U. S. DEPARTMENT OF COMMERCE
R. P. LAMONT, Secretary
BUREAU OF MINES
SCOTT TURNER, Director

Bulletin 279

LIMITS OF INFLAMMABILITY OF GASES AND VAPORS

BY

H. F. COWARD and G. W. JONES

FIRST EDITION, 1928
REVISED AND ENLARGED, 1930

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1931

For sale by the Superintendent of Documents, Washington, D. C. - - - Price 20 cents

FOREWORD

This bulletin is one of a series of publications issued as a result of cooperation between the Safety in Mines Research Board, of Great Britain, and the Bureau of Mines, Department of Commerce, of the United States of America. Under this cooperation, begun in 1924, the exchange of personnel and data permits the intensive investigation of specific problems dealing with the prevention or abatement of accidents in mines. The determination of constants such as the limits of inflammability and explosibility of gases and dusts encountered in mines and the mineral industries is part of the cooperative program.

Dr. H. F. Coward, of Sheffield, England, was detailed by the British Safety in Mines Research Board in April, 1925, to the experimental station of the Bureau of Mines, at Pittsburgh, Pa., to make a cooperative study of certain chemical and physical factors connected with the initiation and propagation of flame in different gases under various conditions. G. W. Jones, of the Bureau of Mines, was detailed to work in association with Doctor Coward and other members of the staff of the Pittsburgh Experiment Station under the supervision of its superintendent, A. C. Fieldner.

Unquestionably the results are of great value to industries handling inflammable gas and are especially valuable in problems concerning safety in coal mining, for they determine with some precision the limits of inflammability of inflammable gas mixtures. Some of the tests give new figures; others confirm former determinations.

Certain reports on cooperative investigations carried on in Great Britain with the assistance of representatives from the United States have been published by the Safety in Mines Research Board.[1]

GEORGE S. RICE,
Chief Mining Engineer,
(Liaison Officer for Bureau of Mines).

---

[1] Rice, G. S., and Wheeler, R. V., Stone Dust as a Preventive of Coal Dust Explosions; Comparative Tests: Paper 13, Safety in Mines Research Board, 1925.
Greenwald, H. P., and Wheeler, R. V., Coal Dust Explosions; Effect of Release of Pressure on Their Development: Paper 14, Safety in Mines Research Board, 1925.
Ketz, S. H., and Grice, C. S. W., Mine Rescue Apparatus; the S. M. R. B. Gas Mask: Paper 57, Safety in Mines Research Board, 1930.

CONTENTS

ILLUSTRATIONS

PREFACE

A knowledge of the limits of inflammability of methane, and indeed of the products of distillation of coal, in air and in partly vitiated atmosphere, is of fundamental importance in the study of mine explosions and their prevention. Likewise, a knowledge of the inflammable limits of gasoline and benzol vapors, natural and manufactured gas, blast-furnace gas, hydrogen, acetylene, and many other gases is of equal importance in the prevention of gas explosions and fires in the metallurgical, petroleum, gas-manufacturing, and related industries.

The importance of such data is shown by the increasingly frequent inquiries received at the Bureau of Mines for information on the limits of inflammability of various gases and vapors when mixed with air or other "atmosphere."

Substances that a short time ago were found infrequently, even in the laboratory, are being used on a large scale, and some of them form dangerously explosive mixtures with air. Data concerning their limits of inflammability are widely scattered in the literature, and many of the figures seem contradictory. In the following pages a comprehensive survey has been made which, it is hoped, includes all available results; the latter have been arranged, coordinated, and critically reviewed. The opportunity has been taken to include a number of results that have not hitherto been published.

A. C. FIELDNER,
Chief Engineer,
Experiment Stations Division.

LIMITS OF INFLAMMABILITY OF GASES AND VAPORS[2]

By H. F. Coward[3] and G. W. Jones[4]

DEFINITIONS

An inflammable mixture of gases, such as methane and air, may be diluted with one or another of its constituents or with other gases until it is no longer inflammable. The dilution limit of inflammability, or simply the limit of inflammability, is the border-line composition; a slight change in one direction produces an inflammable mixture, in the other direction a noninflammable mixture.

There are clearly two limits of inflammability, a higher and a lower, for each pair of so-called combustible gas and supporter of combustion. The lower limit corresponds to the minimum amount of combustible gas, the higher or upper limit to the maximum amount of gas capable of conferring inflammability on the mixture. For example, for methane-air mixtures these limits under normal conditions are approximately 5 and 14 per cent methane, respectively. Mixtures within these limits liberate enough energy on combustion of any one layer to ignite the neighboring layer of unburned gas and are therefore capable of self-propagation of flame; others are not. Mixtures richer than 14 per cent methane, however, may burn on contact with external air, for mixtures which contain less than 14 per cent methane are formed in the zone where the gases mingle.

The experimental determination of limits of inflammability is more difficult than may be anticipated, as is shown by the contradictory figures reported from time to time. It is the object of this paper to present the results of a critical review of all figures published on the limits of inflammability of combustible gases and vapors when in admixture with air, oxygen, or other "atmosphere." Suspended dusts and liquid mists are not considered.

PROPAGATION OF FLAME IN INFLAMMABLE MIXTURES

SOURCE OF IGNITION

When a source of heat of sufficient size and intensity is introduced into a weak mixture, some combustion occurs even when the mixture is incapable of self-propagation of flame. This is usually visible as a "cap" of flame which may be large if the source of heat is ample. The flame cap may be fixed in relative position to the source of ignition, as in a miner's lamp burning in a gassy atmosphere, or may become detached from the source and float for a limited distance in a moving atmosphere, or may travel away for 2 or 3 feet from an initiating spark or flame in a still atmosphere (*72*).[5] Such flames are not self-

[2] Work on manuscript completed, February, 1930.
[3] Assistant director, Safety in Mines Research Board, Sheffield, England.
[4] Chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines.
[5] Numbers in parentheses refer to bibliography at end of this bulletin.

propagating, for they are extinguished when the influence of the source of ignition is lost.

When a somewhat weak source of ignition is employed, some inflammable mixtures, especially those near the limits, may not inflame. The source of ignition is not strong enough to be satisfactory for the test.

As the test concerns the capability of the mixture to propagate flame, not the capacity of the source of energy to initiate flame, it is axiomatic that the limits are unaffected by variations in the nature and strength of the source of ignition. When statements that limits vary according to the means of ignition are made, it may be inferred that the observers used such strong sources of ignition that the caps of flame gave the appearance of general inflammation or that they used such weak sources that flame was not started in mixtures which were, in fact, inflammable. Under these conditions they were determining the limits of ignitibility by the particular sources of ignition which they used, not the limits of inflammability of the mixture itself.

DIRECTION OF FLAME PROPAGATION

When a source of ignition, such as an electric spark or a flame, is introduced into an inflammable mixture, flame tends to travel away from the source in all directions. In a very large volume of mixture the form of the zone of combustion would be a spherical shell of increasing radius, were it not that the hot expanded products of combustion tend to rise and hence to introduce convection currents. Flame can not travel downward when the upward movement of the gases, due to convection, is faster than the speed of flame in a still mixture, as happens in weak mixtures near the limits of inflammability. Hence, near each limit there is a range of mixtures which will propagate flame upward but not downward. These may correctly be termed "inflammable mixtures," as it is only necessary to ignite them near their lower confines to observe self-propagating flame traveling to the higher confines. The gentle convection current set up by the flame increases the apparent speed of flame but, as far as is known, does not enable flame to travel when in the absence of convection effects it would not be propagated (*49*). It seems correct, therefore, to observe upward propagating flames when defining the limits of inflammability of gas mixtures; but for some purposes it is desirable to know the limits of inflammability for propagation of flame in other directions (*54*). Such limits when determined are included in the experimental results given.

For safety in industrial operations it is in general wisest to consider the limits for upward propagation an indication of the danger line, since these limits are wider than those for horizontal or downward propagation of flame.

DIAMETER OF VESSEL

As the propagation of flame depends upon the transfer of energy from the burned to the neighboring unburned gas, and as in a limit mixture the amount of energy available for transfer is only just enough for maintenance of flame propagation, anything that reduces the available energy will affect the limits. Hence, it is necessary to make observations in vessels which are so wide that the cooling effect of their walls is negligible.

The observed limits of inflammability are almost always widened as tube diameter is increased, rapidly at first and more slowly afterward, so that increase of diameter above 5 cm. rarely shows more than a few tenths of 1 per cent increase in the range of inflammability; many examples of this may be found in the tabulated results in the following pages, but there are a few notable exceptions. For example, the higher limit of acetylene-air mixtures is much increased by enlarging the diameter of the vessel beyond 5 cm. Moreover, the abnormal "cool flame" in higher limit acetone-air mixtures appears to be able to travel upward in certain mixtures confined in a 2.5-cm. tube, but not in 5 or 7.5 cm. tubes. Apart from a very few exceptions, however, the general rule holds.

LENGTH OF VESSEL

When flame travels from the open end of a tube toward the closed end its speed is uniform over a distance which depends on the composition of the mixture and on the dimensions of the tube; the inflammation of one layer of gas repeats the inflammation of any other layer in the "uniform movement" of flame. Sooner or later the uniform movement may give place to vibratory movement of the flame; but this is rarely observed in limit mixtures. When it has happened, however, the simple expedient of holding a pad of cotton wool loosely against the open end of the tube has suppressed any tendency to vibration without sensibly hindering the maintenance of constant pressure conditions. The flame then travels throughout the tube at uniform speed; and variation in length of the tube, provided it be long enough (say, 4 feet) for the initial impulse of the source of ignition to be dissipated, has no effect on the limits observed therein.

In experiments with closed tubes, however, it is untrue to say that the length of tube does not affect the results. The longer the tube the smaller must be the pressure attained during propagation of a limit flame, because in longer tubes the gases behind the flame have time to cool more before the flame reaches the end of its journey. Schützenberger (*13*) showed long ago that the observed limits in closed tubes are affected by the length of tube. In experiments with mixtures of 10 per cent hydrogen and 90 per cent oxygen he found that there was "a maximum length of column of gas, beyond which flame is propagated only a short way from the spark, whilst it can be propagated for lesser lengths (of column of gas)." An elaborate experimental study has recently confirmed and extended these observations (*126*). Hence, the results obtained in closed tubes are, at the best, of relative value only.

EFFECT OF SMALL CHANGES IN ATMOSPHERIC COMPOSITION

HUMIDITY

Some gas mixtures are exceedingly difficult to ignite if they have been dried by long-continued contact with phosphorus pentoxide. Such a degree of dryness is peculiar to the laboratory and is not considered in the present review.

Some series of experiments have been conducted with roughly dried mixtures in which the partial pressure of water vapor is less than 1 mm.; in others the mixtures have been saturated with water vapor at the temperature of the laboratory. The condition of humidity has not always been stated, doubtless because it has been assumed to be negligible. Probably the difference is appreciable, for most gases, only in exact work. Thus, the lower limit of methane in air, in certain comparative experiments, was 5.24 per cent for a mixture dried by calcium chloride and 5.22 per cent for one saturated with water vapor at laboratory temperature; these are actual percentages and are equal within experimental error, but, as usually reported from analyses calculated on a dry basis, they appear as 5.24 and 5.33 per cent, respectively. For methane, therefore, the true lower limit is not appreciably affected by the replacement of about 2 per cent of air by an equal volume of water vapor. For the higher limit, however, such a replacement reduces the oxygen content, which is less than the amount required to burn the methane completely, and thus reduces the limit. For example: The corresponding higher limits for methane in dry and in saturated air are 14.02 and 13.54 per cent, respectively; expressed on a dry basis (as reported analytically) these figures become 14.02 and 13.80 per cent, respectively (*105*).

Carbon monoxide shows greater differences than methane. The lower limit of carbon monoxide in air saturated with water vapor at laboratory temperature was 13.1 per cent for upward propagation of flame in a 2-inch tube; if the mixtures of gases were dried by passage through calcium chloride the lower limit became 15.9 per cent (*109*). Such a large difference is exceptional, perhaps unique, for moderate drying of carbon monoxide-air mixtures affects their ignition temperatures and flame speeds more than it affects these properties of any other gas examined hitherto.

OXYGEN CONTENT

The lower limit of methane-air mixtures and of some, probably of all, other mixtures is not appreciably affected by small changes in the oxygen content of the air. The higher limit is noticeably depressed by a small reduction in oxygen content, because a correspondingly less amount of the combustible gas can burn. Thus, a reduction of the oxygen content of the air from 20.9 to 20.6 per cent depressed the higher limit of methane by about 0.3 per cent. (See fig. 7.)

PRESSURE

The normal variations of atmospheric pressure have no appreciable influence on limits of inflammability, as has been shown both by direct observation and by deduction from the course of curves showing the variation of limits over much wider variations of pressure than those of the atmosphere (*28*, *46*, *64*, *81*, *119*, and *135*).

The effect of larger variations in pressure is neither simple nor uniform but is specific for each inflammable mixture. So far as is known, reduction in pressure below 760 mm. always causes a narrowing of the range of inflammability—that is to say, the lower limit rises and the higher limit falls. This change is often imperceptible for the first few hundred millimeters fall in pressure below atmospheric, but thereafter the effect increases until at a suitably low pressure the limits coincide; below this point no mixture is capable of propagating flame (*48*).

The limiting pressure is somewhat difficult to find, because often it is so low that the difficulty of insuring a powerful enough source of ignition has not certainly been overcome. For example, in electrolytic gas a flame that filled a 570-c. c. globe has been produced at 5 mm. pressure, and with the same mixture flame traveled through a cylinder 2 meters long at 8 mm. pressure (*37*). At such pressures the electric discharge used to test the inflammability was diffuse and if made stronger might have produced self-propagating flames at still lower pressures. For this reason the rate at which the lower and higher limit curves approach one another as the pressure is decreased will appear to depend on the strength of the source of ignition, unless the source is carefully made strong enough to insure ignition and the vessel used is large enough for the flame to travel such a distance from the source as will enable observers to see whether the mixture is capable of self-propagation of flame. This has not been done so the course of limit curves at very low pressures is unknown. In attempting to discover the course of such curves, the difficulty of maintaining constant pressure during the inflammation will have to be surmounted. However, it is almost certain that whatever may be the exact course of the curves they do approach and ultimately meet as the pressure is decreased.

Increase of pressure above that of the atmosphere does not always widen the limits. On the contrary, the range of inflammability of some mixtures is narrowed by increase of pressure, so that a mixture which can propagate flame at atmospheric pressure may not do so at higher pressures. For such mixtures there is therefore a pressure (it may be about that of the atmosphere or considerably higher) at which a minimum value of the lower limit is obtained; some mixtures show a maximum value of the higher limit at some definite pressure, not necessarily the same as that for the lower limit (*53*, *82*).

Reference may be made to the details given in the paragraphs on the effect of pressure on the individual mixtures, and more especially to the results obtained for mixtures of air with hydrogen (p. 17), carbon monoxide (p. 29), methane (p.)36, ethane (p. 57), propane (p. 59), butane (p. 60), and ethylene (p. 63). Facts to be explained are, broadly, that for downward propagation of flame at pressures greater than atmospheric the range of inflammability of carbon monoxide in air and of hydrogen in air, over a moderate range of pressure, is narrowed at both limits by increase of pressure; and that under the same conditions the range of each of the gases of the paraffin series, with air, is narrowed at the lower limit side (by moderate increase of pressure beyond a certain critical value) but widened at the higher limit side. Now, the heat loss by convection is greater at high pressures than at low, as density differences are greater at high pressures; hence, the range of inflammability should be narrowed at both limits when flame is traveling downward. This explains the results for hydrogen (both limits, moderate pressures) and carbon monoxide (both limits, all pressures) and those for paraffin gases (low limit only, moderate pressures).

Superposed on the effect just described is another, however. According to the law of mass action, the rate of reaction at constant temperature is greatest in methane-air mixtures when 33.3 per cent methane is present. The mass-action effect becomes a more important factor as the pressure is raised and hence tends to raise the higher limit in methane-air mixtures with increase of pressure. A similar interpretation may be given for higher limit curves of the other paraffin hydrocarbons. For hydrogen and carbon monoxide, however, the mass-action law indicates that the 66.7 per cent mixture is the one of greatest speed of reaction at constant temperature. As the higher limit of each of these gases is greater than 66.7 per cent, the mass-action effect would not tend to reverse the convection effect (*82*). The recently discovered rise in the higher limit of hydrogen at pressures from 10 to 220 atmospheres calls for explanation on other lines (*119*, *135*).

The foregoing argument on the influence of convection on the limits of inflammability was applied to results of experiments on downward propagation of flame. The argument was supported by the discovery that for horizontal propagation, in which the flames could not be retarded by convection and might even be assisted, the lower limit of methane in air remained unaltered between 760 and 5,000 mm. pressure, and the higher limit was increased even more than for downward propagation (*82*).

On account of experimental difficulties no attempt has been made to observe limits of inflammability in other than closed vessels for experiments in which the pressure before inflammation is greater or less than atmospheric. Hence the results relate to the propagation of flame at the stated initial pressures, which increased at an unknown rate and to an unknown extent during the observation. The rate and extent would, however, vary with the size and shape of the container and thus cause differences between results.

The same criticism applies to experiments in closed vessels when the pressure is initially atmospheric; the results obtained are a function of the length of the vessels used, as this governs, in part, the rate and amount of pressure development (*49*).

TEMPERATURE

To propagate flame, the layer of unburned gas next to the burning layer must be brought to such a temperature that it will "burst into flame" rapidly. If the unburned gas is already at a temperature above that of the laboratory, less heat has to be supplied from the burning layer; therefore the lower limit should be decreased by increase of initial temperature and the higher limit should be increased. In other words, the range of inflammability should be widened at both limits by increase of temperature. Experiment has shown this to be true for all mixtures examined hitherto, except in a few instances which can be explained by experimental error—namely, partial combustion of the heated gases before ignition. Details are to be found in the sections dealing with hydrogen in air, in oxygen, and in certain other "atmospheres"; carbon monoxide in air, in oxygen, and in certain other "atmospheres"; ammonia in air and in oxygen; methane in air, in oxygen, and in certain other "atmospheres"; pentane in air; ethylene in air; acetylene in air; ether in air; gasoline in air; coal gas in air, in oxygen, and in certain other "atmospheres."

According to the most recent experiments (*101*) there is for most mixtures a straight-line relation between the limit of inflammability and the initial temperature of the mixture. This relation was obscured in earlier experiments by the change of composition of the gas mixture between the time when it was introduced into the heated vessel and the time when it was tested by sparking; slow combustion at the higher temperatures used was the cause of this change of composition. The same reason apparently explains those cases in which a widening of the range of inflammability under the influence of increased temperature was not observed.

Ordinary variations of laboratory temperature have no appreciable effect on limits of inflammability.

TURBULENCE

Few observations have been made of the effect of turbulence on limits of inflammability, but it has been shown that the lower limits of methane and ethane in air are reduced somewhat by a suitable amount of turbulence produced either by a fan or by stream movement of the mixture, and that the range of inflammability of ether-air mixtures is somewhat widened by stream movements. (See the paragraphs which deal with these mixtures.)

LIMITS IN AIR COMPARED WITH LIMITS IN OXYGEN

In general the lower limit of a gas is nearly the same in oxygen as in air. For downward propagation of flame it is usually slightly higher in oxygen than in air (*69*). This has been thought to be a proof that the mean molecular heat of oxygen is higher than that of nitrogen over the range of temperature between normal heat and the heat of a limit flame—say, 1,200° to 1,400° C.

For upward or horizontal propagation the lower limit of methane is slightly less in oxygen than in air; the ammonia limit is markedly less (*69*).

The higher limits of all inflammable gases are much greater in oxygen than in air; hence the range of inflammability is always greater in oxygen.

MIXTURES OF INFLAMMABLE GASES AND VAPORS

A simple formula, of additive character, was put forward by Le Chatelier (*17*) to connect the lower limits of single gases with the lower limit of any mixture of them. It is

$$\frac{n_1}{N_1}+\frac{n_2}{N_2}=1,$$

in which the N_1 and N_2 are the lower limits in air for each combustible gas separately and n_1 and n_2 are the percentages of each gas in any lower limit mixture of the two in air.

The formula expresses the fact that, for example, a mixture of air, carbon monoxide, and hydrogen, which contains one-quarter of the amount of carbon monoxide and three-quarters of the amount of hydrogen necessary to form a lower limit mixture, will be a lower limit mixture. In other words, if the formula expresses experimental facts, the lower limits of inflammability form a series of inflammability equivalents for the individual gases of a mixture (*66*).

The formula also leads to the deduction that lower limit mixtures if mixed in any proportions give rise to mixtures which are also at their lower limits; or, vice versa, the formula may be deduced from the latter statement as a postulate (*66*).

The formula may be generalized to apply to any number of combustible gases, thus:

$$\frac{n_1}{N_1}+\frac{n_2}{N_2}+\frac{n_3}{N_3}+\cdot\cdot\cdot\cdot=1,$$

and, so far as it expresses experimental results truly, may be applied to higher limit mixtures, with the appropriate rewording of the definitions of n_1 . . . . and N_1 . . . .

A small algebraic transformation gives a more useful formula for calculating the limits of any mixture of combustible gases which obeys it (*66*), as follows:

$$L=\frac{100}{\frac{p_1}{N_1}+\frac{p_2}{N_2}+\frac{p_3}{N_3}+\cdot\cdot\cdot\cdot},$$

in which p_1, p_2, p_3 . . . . are the proportions of each combustible gas present in the original mixture, free from air and inert gases, so that

$$p_1+p_2+p_3+\cdot\cdot\cdot\cdot=100.$$

An example of the use of the formula will make its application clear: To calculate the lower limit of a "natural gas" of the composition

Methane	80 per cent (lower limit 5.3 per cent)
Ethane	15 per cent (lower limit 3.22 per cent)
Propane	4 per cent (lower limit 2.37 per cent)
Butane	1 per cent (lower limit 1.86 per cent)

we have

$$L=\frac{100}{\frac{80}{5.3}+\frac{15}{3.22}+\frac{4}{2.37}+\frac{1}{1.86}}=4.55 \text{ per cent.}$$

The accuracy of the formula has been carefully tested for a number of gas mixtures. The results are discussed separately in the appropriate sections later. In general, it may be said that while the formula is correct or very nearly so in a fair number of cases, there are some marked exceptions. It seems that the limits (lower and higher), of mixtures of hydrogen, carbon monoxide, and methane taken two at a time or all together, and of water gas and coal gas may be calculated with approximate accuracy (*66*). The same is true for mixtures of the simpler paraffin hydrocarbons, including "natural gas" (*111*). Sometimes, however, the differences between calculated and observed values are very large; for examples, see Figures 33 and 34. Many of the greater discrepancies are found when upward propagating flames are observed; this is especially true when one of the constituents is a vapor, such as ether or acetone, capable of giving rise to the phenomenon known as a "cool flame" (*79*). Le Chatelier's law, therefore, useful when its applicability has been proved, must not be applied indiscriminately.

An extension of the law to apply to other atmospheres than air (*28*, *69*), is that when limit mixtures are mixed the result is a limit mixture, provided that all the constituent mixtures are of the same type; that is, all are either lower limit mixtures or all are higher limit mixtures. This law holds, for example, for methane in a range of oxygen-nitrogen mixtures and in air-carbon dioxide, air-argon, and air-helium mixtures, except near the point at which lower and higher limits meet, when a large amount of inert gas is present. It holds also for mixtures of hydrogen, methane, and carbon monoxide, in a wide range of mixtures of air, nitrogen, and carbon dioxide, and may therefore be used to calculate the limits of inflammability of mine fire gases and of the atmospheres after a mine explosion, of blast-furnace gas, of automobile exhaust gas, and of the gases from solid explosives (*145*, *151*).

A brief account of the method of calculating limits of complex industrial gases, such as those just mentioned, will now be given; greater detail will be found in the original account (*145*).

The chief gases in the complex mixtures are hydrogen, carbon monoxide, methane, nitrogen, carbon dioxide, and oxygen. The operations are as follows:

(1) The composition of the mixture is first recalculated on an air-free basis, the amount of each gas being expressed as a percentage of the total air-free mixture.

(2) A somewhat arbitrary dissection of the air-free mixture is made into simpler mixtures, each of which contains only one inflammable gas and part or all of the nitrogen or carbon dioxide.

(3) The limits of each mixture thus dissected are read from tables or from curves. (Fig. 1.)

(4) The limits of the air-free mixture are calculated from the figures for the dissected mixtures obtained in (3), by means of the equation:

$$L=\frac{100}{\frac{p_1}{N_1}+\frac{p_2}{N_2}+\frac{p_3}{N_3}+\ldots\ldots},$$

where p_1, p_2, p_3 . . . . . are the proportions of the dissected mixtures, in percentages, and N_1, N_2, and N_3 . . . . . are their respective limits.

(5) From the limits of the air-free complex mixture thus obtained, the limits of the original complex mixture are deduced.

The following is an example of the calculation applied to a mine-fire atmosphere. It contained:

Constituent	Per cent	Air free, per cent	Constituent	Per cent	Air free, per cent
Carbon dioxide	13.8	15.9	Methane	3.3	3.8
Oxygen	2.8	.0	Hydrogen	4.9	5.7
Carbon monoxide	4.3	5.0	Nitrogen	70.9	69.6

(1) The composition on an air-free basis, also given above, is found thus: The amount of air in the mixture $=2.8\times100/20.9=13.4$ per cent. The air-free mixture is therefore 86.6 per cent of the whole. When the original amounts of carbon dioxide, carbon monoxide, methane, and hydrogen are divided by 86.6 and multiplied by 100, the "air-free" percentages are obtained. The nitrogen figure is obtained by difference between 100 and the sum of these.

(2) The inflammable gases are paired off with the inert gases separately to give a series of dissected mixtures, as shown on the following page.

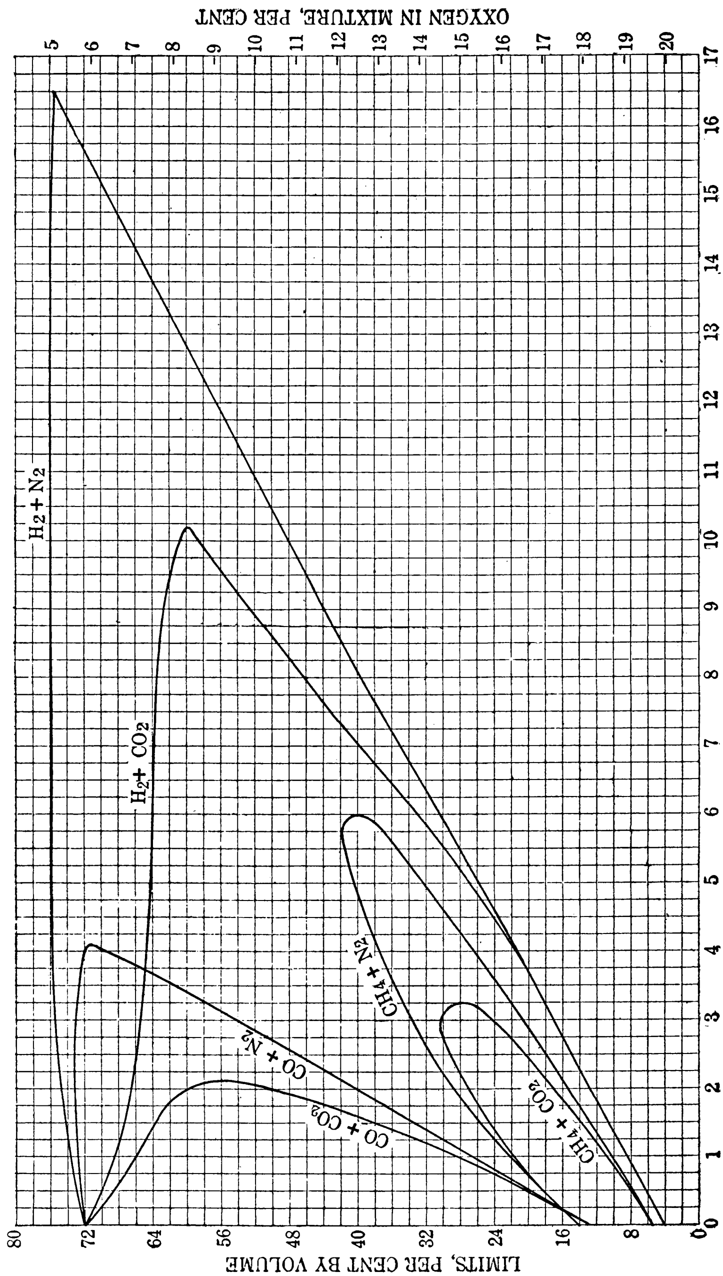

FIGURE 1.—Limits of inflammability of hydrogen, carbon monoxide, and methane, containing various amounts of carbon dioxide and nitrogen

Some discrimination is needed to choose appropriate quantities, but a fair latitude of choice is usually available.

Combustible	Per cent	CO_2, per cent	N_2, per cent	Total, per cent	Ratio of inert to combustible	Limits from Fig. 1	
						Lower	Higher
CO	5.0		17.5	22.5	3.5	61	73
CH_4	3.8		20.9	24.7	5.5	36	41.5
H_2	5.7 {3.0		31.2	34.2	10.4	50	76
	{2.7	15.9		18.6	5.9	32	64
Total		15.9	69.6	100.0			

(3) The limits of the dissected mixtures, read from the curves of Figure 1, are shown in the last two columns above. For example, the first mixture contains 5.0 per cent of carbon monoxide and 17.5 per cent of nitrogen, the ratio between its nitrogen and carbon monoxide is 17.5/5.0 = 3.5, and the limits read from the curve for carbon monoxide-nitrogen mixtures are 61 per cent (lower) and 73 per cent (higher).

(4) The values in the last two columns and in the column "Total, per cent," substituted in the equation, give the two limits of the air-free complex mixture, calculated to 0.5 per cent:

$$\text{Lower limit} = \frac{100}{\frac{22.5}{61}+\frac{24.7}{36}+\frac{34.2}{50}+\frac{18.6}{32}} = 43 \text{ per cent.}$$

$$\text{Higher limit} = \frac{100}{\frac{22.5}{73}+\frac{24.7}{41.5}+\frac{34.2}{76}+\frac{18.6}{64}} = 61 \text{ per cent.}$$

The range of inflammability of the air-free complex mixture is therefore 43 to 61 per cent.

(5) As the air-free mixture is 86.6 per cent of the whole, the limits, in air, of the mine-fire atmosphere are 43 × 100/86.6 and 61 × 100/86.6, or 50 and 70 per cent, respectively.

The novice's difficulty with such calculations is in stage (2), where an appropriate amount of inert gas has to be chosen to pair off with each combustible gas in turn. The ratio of inert to inflammable must not be so high that the mixture falls outside the extreme right of the corresponding curve in Figure 1. A little practice will soon overcome this difficulty.

It need only be added that should the amount of inert gas be so great that a complete series of inflammable mixtures can not be dissected, then the air-free mixture is not inflammable. Moreover, the air-free mixture may be inflammable, but when its limits are multiplied by the appropriate factor in the final stage of the calculation, the result may be greater than 100 for each limit; the original mixture is then not capable of forming an explosive mixture with air, because it contains too much air already. Finally, should the lower limit of the original mixture be less than 100 and the higher limit greater than 100 the mixture is inflammable per se and would explode if a source of ignition were present.

Some 20 examples, covering a wide range of industrial gases, have been tested (*145*) by experiment. The calculated and observed limits agreed within 2 or 3 per cent, except for one higher limit figure. This was for a mixture that contained an unusually large amount of carbon dioxide, nearly 24 per cent.

CHOICE OF EXPERIMENTAL CONDITIONS

In the light of the preceding discussion it seems that limits of inflammability are physicochemical constants of gases and vapors which can be determined when observations are made with quiescent mixtures in vessels of great enough dimensions, with ignition from below (and, if desired, at other points) and with maintenance of constant pressure during the experiment. A somewhat wide experience has shown that if observations are made in a vertical tube 2 inches in diameter and 4 to 6 feet high the results are nearly, but not quite, the same as are obtained in very much larger apparatus. Limits observed in smaller apparatus—for example, tubes of 1 inch or less diameter—are usually significantly narrower. Results obtained in small closed tubes are often so different from normal results, and even from one another, that they may be very misleading.

Effective ignition can usually be obtained equally well by passing an electric spark from an induction coil (say from "2-inch" to "12-inch" as convenient) across a gap several millimeters long, or by drawing the flame of a small spirit lamp or a jet of burning hydrogen across an aperture in the observation vessel. This aperture is conveniently made at the moment preceding ignition by gently sliding away a ground-glass plate which previously had sealed the vessel. When gases of small solubility are tested, a water seal may be used for this purpose. For some gases a small tuft of gun-cotton fired by a spark is a more certain means of ignition (*78*); for others, an electric spark succeeds in firing the mixture when a flame fails (*136*).

Only a few observations have been made on the limits of inflammability of mixtures in motion. For a steady flow of gas the use of a cylindrical tube is indicated, but for general turbulence a more symmetrical vessel of ample dimensions seems necessary. Glass globes of several liters capacity were fitted with internal fans for these observations, and for testing the effect of turbulence due to solid explosives short sections of a cylindrical metal gallery of 6.3 feet diameter were fitted with fans.

THEORETICAL CONSIDERATIONS

No one has succeeded in calculating either a lower or higher limit of inflammability of any mixture from more fundamental physicochemical data. In general terms, the problem is to express quantitatively the fact that in a limit mixture the amount of heat transmitted from the burning layer to the neighboring unburned layer of gas is just enough to inflame the latter. The data required for solving the problem seem to be (1) the heat of reaction of the mixture, (2) the thermal conductivity of the mixture at various temperatures, (3) the heat capacity of the mixture, and (4) the rate of reaction and the temperature coefficient of the rate of reaction of the mixture. Derived functions which may serve to relate dilution limits to simpler, but not the most fundamental, properties are ignition temperatures and the well-known "lags" on ignition.

Some attempts already made to relate limits of inflammability to simpler data may be mentioned. Long ago Humphry Davy (*3*) ascribed to its greater heat capacity the superior effect of carbon dioxide in rendering methane-air mixtures noninflammable; this conclusion has frequently been supported by observations with other inflammable mixtures. Regnault and Reiset (*6*) drew attention to the different effects of hydrogen and oxygen in rendering electrolytic gas noninflammable; they ascribed the difference to the diverse mobility of these gases, which may be put more precisely as a difference due to diverse thermal conductivities. As these gases are not chemically inactive toward the constituents of electrolytic gas, some mass-action effect may play a part. Recently some strictly comparative experiments with mixtures of methane and atmospheres composed of air and equal volumes of either argon or helium have proved that when heats of reaction, rates of reaction, and specific heats are equal there is yet a large difference in the limits in the argon and the helium mixtures. This difference is ascribed to the diverse thermal conductivities of the mixtures (*105*).

Bunsen (*7*, *12*) attempted to calculate ignition temperatures of gas mixtures from their limits of inflammability, with the aid of heats of reaction and specific heats. He assumed that the heat produced by the combustion of one layer (already heated, before burning, to its ignition temperature) was transmitted to the neighboring unburned layer, which was inflamed if the heat thus transmitted sufficed to raise it to its ignition temperature. The reverse procedure, that of calculating dilution limits from the ignition temperatures determined independently, has been frequently attempted. The only result of any value seems to be to show that there is no obvious connection between the two properties.

The heat of combustion of a limit mixture of most gases and vapors is enough to raise an equal volume of the unburned mixture to a temperature far higher than its ignition temperature. A notable exception is the lower limit mixture of hydrogen in air. This produces far too little heat to raise the mixture to its ignition temperature, yet flame will travel upward through the limit mixture indefinitely (*49*). An explanation of this has recently been given by F. Goldmann (*149*). The flame in the limit mixture rises as a luminous ball or balls, consuming only part of the hydrogen. As the hydrogen is consumed, fresh hydrogen diffuses into the flame more rapidly than the other gases, and therefore the mixture that is burning is not the same as that in the rest of the containing vessel. This explanation is rendered highly probable by the observation that particles of finely divided platinum or palladium may be maintained red hot by suspension in a mixture of 4 per cent hydrogen and air. Combustion of the mixture produces a temperature less than 350° C., but the high rate of diffusion of the hydrogen enables a far higher temperature to be maintained at the metallic surface.

Although Goldmann's explanation of the mechanism of flame propagation in these mixtures is entirely acceptable, it seems undesirable, and possibly dangerous, to accept his conclusion that the two limits of inflammability are those observed with downward propagation of flame. If we did so, we should term a 6 per cent hydrogen-air mixture and a 5.6 methane-air mixture noninflammable. Both these mixtures propagate flame upward indefinitely, and if ignited near the floor of a closed room would produce pressures of the order of 1 and 4 atmospheres, respectively, and mean temperatures of about 350° and 1,200° C. Such conditions would burst windows and burn men. It is inconceivable that anyone who has seen a 5.6 per cent methane-air flame traveling up a long tube would term this mixture noninflammable, although it fails to propagate flame downward.

Mallard (*9*) attempted to deduce limits of inflammability from curves expressing the relation between the composition of mixtures in various proportions and the speed of propagation of flame therein. By extrapolating the curves to zero speed of flame he thought to find the composition of the limit mixture; but later it was shown that in a limit mixture the speed of flame was by no means zero.

A few regularities, set forth in the following paragraphs, have been discovered; occasionally they may give a useful indication of the limits of inflammability for mixtures which have not been experimentally investigated.

1. Le Chatelier and Boudouard (*24*) determined the lower limits of some 31 gases and vapors for downward propagation of flame. With the exception of hydrogen and carbon disulphide, which gave low figures, the heats of combustion ranged between 9 and 13 calories per unit volume (23.5 liters at 15° C.) of the limit mixture; for the majority of mixtures the range was 12 to 13 calories.

2. Burgess and Wheeler (*36*) found that for the first five members of the paraffin series of hydrocarbons the calorific values of the lower limit mixtures (propagation of flame throughout a globe) were closely constant; therefore the lower limit of any of these, and probably of other paraffin hydrocarbons, could be calculated from the lower limit of any other. This regularity is, however, not so close for limits for upward propagation of flame for these hydrocarbons (*111*).

