FLAMMABILITY CHARACTERISTICS OF COMBUSTIBLE GASES AND VAPORS

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FLAMMABILITY CHARACTERISTICS OF COMBUSTIBLE GASES AND VAPORS

by

Michael G. Zabetakis[1]

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*)[2] and other publications (*158*).

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.

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[2] Italicized numbers in parentheses refer to items in the bibliography at the end of this report.

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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 nonflammable mixtures (*244*). That is,

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

and

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

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*).

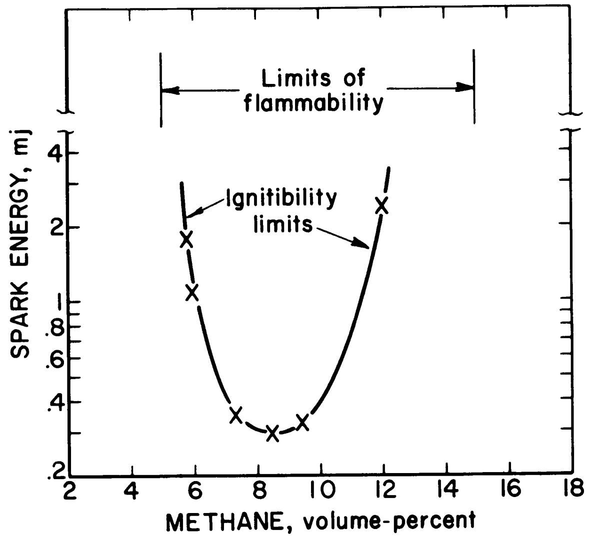

FIGURE 1.—Ignitibility Curve and Limits of Flammability for Methane-Air Mixtures at Atmospheric Pressure and 26° C.

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 ignitibility or more simply ignitibility 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 ignitibility (*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

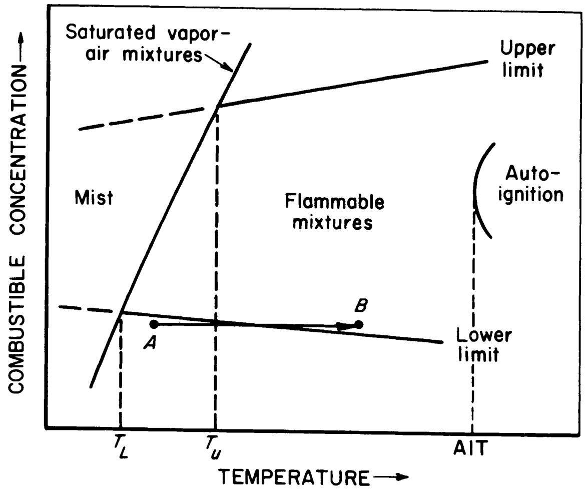

FIGURE 2.—Effect of Temperature on Limits of Flammability of a Combustible Vapor in Air at a Constant Initial Pressure.

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*).

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.

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/cm^3). 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

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

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 τ 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

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

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 samll 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

