules. This implies that there may be a shift from a reaction of the type

$$CH_3\,Br + e \longrightarrow CH_3 + Br^-$$

in the cooler parts of the flame to one of the type

$$CH_3\,Br \longrightarrow CH_3 + {}_+Br^-$$

as more molecules are able to penetrate into the hotter flame zones. This experiment should be repeated using a non-combustible inhibitor.

The interior of a diffusion flame, being surrounded by the reaction zone, should have a higher concentration of electrons than the region just outside of it. The increased field should result in electrons being repelled toward the outside of the flame, where they are more useful, until an equilibrium is established. The addition of methyl bromide to the fuel, resulting in the replacement of electrons with Br^- ions inside the reaction zone, should have little effect on the equilibrium other than to reduce the mobility of the carriers of negative charges and, as a result, should have less effect as an inhibitor than when added to the oxygen supply outside the flame. It is easy to show that concentrations approximately 5 times as great are required for the extinguishment of a propane diffusion flame when the methyl bromide is added to fuel as when it is added to the air supply. Since the rate of diffusion into the reaction zone should be the same from either the fuel side or the oxygen side and the inhibitor is more effective when added from the oxygen side of the reaction zone, it must be concluded that inhibition is connected with the utilization of oxygen.

8. The Efficiency of an Inhibitor

The proposed mechanism requires that an inhibitor be capable of capturing electrons or of removing them from O_2^- ions under flame conditions and, in addition, disposing of them in such a manner that they are no longer available for flame reactions. Because the concentration of electrons is considerably larger than that of O_2^- ions in flames, it is more probable that the mechanism involves capture of free electrons rather than removal of electrons from O_2^- ions, although the latter is not completely ruled out. If the capture of free electrons is involved, the most efficient inhibitor would have the largest possible cross section for capture over an energy range comparable to that found for electrons in flames. From the standpoint of high efficiency of inhibition, the electron would have to be disposed of by the formation of a highly stable negative ion of a kind which does not form compounds with the positive ions found in flames capable of remaining stable at the temperatures involved. This calls for an atomic ion having a high electron affinity and points directly toward the halogens as the best known examples of these characteristics. The cross section for the reactions

$I_2 + \epsilon \longrightarrow I + I^-$ as a function of electron energy, as given by Buchdahl [17] is shown in Figure 4, along with similar results on $O_2 + \epsilon \longrightarrow O_2^-$ taken from Burch, Smith and Branscomb [5] and for $O + \epsilon \longrightarrow O^-$ from Branscomb and Smith [8]. It seems obvious from these curves that I_2 is a better electron sink for low energy electrons than O_2. Hickam and Berg [18] and Buchel'nikova [19] give results on the electron energy for maximum capture cross section and the range of energies of the electrons capable of capture for a number of compounds, some of which have been rated as extinguishing agents by Malcolm [20]. These results are shown in Table 3, along with results on HCl from Fox [21] and on I_2 from Frost and McDowell [22]. The last column is taken from Malcolm's report and is the concentration of extinguishing agent above which a flame of n-heptane will not burn in air. The smaller the value the more effective the inhibitor. The table shows the combined effects of the position of the maximum cross section for capture and the range on the efficiency as an extinguishing agent. The information given by Hickam and Berg and by Fox does not permit the estimation of the cross section for capture so that no inferences can be drawn on this basis. However, the table shows that poor extinguishing efficiency results if the maximum cross section for capture occurs at energies which are either too high or too low, or if the range of energies covered is too small.

Rosser Inami and Wise's results on the CH_4 -NO_2 flame indicate that, compared to CH_3 Br and CF_3 Br NO_2 is a very efficient electron sink. The end product of the capture of an electron, the O^- ion, should take part actively in flame reactions, and evidently has a high enough electron affinity so that it cannot lose its electron to CH_3 Br or CF_3 Br molecules under flame conditions. It is possible that its lifetime is too short for such a transfer to occur with any reasonable probability.

Hickam and Berg point out that there may be strong temperature coefficients with respect to both cross section and the position of the maximum on the electron energy scale. They cite carbon tetrachloride as an example. It has two maxima, one of which decreases with an increase in temperature, the other increases, but at a slower rate. The net result is a shift of the range to higher electron energies. The temperature coefficient must undoubtedly be considered in predicting extinguishing efficiency.

9. Dry Powders

Several mechanisms have been proposed to account for the effectiveness of dry powders as extinguishing agents. Dolan [23] has shown that for a given chemical compound, the effectiveness is a function of surface area and chemical composition and bears no relationship to particle weight or volume. Because absorption of thermal energy is a function of surface area, he proposes that extinguishment is produced by a thermal mechanism. However, since the heat capacity is a function of the weight of the particle, and there appears to be no correlation of effectiveness with weight, this mechanism does not appear to be too promising. McCamy, Shoub, and Lee [24] investigated the effects of infrared shielding by dry powder clouds and concluded that, while the effectiveness of dry powders could not be attributed wholly to infrared shielding, the effect should be considered in any proposed mechanism.

Surface effects in general correlate with adsorption phenomena. Free radicals, being very reactive, should be readily adsorbed on surfaces, including those of dry powder clouds. While the main flame reactions appear to be ionic, it is possible that preignition reactions between free radicals and oxygen lead to oxygenated compounds which may have low ionization temperatures. Adsorption of free radicals in these early reactions would reduce the concentration of compounds producing positive ions and electrons in the reaction zone and thus produce inhibition. This possibility has not yet been investigated.

Surfaces may also be active in removal of electrons from the reaction zone. The detailed process is somewhat as follows: Because of their high energy and small mass, electrons can rapidly leave the region in which they are freed and collect on surfaces, charging them negatively with respect to the plasma. The charge would have two effects. It would repel electrons and it would attract positive ions, which would fall freely to the surface as a result of the electric fields in which they would happen to be on formation. The electrons make so many collisions that they would rapidly establish a Maxwellian distribution among themselves. A steady state would finally be reached in which positive ions would be attracted to the surfaces while only electrons having sufficient energy to scale the sheath could reach the surface. Under these conditions, surfaces would develop a finite negative charge relative to the space surrounding them. Positive ions would thus be reunited with electrons instead of oxygen molecules and the excess of electrons present on the surfaces would be removed from the reaction zone.

