

TECHNICAL REPORT

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**Flammability Characteristics of
Combustible Gases and Vapors**

Reaffirmed

ANSI/ISA–TR12-13-01–1999 (R2013)
Flammability Characteristics of Combustible Gases and Vapors

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FOREWORD

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As a service to industry, the accompanying document, Bureau of Mines Bulletin 627 - Flammability Characteristics of Combustible Gases and Vapors, by Zabetakis 1965, is hereby reprinted in its entirety.

This compendium, formerly available from the U.S. Bureau of Mines, contains information essential to an understanding of detection, measurement and handling of flammable gases and vapors.

For further information, refer to ANSI/ISA-TR12.13.02.

The reader should be aware that more recent LFL/UFL figures are available in NFPA 497, and IEC 60079-20-1.

ABSTRACT

This technical report includes theoretical and practical work carried out and collected by the U.S. Bureau of Mines relating to ignition and explosive properties of flammable gas mixtures. Flammability limits, under varying conditions of proportion, temperature and pressure, are presented.

While the primary emphasis is on methane-air mixtures as found in coal mines, a full treatment of many other gases and vapors is included.

KEY WORDS

Methane
Fire
Explosion
Flammability limits
Flammable
Combustible
LEL, UEL
LFL, UFL
Gas

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APPENDIX I

The following document, *Flammability Characteristics of Combustible Gases and Vapors*, is reprinted in its entirety by permission of the publisher, the Bureau of Mines, U.S. Department of the Interior.

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By Michael G. Zabetakis

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FLAMMABILITY CHARACTERISTICS OF COMBUSTIBLE GASES AND VAPORS

by

Michael G. Zabetakis["]

Abstract

This is a summary of the available limit of flammability, autoignition, and burning-rate data for more than 200 combustible gases and vapors in air and other oxidants, as well as of empirical rules and graphs that can be used to predict similar data for thousands of other combustibles under a variety of environmental conditions. Specific data are presented on the paraffinic, unsaturated, aromatic, and alicyclic hydrocarbons, alcohols, ethers, aldehydes, ketones, and sulfur compounds, and an assortment of fuels, fuel blends, hydraulic fluids, engine oils, and miscellaneous combustible gases and vapors.

Introduction

Prevention of unwanted fires and gas explosion disasters requires a knowledge of flammability characteristics (limits of flammability, ignition requirements, and burning rates) of pertinent combustible gases and vapors likely to be encountered under various conditions of use (or misuse). Available data may not always be adequate for use in a particular application since they may have been obtained at a lower temperature and pressure than is encountered in practice. For example, the quantity of air that is required to decrease the combustible vapor concentration to a safe level in a particular process carried out at 200°C should be based on flammability data obtained at this temperature. When these are not available, suitable approximations can be made to permit a realistic evaluation of the hazards associated with the process being considered; such approximations can serve as the basis for designing suitable safety devices for the protection of personnel and equipment.

The purpose of this bulletin is to present a general review of the subject of flammability, and to supply select experimental data and empirical rules on the flammability characteristics of various families of combustible gases and vapors in air and other oxidizing atmospheres. It contains what are believed to be the latest and most reliable data for more than 200 combustibles of interest to those concerned with the prevention of disastrous gas explosions. In addition, the empirical rules and graphs presented here can be used to predict similar data for other combustibles under a variety of conditions. This bulletin supplements Bureau bulletins (40)^N and other publications (158).

["]Physical chemist, project coordinator, Gas Explosion, Explosives Research Center, Bureau of Mines, Pittsburgh, Pa.

Work on manuscript completed May 1964.

^NItalicized numbers in parentheses refer to items in the bibliography at the end of this report.

Basic knowledge of combustion is desirable for a thorough understanding of the material, which can be found in numerous publications (69, 199, 202). Therefore, only those aspects required for an understanding of flammability are considered here; even these are considered from a fairly elementary viewpoint.

Definitions and Theory

LIMITS OF FLAMMABILITY

A combustible gas-air mixture can be burned over a wide range of concentrations—when either subjected to elevated temperatures or exposed to a catalytic surface at ordinary temperatures. However, homogeneous combustible gas-air mixtures are flammable, that is, they can propagate flame freely within a limited range of compositions. For example, trace amounts of methane in air can be readily oxidized on a heated surface, but a flame will propagate from an ignition source at ambient temperatures and pressures only if the surrounding mixture contains at least 5 but less than 15 volume-percent methane. The more dilute mixture is known as the lower limit, or combustible-lean limit, mixture; the more concentrated mixture is known as the upper limit, or combustible-rich limit, mixture. In practice, the limits of flammability of a particular system of gases are affected by the temperature, pressure, direction of flame propagation, gravitational field strength, and surroundings. The limits are obtained experimentally by determining the limiting mixture compositions between flammable and non-flammable mixtures (244). That is,

$$L_{T,P} = 1/2[C_{gn} + C_{1f}], \quad (1)$$

and

$$U_{T,P} = 1/2[C_{gf} + C_{1n}], \quad (2)$$

where $L_{T,P}$ and $U_{T,P}$ are the lower and upper limits of flammability, respectively, at a specified temperature and pressure, C_{gn} and C_{1n} are the greatest and least concentrations of fuel in oxidant that are nonflammable, and C_{1f} and C_{gf} are the least and greatest concentrations of fuel in oxidant that are flammable. The rate at which a flame propagates through a flammable mixture depends on a number of factors including temperature, pressure, and mixture composition. It is a minimum at the limits of flammability and a maximum at near stoichiometric mixtures (130).

The Bureau of Mines has adopted a standard apparatus for limit-of-flammability determinations (40). Originally designed for use at atmospheric pressure and room temperature, it was later modified for use at reduced pressures by incorporating a spark-gap ignitor in the base of the 2-inch, glass, flame-propagation tube. This modification introduced a difficulty that was not immediately apparent, as the spark energy was not always adequate for use in limit-of-flammability determinations. Figure 1 illustrates the effect of mixture composition on the electrical spark energy requirements for ignition of methane-air mixtures (75). For example, a 0.2-millijoule (mj) spark is inadequate to ignite even a stoichiometric mixture at atmospheric pressure and 26°C; a 1-mj spark can ignite mixtures containing between 6 and 11.5 volume-percent methane, etc. Such limit-mixture compositions that depend on the ignition source strength may be defined as limits of ignitability or more simply ignitability limits; they are thus

indicative of the igniting ability of the energy source. Limit mixtures that are essentially independent of the ignition source strength and that give a measure of the ability of a flame to propagate away from the ignition source may be defined as limits of flammability. Considerably greater spark energies are required to establish limits of flammability than are required for limits of ignitability (218); further, more energy is usually required to establish the upper limit than is required to establish the lower limit. In general, when the source strength is adequate, mixtures just outside the range of flammable compositions yield flame caps when ignited. These flame caps propagate only a short distance from the ignition source in a uniform mixture. The reason for this may be seen in figure 2 which shows the effect of temperature on limits of flammability at a constant initial pressure. As the temperature is increased, the lower limit decreases and the upper limit increases. Thus, since a localized energy source elevates the temperature of nearby gases, even a nonflammable mixture can propagate flame a short distance from the source. That is, a nonflammable mixture (for example, composition-temperature point A, fig. 2) may become flammable for a time, if its temperature is elevated sufficiently (composition-temperature point B).

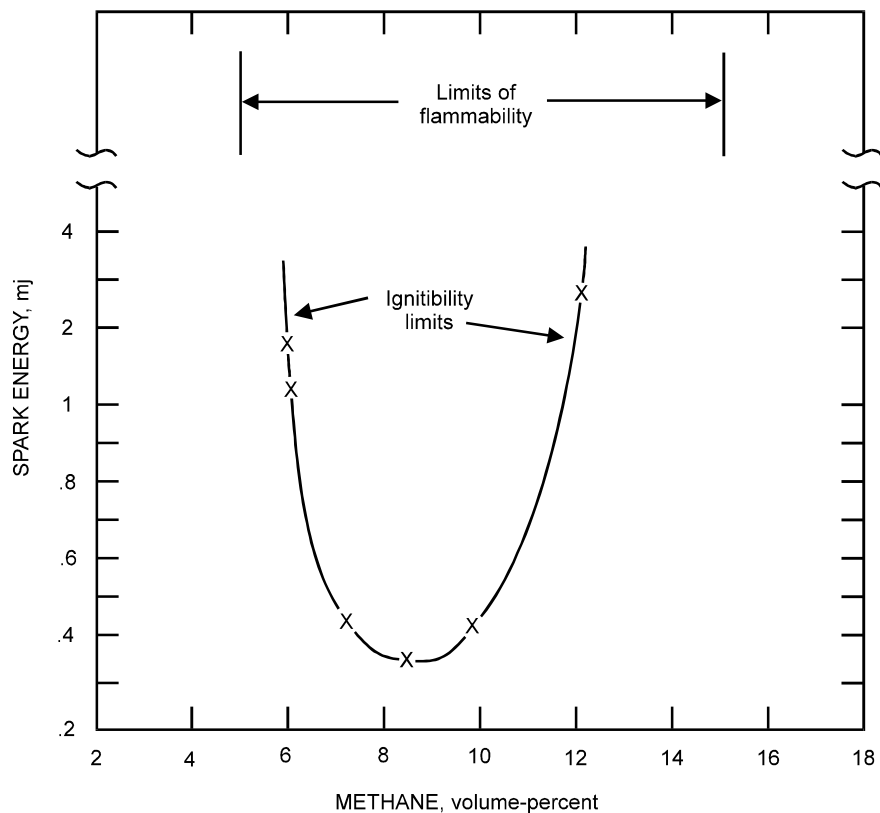


Figure 1—Ignitability Curve and Limits of Flammability for Methane-Air Mixtures at Atmospheric Pressure and 26°C.

Flammable mixtures considered in figure 2 fall in one of three regions. The first is left of the saturated vapor-air mixtures curve, in the region labeled "Mist". Such mixtures consist of droplets suspended in a vapor-air mixture; they are discussed in greater detail in the section on formation of flammable mixtures. The second lies along the curve for saturated vapor-air

mixtures; the last and most common region lies to the right of this curve. Compositions in the second and third regions make up the saturated and unsaturated flammable mixtures of a combustible-oxidant system at a specified pressure.

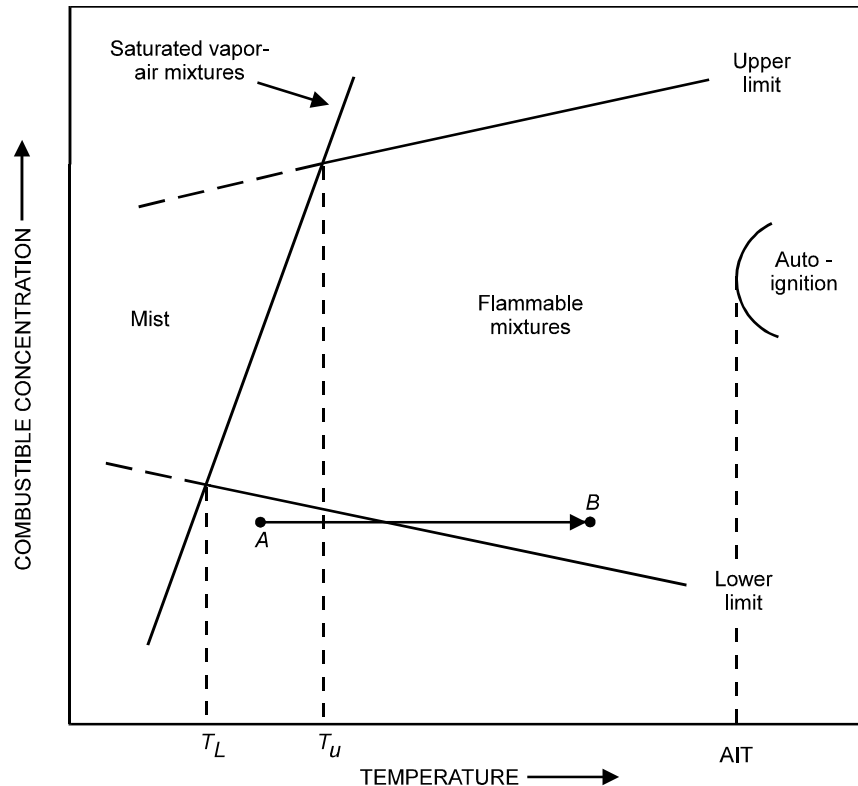


Figure 2—Effect of Temperature on Limits of Flammability of a Combustible Vapor in Air at a Constant Initial Pressure.

In practice, complications may arise when flame propagation and flammability limit determinations are made in small tubes. Since heat is transferred to the tube walls from the flame front by radiation, conduction, and convection, a flame may be quenched by the surrounding walls. Accordingly, limit determinations must be made in apparatus of such a size that wall quenching is minimized. A 2-inch-ID vertical tube is suitable for use with the paraffin hydrocarbons (methane, ethane, etc.) at atmospheric pressure and room temperature. However, such a tube is neither satisfactory under these conditions for many halogenated and other compounds nor for paraffin hydrocarbons at very low temperatures and pressures (197, 244).

Because of the many difficulties associated with choosing suitable apparatus, it is not surprising to find that the very existence of the limits of flammability has been questioned. After a thorough study, Linnett and Simpson concluded that while fundamental limits may exist there is no experimental evidence to indicate that such limits have been measured (132). In a more recent publication, Mullins reached the same conclusion (154). Accordingly, the limits of flammability obtained in an apparatus of suitable size and with a satisfactory ignition source should not be termed fundamental or absolute limits until the existence of such limits has been established. However, as long as experimentally determined limits are obtained under conditions similar to

those found in practice, they may be used to design installations that are safe and to assess potential gas-explosion hazards.

Industrially, heterogeneous single-phase (gas) and multi-phase (gas, liquid, and solid) flammable mixtures are probably even more important than homogeneous gas mixtures. Unfortunately, our knowledge of such mixtures is rather limited. It is important to recognize, however, that heterogeneous mixtures can ignite at concentrations that would normally be nonflammable if the mixture were homogeneous. For example, 1 liter of methane can form a flammable mixture with air near the top of a 100-liter container, although a nonflammable (1.0 volume-percent) mixture would result if complete mixing occurred at room temperature. This is an important concept, since layering can occur with any combustible gas or vapor in both stationary and flowing mixtures. Roberts, Pursall, and Sellers (176-180) have presented an excellent series of review articles on the layering and dispersion of methane in coal mines.