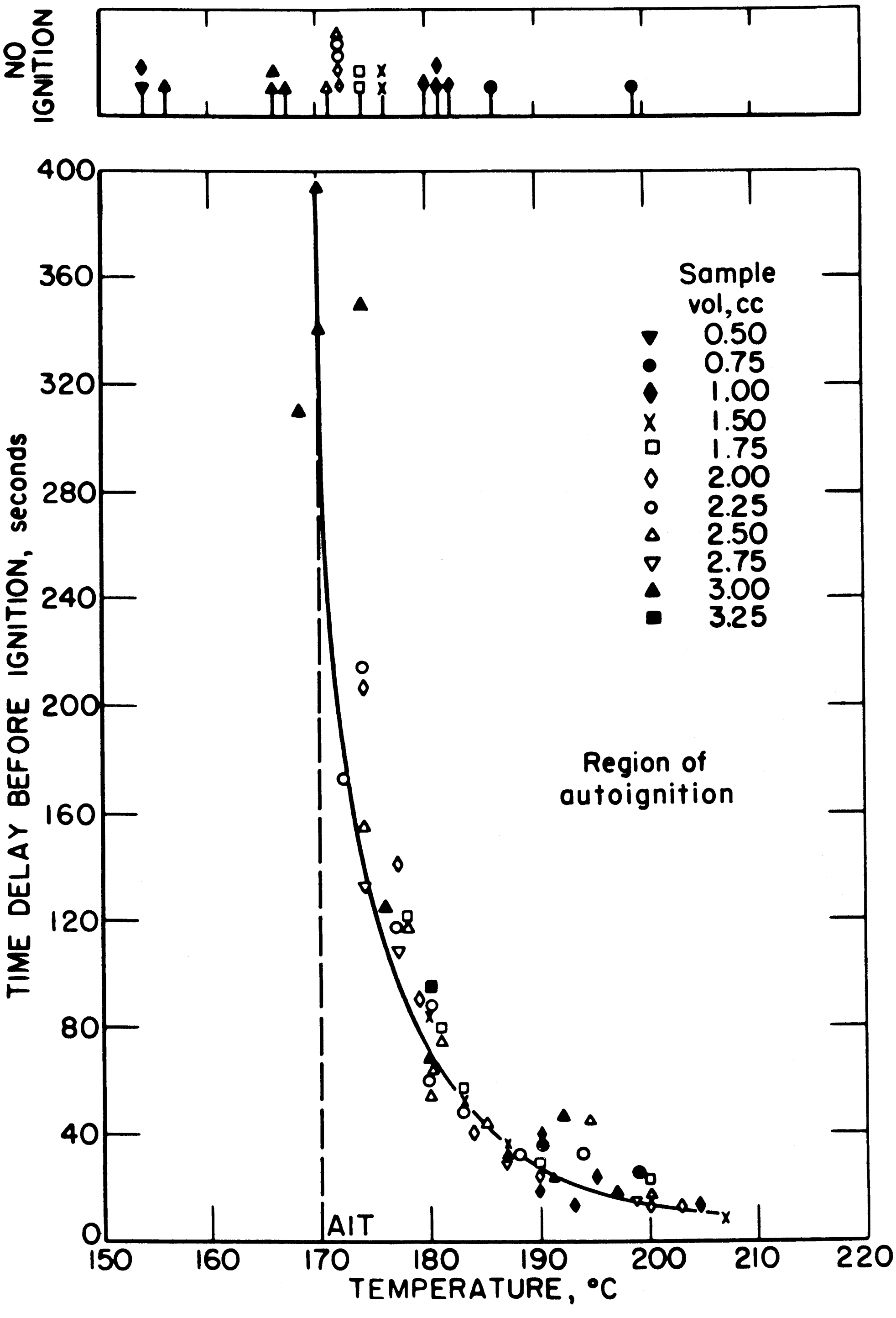

FIGURE 3.—Time Delay Before Ignition of NPN in Air at 1,000 Psig in the Temperature Range From 150° to 210° C. (1–33 apparatus; type-347, stainless steel test chamber.)

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

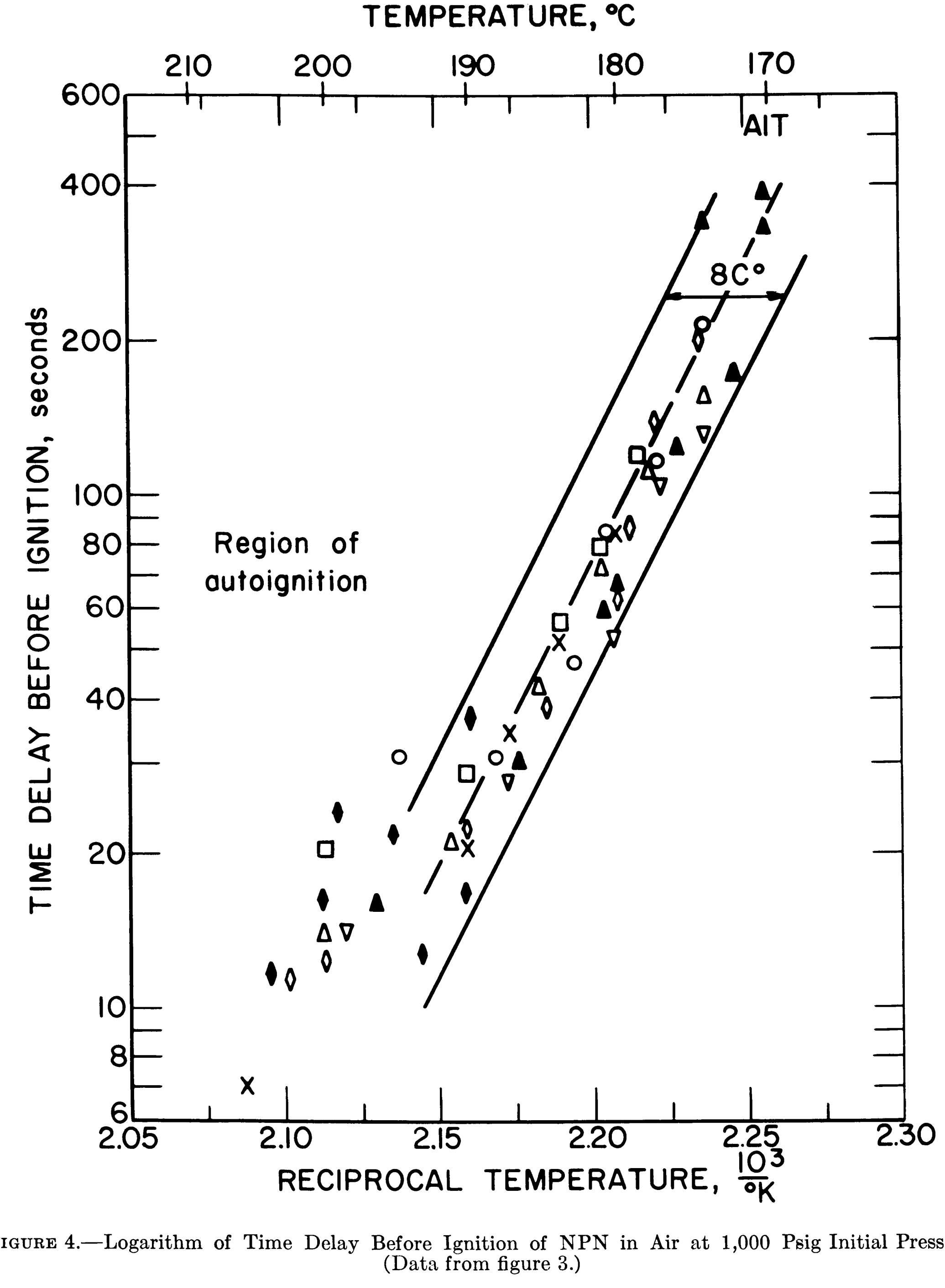

FIGURE 4.—Logarithm of Time Delay Before Ignition of NPN in Air at 1,000 Psig Initial Pressure. (Data from figure 3.)