3. White (*78*) found approximately constant calorific values for 11 of 12 volatile solvents, for propagation of flame upward or downward in lower limit mixtures, or downward in higher limit mixtures; the values are different for different directions of propagation of flame. Carbon disulphide was the exception. For the other 11 solvents the products of combustion were similar (nitrogen, carbon dioxide, water vapor, etc.), therefore the temperatures attained were approximately equal. Hence, the effective ignition temperature for propagation of flame in these gases seems to be approximately constant for the same direction of propagation of flame. The actual ignition temperatures of these vapors are much lower, presumably because normally a much longer time is available for ignition than is available when flame is self-propagating through a mixture. The effective ignition temperature for downward propagation for the 11 solvents, the 5 paraffins, for ethylene, propylene, butylene, and carbon monoxide, is about 1,400° C., uncorrected for radiation losses. The figures are much less (*98*) for hydrogen, hydrogen sulphide, and acetylene.

When the initial temperature of the mixture was increased several hundred degrees (*44*, *101*), the limits were widened and therefore the heat of combustion at each limit was less; but the two factors usually balanced each other so that the flame temperature of the limit mixture remained constant. This was true for the lower limits of methane, ethylene, acetylene, and pentane, and for the higher limits of hydrogen and carbon monoxide. The lower limit temperatures of hydrogen rose nearly 100° and those of carbon monoxide fell nearly 100° as the initial temperature of the mixture was increased.

4. Le Chatelier's law, expressing the limits of mixed inflammable gases and vapors in terms of the limits of the individual gases and vapors, is fairly accurate for many mixtures but inaccurate for others.

Y. Nagai has offered an explanation for certain deviations from Le Chatelier's law (*143*). He assumes that if two gases individually have the same calculated temperature of their limit-mixture flames, which he calls the theoretical flame-propagation temperatures (TFPT), the mixtures of these gases will obey the law. If, however, the TFPT's are not equal, the mixed gases will not obey the law. The gas of higher TFPT does not play the part suggested by Le Chatelier's law until the amount of the other gas is increased in lower

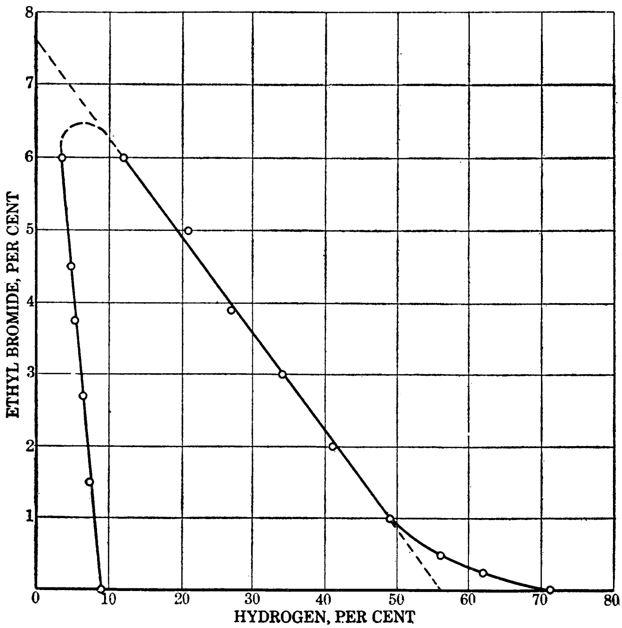

FIGURE 2.—Limits of inflammability of mixtures of hydrogen and ethyl bromide

limit mixtures or decreased in higher limit mixtures. Over a greater or less middle range of composition the limit mixtures of some pairs of gases have constant TFPT's, and therefore these mixtures obey the law over that range. To calculate the composition of any limit mixture in the middle range it is therefore only necessary to assume for the limit mixture of one of the gases a composition which would have the same TFPT as the other gas.

Mixtures of hydrogen and ethyl bromide (*113*) provide a good example in support of Nagai's argument. In Figure 2 are plotted the lower and higher limits of mixtures of hydrogen and ethyl bromide; for example, one higher limit mixture contains about 41 per cent hydrogen and 2 per cent ethyl bromide, the rest of the mixture being air. If Le Chatelier's law were followed by the whole range of these mixtures, then the straight line joining the lower or higher limit point for hydrogen with the corresponding (undetermined) limit point for ethyl bromide would give the corresponding limits of all mixtures of these gases. The theoretical flame-propagation temperature of hydrogen is presumably less than that of ethyl bromide; hence, the addition of the first 1 per cent of ethyl bromide to the higher limit hydrogen mixture necessitates a rapid fall in the hydrogen present in order that the flame temperature shall approach that of ethyl bromide. Thereafter, from 1 to 6 per cent of ethyl bromide, the limits fall on a straight line, as required by Le Chatelier's law, because the flame temperatures are equal. Extrapolation of this line cuts the x axis at $x=56$. The TFPT of the mixtures is therefore equal to that of a 56 per cent hydrogen-air mixture, which can be calculated. Moreover, the position of any point on the straight part of the higher limit curve can be calculated on the assumption that the effective limit of hydrogen is 56 per cent and of ethyl bromide 7.6 per cent.

Although Nagai has adduced many instances of pairs of gases or vapors which appear to support his views (*113, 115, 116, 124, 125, 127, 140*) there are others which can not fall into line. For example, the hydrogen-methane mixtures follow the law of Le Chatelier fairly well, but their TFPT's are far apart. Again, the hydrogen sulphide-hydrogen mixtures (fig. 33) and the hydrogen sulphide-methane mixtures (fig. 34) present such results as can not be interpreted by Nagai's ideas.

5. The lower limits of methane, ethane, propane, and butane (observed in a 3-inch tube, upward inflammation) are given by the empirical formula 8.62 $(n+0.647)$, when $n=1, 2, 3$, or 4, respectively, in the general formula of the paraffins, C_nH_{2n+2}. The empirical formula holds also for any mixture of these gases, n being, then, the average value for the mixture. It is not improbable that the same formula is satisfactory for all paraffins and for all mixtures of paraffins. (See p. 62.)

It is apparent that the theoretical treatment of limits of inflammability is meager; it is bound up with the unsolved problem of the theory of flame propagation in general.

EXPERIMENTAL RESULTS

In accord with the preceding argument the results collected for individual gases will be found arranged as follows: First, the results of experiments on propagation of flame upward in large volumes of quiescent gas which are at atmospheric pressure during the passage of the flame; second, the results for other directions of propagation in similar circumstances; third, the results observed in smaller vessels open at one end, so that the pressure is constant during the experiment, or totally closed, so that pressure varies at a rate and to an extent which depends on the dimensions of the vessel used. The first results may be considered the limits of inflammability of the components named, a physicochemical property independent of external conditions, at atmospheric temperature and pressure; the second are the limits under restricting conditions of direction of propagation; the third are the limits under still more restricted conditions, such as the dimensions of the vessel used for observation.

HYDROGEN

HYDROGEN IN AIR

Flames in hydrogen-air mixtures are exceedingly pale; the flame in a limit mixture is almost or quite invisible even in a completely darkened room. Ignition by a "fat" electric spark gives rise to a very pale flame, but a "thin" blue spark gives an invisible flame. Proof that an invisible flame has traveled to the top of a vertical tube may be obtained by admitting a small quantity of pure hydrogen to the top of the tube a second or so before the flame is expected to arrive there. If the flame reaches the rich mixture, a sharp explosion is observed. Analysis of a limit mixture after the passage of a flame would not prove whether flame had traveled throughout the length of the tube, for the flames in weak mixtures burn only a fraction of the hydrogen in the tube.

When a spark was passed near the lower confines of a weak hydrogen-air mixture contained in a large receiver 6 feet high and 12 inches square in section, the following observations were made:

Four per cent hydrogen.—A vortex ring of flame was seen just above the spark gap; it rose, expanding for about 16 inches, then broke and disappeared.

Four and two-tenths per cent hydrogen.—A similar ring of flame was formed. On breaking it resolved itself into an exceedingly faint cloud, or collection of small balls of flame, which traveled steadily to the top of the containing vessel—a distance of more than 5 feet.

Four and four-tenths, 4.6, 4.8, 5.2, and 5.6 per cent hydrogen.—In each mixture a vortex ring of flame rose about 16 inches, then broke into segments which subdivided into balls of flame that traveled to the top of the vessel. An increasing fraction of the hydrogen present was burned as the amount of hydrogen present was increased; the strongest mixture, 5.6 per cent hydrogen, showed about 50 per cent combustion.

When a longer narrower tube, 15 feet long and 2 inches in diameter, was used, no flame was seen with 4.2 per cent hydrogen, but with 4.4 per cent a globular flame traveled at uniform speed through the whole length of the tube. There seems to be no doubt, therefore, that these flames were self-propagating and capable of traveling indefinitely. They left much unburned gas behind because their lateral speed of propagation was much less than their vertical speed, which was largely due to convection.

In a wide space, therefore, the lower limit of inflammability of hydrogen in air is 4.1 ± 0.1 per cent.

The hydrogen was not wholly burned in an upward propagating flame in a tube 2 inches in diameter until present to the extent of 10 per cent (*49*).

With a continued source of ignition, such as a succession of sparks or a small flame burning from a jet, the appearance presented in weak mixtures was that of a continued thin thread of flame shooting upward and expanding into a flame cloud. As the hydrogen became consumed the thin flame gradually shortened until it disappeared.

Complete combustion of a layer of the limit mixture, 4.1 per cent hydrogen, would heat the products to a temperature less than 350° C. The ignition temperature of hydrogen in air is about 585° C. An ingenious explanation of this anomaly has recently been given. (See p. 13.)

The higher limit of inflammability in large vessels has not been determined, but experiments in a wide, short vessel and in a long, narrow vessel have indicated (*66*) that the higher limit in a large volume is about 74.2 per cent hydrogen. The figures for both limits refer to gases saturated with water vapor at 18° to 19° C. A recent determination in a tube 7 cm. in diameter and 150 cm. in length gave the higher limit as 74.4 per cent hydrogen (*149*).

The limits for downward propagation have not been determined in large vessels.

Observations in small vessels.—The lower limit, upward propagation, was not raised above 4.3 per cent hydrogen as the diameter of the observation tube was reduced to 1 inch, whether the tube was open or closed behind the flame (*66*, *67*, *90*). The higher limit, upward propagation, was reduced to 73 per cent in a closed tube 1 inch in diameter (*90*). Table 1 gives the results observed for other directions of propagation of flame.

TABLE 1.—*Limits of inflammability of hydrogen-air mixtures in small vessels*

HORIZONTAL PROPAGATION OF FLAME

Dimensions of tube, cm.		Firing end	Limits, per cent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
7.5	150	Closed	6.5		Half saturated	*90*
5.0	150	do	6.7		do	*90*
2.5	150	do	7.15		do	*90*
2.5	150	Open	6.2		Saturated	*69*
.9	150	do	6.7	65.7	do	*66*

DOWNWARD PROPAGATION OF FLAME

Diameter	Length	Firing end	Lower	Higher	Content of aqueous vapor	Reference No.
21.0	31	Open	9.3		Saturated	*49*
8.0	37	Closed	8.9	[1] 68.8	do	*53*
7.5	150	do	8.8	74.5	Half saturated	*90*
7.0	150	do		74.5		*149*
6.2	33	Open	8.5		Saturated	*28*
5.0	150	Closed	9.0	74.0	Half saturated	*90*
5.0	65	Open	8.9	71.2		*113*
4.0	50	Closed	8.8		Saturated	*49*
2.5	150	do	9.4	71.5	Half saturated	*90*
2.5	150	Open	9.7		Saturated	*69*
1.9	40	Closed	9.45	66.4	do	*90*
1.9	40	do	9.45	65.25	do	*73*

PROPAGATION THROUGHOUT A SPHERICAL VESSEL

	Firing end	Lower	Higher	Content of aqueous vapor	Reference No.
Capacity, not stated	Closed	9.2		Saturated	*69*
Capacity, 1,000 c. c	do	8.7	75.5	do	*28*
Capacity, 35 c. c	do	9.4	[1] 64.8	do	*18*

[1] This figure would probably have been increased had a stronger spark been used; a spark which is strong enough to ignite a lower limit mixture may be too weak to ignite a higher limit mixture (*66*).

In round figures, therefore, the limits for hydrogen in air may be stated as follows for gases saturated with water vapor at laboratory temperature and pressure; the figures for the higher limit, downward propagation, are based on observations in closed tubes, in which the mixture was under rapidly varying pressure during the experiment:

Limits for hydrogen-air mixtures saturated with water vapor

	Per cent
Upward propagation	4. 1–74
Horizontal propagation	6. 0 --
Downward propagation	9–74

Influence of pressure.—Figure 3 shows the various results obtained in determinations of the limits of hydrogen in air under pressures greater than atmospheric (*53, 119, 135*), except for one series (*28*),

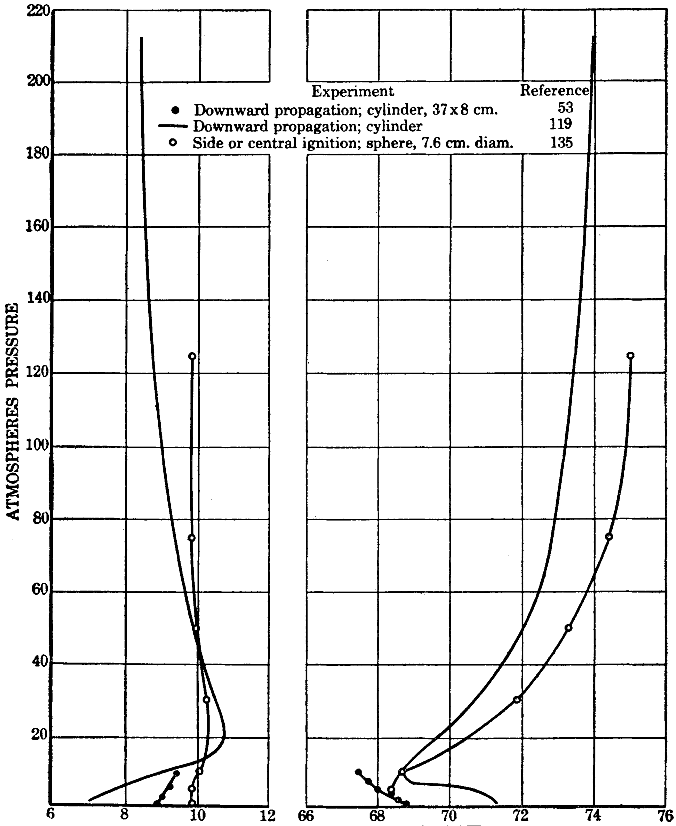

FIGURE 3.—Effect of pressure above normal on the limits of hydrogen in air

which showed no change in the lower limit over a range from 0.5 to 4 atmospheres. The differences are not as considerable as may appear at first sight, except for lower-limit mixtures at pressures of 1 to 5 atmospheres. Apparently, these differences are to be ascribed to different interpretations of experimental results rather than to the experiments themselves; the criterion was 100 per cent combustion for the series indicated in the figure by small circles but only about 80 per cent for the series represented by the unbroken line. In general, it appears that the limits are at first narrowed by increase of pressure above atmospheric, but at higher pressures are steadily widened.

Influence of temperature.—Three sets of temperature observations have been made (*18, 87, 101*). Table 2 gives those that are probably

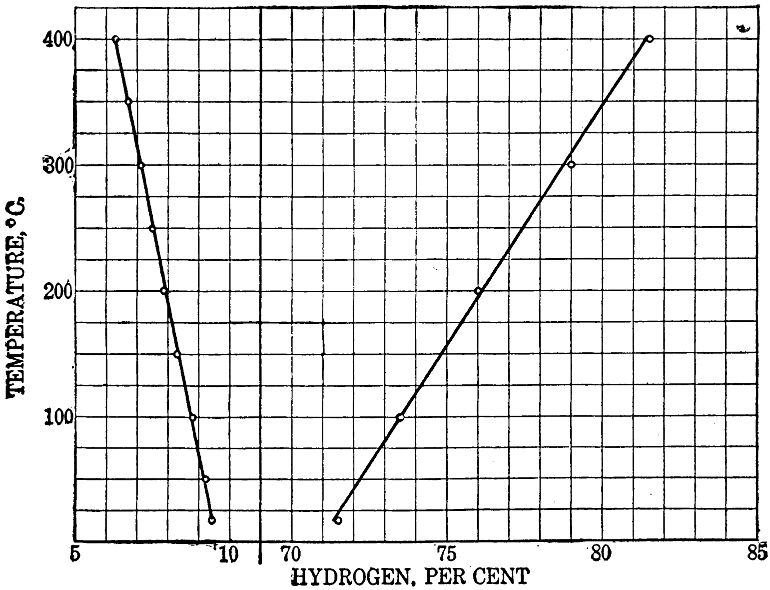

FIGURE 4.—Limits of inflammability of hydrogen in air (downward propagation), showing influence of temperature

the most reliable (*101*), determined in a closed tube 2.5 cm. in diameter and 150 cm. long, with downward propagation of flame.

TABLE 2.—*Influence of temperature on the limits of hydrogen in air, downward propagation of flame*

Temperature, ° C.	Limits of inflammability, per cent hydrogen		Calculated flame temperatures, ° C.	Temperature, ° C.	Limits of inflammability, per cent hydrogen		Calculated flame temperatures, ° C.
	Lower	Higher			Lower	Higher	
17±3	9.4	71.5	815–980	250	7.5		860
50	9.2		820	300	7.1	79.0	875–970
100	8.8	73.5	835–970	350	6.7		890
150	8.3		830	400	6.3	81.5	900–980
200	7.9	76.0	845–975				

These results are shown graphically in Figure 4. An independent result (*141*) extends the higher limit curve to 540° C., at which a 90.45 per cent mixture was inflamed.

The flame temperature necessary to insure propagation of flame downward is apparently much above the ignition temperature of hydrogen in air, 585° C.; and, what is more important, increase in initial temperature of the mixture does not cause the calculated flame temperature to fall toward the ignition temperature but has the opposite effect for lower limit mixtures; this observation awaits explanation.

HYDROGEN IN OXYGEN

That the lower limit of hydrogen in an "atmosphere" of pure oxygen will differ little, if at all, from the lower limit in air is to be expected; but the higher limit in oxygen will be much greater than in air.

Experiments with hydrogen-oxygen mixtures have not been conducted in large vessels, but one observation (*4*) in a small vessel gave a figure as low as 5 per cent for the lower limit; probably a mixture which contains a few tenths more than 4 per cent will prove to be the lower limit for upward propagation. The flame will presumably travel in isolated fragments as in the corresponding hydrogen-air mixtures, and will be invisible. The higher limit figure for upward propagation seems to be about 96 per cent hydrogen (*3*, *4*).

For downward propagation of flame in small vessels the lower limit appears to be about 9 or 10 per cent hydrogen and the higher limit about 92 or 93 per cent (*6*, *10*, *12*, *28*, *73*).

For complete combustion of the gas in a 35-c. c. spherical globe with side ignition the limits were 9.6 to 90.9[6] per cent hydrogen (*18*).

Influence of pressure.—Experiments in a steel cylinder 3 inches in diameter and 5 inches long, axis vertical, indicated that the lower limit of hydrogen in oxygen was not materially altered by increase of pressure to 122 atmospheres but lay between 8 and 9 per cent throughout this range of pressure. Ignition was by spark or hot wire, and the direction of propagation of flame was apparently downward (*75*).

At pressures less than atmospheric the higher limit of hydrogen in oxygen is slightly reduced as the pressure falls. The higher limit does not fall below 90 per cent hydrogen (central ignition in a globe) until the pressure is about 100 mm., and at that stage the insuring of an adequate source of ignition becomes a difficult problem; a powerful source of ignition might insure propagation of flame indefinitely in a hydrogen-oxygen mixture of 90 per cent or a little more hydrogen at pressures below 100 mm. (*48*). The lower limit does not rise above 11 per cent hydrogen until the pressure is below 9 mm.

Influence of temperature.—The limits were found to be widened appreciably by increase of temperature from 15° to 300° C. In a 35-c. c. closed bulb the limits were 9.6 to 90.9 per cent at 15° C. and 9.1 to 94 per cent at 300° C. (*18*).

HYDROGEN IN OTHER ATMOSPHERES

Atmospheres of composition between air and pure oxygen.—For downward propagation of flame in a Bunte burette the lower limit fell gradually from 9.45 per cent of hydrogen in air to 9.15 per cent in nearly pure oxygen. The higher limit rose from 65 per cent hydrogen in air to 81 per cent in a 40 per cent oxygen mixture, 86 per cent in a 56 per cent oxygen mixture, and 91.6 per cent in nearly pure oxygen (*73*).

Atmospheres of air and nitrogen (air deficient in oxygen).—The limits of inflammability of hydrogen in all mixtures of air and nitrogen, or air from which part of the oxygen has been removed, can be read from one of the curves in Figure 5. The determinations were made in

---

[6] Probably too low. See footnote, Table 1, p. 18.

a tube 6 feet long, 2 inches in diameter, with upward propagation of flame at atmospheric pressure during propagation (*145*). From the ordinates of the "nose" of this curve it may be calculated that no mixture of hydrogen, nitrogen, and air is capable of propagating flame at atmospheric pressure and temperature if it contains less than 4.9 per cent of oxygen (*123*).

For some purposes the results are more useful when expressed (*148*) as in Figure 6.

For example, a mixture that contains $H_2=20$ per cent, $O_2=6$ per cent, and $N_2=74$ per cent is inflammable. If 2 per cent of the

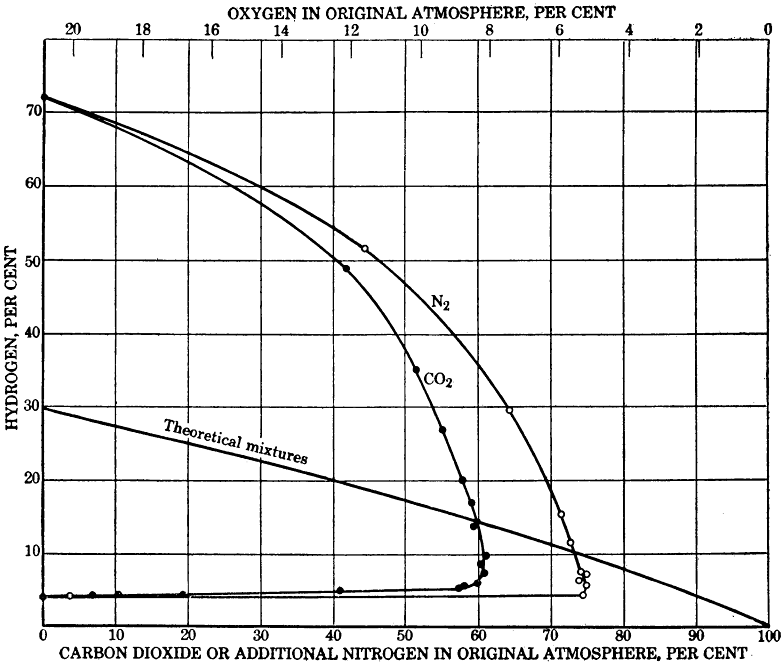

FIGURE 5.—Limits of inflammability of hydrogen in atmospheres of air and carbon dioxide or nitrogen

oxygen were replaced by nitrogen the mixture would not be inflammable but would become so by admixture with a suitable amount of air. In Figure 6 "impossible" mixtures mean those that can not be produced by mixing air, nitrogen, and hydrogen. For more detailed explanations, reference may be made to the corresponding section on methane limits in mixtures of air and nitrogen (pp. 44 to 49).

Atmospheres of air and water vapor.—The effect of considerable quantities of water vapor on the limits of hydrogen in air was shown by the following results obtained in a Bunte burette with downward propagation of flame (*28*). The limits are expressed as percentages of hydrogen in the dry gases.

Effect of water vapor on limits of hydrogen in air

Temperature, ° C.	Hydrogen in the dry gases, per cent		Water vapor present, mm.	Temperature, ° C.	Hydrogen in the dry gases, per cent		Water vapor present, mm.
	Lower	Higher			Lower	Higher	
17	9.45	66.4	14.4	60.5	11.9	61.2	152.4
34.5	9.7	63.6	40.6	78.1	19.4	38.5	328.4

Atmospheres of oxygen and carbon dioxide.—For experiments in a closed 35-c. c. globe with side ignition the limits were 11.9 to 68.2

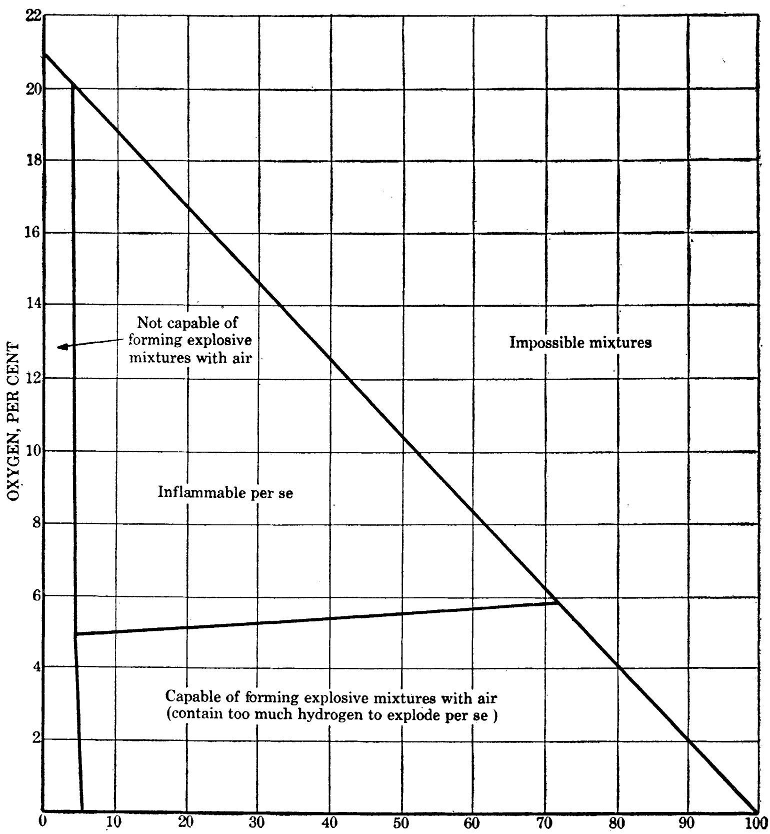

FIGURE 6.—Relation between the quantitative composition and the explosibility of mixtures of hydrogen, oxygen, and nitrogen

per cent hydrogen in a mixture of 20.9 per cent oxygen and 79.1 per cent carbon dioxide, in comparison with 9.4 to 64.8 per cent in air, in the same apparatus (*18*). The higher limit result is unexpectedly greater in the artificial atmosphere than in air; a similar result, however, had been obtained earlier (*10*). Reasons have already been given (footnote, Table 1, p. 18) for thinking that the figure 64.8, higher limit in air, is too low.

Influence of temperature.—Some irregular results have been obtained for hydrogen limits at various temperatures in an atmosphere of 21 per cent oxygen and 79 per cent carbon dioxide, but these results require confirmation (*18*).

Atmospheres of air and carbon dioxide.—The limits of inflammability of hydrogen in all mixtures of air and carbon dioxide can be read from one of the curves in Figure 5. The determinations were made in a tube 6 feet long and 2 inches in diameter, with upward propagation of flame at atmospheric pressure during propagation (*123, 145*).

Some earlier observations (*28*) show, as might be expected, a more rapid narrowing of the limits in Bunte burette experiments. Others (*83*) may be mentioned, but they can hardly be accepted without confirmation, because they indicate several improbable conclusions—for example, the conclusion that the lower limit of hydrogen is reduced from 6.5 per cent in air to 3 per cent in an atmosphere composed of air and 3 or 4 per cent of carbon dioxide.

Air mixed with vapors of various chlorinated hydrocarbons.—A series of results showing the lower and higher limits of hydrogen in air containing increasing amounts of trichlorethylene at 14°, 25°, and 35° C. have been reported. They were observed in small burettes 15 mm. in diameter and so are of limited value (*96*). Similar experiments with the vapors of other chloro derivatives at laboratory temperatures were reported in an earlier communication (*94*).

Atmospheres of air and helium.—When thin rubber balloons 2.5 inches in diameter were filled with various mixtures of hydrogen and helium and a lighted match or a white-hot platinum spiral was used to burn a hole in the fabric, the hydrogen could be raised to 26 per cent before the mixture became inflammable, but if the hydrogen exceeded 28 per cent the mixture would burn. Hence, to dilute the helium used for airships with more than about 26 per cent of hydrogen (*71*) would not be safe.

Experiments by the present writers show that homogeneous mixtures of helium, hydrogen, and air will propagate flame when the proportion of hydrogen to helium is much less than that indicated above. When so little as 8.7 per cent hydrogen is present in admixture with helium, it is possible to make with this mixture a blend with air which will propagate a weak flame up through the central part of a tube 6 feet long and 2 inches in diameter. The complete set of observations is shown in Table 3.

TABLE 3.—*Limits of inflammability of mixtures of hydrogen and helium in air, upward propagation of flame in a 6-foot tube 2 inches in diameter*

Original gas mixture, per cent		Limits of inflammability, per cent	
Hydrogen	Helium	Lower	Higher
100	0	4.2	71.5
58.1	41.9	7.1	76.2
27.9	72.1	16.6	79.2
19.3	80.7	24.9	81.2
10.7	89.3	51.3	80.3
8.7	91.3	69.8	

The mixture which contained 19.3 per cent hydrogen, the rest being helium, had very wide limits of inflammability. Flame traveled rapidly and with some violence through mixtures with air which lay well within these limits, although the earlier balloon experiments had seemed to show that these mixtures were not inflammable. No mixture is safe for use in an airship unless it contains less than 8.7 per cent hydrogen in admixture with helium.

Dilution of electrolytic gas ($2H_2+O_2$) with gases, inert or otherwise.—In the early part of the last century the question of the amount of diluent which, mixed with electrolytic gas, would bring a mixture to its limit of inflammability aroused much interest, which has been revived from time to time since. Some of the diluents were inert, others were not. Table 4 gives the results.

TABLE 4.—*Percentage of electrolytic gas which, with the diluent named, is at the limit of inflammability*[1]

Diluent	Percentage and authority				
	Davy (*3*)	Turner (*4*)			
Hydrogen	11–14	10–12.5	21–23 (Bunsen, *12*)		
Oxygen	10–12.5	6.7–7.7	8.6–9.7 (Bunsen, *12*)	13.9 (Eitner, *28*)	
Air		7.7–9.1			
Nitrogen			14.3 (Henry, *5*)	19.2 (Eitner, *28*)	
Carbon dioxide		25–33	25–27 (Regnault and Reiset, *6*).	25.7–26.2 (Bunsen, *12*)	30.0 (Eitner, *28*)
Hydrochloric acid	30–40	20–25			
Silicon fluoride	55–57				
Sulphur dioxide		33–50			
Nitrous oxide	8–9	10–12.5			
Carbon monoxide		20–25			
Hydrogen sulphide	33–40	67–80	50 approx. (Budde, *38*)		
Ammonia		50–67			
Methane	50–57		76–78 (Tanatar, *26*)	76 (Misteli, *29*)	
Ethane			85.4–85.7 (E. von Meyer, *8*).		
Ethylene	67–75	50–67	78.6–80.8 (E. von Meyer, *8*).	75 (Misteli, *29*)	80 (Jorissen, *98*)
Propylene			88–89 (Tanatar, *26*)	85–86 (Misteli, *29*)	
Trimethylene			88–89 (Tanatar, *26*)		
Acetylene			50 (Tanatar, *26*)		
Cyanogen			40 (Henry, *5*)		
Coal gas		67–80			

[1] Of 2 figures, the lower represents a noninflammable mixture, the higher an inflammable mixture.

Limit mixtures made by diluting electrolytic gas with hydrogen and oxygen become higher and lower limits, respectively, of hydrogen in oxygen. On this basis some correlation of the results can be made. Davy's figures for hydrogen and oxygen dilution suggest upward inflammation for the former and downward for the latter; possibly his usual practice was to test a mixture for downward propagation, but when using a very light mixture he inverted the experimental tube to prevent the gases from streaming out. Turner's figures for hydrogen and oxygen dilution suggest upward inflammation. Bunsen's figures are probably for upward propagation, but it seems that he used a very weak source of ignition for the hydrogen experiments. Regnault and Reiset, Von Meyer, Tanatar, Misteli, Eitner, and Jorissen observed downward propagation.

Uncertainty as to some of the methods used and the small scale of the experiments make it impossible to draw exact conclusions from the results in Table 4. In general, however, it is evident that the inert gases of higher heat capacity are more effective in rendering electrolytic gas nonexplosive than those of lower heat capacity. Moreover, when the diluent is itself inflammable and therefore is in competition with the hydrogen for the oxygen of the electrolytic gas, it is even more extinctive of flame than the inert gases, provided that it contains several atoms capable of uniting with oxygen.

Atmosphere of chlorine.—In a eudiometer tube about 1 cm. in diameter, with gases standing over sulphuric acid, the limits of hydrogen in chlorine, apparently for downward propagation of flame, were 8.1 to 85.7 per cent. Radiation from burning magnesium ignited mixtures containing between 9.8 and 52.5 per cent hydrogen (*63*).

AMMONIA

AMMONIA IN AIR

In a spherical bulb of 0.5 liter capacity the limits of ammonia in air were 16.5 to 26.8 per cent; the mixture contained 1 per cent water vapor. No explosion was obtained in a Bunte burette with a 2-mm. spark gap, but continuous combustion was observed during the passage of a succession of sparks when the composition of the gas mixture lay between 19 and 25 per cent ammonia (*51*).

In a closed tube 7.5 cm. in diameter the limits for upward propagation were 17.1 to 26.4 per cent and for horizontal propagation almost the same; but no mixture was capable of propagating flame downward at atmospheric temperature. In a narrower tube 5 cm. in diameter the limits for upward propagation were 16.1 to 26.6 per cent ammonia and for horizontal propagation 18.2 to 25.5 per cent (*80*).

Influence of temperature.—The range of inflammability of ammonia-air mixtures is widened as the temperature is raised to 450° C., as shown by Figure 7. A closed tube 5 cm. in diameter was used. The calculated flame temperature for the lower limits, horizontal propagation, is almost constant; therefore the preliminary heating of the mixture seems merely to save the necessity, so to speak, for the liberation of an equivalent amount of heat by combustion (*80*).

AMMONIA IN OXYGEN

From observations with a split Bunsen flame the lower limit of ammonia in oxygen was given as somewhat less than 15 per cent and the higher limit as somewhat greater than 80 per cent (*52*).

In a closed tube 7.5 cm. in diameter the lower limit for upward propagation was 14.8 per cent ammonia, and for horizontal and downward propagation was 15.6 and 17.3 per cent, respectively. In a narrower tube, 5 cm. in diameter, the limits for the three directions were (*80*): Upward, 15.3 to 79 per cent ammonia; horizontal, 16.7 to 79 per cent; and downward, 18.1 to 79 per cent. In a narrower tube, probably about 1.5 cm. in diameter, the figures for downward propagation were 18.9 to 69.5 per cent ammonia (*99*).

Influence of temperature.—In a closed tube 5 cm. in diameter the following figures were obtained for the lower limit (*80*):

Lower limit of ammonia in oxygen in closed tube

Temperature ° C.	18	250	450
Horizontal propagation per cent	16.7	14.8	12.6
Downward propagation do	18.1	15.8	13.5

AMMONIA IN OTHER ATMOSPHERES

Atmospheres of nitrogen and oxygen.—The gradual approach of the limits of ammonia in nitrogen-oxygen mixtures, as the atmosphere becomes less rich in oxygen, has been shown in curves to be found in the original publication (*99*).

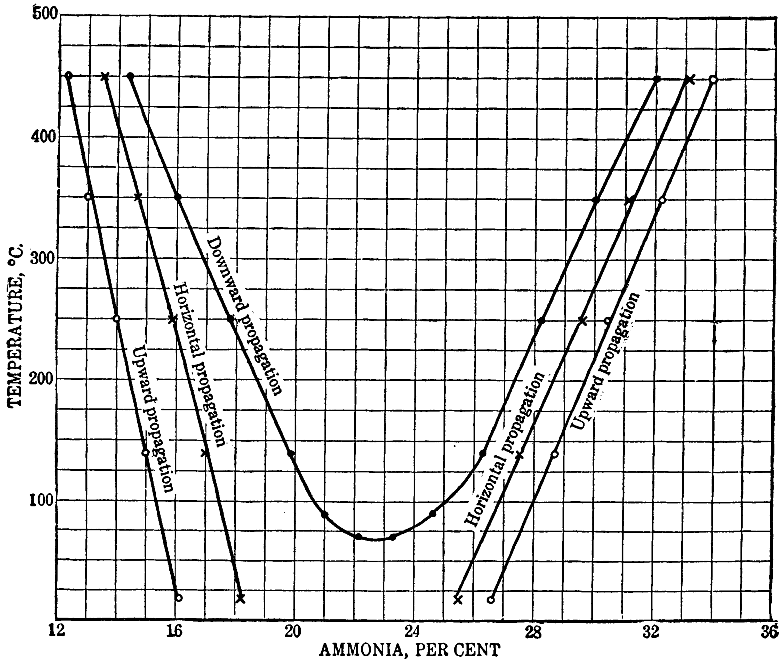

FIGURE 7.—Limits of inflammability of ammonia in air, showing influence of temperature and of direction of propagation of flame

HYDROGEN SULPHIDE

HYDROGEN SULPHIDE IN AIR

In a horizontal tube 6 cm. in diameter and open at both ends the limits of hydrogen sulphide in air were 5.9 to 27.2 per cent (*85*).

In closed tubes 1.5 meters in length and of different diameters the limits observed for mixtures containing 1 per cent water vapor were as follows (*90*):

Limits of hydrogen sulphide in air, 1 per cent water vapor, in closed tubes, per cent

Diameter of tube, cm.	Direction of propagation					
	Upward		Horizontal		Downward	
	Lower	Higher	Lower	Higher	Lower	Higher
	4.40	44.5	5.40	26.6	6.05	19.8
7.5	4.30	45.5	5.30	35.0	5.85	21.3

HYDROGEN SULPHIDE IN OTHER ATMOSPHERES

Atmospheres of nitrogen and oxygen.—The lower limit of hydrogen sulphide, observed in a closed glass tube 150 cm. long and 5 cm. in diameter, with downward propagation of flame, fell steadily from 6.60 per cent in 15.6 per cent oxygen to 4.93 in 66.6 per cent oxygen (*133*).