The subject of flammable sprays, mists, and foams is well-documented (5, 18, 22, 27, 76, 205, 215, 245). Again, where such heterogeneous mixtures exist, flame propagation can occur at so-called average concentrations well below the lower limit of flammability (86); thus, the term "average" may be meaningless when used to define mixture composition in heterogeneous systems.

IGNITION

Lewis and von Elbe (130), Mullins (153,154), and Belles and Swett (156) have prepared excellent reviews of the processes associated with spark-ignition and spontaneous-ignition of a flammable mixture. In general, many flammable mixtures can be ignited by sparks having a relatively small energy content (1 to 100 mj) but a large power density (greater than 1 megawatt/cm³). However, when the source energy is diffuse, as in a sheet discharge, even the total energy requirements for ignition may be extremely large (79, 82, 85, 123, 181, 228). There is still much to be learned in this field, however, since electrical discharges are not normally as well defined in practice as they are in the laboratory.

When a flammable mixture is heated to an elevated temperature, a reaction is initiated that may proceed with sufficient rapidity to ignite the mixture. The time that elapses between the instant the mixture temperature is raised and that in which a flame appears is loosely called the time lag or time delay before ignition. In general, this time delay decreases as the temperature increases. According to Semenov (193), these quantities are related by the expression

$$\log \tau = \frac{0.22E}{T} + B, \quad (3)$$

where τ is the time delay before ignition in seconds; E is an apparent activation energy for the rate controlling reaction in calories per mole; T is the absolute temperature, expressed in degrees, Kelvin; and B is a constant. Two types of ignition temperature data are found in the current literature. In the first, the effect of temperature on time delay is considered for delays of less than 1 second (127, 153). Such data are applicable to systems in which the contact time between the heated surface and a flowing flammable mixture is very short; they are not satisfactory when the contact time is indefinite. Further, equation (3) is of little help, because it gives only the time delay for a range of temperatures at which autoignition occurs; if the temperature is reduced sufficiently, ignition does not occur. From the standpoint of safety, it is the lowest temperature at which ignition can occur that is of interest. This is called the minimum

spontaneous-ignition, or autoignition, temperature (AIT) and is determined in a uniformly heated apparatus that is sufficiently large to minimize wall quenching effects (194, 237). Figures 3 and 4 illustrate typical autoignition-temperature data. In figure 3 the minimum autoignition-temperature or AIT value for *n*-propyl nitrate is 170° C at an initial pressure of 1,000 psig (243). Data in this figure may be used to construct a $\log \tau$ versus $\frac{1}{T}$ plot such as that in figure 4. Such graphs illustrate the applicability of equation (3) to autoignition temperature data. The equation of the broken line in figure 4 is

$$\log \tau = \frac{12.3 \times 10^3}{T} - 25.1. \quad (4)$$

In this specific case, equation (4) is applicable only in the temperature range from 170° to 195°C; another equation must be used for data at higher temperatures. The solid lines in figure 4 define an 8°C band that includes the experimental points in the temperature range from 170° to 195°C.

FORMATION OF FLAMMABLE MIXTURES

In practice, heterogeneous mixtures are always formed when two gases or vapors are first brought together. Before discussing the formation of such mixtures in detail, a simplified mixer such as that shown in figure 5 will be considered briefly. This mixer consists of chambers 1 and 2 containing gases *A* and *B*, respectively; chamber 2, which contains a stirrer, is separated from chamber 1 and piston 3 by a partition with a small hole, *H*. At time t_o , a force *F* applied to piston 3 drives gas *A* into chamber 2 at a constant rate. If gas *A* is distributed instantaneously throughout chamber 2 as soon as it passes through *H*, a composition diagram such as that given in figure 6 results; the (uniform) piston motion starts at t_o , and stops at t_F . However, if a time interval Δt is required to distribute a small volume from chamber 1 throughout chamber 2, then at any instant between t_o and $t_F + \Delta t$, a variety of mixture compositions exists in chamber 2. This situation is represented schematically in figure 7. The interval of time during which heterogeneous gas mixtures would exist in the second case is determined in part by the rate at which gas *A* is added to chamber 2, by the size of the two chambers, and by the efficiency of the stirrer.

In practice, flammable mixtures may form either by accident or design. When they are formed by accident, it is usually desirable to reduce the combustible concentration quickly by adding enough air or inert gas to produce nonflammable mixtures. Under certain conditions, it may be possible to increase the combustible concentration so as to produce a nonflammable mixture. Such procedures are discussed in greater detail in the following section.

Flammable mixtures are encountered in production of many chemicals and in certain physical operations. These include gasfreeing a tank containing a combustible gas (232), drying plastic-wire coating, and recovering solvent from a solvent-air mixture. When layering can occur, as in drying operations, it is not enough to add air at such a rate that the overall mixture composition is below the lower limit of flammability (assuming that uniform mixtures result). Special precautions must be taken to assure the rapid formation of nonflammable mixtures (235). When a batch process is involved, an added precaution must be taken; a constituent at a partial pressure near its vapor pressure value may condense when it is momentarily compressed by addition of other gases or vapors. Accordingly, mixtures that are initially above the upper limit of flammability may become flammable. A similar effect, must be considered when mixtures are sampled with equipment that is cooler than the original sample; if vapor condenses in the sampling line, the

test sample will not yield accurate data. A flammable mixture sampled in this manner may appear to be nonflammable and thus create a hazardous situation (236).

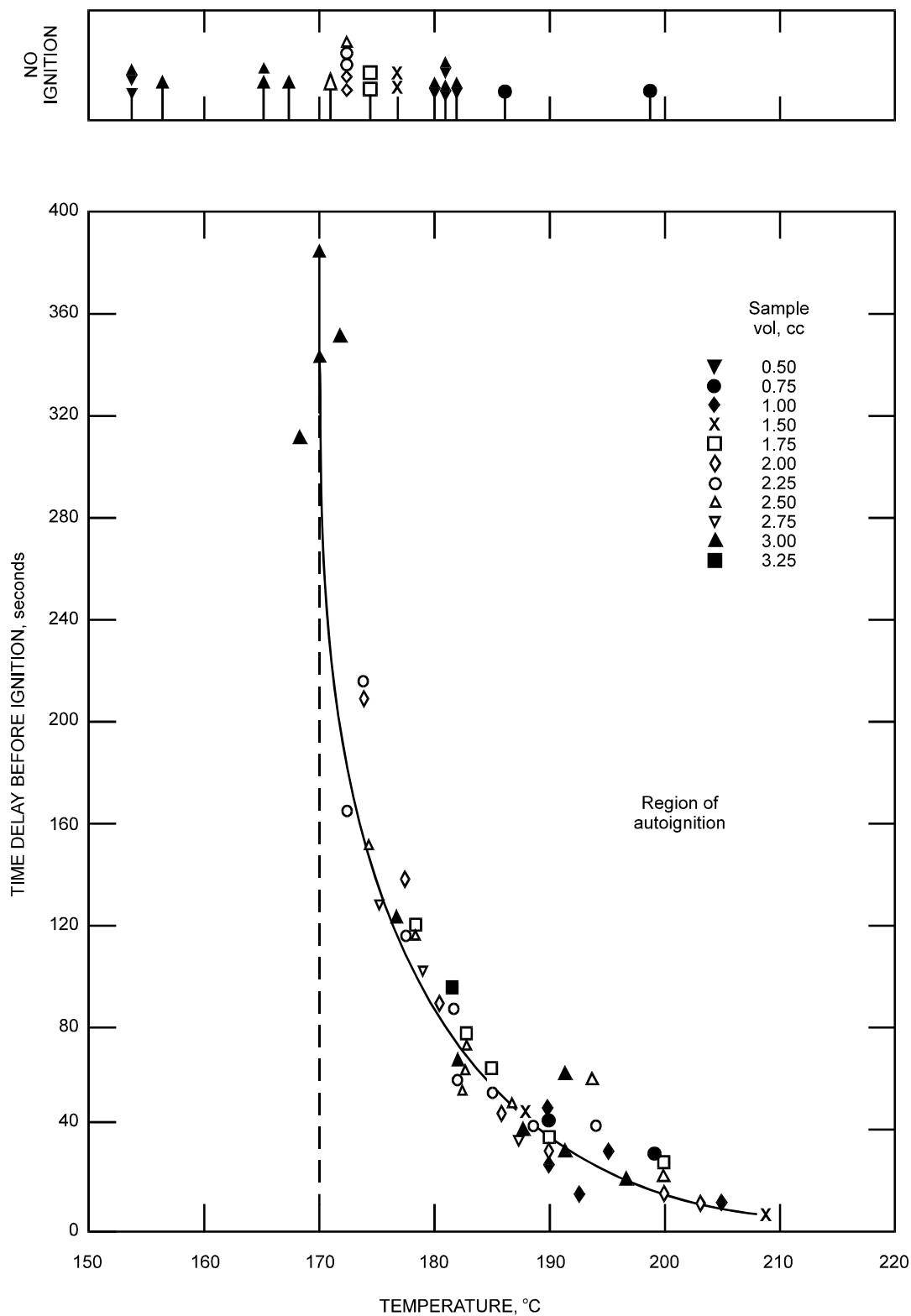


Figure 3—Time Delay Before Ignition of NPN in Air at 1,000 Psig in the Temperature Range From 150° to 210°C. (1-33 apparatus; type-347, stainless steel test chamber.)

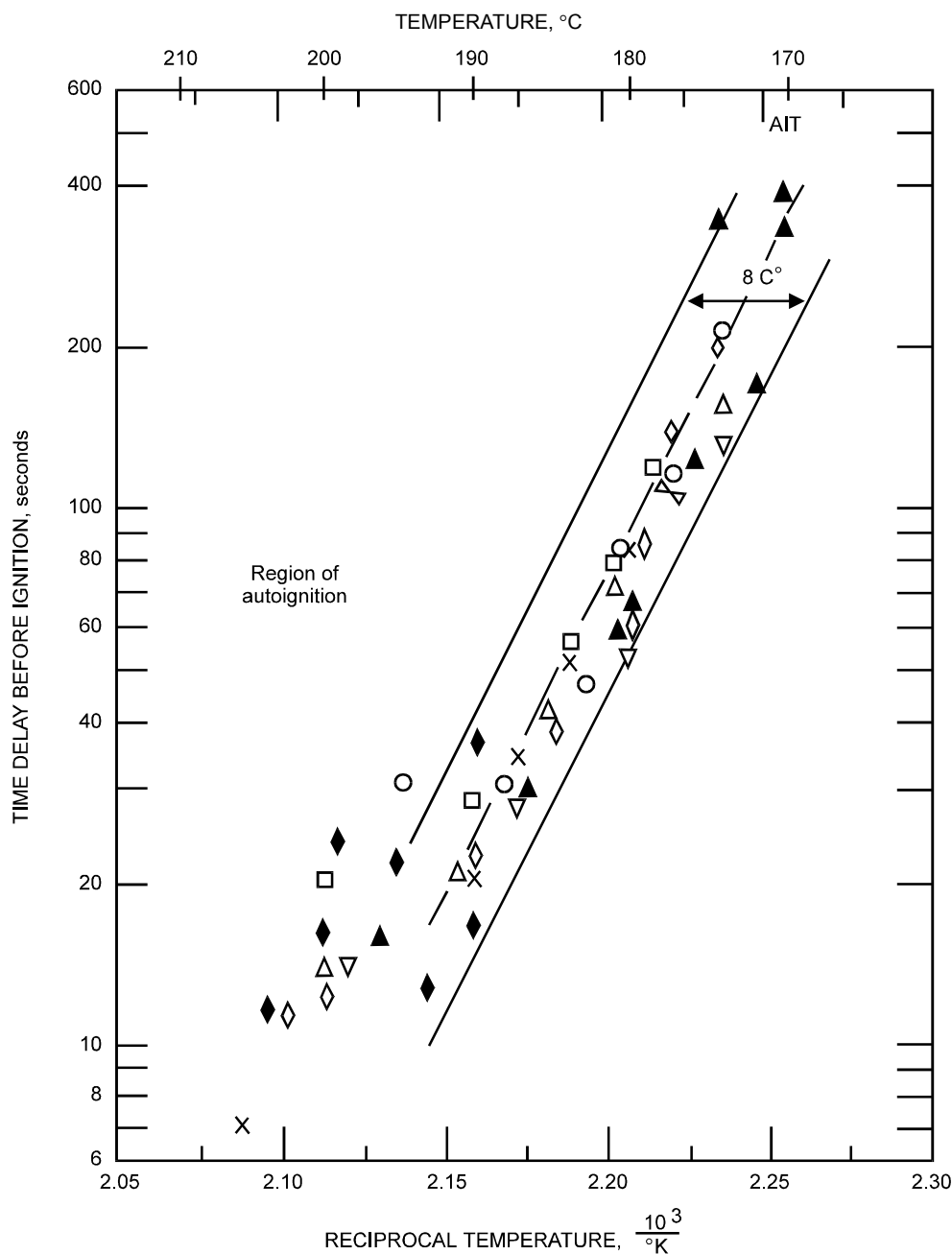


Figure 4—Logarithm of Time Delay Before Ignition of NPN in Air at 1,000 Psig Initial Pressure. (Data from figure 3.)

A flammable mixture can also form at temperatures below the flash point of the liquid combustible either if the latter is sprayed into the air, or if a mist or foam forms. With fine mists

and sprays (particle sizes below 10 microns), the combustible concentration at the lower limit is about the same as that in uniform vapor-air mixtures (17, 18, 22, 24, 76, 245). However, as the droplet diameter increases, the lower limit appears to decrease. In studying this problem, Burgoyne found that coarse droplets tend to fall towards the flame front in an upward propagating flame, and as a result the concentration at the flame front actually approaches the value found in lower limit mixtures of fine droplets and vapors (24). With sprays, the motion of the droplets also affects the limit composition, so that the resultant behavior is rather complex. The effect of mist and spray droplet size on the apparent lower limit is illustrated in figure 8. Kerosine vapor and mist data were obtained by Zabetakis and Rosen (245); tetralin mist data, by Burgoyne and Cohen (24); kerosine spray data, by Anson (5); and the methylene bistearamide data, by Browning, Tyler, and Krall (18).