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*).

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

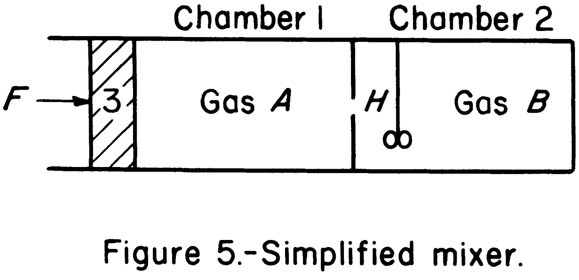

FIGURE 5.—Simplified Mixer.

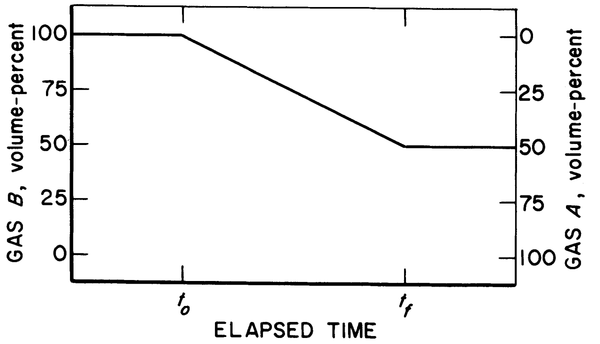

FIGURE 6.—Composition of Gas in Chamber 2, Figure 5 (Instantaneous Mixing).

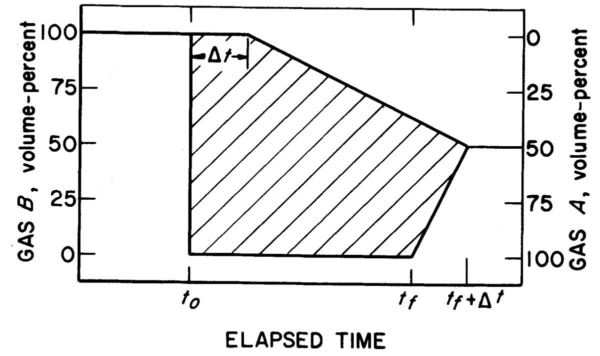

FIGURE 7.—Composition of Gas in Chamber 2, Figure 5 (Delayed Mixing).

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 pro-

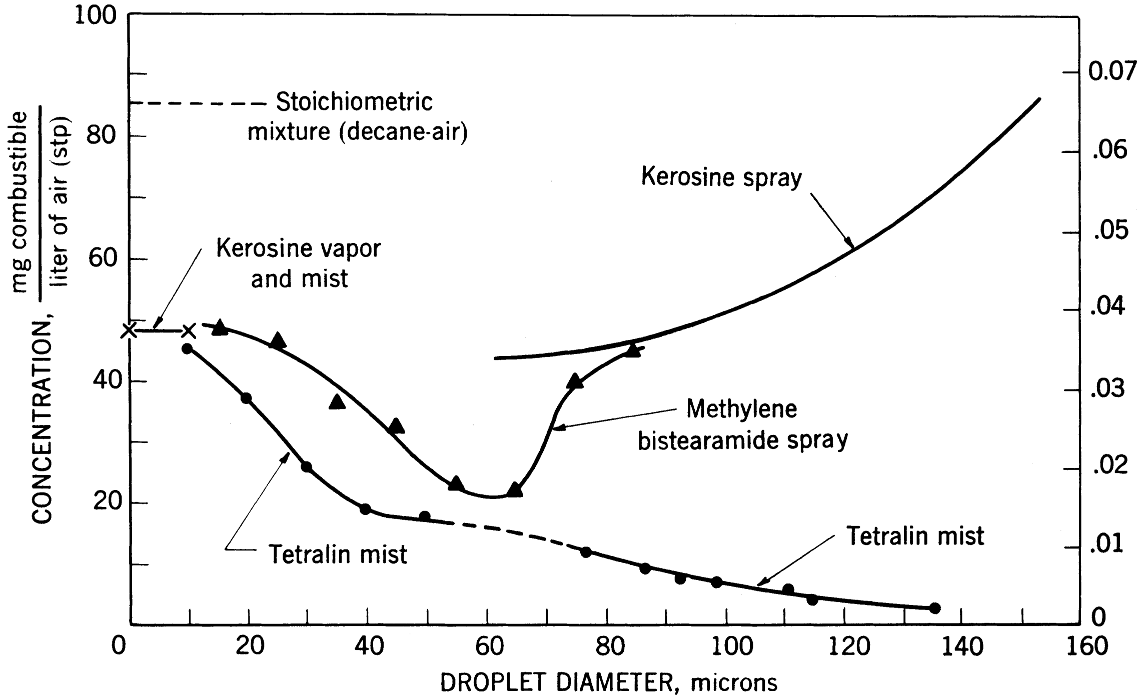

FIGURE 8.—Variation in Lower Limits of Flammability of Various Combustibles in Air as a Function of Droplet Diameter.

duced 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

$$\Delta P \propto \frac{h_f}{h_a}. \tag{5}$$

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*).