HYDROGEN CYANIDE (PRUSSIC ACID)

The limits of hydrogen cyanide in air are said to be 12.75 to 27 per cent, but the experimental conditions are not stated (*93*).

CARBON DISULPHIDE

CARBON DISULPHIDE IN AIR

The widest limits recorded for carbon disulphide in air are a lower limit of 1.06 per cent for a 7.5-cm. tube and limits of 1.41 to 50 per cent at 60° C. for a closed 5-cm. tube; these limits are for upward propagation in a roughly dried mixture (*78*).

For downward propagation in a closed 7.5-cm. tube the limits were 1.91 to 35 per cent; they were but slightly narrowed in narrower tubes—for example, in a 2.5-cm. tube the limits were 2.08 to 31 per cent (*78*). Two older determinations are replaced by the foregoing results (*27, 31*).

In an open 2-liter bottle the lower limit for downward propagation of flame was 1.94 per cent carbon disulphide (*24*).

It seems that in a large space at atmospheric pressure the lower limit of carbon disulphide will prove to be about 1.0 per cent for upward propagation and 1.9 per cent for downward propagation. The higher limit will be somewhat over 50 per cent.

Abnormal influence of small quantities of a third substance.—Introduction into the air of 0.1 or 0.2 per cent of certain substances raises the lower limit (downward propagation) of carbon disulphide from 2.0 to about 3.0. Examples of these are pentane, ether, acetaldehyde, ethylene, alcohol, and acetylene. Other substances of similar action, but not so marked, are benzene, acetone, hydrogen sulphide, acetic acid, methane, and hydrogen. Carbon monoxide, cyanogen, and nitrogen have little, if any, such action. It has been suggested that, as the lower limit of carbon disulphide is much less than would be expected from its heat of combustion in comparison with most other substances, its combustion is catalyzed by some such intermediate compound as carbon monosulphide. The effect of pentane, etc., on the lower limit of carbon disulphide is then due to the poisoning of the catalyst by the third substance (*133*).

CARBON DISULPHIDE IN OTHER ATMOSPHERES

Atmospheres of nitrogen and oxygen.—The lower limit of carbon disulphide, observed in a closed glass tube 150 cm. long and 5 cm. in diameter, with downward propagation of flame, fell steadily from 2.63 per cent in 11.8 per cent oxygen to 2 in air, and 1.24 in 93 per cent oxygen (*133*).

CARBON OXYSULPHIDE

One determination with carbon oxysulphide-air mixtures gave limits of 11.9 to 28.5 per cent, observed, perhaps, in a eudiometer tube (*42*).

CARBON MONOXIDE

CARBON MONOXIDE IN AIR

When a small spark was passed near the lower confines of a carbon monoxide-air mixture standing over water in a large receiver 6 feet high and 12 inches square in section, the following observations were made (*49*):

12.3 and 12.33 per cent carbon monoxide: A stout ring of flame was formed, but flame did not travel the whole length of the vessel.

12.5 and 12.7 per cent carbon monoxide: A ring of flame first formed, then broke and filled the upper part of the vessel with striæ of flame.

12.9 per cent carbon monoxide: A flame as wide as the vessel itself, with a strongly curved convex front, passed slowly and steadily up through the whole mixture.

In a wide space, therefore, the lower limit of carbon monoxide in air was concluded to be 12.5 per cent carbon monoxide.

The higher limit of inflammability has not been determined in large vessels, but experiments in a wide, short vessel and in a long, narrow vessel have indicated (*66*) that the higher limit in a large volume is about 74.2 per cent carbon monoxide.

The figures for both limits refer to gases saturated with water vapor at 18° to 19° C. When water vapor is removed as completely as is possible in laboratory experiments, the most explosive mixtures of carbon monoxide and oxygen can be ignited only by unusually powerful electric sparks; but simple drying by passage over calcium chloride has proved sufficient to raise the lower limit of carbon monoxide in air from 13.1 to 15.9 per cent (*109*). These results, obtained in a tube 2 inches in diameter, would doubtless be paralleled in large-scale experiments.

The limits for downward propagation of flame have not been determined in large vessels.

Observations in small vessels.—The lower limit for upward propagation observed in closed vessels rose somewhat as the diameter of the container was decreased; the limits were 12.8, 13.1, and 13.2 per cent in 3-inch, 2-inch, and 1-inch tubes, respectively. The corresponding higher limits were 72, 72, and 71 per cent (*90*).

Figure 8 indicates the limits for downward propagation in tubes of various diameters. For narrower tubes the observations were made with the upper end of the tube open; for the wider tubes both ends were closed (*24, 28, 53, 73, 90*). The limits narrow rapidly when the tube diameter falls below 1 cm. and coincide at a little above 2 mm.

The lower limit for horizontal propagation (*90*) for closed tubes is: 15.9 per cent CO for a tube 25 mm. in diameter, 14.1 per cent CO for a 50-mm. tube, and 13.6 per cent CO for a 75-mm. tube. The limits for propagation throughout a closed 35-c. c. globe with side ignition are 14.2 to 74.7 per cent (*18*).

In round figures, therefore, the limits for carbon monoxide in air saturated with water vapor at laboratory temperature and pressure are 12.5 to 74 per cent CO for upward propagation, 13.5 per cent CO (lower limit) for horizontal propagation, and 15 to 71 per cent CO for downward propagation. The figures for horizontal and downward propagation are based on observations in closed tubes in which the gases were under variable pressure during the experiment.

Influence of pressure.—Some old observations below atmospheric pressure showed limiting pressures of inflammability for downward propagation of flame in several carbon monoxide-air mixtures (*24*), as follows:

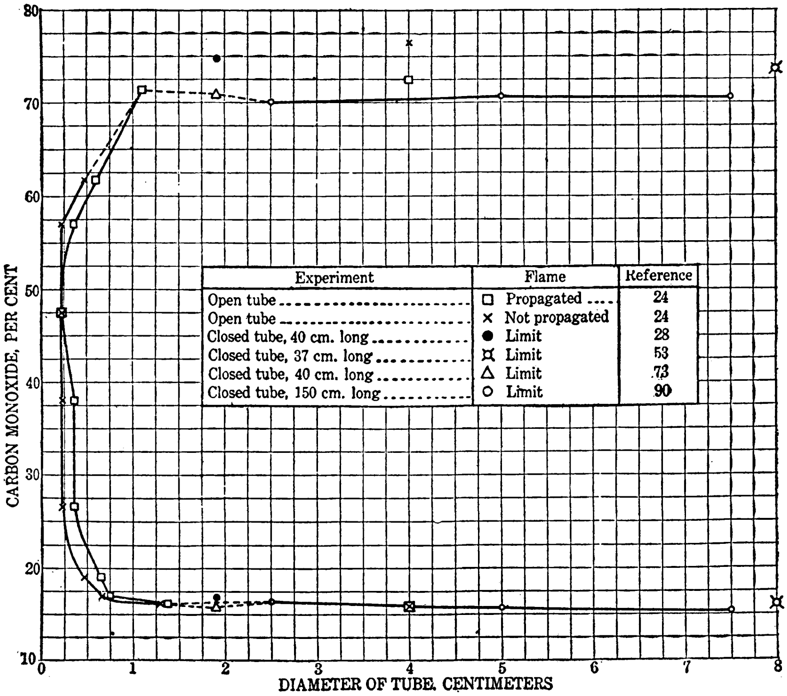

FIGURE 8.—Limits of inflammability of carbon monoxide in air (downward propagation), showing effect of diameter of tube

Limiting pressures for downward propagation of flame, carbon monoxide-air mixtures

Carbon monoxide	Pressure at which flame was propagated, mm.	Pressure at which flame was not propagated, mm.	Carbon monoxide	Pressure at which flame was propagated, mm.	Pressure at which flame was not propagated, mm.
16.4 per cent	454	411	27.9 per cent	89	79
18.6 per cent	144	112	46.5 per cent [1]	94	79

[1] The last mixture in this list could not be ignited at 76 mm. either by an induction-coil spark or by the flame of guncotton.

Figure 9 shows the limits of carbon monoxide in air under pressures greater than atmospheric (*53, 135, 139*). The effect of raising the initial temperature to 100° C. and of saturation with water vapor at 100° C. is shown for pressures of 32 and 64 atmospheres. The range of inflammability of dry mixtures is narrowed by increase of pressure.

Influence of temperature.—Four sets of observations have been made (*18, 24, 87, 101*) on the influence of temperature. Probably the most reliable data are those (*101*) in Table 5, determined in a closed tube 2.5 cm. in diameter and 150 cm. long, with downward propagation of flame.

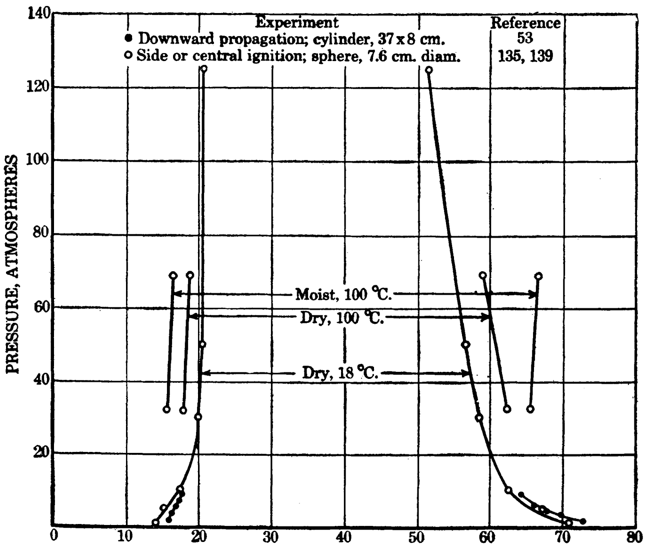

FIGURE 9.—Effect of pressures above normal on the limits of carbon monoxide in air

TABLE 5.—*Influence of temperature on limits of inflammability of carbon monoxide in air*

Temperature, ° C.	Limits of inflammability, carbon monoxide, per cent		Calculated flame temperatures, ° C.	Temperature, ° C.	Limits of inflammability, carbon monoxide, per cent		Calculated flame temperatures, ° C.
	Lower	Higher			Lower	Higher	
17±3	16.3	70.0	1,490–1,120	250	12.9		1,405
50	15.7		1,465	300	12.4	75.0	1,405–1,170
100	14.8	71.5	1,435–1,130	350	12.0		1,410
150	14.2		1,425	400	11.4	77.5	1,410–1,170
200	13.5	73.0	1,410–1,160				

The results shown in Table 5 are plotted in Figure 10 with two older approximate observations indicated by stars (*24*) which extend the lower limit results to nearly 600° C. A recent result (*142*) extends the higher limit curve to 727° C., at which a 92.9 per cent mixture was inflamed.

The flame temperature necessary to propagate flame downward is much above the ignition temperature (650° C.) of a jet of carbon monoxide in air. It is remarkable that the calculated flame temperatures for the higher limit mixtures should be so much lower than those for the lower limits; an ad hoc explanation is that the higher limit mixtures react more rapidly than those of the lower limit, as the law of mass action points to most rapid reaction, at constant temperature, in the mixture which contains 66.7 per cent carbon monoxide; but the difference in flame temperatures for the two limits seems too great to be explained thus.

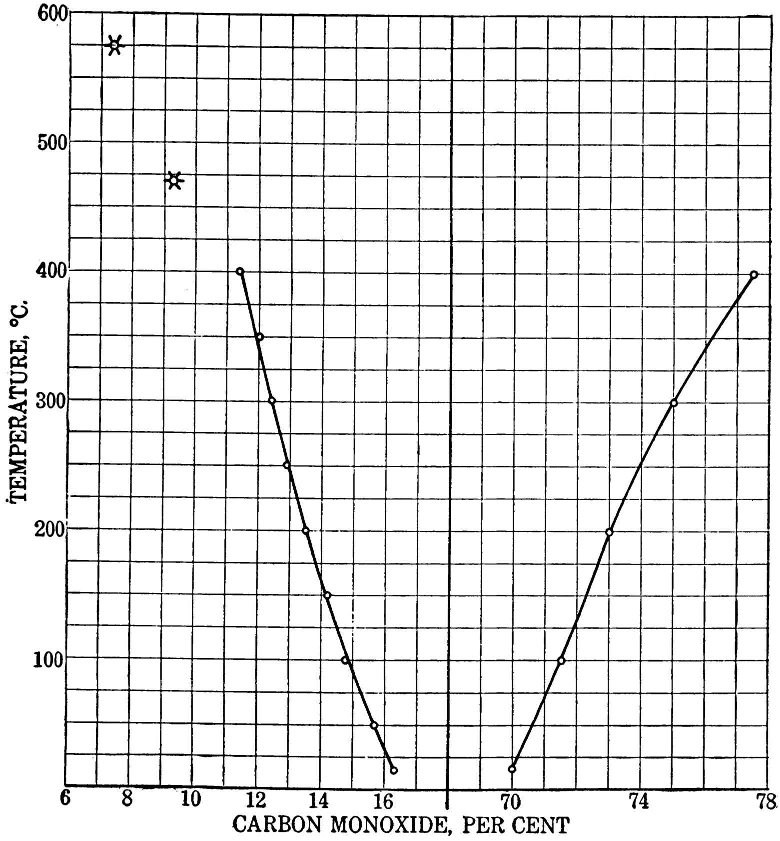

FIGURE 10.—Limits of inflammability of carbon monoxide in air (downward propagation), showing influence of temperature

The influence of temperature on the limits at high pressures is shown in Figure 9.

CARBON MONOXIDE IN OXYGEN

No experiments with carbon monoxide-oxygen mixtures in large vessels have been reported.

For downward propagation in a Bunte burette 19 mm. in diameter the limits found were 16.7 to 93.5 per cent in nearly pure oxygen (*73*). For propagation throughout a 35-c. c. globe with side ignition the limits were 15.5 to 93.9 per cent (*18*). Earlier observations are consistent with these figures, except that Wagner's low-limit figure was unduly high on account of his use of a weak source of ignition (*8, 10*).

Effect of pressure.—The limits were not appreciably narrowed until the pressure was reduced below 150 mm., when a moderately strong igniting spark was used. At lower pressures ignition becomes difficult to insure (*48*).

Influence of temperature.—The limits were found to be widened appreciably by increase of temperature (*18*). In a 35-c. c. closed bulb they were 15.5 to 93.9 per cent at 15° C. and 14.2 to 95.3 at 200° C.

CARBON MONOXIDE IN OTHER ATMOSPHERES

Atmospheres of composition between pure air and pure oxygen.—For downward propagation of flame in a Bunte burette 1.9 cm. in

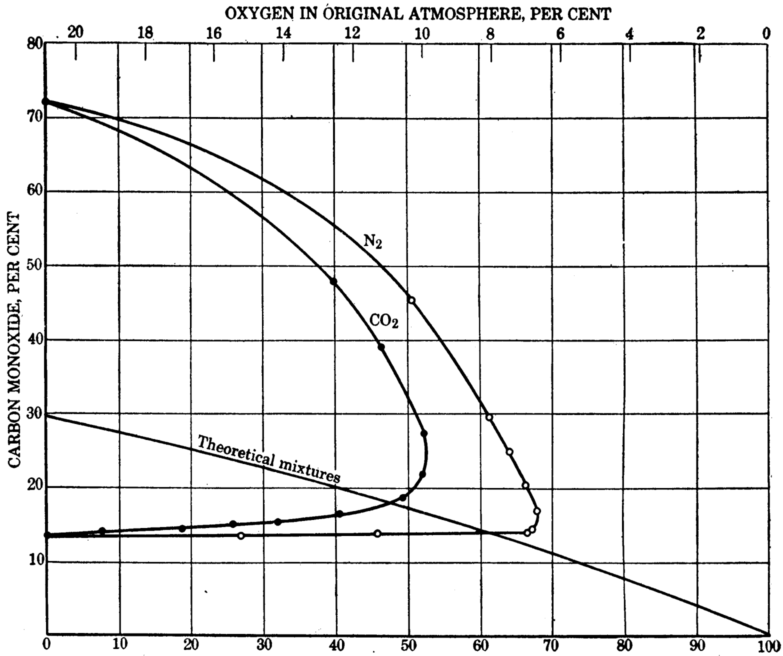

FIGURE 11.—Limits of inflammability of carbon monoxide in atmospheres of air and carbon dioxide or nitrogen

diameter the lower limit rose gradually from 15.6 per cent carbon monoxide in air to 16.7 per cent in nearly pure oxygen. The higher limit rose from 70.9 per cent carbon monoxide in air to 87.6 in a 51 per cent oxygen mixture, 91 per cent in a 71 per cent oxygen mixture, and 93.5 per cent in nearly pure oxygen (*73*).

Atmospheres of air and nitrogen (air deficient in oxygen).—The limits of inflammability of carbon monoxide in all mixtures of air and nitrogen, or air from which part of the oxygen has been removed, can be read from one of the curves in Figure 11. The determinations were made in a tube 6 feet long and 2 inches in diameter, with upward propagation of flame at atmospheric pressure during propagation

(*145*). From the ordinates of the nose of this curve it may be calculated that no mixture of carbon monoxide, nitrogen, and air is capable of propagating flame at atmospheric pressure and temperature if it contains less than 5.6 per cent of oxygen (*123*).

For some purposes the results are more useful when expressed (*148*) as in Figure 12. For example, a mixture that contains 20 per cent carbon monoxide and 8 per cent oxygen, the rest being nitrogen, is explosive. If the oxygen is reduced to 4 per cent, the carbon monoxide remaining at 20 per cent, the mixture is no longer explosive but

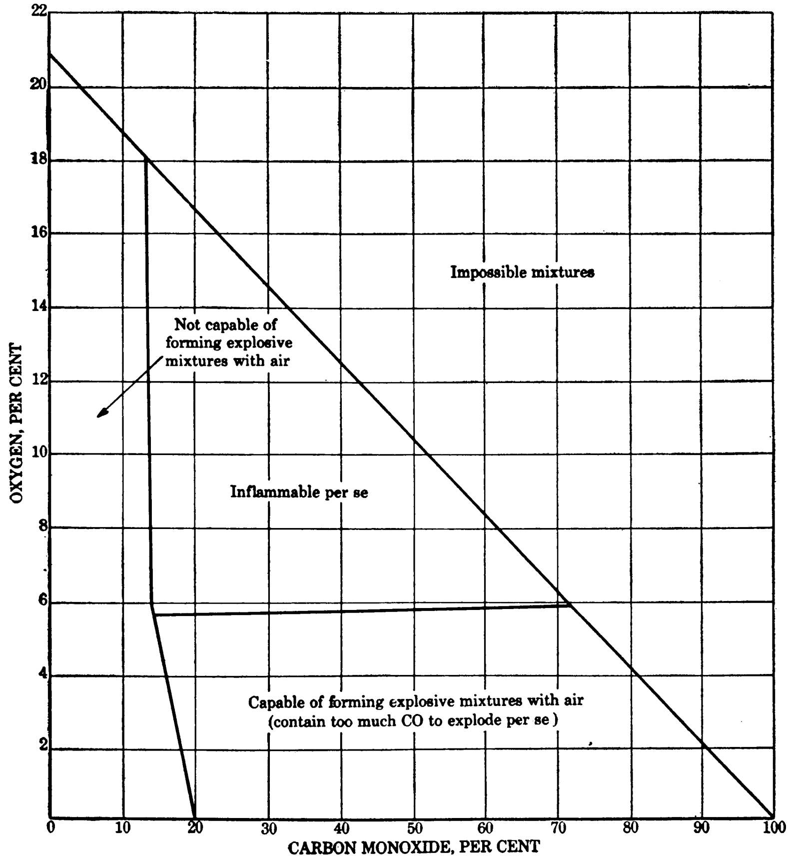

FIGURE 12.—Relation between the quantitative composition and the explosibility of mixtures of carbon monoxide, air, and nitrogen

will become so on admixture with suitable amounts of air. If the carbon monoxide is less than 20 per cent and oxygen is absent, no mixture with air is inflammable, whatever the proportions.

In Figure 12 "impossible" mixtures are those that can not be produced by mixing air, nitrogen, and carbon monoxide. For more detailed explanations, reference may be made to the corresponding section on methane limits in mixtures of air and nitrogen.

Atmospheres of air and water vapor.—The effect of considerable amounts of water vapor on the limits of carbon monoxide in air was shown by the following results obtained in a Bunte burette with downward propagation (*28*); the limits are expressed as percentages of carbon monoxide in the dry gases.

Effect of water vapor on limits of carbon monoxide in air

Temperature, ° C.	Carbon monoxide in dry gases, per cent		Water vapor present, mm.	Temperature, ° C.	Carbon monoxide in dry gases, per cent		Water vapor present, mm.
	Lower	Higher			Lower	Higher	
14	16.2	74.1	11.9	60.5	20.0	68.4	152.4
34.5	16.9	73.5	40.6	78.1	29.4	50.4	328.4

Atmospheres of oxygen and carbon dioxide.—For experiments in a closed 35-c. c. globe with side ignition, the limits were 21.8 to 72.8 per cent carbon monoxide in a mixture of 20.9 per cent oxygen and 79.1 per cent carbon dioxide, compared with 14.2 to 74.7 per cent in air in the same apparatus (*18*). Results showing the influence of temperature on limits in this series are irregular. Some earlier figures (*10*) may be regarded as supplanted by those just quoted.

Atmospheres of air and carbon dioxide.—The limits of inflammability of carbon monoxide in all mixtures of air and carbon dioxide can be read from one of the curves in Figure 11. The determinations were made in a tube 6 feet long and 2 inches in diameter, with upward propagation of flame at atmospheric pressure during propagation (*123, 145*).

Some earlier observations (*28*) show, as might be expected, more rapid narrowing of the limits in Bunte burette experiments.

Atmospheres of air mixed with vapors of chlorinated hydrocarbons.—Series of results showing the lower and higher limits of carbon monoxide in air containing increasing amounts of the vapors of dichloroethylene and trichloroethylene have been reported; they were observed in small burettes of 15-mm. diameter, and so are of limited value (*94*). Similar experiments have been made with the vapors of other halogen derivatives (*147*).

Dilution of $2CO+O_2$.—The following results were obtained for downward propagation of flame in diluted $2CO+O_2$ in a Bunte burette 19 mm. in diameter (*28*).

Downward propagation in diluted $2CO+O_2$ in a Bunte burette

Diluent	Percentage of $2CO+O_2$ which, with the diluent named, is at the limit of inflammability
Oxygen	23.4
Nitrogen	25.6
Carbon dioxide	35.3

Nitrogen evidently has a slightly greater extinctive action than oxygen, although the two gases are of equal heat capacity; carbon dioxide, which is of greater heat capacity, has a greater extinctive action.

METHANE

METHANE IN AIR

When a spark was passed near the lower confines of methane-air mixtures standing over water in a large receiver 6 feet high and 12 inches square in section, the following observations were made (*49*):

5.1 per cent methane: A vortex ring of flame traveled upward about 12 inches, broke, and died out as a tongue of flame about 12 inches higher.

5.3 per cent methane: In one experiment the ring of flame resolved itself into a flame which traveled steadily to the top of the vessel; in other experiments the flame became extinguished in the course of a violent uprush on one side.

5.6 per cent methane: A steady flame with a convex front passed throughout the mixture.

A repetition of these experiments has recently been made with slight alteration in the vessel, a glass cylinder 7 feet high and 10 inches in diameter. The limit observed was 5.32 per cent methane. Steady conditions were more easily obtained in the 10-inch tube than in the box (*109*).

Independent observers conducted experiments in a vessel similar to that first described, which led them to conclude that the lower limit with inflammation upward was about 4.9 per cent methane (*57*). A comparison of the two sets of experiments shows, however, that they were conducted differently. In each set the gas was ignited electrically at the lower end of the vessel; in the first set the flame traveled toward a closed end with a water-seal release behind the flame, but in the second set the flame traveled from a closed end toward a paper diaphragm which "upon ignition broke and gave a vent for the burned gases." The authors have recently repeated both sets of experiments and confirmed both results; the figures obtained were 5.28 per cent for propagation upward, away from the open end, and 5.01 per cent for propagation in the same vessel, upward toward the open end. The mixture was about 70 per cent saturated with water vapor at 20° to 22° C.

There was a great difference between the appearance of the limit flames in the two tests, however. In the first they appeared, after traveling 12 inches or so, to be spreading from side to side of the vessel with a strongly convex front and to travel at uniform speed; in the second the flame was apparently not continuous from side to side but consisted of innumerable vertical streaks of flame, traveling much faster and evidently in a turbulent mixture. It was difficult to be sure that the flame would travel indefinitely and not be extinguished.

In the former experiments the flame traveled into quiescent gas; in the latter the flame traveled into gas which had considerable motion on account of the upward expansion of the heated gas.

Hence, the conclusion is that in a wide space the lower limit of methane in air saturated with water vapor at laboratory temperature is 5.3 per cent methane; but that if the flame is traveling upward from closed to open end of a vessel in gas which is therefore in motion it may travel at least 6 feet when the proportion of methane is not less than 5 per cent. Furthermore, in certain circumstances "the flames of mixtures containing 5.3 to 5.6 per cent of methane are very sensitive to extinction by shock" (*49*).

The higher limit of methane in air, saturated with water vapor, has been determined in a glass tube 7 feet long and 10 inches in diameter to be 13.87 per cent methane (*109*). This figure may be taken as correcting an earlier estimate (*66*), a higher value, based on observations in wide short vessels and long narrow vessels.

In a similar vessel with a paper release at the top equivalent to an open end, the higher limit was 15.2 per cent under the conditions of movement imparted to the gases (*57*).

Downward propagation of flame.—In a large box nearly 6 feet long and 12 inches square in section, the limits for downward propagation of flame in a quiescent mixture were 5.75 and 13.6 per cent methane; when the box was closed at the top and open at the bottom, so that motion was imparted to the mixture by the expansion on burning, the lower limit for downward propagation was 5.45 per cent (*57*).

Horizontal propagation of flame.—In the box mentioned in the preceding paragraph the lower limit for horizontal propagation was 5.55 per cent methane. The position of the open end, whether behind or ahead of the flame, was not stated (*57*).

In a horizontal glass cylinder 7 feet long and 10 inches in diameter the limits for propagation through the whole length of the tube from open to closed end were 5.42 to 14.03 per cent methane. The mixtures were only partly saturated with water vapor; if completely saturated, the higher limit would be reduced somewhat, probably to a value not exceeding 13.87 per cent methane—that for upward propagation in the same vessel (*109*).

Observations in small vessels.—A large number of observations of the limits of methane in small vessels have been made in the course of a century. On the whole, the conclusions are fairly concordant, as shown by Table 6, when allowance is made for variation in experimental conditions. Outstanding discrepant figures are not quoted here, because they have been explained as due to faulty experiment or faulty interpretation. For instance, in at least one instance it is certain that incomplete admixture of the methane and air was obtained; in another (*35*) the observation of a small pressure change on sparking was erroneously interpreted as an indication of inflammability; in a third (*9*) the flame speeds in a series of inflammable mixtures of methane and air were extrapolated to zero speed, the composition corresponding to which was taken as the limit of inflammability—an error, because a "limit" mixture still shows a flame speed which is far from zero. Many of the older figures are omitted because they are but rough approximations in comparison with more recent results, with which, however, they are not at variance.

Upward propagation.—Table 6 shows the limits for methane-air mixtures in the smaller vessels with upward propagation. It is evident that the limits found in wide vessels open behind the flame—namely, 5.3 to 13.87 for gases saturated with water vapor—are not appreciably narrower in open tubes 5 cm. in diameter. There is, however, a marked difference in the higher limit figures for completely closed tubes; the tendency is for the higher limit to be distinctly greater in closed than in open tubes of equal diameter. This is explained by the observation that increase of pressure markedly increases the higher limit; enough pressure is developed in closed tubes in the earlier stages of propagation while the flame is still assisted by the initial impulse from the source of ignition. This explanation is confirmed by a comparison of two experiments in tubes whose diameters (5 cm.) were equal but whose lengths were very different. The shorter tube gave a greater higher limit figure than the longer tube; the reason for this is that the pressure must rise faster and to a greater amount in the shorter tube.

TABLE 6.—*Limits of inflammability of methane in air, in glass tubes, with upward propagation of flame*

Dimensions of tube, cm.		Firing end	Limits, per cent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
7.5	150	Closed	5.35	14.85	Half saturated	90
6.2	33	Open	5.45	13.5	Saturated	28
6.0	200	Closed	5.40	14.8	Small	54
5.0	50	do		15.11		82
5.0	150	do	5.40	14.25	Half saturated	90
5.0	180	Open	5.24	14.02	Dry	105
5.0	180	do	5.33	13.80	Saturated	105
2.7		do	5.28		Dry	46
2.5	150	do	5.5		Saturated	69
2.5	150	Closed	5.80	13.20	Half saturated	90

Horizontal propagation.—Table 7 shows the limits for horizontal propagation in the smaller vessels. The limits for closed tubes are appreciably narrowed by reducing the diameter of the tube to 2.5 cm. In open tubes the limits meet when the diameter of the tube is reduced to 0.36 cm. Flame is not propagated, except for a short distance from the source of ignition, along a tube 0.36 cm. in diameter.

TABLE 7.—*Limits of inflammability of methane in air, in glass tubes with horizontal propagation of flame*

Dimensions of tube, cm.		Firing end	Limits, per cent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
7.5	150	Closed	5.40	13.95	Half saturated	90
6.0	200	do	5.4	14.3	Small	54
5.0	150	do	5.65	13.95	Half saturated	90
5.0	50	do	5.39	14.28		82
2.7		Open	5.64		Dry	46
2.5	150	do	5.85	13.3	Saturated	69
2.5	150	Closed	6.20	12.90	Half saturated	90
2.0	40	do	5.59	13.31		82
.90	300	Open	7.8	11.6	Saturated	65
.81	300	do	8.3	10.9	do	65
.72	300	do	8.4	10.6	do	65
.56	300	do	8.4	10.6	do	65
.45	300	do	[1] 9.95		do	65
.36	300	do	Nil.		do	65

[1] The limits coincide at this composition.

Downward propagation.—Table 8 shows the limits for downward propagation of flame in the smaller vessels. The limits throughout are somewhat narrower than those found in the largest vessel for the same direction of propagation.

TABLE 8.—*Limits of inflammability of methane in air, in glass tubes with downward propagation of flame*

Dimensions of tube, cm.		Firing end	Limits, per cent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
8.0	37	Closed	5.9	12.9	Saturated	*53*
7.5	150	do	5.95	13.35	Half saturated	*90*
6.2	33	Open	6.3		Saturated	*28*
6.0	200	Closed	6.0	13.4	Small	*54*
5.0	50	do	5.80	13.38		*82*
5.0	150	do	6.12	13.25	Half saturated	*90*
2.7		Open	5.84		Dry	*46*
2.5	150	do	6.1		Saturated	*69*
2.5	150	Closed	6.30	12.80	Half saturated	*90*
1.9	40	do	6.1	12.8	Saturated	*28*
1.9	40	do	6.15	12.0	do	*73*
.815		Open	6.25		Dry	*46*
.515		do	7.03		do	*46*

Table 9 shows the limits for propagation of flame throughout mixtures of methane and air contained in closed spherical vessels of various sizes. The limits become somewhat narrower as the size of container is decreased and generally correspond more nearly with the limits observed in tubes with downward propagation than in those with either horizontal or upward propagation.

TABLE 9.—*Limits of inflammability of methane in air, in small spherical vessels*

Capacity of vessel, c. c.	Point of ignition	Limits, per cent		Content of aqueous vapor	Reference No.
		Lower	Higher		
2,000	Central	5.6	14.8	Small	*36*
2,500	do	5.77		Saturated	*47*
100	Above	5.5	14.0		*59*
35	Side	6.0	12.6	Dry	*18*
35	do	5.9	13.1	Saturated	*18*

Influence of turbulence and of streaming movement on the limits of inflammability.—When a small fan was rotated rapidly enough but not too fast in methane-air mixtures contained in a 4-liter globe, the lower limit of methane was 5. 0 per cent, as compared with 5.6 per cent observed for quiescent mixtures in the same vessel. If the turbulence was too violent, however, even a 5.6 per cent mixture did not propagate more than a short tongue of flame (*54*).

A streaming movement of the gas mixture produces similar effects on the lower limit. Within the range of speed from 35 to 65 cm. a second (69 to 128 feet a minute) flame was propagated in a 5.02 per cent methane-air mixture, although a 5.00 per cent mixture failed to propagate flame at any speed of movement of the gas (*72*). Hence, under appropriate conditions of movement of the gas mixture, the lower limit of methane is 5.0 per cent. The same figure was obtained (see above) when movement of the mixture was produced by expansion caused by its own combustion, in experiments on the propagation of flame from closed to open end of a large vessel.

Reference may be made to observations of the effect of turbulence, in somewhat different circumstances, on the lower limit of natural gas in air, page 93.

Influence of pressure.—No measurable change in the limits of methane in air could be discovered when the pressure varied between 753 and 794 mm. (*46*).

An interesting comparison has been made between the effect of pressure change from 1 to 6 atmospheres on the limits for downward and for horizontal propagation in tubes 2 cm. in diameter (*64*, *82*). For downward propagation the range changes steadily from 6.00 to 13.00 per cent at 1 atmosphere to 6.40 to 14.05 per cent at about 6 atmospheres. For horizontal propagation the lower limit remained nearly constant, 5.6 per cent, over this range of pressure; the higher limit rose steadily from 13.31 per cent at 1 atmosphere to 16.12 per cent at about 6.5 atmospheres.

In these experiments, therefore, the lower limit for horizontal propagation was unchanged but for downward propagation increased

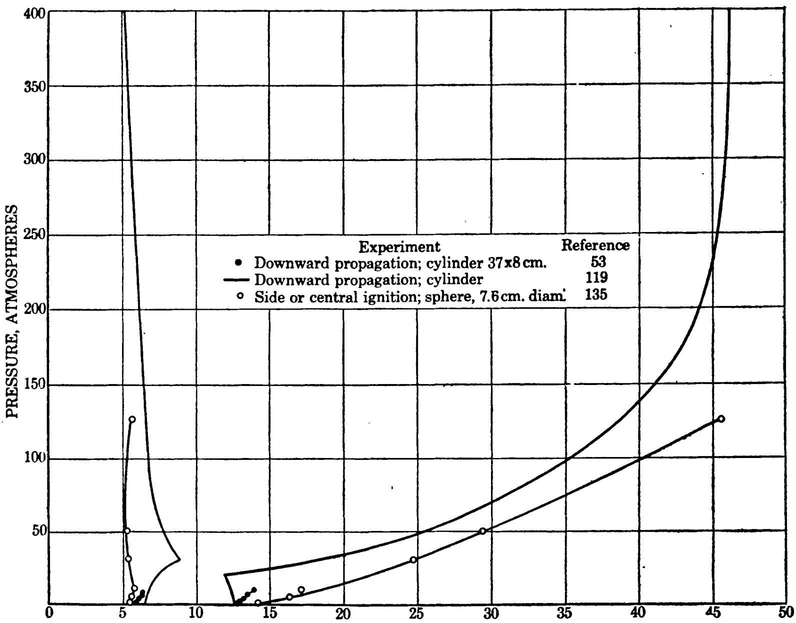

FIGURE 13.—Effect of pressures above normal on the limits of methane in air

steadily with increasing pressure. The higher limit for horizontal propagation increased more rapidly than for downward propagation. For an interpretation of this see page 5.

The limits observed under very high pressures (*53*, *119*, *135*) are shown in Figure 13. The rapid increase in the higher limit is remarkable. The differences between the three series of results are to be ascribed to differences in experimental method and in interpretation. Experiments had almost of necessity to be conducted in small vessels; but the results are doubtless a fair indication of the possibilities of explosion in larger vessels holding mixtures of compressed gases, if a source of ignition should be present.

Limits at less than atmospheric pressure, at various temperatures, in a tube 50 cm. long and 2 cm. in diameter, with downward propagation of flame, are shown in Figure 14. The curve for 20° C. in this figure shows much wider limits at low pressures and extends to much lower pressures than were observed in an older series of tests (*58*). The more recent results were obtained with a stronger igniting spark; sparks which will ignite an inflammable mixture at normal pressures may be far too weak to ignite the same mixtures at low pressures.

Experiments in a wider tube, 5 cm. in diameter and 50 cm. long, show a comparison of the limits for different directions of propagation of flame at pressures less than atmospheric (*82*). The curves for these limits are plotted in Figure 15. Data were not obtained for

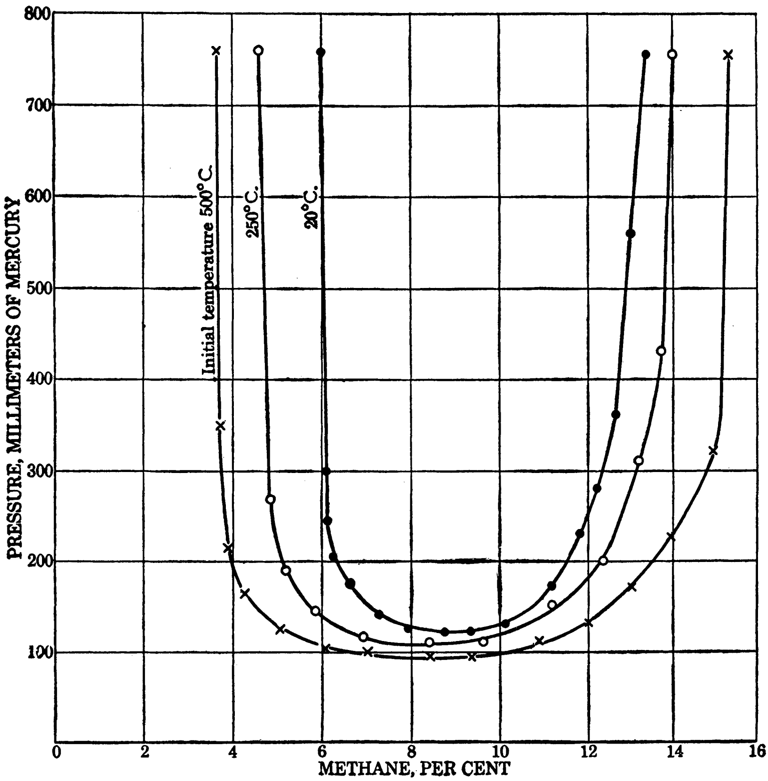

FIGURE 14.—Limits of inflammability of methane in air (downward propagation) showing influence of pressure (below normal) and temperature

upward propagation at the lower limit because in the rather short vessel used the issue was confused by the large "caps" of flame above the igniting spark.