Flammable mist-vapor-air mixtures may occur as the foam on a flammable liquid collapses. Thus, when ignited, many foams can propagate flame. Bartkowiak, Lambiris, and Zabetakis found that the pressure rise ΔP produced in an enclosure by the complete combustion of a layer of foam of thickness h_f is proportional to h_f and inversely proportional to h_a , the height of the air space above the liquid before foaming (7). That is

$$\Delta P \propto \frac{h_f}{h_a} \quad (5)$$

Pressures in excess of 30 psi were produced by the ignition of foams in small containers.

Thomas found that an additional hazard could arise from production of foams by oxygen-enriched air at reduced pressures (215). Air can become oxygen-enriched as the pressure is reduced, because oxygen is more soluble than nitrogen in most liquids (83). Thus the presence of foams on combustible liquids are a potential explosion hazard.

A flammable foam can also form on nonflammable liquid if the foam is generated by a flammable gas mixture instead of air. Burgoyne and Steel, who studied this problem, found that the flammability of methane-air mixtures in water-base foams was affected by both the wetness of the foam and the bubble size (28).

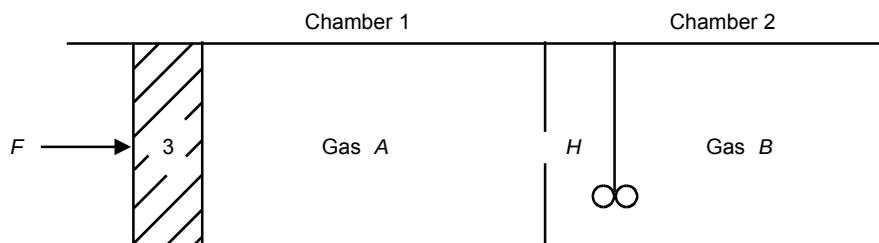


Figure 5—Simplified mixer

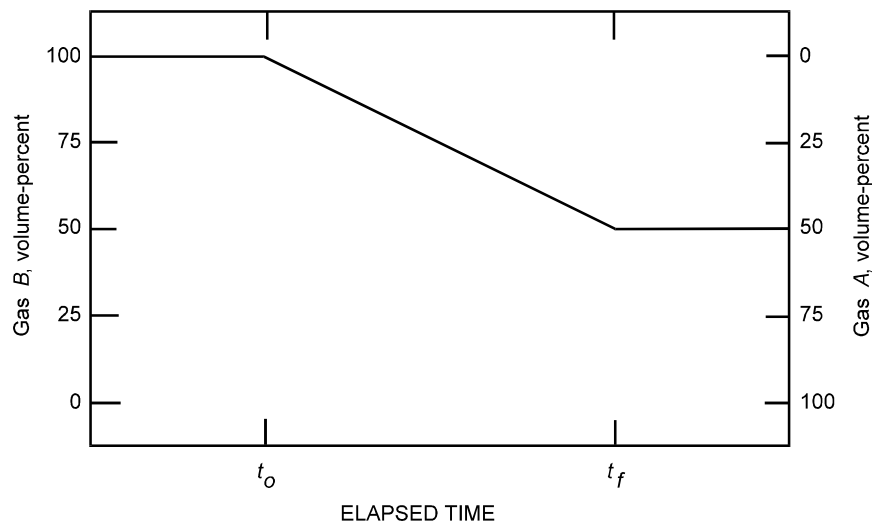


Figure 6—Composition of Gas in Chamber 2, Figure 5 (Instantaneous Mixing).

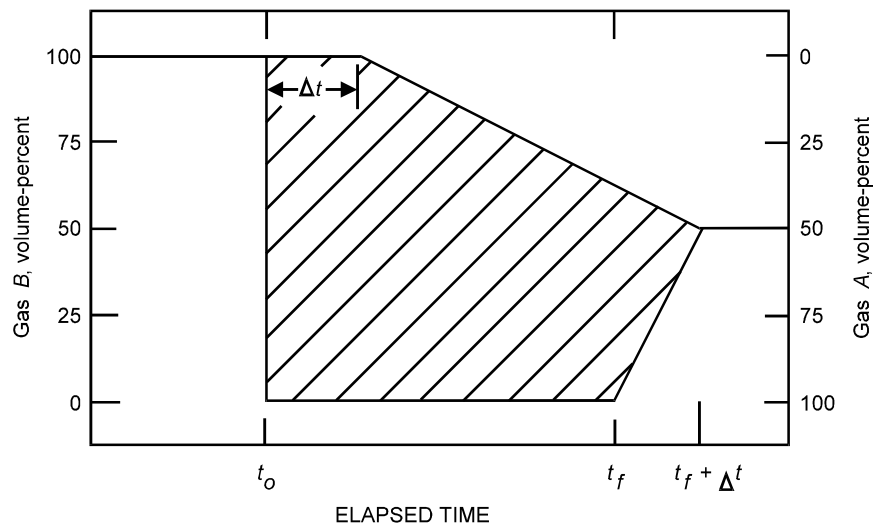


Figure 7—Composition of Gas in Chamber 2, Figure 5 (Delayed Mixing).

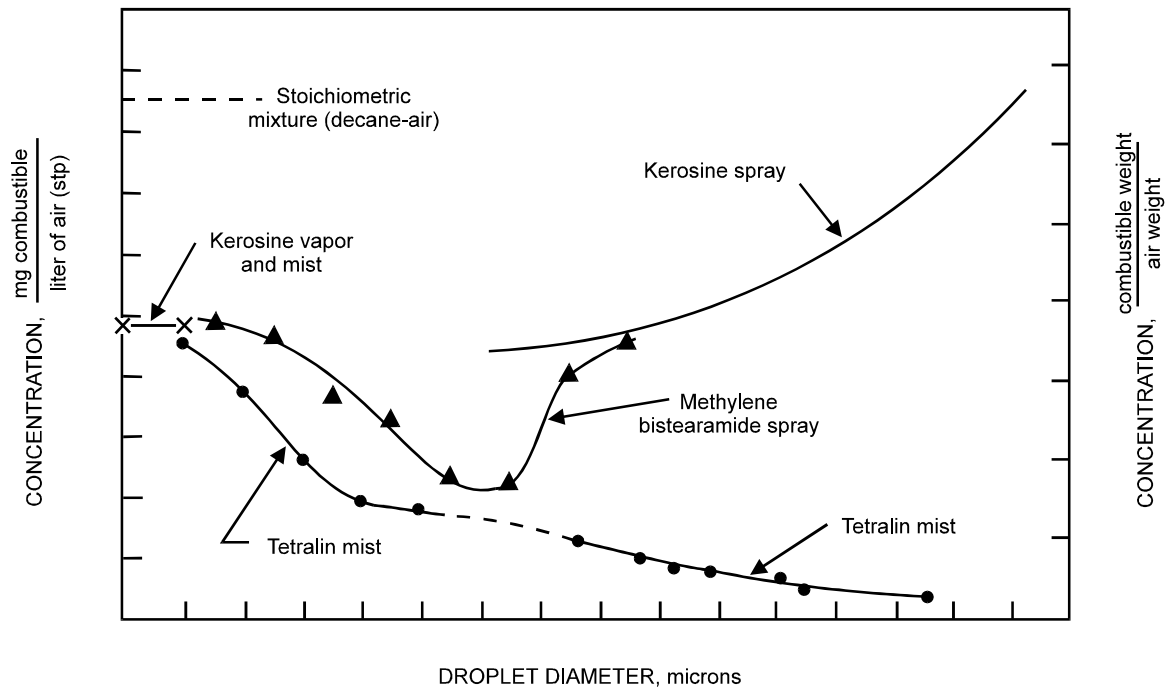


Figure 8—Variation in Lower Limits of Flammability of Various Combustibles in Air as a Function of Droplet Diameter.

Presentation of Data

Limit-of-flammability data that have been obtained at a specified temperature and pressure with a particular combustible-oxidant-inert system may be presented on either a triangular or a rectangular plot. For example, figure 9 shows a triangular flammability diagram for the system methane-oxygen-nitrogen. This method of presentation is frequently used because all mixture components are included in the diagram. However, as the sum of all mixture compositions at any point on the triangular plot is constant (100 pct) the diagram can be simplified by use of a rectangular plot (244). For example, the flammable area of figure 9 may be presented as illustrated in figure 10. As noted, the oxygen concentration at any point is obtained by subtracting the methane and nitrogen concentrations at the point of interest from 100 as follows:

$$\text{Pct O}_2 = 100 \text{ pct} - \text{pct CH}_4 - \text{pct N}_2. \quad (6)$$

With either type of presentation, addition of methane, oxygen, or nitrogen to a particular mixture results in formation of a series of mixtures that fall along the line between the composition point (for example, *M1* in figures 9 and 10) and the vertices of the bounding triangle. For example, addition of methane (+CH₄) to mixture *M1* yields initially all mixture compositions between *M1* and C (100 pct CH₄). After a homogeneous mixture is produced, a new mixture composition point, such as *M2*, is obtained. Similarly, if oxygen is added (+O₂) to the mixture represented by point *M1*, all compositions between *M1* and O (100 pct O₂) are obtained initially; if nitrogen is added, all compositions between *M1* and N (100 pct N₂) are obtained initially. If more than one gas is added to *M1*, for example, methane and oxygen, the resultant composition point may be obtained by considering that the mixing process occurs in two steps. First, the methane is added to *M1* and the gases are mixed thoroughly to give *M2*. Oxygen is then added to *M2* with mixing to give a new (flammable) mixture, *M3*. If the methane and oxygen were added to a fixed volume at constant pressure, some of *M1* and then of *M2* would escape and mix with the surrounding atmosphere. In many instances this is an important consideration because the resulting mixtures may be flammable. For example, even if an inert gas is added to a constant-volume tank filled with methane, flammable mixtures can form outside the tank as the displaced methane escapes into the atmosphere. If the methane is not dissipated quickly, a dangerous situation can arise.

When a mixture component is removed by condensation or absorption, the corresponding composition point (for example, *M1* in figures 9 and 10) shifts away from the vertices C, O, and N along the extensions to the lines *M1*—C, *M1*—O and *M1*—N, indicated in figures 9 and 10 by the minus signs. The final composition is determined by the percentage of each component removed from the initial mixture.

Mixtures with constant oxygen-to-nitrogen ratio (as in air), are obtained in figures 9 and 10 by joining the apex, C, with the appropriate mixture composition along the baseline, ON. Thus, the Air line, CA, (fig. 10) is formed by joining C with the mixture A (21 percent O₂ + 79 percent N₂). Using this latter point, A, one can readily determine the mixture compositions that are formed when mixture *M1* is displaced from an enclosure and mixed with air. Initially, all mixture compositions between *M1* and A would form. Since these would pass through the flammable mixture zone, a hazardous condition would be created. Similarly, if pure combustible CH₄ were dumped into the atmosphere (air), all mixtures between C and A would form. These would include the flammable mixtures along CA so that a hazardous condition would again be created, unless the combustible were dissipated quickly.

Mixtures with constant oxidant content are obtained by constructing straight lines parallel to zero oxidant line; such mixtures also have a constant combustible-plus-inert content. One particular

constant oxidant line is of special importance—the minimum constant oxidant line that is tangent to the flammability diagram or, in some cases, the one that passes through the extreme upper-limit-of-flammability value. This line gives the minimum oxidant (air, oxygen, chlorine, etc.) concentration needed to support combustion of a particular combustible at a specified temperature and pressure. In figures 9 and 10, the tangent line gives the minimum oxygen value (Min $O_{2,12}$ volume-percent) required for flame propagation through methane-oxygen-nitrogen mixtures at 26°C and 1 atmosphere.

Another important construction line is that which gives the maximum nonflammable combustible-to-inert ratio (critical C/N). Mixtures along and below this line form nonflammable mixtures upon addition of oxidant. The critical C/N ratio is the slope of the tangent line from the origin (Figs. 9 and 10), 100 percent oxidant, to the lean side of the flammable mixtures curve. The reciprocal of this slope gives the minimum ratio of inert-to-combustible at which nonflammable mixtures form upon addition of oxidant. It is of interest in fire extinguishing.

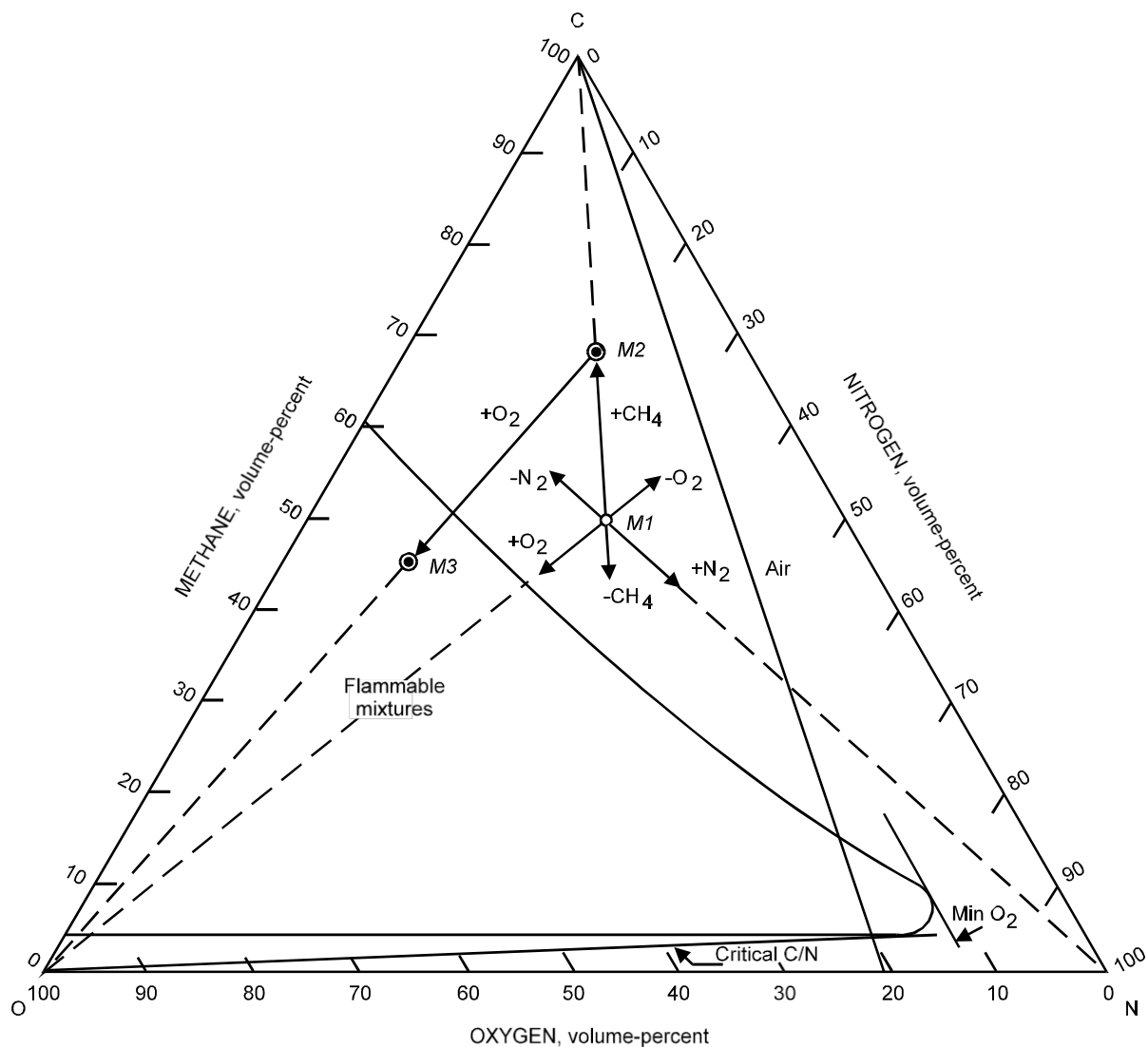


Figure 9—Flammability Diagram for the System Methane-Oxygen-Nitrogen at Atmospheric Pressure and 26°C.