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, *M*1 in figures 9 and 10) and the vertices of the bounding triangle. For example, addition of methane (+CH_4) to mixture *M*1 yields initially all mixture compositions between *M*1 and C (100 pct CH_4). After a homogeneous mixture is produced, a new mixture composition point, such as *M*2, is obtained. Similarly, if oxygen is added (+O_2) to the mixture represented by point *M*1, all compositions between *M*1 and O (100 pct O_2) are obtained initially; if nitrogen is added, all compositions between *M*1 and N (100 pct N_2) are obtained initially. If more than one gas is added to *M*1, for example, methane and oxygen, the resultant composition point may be obtained by considering that the mixing process

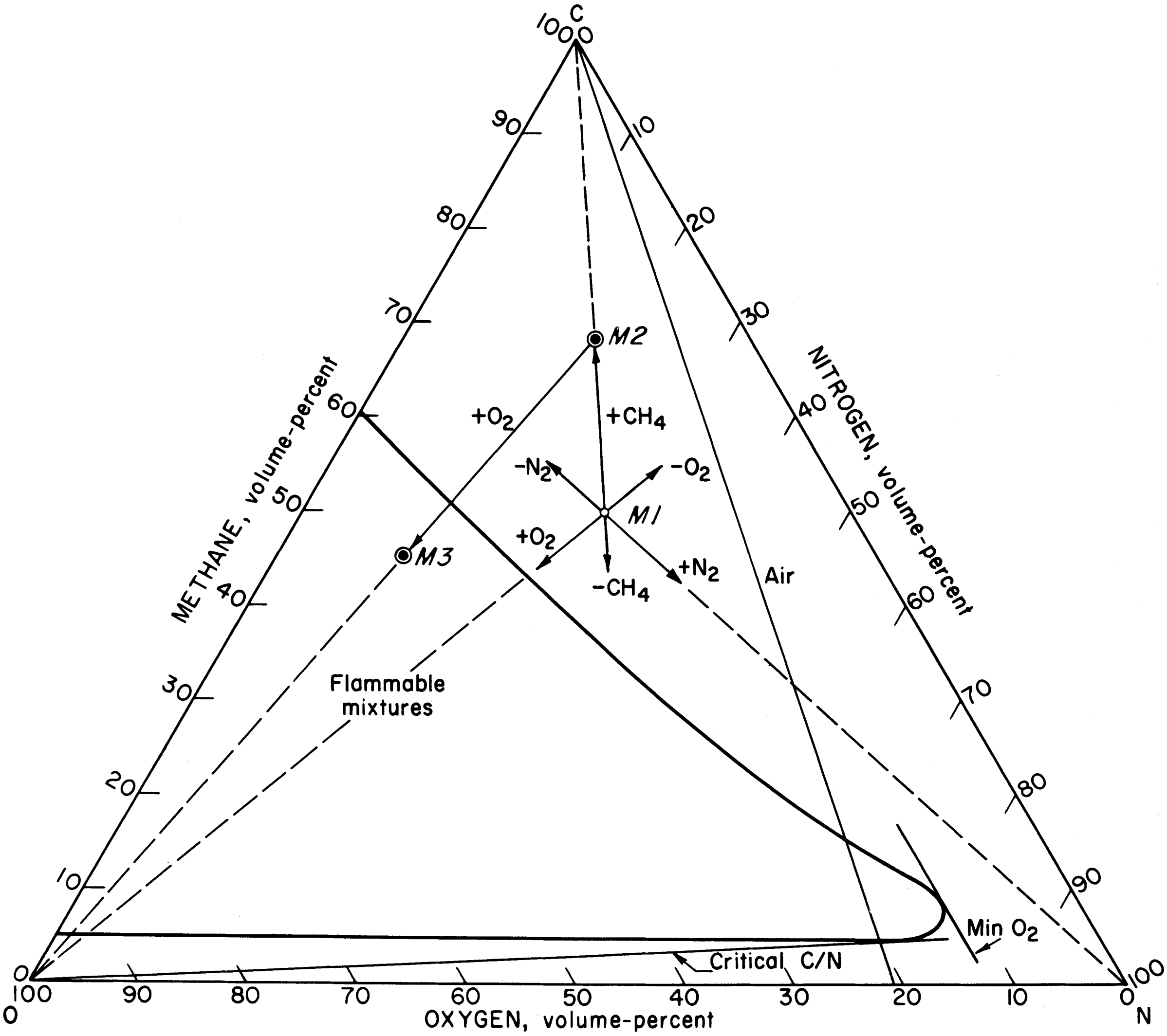

FIGURE 9.—Flammability Diagram for the System Methane-Oxygen-Nitrogen at Atmospheric Pressure and 26° C.