Influence of temperature.—Several of the older observations have been unfavorably criticized because before being ignited the mixture under test was allowed to remain in the heated experimental vessel so long as to cause some general slow combustion, and thus to change the composition of the mixture enough to affect the results. A comparison of the less exceptionable results is made in Figure 16, which shows lower and higher limits up to temperatures at which almost instantaneous inflammation of the mixtures was observed. The conditions of experiment for the various series were as follows:

Conditions of various experiments on influence of temperature

Curve No.	Condition	Reference No.
1	Hempel pipette, 100 c. c., ignition near top	*58*
2	Closed tube, 2 cm. diameter, 50 cm. long, downward propagation [1]	*64*
3	Closed tube, 2.5 cm. diameter, 150 cm. long, downward propagation	*101*
4	Closed tube, 1.8 cm. diameter, 150 cm. long, downward propagation	*101*

[1] Another series of lower limits, observed in a tube, dimensions unspecified and propagation apparently downward, gave results which are closely expressed by curve 2 (*44*).

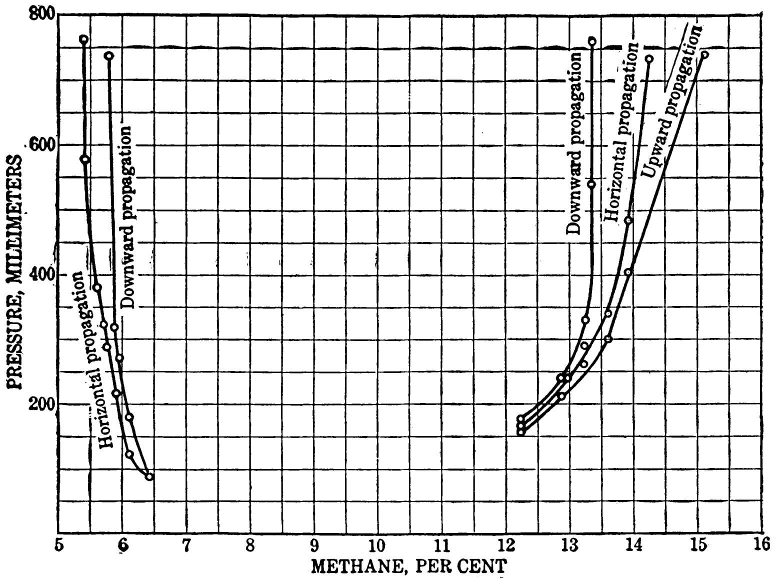

FIGURE 15.—Limits of inflammability of methane in air, showing influence of pressure and of direction of propagation of flame

The range of inflammability, as will be noted, is much widened at both limits by increase of temperature, but ordinary variations of atmospheric temperature have an insignificant effect on either limit.[7]

Figure 14 shows that the temperature effect remains the same at pressures less than the normal.

The differences between the results of the several sets of tests, although small for lower limits and not very large for higher limits, are real and must be due to the use of different apparatus. In higher limits the length of tube used seems to be the determining factor, as shown by series 2 and 4 with tubes of nearly the same diameter. Hence all the results are relative to the apparatus used and do not show the influence of temperature on limits defined as a property of

[7] Formulas to express the influence of temperature on the limits have been given (*46*) for the range 0° to 49° C. They are: Lower limit, $n=n_o-0.0042t$; higher limit, $n'=n'_o+0.0036t$.

the gas mixture alone. The results may, however, be taken as an indication of the effect of temperature on the true limits.

An unconfirmed observation has been made which indicates that, although the limits in moist methane-air mixtures are widened by increase in temperature, the lower limit as well as the higher limit is much raised by increase of temperature when the mixtures are dried with phosphorus pentoxide (*18*).

Influence of pressure at various temperatures.—The curves of Figure 14 show the limits of inflammability of methane-air mixtures

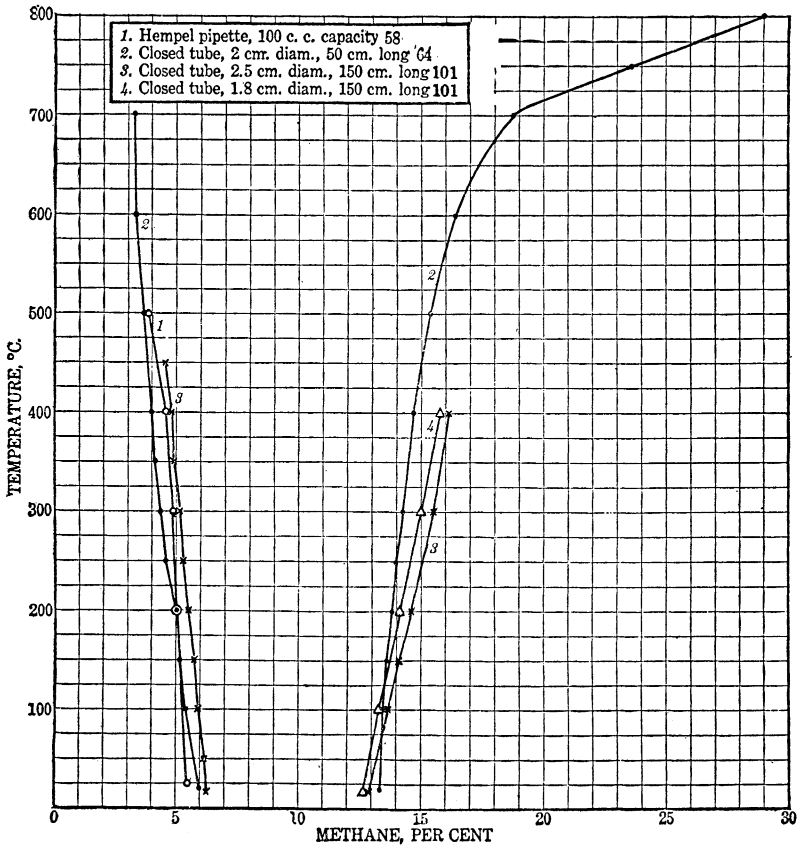

FIGURE 16.—Limits of inflammability of methane in air (downward propagation), showing influence of temperature

at 20°, 250°, and 500° C. at all pressures below atmospheric. The limits were observed in a closed tube 2 cm. in diameter and 50 cm. long (*64*).

METHANE IN OXYGEN

The lower limit of methane in oxygen, observed in small vessels, was found to be as follows: In an open tube 1 inch in diameter (*69*), 5.4 per cent methane for upward propagation, 5.8 per cent for horizontal, and 6.3 per cent for downward propagation; and in a closed globe of 2.5 liters capacity with central ignition, 6.0 per cent methane (*47*). The corresponding figures for methane-air mixtures are 5.5, 5.9, 6.1, and 5.8 per cent, which are slightly higher for upward and horizontal propagation, although slightly lower for downward propagation and for propagation throughout a closed globe.

The lower limit in oxygen for downward propagation in a 1.9 cm. closed tube (Bunte burette) was 6.4 or 6.45 per cent (*28*, *73*).

The higher limit of methane in oxygen, observed in some old experiments, appears to lie between 53 and 57 per cent methane for downward propagation of flame (*8*, *10*, *18*); it is 59.2 per cent for horizontal propagation in a 1-inch tube open at the firing end (*69*).

Influence of pressure.—The limits of methane in oxygen were not appreciably narrowed until the pressure was reduced below 150 mm. A moderately strong igniting spark was used (*48*).

The higher limit is increased by increase of pressure above atmospheric. One observation (*120*), incidental to other work, is that at 10 atmospheres pressure a mixture containing 71 per cent methane slowly propagated flame. A series of determinations (*154*) in a small bomb indicated rapid rise of the higher limit from 58.4 per cent at 1 atmosphere to 81.7 per cent at 60 atmospheres, followed by a slower rise to 84 per cent at about 145 atmospheres; but the experimental mixtures contained about 4.5 per cent of nitrogen, and the figures would be somewhat higher in pure oxygen. Combustion was far from complete in such mixtures under moderately high pressure.

Influence of temperature.—The limits were widened somewhat by increase of temperature from 15° to 300° C. In a 35-c. c. closed bulb the limits were 6.2 to 57.1 at 15° C. and 5.1 to 57.8 at 300° C. (*18*).

Influence of temperature at high pressures.—The higher limit of methane in oxygen was raised by increase of temperature at high pressures. For example, the limit in a small bomb was 81.7 per cent methane at atmospheric temperature and 60 atmospheres, and was the same at 332° C. and about 21 atmospheres (*154*). Curves that show the higher limit at elevated temperatures and pressures, are given in the original paper.

METHANE IN OTHER ATMOSPHERES

Atmospheres of composition between air and pure oxygen.—The limits of methane in mixtures of nitrogen and oxygen richer in oxygen than ordinary air have been found as follows: (1) In a closed globe of 2.5 liters capacity the lower limit rose regularly from 5.8 to 6 per cent methane as the oxygen content of the atmosphere rose from 20.9 to 100 per cent (*47*); (2) in a horizontal glass tube 2.5 cm. in diameter, open at the firing end, the lower limit fell from 5.8 to 5.7 per cent methane and the higher limit rose linearly from 13.3 to 59.2 per cent methane in the same range of oxygen content (*69*); (3) in a closed tube 1.9 cm. in diameter the lower limit for downward propagation of flame rose regularly from 6.15 per cent in air to 6.45 per cent in oxygen. The higher limit rose from 12 per cent in air to 38 per cent in a 62 per cent oxygen mixture and to 52 per cent in a 95 per cent oxygen mixture (*73*).

Atmospheres of air and nitrogen (air deficient in oxygen).—Large-scale observations with mixtures of methane, air, and nitrogen have been made in a tube 7 feet long and 10 inches in diameter for upward propagation of flame from the open end of the tube; the mixtures throughout were at atmospheric pressure and saturated with water vapor. The range of observations, shown in Figure 17, covers all compositions ranging from air (20.9 per cent oxygen) to mixtures in which the amount of oxygen is too small for flame propagation, whatever be the amount of methane present. The abscissas represent the "atmosphere" in each mixture as composed of air and nitrogen; for example, 25 per cent "additional nitrogen" means that

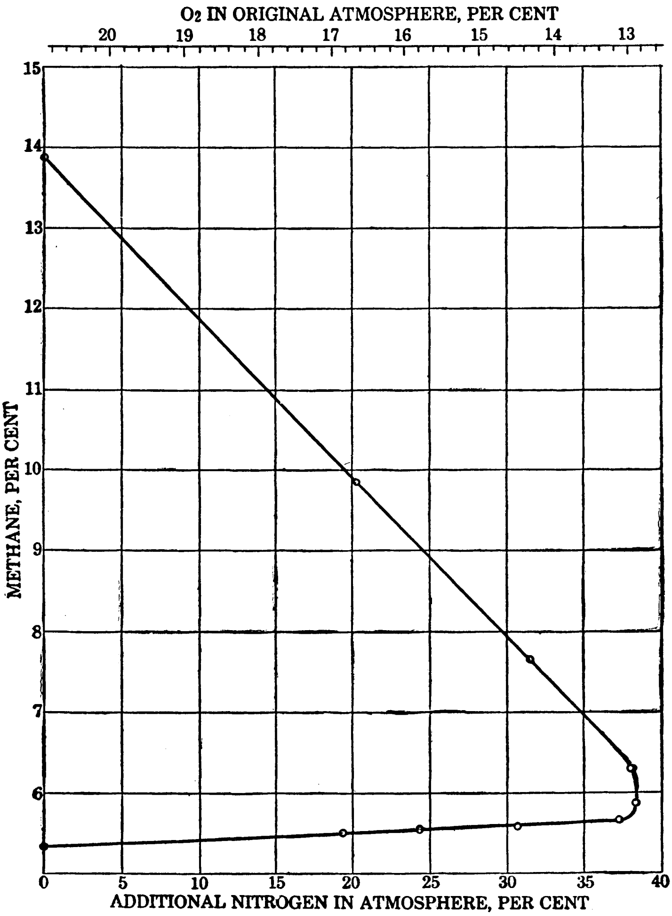

FIGURE 17.—Limits of inflammability of methane in mixtures of air and nitrogen (upward propagation), showing results of experiments in large vessel

the "atmosphere" used for the observations was composed of 75 per cent air and 25 per cent nitrogen. Along the top of the diagram the corresponding percentages of oxygen present in the whole atmosphere may be read. It is evident that no mixture of methane is inflammable at ordinary temperatures and pressures when the atmosphere contains less than 12.8 per cent oxygen and the remainder is nitrogen (*109*).

Observations made in smaller apparatus are shown in Figure 18. The results obtained in a 5-cm. tube, with upward propagation of flame in a dry mixture, are nearly coincident with those plotted in Figure 17. The three curves that show narrower limits represent experiments in various types of apparatus with downward propagation of flame. One curve shows greater values over part of the higher limit range. These experiments were conducted in a closed vessel

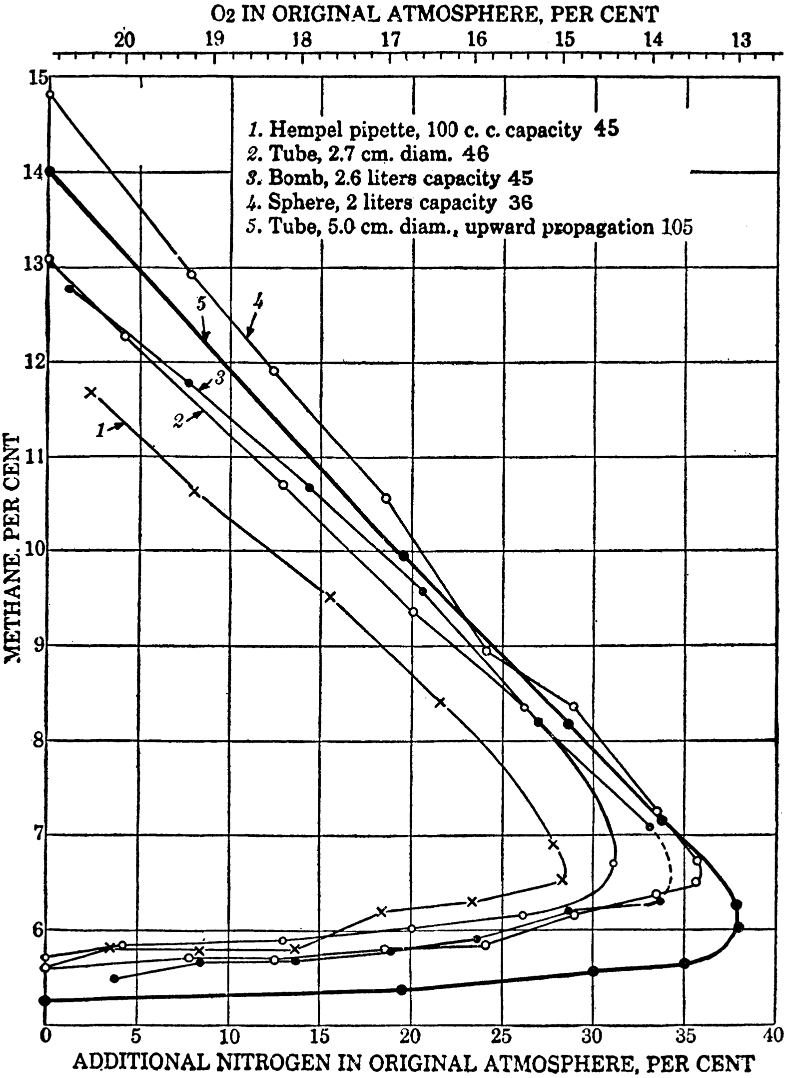

FIGURE 18.—Limits of inflammability of methane in mixtures of air and nitrogen; comparison of results obtained in smaller vessels

in which the pressure rose considerably during the inflammation; increase of pressure is known to increase markedly the upper limit for methane. (See p. 40.)

For some purposes the results are more useful when expressed (*148*) as in Figure 19.

For example, it is not deducible at a glance from Figure 17 that the mixture—

	Per cent
Methane	12
Oxygen	2
Nitrogen	86

is not capable of forming an explosive mixture with air, whatever the proportions used, whereas the mixture—

	Per cent
Methane	9
Oxygen	12
Nitrogen	79

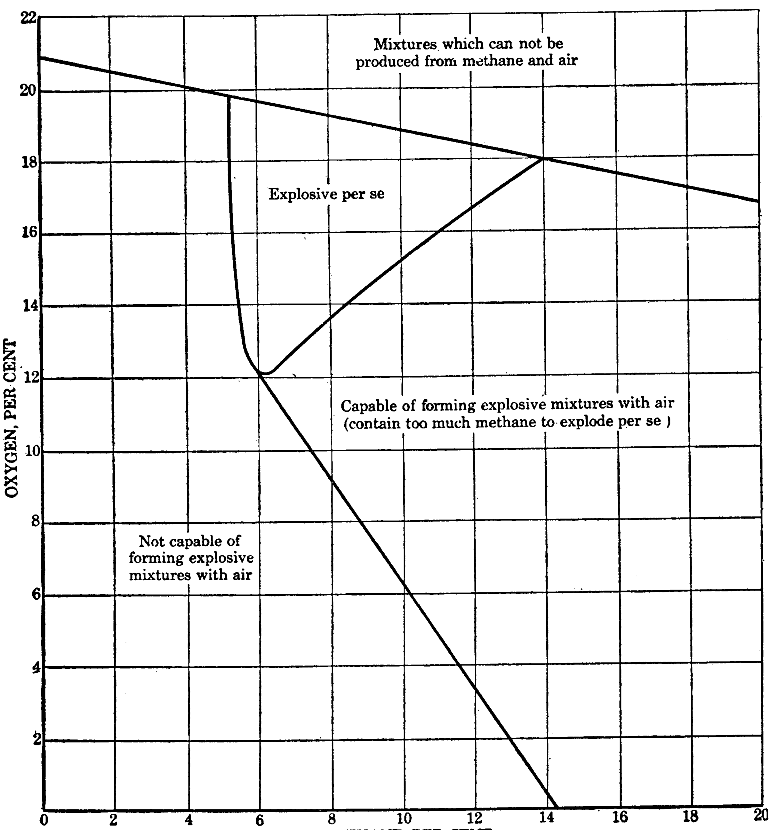

FIGURE 19.—Relation between the quantitative composition and the explosibility of mixtures of methane, air, and nitrogen

though not itself explosive may form a series of explosive mixtures with air. Figure 19 gives this information at a glance.

Explanation of Figure 19.—Figure 20 serves to explain Figure 19. The straight line *AD* (fig. 20) represents the composition of all mixtures of methane and pure air which contain up to 20 per cent of methane. No mixture of methane and air can fall above this line, and all mixtures of methane, air, and nitrogen must fall below it. The line *BE* is the line of lower limits of inflammability of methane, and *CE* the line of higher limits. As the oxygen content falls, *BE* and *CE* approach until they meet at *E*. No mixture which contains less oxygen than that corresponding with the point *E* is explosive per se; but all mixtures in the area *BEC* are within the limits of inflammability, and are therefore explosive.

Next consider any mixture to the right of the line *CEF*—for example, the mixture represented by the point *G*. Join *GA*. Then *GA* represents the mixtures formed, in succession, as *G* is diluted with air. Then because *GA* passes through the area *BEC*, the mixture, as it

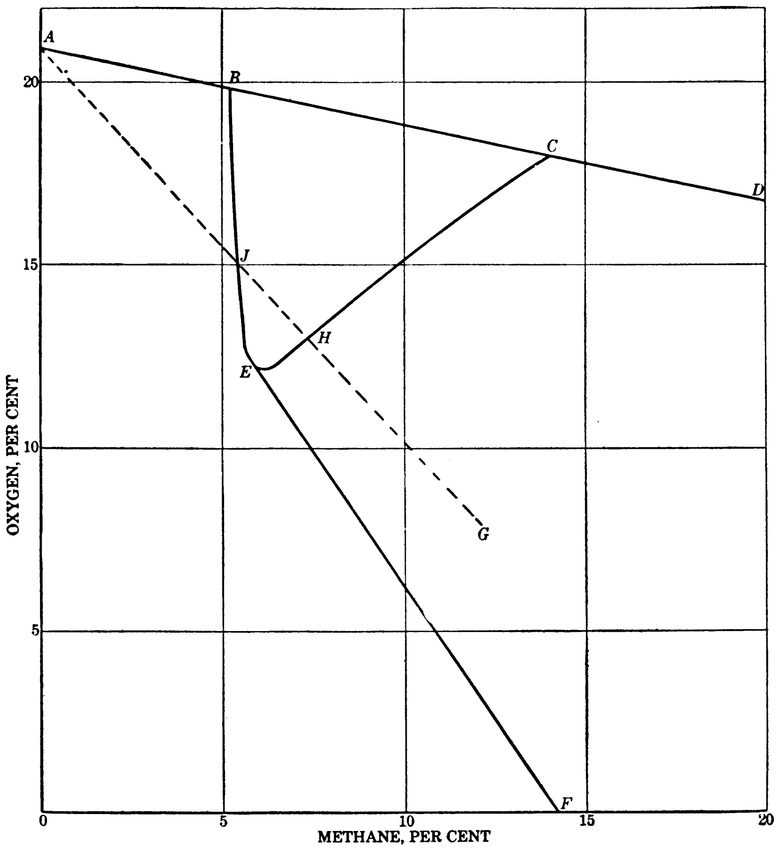

FIGURE 20.—Expla atory of Figure 19

is diluted with air, becomes explosive, and remains explosive so long as its composition is represented by any point within that area.

It will now be clear that the position of *FE* is exactly defined by drawing a tangent from *A* to the curve *BEC*, and producing the tangent to meet the axis of abscissas in *F;* becauset he line joining any point above and to the right of *FE*, to *A*, must pass through *BEC*, while the line joining any point below and to the left of *FE*, to *A*, must fail to pass through the explosive region *BEC*. *FE* is therefore the boundary of those mixtures capable of forming explosive mixtures with air.

It is clear from Figure 19 that any mixture of methane and nitrogen which contains more than about 14.3 per cent of methane can form explosive mixtures with air. If there be oxygen present, a correspondingly smaller amount of methane suffices.

Mixtures of methane, nitrogen, and oxygen which are represented by any point in the area *DCEF* of Figure 20 are capable of forming explosive mixtures when mixed with air in suitable proportions. If it be of interest to know what these proportions are—and if there is a wide range of explosive mixtures possible, the danger is so much the greater—then they can be found from the following considerations:

Suppose the mixture of methane, nitrogen, and oxygen to be represented by the point *G* in the area *DCEF*, the straight line *GA* represents all the possible mixtures of original mixture and air. As the original mixture is diluted step by step with air, the composition of the new mixture is represented by points farther and farther along *GA*. The air mixture first becomes explosive per se at the point *H* where *GA* crosses *EC*. The higher limit of the original mixture is defined by this point; the lower limit of the original mixture is defined by the point *J* at which *GA* cuts *EB*.

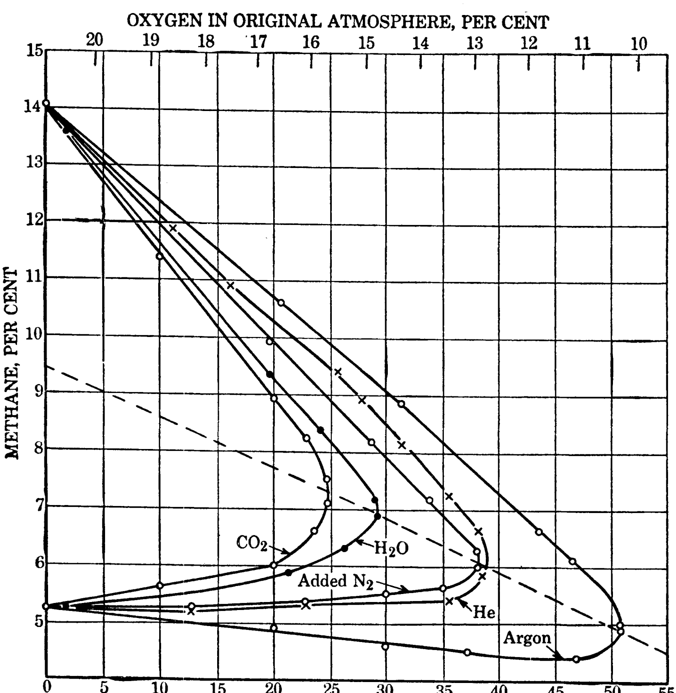

FIGURE 21.—Limits of inflammability of methane in separate mixtures of air with carbon dioxide, water vapor, nitrogen, helium, and argon

Now the ratio *AH* : *HG* is the ratio of original mixture to air in the upper limit mixture; and the ratio *AJ* : *JG* is the ratio for the lower limit mixture. Hence the limits of inflammability of the original mixture are given (in percentages) by 100 *AJ*/*AG* (lower limit) and 100 *AH*/*AG* (higher limit) (*148*).

Atmospheres of air and water vapor.—Observations that show the small difference in the limits of methane in dry air and in air saturated with water vapor at laboratory temperatures are quoted under "Effect of small changes in atmospheric composition," page 3.

The effect of large amounts of water vapor on the limits of methane in air is shown by a curve in Figure 21. The determinations were made in a tube 3 feet long and 2 inches in diameter, with upward propagation of flame at atmospheric pressure during propagation (*155*). For each experiment the tube was heated to the tempera-

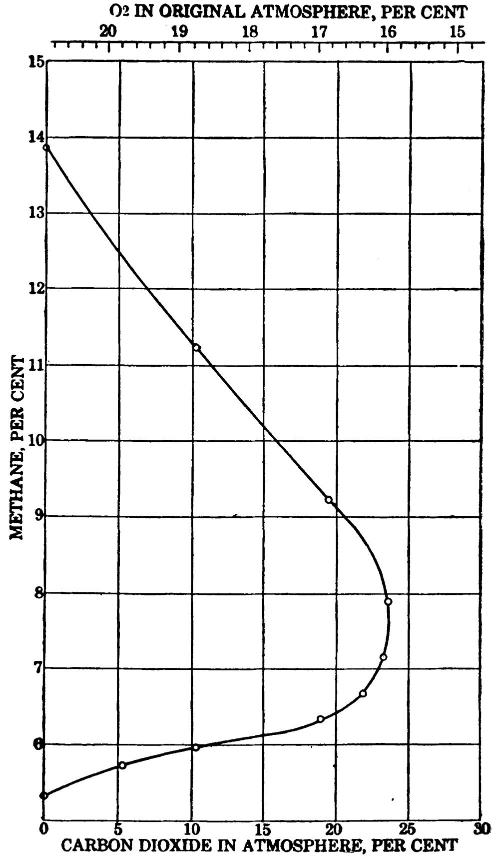

FIGURE 22.—Limits of inflammability of methane in mixtures of air and carbon dioxide (upward propagation), showing results of experiments in large vessel

ture necessary to maintain in the vaporous state the required amount of water. Hence, most of the observations in the water curve of Figure 21 were made at temperatures above normal. Had it been possible to experiment at normal temperature, the curve would probably have lain a little to the right of the carbon dioxide curve over the lower limit range and at the nose, but the two curves would have coincided over most of the higher limit range.

Atmospheres of air and carbon dioxide.—Figure 22 shows the limits of methane in mixtures of air and carbon dioxide saturated with water vapor. The tests were made in a tube, 7 feet long and 10 inches in diameter, with upward propagation of flame from the open end of the tube. Under these circumstances no mixture of methane with an atmosphere composed of air and 24 per cent or more carbon dioxide is capable of propagating flame far from the source of ignition (*109*).

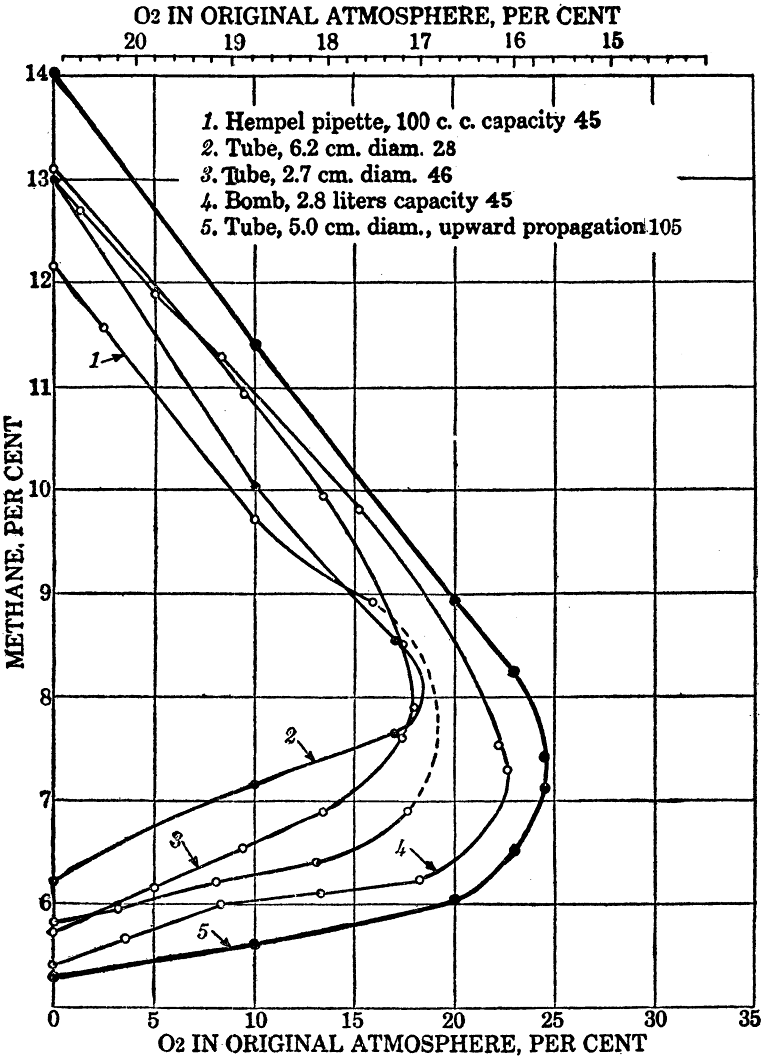

FIGURE 23.—Limits of inflammability of methane in mixtures of air and carbon dioxide; comparison of results obtained in smaller vessels

Observations made in smaller apparatus are shown in Figure 23. Those obtained in a 5-cm. open tube with upward propagation of flame through dry gases show, in general, a slightly wider range of inflammability than those of Figure 22; the completely extinctive atmosphere in the 2-inch tube contains 25 per cent carbon dioxide, compared with 24 per cent carbon dioxide contained in the widest vessel. The four curves showing narrower limits represent experiments in various vessels with downward propagation of flame.

Influence of temperature.—The limits of fire damp in atmospheres of air and carbon dioxide from 100° to 600° C. have been determined. The fire damp used contained 73.8 per cent of methane and 26.2 per

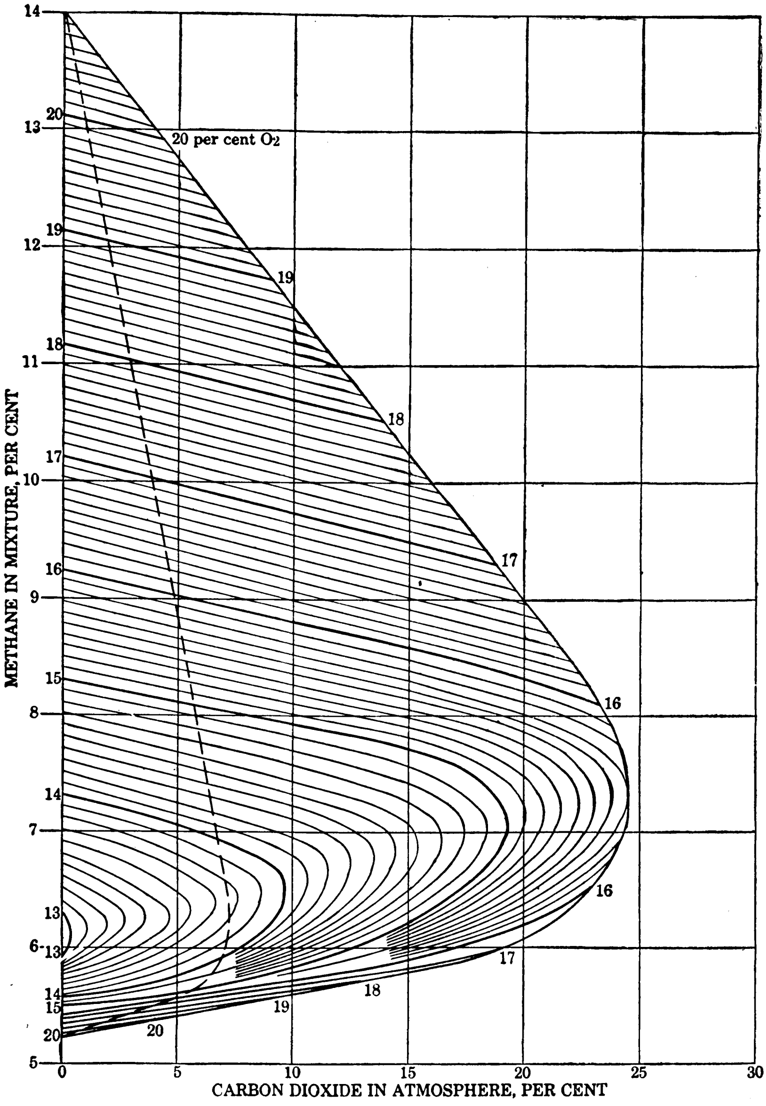

FIGURE 24.—Limits of inflammability of methane in mixtures of air, nitrogen, and carbon dioxide

cent of nitrogen. The observations were made in a horizontal glass tube 2 cm. in diameter and 100 cm. long. The results are expressed in curves showing the limits of methane in the various atmospheres of air, carbon dioxide, and such additional nitrogen as was due to the fire damp itself. The curves are of the same type as those of Figure

22 and show the increased range of inflammability of all mixtures due to increased temperature (*131*).

Atmospheres of air, nitrogen, and carbon dioxide (including mixtures of air and black damp).—Observations on the limits of inflammability of methane in atmospheres composed of air, nitrogen, and carbon dioxide are plotted in Figure 24; they were obtained with roughly dried gases in a tube 2 inches in diameter, with upward propagation of flame from the open end of the tube. The curve bounding the series of curves to the right reproduces the limits of inflammability of methane in all atmospheres of ordinary air and carbon dioxide mixed in any proportions. The straight line bounding the series of curves to the left gives, with the oxygen figures inserted thereon, the limits in all atmospheres of air and nitrogen mixed in any proportions. The whole area between represents the limits in atmospheres which are deficient in oxygen and also contain carbon dioxide. When the deficiency of oxygen is replaced by an equal amount of carbon dioxide, as would occur very nearly in the combustion of coke, these atmospheres and the corresponding methane limits are all represented by points on the broken curve.[8] The region to the right of the broken curve represents limits in atmospheres formed by the replacement of oxygen with more than an equal volume of carbon dioxide. The region to the left of the broken curve represents limits in atmospheres formed by the replacement of oxygen with less than an equal volume of carbon dioxide. Atmospheres of this type are produced by ordinary combustion and by respiration. This region, therefore, contains the limits for atmospheres composed of air and black damp mixed (*104*).

As the composition of black damp is somewhat variable, to draw one curve representing its effect on the limits of methane is impossible, but Figure 25 shows the limits for a range of variations in the composition of black damp. These curves clearly show that the danger of an explosion of fire damp is but slightly decreased by the presence of black damp in any proportions, unless the proportions are so high that the atmosphere is not fit to work in, even if gas masks are worn. An artificial supply of oxygen or air would be necessary for respiration in a black damp-air atmosphere incapable of propagating explosions of fire damp (*104*).

Figure 19 may be used to determine whether any given mixture of fire damp, black damp, and air is explosive or is capable of exploding if mixed with a suitable amount of air. The mixture is analyzed to determine the proportions of methane, oxygen, nitrogen, and carbon dioxide present. If the carbon dioxide is assumed to be replaced by an equal volume of nitrogen, the figure gives exact information, as described on page 47; in a coal mine the amount of carbon dioxide in such mixtures is of the order 5 or 6 per cent (often less, rarely more), and the error introduced by considering as nitrogen this small amount of carbon dioxide has been shown to be small and on the side of safety (*148*).

Experiments with the same gases in small apparatus, downward propagation of flame, have been reported, but on account of the experimental conditions the limits throughout are narrower, and the

[8] See reference *28* for earlier observations, made in a Bunte burette.

extinctive amounts of inert gas much less than those quoted above (*81*).