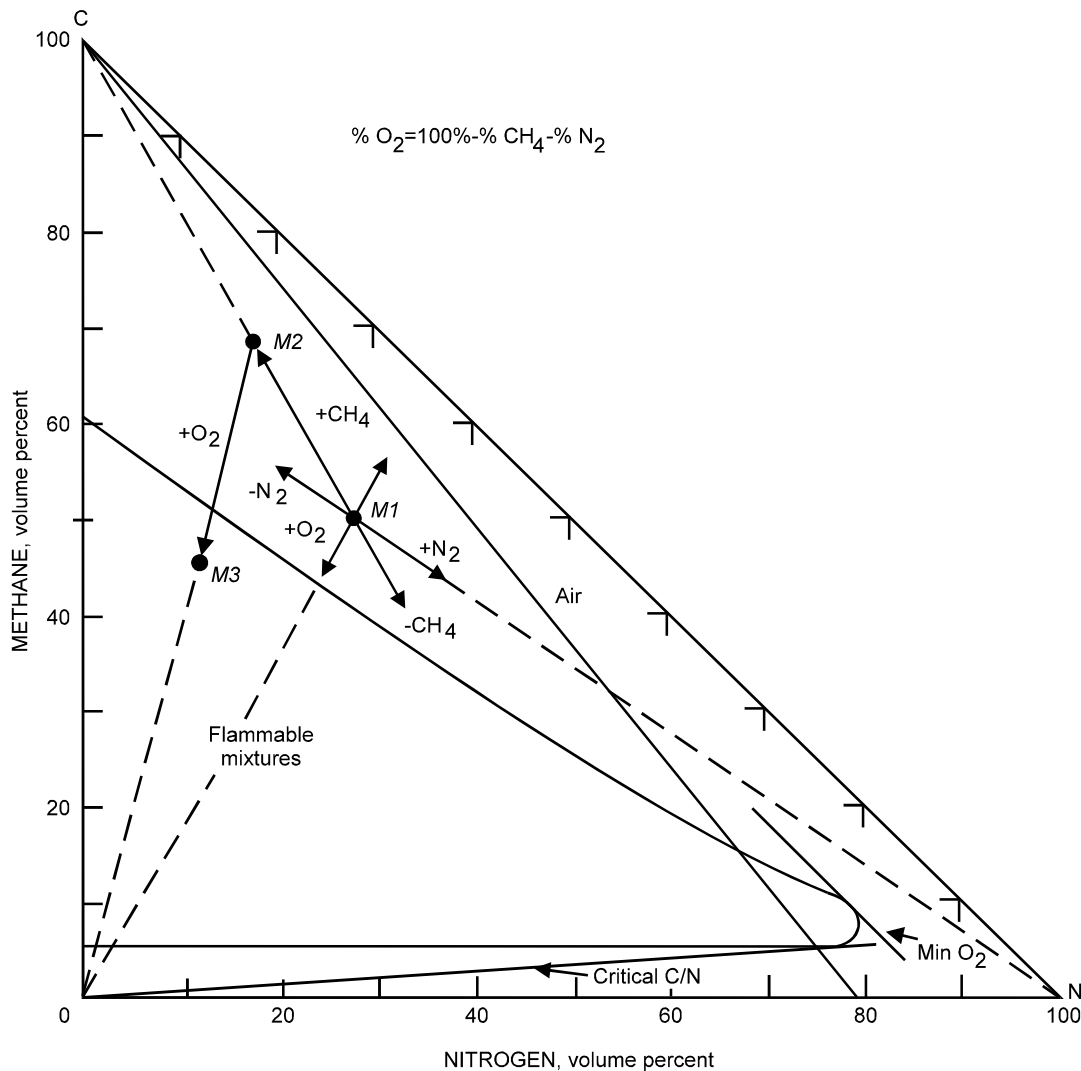


Figure 10—Flammability Diagram for the System Methane-Oxygen-Nitrogen at Atmospheric Pressure and 26°C. (Data from fig. 9).

An increase in temperature or pressure usually widens the flammable range of a particular combustible-oxidant system. The effect of temperature is shown in figure 11; two flammable areas, T_1 , and T_2 , are defined for a combustible-inert-oxidant system at constant pressure. The effect of temperature on the limits of flammability of a combustible in a specified oxidant was previously shown in figure 2. This type of graph is especially useful since it gives the vapor pressure of the combustible, the lower and upper temperature limits of flammability (T_L and T_U), the flammable region for a range of temperatures, and the autoignition temperature (AIT). Nearly 20 of these graphs were presented by Van Dolah and coworkers for a group of combustibles used in flight vehicles (218).

The lower temperature limit, T_L , is essentially the flash point of a combustible, in which upward propagation of flame is used; in general, it is somewhat lower than the flash point, in which downward propagation of flame is used. Since T_L is the intersection of the lower-limit and vapor-pressure curves, a relationship can be developed between T_L , or the flash point, and the constants defining the vapor pressure of a combustible liquid. An excellent summary of such relationships has been presented by Mullins for simple fuels and fuel blends (154).

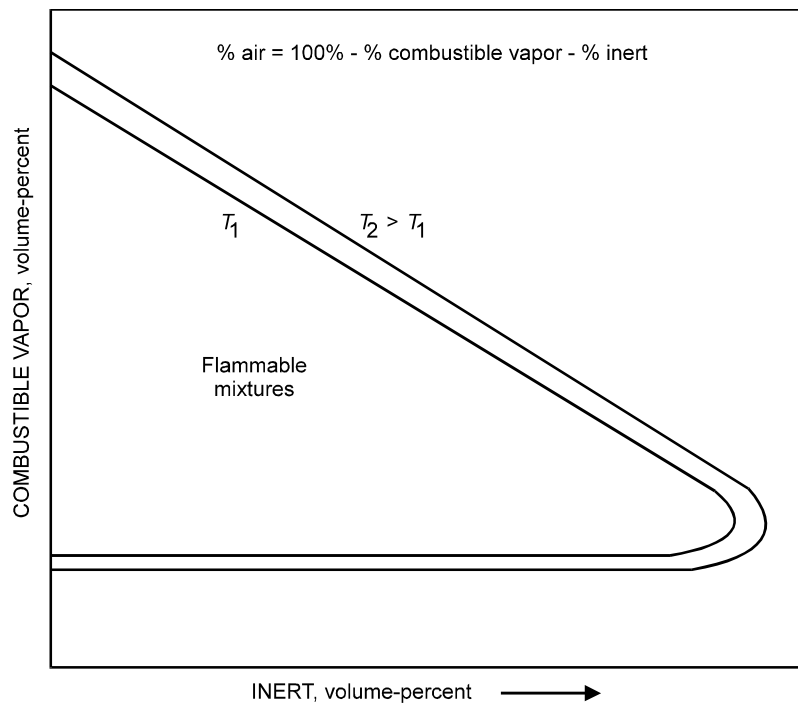


Figure 11—Effect of Initial Temperature on Limits of Flammability of a Combustible Vapor-Inert-Air System at Atmospheric Pressure.

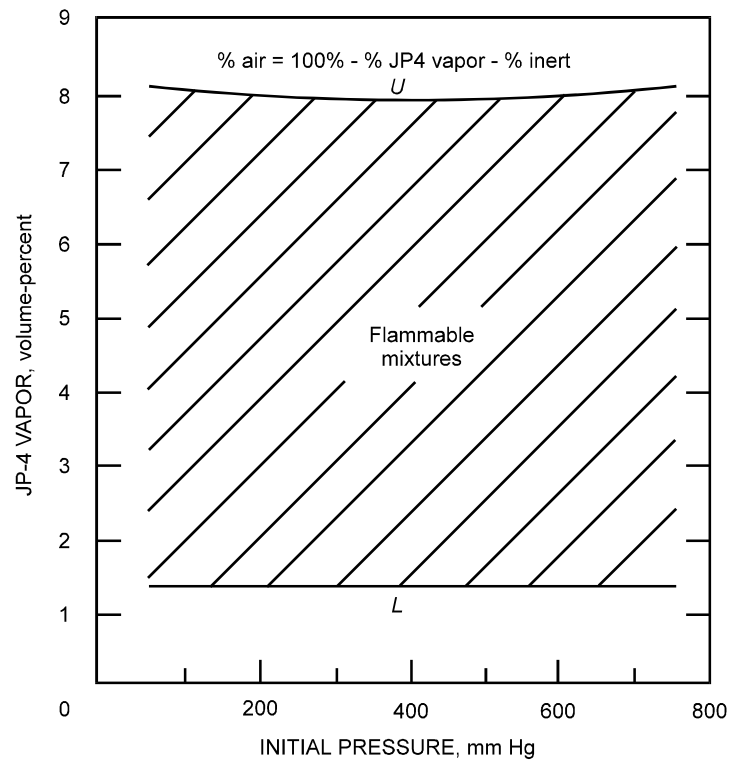


Figure 12—Effect of Initial Pressure on Limits of Flammability of JP-4 (Jet Fuel Vapor) in Air at 26°C.

At constant temperature, the flammable range of a combustible in a specified oxidant can be represented as in figure 12. Here the flammable range of JP-4 vapor-air mixtures is given as a function of pressure (241). A more generalized flammability diagram of a particular combustible-oxidant system can be presented in a three dimensional plot of temperature, pressure, and combustible content—as illustrated in figure 13 (244). Here, composition is given as the ratio of partial pressure of the combustible vapor, p_{VAPOR} , to the total pressure, P . For any value of P , the limits of flammability are given as a function of the temperature. For example, at 1 atmosphere ($P=1$), the flammable range is bounded by the lower limit curve $L_1L_2L_3L_4$, and the upper limit curve U_1U_2 ; all mixtures along the vapor pressure curve $L_4U_3''U_2$ are flammable. The flammable range is the same as that depicted in figure 2. At constant temperature (for example, T_1), the flammable range is bounded by the lower limit curve L_1P_{L1} and the upper limit curve U_1P_{U1} ; the broken curve $P_{L1}P_{U1}$ represents the low pressure, (quenched) limit.

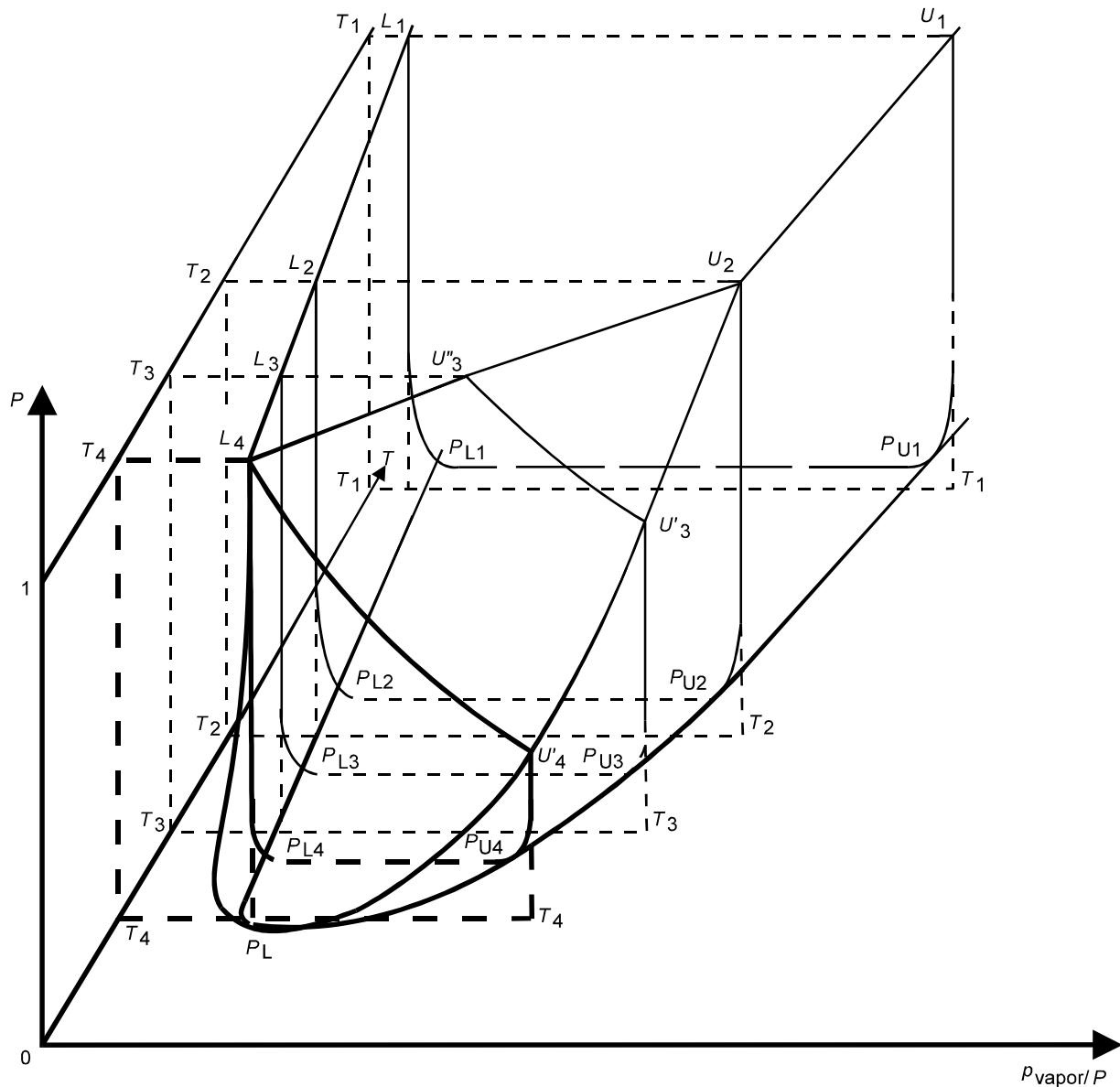


Figure 13—Effect of Temperature and Pressure on Limits of Flammability of a Combustible Vapor in a Specified Oxidant.