It should be noted that, because the energy of the electrons increases with temperature, the electron sheath formed by this process will become thicker and more electrons will be removed at higher temperatures. This is quite a different effect from that of wall-quenching of flames which has a temperature coefficient in the opposite direction [25]. The two effects differ in another respect. If the surfaces are made of materials which can conduct electrons away as rapidly as collected, no electron sheath can form. Wall-quenching effects are independent of the material of which the wall is made and appear to be purely thermal in nature.

Dry powders of different chemical composition have different efficiencies as extinguishing agents. It is to be expected that the electrical properties of different chemical entities would be different and particularly so at flame temperatures where such differences may very well be exaggerated. For a single chemical compound inhibition by absorption of electrons should be a function of oxygen concentration for dry powders, just as it is with halogen compounds. In addition, particles of dry powder which have passed near a diffusion flame should bear negative charges and should be readily precipitated on a positively charged electrode. Only qualitative results are available, at present, on these two effects, but they substantiate the proposed mechanism.

The apparatus shown in Figure 5 was used to disperse dry powder into a stream of air to which had been added oxygen or nitrogen. Air was supplied through the fritted disk and powder bed at various rates and it was assumed that the rate of powder application was proportional to the rate of air supply. The powder bed was agitated, to prevent channeling, by means of a buzzer attached to the tube. It was further assumed that mixing of the air-oxygen or air-nitrogen mixture supplied through the side tube would be reasonably complete by the time the flame was reached. The flame position was approximately 10 diameters above the side tube and the powder streamlines indicated that reasonably good mixing occurred. Propane was supplied at approximately 50 cm^3/min. Linear air flow rates of 20 to 50 cm/sec in the area surrounding the flame did not appreciably change the flame characteristics. The relative rates of powder application were indicated by the rate of air supplied through the powder bed and a dilution factor based on the volume of mixture entering from the side tube. The powder used was of 4 micron average diameter, potassium bicarbonate base, and fresh powder was used for each run. Each determination was made by setting the desired mixture composition supplied through the side tube, lighting the flame, starting the buzzer and slowly increasing the air rate through the powder bed until the flame was extinguished. The results are shown in Figure 6.

The curvature shown in the figure is undoubtedly caused by the lack of a linear relationship between the velocity of the airflow through the powder bed and the amount of powder it is capable of carrying. In spite of this difficulty, the curve shows that it is necessary to apply more powder to produce extinguishment as the oxygen concentration is increased, and thus supports the proposed mechanism.

The same apparatus was used to show that powder particles which have passed near the flame bear negative charges. Two electrodes 1.4 x 3.5 cm were supported vertically above the top of the tube with a separation of 1.4 cm. A d-c potential of 500 volts was applied between them. With the flame burning in air and a rather low rate of powder application, about 80-90% of the particles collected by the electrodes, as estimated visually, were collected by the positive electrode. Streamers of particles 1 -2 mm long formed at the upper (downstream) edge of the electrode. When the flame was extinguished only a very small fraction of the powder was collected by either electrode and about equal amounts were collected by each. With the flame burning and oxygen added to the air stream, no powder was collected by either electrode until rather high rates of application were used, when rather small amounts of powder were collected, a slightly larger deposit appearing on the positive electrode. When nitrogen was added to the air stream, the collection differed from that for unmodified air only in that the deposition appeared to be a little more rapid.

Some of the powder which collected at the positive electrode was analyzed and found to be predominantly potassium hydroxide, indicating that decomposition takes place along with acquisition of negative charges. Since the powder particles passed near the diffusion flame where a relatively higher density of electrons would be expected, the sign of the charge mighthave been predicted. Because of the difficulty of producing a suspension of dry powder in a slowly moving gas stream, no attempt was made to determine the sign of the charge acquired when the powder was passed through a diffusion flame. No information is available on the average number of charges per particle, in the experiment reported here.

The above facts seem to provide rather conclusive evidence, not only of the mechanism of inhibition by dry powders, but also they are evidence of the ionic nature of one step in the combustion process.

10. Discussion

Several arguments have been presented in apposition to the ionic mechanism. They resolve themselves into three general classes. It is argued that ions are produced only incidentally as a by-product of some other, non-ionic, process and serve as an indicator of the other process [267]. If this were the case, it would be possible to deflect the ionic indicator by means of an electric field without disturbing the reaction zone itself. That this is not the case can be shown by probing a flame with a small thermocouple under conditions of deflection and non-deflection.

Secondly, it is argued that ions may be catalytic. Catalysis in a homogeneous mixture of reacting molecules A and B by a catalyst C, can take place by one of two processes:

$$A + B + C \longrightarrow ABC^* \longrightarrow AB + C \qquad (1)$$

$$\left.\begin{array}{l} A + C \longrightarrow AC^* \\ AC^* + B \longrightarrow AB + C \end{array}\right) \qquad (2)$$

Reaction (1) involves a 3-body collision whereas reactions (2) require two 2-body collisions in rapid succession. The activated complex, which can exist only momentarily because of its excess energy, is designated by the asterisk. If the concentration of catalyst is low enough that each catalyst molecule is in constant circulation, the reaction rate must be a function of catalyst concentration. The ionic concentration data of Table 1 is of the order of 10^5 ions per cm^2 in a molecular concentration of approximately 10^{19} which would seem to fulfill the requirement of constant circulation of catalyst, yet a 5-fold change in ionic concentration produced negligible change in reaction rate. On this basis it seems improbable that ions can be catalysts for reactions between neutral particles in a flame.

The third objection to an ionic mechanism in flames is that the concentration of ions is too low to provide the number of collisions required by the observed reaction rate.

Rates for both free radical and ionic reactions are dependent not only on concentrations but also on the reaction cross sections. Cross sections for reacting neutral molecules are functions of the relative velocities of the molecules and are therefore related to temperature. They vary between wide limits, depending on the activation energy required by the particular reacting species. In the case of species requiring a low but finite activation energy, as is the case with some free radicals, the cross section is zero at zero velocity, goes through a maximum at some particular velocity and returns to zero asymtotically at larger velocities. Because of the strong forces between ions of opposite charge the cross section approaches infinity as the velocity approaches zero and decreases as the relative velocities increase, approaching zero at higher velocity. The situation is further complicated by the fact that some molecules, notably the O_2 molecule, can readily exchange charges, so that charges which started at some distance apart can migrate, through charge exchange reactions, until they are close enough together that neutralizing reactions can take place. It therefore appears that large effective reaction cross sections can compensate for low concentrations.