Atmospheres composed of air mixed with argon and helium.—Figure 21 reproduces the curves showing the influence of nitrogen, water vapor, and carbon dioxide on the limits of inflammability of methane as found in a tube 2 inches in diameter, for upward propagation of flame, with the lower end of the tube open. The

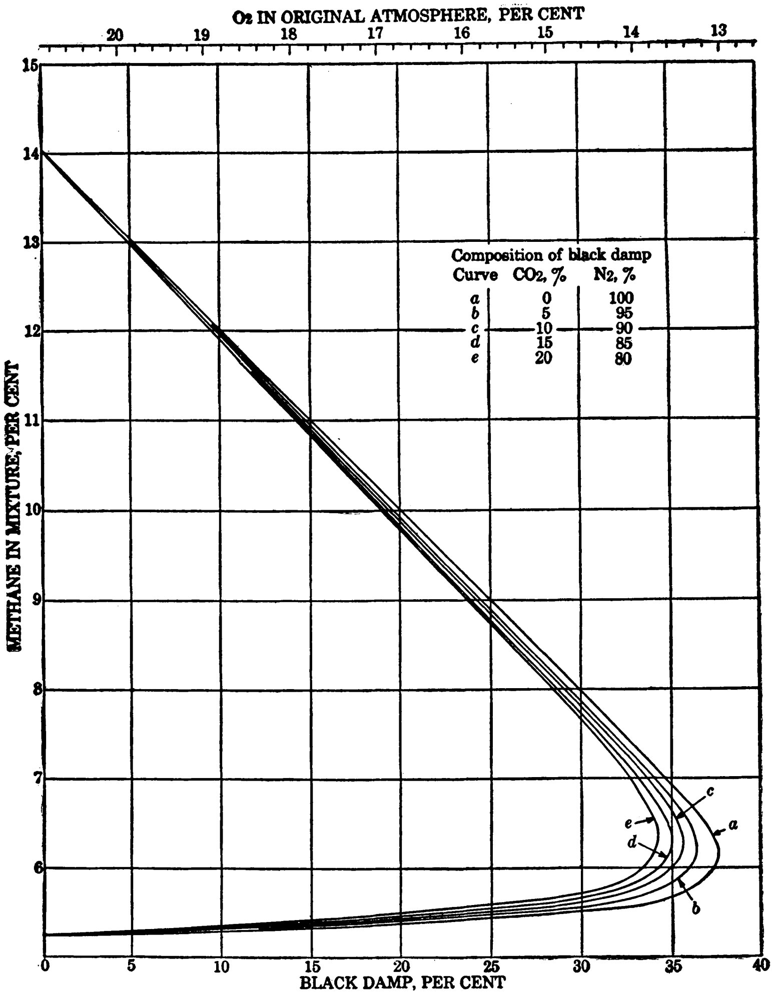

FIGURE 25.—Limits of inflammability of methane in mixtures of air and black damp

differences between the three gases are ascribed to their different heat capacities; as carbon dioxide has the greatest heat capacity, it has the greatest extinctive effect on flame. The corresponding curve for argon in the same figure is in agreement with this supposition, as argon has a smaller heat capacity than nitrogen. The curve for helium, a gas of equal heat capacity to argon, shows that this factor is not the only one determining the extinctive effect of an inert gas; apparently the high thermal conductivity of helium makes it a more efficient flame extinguisher than argon. It seems, however, that the effect of thermal conductivity becomes marked only when comparisons are made between gases of such very great difference in thermal conductivity as exists between argon and helium (*105*).

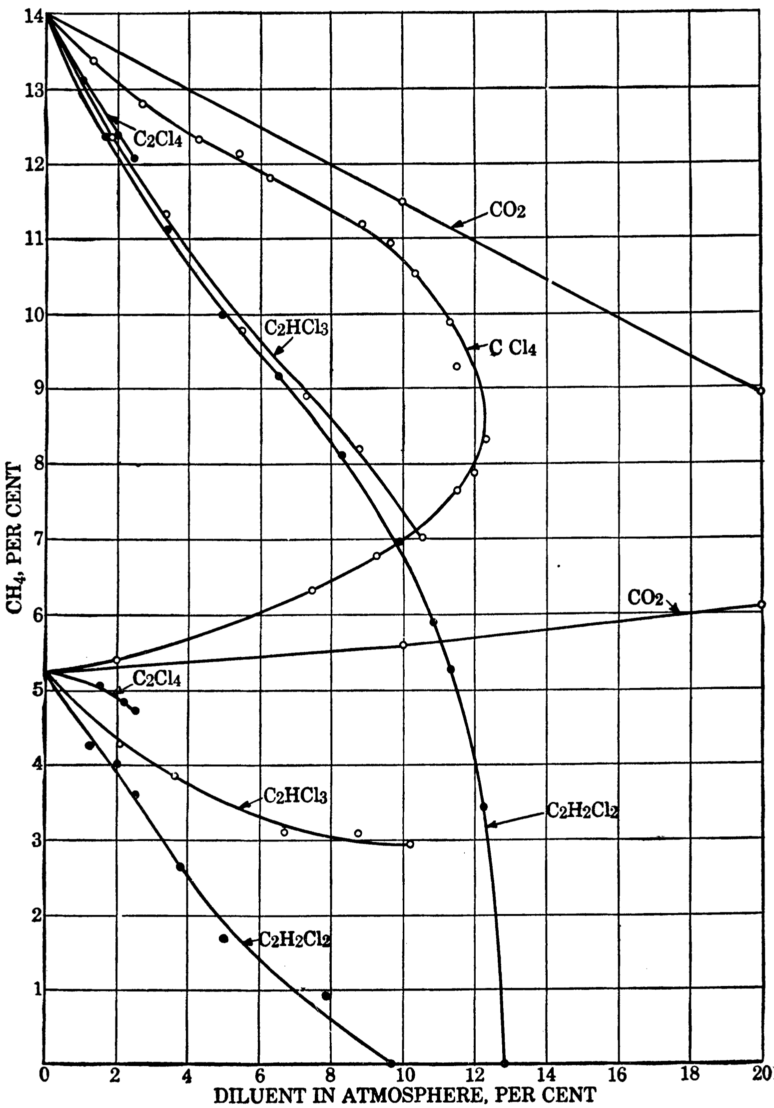

FIGURE 26.—Limits of inflammability of methane in mixtures of air with certain chlorinated hydrocarbons and with CO_2

The broken line in Figure 21 is the locus of mixtures in which the ratio between methane and oxygen is exactly that required for complete combustion, CH_4: $2O_2$.

Atmospheres of air and certain chlorinated hydrocarbons.—Figure 26 shows the influence of certain chlorinated hydrocarbons, mixed in the stated amounts with air, on the limits of inflammability of methane, as found in a tube 2 inches in diameter for upward propagation of flame from the open end. Part of the carbon dioxide curve is inserted for comparative purposes (*106*).

The curves for trichlorethylene and tetrachlorethylene are incomplete; the experiments were carried to the point at which the atmosphere was saturated with these vapors at laboratory temperature. The effects of tetrachlorethane and pentachlorethane were also investigated up to the saturation point. The two ethane derivatives behave like inert diluents whose effect is to be attributed to their thermal capacities. The ethylene derivatives, however, contribute to the inflammability of the mixture; hence the lower limit of methane falls with increase in the proportion of vapor; the higher limit also falls rapidly, for the same reason. The order of increasing combustibility is $C_2Cl_4 \rightarrow C_2HCl_3 \rightarrow C_2H_2Cl_2$; the last vapor forms inflammable mixtures with air without the help of any methane.

The extinctive effect of carbon tetrachloride on methane flames is apparently entirely due to its high thermal capacity. Volume for volume, carbon tetrachloride vapor is twice as extinctive as carbon dioxide; the presence of 12.5 per cent carbon tetrachloride in air renders the mixture incapable of propagating flame, whereas 25 per cent carbon dioxide is necessary for the same effect. Equal volumes of the two liquids, however, have approximately equal extinctive effect.

Series of experiments with chlorine derivatives, in narrow vessels with downward propagation of flame, have been reported (*92*, *94*, *96*, *121*) and discussed (*122*).

Atmospheres in which the nitrogen (of air) is replaced by an inert gas.—In a closed globe of 35 c. c. capacity, with side ignition, the limits were 8.9 to 11.7 per cent methane in a mixture of 20.9 per cent oxygen and 79.1 per cent carbon dioxide, compared with 5.9 to 13.1 per cent methane in air in the same apparatus. The influence of temperature was irregular (*18*).

In a tube 2.5 cm. in diameter, with horizontal propagation from the open end, the methane limits were as follows:

Methane limits in tube 2.5 cm. in diameter

Atmosphere	Methane limits, per cent		Reference No.
	Lower	Higher	
20.9 per cent O_2, 79.1 per cent N_2 (air)	5.85	13.3	*68*
20.9 per cent O_2, 79.1 per cent A	4.40	15.80	*111*
20.9 per cent O_2, 79.1 per cent He	5.55	14.25	*111*

The influence of heat capacity and thermal conductivity are illustrated by these examples. (See under "Atmospheres composed of air mixed with argon and helium.")

Influence of temperature.—In an atmosphere of 20.9 per cent oxygen and 79.1 per cent carbon dioxide the limits observed (*18*) in a closed 35-c. c. globe were slightly widened by increase of temperature to 300° C.

Dilution of CH_4+2O_2 with diluents, inert or otherwise.—The following results were obtained for downward propagation of flame in a Bunte burette 1.9 cm. in diameter.

Effect of diluents upon inflammability of CH_4+2O_2

Diluent	Amount of CH_4+2O_2 which, with the diluent named, is present at the limit of inflammability, per cent
Oxygen	19.3
Nitrogen	23.3
Carbon dioxide	31.9

Nitrogen has a greater extinctive action than oxygen, although it is of equal heat capacity; carbon dioxide, of greater heat capacity, has a greater extinctive action (*28*).

For upward propagation in a tube 5 cm. in diameter the limits were found by the authors to be 3.95 per cent methane with argon and 5 per cent methane with helium. The thermal conductivity effect is noteworthy.

ETHANE

ETHANE IN AIR

The limits of ethane in air, nearly dry, for upward propagation in a tube 5 cm. in diameter, open at the firing end, were 3.22 to 12.45 per cent ethane. The methane-air results in the same and in larger vessels indicate that the figures just given for ethane are close to its true limits in large volumes (*111*). Table 10 summarizes other determinations of the limits of ethane in air.

TABLE 10.—*Summary of other determinations of limits of ethane in air*

Dimensions of tube, cm.		Firing end	Limits, per cent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
UPWARD PROPAGATION OF FLAME						
7.5	150	Closed	3.12	14.95	Half saturated	*90*
5.0	150	do	3.15	14.8	do	*90*
HORIZONTAL PROPAGATION OF FLAME						
7.5	150	Closed	3.15	12.85	Half saturated	*90*
5.0	150	do	3.22	11.75	do	*90*
2.5	150	Open	3.3	10.6	Saturated	*69*
DOWNWARD PROPAGATION OF FLAME						
7.5	150	Closed	3.26	10.15	Half saturated	*90*
5.0	150	do	3.32	10.0	do	*90*
2.0	40	do	3.13	9.85		*82*
1.9	40	do	4.05	9.55	Saturated	*73*
PROPAGATION IN GLOBES						
Capacity, "large"		Closed	3.4	10.7		*68*
Capacity, 4,000 c. c.		do	3.1			*103*

The higher limit varies more than the lower with the direction of propagation of flame. The influence of pressure on the higher limit is unusually great, for upward propagation in a closed tube is possible when the ethane content is more than 2 per cent above the higher limit in a corresponding tube in which, by having the end of the tube open behind the flame, atmospheric pressure is maintained during the progress of the flame.

Influence of turbulence.—In a 4-liter globe the lower limit for a quiescent mixture was 3.10 per cent ethane; with a fan running at

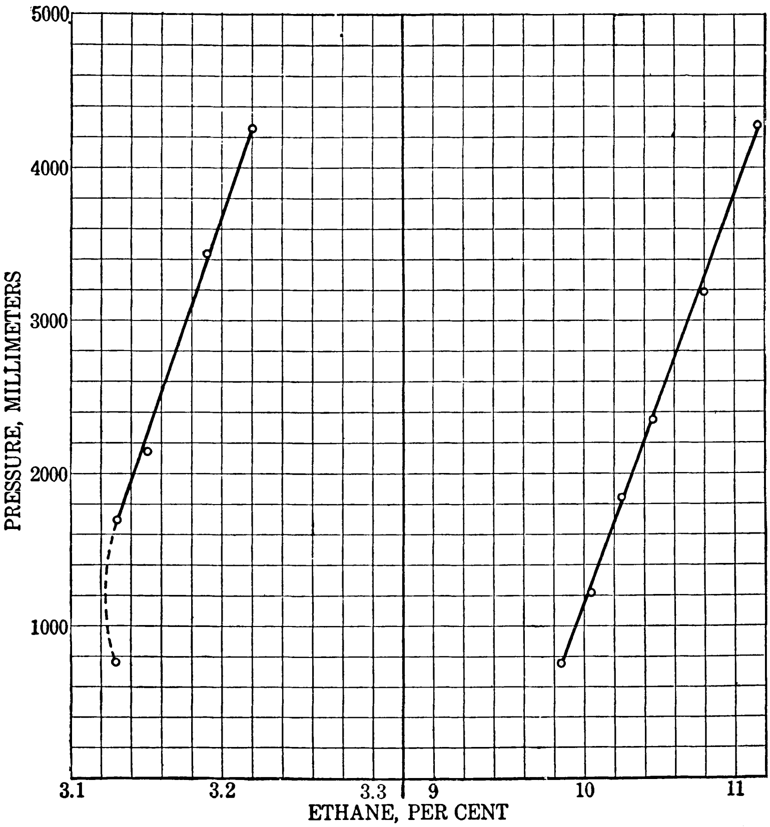

FIGURE 27.—Limits of inflammability of ethane in air (downward propagation), showing influence of pressure

high speed inside the vessel a 3.2 per cent mixture did not ignite, but when the fan was run at a moderate speed a 3.0 per cent mixture exploded, giving rise to a pressure of 4.3 atmospheres (*68*).

Influence of pressure.—Observations (*82*) in a closed tube 2 cm. in diameter and 40 cm. long, with downward propagation of flame, are plotted in Figure 27. For a discussion of these see page 5.

ETHANE IN OXYGEN

An old observation placed the higher limit at 50.5 per cent ethane for downward propagation in a 2-cm. eudiometer (*8*).

ETHANE IN OTHER ATMOSPHERES

Experiments with nitrogen-oxygen atmospheres, richer in oxygen than ordinary air, were made in a Bunte burette 1.9 cm. in diameter with downward propagation. The lower limit of ethane was hardly altered as the oxygen in the atmosphere was increased to 94 per cent; the higher limit rose gradually from 9.5 in air and 33.4 in 60 per cent oxygen to 46 in 94 per cent oxygen atmospheres (*73*).

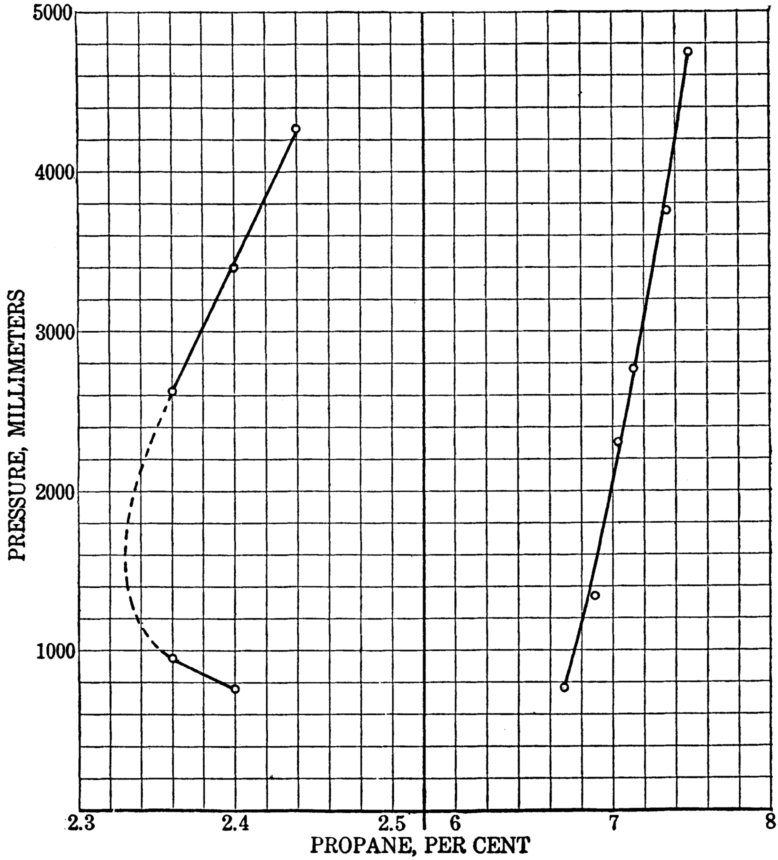

FIGURE 28.—Limits of inflammability of propane in air (downward propagation), showing influence of pressure

PROPANE

The limits of propane-air mixtures, nearly dry, for upward propagation in a tube 5 cm. in diameter, open at the firing end, were 2.37 to 9.50 per cent propane. The methane-air results in the same and in larger vessels indicate that the figures just given for propane are close to its true limits in large volumes (*111*). Table 11 gives other determinations of the limits.

9959°—31——5

TABLE 11.—*Summary of other determinations of limits of propane in air*

Dimensions of tube, cm.		Firing end	Limits, per cent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
HORIZONTAL PROPAGATION OF FLAME						
2.5	150	Open	2.4	7.3	Saturated	*69*
DOWNWARD PROPAGATION OF FLAME						
2.0	40	Closed	2.40	6.69		*82*
PROPAGATION IN GLOBE						
Capacity, "large"		Closed	2.3	7.3		*69*

Influence of pressure.—Observations (*82*) in a closed tube 2 cm. in diameter and 40 cm. long, with downward propagation of flame, are plotted in Figure 28. For a discussion of these see page 5.

BUTANE

The limits of butane-air mixtures, nearly dry, for upward propagation in a tube 5 cm. in diameter, open at the firing end, were 1.86 to 8.41 per cent butane. The methane-air results in the same and in larger vessels indicate that these figures are close to the true limits in large volumes (*111*). Table 12 gives other determinations of the limits of butane-air mixtures.

TABLE 12.—*Summary of other determinations of limits of butane in air*

Dimensions of tube, cm.		Firing end	Limits, per cent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
HORIZONTAL PROPAGATION OF FLAME						
2.5	150	Open	1.9	6.5	Saturated	*69*
DOWNWARD PROPAGATION OF FLAME						
2.0	40	Closed	1.92	5.50		*82*
PROPAGATION IN GLOBE						
Capacity, "large"		Closed	1.6	5.7		*69*

Influence of pressure.—Observations (*82*) in a closed tube 2 cm. in diameter and 40 cm. long, with downward propagation of flame, are plotted in Figure 29. For a discussion of these curves, see page 5

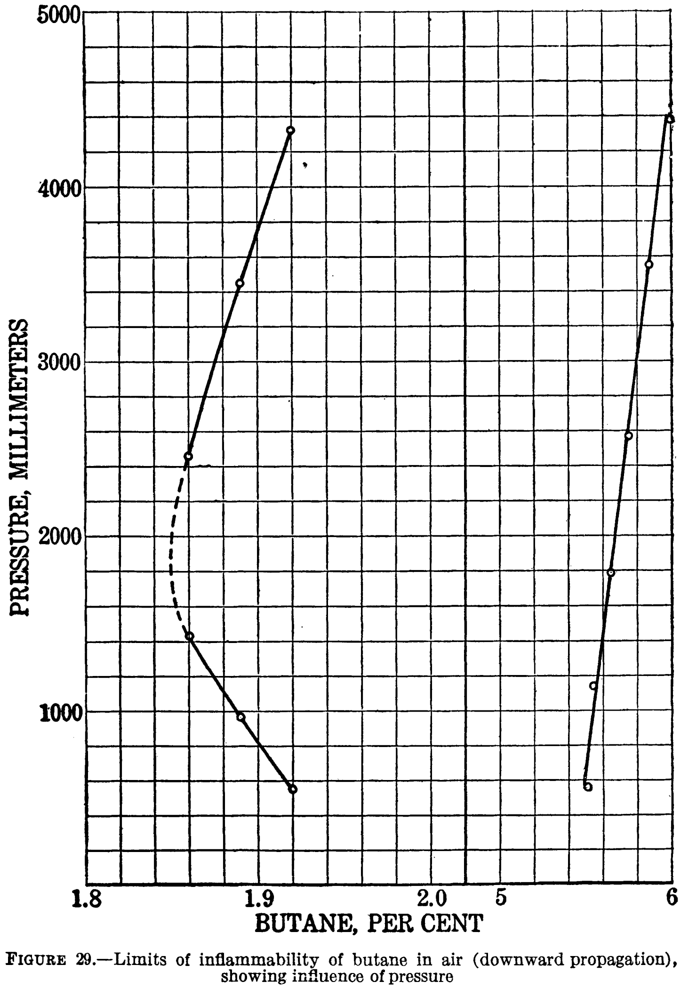

FIGURE 29.—Limits of inflammability of butane in air (downward propagation), showing influence of pressure

PENTANE

The limits of pentane in air, upward propagation of flame in a tube 5 cm. in diameter, open at the firing end, were 1.45 to 7.50 per cent (*157*).

Table 13 summarizes other determinations of the limits of pentane in air.

TABLE 13.—*Summary of other determinations of the limits of pentane in air*

Dimensions of tube, cm.		Firing end	Limits, per cent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
UPWARD PROPAGATION OF FLAME						
7.5	150	Closed	1.42	8.0	Half saturated	*90*
5.0	150	do	1.43	8.0	do	*90*
HORIZONTAL PROPAGATION OF FLAME						
7.5	150	Closed	1.44	7.45	Half saturated	*90*
5.0	150	do	1.46	6.70	do	*90*
2.5	150	Open	1.6	5.4	Saturated	*69*
DOWNWARD PROPAGATION OF FLAME						
7.5	150	Closed	1.48	4.64	Half saturated	*90*
6.2	33	Open	1.3		Saturated	*28*
5.0	150	Closed	1.49	4.56	Half saturated	*90*
5.0	65	do	1.43	4.6	Dry	*140*
2.0	40	do	1.75	4.68		*82*
1.9	40	do	2.4	4.9	Saturated	*28*
PROPAGATION IN GLOBES						
Capacity, 14.5 liters		Closed	1.2			*28*
Capacity, "large"		do	1.4	4.5		*69*

An old observation gave the lower limit for pentane-air mixtures as 1.1 per cent in a 2-liter bottle, apparently for downward propagation of flame (*24*).

Influence of pressure.—Observations (*82*) in a closed tube 2 cm. in diameter and 40 cm. long, with downward propagation of flame, are plotted in Figure 30. For a discussion of these tests see page 5.

Influence of temperature.—Determinations (*101*) in a closed tube 2.5 cm. in diameter and 150 cm. long, with downward propagation of flame, showed that the lower limit decreased linearly from 1.53 per cent at about 17° C. to 1.22 per cent at 300° C.; the higher limit increased linearly from 4.50 per cent at about 17° C. to 5.35 per cent at 300° C.

HIGHER PARAFFIN HYDROCARBONS

Observations (*24*) with hydrocarbon-air mixtures, made in a 2-liter open bottle, apparently with downward propagation of flame, gave the following lower limit figures: Hexane, 1.3 per cent; heptane, 1.1 per cent; octane, 1.0 per cent; and nonane, 0.83 per cent.

The lower limits of the first four members of the paraffin series, observed in a 2-inch tube, upward propagation of flame, are given by the empirical formula $8.62/(n+0.647)$, where n is the number of carbon atoms in the molecule. It is not improbable that this formula will give the lower limits of higher members of the series. Alternatively, the lower limit may be read from the broken part of the curve in Figure 35, as described on page 92.

ETHYLENE

ETHYLENE IN AIR

The limits of ethylene in air, upward propagation of flame in a tube 5 cm. in diameter, open at the firing end, were 3.05 to 28.6 per cent (*159*).

Table 14 summarizes other determinations of the limits of ethylene in air.

TABLE 14.—*Summary of other determinations of the limits of ethylene in air*

Dimensions of tube, cm.		Firing end	Limits, per cent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
UPWARD PROPAGATION OF FLAME						
7.5	150	Closed	3.02	34	Half saturated	*90*
6.2	33	Open	3.4	20.55	do	*28*
5.0	150	Closed	3.13	33.3	do	*90*
2.5	150	do	3.15	27.6	do	*90*
2.5	150	Open	3.3	25.6	Small	*74*
HORIZONTAL PROPAGATION OF FLAME						
7.5	150	Closed	3.20	23.7	Half saturated	*90*
5.0	150	do	3.25	22.4	do	*90*
2.5	150	do	3.30	14.0	do	*90*
2.5	150	Open	3.4	14.1	Small	*74*
2.5	150	do	3.30	18.25	do	*156*
DOWNWARD PROPAGATION OF FLAME						
7.5	150	Closed	3.33	15.5	Half saturated	*90*
6.2	33	Open	3.4		Saturated	*28*
5.0	150	Closed	3.42	15.3	Half saturated	*90*
2.5	150	do	3.45	13.7	do	*90*
2.5	150	Open	3.6	13.7	Small	*74*
1.9	40	Closed	4.1	14.6	Saturated	*28*
1.9	40	do	3.9	14.1	do	*73*

The results obtained in closed tubes show great variability with the diameter of tube and apparently are much affected by the pressure changes which occur during inflammation.

Influence of pressure.—Experiments in a small cylindrical bomb (*119*) showed a pronounced effect of pressure on the limits of ethylene in air. The lower limit rose from 3.5 per cent at normal pressure to 5 per cent at 20 atmospheres and then fell to 1.5 per cent at 380 atmospheres. The higher limit rose rapidly from 16 per cent at normal pressure to 68 per cent at 90 atmospheres and then rose slowly to 71 per cent at 380 atmospheres.

Influence of temperature.—Of two sets of observations (*87*, *90*) on the influence of temperature one appears to be reliable (*90*). Determinations were made in a closed tube 2.5 cm. in diameter and 150 cm. long with downward propagation of flame. The lower limit decreased linearly from 3.45 per cent ethylene at about 17° C. to 2.50 per cent at 400° C. The higher limit increased from 13.7 per cent at about 17° C. to 17.9 per cent at 300° C.; the rate of increase became faster as the temperature was raised.

ETHYLENE IN OXYGEN

The limits of ethylene in oxygen, upward propagation of flame in a tube 5 cm. in diameter, open at the firing end, were 3.10 to 79.9 per cent *(159)*.

Some older observations *(8, 10, 98)* gave somewhat narrower limits in small vessels.

Influence of pressure.—Certain ethylene-oxygen mixtures are still inflammable at 30 mm. pressure *(48)*.

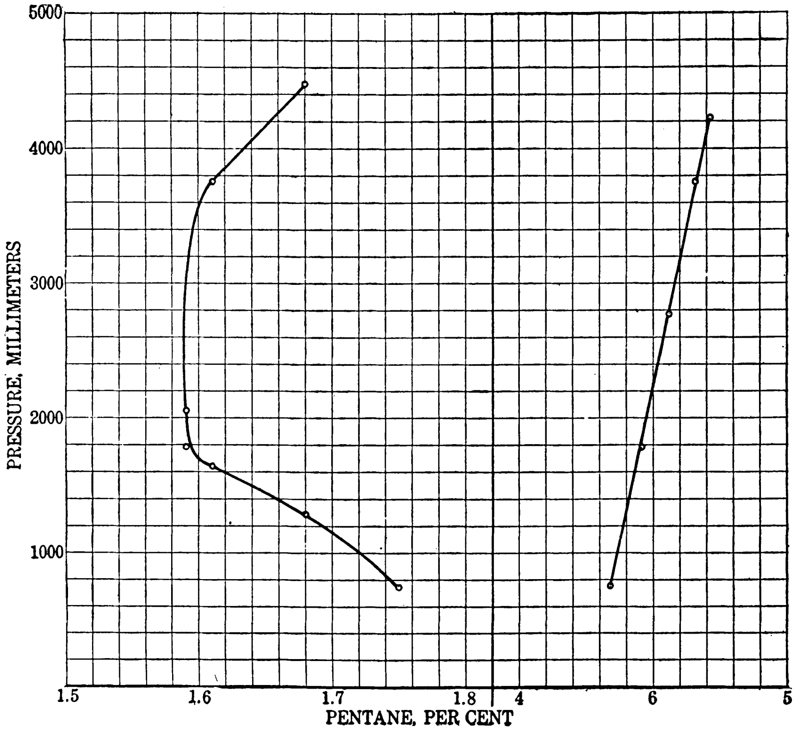

FIGURE 30.—Limits of inflammability of pentane in air (downward propagation), showing influence of pressure

ETHYLENE IN OTHER ATMOSPHERES

Atmospheres of composition between air and pure oxygen.—Observations made in a Bunte burette 1.9 cm. in diameter, with downward propagation, were as follows: The lower limit was slightly increased as the oxygen in the atmosphere was increased to 94 per cent; the higher limit rose gradually from 14.1 per cent in air, and 47.6 per cent in 60 per cent oxygen to 62 per cent in 94 per cent oxygen atmospheres *(73)*.

Atmospheres of air and nitrogen (air deficient in oxygen).—The limits of inflammability of ethylene in all mixtures of air and nitrogen or air from which part of the oxygen has been removed, can be read from one of the curves of Figure 31. The determinations were made in in a tube 6 feet long and 2 inches in diameter, with upward propagation of flame at atmospheric pressure during propagation (*159*).

Atmospheres of air and carbon dioxide.—The limits of inflammability of ethylene in all mixtures of air and carbon dioxide can be read from one of the curves of Figure 31. The determinations were made as described in the previous paragraph.

Some earlier observations (*28*) show, as might be expected, more rapid narrowing of the limits in Bunte burette experiments.

Atmospheres of carbon dioxide and oxygen.—For limits of ethylene in carbon dioxide-oxygen atmospheres, reference may be made to some old experiments of doubtful accuracy (*10*).

Dilution of $C_2H_4+3O_2$ with gases, inert or otherwise.—The following results of experiments with diluted mixtures of $C_2H_4+3O_2$ were obtained in a Bunte burette (*28*).

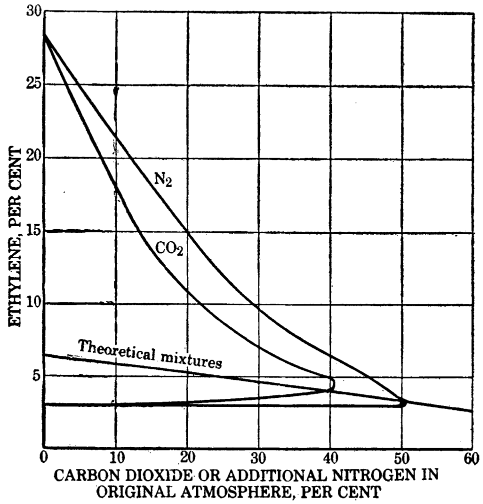

FIGURE 31.—Limits of inflammability of ethylene in atmospheres of air and carbon dioxide or nitrogen

Effect of dilution on inflammability of $C_2H_4+3O_2$

Diluent	Amount of $C_2H_4+3O_2$ which, with the diluent named, is present at the limit of inflammability, per cent
Oxygen	15.4
Nitrogen	18.5
Carbon dioxide	22.1

PROPYLENE

PROPYLENE IN AIR

Table 15 gives the observed limits of inflammability of propylene in air.

TABLE 15.—*Limits of inflammability of propylene in air*

Dimensions of tube, cm.		Firing end	Limits, per cent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
UPWARD PROPAGATION OF FLAME						
7.5	150	Closed	2.18	9.7	Half saturated	*90*
5.0	150	do	2.21	9.6	do	*90*
HORIZONTAL PROPAGATION OF FLAME						
7.5	150	Closed	2.22	9.3	Half saturated	*90*
5.0	150	do	2.26	8.4	do	*90*
2.5	150	Open	2.6	7.4	Small	*74*
2.5	150	do	2.58	7.5	do	*156*
DOWNWARD PROPAGATION OF FLAME						
7.5	150	Closed	2.26	7.4	Half saturated	*90*
5.0	150	do	2.29	7.2	do	*90*

PROPYLENE IN OXYGEN

The higher limit of propylene in oxygen, upward propagation of flame in a tube 5 cm. in diameter, open at the firing end, was 52.8 per cent (*159*).

BUTYLENE

Table 16 gives the observed limits of inflammability of butylene in air.

TABLE 16.—*Limits of inflammability of butylene in air*

Dimensions of tube, cm.		Firing end	Limits, per cent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
UPWARD PROPAGATION OF FLAME						
7.5	150	Closed	1.70	9.0	Half saturated	*90*
5.0	150	do	1.80	9.0	do	*90*
HORIZONTAL PROPAGATION OF FLAME						
7.5	150	Closed	1.75	9.0	Half saturated	*90*
5.0	150	do	1.82	7.4	do	*90*
2.5	150	Open	1.93	6.0	Small	*156*
DOWNWARD PROPAGATION OF FLAME						
7.5	150	Closed	1.80	6.25	Half saturated	*90*
5.0	150	do	1.84	6.10	do	*90*

AMYLENE

One observation in a 2-liter bottle, apparently with downward propagation of flame, gave 1.6 per cent as the lower limit of amylene in air (*24*).

ACETYLENE

ACETYLENE IN AIR

The lower limit of acetylene in air, in a tube 5 cm. in diameter and 150 cm. long, upward propagation of flame from an open end, is 3.00 per cent (*157*).

In a box about 4.6 feet high and 12 inches square in cross section the lower limit for propagation of flame upward toward the open top was 2.53 per cent acetylene (*55*). It has been pointed out that the lower limit of methane is reduced from 5.3 per cent in a quiescent mixture to 5.0 per cent if turbulence is imparted to the mixture as the result of expansion of the gases when flame travels upward toward the open end of the tube. Hence, the lower limit of acetylene in a quiescent mixture in a large space may be nearer 3.00, as observed in the 5-cm. tube, than 2.53. In a bell jar, with turbulence, the figure 2.30 was obtained (*157*).

For downward propagation of flame in the box, presumably toward the closed end, the lower limit was about 2.8 per cent (*55*). An earlier determination in a 90-liter vessel 41 cm. in diameter and 80 cm. in height gave limits of 3 to 80 per cent acetylene (*25*).

Table 17 gives other determinations of the limits.

TABLE 17.—*Summary of other determinations of limits of acetylene in air*

UPWARD PROPAGATION OF FLAME

Dimensions of tube, cm.		Firing end	Limits, per cent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
7.5	150	Closed	2.60	80	Half saturated	*90*
5.0	150	do	2.60	78	do	*90*
2.5	150	do	2.73	70	do	*90*

HORIZONTAL PROPAGATION OF FLAME

Diameter	Length	Firing end	Lower	Higher	Content of aqueous vapor	Reference No.
7.5	150	Closed	2.68	78.5	Half saturated	*90*
5.0	150	do	2.68	68.5	do	*90*
4.0			[1] 2.9	64		*20*
3.0			[1] 3.1	62		*20*
2.5	150	Closed	2.87	59.5	Half saturated	*90*
2.0			[1] 3.5	55		*20*
.6			[1] 4.0	40		*20*
.4			[1] 4.5	25		*20*
.2			[1] 5.0	15		*20*
.08			[1] 7.7	10		*20*
.05			No propagation [1]			*20*

DOWNWARD PROPAGATION OF FLAME

Diameter	Length	Firing end	Lower	Higher	Content of aqueous vapor	Reference No.
12.2	21	Open		75	Saturated	*28*
10.0	13	do		70	do	*28*
7.5	150	Closed	2.78	71.0	Half saturated	*90*
5.0	150	do	2.80	63.5	do	*90*
4.4	26	Open		60	Saturated	*28*
2.5	150	do	2.90	55.0	Half saturated	*90*
1.9	40	do	3.45	52.2	Saturated	*28*
1.9	40	do	3.45	52.4	do	*73*

[1] Direction of flame propagation not stated in original reference; it may be downward, not horizontal.

Limits in vessels other than tubes were as follows: In a 2.8-liter bottle with central ignition, 3.0 to 73 per cent (*55*); in a 2-liter rubber balloon with flame ignition, 75 per cent (higher limit) (*28*); and in a 100 c. c. Hempel pipette with downward propagation, 2.9 to 51 per cent (*55*).

A few experiments have been reported on the "inflammability of acetylene mixed with about 30 per cent of air," but this mixture is well within the limits of inflammability and the report (*39*) is only concerned with conditions for ignition.

Influence of pressure.—The lower limit, observed in a Hempel pipette, was unchanged by increase of pressure to 5 atmospheres (*55*).

Influence of temperature.—Determinations (*101*) in a closed tube 2.5 cm. in diameter and 150 cm. long, with downward propagation of flame, showed that the lower limit decreased linearly from 2.90 per cent at about 17° C. to 2.19 per cent at 300° C. The higher limit increased from 55 per cent at about 17° C. to somewhat over 81 per cent at 200° C.

In an older observation (*28*) the higher limit in a cylinder 4.4 cm. in diameter and 26 cm. long, with downward propagation from an open end, was 60 per cent acetylene at laboratory temperature and 75 per cent at 200° C.

ACETYLENE IN OXYGEN

An old experiment with acetylene-oxygen mixtures gave the higher limit for downward propagation as 83 per cent acetylene (*8*); an estimate for "an infinite mass" (not cooled by walls of confining vessel) gave limits of 2.8 to 93 per cent acetylene (*20*).

Experiments with downward propagation in a Bunte burette 1.9 cm. in diameter gave a lower limit of 3.1 per cent in oxygen, compared with 3.45 per cent in air (*28*).

ACETYLENE IN OTHER ATMOSPHERES

Atmospheres of composition between air and pure oxygen.—Experiments with acetylene in nitrogen-oxygen atmospheres, richer in oxygen than ordinary air, in a Bunte burette 1.9 cm. in diameter with downward propagation, showed that the lower limit was unchanged as the oxygen in the atmosphere increased to 97 per cent; the higher limit rose gradually from 52.4 per cent in air, 82.2 per cent in 58 per cent oxygen, to 89.7 per cent in 96.8 per cent oxygen (*73*).

Atmospheres of nitrogen, oxygen and carbon dioxide.—A few experiments in a Bunte burette show the narrowing of the range of inflammable mixtures in which (1) the oxygen is gradually replaced by carbon dioxide, and (2) increasing amounts of carbon dioxide are added to air. In the first series no inflammable mixture could be made when the oxygen was reduced to 8 per cent (carbon dioxide, 13 per cent). In the second series no inflammable mixture could be made in an atmosphere composed of 54 per cent air and 46 per cent carbon dioxide (*28*).

Atmospheres of air mixed with vapors of chlorinated hydrocarbons.—Limits of acetylene in air containing the vapors of various chloro derivatives of hydrocarbons have been reported; they were observed in small burettes 15 mm. in diameter, and so are of limited value (*92*).

Dilution of $2C_2H_2+5O_2$ with gases, inert or otherwise.—The following results of experiments on the dilution of $2C_2H_2+5O_2$ were obtained for downward propagation of flame in a Bunte burette (*28*):

Effect of diluents on inflammability of $2C_2H_2+5O_2$

Diluent	Amount of $2C_2H_2+5O_2$ which, with the diluent named, is present at the limit of inflammability, per cent
Oxygen	10.9
Nitrogen	13.0
Carbon dioxide	18.7

BENZENE

BENZENE IN AIR

The limits of benzene in air, upward propagation of flame in a tube 5 cm. in diameter, open at the firing end, were 1.40 to 6.75 per cent (*157*), 1.55 per cent (lower limit only) (*158*).

Table 18 summarizes other determinations of the limits of benzene in air.