The flammable range is the same as that depicted in figure 12. A similar range is defined at temperatures T_2 , T_3 , and T_4 which are less than T_1 . However, at T_3 and T_4 the upper limit curves intersect the vapor pressure curves, so that no upper limits are found above U'_3 and U'_4 . In other words, all compositions $U'_3U''_3$ and U'_4L_4 are flammable. The curve $L_4P_LU'_4U'_3U_2$ defines the range of limit mixtures which are saturated with fuel vapor. Further, since L_4 is the saturated lower limit mixture at one atmosphere, T_4 is the flash point.

Some of the points considered in this and the previous section are illustrated in figure 14 (232). This is the flammability diagram for the system gasoline vapor-water vapor-air at 70°F (21°C) and

212° F (100°C) and atmospheric pressure. The air saturation temperature, that is, the temperature at which saturated air contains the quantity of water given on the water vapor axis, is also included. For precise work, a much larger graph or an enlargement of the region from 0 to 8 percent gasoline vapor and from 0 to 30 percent water vapor would be used. However, figure 14 is adequate here. If water vapor is added to a particular mixture A, all mixture compositions between A and pure water vapor will form as noted (if the temperature is at least 212°F), and the composition point will shift towards the 100-percent-water-vapor point. If water vapor is removed by condensation or absorption, the composition point will move along the extension to the line drawn from A to the 100-percent-water-vapor point. The same applies to the other components, air and gasoline, as indicated earlier. Moreover, if more than one component is involved, the final composition point can be found by considering the effect of each component separately.

Figure 14 is of special interest since it can be used to evaluate the hazards associated with a gas-freeing operation. For example, mixture A represents a saturated gasoline vapor-air-water vapor mixture at 70°F. A more volatile gasoline than the one used here would give a saturated mixture with more gasoline vapor and less air in a closed tank; a less volatile gasoline would give less gasoline vapor and more air. In any event, if a continuous supply of air saturated with water vapor is added to a tank containing mixture A, all compositions between A and B (air plus water vapor) will be formed until all the gasoline vapor is flushed from the tank, and mixture B alone remains. If steam is used to flush mixture A from the tank, all compositions between A and C will form until all the gasoline vapor has been flushed from the tank and only steam remains (at 212°F or higher). If the tank is permitted to cool, the steam will condense and air will be drawn into the tank giving mixtures along C–B. At 70°F, only air plus a small amount of water vapor will remain.

If hot water and water vapor at 175°F are used to flush mixture A from the tank, the mixture composition can only shift along AC to E. Mixtures between A and E that are flushed from the tank mix with air to give mixtures between points along AE and B. Again, as the water vapor in these mixtures condenses outside the tank, the composition of the resultant mixtures will shift away from the 100-percent-water-vapor point, C. The mixture in the tank will remain at E unless air is used to flush the tank, in which case mixture compositions between E and B will form. Again, if the water vapor within the tank condenses, the mixture composition will shift away from C. In any event, at this temperature (175°F), the addition of air to mixture E will lead to formation of flammable mixtures. Thus, mixture A cannot be flushed from a tank without forming flammable mixtures, unless steam or some other inert vapor or gas is used.

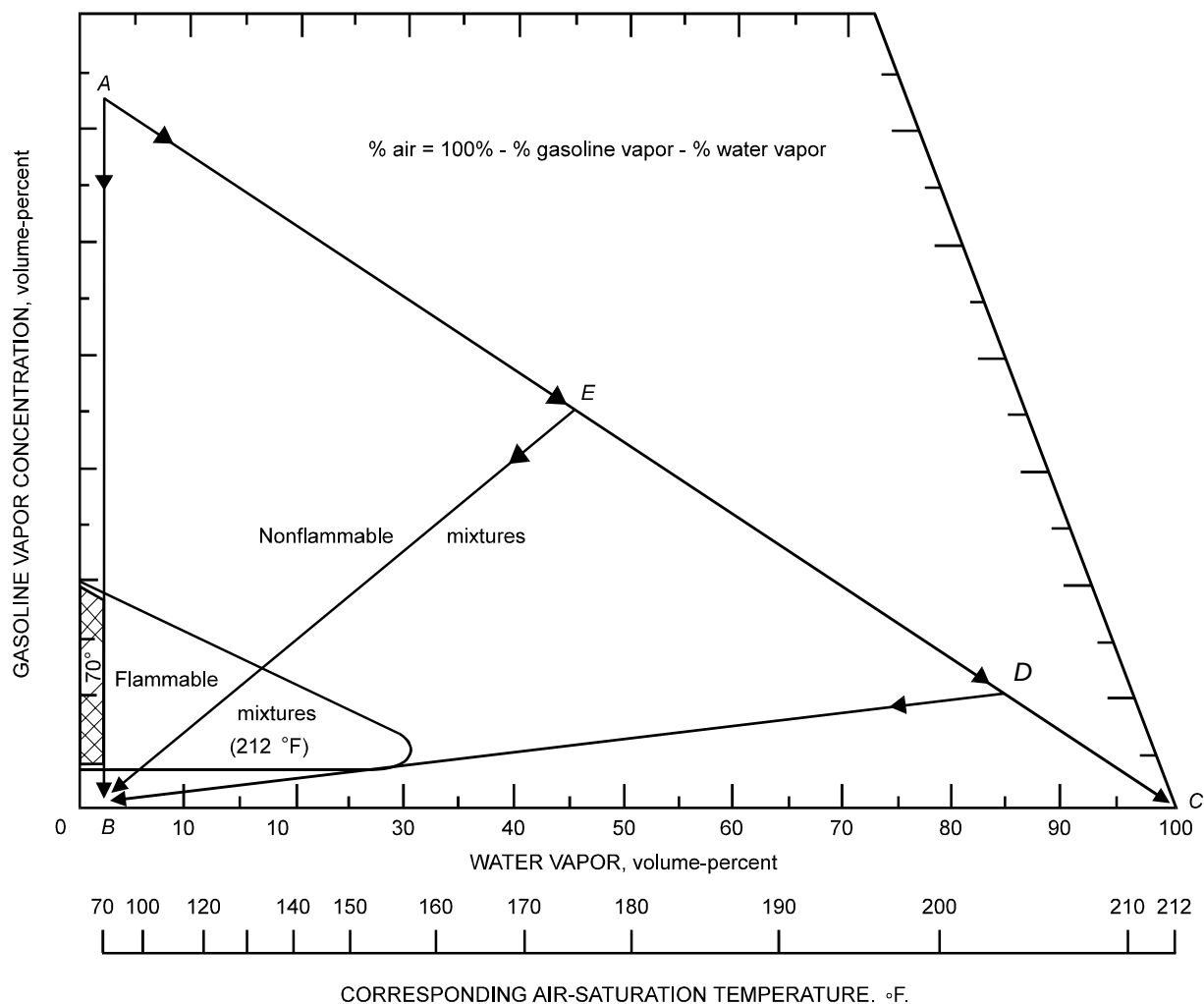


Figure 14—Flammability Diagram for the System Gasoline Vapor-Water Vapor-Air at 70°F (21°C) and at 212°F (100°C) and Atmospheric Pressure.

Deflagration and Detonation Processes

Once a flammable mixture is ignited, the resulting flame, if not extinguished, will either attach itself to the ignition source or propagate from it. If it propagates from the source, the propagation rate will be either subsonic (deflagration) or supersonic (detonation) relative to the unburned gas. If it is subsonic, the pressure will equalize at the speed of sound throughout the enclosure in which combustion is taking place so that the pressure drop across the flame (reaction) front will be relatively small. If the rate is supersonic, the rate of pressure equalization will be less than the propagation rate and there will be an appreciable pressure drop across the flame front. Moreover, with most combustible-air mixtures, at ordinary temperatures, the ratio of the peak-to-initial pressure within the enclosure will seldom exceed about 8:1 in the former, but may be more than 40:1 in the latter case. The pressure buildup is especially great when detonation follows a

large pressure rise due to deflagration. The distance required for a deflagration to transit to a detonation depends on the flammable mixture, temperature, pressure, the enclosure, and the ignition source. With a sufficiently powerful ignition source, detonation may occur immediately upon ignition, even in the open. However, the ignition energy required to initiate a detonation is usually many orders of magnitude greater than that required to initiate a deflagration (32, 249).

DEFLAGRATION

Where a deflagration occurs in a spherical enclosure of volume V with central ignition, the approximate pressure rise ΔP at any instant t after ignition is given by the expressions:

$$\Delta P = KP_1 \frac{S_u^3 t^3}{V} \leq P_m, \quad (7)$$

and

$$P_m = P_1 \frac{n_b T_b}{n_1 T_1} = P_1 \frac{\bar{M}_1 T_b}{\bar{M}_b T_1} \quad (8)$$

where K is a constant, S_u is the burning velocity, P_1 is the initial pressure P_m is the maximum pressure, T_1 is the initial temperature, n_1 is the number of moles of gas in the initial mixture, n_b is the number of moles of gas in the burned gases, $\bar{M}_1$ is the average molecular weight of the initial mixture, $\bar{M}_b$ is the average molecular weight of the burned gases, and T_b is the final (adiabatic) temperature of the products. With other enclosures, or with noncentral ignition, the flame front is disturbed by the walls before combustion is completed, so that calculated pressure cannot be expected to approximate actual pressure. Even with spherical enclosures, the flame front is not actually spherical, so that the walls tend to disturb the flame before combustion is complete (118, 130). A graph of the pressure developed by the combustion of a stoichiometric methane-air mixture (central ignition) in a 19.7 cm diameter, 9-liter cylinder is given in figure 15. The calculated pressure for a 9-liter sphere is included for comparison; K in equation (7) was evaluated from the experimental curve at 70 milliseconds. The calculated curve follows the experimental curve closely about 75 milliseconds, when the latter curve has a break. This suggests that the flame front was affected by the cylinder walls in such a way that the rate of pressure rise decreased, and the experimental curve fell below the calculated curve. Further, since the combustion gases were being cooled, the maximum pressure fell below the calculated value. The minimum elapsed time (in milliseconds) required to reach the maximum pressure appears to be about $75 \sqrt[3]{V}$ for the paraffin hydrocarbons and fuel blends such as gasoline; V is the volume in cubic feet in this case.

DETONATION

Wolfson and Dunn (52, 230) have expressed the pressure ratio P_2/P_1 across a detonation front as

$$\frac{P_2}{P_1} = \frac{1}{\gamma_2 + 1}(\gamma_1 M_1^2 + 1), \quad (9)$$

where γ_2 is the specific heat ratio of the burned gases, γ_1 is the specific heat ratio of the initial mixture, and M_1 is the Mach number of the detonation wave with respect to the initial mixture. M_1 is given in terms of the temperatures T and molecular weights W of the initial and final mixtures by the expression:

$$\frac{(\gamma_1 M_1^2 + 1)^2}{\gamma_1 M_1^2} = \frac{(\gamma_2 + 1)^2 T_2 W_1}{\gamma_2 T_1 W_2}. \quad (10)$$

Wolfson and Dunn have developed generalized charts that simplify the operations involved in obtaining the pressure ratio as well as the density and temperature/molecular weight ratios across the detonation wave and the energy release in the detonation wave.

Many investigators have measured and calculated detonation and reflected pressures resulting from detonation waves (54, 57, 204). Figure 16 from the data of Stoner and Bleakney (204) gives the detonation velocity, the static or detonation pressure, and the reflected pressure developed by a detonation wave propagating through hydrogen-oxygen mixtures at atmospheric pressure and 18°C.

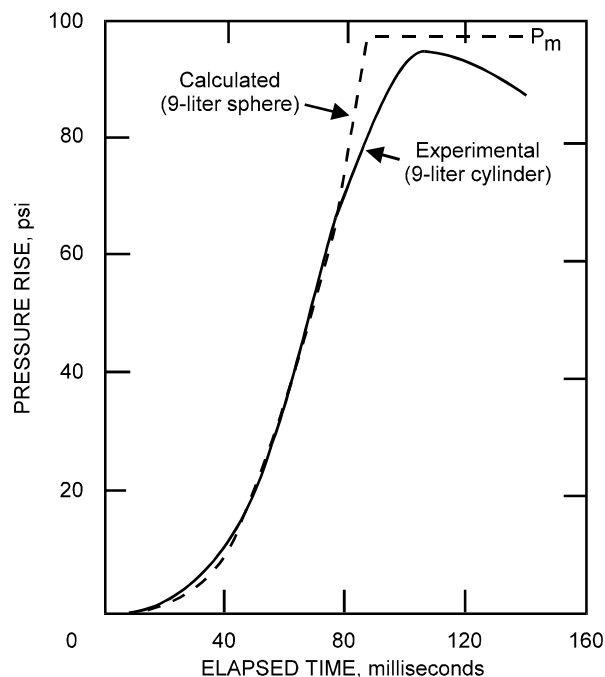


Figure 15—Pressure Produced by Ignition of a 9.6 Volume-Percent Methane-Air Mixture in a 9-Liter Cylinder (Experimental).