In a hydrocarbon gas-oxygen flame, positive ions can come only from the fragmentation of fuel molecules. When air is substituted for oxygen it seems probable that the fuel molecules are still the only source of positive ions. Because of this, it has been postulated that the rate of formation of positive ions depends upon the rate of fuel supply. Under steady-state conditions the rate of recombination is equal to the rate of formation of ions and steady-state concentration of ions must be that required to produce the observed rate of recombination. The low steady-state concentration observed is an indication of very large effective reaction cross section.

The fact that a 5-fold increase in oxygen concentration produced an almost identical decrease in the concentration of positive ions seems to be evidence for the applicability of the mass-action law to the capture of electrons by neutral oxygen molecules. It should also provide a correspondingly larger number of possible charge exchange chains and a greater chance for neutralization of the positive ions, and explain the resultant decrease in their steady-state concentration.

In order that a dynamic reaction like a flame may continue to go, it is necessary that energy be fed back from the reacting particles to those about to react. This activation energy may be of two kinds, kinetic or radiant. In the case of the Egerton-Powling burner some of the feed-back is by way of radiant energy as can be demonstrated by changing the position of the upper screen and noting that the flame follows the movement of the screen.

When a flame is deflected by means of an electric field, the movement is in the direction that positive ions would travel under the influence of the field. This seems to indicate that positive ions are important in the kinetic feed-back of activation energy. One may envisage several mechanisms by which such energy might be transported, some of which do not appear to be very probable.

The presence of the field produces a motion of the positive ion which gives it energy in addition to its thermal energy. However, the drift velocity is so small compared to its thermal velocity that it seems unlikely that enough energy could be acquired from the field to explain the observed deflections.

If activation energy is transported from product molecules to reactant molecules by a purely thermal process and positive ions are postulated to carry only thermal energies, one may consider that a certain amount of thermal energy could be directed because of the charges on the ions and the presence of the field. However, because of a small number of particles capable of being directed in this way, it seems unlikely that deflection of flames can be explained on this basis.

It is possible that an ion can carry more vibrational energy than a neutral molecule of the same species because it may have more internal degrees of freedom caused by the removal of an electron. This is particularly true if the ion is excited above its ground state. However, the additional energy above thermal and exclusive of that associated with the charge is likely to be small and cannot explain the observed effect.

The largest energy carried by a positive ion is associated with its charge. However, if this energy is to be imparted to a molecule in the process of activating it, the charge must also be transferred to the molecule being activated, since the

energy goes along with the charge. Since positive ions disappear continuously by recombination, it is implied that every positive ion must produce more than one positive ion in the activation process. This, in turn, implies that energy in excess of that associated with the charge must be transferred at the time the charge is transferred.

So little information is available on cross sections for charge transfer between positive ions that it is useless to speculate further. We can only conclude that the motion of a reaction zone in an electric field indicates that positive ions are implicated in the activation process.

11. Summary

It must be concluded, on the basis of deflection experiments, that ionic reactions are important in the mechanism of combustion. The work of Rosser, Inami and Wise [2] interpreted on the basis of ionic reactions, indicates that inhibitions interferes with the activation of oxygen molecules. The work of Branscomb et al. [5, 8], and Crain [4], and Chanin, Phelps and Biondi [6] indicates that a possible activation process for oxygen molecules is through the formation of the O_2^- ion. This proposal is supported by additional evidence which relates the oxygen concentration to the positive ion concentration, as measured with Longmuir probes, and the lifetime of positive ions, as measured by deflection of the flame by an electric field. Additional evidence for an ionic mechanism is provided by the proposed mechanism of inhibition in which electrons, O_2^- ions and possibly positive ions are captured by the inhibitor and permanently removed from the system. Sugden [16] has shown that halogenated inhibitors reduce the electron concentrations. Hickam and Berg [18] and Buchel'nikova [19] have shown that halogenated inhibitors have captured cross sections appropriate for the removal of thermal electrons from flames. Evidence is presented in this report that dry powder extinguishing agents acquire negative charges when mixed with the air supplied to a diffusion flame, that a halogenated inhibitor is more effective when mixed with the air supplied to a diffusion flame than when mixed with fuel, and that inhibition efficiency is more intimately connected with oxygen concentration than with the nature of the fuel supplied to a flame.

Because a reaction zone is displaced in an electric field in the direction that positive ions would be displaced, it is concluded that positive ions are connected with the transport of activation energy between products and reactants.

[1] S. N. Foner and R. L. Hudson, J. Chem. Phys, 21, 1374-1382 (1953).

[2] W. A. Rosser, Jr., S. H. Inami, and H. Wise, Study of the Mechanisms of Fire Extinguishment of Liquid Rocket Propellants, WADC Tech. Report, 59-206.

[3] F. E. Belles, Nat. Advisory Committee for Aeronautics, Tech. Note 3565, (1955).

[4] C. M. Crain, J. Applied Phys. 29, 1605 (1958).

[5] D. S. Burch, S. J. Smith and L. M. Branscomb, Phys. Rev. 112, 171-5 (1958).

[6] L. M. Chanin, A. V. Phelps, and M. A. Biondi, Bull Am. Phys. Soc. 4, 316 (1959).

[7] L. M. Branscomb, Advances in Electron Physics IX, 43-94, (1957).

[8] L. M. Branscomb and S. J. Smith, Phys. Rev. 98, 1127-8 (1955).

[9] R. E. Fox, Bul. Am. Phys. Soc. 4, 318 (1959).

[10] M. J. Breton, Ann. office combustibles liquides, 11, 487-548 (1936).

[11] J. Powling, Fuel, 28, 25-8 (1949).

[12] B. Lewis, J. Am. Chem. Soc., 53, 1304 (1931).

[13] P. F. Knewstubb and T. M. Sugden, Seventh Symposium (International) on Combustion, 247-253 (1959).