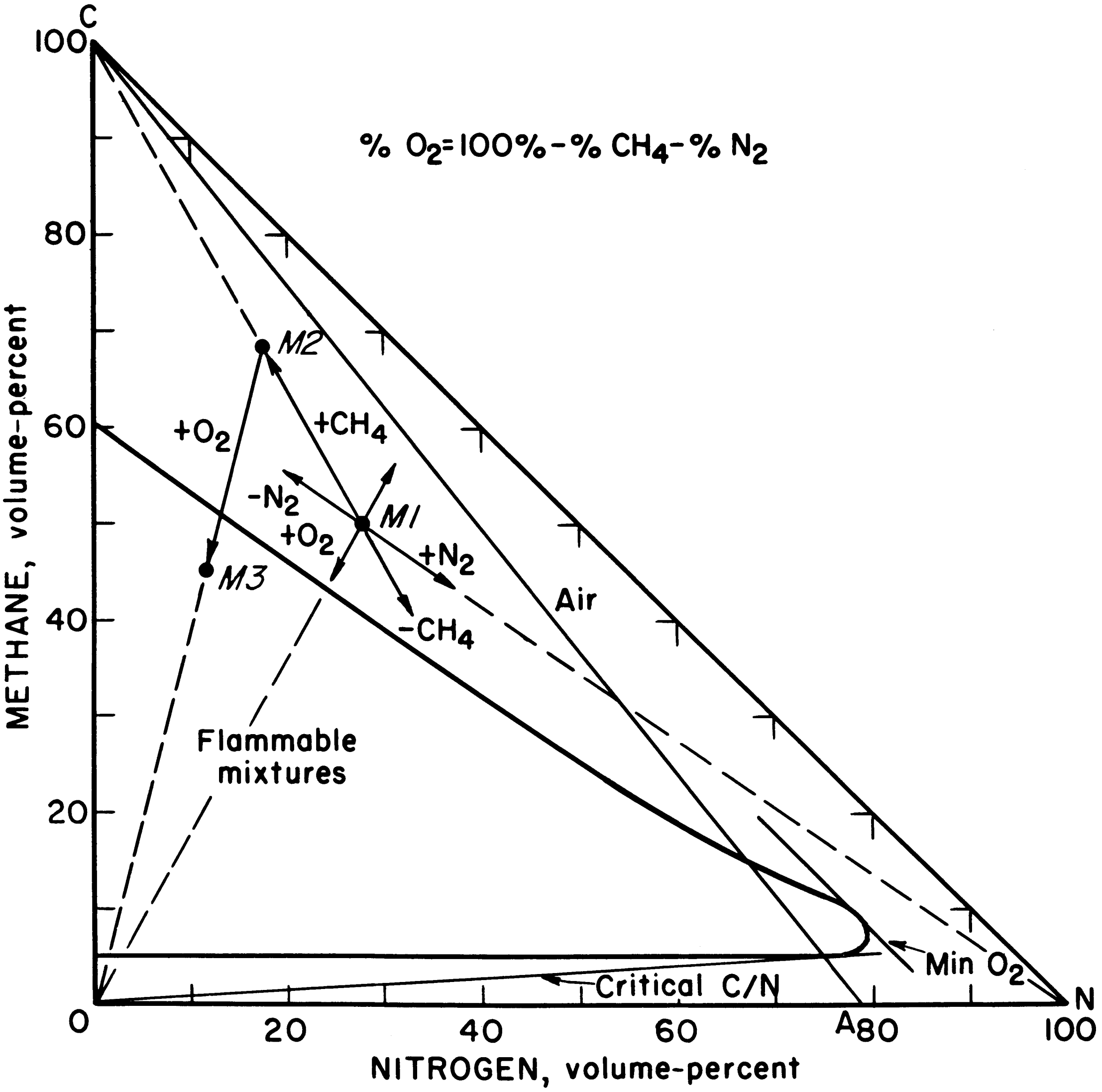

Figure 10.—Flammability Diagram for the System Methane-Oxygen-Nitrogen at Atmospheric Pressure and 26° C. (Data from fig. 9).

occurs in two steps. First, the methane is added to *M*1 and the gases are mixed thoroughly to give *M*2. Oxygen is then added to *M*2 with mixing to give a new (flammable) mixture, *M*3. If the methane and oxygen were added to a fixed volume at constant pressure, some of *M*1 and then of *M*2 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, *M*1 in figures 9 and 10) shifts away from the vertices C, O, and N along the extensions to the lines *M*1—C, *M*1—O and *M*1—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, C*A*, (fig. 10) is formed by joining C with the mixture *A* (21 percent O_2 +79 percent N_2). Using this latter point, *A*, one can readily determine the mixture compositions that are formed when mixture *M*1 is displaced from an enclosure and mixed with air. Initially, all mixture compositions between *M*1 and A would form. Since these would pass through the flammable mixture zone, a hazardous condition would be created. Similarly, if pure combustible CH_4 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.

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*).