BLAST PRESSURE

The pressures produced by a deflagration or a detonation are often sufficient to demolish an enclosure (reactor, building, etc.). As noted, a deflagration can produce pressure rises in excess of 8:1, and pressure rises of 40:1 (reflected pressure) can accompany a detonation. As ordinary structures can be demolished by pressure differentials of 2 or 3 psi, it is not surprising that even reinforced concrete structures have been completely demolished by explosions of near-limit flammable mixtures.

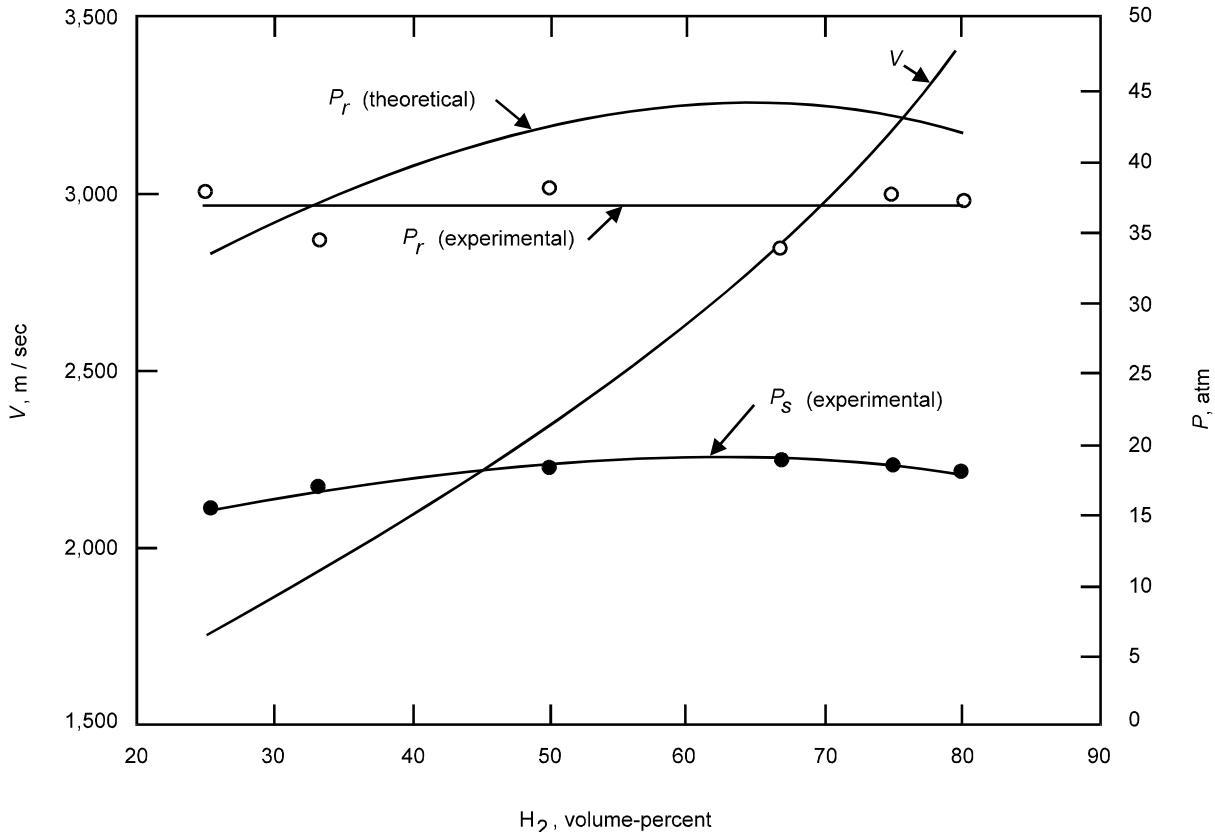


Figure 16—Detonation Velocity, V ; Static Pressure, P_s ; and Reflected Pressure, P_r , Developed by a Detonation Wave Propagating Through Hydrogen-Oxygen Mixtures in a Cylindrical Tube at Atmospheric Pressure and 18°C.

Jacobs and coworkers have studied the damage potential of detonation waves in great detail (91, 170). They have considered the principles involved in rupturing of pipes and vessels by detonations and the relevance of engineering and metallurgical data to explosions. More recently, Randall and Ginsburg (171) have investigated bursting of tubular specimens at ordinary and reduced temperatures. They found that the detonation pressure required to burst such specimens was, in general, slightly higher than the corresponding static-bursting pressure. Ductility of the test specimen appeared to have little effect on the bursting pressure, but ductility increased the strength of pipes containing notches or other stress raisers.

When a detonation causes an enclosure to fail, a shock wave may propagate outward at a rate determined by characteristics of the medium through which it is transmitted, and the available energy. If the shock velocity, V , is known, the resulting overpressure, $(P - P_o)$, is given by the expression (204)

$$P - P_o = P_o \left[\frac{2\gamma}{\gamma - 1} \right] \left[\frac{V}{a} - 1 \right], \quad (11)$$

where γ is the ratio of specific heats, and a is the velocity of sound in the medium through which the shock wave passes. The approximate damage potential can be assessed from the data in table 1 (217).

In conducting experiments in which blast pressures may be generated, special precautions must be taken to protect the personnel and equipment from blast and missiles. Browne, Hileman, and Weger (16) have reviewed the design criteria for suitable barricades. Other authors have considered the design of suitable laboratories and structures to prevent fragment damage to surrounding areas (44, 174, 203, 220).

Table 1 — Conditions of failure of peak over pressure-sensitive elements (217)

Structural element	Failure	Approximate incident blast overpressure (psi)
Glass windows, large and small.	Usually shattering, occasional frame failure.	0.5-1.0
Corrugated asbestos siding.	Shattering.	1.0-2.0
Corrugated steel or aluminum paneling.	Connection failure, followed by buckling.	1.0-2.0
Wood siding panels, standard house construction.	Usually failure occurs at main connections, allowing a whole panel to be blown in.	1.0-2.0
Concrete or cinderblock wall panels, 8 or 12 inches thick (not reinforced).	Shattering of the wall.	2.0-3.0
Brick wall panel, 8 or 12 inches thick (not reinforced).	Shearing and flexure failures.	7.0-8.0

Preventive Measures

INERTING

In principle, a gas explosion hazard can be eliminated by removing either all flammable mixtures or all ignition sources (23, 240). However, this is not always practical, as many industrial operations require the presence of flammable mixtures, and actual or potential ignition sources. Accordingly, special precautions must be taken to minimize the damage that would result if an accidental ignition were to occur. One such precaution involves the use of explosive actuators

which attempt to add inert material at such a rate that an explosive reaction is quenched before structural damage occurs (70, 72). Figure 17 shows how the pressure varies with and without such protection. In the latter case, the pressure rise is approximately a cubic function of time, as noted earlier. In the former case, inert is added when the pressure or the rate of pressure rise exceeds a predetermined value. This occurs at the time t_i in figure 17 when the explosive actuators function to add the inert. As noted, the pressure increases momentarily above the value found in the unprotected case and then falls rapidly as the combustion reaction is quenched by the inert.

FLAME ARRESTORS AND RELIEF DIAPHRAGMS

Inert atmospheres must be used when not even a small explosive reaction can be tolerated. However, when the ignition of a flammable mixture would create little hazard if the burning mixture were vented, flame arrestors and relief diaphragms could be used effectively. The design of such systems is determined by the size and strength of the confining vessels, ducts, etc.

In recent studies of the efficiency of wire gauze and perforated block arrestors (161, 162), Palmer found the velocity of approach of the flame to be the major factor in determining whether flame passed through an arrestor. For these two types of arrestors, he found the critical approach velocity to be

$$V' = \frac{1.75k(T_h - T_o)}{m^{0.9}Q/x_o}, \quad (12)$$

and

$$V = \frac{9.6kA't(T_h - T_o)}{d^2Q/x_o}, \quad (13)$$

where k is the thermal conductivity of the gas; m is the mesh width; T_h is the mean bulk temperature of the flame gases through the arrestor; T_o is the initial temperature of the arrestor; Q is the heat lost by unit area of flame; x_o is the thickness of the flame propagating at the burning velocity, S ; d is the diameter of an aperture; A' is the area of a hole in unit area of the arrestor face; and t is the arrestor thickness.

Equations (12) and (13) can be used to determine the mesh width or aperture diameter needed to stop a flame having a particular approach velocity. In practice, application of these equations assumes a knowledge of the flame speed in the system of interest. Some useful data have been made available by Palmer and Rasbash and Rogowski (172, 173), as well as by Jost (118) and Lewis and von Elbe (130).

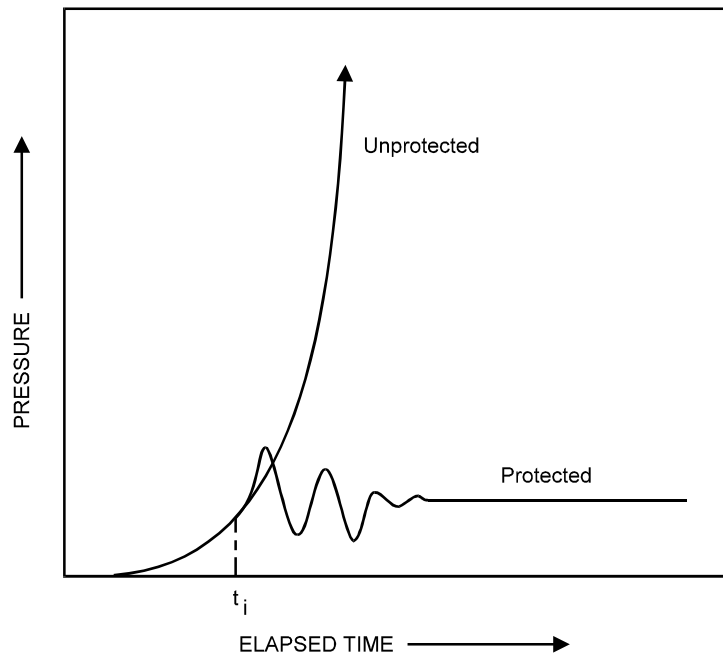


Figure 17—Pressure Variation Following Ignition of a Flammable Mixture in Unprotected and Protected Enclosures.

Tube bundles also may be used in place of wire screens. Scott found that these permit increased aperture diameters for a given approach velocity (192).

In practice, it may be desirable to install pressure relief vents to limit damage to duct systems where flame may propagate. Rasbash and Rogowski (173) found that with propane-and pentane-air mixtures, the maximum pressure P_M , (pounds per square inch) developed in an open-ended duct, having a cross section of 1 ft² is:

$$P_M = 0.07 \frac{L}{D}, \text{ and } 6 \leq \frac{L}{D} \leq 48, \quad (14)$$

where $\frac{L}{D}$ is the ratio of duct length to diameter. However, the presence of an obstacle (bend, constriction, etc.) in the path of escaping gases increased the pressure due to resistance to fluid flow by the obstacle. Location of a relief vent near the ignition source decreased the maximum pressure as well as the flame speed. For values of K (cross-section area of duct/area of vent) greater than 1, these authors found

$$0.8K \leq P_M \leq 1.8K, \quad (15)$$

where $2 \leq K \leq 32$, and $6 \leq \frac{L}{D} \leq 30$. To keep the pressure at a minimum either many small vents or a continuous slot was recommended rather than a few large vents. In addition, vents should be located at positions where ignition is likely to occur and should open before the flame has traveled more than 2 feet.

When possible, relief vents should be used with flame arrestors. The vents tend not only to reduce the pressure within a system following ignition but also to reduce the flame speed, thus making all arrestors more effective. Unfortunately, in certain large applications (for example, drying ovens), it is difficult to use flame arrestors effectively. In such cases, greater reliance must

be placed on the proper functioning of relief vents. Simmonds and Cubbage (42, 43, 195) have investigated the design of effective vents for industrial ovens. They found two peaks in the pressure records obtained during the venting of cubical ovens (fig. 18). The first peak, P_1 ; the oven volume, V ; the factor, K ; and the weight per unit area (lb/ft^2) of relief, w , were related as follows for a 25 percent town gas¹-air mixture:

$$P_1 V^{1/3} = 1.18Kw + 1.57. \quad (16)$$

More generally,

$$P_1 V^{1/3} = S_o (0.3Kw + 0.04), \quad (17)$$

where S_o is the burning velocity of the mixture at the oven temperature.

The first pressure pulse was ascribed to the release and motion of the relief vent following ignition; the second pulse, to continued burning at an increased rate. The second pulse represents the pressure drop across the vent, and it is thus proportional to K . For small values of K it was found that

$$P_2 = K. \quad (18)$$

As with ducts, larger pressures were obtained when obstructions were placed in the oven.

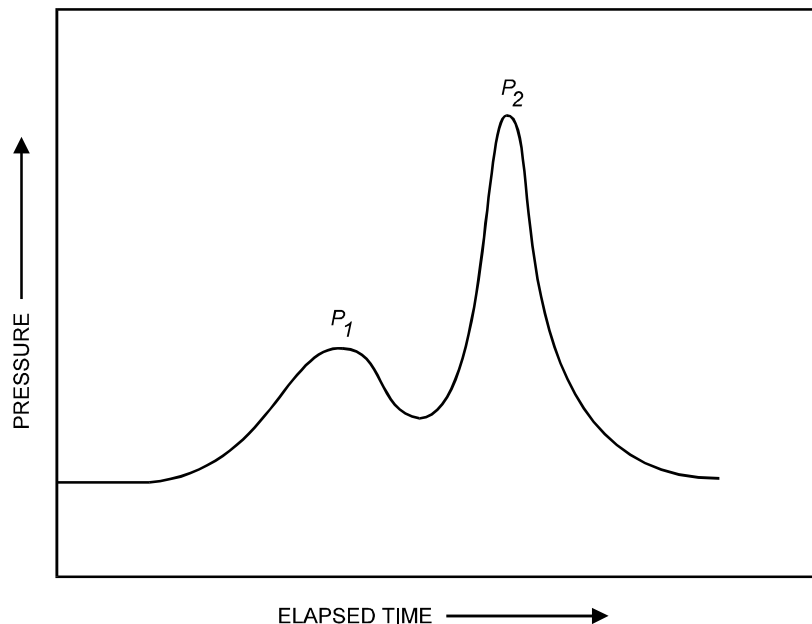


Figure 18—Pressure Produced by Ignition of a Flammable Mixture in a Vented Oven.