[14] T. Kimbara and H. Ikegami, Combustion and Flame, 1, 199 (1957).

[15] L. B. Loeb, Basic Processes of Gaseous Electronics, Univ. of California Press, Berkeley, California (1955).

[16] T. M. Sugden, Fifth Symposium (International) on Combustion, 406-11 (1955).

[17] R. Buchdahl, J. Chem. Phys., 9, 146-52 (1941).

[18] W. M. Hickam and D. Berg, J. Chem. Phys. 29, 517-23 (1958).

[19] I. S. Buchel'nikova, J. Exptl. Theoret. Phys. (USSR) 35. 783 (1959).

[20] J. E. Malcolm, Report 1177, Interim Report on Vaporizing Fire Extinguishing Agents, Engineer Research and Development Laboratories, Ft. Belvoir, Va.

[21] R. E. Fox, J. Chem. Phys. 26, 1281-4, (1957).

[22] D. C. Frost and C. A. McDowell, J. Chem. Phys. 29, 964 (1958).

[23] J. E. Dolan, Sixth Symposium (International) on Combustion, 487-94 (1956).

[24] C. S. McCamy, H. Shoub and T. G. Lee, Sixth Symposium (International) on Combustion, 795-801 (1956).

[25] R. Friedman and W. C. Johnson, J. Applied Phys. 21, 791-5, (1950).

[26] J. O. Hirschfelder, Private Communication.

USCOMM-NBS-DC

Table 1. Positive ion concentration and calculated flame temperature as a function of oxygen concentration at constant rate of fuel supply and mixture velocity.

% Propane	% O_2	% N_2	Mixture Velocity cm/sec	Positive ion Concentration Arbitrary Units	Calc. Temp °C
1.97	12.9	85.2	7.98	5.6	1012
2.06	16.2	81.8	7.78	6.2	1067
2.05	18.6	79.4	7.88	6.0	1055
1.93	20.5	77.6	7.88	5.8	982
1.96	23.6	74.5	8.05	4.9	997
1.97	27.8	70.3	8.01	4.2	929
1.95	32.1	66.0	8.06	4.2	1002
1.94	35.1	63.0	7.98	3.8	969
1.96	39.7	58.5	8.03	2.96	1007
1.96	44.7	53.4	8.04	2.15	989
1.86	54.7	43.4	8.01	1.26	962

Table 2. Deflection of a flame as a function of oxygen concentration at constant mixture velocity.

	1	2	3
Propane concentration in per cent	1.96	2.00	2.01
Mixture velocity in cm/sec	7.88	7.85	7.84
Oxygen concentration in per cent	12.07	20.52	51.5
Deflection in mm for a 500 v field	8+	3	$<\frac{1}{2}$

Table 3. Cross section and width of electron capture band for selected compounds.

Compound	Ion	Onset of Capture ev	Width of Capture Band ev	% of Peak Flammability
SF_6	SF_6^-	0	0	20.5
SF_6	SF_5^-	0.05	1.4	20.5
$C\ Cl_2F_2$	Cl^-	0.5	0.4	14.9
$C\ Cl_4$	Cl^-	0.2	1.0	11.5
$CF_2\ Cl_2\ CF_2\ Cl_2$	Cl^-	0.2	2.8	9.0
HCl	Cl^-	0.66	1.0	25.5
I_2	I^-	0.34	1.0	--