TABLE 18.—*Summary of other determinations of the limits of inflammability of benzene in air*

UPWARD PROPAGATION OF FLAME

Dimensions of tube, cm.		Firing end	Limits, per cent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
7.5	150	Closed	1.41		Dry	*78*
5.0	150	do	1.45	[1] 7.45	do	*78*
5.0	91	do	1.50	8.0	do	*110*
2.5	150	do	1.55		do	*78*
2.5	25	(Central ignition)	[2] 1.5	9.5	Undried	*134*

HORIZONTAL PROPAGATION OF FLAME

Diameter	Length	Firing end	Lower	Higher	Content of aqueous vapor	Reference No.
7.5	150	Closed	1.46		Dry	*78*
5.0	150	do	1.46	[1] 6.65	do	*78*
5.0	91	do	1.55	6.5	do	*110*
2.5	150	do	1.55		do	*78*

DOWNWARD PROPAGATION OF FLAME

Diameter	Length	Firing end	Lower	Higher	Content of aqueous vapor	Reference No.
7.5	150	Closed	1.46		Dry	*78*
6.2		Open	1.4		Saturated	*28*
5.0	150	Closed	1.48	[1] 5.55	Dry	*78*
5.0	91	do	1.60	5.0	do	*110*
5.0	65	do	1.47	5.45	do	*140*
2.5	150	do	1.58		do	*78*
1.9	40	do	2.65	6.5	Saturated	*28*
1.9	40	do	2.7	7.0	do	*73*

[1] At 60° C. [2] For "90% benzene," b. p. 77°–118° C.

In a globe of 14.5 liters capacity the lower limit observed was 1.3 per cent (*28*).

The lower limits in a 5-cm. tube closed at both ends differed only in the second decimal place from those obtained when a small stopcock was opened at one end or the other. Similar differences were observed when the length of tube was varied between the limits of 100 and 250 cm. and when the position of the point of ignition was brought forward about 6 cm. (*78*).

It appears that the lower limit in a large space at atmospheric pressure will prove to be about 1.3 or 1.4 per cent benzene, but it is not possible, from the results quoted, to define the higher limit closely in these circumstances.

Influence of pressure.—The range of inflammability of benzene in air is widened at both sides by increase of pressure above atmospheric, provided the temperature be raised to maintain enough vapor for the test. The effect may be due to the temperature change more than to the pressure change (*119*).

BENZENE IN OTHER ATMOSPHERES

In nitrogen-oxygen atmospheres, richer in oxygen than ordinary air, in a spherical vessel with ignition near the top, the lower limit of benzene was unchanged as the oxygen in the atmosphere was increased to 97 per cent; the higher limit rose gradually from 7 per cent in air, 20.7 per cent in 58 per cent oxygen, to 30 per cent in 97 per cent oxygen (*73*).

TOLUENE

The lower limit of toluene in air, upward propagation of flame, in a tube 5 cm. in diameter, open at the firing end, was 1.45 per cent (*157*), or 1.49 per cent (*158*).

Table 19 summarizes other determinations of the limits of toluene in air.

TABLE 19.—*Summary of other determinations of the limits of inflammability of toluene in air*

UPWARD PROPAGATION OF FLAME

Dimensions of tube, cm.		Firing end	Limits, per cent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
7.5	150	Closed	1.27		Dry	*78*
5.0	150	do	1.31	[1] 6.75	do	*78*
2.5	25	(Central ignition)	1.3	7.0	Undried	*134*

HORIZONTAL PROPAGATION OF FLAME

Diameter	Length	Firing end	Lower	Higher	Content of aqueous vapor	Reference No.
7.5	150	Closed	1.28		Dry	*78*
5.0	150	do	1.30	[1] 5.80	do	*78*

DOWNWARD PROPAGATION OF FLAME

Diameter	Length	Firing end	Lower	Higher	Content of aqueous vapor	Reference No.
7.5	150	Closed	1.28		Dry	*78*
5.0	150	do	1.32	[1] 4.60	do	*78*

[1] At 60° C.

Earlier figures gave approximate values of 1.3 and 1.4 per cent for the lower limit, probably for downward propagation of flame (*24*, *27*).

The lower limit in a large space at atmospheric pressure is probably about 1.3 per cent, but it is not possible from the results quoted, to define the higher limit in these circumstances.

CYCLOHEXANE

The limits of cyclohexane in air, upward propagation of flame, in a tube 5 cm. in diameter, open at the firing end, were 1.33 to 8.35 per cent (*158*). In a closed tube 5 cm. wide and 65 cm. long, downward propagation of flame, they were 1.31 to 4.5 per cent (*140*).

METHYL CYCLOHEXANE

The lower limit of methyl cyclohexane in air, in a tube 5 cm. wide, was 1.25 per cent for upward propagation of flame (*158*) and 1.15 per cent for downward propagation (*115*). In the former observations the tube was open at the firing end, in the latter it was partially opened (by means of stopcocks) at both ends.

Influence of impurities.—The lower limit was unaffected by small additions of diethyl selenide or lead tetraethyl. The effect of pyridine and of diethyl selenide was in accord with Le Chatelier's formula (*116*).

METHYL ALCOHOL

METHYL ALCOHOL IN AIR

The lower limit of methyl alcohol in air, upward propagation of flame, in a tube 5 cm. in diameter, open at the firing end, was 7.35 per cent (*157*).

Table 20 summarizes other determinations of the limits of methyl alcohol in air.

TABLE 20.—*Summary of other determinations of the limits of inflammability of methyl alcohol in air*

Dimensions of tube, cm.		Firing end	Limits, per cent		Contents of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
UPWARD PROPAGATION OF FLAME						
7.5	150	Closed	7.05		Dry	*78*
5.0	150	do	7.10	[1] 36.5	do	*78*
5.0	91	do	6.0		do	*110*
2.5	150	do	7.9		do	*78*
2.5	25	(Central ignition)	5.5	21.0	Undried	*134*
HORIZONTAL PROPAGATION OF FLAME						
7.5	150	Closed	7.30		Dry	*78*
5.0	150	do	7.35	[1] 30.5	do	*78*
5.0	91	do	6.40	13.50	do	*110*
2.5	150	do	7.9		do	*78*
DOWNWARD PROPAGATION OF FLAME						
7.5	150	Closed	7.45		Dry	*78*
5.0	150	do	7.65	[1] 26.5	do	*78*
5.0	91	do	6.80		do	*110*
2.5	150	do	8.0		do	*78*

[1] At 60° C.

The lower limit in a 2-liter flask with ignition near the base has recently been given as 6.1 per cent (*102*). Two older figures (*24*, *27*), probably for downward propagation, are 6 and 7.8 per cent.

Influence of temperature.—Two series of experiments on the influence of temperature on the limits of methyl alcohol have been reported (*152*, *153*). The latter, which seem to be reliable, show that for downward propagation of flame in a 2½-liter bottle the lower limit falls steadily from 7.5 per cent at 50° to 5.9 per cent at 250° C. The higher limit rose from 24.9 per cent at 100° to 36.8 per cent at 200° C.

Influence of water.—The lower limits of mixtures of methyl alcohol and water rise steadily as the amount of water increases from 0 to 60 per cent, but the amount of methyl alcohol itself is approximately constant in the limit mixture. When 80 per cent of water was present it was difficult to inflame any mixture of the vaporized liquid and air at 105° C., and 85 per cent water made inflammation practically impossible (*152*).

METHYL ALCOHOL IN OTHER ATMOSPHERES

Atmospheres of nitrogen and oxygen and of carbon dioxide and oxygen.—The limits of methyl alcohol in "atmospheres" of nitrogen and oxygen and of carbon dioxide and oxygen, containing oxygen ranging from 20.9 per cent downward, have been determined in a 2-liter flask, with ignition near the base. Curves extending as far as could be determined at laboratory temperatures are given in the original paper (*102*). (The higher limit, over part of the range, requires more methyl alcohol than is present in the saturated vapor.) When the oxygen content of a nitrogen-oxygen "atmosphere" was reduced below 10.9 per cent, no mixture of methyl alcohol would propagate flame (*102*).

Atmospheres of air and carbon dioxide.—The limits of methyl alcohol in mixtures of air and carbon dioxide, downward propagation of flame in a 2-liter cylinder, approach one another as the proportion of carbon dioxide is increased. When more than 26 per cent carbon dioxide is present in the "atmosphere," no mixture with methyl alcohol will propagate flame in these circumstances (*152*).

ETHYL ALCOHOL

ETHYL ALCOHOL IN AIR

The lower limit of ethyl alcohol in air, upward propagation of flame in a tube 5 cm. in diameter, open at the firing end, is 4.25 per cent (*157*), or 4.40 per cent (*158*).

Table 21 summarizes other determinations of the limits of ethyl alcohol in air.

TABLE 21.—*Summary of other determinations of the limits of inflammability of ethyl alcohol in air*

UPWARD PROPAGATION OF FLAME

Dimensions of tube, cm.		Firing end	Far end	Limits, per cent		Content of aqueous vapor	Reference No.
Diameter	Length			Lower	Higher		
15	300 (iron)	Closed	Open	4.16		Dry	*70*
7.5	150 (glass)	do	Closed	3.56		do	*78*
5	150 (glass)	do	Open	4.24	[1] 18.95	do	*70*
5	150 (glass)	do	Closed	3.69	[1] 18.00	do	*78*
5	91 (glass)	do	do	4.30		do	*110*
2.5	150 (glass)	do	Open	5.02		do	*70*
2.5	25 (glass)	(Central ignition)	Closed	4.0	14.0	Undried	*134*

HORIZONTAL PROPAGATION OF FLAME

Diameter	Length	Firing end	Far end	Lower	Higher	Content of aqueous vapor	Reference No.
15	300 (iron)	Closed	Open	4.23		Dry	*70*
7.5	150 (glass)	do	Closed	3.70		do	*78*
5	150 (glass)	do	Open	4.32	[1] 13.80	do	*70*
5	150 (glass)	do	Closed	3.75	[1] 13.80	do	*78*
5	91 (glass)	do	do	4.40		do	*110*
2.5	150 (glass)	do	Open	5.18		do	*70*

DOWNWARD PROPAGATION OF FLAME

Diameter	Length	Firing end	Far end	Lower	Higher	Content of aqueous vapor	Reference No.
15	300 (iron)	Closed	Open	4.37		Dry	*70*
7.5	150 (glass)	do	Closed	3.75		do	*78*
6.2	33 (glass)	Open	do	3.70		Saturated	*28*
5	150 (glass)	Closed	Open	4.44	[1] 11.50	Dry	*70*
5	150 (glass)	do	Closed	3.78	[1] 11.50	do	*78*
5	91 (glass)	do	do	4.50		do	*110*
5	70 (glass)	Partly open	Partly open	3.81		do	*118*
2.5	150 (glass)	Closed	Open	5.21		do	*70*
1.9	40 (glass)	do	Closed	3.95	13.65	Saturated	*28*

[1] At 60° C.

Influence of temperature.—The lower limit of ethyl alcohol in air, upward propagation of flame in a tube 5 cm. in diameter, is 4.25 per cent at laboratory temperature (*157*) and 3.85 per cent at 125° C. (*150*). Three other series of observations have been recorded (*77*, *152*, *153*). The last set, which seems to be reliable, shows that for downward propagation of flame in a 2½-liter bottle the lower limit falls steadily from 3.80 per cent at 50° to 2.75 per cent at 225° C. At 250° C. the lower limit rose to 3.05 per cent, but this was presumably due to slow combustion of part of the mixture before ignition.

Influence of impurities.—The lower limit of ethyl alcohol in air was unaffected by small additions of water vapor, diethyl selenide, or lead tetraethyl. The effect of a little pyridine was in accord with Le Chatelier's formula (*116*).

Influence of water.—The lower limits of mixtures of ethyl alcohol and water rise steadily as the amount of water increases from 0 to 60 per cent, but the amount of ethyl alcohol itself is approximately constant in the limit mixture. When 80 per cent of water was present it was difficult to inflame any mixture of the vaporized liquid and air at 105° C., and 85 per cent water made inflammation practically impossible (*152*).

ETHYL ALCOHOL IN OTHER ATMOSPHERES

Atmospheres of air and carbon dioxide.—The limits of ethyl alcohol in mixtures of air and carbon dioxide, downward propagation of flame in a 2-liter cylinder, approach one another as the proportion of carbon dioxide is increased. When more than 36 per cent carbon dioxide is present in the "atmosphere," no mixture with ethyl alcohol will propagate flame in these circumstances (*152*).

HIGHER ALCOHOLS

Lower limits of some higher alcohols in air, apparently for downward propagation of flame, have been determined in a ½-liter flask (*24*). The lower limits were 2.55 per cent propyl alcohol, 2.65 per cent isopropyl alcohol, 1.68 per cent isobutyl alcohol, 1.19 per cent amyl alcohol, and 3.04 per cent allyl alcohol.

The lower limit of isopropyl alcohol in air, in a closed tube 25 cm. long and 2.5 cm. in diameter, central ignition, upward propagation, was 2.5 per cent (*134*).

METHYL ETHER

An old observation placed the higher limit of methyl ether in oxygen, with downward propagation in a 2-cm. tube, between 42 and 49 per cent methyl ether (*8*).

ETHYL ETHER

ETHYL ETHER IN AIR

The limits of ethyl ether in air, upward propagation of flame in a tube 5 cm. in diameter, open at the firing end, were 1.85 to 25.9 per cent (*157*), or 1.92 to 48.5 per cent (*158*).

Table 22 summarizes other determinations of the limits of ethyl ether in air.

TABLE 22.—*Summary of other determinations of the limits of inflammability of ethyl ether in air*

UPWARD PROPAGATION OF FLAME

Dimensions of tube, cm.		Firing end	Far end	Limits, per cent		Content of aqueous vapor	Reference No.
Diameter	Length			Lower	Higher		
15	300 (iron)	Closed	Open	1.73	23.30	Dry	*70*
7.5	150 (glass)	do	Closed	1.71	48	do	*78*
5	150 (iron)	do	Open	2.24	15.45	do	*70*
5	150 (glass)	do	do	1.93	15.75	do	*70*
5	150 (glass)	do	Closed	1.84	48	do	*78*
5	91 (glass)	do	do	1.95	15.60	do	*110*
2.5	150 (glass)	do	do	2.00	47	do	*78*
2.5	25 (glass)	(Central ignition)	do	1.25	10.0	Undried	*134*

HORIZONTAL PROPAGATION OF FLAME

Diameter	Length	Firing end	Far end	Lower	Higher	Content of aqueous vapor	Reference No.
15	300 (iron)	Closed	Open	1.80	22.30	Dry	*70*
7.5	150 (glass)	do	Closed	1.75	40	do	*78*
5	150 (iron)	do	Open	2.29	7.95	do	*70*
5	150 (glass)	do	do	2.05	8	do	*70*
5	150 (glass)	do	Closed	1.88	33	do	*78*
5	91 (glass)	do	do	2.05	8	do	*110*
2.5	150 (glass)	do	do	{1.98 14	6.25 25}	do	*78*

TABLE 22.—*Summary of other determinations of the limits of inflammability of ethyl ether in air*—Continued

DOWNWARD PROPAGATION OF FLAME

Dimensions of tube, cm.		Firing end	Far end	Limits, per cent		Content of aqueous vapor	Reference No.
Diameter	Length			Lower	Higher		
15	300 (iron)	Closed	Open	1.93	6.50	Dry	*70*
7.5	150 (glass)	do	Closed	1.85	6.40	do	*78*
6.2	33 (glass)	Open	do	1.6		Saturated	*28*
5	150 (iron)	Closed	Open	2.34	6.70	Dry	*70*
5	150 (glass)	do	do	2.15	6.15	do	*70*
5	91 (glass)	do	Closed	2.15	6.15	do	*110*
5	65 (glass)	do	do	1.89	6.7	do	*140*
5	65 (glass)	Partly open	Partly open	1.93	6.66	do	*115*
2.5	150 (glass)	Closed	Closed	1.97	6.15	do	*78*
1.9	33 (glass)	Open	do	2.75	7.70	Saturated	*28*

The lower limits in a 5-cm. glass tube closed at both ends differed only in the second decimal place from those obtained when a small stopcock was opened at one end or the other; the higher limits differed by not more than 1 per cent. Similar differences were observed when the length of the tube was varied between the limits of 100 and 250 cm. and when the point of ignition was brought forward about 6 cm. (*78*).

The lower limit figures are fairly consistent among themselves; they are greater for downward than for horizontal propagation and greater for horizontal than for upward propagation. They are somewhat greater in an iron tube than in a glass tube, presumably on account of the greater cooling action of the metal. In a large space at atmospheric pressure the lower limit is probably about 1.7 per cent ether.

The higher limit figures seem to be extremely irregular, but the explanation lies in the appearance of the "cool flame" of ether which is propagated through some mixtures very deficient in oxygen. This is noticeable in the 2.5-cm. tube with horizontal propagation, in which the range of inflammability for the ordinary flame is separated by a large interval from the range for the "cool flame" (the higher figures in Table 22). Further details are to be found in the original communication (*78*).

Influence of pressure.—As the pressure is reduced below normal, the range of inflammable mixtures in a horizontal tube 5 cm. in diameter divides into two ranges. At 500 mm. pressure the limits are 1.88 to 9.25 per cent for the ordinary flame, 13 to 33 per cent for the cool flame. As the pressure is lowered further, each range contracts and a little below 400 mm. the cool flame is no longer propagated. At 90 mm. the range for the ordinary flame had contracted to 2.32 to 6.1 per cent (*132*).

Increase of pressure above atmospheric widened the range at both sides, when the temperature was raised to maintain enough ether in the vaporous state for the test. The effect may be due to the temperature change more than to the pressure change (*119*).

Influence of temperature.—A rise of 40° caused a decided increase in the higher limit (*70*).

Influence of streaming movement of the mixture.—The limits were appreciably widened (several tenths of 1 per cent) when velocities up to 9 cm. a second were imparted to the mixtures (*70*).

Influence of impurities.—The presence of the peroxides of ether scarcely affected the lower limit, but any large quantity raised the higher limit (*70*). The lower limit was unaffected by small additions of diethyl selenide or lead tetraethyl. The effect of pyridine (one experiment) was in accord with Le Chatelier's formula (*117*).

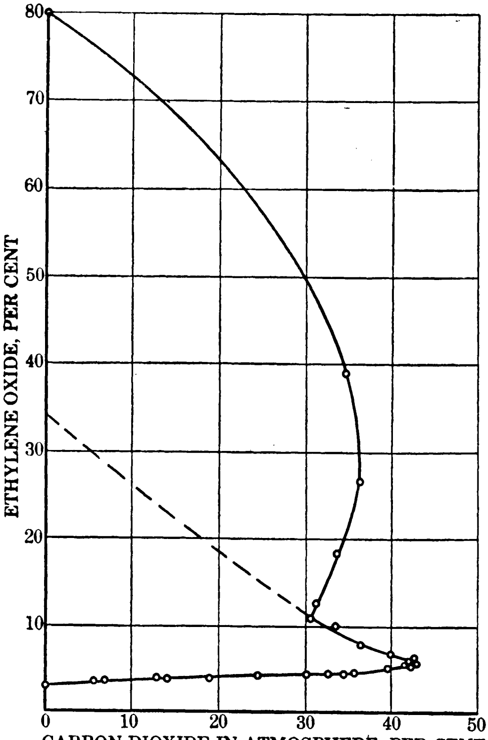

FIGURE 32.—Limits of inflammability of ethylene oxide in atmospheres of air and carbon dioxide

ETHYL ETHER IN OXYGEN

The limits of ethyl ether in oxygen, downward propagation of flame in a narrow burette, are 1.7 to 39.5 per cent ether (*112*).

ETHYL ETHER IN NITROUS OXIDE

The limits of ethyl ether in nitrous oxide, downward propagation of flame in a narrow burette, are 3.8 to 25.7 per cent ether (*112*).

ETHYL ETHER IN AIR, OR OXYGEN, AND NITROUS OXIDE

The limits of ethyl ether in a series of mixtures of air, or oxygen, and nitrous oxide have been determined for downward propagation of flame in a narrow burette (*112*). The results are not such as would be obtained if the generalized form of Le Chatelier's law held for these mixtures.

ETHYLENE OXIDE

ETHYLENE OXIDE IN AIR

The limits of ethylene oxide in air, in a tube 5 cm. in diameter and 150 cm. long, with upward propagation of flame from the open end, are 3.00 to 80.0 per cent (*157*). The richer mixtures in this range burn at the bottom of the explosion tube for perhaps as long as 30 seconds and then a very pale blue flame passes slowly to the top of the tube.

ETHYLENE OXIDE IN OTHER ATMOSPHERES

Atmospheres of air and carbon dioxide.—The limits of inflammability of ethylene oxide in all mixtures of air and carbon dioxide are shown in Figure 32. The determinations were made as described in the previous paragraph. The upper part of the curve in Figure 32 applies to the curious type of flame just described, which is apparently analogous to the "cool flame" of ether (*157*).

ACETALDEHYDE

ACETALDEHYDE IN AIR

Table 23 gives the observed limits of inflammability of acetaldehyde in air.

TABLE 23.—*Limits of inflammability of acetaldehyde in air*

Dimensions of tube, cm.		Firing end	Limits, per cent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
UPWARD PROPAGATION OF FLAME						
7.5	150	Closed	3.97	57	Dry	*90*
5	150	do	4.21	57		*90*
HORIZONTAL PROPAGATION OF FLAME						
7.5	150	Closed	4.23 [1] 21	16.7 48	Dry	*90*
5	150	do	4.32 [1] 25	16 45	do	*90*
DOWNWARD PROPAGATION OF FLAME						
7.5	150	Closed	4.27	13.4	Dry	*90*
5	150	do	4.36	12.8	do	*90*
1.7		do	5.7	13.5		*76*

[1] This range is for the "cool flame."

In a large space at atmospheric pressure the lower limit of acetaldehyde in air is probably about 4 per cent, the higher limit perhaps merging into the region of "cool flames," of which the higher limit is about 57 per cent acetaldehyde.

ACETALDEHYDE IN OTHER ATMOSPHERES

The limits of acetaldehyde in an atmosphere composed of 21 per cent oxygen, 19 per cent nitrogen, and 60 per cent carbon dioxide were 8.1 to 11 per cent for downward propagation in a 1.7-cm. tube (*76*).

In an atmosphere composed of 21 per cent oxygen and 79 per cent carbon dioxide no mixture with acetaldehyde was inflammable in a 1.7-cm. tube with downward propagation (*76*).

FURFURAL

The lower limit of furfural in air is 2.10 per cent at 125° C. The determination was made in a tube 150 cm. long and 5 cm. in diameter, propagation of flame upward from the open end of the tube (*150*).

ACETONE

ACETONE IN AIR

The limits of acetone in air, upward propagation of flame in a tube 5 cm. in diameter, open at the firing end, were 3.00 to 10.80 per cent (*157*) or 3.1 to 11.15 per cent (*158*).

Table 24 summarizes other determinations of the limits of acetone in air.

TABLE 24.—*Summary of other determinations of the limits of inflammability of acetone in air*

Dimensions of tube, cm.		Firing end	Far end	Limits, per cent		Content of aqueous vapor	Reference No.
Diameter	Length			Lower	Higher		
UPWARD PROPAGATION OF FLAME							
15	300 (iron)	Closed	Open	2.88	12.40	Dry	*70*
10	75 (glass)	do	Closed	2.15	9.70	do	*62*
7.5	150 (glass)	do	do	2.89	11.80	do	*78*
5	150 (iron)	do	Open	3.80		do	*70*
5	150 (glass)	do	do	2.89	12.20	do	*70*
5	150 (glass)	do	Closed	2.90	12.60	do	*78*
5	150 (glass)	do	do	2.20	9.50	do	*62*
2.5	150 (glass)	do	do	3.12	12.95	do	*78*
2.5	60 (glass)	do	do	2.30	7.50	do	*62*
2.5	25 (glass)	(Central ignition)	do	2.5	9.0	Undried	*134*
HORIZONTAL PROPAGATION OF FLAME							
15	300 (iron)	Closed	Open	2.89	12.40	Dry	*70*
10	75 (glass)	do	Closed	2.20	9.50	do	*62*
7.5	150 (glass)	do	do	2.92	11.90	do	*78*
5	150 (iron)	do	Open	3.90		do	*70*
5	150 (glass)	do	do	3.04	9.15	do	*70*
5	150 (glass)	do	Closed	2.96	9.90	do	*78*
5	150 (glass)	do	do	2.25	9.30	do	*62*
2.5	150 (glass)	do	do	3.10	8.25	do	*78*
2.5	60 (glass)	do	do	2.40	6.70	do	*62*
DOWNWARD PROPAGATION OF FLAME							
15	300 (iron)	Closed	Open	3.11	10.90	Dry	*70*
10	75 (glass)	do	Closed	2.35	8.50	do	*62*
7.5	150 (glass)	do	do	2.93	8.60	do	*78*
5	150 (iron)	do	Open	4.00		do	*70*
5	150 (glass)	do	do	3.15	8.35	do	*70*
5	150 (glass)	do	Closed	2.99	8.40	do	*78*
5	150 (glass)	do	do	2.40	8.30	do	*62*
5	65 (glass)	do	do	3.00		do	*140*
2.5	150 (glass)	do	do	3.15	8.25	do	*78*
2.5	60 (glass)	do	do	2.75	6.50	do	*62*

The limits in a 2-liter flask and in a 13-liter flask, with ignition near the base, were 2.5 to 10.4 per cent (*102*). Two older figures for the lower limit, probably with downward propagation of flame, are 2.9 and 2.7 per cent (*24*, *27*). The agreement of the figures in Table 24 is poor.

Unusual difficulties have arisen in the interpretation of observations of the nature and progress of flame in acetone-air mixtures. Thus, one observer writes (*78*):

The greatest difficulty was found with acetone * * *. The (higher limit) figures finally taken were the highest values obtained in any of a great number of trials. Below the values given an ignition would often occur and a flame only go halfway up the tube * * *. The fact that a flame goes only halfway or less along a tube is no proof that the mixture is above the limit in that tube * * *. In a 7.5 cm. tube near the upper limit upward a mixture which only propagated flame 50 cm. or less would often propagate flame much farther at the second trial and at the third all the way to the top.

It is perhaps correct to say that the lower limit of acetone in air is not less than 2.5 per cent and the higher limit not more than 13 per cent.

Influence of temperature.—The lower limit of acetone in air, upward propagation of flame in a tube 2 inches in diameter is 3.00 at laboratory temperature (*157*) 2.92 at 125° C. (*150*).

ACETONE IN OTHER ATMOSPHERES

For "atmospheres" of nitrogen and oxygen, of carbon dioxide and oxygen, and of equal volumes of nitrogen and carbon dioxide mixed with oxygen, the mixtures containing oxygen in amounts ranging from 20.9 per cent downward, the limits of acetone have been determined in a 2-liter flask with ignition near the base. Curves are given in the original paper (*102*) for the whole region of explosibility. It appears that when the oxygen content of a nitrogen-oxygen "atmosphere" is reduced below 13.5 per cent no mixture with acetone will propagate flame (*102*).

METHYL ETHYL KETONE

Table 25 gives the observed limits of inflammability of methyl ethyl ketone in air.

TABLE 25.—*Limits of inflammability of methyl ethyl ketone in air*

UPWARD PROPAGATION OF FLAME

Dimensions of tube, cm.		Firing end	Limits, per cent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
7.5	150	Closed	1.97	10.0	Dry	*78*
5.0	150	do	2.05	9.9	do	*78*
5.0	91	do	2.15	11.5	do	*110*
2.5	150	do	2.12	10.1	do	*78*
HORIZONTAL PROPAGATION OF FLAME						
7.5	150	Closed	1.97	10.2	Dry	*78*
5.0	150	do	2.05	8.5	do	*78*
5.0	91	do	2.25	10.5	do	*110*
2.5	150	do	2.12	6.6	do	*78*
DOWNWARD PROPAGATION OF FLAME						
7.5	150	Closed	2.05	7.6	Dry	*78*
5.0	150	do	2.10	7.4	do	*78*
5.0	91	do	2.40	5.8	do	*110*
2.5	150	do	2.17	6.3	do	*78*

The lower-limit figures in the preceding table are moderately consistent. In a large space at atmospheric pressure, the lower limit is probably just below 2 per cent, the higher not greater than 12 per cent.

ACETIC ACID

The lower limit of acetic acid in air in a 500-c. c. flask, apparently for downward propagation of flame, is 4.05 per cent at 36° C. (*24*).

METHYL FORMATE

The limits of methyl formate in air, upward propagation of flame in a tube 6 cm. in diameter, open at the firing end, are 5.9 to 20.4 per cent (*158*).

ETHYL FORMATE; METHYL ACETATE

The limits of inflammability for ethyl formate in air and for methyl acetate in air, in a closed tube 91 cm. long and 5 cm. in diameter, are (*110*) as follows:

Limits of inflammability of ethyl formate in air and of methyl acetate in air

Direction of propagation	Ethyl formate, per cent		Methyl acetate, per cent	
	Lower	Higher	Lower	Higher
Upward	3.5	16.4	4.1	13.9
Horizontal	3.7	14.6	4.25	11.9
Downward	3.9	11.8	4.4	10.1

ETHYL ACETATE

The lower limit of ethyl acetate in air, upward propagation of flame in a tube 6 cm. in diameter, open at the firing end, is 2.55 per cent (*158*).

Other determinations of the limits of ethyl acetate in air are as follows:

Summary of other determinations of the limits of inflammability of ethyl acetate in air

Dimensions of tube, cm.		Tube	Limits for propagation, per cent						Reference No.
			Upward		Horizontal		Downward		
Diameter	Length		Lower	Higher	Lower	Higher	Lower	Higher	
7.5	150	Closed	2.26		2.29		2.33		*78*
5.0	150	do	2.32	[1] 11.40	2.35	[1] 9.80	2.37	[1] 7.10	*78*
2.5	150	do	2.44		2.44		2.50		*78*
2.5	25	do	2.25	11.0					*134*

[1] At 60° C.

Older experiments with ethyl acetate and air in a 2-liter bottle, probably with downward propagation, gave a lower limit of 2.3 per cent (*24*).

PROPYL ACETATE

The lower limit of propyl acetate in air, upward propagation of flame in a tube 6 cm. in diameter, open at the firing end, is 2.05 per cent (*158*).

ISOPROPYL ACETATE

The lower limit of isopropyl acetate in air, in a closed tube 25 cm. long and 2.5 cm. in diameter, central ignition, upward propagation of flame, was 2.0 per cent (*134*).

BUTYL ACETATE

The lower limit of butyl acetate (b. p. 124° to 124.5° C.) in air, upward propagation of flame in a tube 6 cm. in diameter. open at the firing end, was 1.7 per cent, at 30° C. (*158*).

ETHYL NITRATE

The lower limit of ethyl nitrate in air in a 2-liter bottle apparently for downward propagation, is 3.8 per cent (*24*).

ETHYL NITRITE

The observed limits of inflammability for dry ethyl nitrite in air, in a closed tube 150 cm. long, are as follows:

Limits of inflammability of dry ethyl nitrite in air

Tube diameter, cm.	Limits for propagation, per cent					
	Upward		Horizontal		Downward	
	Lower	Higher	Lower	Higher	Lower	Higher
7.5	3.01	----------	3.51	----------	3.83	15.1
5.0	3.51	>50	3.63	>45	3.91	14.4

In all probability the higher limit upward propagation is much higher than the figure shown. White (*78*) says:

> That this compound is capable of transmitting two different flames through the same mixture was shown during an attempted downward ignition in a 5 cm. tube at the upper limit. This mixture, which would have burned downwards violently in normal circumstances, on sparking gave a pale blue flame which moved gently upwards through the 15 cm. between the electrodes and the top of the tube.

METHYL CHLORIDE

Mixtures of methyl chloride and air ranging from 10.75 to 17.40 per cent methyl chloride were ignited in a glass tube 2 inches in diameter and 6 feet long, and flame traveled upward throughout the tube at atmospheric pressure during propagation. The range appeared to be wider when an induction-coil spark was used, in a 2½-liter bell jar—8.25 to 18.70 per cent (*136*).

The range in a spherical bomb (size not stated), spark ignition, was from 8.9 to 15.5 per cent methyl chloride (*86*).

METHYL BROMIDE

Methyl bromide-air mixtures appear to be incapable of ignition and propagation of flame in a tube 2 inches in diameter, but mixtures containing between 13.5 and 14.5 per cent methyl bromide were inflamed by an induction-coil spark in a 2½-liter bell jar (*136*).

CHLOROFORM

No mixture of chloroform and oxygen or nitrous oxide, or of all three together, is capable of propagating flame downward in a small burette (*112*).

ETHYL CHLORIDE

Mixtures of ethyl chloride and air ranging from 4.25 to 14.35 per cent ethyl chloride were ignited in a glass tube 2 inches in diameter and 6 feet long, and flame traveled upward throughout the tube at atmospheric pressure. The range appeared to be somewhat wider when an induction-coil spark was used in a 2½-liter bell jar—4.00 to 14.80 per cent (*136*). Another observation (*115*) gives the lower limit 3.95 per cent for downward propagation in a tube 2 inches in diameter and 2 feet long, both ends partly open during inflammation.

The range in an explosion pipette, downward propagation, spark ignition was 3.6 to 11.2 per cent. For upward propagation in a eudiometer tube, flame ignition, the range was 6.4 to 11.2 per cent of ethyl chloride (*84*).

ETHYL BROMIDE

Ethyl bromide-air mixtures appear to be incapable of ignition and propagation of flame in a tube, 2 inches in diameter, but mixtures containing between 6.75 and 11.25 per cent ethyl bromide were inflamed by an induction-coil spark in a 2½-liter bell jar (*136*).

ETHYLENE DICHLORIDE

The limits of ethylene dichloride in air, in a tube 2 inches in diameter and 6 feet long, upward propagation of flame at atmospheric pressure during inflammation, are 6.20 to 15.9 per cent (*157*). The higher limit figure was obtained at 125° C.

DICHLORETHYLENE

The limits of inflammability of dichlorethylene in air, observed in a tube 5 cm. in diameter with upward propagation at atmospheric pressure throughout, are 9.7 to 12.8 per cent (*106*).

VINYL CHLORIDE

The limits of vinyl chloride in air in a tube 2 inches in diameter and 6 feet long, upward propagation of flame, at atmospheric pressure during inflammation, are 4.00 to 21.7 per cent (*157*).

DIETHYL SELENIDE

The lower limit of diethyl selenide in air, in a tube 5 cm. wide and 65 cm. long, downward propagation of flame, was 2.81 per cent, tube partly opened during propagation (*117*), and 2.5 per cent, tube closed (*127*).

TIN TETRAMETHYL; LEAD TETRAMETHYL

The lower limits of tin tetramethyl and lead tetramethyl in air, in a closed tube 5 cm. wide and 65 cm. long, downward propagation of flame, were 1.90 and 1.80 per cent, respectively (*125*).

PYRIDINE

The limits of inflammability of dry pyridine in air in a closed tube 150 cm. long and 5 cm. in diameter are as follows (*78*): Upward, 1.81 to 12.4 per cent; horizontal, 1.84 to 9.8 per cent; and downward, 1.88 to 7.2 per cent. The lower limits were determined at 60° C. and the higher at 70° C.

HYDROGEN AND CARBON MONOXIDE

HYDROGEN AND CARBON MONOXIDE IN AIR

The lower limits of various mixtures of hydrogen and carbon monoxide in air, observed in a vessel 6 feet high and 12 inches square in section with upward propagation at atmospheric pressure (*66*), were as follows:

Lower limits of inflammability in a large vessel

Hydrogen	Carbon monoxide	Lower limit, per cent		
		Observed	Calculated	Difference
100	0	4.10		
75	25	4.70	4.9	−0.20
50	50	6.05	6.2	−.15
25	75	8.20	8.3	−.10
10	90	10.80	10.4	+.40
0	100	12.50		

In a small vessel 4 cm. in diameter and 25 cm. high, presumably with downward propagation, the lower limits observed were (*24*):

Lower limits of inflammability in a small vessel

Hydrogen	Carbon monoxide	Lower limit, per cent		
		Observed	Calculated	Difference
100	0	10		
63.9	36.1	11.9	11.5	+0.4
41.5	58.5	13.25	12.8	+.45
18.4	81.6	14.7	14.4	+.3
0	100	15.9		

Other observers obtained similar results in a Bunte burette 19 mm. in diameter, with downward propagation of flame, using a mixture of equal volumes of hydrogen and carbon monoxide (*28, 73*).

The higher limit in air of a 50:50 mixture of hydrogen and carbon monoxide, observed in a tube 5 feet high and 2 inches in diameter, with upward propagation at atmospheric pressure, was 71.8 per cent, which is 0.7 per cent less than the calculated value (*66*).

The differences between the observed figures and those calculated from Le Chatelier's law just exceed the experimental errors, for lower and for higher limits.

HYDROGEN AND CARBON MONOXIDE IN OTHER ATMOSPHERES

The limits of inflammability of a mixture of hydrogen and carbon monoxide in almost equal volumes, in atmospheres of nitrogen and oxygen ranging from air to almost pure oxygen, were determined for downward propagation in a burette 19 mm. in width. The lower limit rose slightly from 12.4 per cent of the mixture in air to 12.6 per cent in oxygen; the higher limit rose from 66.1 per cent in air to 92 per cent in 98 per cent oxygen (*73*).

WATER GAS

The limits for a mixture of equal volumes of carbon monoxide and hydrogen calculated by the use of Le Chatelier's formula are nearly correct. Water gas contains other constituents, nitrogen, carbon dioxide, and methane. The method of calculation expounded on pages 8 to 12 takes account of these constituents and gives results in fair agreement with experiment (*151*).

The limits of water gas were approximately 9 to 55 per cent for upward propagation in a tube 7.5 cm. in diameter open at the firing end (*21*). The water gas used contained hydrogen, 49.6 per cent; carbon monoxide, 40.8 per cent; carbon dioxide, 2.6 per cent; and nitrogen, 7.0 per cent.

Another sample of water gas (*138*) gave the limits 11.9 to 65.4 per cent for downward propagation of flame in a small tube.

Another sample gave the limits 6.9 to 69.5 per cent in a small bulb in comparison with 6.1 to 65.4 per cent calculated by the method expounded on page 8, but based on limits of the individual gases obtained in larger apparatus (*151*). A carbureted water gas in the same conditions gave the limits 6.4 to 37.7 per cent. The relatively low higher limit is due to the presence of hydrocarbons in the carbureted gas (*151*).