¹Town gas contained approximately 52% hydrogen, 17% carbon monoxide, 15% methane; the balance was other hydrocarbons, 3%; nitrogen 9%; carbon dioxide, 3%; and oxygen.

In designing explosion reliefs for ovens, Simmonds and Cabbage pointed out that (1) the reliefs should be constructed in such a way that they do not form dangerous missiles if an explosion occurs; (2) the weight of the relief must be small so that it opens before the pressure builds up to a dangerous level; (3) the areas and positions of relief openings must be such that the explosion pressure is not excessive; (4) sufficient free space must be utilized around the oven to permit satisfactory operation of the relief and minimize risk of burns to personnel; and (5) oven doors should be fastened securely so that they do not open in the event of an explosion.

Burgoyne and Wilson have presented the results of an experimental study of pentane vapor-air explosions in vessels of 60- and 200-cubic-foot volume (30). They found the rates of pressure rise greater than could be predicted from laminar burning velocity data, so that the effect of a relief area in lowering the peak pressure was less than expected. All experiments were conducted at an initial pressure of 1 atmosphere. Vent data for use at higher initial pressures are summarized in an article by Block (10); a code for designing pressure relief systems has been proposed in this article. Other authors have considered the effects of temperature and characteristics of the flammable mixture on vent requirements (14, 35, 38, 45, 46, 134, 145, 168, 221).

Flammability Characteristics

The flammability data (limits of flammability, flash point, ignition temperature and burning velocity) of the various chemical families exhibit many similarities. Accordingly, the data presented here are grouped under the various commercially important families, blends, and miscellaneous combustibles.

PARAFFIN HYDROCARBONS (C_nH_{2n+2})

Limits in Air

Lower and upper limits of flammability at 25°C (or at the temperature noted) and 1 atmosphere (L_{25} and U_{25}) for many members of the paraffin hydrocarbon series are given in table 2, together with the molecular weight, M , vapor specific gravity, sp gr, stoichiometric composition in air, C_{st} (appendix B) and heat of combustion, ΔH_c (183). At room temperature and atmospheric or reduced pressure, the lower limits of flammability of most of this series fall in the range from 45 to 50 mg combustible vapor per liter of air at standard conditions, that is, 0°C and 760 mm Hg (0.045 to 0.050 oz combustible vapor per cubic foot of air) (247). This is illustrated in figure 19 in which some lower limits of flammability are plotted against molecular weight; except for methane, ethane, and propane all limit values fall in a band between concentrations of approximately 45 and 50 mg/lr.

The following expression may be used to convert from a lower limit L in volume-percent of vapor in the vapor-air mixture to one in milligrams of combustible, per liter of air at standard conditions:

$$L\left(\frac{\text{mg}}{1}\right) = \frac{L \text{ (vol pct)}}{[100 - L \text{ (vol pct)}] \left[\text{sp vol} \frac{1}{\text{mg}}\right]}, \quad (19)$$

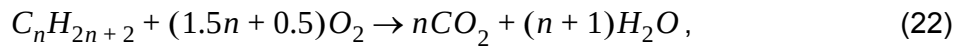
specific volume being volume of combustible vapor per milligram of combustible. At standard conditions (0°C and 760 mm Hg) this is about 22.414/1,000*M*, where *M* is the molecular weight of the combustible. Since *L* (vol pct) of most members of this series is much less than 100 percent, the lower limit can be expressed as

$$L\left(\frac{\text{mg}}{1}\right) \approx 0.45ML \text{ (vol pct)} . \quad (20)$$

At any specified temperature, the ratio of the lower limit to the amount of combustible needed for complete combustion, C_{st} , also is approximately constant. This was first noted by Jones (95) and later by Lloyd (133), who found that for paraffin hydrocarbons at about 25°C,

$$L_{25^\circ} \approx 0.55C_{st} . \quad (21)$$

For the complete combustion of the paraffin hydrocarbons, we have:



so that in air

$$C_{st} = \frac{100}{1 + 4.773(1.5n + 0.5)} \text{ vol pct} , \quad (23)$$

where 4.773 is the reciprocal of 0.2095, the molar concentration of oxygen in dry air. The values of C_{st} (appendix B) are included in table 2. By weight these become

$$C_{st} = \frac{1000[12.01n + 1.008(2n + 2)]\text{mg}}{22.414 \times 4.773(1.5n + 0.5)} \frac{1}{1} , \quad (24)$$

or

$$C_{st} = 9.34 \left[\frac{14.03n + 2.02}{1.5n + 0.5} \right] \frac{\text{mg}}{1} . \quad (25)$$

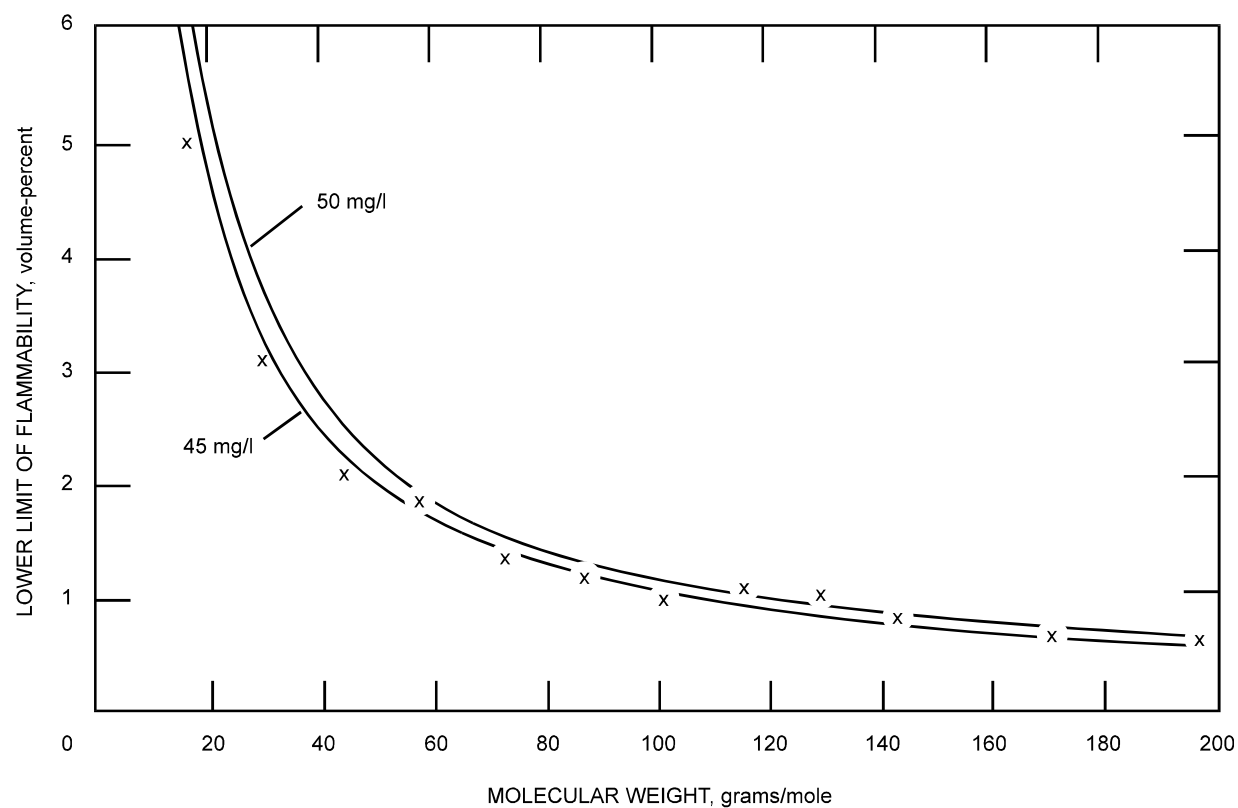


Figure 19—Effect of Molecular Weight on Lower Limits of Flammability of Paraffin Hydrocarbons at 25°C.

Table 2 — Properties of paraffin hydrocarbons

Combustible	Formula	<i>M</i>	Sp gr (Air=1)	<i>C_{st}</i> in air (vol pct)	Net ΔH_c ($\frac{\text{Kcal}}{\text{mole}}$)	Lower limit in air				Upper limit in air			
						<i>L₂₅</i> (vol pct)	$\frac{L_{25}}{C_{st}}$	$L(\frac{\text{mg}}{\text{l}})$	Ref.	<i>U₂₅</i> (vol pct)	$\frac{U_{25}}{C_{st}}$	$U(\frac{\text{mg}}{\text{l}})$	Ref.
Methane	CH ₄	16.04	0.55	9.48	191.8	5.0	0.53	38	(40)	15.0	1.6	126	(40)
Ethane	C ₂ H ₆	30.07	1.04	5.65	341.3	3.0	.53	41	(40)	12.4	2.2	190	(41)
Propane	C ₃ H ₈	44.09	1.52	4.02	488.5	2.1	.52	42	(115)	9.5	2.4	210	(41)
<i>n</i> -Butane	C ₄ H ₁₀	58.12	2.01	3.12	635.4	1.8	.58	48	(113)	8.4	2.7	240	(41)
<i>n</i> -Pentane	C ₅ H ₁₂	72.15	2.49	2.55	782.0	1.4	.55	46	(40)	7.8	3.1	270	(40)
<i>n</i> -Hexane	C ₆ H ₁₄	86.17	2.98	2.16	928.9	1.2	.56	47	(246)	7.4	3.4	310	(40)
<i>n</i> -Heptane	C ₇ H ₁₆	100.20	3.46	1.87	1075.8	1.05	.56	47	(246)	6.7	3.6	320	(40)
<i>n</i> -Octane	C ₈ H ₁₈	114.23	3.94	1.65	1222.8	.95	.58	49	(246)	—	—	—	—
<i>n</i> -Nonane	C ₉ H ₂₀	128.25	4.43	1.47	1369.7	¹ .85	.58	49	(246)	—	—	—	—
<i>n</i> -Decane	C ₁₀ H ₂₂	142.28	4.91	1.33	1516.6	² .75	.56	48	(246)	³ 5.6	4.2	380	—
<i>n</i> -Undecane	C ₁₁ H ₂₄	156.30	5.40	1.22	1663.6	.68	.56	48	(⁴)	—	—	—	—
<i>n</i> -Dodecane	C ₁₂ H ₂₆	170.33	5.88	1.12	1810.5	.60	.54	46	(⁴)	—	—	—	—
<i>n</i> -Tridecane	C ₁₃ H ₂₈	184.36	6.37	1.04	1957.4	.55	.53	46	(⁴)	—	—	—	—
<i>n</i> -Tetradecane	C ₁₄ H ₃₀	198.38	6.85	.97	2104.3	.50	.52	44	(⁴)	—	—	—	—
<i>n</i> -Pentadecane	C ₁₅ H ₃₂	212.41	7.33	.90	2251.2	.46	.51	46	(⁴)	—	—	—	—
<i>n</i> -Hexadecane	C ₁₆ H ₃₄	226.44	7.82	.82	2398.2	.43	.51	44	(⁴)	—	—	—	—

¹*t*=43° C.²*t*=53° C.³*t*=86° C.⁴Calculated value extrapolated to 25°C at Explosives Res. Center, Federal Bureau of Mines.

Thus,

$$C_{st} \approx 87 \text{ mg/l, } n \geq 4. \quad (26)$$

Combining this equation with equation (21), we have

$$L_{25^\circ} \left(\frac{\text{mg}}{1} \right) \approx 48 \left(\frac{\text{mg}}{1} \right), \quad (27)$$

for paraffin hydrocarbons, except methane, ethane, and propane. Substitution of this value into equation (20) gives

$$L_{25^\circ}(\text{vol pct}) \approx \frac{107}{M}. \quad (28)$$

The following expression may be used to convert a lower limit value in volume-percent to a fuel-air (weight) ratio:

$$L(F/A) = \frac{M}{28.96} \left[\frac{L(\text{vol pct})}{100 - L(\text{vol pct})} \right]. \quad (29)$$

The reciprocal expression gives the air-fuel (weight) ratio:

$$L(A/F) = \frac{28.96}{M} \left[\frac{100}{L(\text{vol pct})} - 1 \right]. \quad (30)$$

As noted, the lower limits given in figure 19 were determined at room temperature and atmospheric or reduced pressure. Lower limits vary with temperature as shown for methane in figure 20. The limit values obtained with upward propagation of flame (21) fall fairly close to a straight line that passes through the lower limit value at 25°C and the flame temperature (1,225°C). This is in accordance with the White criterion that the flame temperature is constant at the lower limit (222). The data obtained by White with downward propagation of flame fall along a line parallel to the line through the limit values obtained with upward propagation. Taking the value 1,300°C as the approximate flame temperature for the paraffin hydrocarbon series (55), and using the lower limit values at room temperature in table 2, the limits of the first 10 paraffin hydrocarbons are represented as in figures 21 and 22. Figure 21 gives the lower limits in volume-percent and figure 22 in milligrams per liter. By weight, the lower limits of most members of this series again fall in a fairly narrow band ("higher hydrocarbons" region). Individual adiabatic flame temperatures can be determined for lower limit mixtures using the data in table 2 and appendix C (55).

The straight lines of figures 21 and 22 are given by:

$$L_t = L_{25^\circ} - \frac{L_{25^\circ}}{1300^\circ - 25^\circ} (t - 25^\circ), \quad (31)$$

or

$$\frac{L_t}{L_{25^\circ}} = 1 - 0.000784(t - 25^\circ). \quad (32)$$

They are described in more general terms by a plot of L_t/L_{25° against the temperature (fig. 23, solid line).