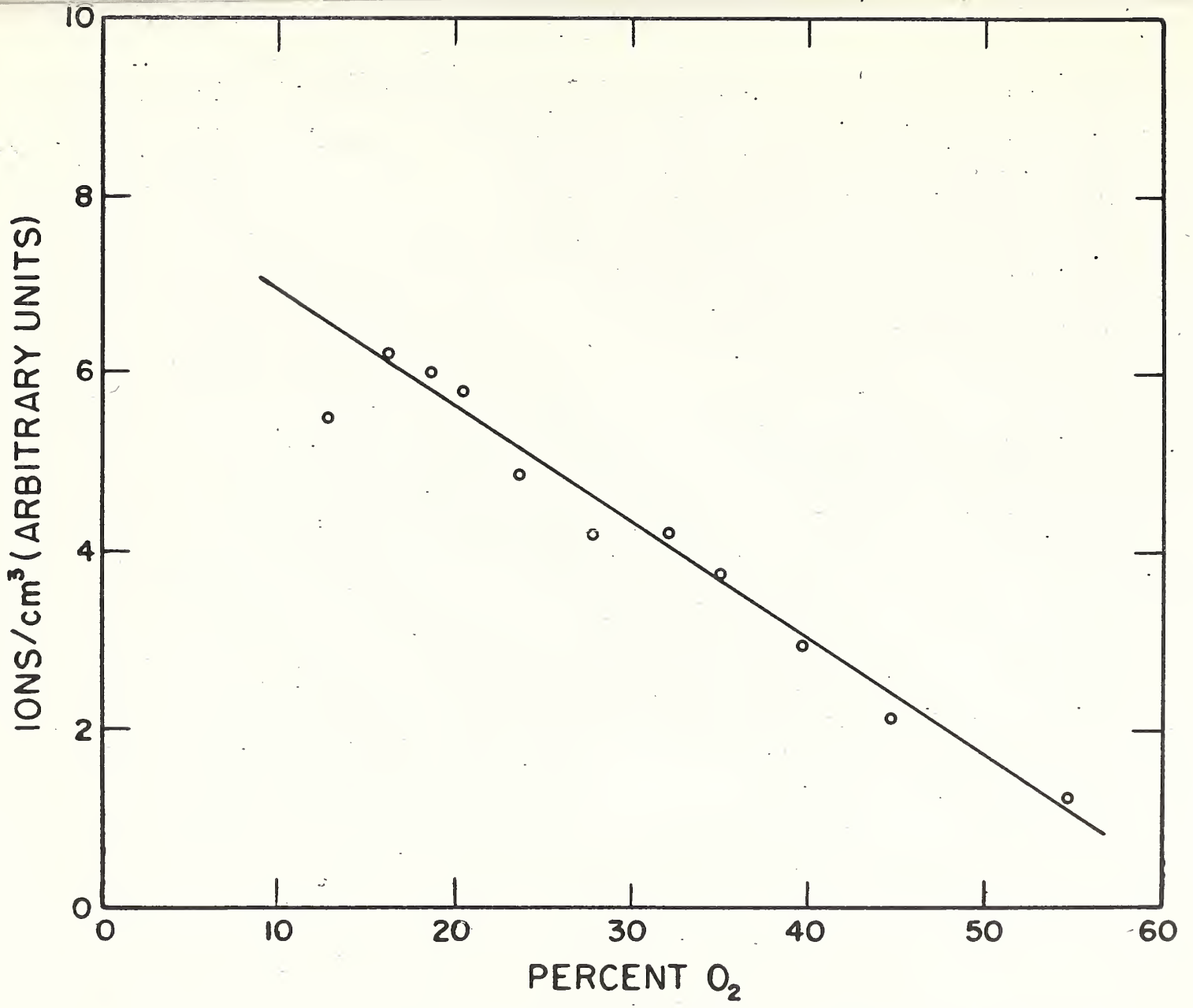


Figure 1. Ion concentration as a function of oxygen concentration.

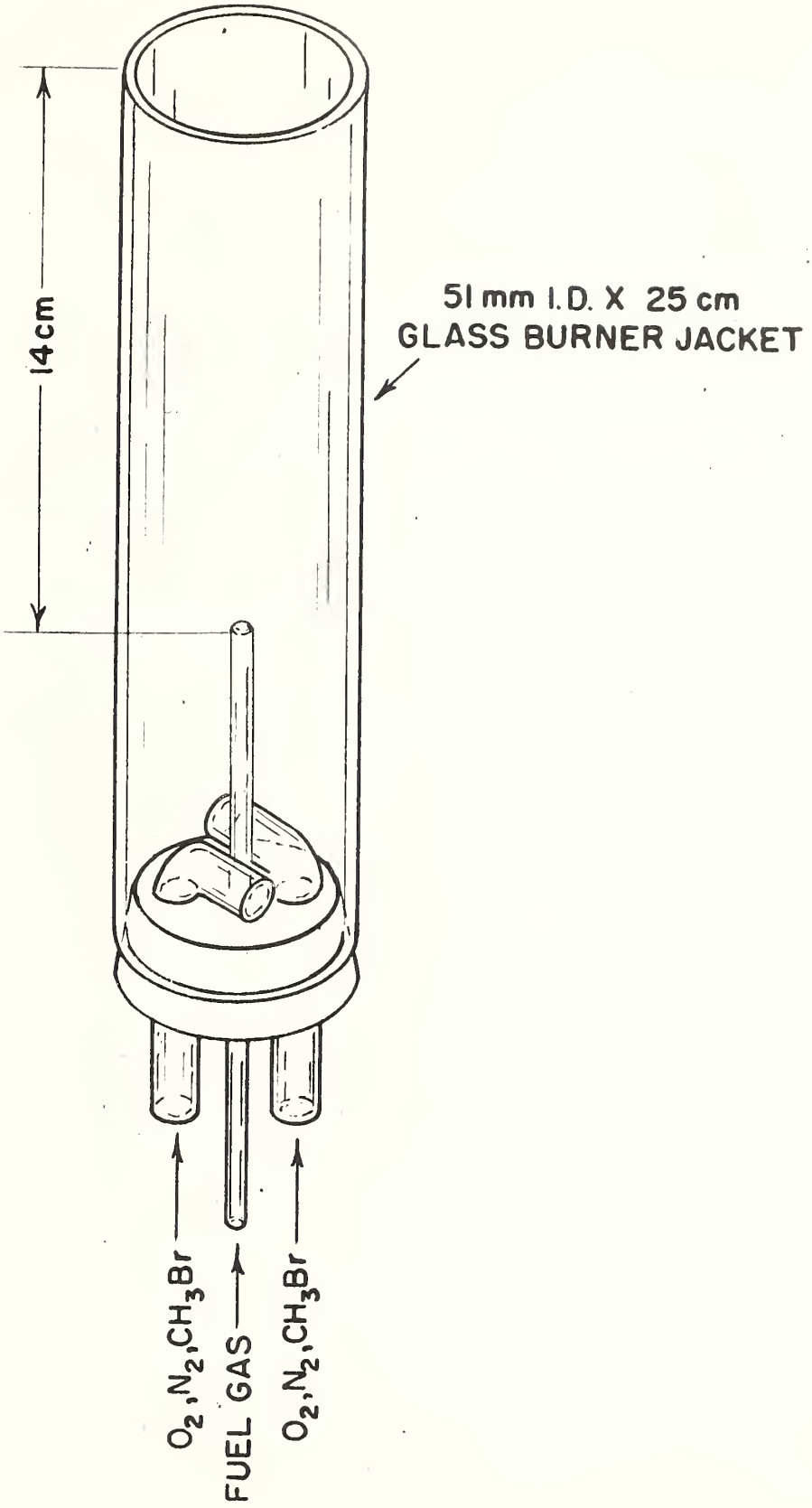


Figure 2. Burner for supplying atmospheres of various compositions to a diffusion flame.