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

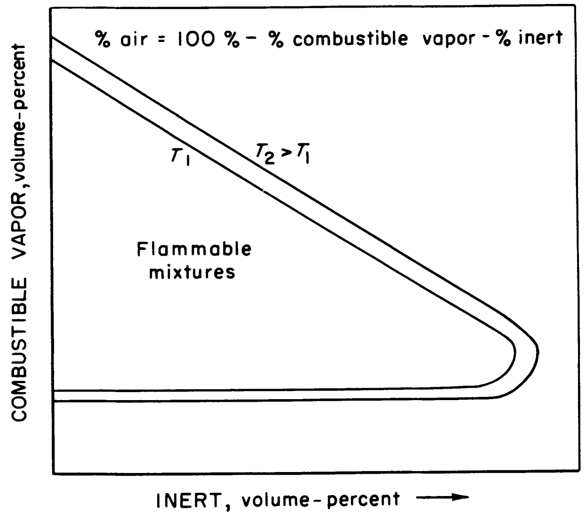

FIGURE 11.—Effect of Initial Temperature on Limits of Flammability of a Combustible Vapor-Inert-Air System at Atmospheric Pressure.

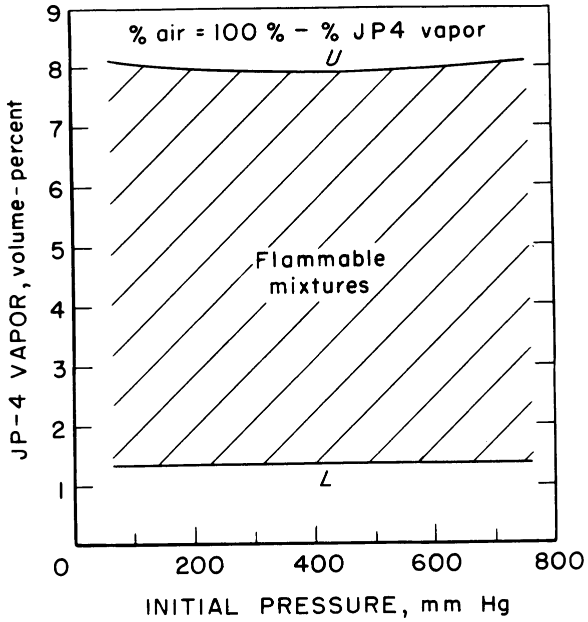

FIGURE 12.—Effect of Initial Pressure on Limits of Flammability of JP-4 (Jet Fuel Vapor) in Air at 26° C.