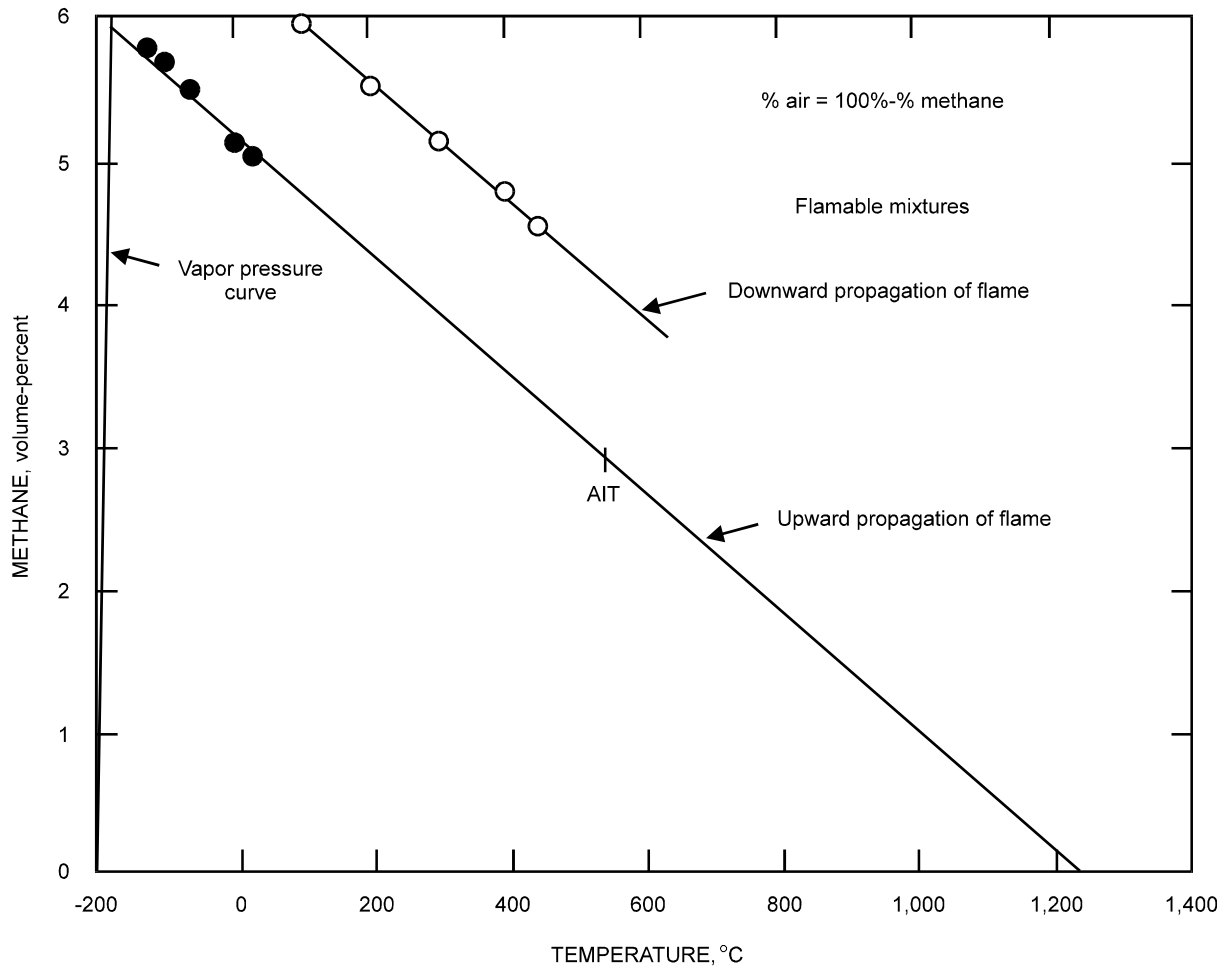


Figure 20—Effect of Temperature on Lower Limit of Flammability of Methane in Air at Atmospheric Pressure.

These data are also correlated fairly well with the modified Burgess-Wheeler Law suggested by Zabetakis, Lambiris, and Scott (242):

$$L_t = L_{25^\circ} - \frac{0.75}{\Delta H_c} (t - 25^\circ), \quad (33)$$

where t is the temperature in $^\circ\text{C}$ and ΔH_c is the net heat of combustion in kilocalories per mole. Then,

$$\frac{L_t}{L_{25^\circ}} = 1 - \frac{0.75}{L_{25^\circ} \cdot \Delta H_c} (t - 25^\circ). \quad (34)$$

Substituting the value 1,040 for $L_{25^\circ} \cdot \Delta H_c$ obtained by Spakowski (201), we have

$$\frac{L_t}{L_{25^\circ}} = 1 - 0.000721(t - 25^\circ), \quad (35)$$

which is also given in figure 23 for a limited temperature range with the broken line.

Only the lower limit at 25°C and atmospheric pressure is needed to use figure 23. For example, assuming a constant flame temperature, the ratio L_t/L_{25° at 600°C is 0.55. The calculated lower limit of methane at 600°C therefore is 5.0 x 0.55, or 2.75 volume-percent. The same value can be obtained directly from figure 21. From the modified Burgess-Wheeler Law curve, $L_t/L_{25^\circ}=0.585$ at 600°C, so that $L_{600^\circ}=2.92$ volume-percent.

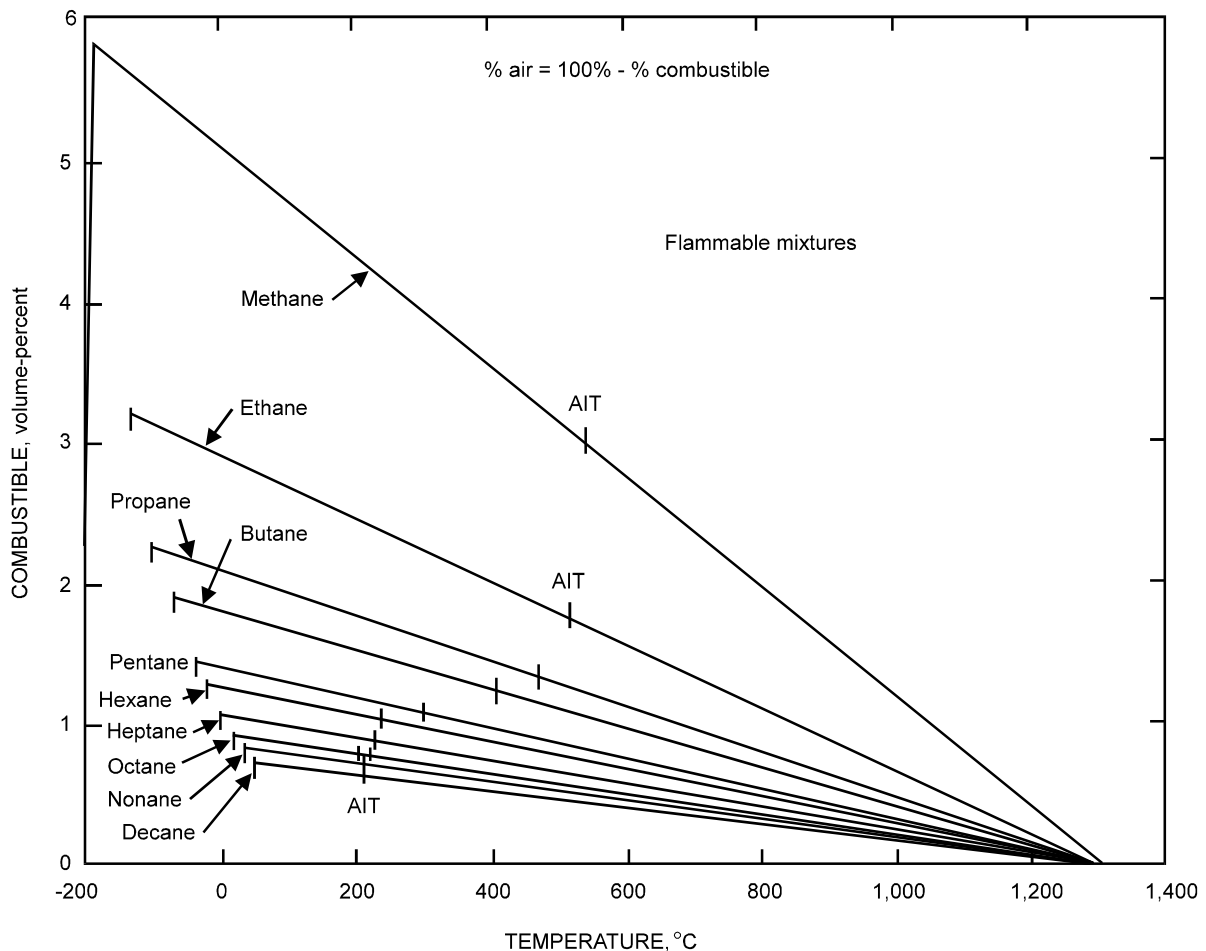


Figure 21—Effect of Temperature on Lower Limits of Flammability of 10 Paraffin Hydrocarbons in Air at Atmospheric Pressure.

Limit-of-flammability measurements are complicated by surface and vapor-phase reactions that occur at temperatures above the autoignition temperature. For example, Burgoyne and Hirsch (25) have shown that methane-air mixtures containing up to 5 percent methane burn readily at

1,000° C. Experiments were conducted with mixtures containing as little as 0.5 percent methane; figure 20 predicts that a flame would not propagate through such a mixture.

Flammability experiments at elevated temperatures indicate that in the absence of cool flames (87, 88), the upper limit also increases linearly with temperature. The effect of temperature appears to be fairly well correlated by the modified Burgess-Wheeler law:

$$U_t = U_{25^\circ} + \frac{0.75}{\Delta H_c}(t - 25^\circ) . \quad (36)$$

If we assume that the heat release at the upper limit is equal to that at the lower limit, then

$$\frac{U_t}{U_{25^\circ}} = 1 + 0.000721(t - 25^\circ) . \quad (37)$$

A plot of U_t/U_{25° against temperature (fig.24) was used to compare recent experimental values of Rolingson and coworkers (182) for methane-air mixtures at 15 psig with those predicted by the modified Burgess-Wheeler law. The experimental and calculated upper limits are given in table 3 together with the difference, $U_{\text{calc}} - U_{\text{exper}}$. In each case, the difference is less than 4 percent of the experimental value, which is approximately within the limit of experimental error. Earlier experiments of White (222) at temperatures to 400° C, with downward flame propagation, also are represented quite adequately by equation (37). For example, White found that the upper limit of pentane in air (downward propagation) increased linearly from 4.50 volume-percent at about 17° C to 5.35 volume-percent at 300° C. The ratio of 5.35: 4.50 is 1.17, which compares quite well with $U_{300^\circ}/U_{25^\circ} \approx 1.20$ obtained from figure 24.

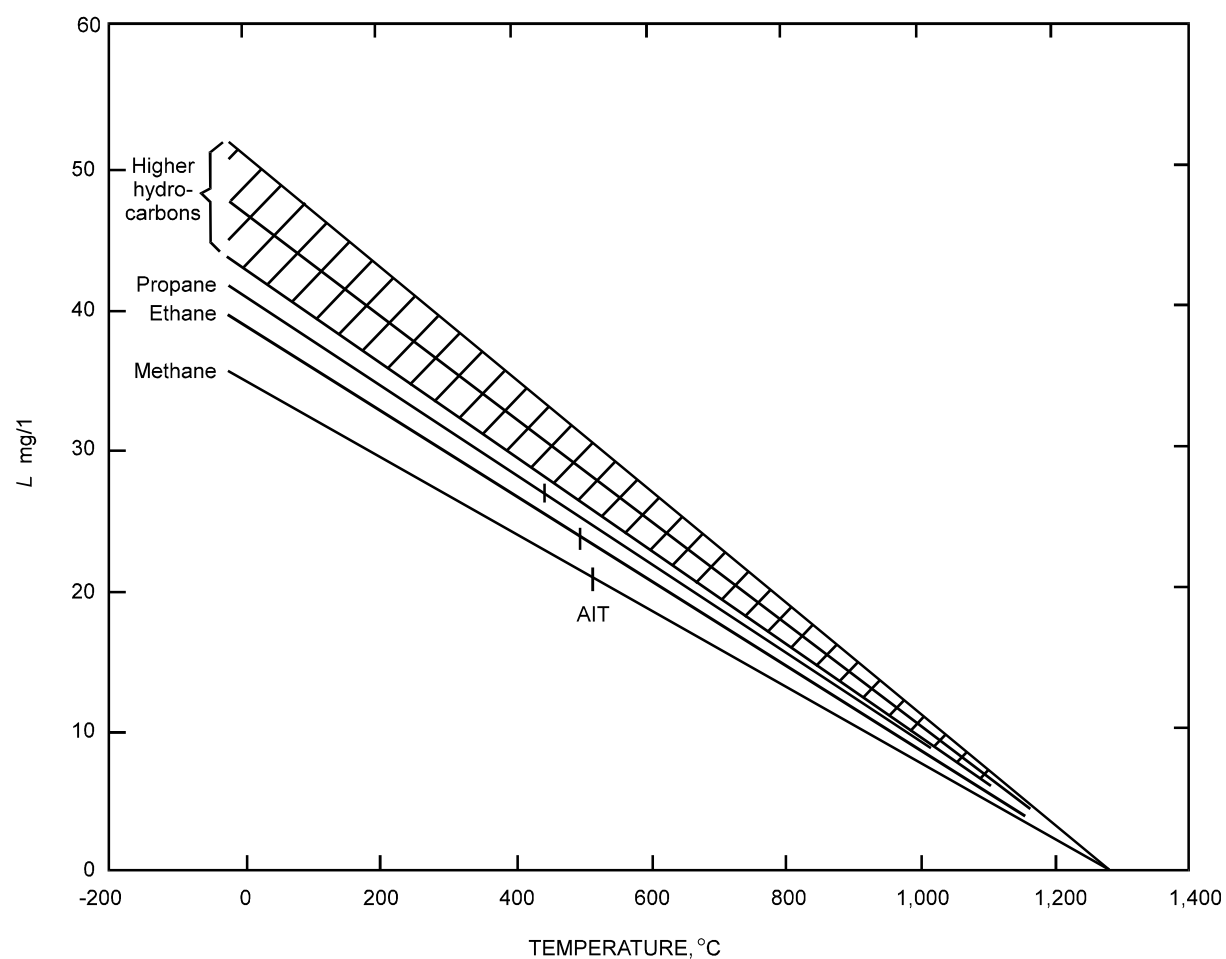


Figure 22—Effect of Temperature on Lower Limits of Flammability of 10 Paraffin Hydrocarbons in Air at Atmospheric Pressure by Weight.