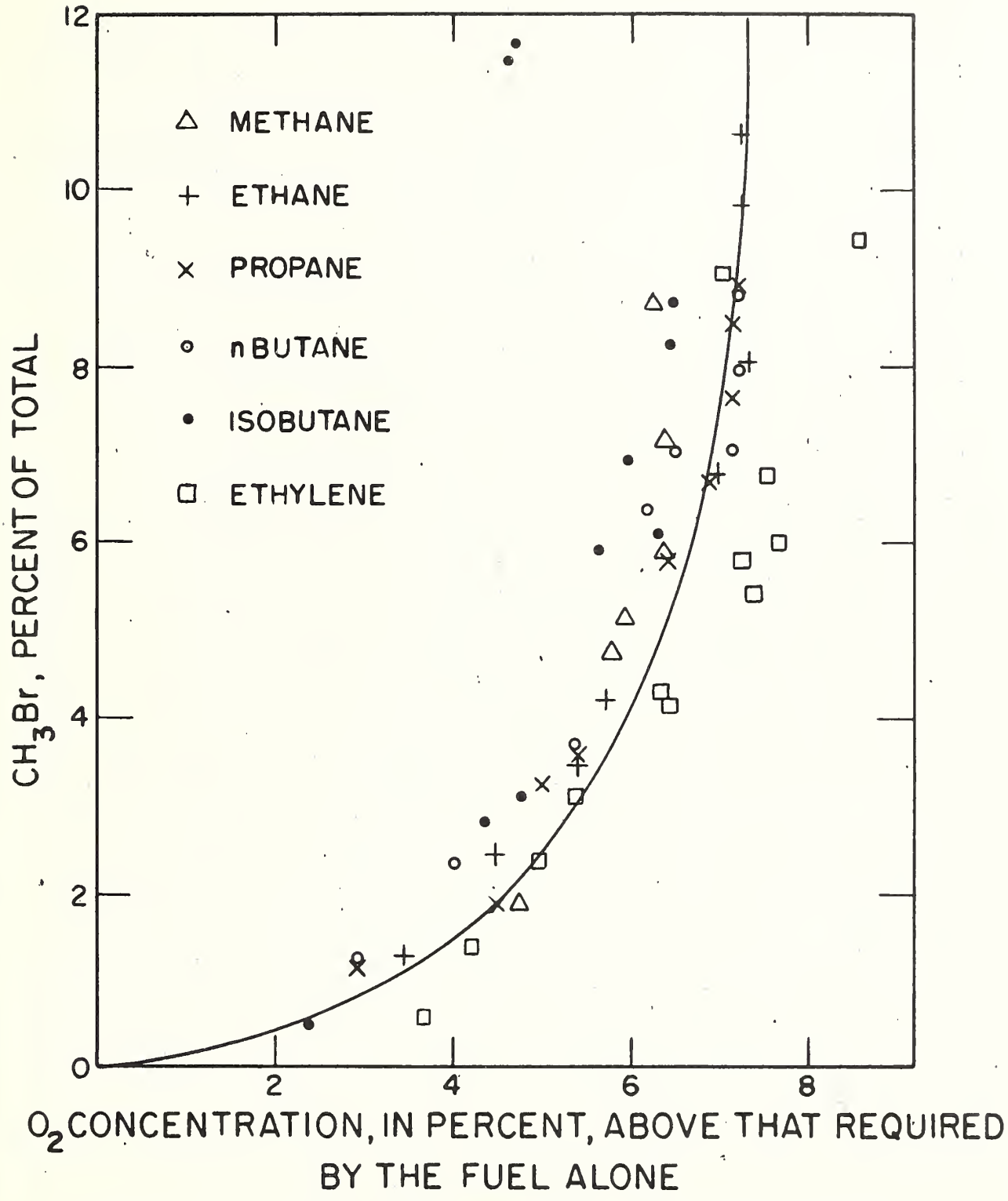


Figure 3. Extinguishing efficiency of methyl bromide as a function of oxygen concentration for diffusion flames of various gases.

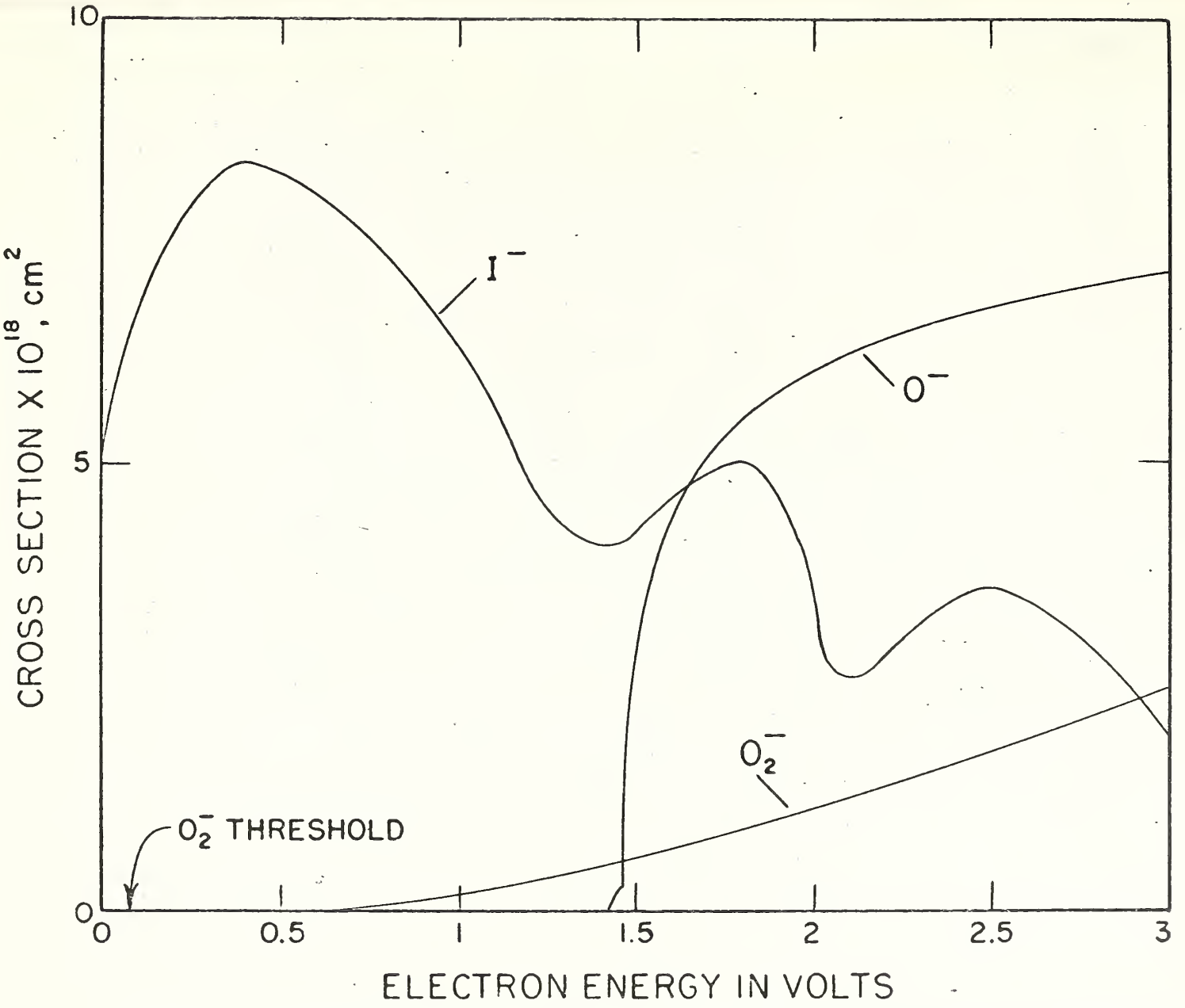


Figure 4. Absorption cross section as a function of electron energy for the reactions $I_2 + \epsilon \rightarrow I^- + I$, $O + \epsilon \rightarrow O^-$ and $O_2 + \epsilon \longrightarrow O_2^-$