The limits of various samples of semiwater gas and Mond gas have been determined in a Bunte burette, with both upward and downward propagation of flame. Analyses and results may be found in the original paper (*146*).

HYDROGEN AND AMMONIA

The limits of hydrogen-ammonia mixtures in air and in oxygen have been determined in very small tubes with downward propagation of flame. Apparently the higher limit mixtures in oxygen give results in fair agreement with Le Chatelier's law (*99*).

HYDROGEN AND HYDROGEN SULPHIDE

Both lower and higher limits of hydrogen-hydrogen sulphide mixtures in air have been found to diverge widely from Le Chatelier's law throughout the whole range of mixtures. The limits are narrower than those calculated and therefore limit mixtures of the individual gases when blended give noninflammable mixtures. The results, obtained in closed tubes 5 cm. in diameter, are plotted in Figure 33 for both limits and for both upward and downward propagation of flame; the curves calculated from the law are also shown (*100*).

The results that would be obtained if experiments were so conducted that atmospheric pressure was maintained throughout are not known. It seems unlikely, however, that the wide differences between actual results and those calculated would disappear.

HYDROGEN AND METHANE

The lower limits of various mixtures of hydrogen and methane in air were observed in a vessel 6 feet high and 12 inches square in section with upward propagation of flame. At atmospheric pressure the limits were (*66*):

Lower limits of inflammability with upward propagation

Hydrogen	Methane	Lower limit, per cent		
		Observed	Calculated	Difference
100	0	4.1	----------	----------
90	10	4.1	4.2	−0.1
75	25	4.1	4.4	−.3
50	50	4.6	4.7	−.1
25	75	4.7	5.0	−.3
0	100	5.6	----------	----------

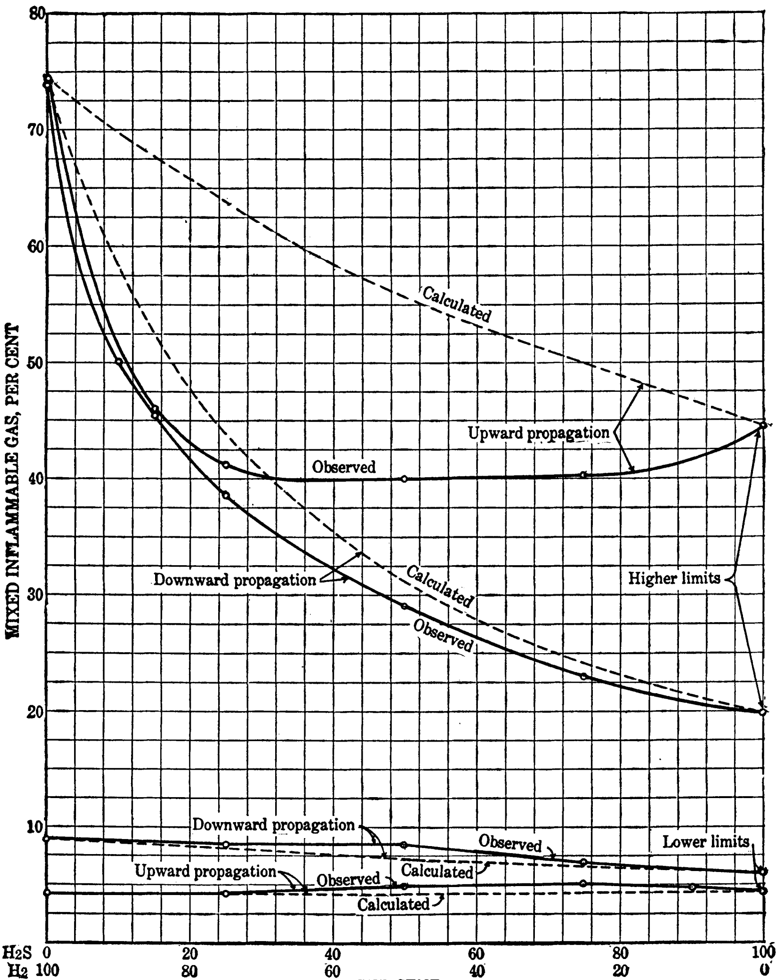

FIGURE 33.—Limits of inflammability of hydrogen-hydrogen sulphide mixtures in air

The higher limit of a mixture of hydrogen, methane, and air, observed in a tube 5 feet high and 2 inches in diameter with upward propagation of flame at atmospheric pressure, was (*66*):

Higher limits of inflammability with upward propagation

Hydrogen	Methane	Higher limit, per cent		
		Observed	Calculated	Difference
100	0	71.5	----------	----------
48.5	51.5	22.6	22.7	−0.1
0	100	13.8	----------	----------

The differences between the observed and calculated values in the foregoing tables are beyond the experimental error in two tests; the calculated results may be termed a fair approximation. Differences rather greater than these were observed in closed tubes 5 cm. in diameter for both upward and downward propagation of flame (*100*).

The approximate limits for a mixture of equal volumes of hydrogen and methane have been determined (*67*) in narrow tubes 0.9 to 0.2 cm. in diameter.

HYDROGEN, CARBON MONOXIDE, AND METHANE

Lower and higher limits for hydrogen-carbon monoxide-methane mixtures in air can be calculated as accurately as for mixtures of any two of these combustible gases (*66*).

HYDROGEN AND ETHANE

An old observation in a eudiometer tube 2 cm. in diameter gave the higher limit in oxygen of a mixture of equal volumes of hydrogen and ethane, with downward propagation, as being between 56 and 57 per cent (*8*).

HYDROGEN AND PENTANE

The limits for a mixture of 3 volumes of pentane and 2 volumes of hydrogen, observed in a horizontal glass tube 2.5 cm. in diameter with the firing end open, were 2.4 to 8.7 per cent (*69*).

HYDROGEN AND ETHYLENE

HYDROGEN AND ETHYLENE IN AIR

Observations in closed tubes 5 cm. in diameter, with upward and downward propagation of flame, showed that over the whole range of these mixtures the limits were narrower than those calculated by Le Chatelier's law; the differences were a few tenths of 1 per cent at the lower limits and a few per cent at the higher limits (*100*).

HYDROGEN AND ETHYLENE IN OXYGEN

The limits of inflammability of the range of hydrogen-ethylene mixtures in oxygen have been determined. The observations were made in very small apparatus and are therefore of limited value (*98*).

HYDROGEN AND ACETYLENE

Lower limits of hydrogen-acetylene mixtures in air have been determined in closed glass tubes 5 and 7.5 cm. in diameter, with upward and downward propagation of flame. For upward propagation, with amounts of acetylene up to about 43 per cent of the hydrogen-acetylene mixture, the lower limits were markedly greater than those calculated; between 43 and 50 per cent there was a sudden drop, and thereafter the limits almost coincided with the calculated values. For downward propagation the lower limits were consistently a little greater than those calculated (*100*).

HYDROGEN AND OTHER GASES OR VAPORS

The limits of a series of binary mixtures of hydrogen and various gases and vapors have been determined in a tube 5 cm. in diameter, 65 cm. long, downward propagation of flame. The results for each pair of mixtures were of the same general type as for mixtures of hydrogen and ethyl bromide, which have been quoted on page 15, where their significance is discussed.

The gases and vapors used were ethyl bromide (*113*); methyl iodide, methylene bromide, bromoform, ethyl iodide, ethylene bromide (*114*); hydrogen selenide, diethyl selenide (*117*); dimethyl selenide, dimethyl telluride (*124*); tin tetramethyl, lead tetramethyl (*125*); ethyl alcohol, ether, acetone, benzene, pentane, cyclohexane, methyl cyclohexane, and a hydrocarbon mixture (*140*).

From a study of the dew point, density, and range of inflammability of such mixtures of hydrogen and small amounts of other substances, it was concluded that tetramethyl tin is the best explosion suppressor for hydrogen to be used in balloons or airships, followed by dimethyl selenide and ethyl bromide (*144*). The practical importance of these experiments seems, however, to rest in the proof that none of the additions is effective in destroying the inflammability of the hydrogen when mixed with air; when 0.90 per cent of lead tetramethyl is present, the range of inflammability is 9 to 54 per cent, compared with 9 to 71 per cent for pure hydrogen. Moreover, the permeability of a balloon fabric to the explosion suppressors is not considered.

AMMONIA AND ETHYL BROMIDE

The limits of inflammability of a series of ammonia-ethyl bromide-oxygen-nitrogen mixtures have been determined in very small tubes. A diagram in the original paper shows the limits for the two gases, ammonia and ethyl bromide vapor, singly and mixed. Neither gas is inflammable downward in air, but each will burn in oxygen (*107*).

HYDROGEN SULPHIDE AND METHANE

Both limits of hydrogen sylphide-methane mixtures in air, in closed glass tubes 5 cm. in diameter with upward and downward propagation of flame, show large deviations from those calculated. The lower limits are markedly high. The higher limits, on the other hand, are very high for mixtures rich in hydrogen sulphide and low for other mixtures, so that the curves (for both directions of propaga-

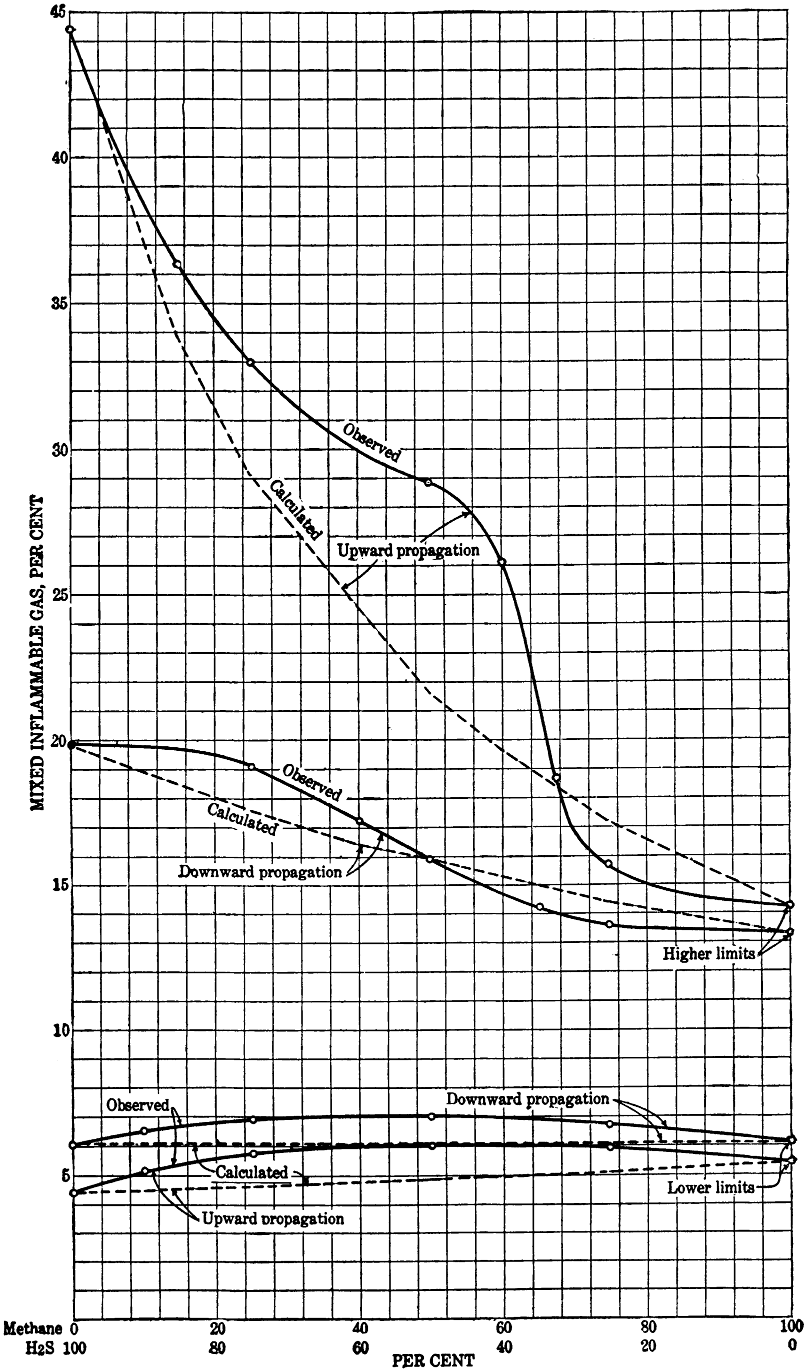

FIGURE 34.—Limits of inflammability of methane-hydrogen sulphide mixtures in air

tion) for experimental and calculated figures cut across one another. These curves are reproduced in Figure 34 (*100*).

HYDROGEN SULPHIDE AND ACETYLENE

The lower limits of hydrogen sulphide-acetylene mixtures in air have been determined in closed glass tubes 5 cm. in diameter for upward and downward propagation of flame. The maximum deviation from the calculated limit was 0.3 per cent (*100*).

CARBON DISULPHIDE AND VARIOUS GASES AND VAPORS

Mixtures of carbon disulphide and air with ether, benzene, acetone, and acetaldehyde, observed in closed tubes 5 cm. in diameter and 150 cm. long, showed no agreement with Le Chatelier's law for either higher or lower limits with downward propagation. It was suggested that the propagation of flame in carbon disulphide-air mixtures may be catalyzed by some product of its combustion and the catalytic effect inhibited by ether, benzene, acetone, and acetaldehyde (*79*).

The abnormal influence of small quantities of certain other inflammable substances on the lower limit of carbon disulphide has already been discussed (p. 28).

CARBON MONOXIDE AND METHANE

The lower limits of various mixtures of carbon monoxide and methane in air in a vessel 6 feet high and 12 inches square in section, with upward propagation of flame at atmospheric pressure throughout, were (*66*):

Lower limits of inflammability with upward propagation

Carbon monoxide	Methane	Lower limit, per cent		
		Observed	Calculated	Difference
100	0	12.5	----------	----------
90	10	11.0	11.1	−0.1
75	25	9.5	9.6	−.1
50	50	7.7	7.7	.0
40	60	7.2	7.1	+.1
25	75	6.4	6.5	−.1
0	100	5.6	----------	----------

The higher limit of a mixture of carbon monoxide and methane in air, in a tube 5 feet high and 2 inches in diameter, with upward propagation at atmospheric pressure (*66*), was as follows:

Higher limit of inflammability with upward propagation

Carbon monoxide	Methane	Higher limit, per cent		
		Observed	Calculated	Difference
100	0	73.0	----------	----------
50	50	22.8	23.2	−0.4
0	100	13.8 (*101*)	----------	----------

The differences between the observed and calculated figures in the two preceding tables are almost within the limits of experimental error.

A series of experiments in a Hempel explosion pipette with downward propagation of flame showed fairly good agreement with the calculated values for the lower limit, but for the higher limit the observed values were always low, sometimes as much as 10 per cent (*59*).

CARBON MONOXIDE AND ACETYLENE

The lower limit of a mixture containing 84 per cent carbon monoxide and 16 per cent acetylene has been determined in a vessel 4 cm. in diameter and 25 cm. high, presumably with downward propagation from an open end. The lower limit was 9.1 per cent in air, closely agreeing with the figure calculated from the limits of carbon monoxide and acetylene (*24*) observed individually in the same circumstances.

METHANE AND HIGHER HYDROCARBONS

METHANE AND ETHANE, METHANE AND PROPANE, METHANE AND BUTANE, AND ETHANE AND BUTANE IN AIR

In a tube 5 cm. in diameter with upward propagation from an open end the lower limits observed for methane-ethane, methane-propane, methane-butane, and ethane-butane mixtures with air were in close agreement with the values calculated from Le Chatelier's law; the higher limits observed were slightly less than those calculated (*111*).

The regularity of the lower limits of such mixtures is further discussed on page 92.

METHANE AND PENTANE IN AIR

Throughout the whole range of methane-pentane mixtures the lower limits for upward or downward propagation in a 5-cm. tube agree with the limits calculated by Le Chatelier's formula from the limits of methane and pentane separately (*100*). A 50: 50 mixture gave a lower limit close to the calculated limit for horizontal propagation in a 2.5-cm. tube open at the firing end (*69*).

The higher limits, observed in the 5-cm. tube, were in general less by a few tenths of 1 per cent than those calculated (*100*).

METHANE AND ETHYLENE

The limits of methane-ethylene mixtures in air in closed tubes 5 cm. in diameter, with upward and downward propagation of flame, were in general slightly narrower than those calculated (*100*).

METHANE AND ACETYLENE

The limits of methane-acetylene mixtures in air were determined in closed glass tubes 5 cm. in diameter, with upward and downward propagation of flame. The lower limits for both directions of propagation were slightly higher than those calculated. The higher limits were a little less than the calculated limits for downward propagation but were much greater for upward propagation. The greatest difference was shown by the 40: 60 acetylene-methane mixture, for which the observed figure was 47 per cent for the higher limit and that calculated was 21 per cent (*100*).

BENZINE

BENZINE IN AIR

The lower limit of benzine in air for upward propagation in a tube 6.2 cm. in diameter and open at the firing end was 1.1 per cent (*28*). The limits for propagation downward in a closed pipette 1.9 cm. in diameter were 2.4 to 4.9 per cent. The benzine all distilled below 105° C. (*28*). A second observer gave limits of 1.9 to 5.1 per cent for benzine having a specific gravity of 0.700 and a boiling range of 67° to 94° C. (*73*).

BENZINE IN OTHER ATMOSPHERES

In a Bunte burette 19 mm. in diameter, with downward propagation of flame, in nitrogen-oxygen atmospheres ranging from air to nearly pure oxygen, the lower limit of benzine ranged between 1.9 and 2.1 per cent; the higher limit rose from 5.1 per cent in air, 19 per cent in 60 per cent oxygen, to 28.6 per cent in 94 per cent oxygen (*73*).

GASOLINE (PETROL)

In a glass jar of 2.8 liters capacity, with upward propagation of flame, the limits of inflammability of gasoline in air were 1.45 to 6.2 per cent gasoline vapor (by volume). The limits in a Hempel pipette of 100 c. c. capacity with downward propagation were 1.95 to 5.25 per cent; upward the lower limit was 1.55 per cent. The gasoline had a specific gravity of 0.689 at 15° C. and a boiling range of 50° to 140° C.; at 140° C. there was 2.7 per cent residue (*56*).

Influence of temperature.—At 400° C. the lower limit, observed in a Hempel pipette of 100 c. c. capacity with upward ignition, was reduced to 1.1 per cent from 1.55 per cent at air temperature (*56*).

Other experiments indicate that temperature has a greater effect on the lower limit; the results seem unreliable, because in a parallel series of tests with alcohol the lower limit found at 20° C. was undoubtedly too high (*77*).

OIL GAS

The limits for oil gas in air are stated to be 6 to 13.4 per cent—observed, perhaps, in a eudiometer tube (*42*).

OIL GAS AND ACETYLENE

The limits for a mixture of 75 per cent oil gas and 25 per cent acetylene in air are stated to be 4 to 15.5 per cent—observed, perhaps, in a eudiometer tube (*42*).

NATURAL GAS

NATURAL GAS IN AIR

The lower limit of natural gas in air in a tube 7 feet high and 12 inches in diameter with upward propagation of flame from open to closed end was found to be 4.91 per cent natural gas in air. The

9959°—31——7

mixture contained about 2 per cent water vapor. The percentage composition of the gas was: Methane, 87.4; ethane, 6.8; propane, 1.55; butane, 0.81; pentane, trace; nitrogen, 3.2; oxygen, 0.1; and carbon dioxide, 0.0. The limit figure represents, for convenience, the proportion of the inflammable constituents of natural gas present in the limit mixture with air. If the nitrogen and oxygen were included, the limit for natural gas would be nearly 5.1 per cent. For propagation of flame upward from closed to open end in the same tube, the lower limit was 4.74 per cent (inflammable constituents).

The limits of natural gas in a tube 2 inches in diameter, with upward propagation of flame from an open end, can be calculated with approximate accuracy by means of Le Chatelier's law. For dry gases the limits of the inflammable part of the natural gas were 4.80 to 13.46 per cent. The figures calculated from the corresponding figures for the individual constituents—namely, methane, 5.24 to 14.02 per cent; ethane, 3.22 to 12.45 per cent; propane, 2.37 to 9.50 per cent; and butane, 1.86 to 8.41 per cent—were, for natural gas, 4.85 to 13.72 per cent. The lower limit figure is nearly in agreement with that calculated. It can not be appreciably affected by the nitrogen which the natural gas introduces, but the higher limit figure will be affected (see fig. 17, showing the influence of nitrogen on the limits of methane in air). An estimate of the influence of nitrogen on the higher limit figure may be made thus: If deduction is made of 0.4 per cent nitrogen corresponding with 0.1 per cent oxygen found in the natural gas, there remains 2.8 per cent nitrogen brought to the mixture with the natural gas. This amount represents, as it is present with the 13.7 per cent hydrocarbons of the whole limit mixture, about 0.4 per cent "additional nitrogen" in the original "atmosphere." From Figure 17 one can see that this amount of additional nitrogen depresses the higher limit for methane by about 0.1 per cent, and doubtless its effect on the higher limit of natural gas is about the same (*111*).

Further evidence that the limits for natural gas may be calculated with fair accuracy from the limits of its various constituents is provided by the data which show that Le Chatelier's law is followed by these constituents when two are taken together. (See the sections on methane-ethane, methane-propane, methane-butane, methane-pentane, and ethane-butane mixtures.)

The lower limit, but not the higher limit, for any mixture of paraffin hydrocarbons exhibits an interesting and useful regularity (*111*); it is constant for all mixtures which have equal values for the analytical ratio C/A, C being the contraction observed on exploding the mixture with excess air, A being the volume of carbon dioxide produced thereby. The lower limit of any mixture of paraffin hydrocarbons can therefore be deduced fairly accurately without an exact knowledge of its composition; all that is required is a determination of the C/A ratio of the mixture and reference to Figure 35, the curve of which is drawn through experimental points. The broken part of this curve may be used to supply the lower limits of mixtures of heavier paraffin hydrocarbons (*111*).

Influence of pressure.—The influence of pressure on the higher limit of a "natural methane" (methane, 80.3; higher paraffins, 11.1; carbon monoxide, 0.4; inert gases, 7.9 per cent) has been determined in narrow tubes (3 or 5 mm. diameter), downward propagation of flame (*130*). The higher limit rose rapidly, from 14.25 per cent "methane" at atmospheric pressure to 39 per cent at 12 atmospheres and 52 per cent at 50 atmospheres.

Influence of turbulence caused by fans or by the detonation of explosives.—Some experiments of a preliminary character have been made to determine whether the lower limit of natural gas in air is affected by turbulence such as that produced by fans or by the detonation of explosives. The use of explosives necessitated experiments on a comparatively large scale, and therefore a 20-foot section of a 100-foot steel tube 6⅓ feet in diameter was used. The explosives were fired near one end of the horizontal axis of the tube. The pipe had paper-covered relief vents along the top, and the end opposite the source of ignition was closed by a paper cover; these paper-covered orifices enabled the extent of an ignition to be roughly judged. The

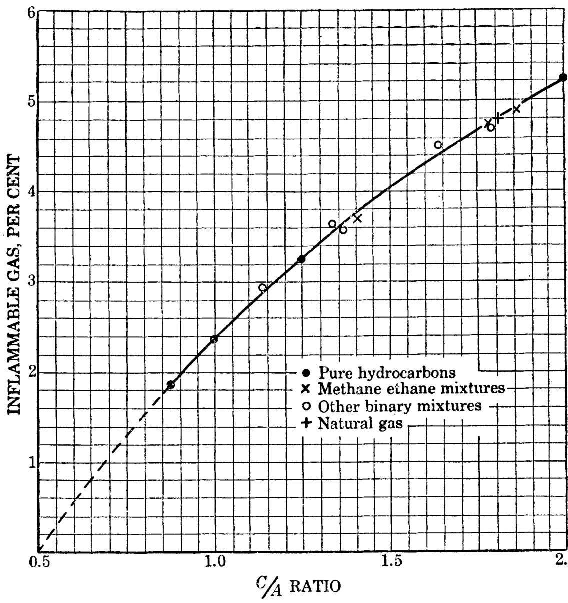

FIGURE 35.—Variation of lower limit of paraffin hydrocarbons with C/A ratio

observations were aided by noting the effect of an experiment on tufts of guncotton placed at various points in the tube.

The results were conveniently classed as (1) explosions, when the paper covers were blown out violently and flame appeared from the relief vents; (2) inflammations, when it was evident that some gas had been ignited, but no great violence was observed; and (3) nonignitions.

A small electric igniter of black blasting powder gave a lower limit of explosion at about 5.6 per cent natural gas and a lower limit of inflammation at about 4.6 per cent.

Black blasting powder, 50 or 200 grams, burning with a long flame, gave limits of 5.1 per cent and less than 4.7 per cent, respectively.

A straight nitroglycerin dynamite, 50 or 200 grams, gave a lower limit of explosion at 5.6 per cent; "inflammation" could not with certainty be observed at lower percentages on account of the violent effects of the detonation on the paper covers.

Turbulence induced by a fan run at appropriate speeds reduced the limit of explosion to 5 per cent. The limit of inflammation was slightly reduced at moderate speeds; at higher speeds inflammation, apart from explosion, could not be observed. The term "inflammation" as used in the preceding paragraphs apparently covered the range of mixtures capable of propagating flame from the source of ignition for some distance upward, spreading more or less laterally; "explosion" was used to designate a sufficiently great amount of inflammation at sufficient speed to cause the effects described. The reduction of the limit of explosion by the long flames of gunpowder was the effect of the greater amount of burning induced by them; a similar effect was produced by turbulence.

The natural gas used in these experiments contained 87.8 per cent methane, 6.9 per cent ethane, 2.6 per cent propane, 0.8 per cent butane, 1.9 per cent nitrogen, and no oxygen or carbon dioxide.

The percentages of natural gas in the limit mixtures refer to "nitrogen-free" gas (*108*).

NATURAL GAS IN OTHER ATMOSPHERES THAN AIR

An extensive series of observations in a 100-c. c. Hempel pipette and in a short steel cylinder of 2.8 liters capacity has been made with atmospheres which contain oxygen, nitrogen, and carbon dioxide. The composition of the mixtures used, including the natural gas, ranged from 19.9 per cent to 14 per cent oxygen and from no carbon dioxide to 61 per cent. The results are plotted in comprehensive curves in the original paper (*45*).

COAL GAS (ILLUMINATING GAS)

COAL GAS IN AIR

The lower limit of a "town gas" (*66*) in a vessel 6 feet high and 12 inches square in section, with upward propagation from open to closed end, was 5.35 per cent. The figure calculated from the analysis given below in conjunction with the limits of the individual constituents of the gas was 5.36 per cent.

The higher limit of a coal gas (*66*), in a tube 5 feet high and 2 inches in diameter, with upward propagation from open to closed end, was 30.9 per cent. The calculated figure was 28.8 per cent, uncorrected for inert constituents of the gas.

The town gas and the coal gas contained the following constituents:

Analyses of town gas and coal gas, per cent

	Town gas	Coal gas		Town gas	Coal gas
Benzene, etc.	0.8	1.2	Hydrogen	46.6	50.6
Carbon dioxide	2.6	0.1	Methane	19.4	29.7
Oxygen	0.5	0.1	Ethane	4.0	3.2
Ethylene, etc.	2.8	2.9	Nitrogen	9.2	4.9
Carbon monoxide	14.1	7.3			

The recorded limits of town and coal gas in smaller vessels and for other directions of propagation are such as might be expected from mixtures containing a large proportion of hydrogen (*16, 17, 18, 21, 22, 28, 60, 67, 73, 130, 138, 151*). Thus, for the lower limit the figures range between 5 per cent for upward propagation and nearly 10 per cent for downward propagation; the higher limit figures range between 18.5 per cent for downward and 31 per cent for upward propagation.

An old set of comparative experiments showed a rise from 8.1 to 8.7 per cent in the lower limit of a coal gas as the diameter of the experimental tube was decreased from 30 to 10 mm. (*17*). Some more recent experiments showed that flame would still travel, apparently indefinitely, in a tube 3 mm. in diameter when one of the most explosive mixtures was used, but would not travel in a tube 2 mm. in diameter (*67*). It is hardly possible to compare the recorded results more closely, because the composition of the illuminating gas varied.

Influence of pressure.—The higher limit of a French town gas rose rapidly with increasing pressure. At atmospheric pressure the higher

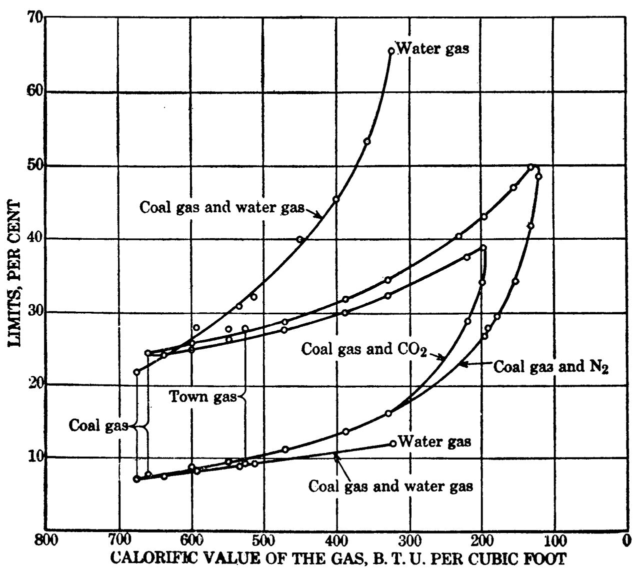

FIGURE 36.—Limits of inflammability of coal gas with various admixtures

limit was 18.5 per cent, at 10 atmospheres 37.5 per cent, and at 22 atmospheres 51 per cent. Further increase in pressure had a diminishing effect, for at 54 atmospheres the limit was 56.5 per cent gas. The experiments were made with gas compressed into tubes of 3 or 5 mm. diameter, with downward propagation of flame, and reasons are given for concluding that the results would not be different in wider vessels. The observations are of importance in relation to the use of compressed gas (*130*).

Influence of temperature.—In a 35-c. c. bulb, side ignition, the lower limit fell gradually from 6.9 to 6.3 per cent, the higher limit rose from 22.8 to 28.7 per cent, as the temperature was increased from 15 to 300° C. The composition of the gas used is given in the following paragraph (*18*).

Influence of impurities (nitrogen and carbon dioxide).—Two curves in Figure 36 show the limits of a coal gas polluted by nitrogen and by carbon dioxide, as observed in a Bunte burette, downward propagation of flame. The abscissas represent the composition of the gas in terms of its calorific value (*138*). These can readily be converted into percentage composition, for the calorific value of each mixture is proportional to its content of coal gas.

COAL GAS IN OXYGEN

In a 35-c. c. bulb, with side ignition, the limits observed (*18*) were 7.4 to 69.7 per cent coal gas. The percentage composition of the coal gas was: Heavy hydrocarbons, 5.3; carbon dioxide, 2.0; carbon monoxide, 6.4; methane, 34.5; hydrogen, 49.4; and nitrogen, 2.4.

Influence of temperature.—In the same series of experiments it was found that as the temperature was raised to 300° C. the lower limit fell gradually to 6.9 per cent and the higher limit rose to 72 per cent.

Influence of pressure.—The higher limit of a French town gas in oxygen was 78.6 per cent at atmospheric pressure; 85 per cent at 10 atmospheres; and 89.1 per cent at 43 atmospheres. The experiments were made as described in the corresponding paragraph on coal gas in air. At 74 atmospheres pressure, a mixture of 89.6 per cent gas and 10.4 per cent oxygen could not be exploded. It was concluded that mixtures of town gas and oxygen, compressed in tanks up to 200 atmospheres pressure, could not explode if they contained less than 10 per cent oxygen; but that it would be prudent not to exceed 5 or 6 per cent oxygen. The act of compressing such mixtures must, however, be conducted in such a way as to avoid undue rise in their temperature, which would widen the limits. Up to 80° C., however, the higher limit is not appreciably altered (*129, 130*).

COAL GAS IN OTHER ATMOSPHERES

Atmospheres of composition between air and pure oxygen.—The limits of a synthetic illuminating gas in air were 9.7 to 25.1 per cent in a Bunte burette; the lower limit rose to 9.9 in 96 per cent oxygen and 4 per cent nitrogen, and the higher limit rose to 73.7 in the same mixture (*73*). The percentage composition of the gas used was: Carbon dioxide, 2.0; ethylene, 3.8; carbon monoxide, 9.0; methane, 30.2; hydrogen, 51.0; and nitrogen, 4.0.

Atmospheres of air and nitrogen (air deficient in oxygen) and of air and carbon dioxide.—From the data presented in Figure 36 may be calculated the composition of the atmosphere which is just incapable of forming an inflammable mixture with coal gas. If the air contains less than 11.5 per cent of oxygen, it can not form an inflammable mixture with coal gas; if the oxygen content of the air is reduced by the addition of carbon dioxide, then when the mixture contains more than 31 per cent carbon dioxide and consequently less than 14.4 per cent oxygen, it can not form an inflammable mixture with coal gas. (In close agreement with the analytical figures of an old observation (*28*).) These conclusions may be fairly representative of a normal coal gas, but they are based on observations of flame traveling downward in a narrow burette; in wider vessels and especially when ignition occurs near the lower part of the vessel, the oxygen figures would doubtless be several per cent less.

Atmospheres of oxygen and carbon dioxide.—In an atmosphere composed of 21 per cent oxygen and 79 per cent carbon dioxide, in a 35-c. c. bulb with side ignition, the limits of coal gas were 7.6 to 25.2 per cent. At 300° C. the limits became 9.3 to 18.2 per cent. The composition of the gas used is given in the paragraph on coal gas-oxygen mixtures (*18*).

COAL GAS AND METHANE

Mixtures of coal gas and methane have been shown to give lower limits, for downward propagation, which can be calculated from the limits observed for coal gas and methane separately (*17*).

COAL GAS AND WATER GAS

Figure 36 shows the limits in air of all mixtures of a typical coal gas and a water gas, as observed in a Bunte burette, downward propagation of flame (*138*). The abscissas represent the composition of the gas in terms of its calorific value. The addition of water gas to coal gas widens the range of inflammability and in consequence increases the chance of an explosion. The range would doubtless be found wider by several per cent at each limit for upward propagation of flame in these mixtures.

MINE-FIRE GASES AND GASES FROM MINE EXPLOSIONS

The limits of inflammability of mine-fire gases and of the atmospheres after explosions, highly variable though they are in composition, may be calculated with approximate accuracy by the method given on page 8. Some examples (*145*) are given in Table 26.

TABLE 26.—*Typical samples of mine-fire atmospheres found in coal mines*

Sample No.	Composition of atmosphere, per cent by volume						Limits of inflammability	
	CO_2	O_2	CO	CH_4	H_2	N_2	Lower	Higher
1	13.8	2.8	4.3	3.3	4.9	70.9	45.1	70.4
2	1.6	14.1	1.0	7.2	0	76.1	69.2	100.0
3	.5	17.4	0	12.6	0	69.5	40.1	100.0
4	1.3	17.0	1.9	4.0	0	75.8	(1)	(1)
5	6.4	1.4	1.1	16.7	.2	74.2	30.5	41.3
6	5.9	1.4	1.4	22.3	0	69.0	23.1	37.0
7	2.6	8.8	0	8.1	0	80.5	(1)	(1)

1 Noninflammable.

If the atmosphere contains methane and negligible amounts of hydrogen and carbon monoxide, the necessary information may be obtained from Figure 19.

AUTOMOBILE EXHAUST GASES

The usual adjustment of an automobile carburetor gives an air-fuel ratio of about 12.5 : 1, and the exhaust is not inflammable. If, however, the air-fuel ratio is reduced below about 11.7 : 1 the exhaust is inflammable and there is danger of explosion as well as poisoning when the engine is run in a place of limited ventilation. The limits of inflammability of the exhaust gas may be calculated with approximate accuracy by the method given on page 8 (*137*, *145*).

BLAST-FURNACE GAS

The limits of two typical blast-furnace gases, in a glass tube 6 feet long and 2 inches in diameter, upward propagation of flame at atmospheric pressure during propagation, were (1) 36 to 72 per cent, and (2) 35 to 73.5 per cent. These figures agree approximately with those calculated from the analysis of the gas by the method given on page 8 (*145*).

An older observation in a closed tube 8½ inches long and 3 inches wide, central ignition, gave the limits of a blast-furnace gas as 45 to 65 per cent (*60*). A more recent observation in a Bunte burette gave the limits 35.8 to 71.9 per cent for upward propagation and 43.9 to 67.8 per cent for downward propagation of flame (*146*).

The composition of the gases used in the foregoing experiments was:

Analyses of blast-furnace gases, per cent

Reference	*145*		*60*	*146*
	(1)	(2)		
Carbon dioxide	15.90	8.30	10.0	8.2
Oxygen	0	0	.5	0
Carbon monoxide	23.70	30.65	27.5	25.6
Methane	.20	.10	.3	0
Hydrogen	4.30	3.00	2.7	4.4
Nitrogen	55.90	57.95	59.0	61.8

PRODUCER GAS

The limits of a producer gas in air, in a Bunte burette, were 35.5 to 80.0 per cent for upward propagation and 40.6 to 76.5 per cent for downward propagation of flame. The gas contained: Carbon dioxide, 2.8; carbon monoxide, 30.9; hydrogen, 4.6; and nitrogen, 61.7 per cent (*146*).

Another sample of producer gas had the limits 20.7 to 73.7 per cent in a small bulb, in comparison with 20.2 to 71.8 per cent calculated by the method expounded on page 8, but based on limits of the individual gases obtained in larger apparatus. The gas contained: Carbon dioxide, 6.2; carbon monoxide, 27.3; hydrogen, 12.4; methane, 0.7; and nitrogen, 53.4 per cent (*151*). The greater amount of hydrogen in this sample is responsible for the fall in its lower limit compared with that of the first sample.

SOME HYDROCARBONS; ETHER; ETHYL CHLORIDE AND BROMIDE; DIETHYL SELENIDE; TIN TETRAMETHYL; AND LEAD TETRAMETHYL

Limits of the following pairs of mixtures, in various proportions, have been determined in a tube 5 cm. wide and 65 cm. long, with downward propagation of flame: Methyl cyclohexane and ethyl chloride (*115*); "hydrocarbon" (isoheptane and dimethyl cyclohexane) and ethyl bromide (*115*); "hydrocarbon" (isoheptane and dimethyl cyclopentane) and diethyl selenide, also with tin tetramethyl and lead tetramethyl (*127*); ethyl ether and ethyl bromide (*115*); ethyl ether and methyl iodide (*115*); ethyl ether and tin tetramethyl (*127*); and ethyl ether and lead tetramethyl (*127*). The results are of the general type shown in Figure 2, and were interpreted similarly.