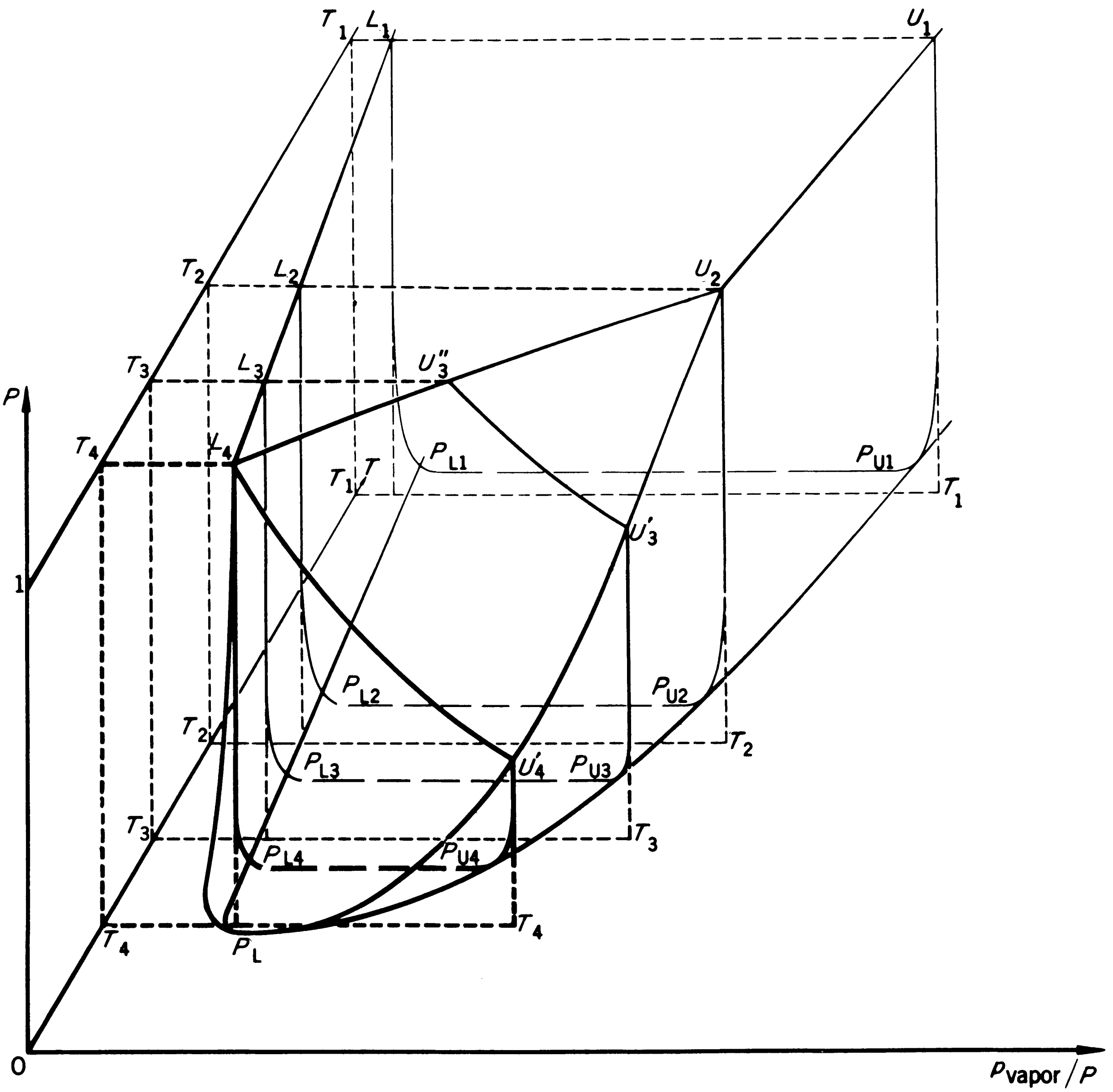

FIGURE 13.—Effect of Temperature and Pressure on Limits of Flammability of a Combustible Vapor in a Specified Oxidant.

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. 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 along $U_3'U_3''$ and $U_4'L_4$ are flammable. The curve

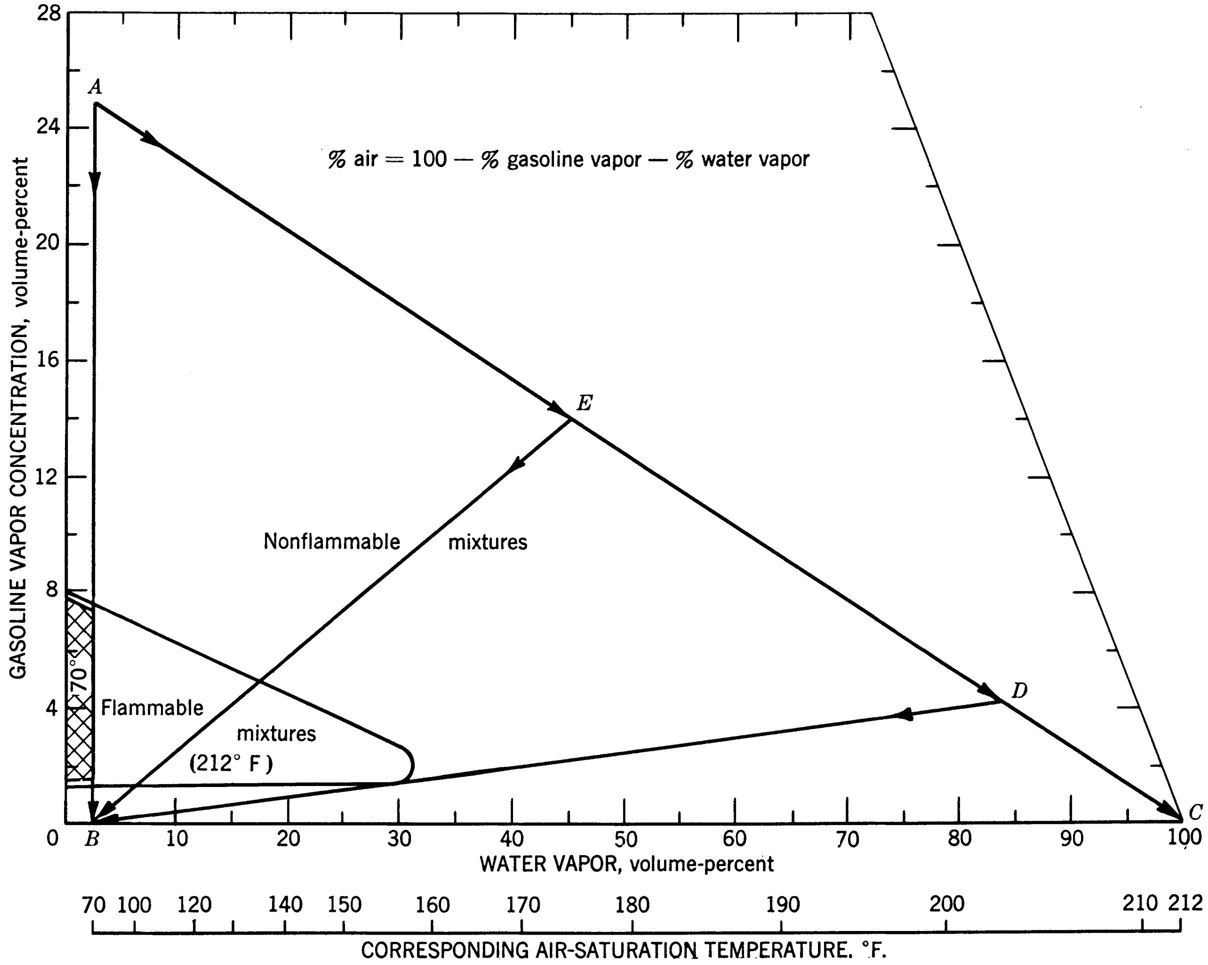

FIGURE 14.—Flammability Diagram for the System Gasoline Vapor-Water Vapor-Air at 70° F (21° C) and at 212° F (100° C) and Atmospheric Pressure.