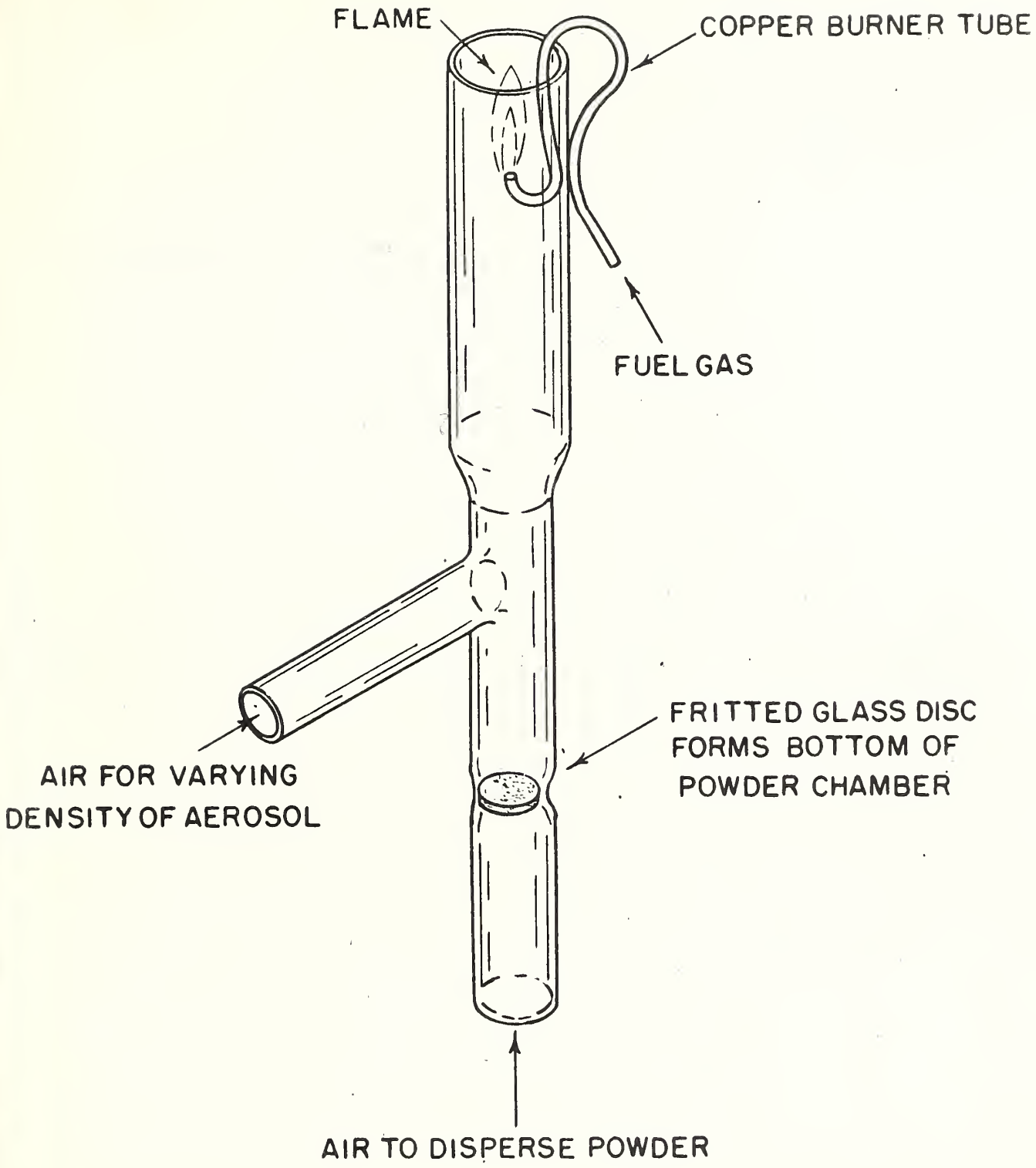


Figure 5. Apparatus for applying dry powder to a diffusion flame

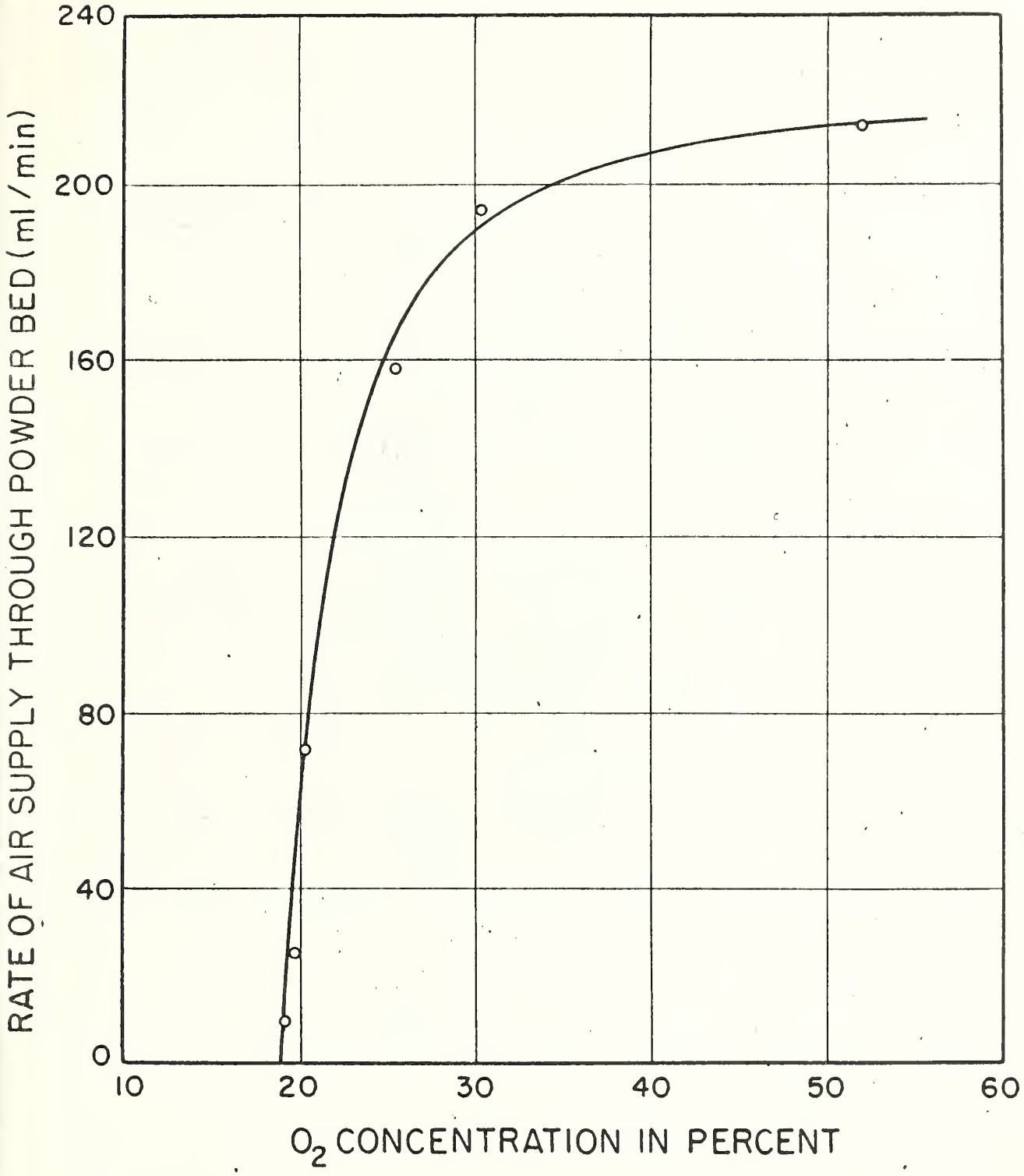


Figure 6. Effect of changing oxygen concentration on the concentration of dry powder required for extinction of a diffusion flame.

U.S. DEPARTMENT OF COMMERCE
Frederick H. Mueller, *Secretary*

NATIONAL BUREAU OF STANDARDS
A. V. Astin, *Director*

THE NATIONAL BUREAU OF STANDARDS

The scope of activities of the National Bureau of Standards at its major laboratories in Washington, D.C., and Boulder, Colorado, is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section carries out specialized research, development, and engineering in the field indicated by its title. A brief description of the activities, and of the resultant publications, appears on the inside of the front cover.

WASHINGTON, D.C.

Electricity and Electronics. Resistance and Reactance. Electron Devices. Electrical Instruments. Magnetic Measurements. Dielectrics. Engineering Electronics. Electronic Instrumentation. Electrochemistry.

Optics and Metrology. Photometry and Colorimetry. Photographic Technology. Length. Engineering Metrology.

Heat. Temperature Physics. Thermodynamics. Cryogenic Physics. Rheology. Molecular Kinetics. Free Radicals Research.

Atomic and Radiation Physics. Spectroscopy. Radiometry. Mass Spectrometry. Solid State Physics. Electron Physics. Atomic Physics. Neutron Physics. Radiation Theory. Radioactivity. X-rays. High Energy Radiation. Nucleonic Instrumentation. Radiological Equipment.

Chemistry. Organic Coatings. Surface Chemistry. Organic Chemistry. Analytical Chemistry. Inorganic Chemistry. Electrodeposition. Molecular Structure and Properties of Gases. Physical Chemistry. Thermochemistry. Spectrochemistry. Pure Substances.

Mechanics. Sound. Mechanical Instruments. Fluid Mechanics. Engineering Mechanics. Mass and Scale. Capacity, Density, and Fluid Meters. Combustion Controls.