METHYL CYCLOHEXANE; ALCOHOL; ETHER

The lower limits of mixtures of methyl cyclohexane, ethyl alcohol, and ethyl ether, taken in pairs or all together, have been determined in a tube 5 cm. wide and 70 cm. long, with downward propagation of flame. The observed results agree with those calculated by Le Chatelier's law (*118*).

GASOLINE; ALCOHOL; ETHER

Series of observations with ethyl alcohol-gasoline and ethyl alcohol-gasoline-air mixtures in a 2,300-c. c. vessel at 50° and 90° C. showed moderated agreement with Le Chatelier's law. The results, expressed in cubic centimeters of liquid vaporized in 1,000 c. c. of air, are throughout probably too high; the result for pure alcohol was undoubtedly too high (*77*).

BENZENE AND TOLUENE

The limits of benzene-toluene mixtures in air in a closed tube 5 cm. in diameter and 150 cm. long were in close agreement with the values calculated by Le Chatelier's formula for upward, horizontal, and downward propagation, lower and higher limits (*79*).

BENZENE AND ETHYL ALCOHOL

The lower limits of mixtures of benzene and ethyl alcohol in air, upward propagation of flame in a tube 5 cm. wide and 150 cm. long, open at the firing end, deviate somewhat from the values calculated by Le Chatelier's formula (*150*).

METHYL ALCOHOL AND ETHYL ALCOHOL

Lower and higher limits of mixtures of methyl and ethyl alcohol in air, downward propagation of flame, in a 2-liter cylinder at 75° C., agreed with the values calculated by Le Chatelier's formula (*152*). All the individual values are, however, probably too high. Another observer (*153*) found that the lower limit of a 50 : 50 mixture of the two alcohols was 0.7 to 0.3 less than that calculated over the range 50° to 250° C. in similar circumstances.

Influence of water.—The lower limits of mixtures of water and the two alcohols rise steadily as the amount of water increases from 0 to 60 per cent, but the amount of the mixed alcohols is approximately constant in the limit mixture. When 80 per cent of water was present it was difficult to inflame any mixture of the vaporized liquid and air at 105° C., and 85 per cent water made inflammation practically impossible (*152*).

METHYL ALCOHOL AND ETHER; METHYL ALCOHOL AND ACETONE; ETHYL ACETATE AND BENZENE; ACETALDEHYDE AND TOLUENE; ETHYL NITRITE AND ETHER

Lower limits of methyl alcohol-ether, methyl alcohol-acetone, ethyl acetate-benzene, acetaldehyde-toluene, and ethyl nitrite-ether in air were determined in closed tubes 5 cm. in diameter and 150 cm. long. Each pair of these combustible substances showed close agreement with Le Chatelier's law. No figures are quoted in the original communication (*79*).

For methyl alcohol-acetone mixtures with air the law has been shown to apply to higher as well as lower limits by experiments in a closed 2-liter spherical flask with ignition in the lower part of the flask (*102*).

ETHYL ALCOHOL AND ETHER; ACETONE AND ETHER

Observations with ethyl alcohol-ether-air and acetone-ether-air mixtures in closed tubes 5 cm. in diameter and 150 cm. long showed close agreement with the values calculated by Le Chatelier's formula, for lower limits, upward, horizontal, and downward propagation, and for higher limits, downward propagation. The higher limits, upward or horizontal propagation, differ greatly from the calculated values; these differences are ascribed to the irregular intervention of the "cool flame" of ether. Details of the results may be obtained in the original communications (*70*, *79*, *118*).

ETHYL ALCOHOL AND FURFURAL

The lower limits of two mixtures (3 : 1 and 1:3) of ethyl alcohol and furfural, upward propagation of flame in a tube 5 cm. wide and 150 cm. long, open at the firing end, deviate somewhat from the values calculated by Le Chatelier's formula (*150*).

ETHYL ALCOHOL AND ACETONE

The lower limit of a 4 : 1 mixture of ethyl alcohol and acetone, upward propagation of flame in a tube 5 cm. wide and 150 cm. long, open at the firing end, was nearly in agreement with the value calculated by Le Chatelier's formula (*150*).

ETHER AND ACETALDEHYDE

Observations with ether-acetaldehyde-air mixtures in closed tubes 5 cm. in diameter and 150 cm. long showed close agreement with the values calculated by Le Chatelier's formula for lower limits, upward and downward propagation, and for higher limits, downward propagation. The observed values for higher limits, upward propagation, are definitely lower than those calculated. Both ether and acetaldehyde give rise to "cool flames" in the richer mixtures, and the higher limits reported are those of the "cool flames." The propagation of the "cool flame" by either constituent is not assisted by that of the other to the extent that an additive law would indicate (*79*).

ACETONE AND METHYL ETHYL KETONE

Observations with acetone-methyl ethyl ketone-air mixtures in closed tubes 5 cm. in diameter and 150 cm. long for both limits showed close agreement with the values calculated by Le Chatelier's formula, for horizontal and downward propagation. For upward propagation the lower limits were slightly higher than those calculated; the higher limits were several tenths of 1 per cent higher than those calculated (*79*).

PARAFFIN HYDROCARBON HALIDES

The limits of the following mixtures have been determined in air, in a 2½-liter bell jar, electric spark ignition: Methyl chloride and ethyl chloride; methyl chloride and methyl bromide; methyl bromide and ethyl chloride. All mixtures of each pair are capable of violent explosion when mixed with appropriate amounts of air. The observed limits differ appreciably from those calculated by Le Chatelier's law (*136*).

SOME MIXED SOLVENTS FOR LACQUERS

Table 27 gives lower limits, in grams per liter, of a series of mixtures of hydrocarbons, esters (active nitro cellulose solvents), and alcohols. The limits were determined in a closed tube 25 cm. long and 2.5 cm. in diameter, central ignition, with upward propagation of flame (*134*).

TABLE 27.—*Mixed solvents, composition and limits*

Mixture No.	1	2	3	4	5	6	7	8
Benzene	50	60	20			20		
Toluene			40	60	60	40	30	30
V. M. P. naphtha							30	
Ethyl acetate	50	30	15	15		10		
Butyl acetate			15		15	10		
Butyl propionate				15	15	10	30	40
Ethyl alcohol		10	5	5				
Butyl alcohol			5	5	10	10	10	30
Lower limit, gram per liter	0.070	0.057	0.071	0.098	0.082	0.062	0.059	0.077

SUMMARY OF LIMITS OF INFLAMMABILITY

Tables 28 and 29 contain chosen values for the limits of inflammability of single gases and vapors and of some industrial mixtures in air at ordinary temperatures and pressures. The values observed for upward propagation of flame in large vessels are chosen as most generally useful for reasons given earlier.

The figures in italics represent experiments with mixtures contained in closed or small vessels; they are therefore not applicable with certainty to conditions in which normal pressure is maintained during the passage of flame but are useful approximations. Reference to the text will give more exact definition of the conditions of observation.

TABLE 28.—*Approximate limits of inflammability of single gases and vapors in air at ordinary temperatures and pressures, per cent*

Gas or vapor	Lower limit, by volume	Higher limit, by volume	Gas or vapor	Lower limit, by volume	Higher limit, by volume
Hydrogen	4.1	74	Ethylene oxide	3.0	80
Ammonia	*16*	*27*	Acetaldehyde	*4*	*57*
Hydrogen sulphide	*4.3*	*46*	Furfural (125° C.)	2	----------
Carbon disulphide	*1.0*	*50*	Acetone	3	*11*
Carbon monoxide	12.5	74	Acetone (turbulent mixture)	*2.5*	----------
Methane	5.3	14.0	Methyl ethyl ketone	*2*	*12*
Methane (turbulent mixture)	5.0	15	Methyl formate	6	20
Ethane	3.2	12.5	Ethyl formate	*3.5*	*16.5*
Propane	2.4	9.5	Methyl acetate	*4.1*	*14*
Butane	1.9	8.5	Ethyl acetate	2.5	*11.5*
Pentane	1.45	7.5	Propyl acetate	2.0	----------
Ethylene	3.0	29	Butyl acetate (30° C.)	1.7	----------
Acetylene	3.0	----------	Ethyl nitrite	*3*	----------
Acetylene (turbulent mixture)	2.3	----------	Methyl chloride	8	19
Benzene	1.4	7	Methyl bromide	13.5	14.5
Toluene	1.4	*7*	Ethyl chloride	4	15
Cyclohexane	1.3	8.3	Ethyl bromide	7	11
Methyl cyclohexane	1.2	----------	Ethylene dichloride	6	[1] *16*
Methyl alcohol	7	----------	Dichlorethylene	10	13
Ethyl alcohol	4	*19*	Vinyl chloride	4	22
Ethyl ether	1.7	26 (*48*)	Pyridine (70° C.)	*1.8*	*12.5*

[1] 125° C.

TABLE 29.—*Approximate limits of inflammability of some industrial mixtures of gases and vapors in air at ordinary temperatures and pressures, per cent*

Gas or vapor	Lower limit, by volume	Higher limit, by volume	Gas or vapor	Lower limit, by volume	Higher limit, by volume
Benzine	1.1	----------	Natural gas	4.8	13.5
Gasoline	1.4	6	Illuminating gas	5.3	31
Water gas	6 to 9	55 to 70	Blast-furnace gas	*35*	74

The limit figures in Table 29 apply only to particular samples of mixture; analytical data will be found in the text. By the use of Le Chatelier's law the limits of samples of similar mixtures can be calculated.

Further information about the limits of gases and vapors will be found in the text; it is not suitable for inclusion in Tables 28 and 29 but may be useful if the conditions of determination are kept in mind.

Much information about the limits of certain gases and vapors in other atmospheres than air has been assembled. The influence of pressure and temperature and the effect of turbulence on limits of inflammability have been shown.

BIBLIOGRAPHY

(Some titles, insufficiently explicit, have been replaced by short statements which are put within parentheses)

1. HUMBOLDT, F. H. A., and GAY-LUSSAC, L. J., Experiments on eudiometry. Jour. phys. théor. et appl., t. 60, 1804, p. 129: trans. in Ann. Phys. (Gilbert), vol. 20, 1805, p. 38.

2, 3. DAVY, H., The fire damp of coal mines and methods of lighting the mines so as to prevent its explosion. Phil. Trans., vol. 106, 1816, p. 1. Some researches on flame. Phil. Trans., vol. 107, 1817, p. 45.

4. TURNER, E. (Experiments on rendering electrolytic gas noninflammable by the addition of other gases). Edinburgh Phil. Jour., vol. 11, 1824, p. 311.

5. HENRY, W. (Dilution of electrolytic gas until no longer inflammable). Ann. Phil., vol. 25 (vol. 9, n. s.), 1825, p. 416.
6. REGNAULT, V., and REISET, J., Some hydrogen-oxygen limits in various gases. Ann. Chem. Pharm., vol. 73, 1850, p. 129.
7. BUNSEN, R., Gasometry. 1857, p. 247.
8. MEYER, E. VON, The incomplete combustion of gases. Jour. prakt. Chem., Jahrg. 10, n. s., 1874, p. 273.
9. MALLARD, E., Speed of flame in air and fire-damp mixtures. Ann. mines, t. 7 (ser. 7), 1875, p. 355.
10. WAGNER, A., Explosion limits of mixtures of combustible gases with oxygen or air. Bayer. Indus. u. Gewerbeblatt, Jahrg. 8, 1876, p. 186.
11. COQUILLON, J. J., Limits of explosibility of fire damp. Compt. rend., t. 83, 1876, p. 709.
12. BUNSEN, R., Gasometry. 2d. ed., 1877.
13. SCHÜTZENBERGER, P., Combustion of gases. Compt. rend., t. 86, 1878, p. 598.
14. MALLARD, E., and LE CHATELIER, H., Experimental and theoretical researches on the combustion of explosive gaseous mixtures. Ann. mines, t. 4 (ser. 8), 1883, p. 347.
15. WÜLLNER, A., and LEHMANN, O. (Methane-air limits). Ber. preuss. Schlagwetterkommission, Berlin, Jahrg. 3, 1886, p. 193.
16. BROOCKMANN, E., Combustion of gases. Jour. Gasbel., Jahrg. 32, 1889, p. 189.
17. LE CHATELIER, H. Estimation of fire damp by inflammability limits. Ann. mines, t. 19 (ser. 8), 1891, p. 388.
18. ROSZKOWSKI, J., The effect of temperature on the explosion limits of inflammable gas mixtures. Jour. Gasbel., Jahrg. 33, 1890, pp. 491, 524, 535, 553; Ztschr. physikal. Chem., Jahrg. 7, 1891, p. 485.
19. HALDANE, J. S., and ATKINSON, W. N., Composition, occurrence, and properties of black damp. Trans. Inst. Min. Eng., vol. 8, 1894–95, p. 549.
20. LE CHATELIER, H., Combustion of acetylene. Compt. rend., t. 121, 1895, p. 1144.
21. CLOWES, F., The limiting explosive mixtures of various combustible gases with air. Trans. Inst. Min. Eng., vol. 9, 1894–95, pp. 373, 382; Jour. Soc. Chem. Ind., vol. 14, 1895, p. 1024; vol. 15, 1896, p. 418.
22. BUNTE, H. (Limits of several gases in air). Ber. Deut. chem. Gesell., Jahrg. 31, 1898, p. 19.
23. COURIOT, H., and MEUNIER, J., Explosion of methane mixtures by the electric current. Compt. rend., t. 126, 1898, p. 750.
24. LE CHATELIER, H., and BOUDOUARD, O., Limits of inflammability of carbon monoxide. Compt. rend., t. 126, 1898, p. 1344. Limits of inflammability of combustible vapors. Compt. rend., t. 126, 1898, p. 1510. Limits of inflammability of gaseous mixtures. Bull. Soc. chim. Paris, t. 19, 1898, p. 483.
25. GERDES, H. (Acetylene-air limits). Ann. Gewerbe u. Bauwesen, Jahrg. 43, 1898, p. 105.
26. TANATAR, S., Burning of gases. Ztschr. physikal. Chem., Jahrg. 35, 1900, p. 340; Jahrg. 36, 1901, p. 225.
27. KUBIERSCHKY, K., Explosion of mixtures of inflammable vapors or mists with air. Ztschr. angew. Chem., Jahrg. 14, 1901, p. 129.
28. EITNER, P., Explosion limits of inflammable gases and vapors. Habilitationsschrift, München, 1902; Jour. Gasbel., Jahrg. 45, 1902, pp. 21, 69, 90, 112, 221, 244, 265, 345, 362, 382, 397.
29. MISTELI, W., Incomplete combustion of gases. Jour. Gasbel., Jahrg. 48, 1905, p. 802.
30. TECLU, N., Determination of the limiting explosive mixtures of gases. (Erroneous results in part.) Jour. prakt. Chem., Jahrg. 75, n. s., 1907, p. 212.
31. MEUNIER, J., Limits * * * of ether and air. Compt. rend., t. 144, 1907, p. 796. Explosive mixtures of ether and air. Compt. rend., t. 144, 1907, p. 1107.
32. HAUSER, E., Leçons sur le grisou. Madrid, 1908.
33. EPSTEIN, F., and KRASSA, P. (Carbon dioxide seemed to increase explosibility of gases in Bunsen flame). Ztschr. physikal. Chem., Jahrg. 71, 1910, p. 28.
34. FISCHER, F., and WOLF, M. (Hydrogen-oxygen limits). Ber. Deut. chem. Gesell., Jahrg. 44, 1911, p. 2956.

35. PERMAN, E. P., Limits of explosibility in gaseous mixtures. (Erroneous conclusions.) Nature, vol. 87, 1911, p. 416.
36. BURGESS, M. J., and WHEELER, R. V., Lower limit of inflammation of mixtures of the paraffin hydrocarbons with air. Jour. Chem. Soc., vol. 99, 1911, p. 2013.
37. COWARD, H. F., COOPER, C., and WARBURTON, C. H., Ignition of electrolytic gas by the electric discharge. Jour. Chem. Soc., vol. 101, 1912, p. 2278.
38. BUDDE, H. (Amount of hydrogen sulphide required to render electrolytic gas noninflammable). Ztschr. anorg. Chem., Jahrg. 78, 1912, p. 169.
39. DELEPINE, M., Inflammability of acetylene mixed with about 30 per cent of air. 8th Internat. Congr. App. Chem., 1912, sec. 3 B, Orig. Com. 4, p. 25.
40. HARGER, J., Prevention of explosions in mines. Trans. Inst. Min. Eng., vol. 43, 1912, p. 132.
41. PARKER, A., Influence of increase of initial temperature on the explosiveness of gaseous mixtures. Jour. Chem. Soc., vol. 103, 1913, p. 934.
42. HEMPEL, W., Gas analytische Methoden. Braunschweig, 1913.
43. JORISSEN, W. P., Extinction of flames. Chem. Weekblad., vol. 10, 1913, p. 961.
44. TAFFANEL, J., and LEFLOCH, C., Combustion of gaseous mixtures. (Influence of temperature on methane-air limits.) Compt. rend., t. 157, 1913, p. 595.
45. CLEMENT, J. K., Influence of inert gases on inflammable gaseous mixtures. Tech. Paper 43, Bureau of Mines, 1913, 24 pp.
46. LEPRINCE-RINGUET, F., Limits of inflammability of fire damp. Compt. rend., t. 158, 1914, p. 1793. Inflammability of mixtures of fire damp and other gases. Compt. rend., t. 158, 1914, p. 1999.
47. PARKER, A., Lower limits of inflammation of methane with mixtures of oxygen and nitrogen. Jour. Chem. Soc., vol. 105, 1914, p. 1002.
48. COWARD, H. F., COOPER, C., and JACOBS, J., Ignition of some gaseous mixtures by the electric discharge. Jour. Chem. Soc., vol. 105, 1914, p. 1069.
49. COWARD, H. F., and BRINSLEY, F., Dilution limits of inflammability of gaseous mixtures. I, Determination of dilution limits. II, Lower limits for hydrogen, methane, and carbon monoxide in air. Jour. Chem. Soc., vol. 105, 1914, p. 1859.
50. SOMERMEIER, E., Lower limits of combustible and explosive mixtures of gases and air. Jour. Ind. Eng. Chem., vol. 6, 1914, p. 191. Partial and intermittent combustion of gas. Jour. Ind. Eng. Chem., vol. 6, 1914, p. 374.
51. SCHLUMBERGER, E., and PIOTROWSKI, W., Explosibility of mixtures of air and ammonia. Jour. Gasbel., Jahrg. 57, 1914, p. 941.
52. REIS, A., Flames. (Ammonia-oxygen limit.) Ztschr. physikal. Chem., Jahrg. 88, 1914, p. 513.
53. TERRES, E., and PLENZ, F., Influence of pressure on the burning of explosive gas mixtures. Jour. Gasbel., Jahrg. 57, 1914, pp. 990, 1001, 1016.
54. BURGESS, M. J., and WHEELER, R. V., The limits of inflammability of mixtures of methane and air. Jour. Chem. Soc., vol. 105, 1914, p. 2591. Propagation of flame in limit mixtures of methane, oxygen, and nitrogen. J. Chem. Soc., vol. 105, 1914, p. 2596.
55. BURRELL, G. A., and OBERFELL, G. G., Explosibility of acetylene. Tech. Paper 112, Bureau of Mines, 1915, 15 pp.
56. BURRELL, G. A., and BOYD, H. T., Inflammability of mixtures of gasoline vapor and air. Tech. Paper 115, Bureau of Mines, 1915, 18 pp.
57. BURRELL, G. A., and OBERFELL, G. G., Limits of inflammability of mixtures of methane and air. Tech. Paper 119, Bureau of Mines, 1915, 30 pp.
58. BURRELL, G. A., and ROBERTSON, I. W., Effects of temperature and pressure on the explosibility of methane-air mixtures. Tech. Paper 121, Bureau of Mines, 1916, 14 pp.
59. BURRELL, G. A., and OBERFELL, G. G., Explosibility of gases from mine fires. Tech. Paper 134, Bureau of Mines, 1916, 31 pp.
60. BURRELL, G. A., and GAUGER, A. W., Limits of complete inflammability of mixtures of mine gases and of industrial gases with air. Tech. Paper 150, Bureau of Mines, 1917, 13 pp.
61. THORNTON, W. M., The limits of inflammability of gaseous mixtures. Phil. Mag., vol. 33, 1917, p. 190.
62. WHEELER, R. V., and WHITAKER, A., Propagation of flame in mixtures of acetone and air. Jour. Chem. Soc., vol. 111, 1917, p. 267.

63. MATHIEU, P., Proportions of chlorine and hydrogen which limit the explosion of mixtures of these gases. Jour. Phys., t. 7, p. 166, 1917.
64. MASON, W., and WHEELER, R. V., Effect of temperature and of pressure on the limits of inflammability of mixtures of methane and air. Jour. Chem. Soc., vol. 113, 1918, p. 45.
65. PAYMAN, W., and WHEELER, R. V., Propagation of flame through tubes of small diameter. Jour. Chem. Soc., vol. 113, 1918, p. 656.
66. COWARD, H. F., CARPENTER, C., and PAYMAN, W., Dilution limits of inflammability of gaseous mixtures. III, Lower limits of some mixed inflammable gases with air. IV, Upper limits of some gases, singly and mixed, in air. Jour. Chem. Soc., vol. 115, 1919, p. 27.
67. PAYMAN, W., and WHEELER, R. V., Propagation of flame through tubes of small diameter. II. Jour. Chem. Soc., vol. 115, 1919, p. 36.
68. WHEELER, R. V., Inflammation of mixtures of ethane and air in a closed vessel: The effects of turbulence. Jour. Chem. Soc., vol. 115, 1919, p. 81.
69. PAYMAN, W., Propagation of flame in complex gaseous mixtures. I, Limit mixtures. II, Uniform movement of flame in mixtures of air with the paraffin hydrocarbons. Jour. Chem. Soc., vol. 115, 1919, pp. 1436, 1446.
70. WHITE, A. G., and PRICE, T. W., Ignition of ether-alcohol-air and acetone-air mixtures in contact with heated surfaces. Jour. Chem. Soc., vol. 115, 1919, p. 1462.
71. SATTERLY, J., and BURTON, E. F., Combustibility of mixtures of hydrogen and helium. Trans. Roy. Soc. Canada, vol. 13, sec. 3, 1919, p. 211.
72. MASON, W., and WHEELER, R. V., Propagation of flame in mixtures of methane and air. III, Propagation in currents. Jour. Chem. Soc., vol. 117, 1920, p. 1227.
73. TERRES, E., Effect of oxygen on the explosion limits of combustible gases and vapors. Jour. Gasbel., Jahrg. 63, 1920, pp. 785, 805, 820, 836.
74. CHAPMAN, W. R., Propagation of flame in mixtures of ethylene and air. Jour. Chem. Soc., vol. 119, 1921, p. 1677.
75. NUCKOLLS, A. H., Explosive limits of mixtures of hydrogen and oxygen under pressure. Rept. Underwriters' Laboratories, Chicago, 1920.
76. JORISSEN, W. P. (Contains limits of acetaldehyde in certain atmospheres.) Rec. trav. chim. Pays-bas, t. 39, 1920, p. 715.
77. BOUSSU, R. G., (Lower) limit of inflammability of the vapors of the system alcohol-gasoline and of a triple system with a base of alcohol and gasoline. Compt. rend., t. 175, 1922, p. 30.
78, 79. WHITE, A. G., Limits for the propagation of flame in vapor-air mixture. I, Mixtures of air and one vapor at the ordinary temperature and pressure. II, Mixtures of more than one vapor and air at the ordinary temperature and pressure. Jour. Chem. Soc., vol. 121, 1922, pp. 1244, 2561.
80. ——— Limits for the propagation of flame at various temperatures in mixtures of ammonia with air and oxygen. Jour. Chem. Soc., vol. 121, 1922, p. 1688.
81. TAFFANEL, J., Combustion of gaseous mixtures. Chaleur et industrie, t. 4, 1923, p. 598.
82. PAYMAN, W., and WHEELER, R. V., Effect of pressure on the limits of inflammability of mixtures of the paraffin hydrocarbons with air. Jour. Chem. Soc., vol. 123, 1923, p. 426.
83. ASCH, E., Explosive limits of gas mixtures. Ztschr. Tech. Physik., Jahrg. 4, 1923, p. 468.
84. DEISS, E., Certain constants of ethyl chloride. Ztschr. Elektrochem., vol. 29, 1923, p. 586.
85. JONES, G. W., YANT, W. P., and BERGER, L. B., Explosibility of hydrogen sulfide in air. Jour. Ind. Eng. Chem., vol. 16, 1924, p. 353.
86. EDWARDS, H. D., Properties of refrigerants. Refrigerating Engineering, vol. 11, 1924, p. 95.
87. BERL, E., and FISCHER, H., Explosive mixtures of gases and vapors with air. Ztschr. Electrochem., Jahrg. 30, 1924, p. 29.
88. STRACHE, H., Explosion limits and flash points of combustible liquids. Oest. Chem. Ztg., Jahrg. 27, 1924, p. 19.
89. RIEDLER, A., Inflammable liquid fuels and the methods of rendering them industrially safe. Oest. Chem. Ztg., Jahrg. 27, 1924, pp. 91, 100.
90. WHITE, A. G., Limits for the propagation of flame in inflammable gas-air mixtures. I, Mixtures of air and one gas at the ordinary temperature and pressure. Jour. Chem. Soc., vol. 125, 1924, p. 2387.

91. JORISSEN, W. P., and VELISEK, J., Influence of some noninflammable vapors of organic liquids on the limits of inflammability of methane-air mixtures. I. Rec. trav. chim. Pays-bas, t. 43, 1924, p. 80.
92. JORISSEN, W. P., and MEUWISSEN, J. C., Influence of some noninflammable vapors of organic liquids on the limits of inflammability of methane-air mixtures. II. Rec. trav. chim. Pays-bas, t. 43, 1924, p. 591.
93. CHEMISCHE TECHNISCHE REICHSANSTALT (Limits of inflammability of hydrocyanic acid). Jahrg. 4, 1924–1925, p. 52.
94. JORISSEN, W. P., and MEUWISSEN, J. C., Influence of some noninflammable vapors of organic liquids on the limits of inflammability of methane-air mixtures. III, Mixtures of inflammable gases and air. Rec. trav. chim. Pays-bas, t. 44, 1925, p. 132.
95. JORISSEN, W. P., and VALK, J. H. A. P. L. VAN DER, Influence of dichloro and trichloroethylene on the limits of inflammability of carbon monoxide-air mixtures. Rec. trav. chim. Pays-bas, t. 44, 1925, p. 810.
96. JORISSEN, W. P., and ONGKIEHONG, B. L., Influence of trichloroethylene on the limits of inflammability of hydrogen-air mixtures. Rec. trav. chim. Pays-bas, t. 44, 1925, p. 814.
97. JORISSEN, W. P., and ONGKIEHONG, B. L., Graphic representation of limits of mixed gases. Rec. trav. chim. Pays-bas, t. 44, 1925, p. 1039.
98. JORISSEN, W. P., and ONGKIEHONG, B. L., Influence of ethylene on the limits of explosion of electrolytic gas. Rec. trav. chim. Pays-bas, t. 45, 1926, p. 162.
99. JORISSEN, W. P., and ONGKIEHONG, B. L., Explosion regions of hydrogen-ammonia-air and hydrogen-ammonia-oxygen mixtures. Rec. trav. chim. Pays-bas, t. 45, 1926, p. 224.
100, 101. WHITE, A. G., Limits for the propagation of flame in inflammable gas-air mixtures. II, Mixtures of more than one gas and air. III, The effect of temperature on the limits. Jour. Chem. Soc., vol. 127, 1925, pp. 48, 672.
102. CROUCH, H., and CARVER, E. K., Effect of nitrogen and carbon dioxide dilutions on explosion limits of acetone and methanol and their mixtures. Ind. Eng. Chem., vol. 17, 1925, p. 641.
103. BURGESS, M. J., and WHEELER, R. V., Limits of inflammability of fire damp and air. Paper 15, Safety in Mines Research Board (London), 1925.
104. COWARD, H. F., and HARTWELL, F. J., Limits of inflammability of fire damp in atmospheres which contain black damp. Paper 19, Safety in Mines Research Board (London), 1926.
105. COWARD, H. F., and HARTWELL, F. J., Extinction of methane flames by diluent gases. Jour. Chem. Soc., vol. 129, 1926, p. 1522.
106. COWARD, H. F., and JONES, G. W., Extinction of methane-air flames by some chlorinated hydrocarbons. Ind. Eng. Chem., vol. 18, 1926, p. 970.
107. JORISSEN, W. P., and ONGKIEHONG, B. L., The explosion space C_2H_5Br-NH_3-O_2-N_2. Rec. trav. chim. Pays-bas, t. 45, 1926, p. 400.
108. CRAWSHAW, J. E., Lower limits of flammability of natural gas-air mixtures in a large gallery. Unpublished report, Bureau of Mines, Dec. 15, 1925.
109. COWARD, H. F., and HARTWELL, F. J., Unpublished results.
110. WHEELER, R. V., Unpublished results.
111. COWARD, H. F., JONES, G. W., DUNKLE, C. G., and HESS, B. E., The explosibility of methane and natural gas. Bull. 30, Min. Met. Investigations, U. S. Bureau of Mines and Carnegie Inst. of Technology, 1926.
112. JORISSEN, W. P., and ONGKIEHONG, B. L., The explosion regions of nitrous oxide-ether vapor-oxygen and of nitrous oxide-ether vapor-air. Rec. trav. chim. Pays-bas, t. 45, 1926, p. 633.
113. TANAKA, Y., and NAGAI, Y., Influence of ethyl bromide on the limits of inflammability of hydrogen-air mixtures. Proc. Imp. Acad. Tokyo, vol. 2, 1926, p. 280.
114. ——— Influence of organic bromine and iodine compounds on the upper limit of inflammability of hydrogen-air mixtures. Proc. Imp. Acad. Tokyo, vol. 2, 1926, p. 283.
115. NAGAI, Y., The inflammability of alkyl halides and their influence on the limit of inflammability of ethyl ether-air and hydrocarbon-air mixtures. Proc. Imp. Acad. Tokyo, vol. 2, 1926, p. 284.

116. NAGAI, Y., and AKIYAMA, K., Effects of water and antiknock materials on the lower limit for the propagation of flame. Jour. Soc. Chem. Ind. Japan, vol. 29, 1926, p. 91 B.
117. TANAKA, Y., and NAGAI, Y., Influence of diethyl selenide and hydrogen selenide on the limits of inflammability of hydrogen-air mixtures. Proc. Imp. Acad. Tokyo, vol. 2, 1926, p. 494.
118. TANAKA, Y., NAGAI, Y., and AKIYAMA, K., Lower limit of inflammability of ethyl alcohol, ethyl ether, methyl cyclohexane, and their mixtures. Rep. Aeronaut. Res. Inst., Tokyo Imp. Univ., vol. 2, 1927, p. 235.
119. BERL, E., and WERNER, G., Limits of inflammability at high pressures of mixtures, with air, of combustible gases and vapors. Ztschr. angew. Chem., vol. 40, 1927, p. 245.
120. TOWNEND, D. T. A., Gaseous combustion at high pressures. VIII, The explosion of methane with up to its own volume of oxygen at initial pressures up to 150 atmospheres. Proc. Roy. Soc., vol. A116, 1927, p. 637.
121. JORISSEN, W. P., and KAYSER, G. M. A., The influence of mixtures of carbon dioxide and carbon tetrachloride vapor on the inflammability of a methane-air mixture. Rec. trav. chim. Pays-Bas, t. 46, 1927, p. 373.
122. JORISSEN, W. P., COWARD, H. F., and JONES, G. W., Influence of some chlorinated hydrocarbons on the limits of inflammability of methane-air mixtures. Ind. Eng. Chem., vol. 19, 1927, p. 430.
123. JONES, G. W., and PERROTT, G. ST. J., Oxygen required for the propagation of hydrogen, carbon monoxide, and methane flames. Ind. Eng. Chem., vol. 19, 1927, p. 985.
124. TANAKA, Y., and NAGAI, Y., Influence of dimethyl selenide and dimethyl telluride on the limits of inflammability of hydrogen-air mixtures. Proc. Imp. Acad. Tokyo, vol. 3, 1927, p. 348.
125 ——— Influence of tetramethyl tin and tetramethyl lead on the limits of inflammability of hydrogen. Proc. Imp. Acad. Tokyo, vol. 3, 1927, p. 434.
126. TERADA, T., YUMOTO, K., and NAKAYA, U., Combustion of mixtures of hydrogen with air or oxygen in eudiometer. Sci. Papers, Inst. Phys. and Chem. Res. No. 90, vol. 6, 1927, p. 81.
127. NAGAI, Y., Effect of antiknock materials on the limits of inflammability of ethyl ether and hydrocarbon. Proc. Imp. Acad. Tokyo, vol. 3, 1927, p. 664.
128. ——— Effect of pressure on the limits of inflammability and the average life period of activated molecules in combustion. Jour. Fac. Eng., Tokyo Imp. Univ., vol. 17, 1927, p. 89.
129. CHAPPUIS, J., and PIGNOT, A., The compression of town's gas. Compt. rend., t. 185, 1927, p. 1486.
130. PIGNOT, A., Compression of illuminating gas. Advantages of storage under high pressure. Rev. Univ. Mines, t. 20, 1928, p. 221.
131. DE BOOSERE, O., Limits of inflammability. Ann. Mines Belg., vol. 28, 1927, p. 1075.
132. WHITE, A. G., The effect of pressure on the limits for the propagation of flame in ether-air. Jour. Chem. Soc., 1927, p. 498.
133. ——— The burning of carbon disulphide near the limit for the propagation of flame, with some remarks on the ignition point of sulphur. Jour. Chem. Soc., 1927, p. 793.
134. RICHARDSON, E. G., and SUTTON, C. R., Explosive properties of lacquer-solvent vapors. Ind. Eng. Chem., vol. 20, 1928, p. 187.
135. BONE, W. A., NEWITT, D. M., and SMITH, C. M., The influence of pressure upon the explosion limits of inflammable gas-air, etc., mixtures. Proc. Roy. Soc., vol. A117, 1928, p. 553.
136. JONES, G. W., The flammability of refrigerants. Mixtures of methyl and ethyl chlorides and bromides. Ind. Eng. Chem., vol. 20, 1928, p. 367.
137. ——— Inflammability of automobile exhaust gas. Ind. Eng. Chem., vol. 20, 1928, p. 901.
138. BUNTE, K., and STEDING, A., Explosion limits of technical gas mixtures. Gas u. Wasserfach, vol. 71, 1928, p. 821; Gas Jour., vol. 184, 1928, p. 728.
139. BONE, W. A., NEWITT, D. M., and SMITH, C. M., The influence of steam and temperature, respectively, upon the explosion limits of carbon monoxide-air mixtures. Proc. Roy. Soc., vol. A120, 1928, p. 563.

140. Tanaka, Y., and Nagai, Y., Influence of ethyl ether, ethyl alcohol, acetone, and hydrocarbons on the limits of inflammability of hydrogen-air mixtures. Proc. Imp. Acad. Tokyo, vol. 4, 1928, p. 154.
141. Prettre, M., and Laffitte, P., Ignition temperatures of mixtures of hydrogen and air. Compt. rend., t. 187, 1928, p. 763.
142. ——— Ignition temperatures of mixtures of carbon monoxide and air. Compt. rend., t. 188, 1929, p. 1403.
143. Nagai, Y., Flame propagation in gaseous mixtures. Jour. Fuel Soc. Japan, vol. 8, 1929, p. 17.
144. Tanaka, Y., and Nagai, Y., Dew point, density, and range of inflammability of treated hydrogen. Proc. Imp. Acad. Tokyo, vol. 5, 1929, p. 80.
145. Jones, G. W., Inflammability of mixed gases. Tech. Paper 450, Bureau of Mines, 1929, 38 pp.
146. Passauer, H., The normal rate of combusion of gases rich in nitrogen (producer gas and blast-furnace gases). Feuerungstechnik, vol. 17, 1929, pp. 7, 15, 28.
147. Valk, J. H. A. P. L., van der, Explosive regions of some gas and vapor mixtures in which carbon monoxide is the only or the principal inflammable gas. Rec. trav. chim. Pays-Bas, t. 48, 1929, p. 201.
148. Coward, H. F., Explosibility of atmospheres behind stoppings. Trans. Inst. Min. Eng., vol. 77, 1929, p. 94.
149. Goldmann, F., Diffusion phenomena in lower limit hydrogen mixtures. Ztschr. physikal. Chem., vol. B5, 1929, p. 307.
150. Jones, G. W., and Klick, J. R., Inflammability of mixtures of ethyl alcohol, benzene, furfural, and acetone. Ind. Eng. Chem., vol. 21, 1929, p. 791.
151. Yeaw, J., Explosive limits of industrial gases. Ind. Eng. Chem., vol. 21, 1929, p. 1030.
152. Louis, —, Use of methyl and ethyl alcohols as fuel for internal-combustion engines. Ann. combust. liquides, t. 4, 1929, p. 183.
153. Yannaquis, —, Influence of temperature on the limits of inflammability of alcohols. Ann. combust. liquides, t. 4, 1929, p. 303.
154. Cooper, C. M., and Wiezevich, P. J., Effects of temperature and pressure on the upper explosive limit of methane-oxygen mixtures. Ind. Eng. Chem., vol. 21, 1929, p. 1210.
155. Coward, H. F., and Gleadall, J. J., Extinction of methane flames by water vapor. Jour. Chem. Soc., 1930, p. 243.
156. Georgeson, E. H. M., and Hartwell, F. J., Uniform movement of flame in mixtures of air with ethylene, propylene, and butylene. Jour. Chem. Soc., 1930, p. 733.
157. Jones, G. W., Unpublished results.
158. Burgess, M. J., and Greenwood, G., Unpublished results .
159. Jones, G. W., and Kennedy, R. E., Extinction of ethylene flames by carbon dioxide and nitrogen. Anesthesia and Analgesia, vol. 9, 1930, p. 6.

CONTENTS