Organic and Fibrous Materials. Rubber. Textiles. Paper. Leather. Testing and Specifications. Polymer Structure. Plastics. Dental Research.

Metallurgy. Thermal Metallurgy. Chemical Metallurgy. Mechanical Metallurgy. Corrosion. Metal Physics.

Mineral Products. Engineering Ceramics. Glass. Refractories. Enameled Metals. Constitution and Microstructure.

Building Technology. Structural Engineering. Fire Protection. Air Conditioning, Heating, and Refrigeration. Floor, Roof, and Wall Coverings. Codes and Safety Standards. Heat Transfer. Concreting Materials.

Applied Mathematics. Numerical Analysis. Computation. Statistical Engineering. Mathematical Physics.

Data Processing Systems. SEAC Engineering Group. Components and Techniques. Digital Circuitry. Digital Systems. Analog Systems. Application Engineering.

• Office of Basic Instrumentation.

• Office of Weights and Measures.

BOULDER, COLORADO

Cryogenic Engineering. Cryogenic Equipment. Cryogenic Processes. Properties of Materials. Gas Liquefaction.

Radio Propagation Physics. Upper Atmosphere Research. Ionospheric Research. Regular Propagation Services. Sun-Earth Relationships. VHF Research. Radio Warning Services. Airglow and Aurora. Radio Astronomy and Arctic Propagation.

Radio Propagation Engineering. Data Reduction Instrumentation. Modulation Research. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Propagation Obstacles Engineering. Radio-Meteorology. Lower Atmosphere Physics.

Radio Standards. High Frequency Electrical Standards. Radio Broadcast Service. High Frequency Impedance Standards. Electronic Calibration Center. Microwave Physics. Microwave Circuit Standards.

Radio Communication and Systems. Low Frequency and Very Low Frequency Research. High Frequency and Very High Frequency Research. Ultra High Frequency and Super High Frequency Research. Modulation Research. Antenna Research. Navigation Systems. Systems Analysis. Field Operations.


NBS