$L_4P_LU'_4U'_3U_2$ 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 absorbtion, 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 compositons 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.

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:

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

and

$$P_m = P_1 \frac{n_b T_b}{n_1 T_1} = P_1 \frac{\overline{M}_1 T_b}{\overline{M}_b T_1}, \qquad (8)$$

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, $\overline{M}_1$ is the average molecular weight of the initial mixture, $\overline{M}_b$ 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

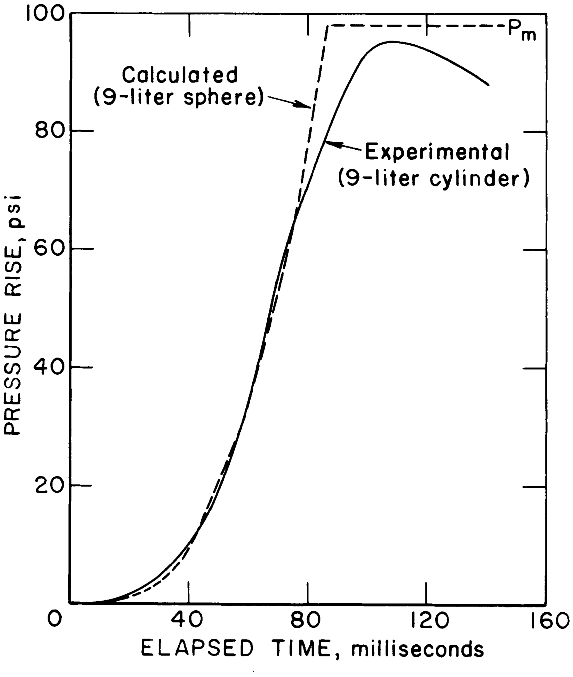

FIGURE 15.—Pressure Produced by Ignition of a 9.6 Volume-Percent Methane-Air Mixture in a 9-Liter Cylinder (Experimental).

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

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

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:

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

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.

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

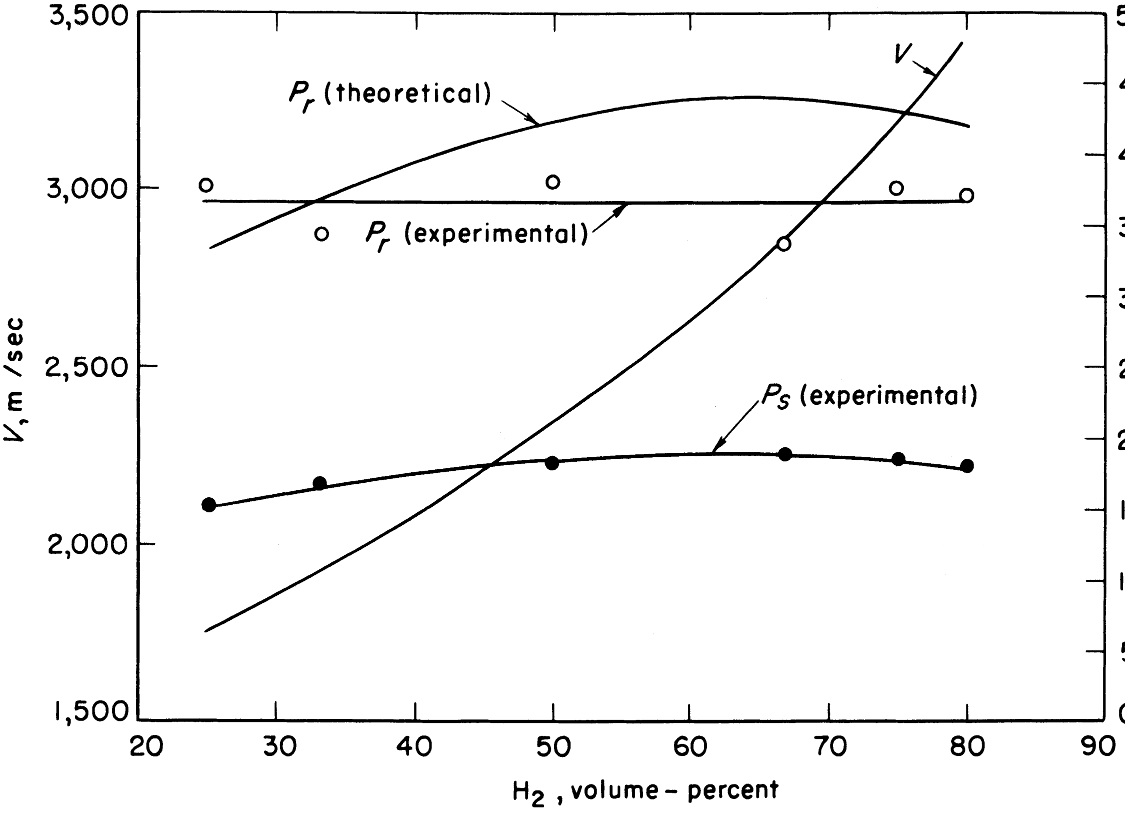

FIGURE 16.—Detonation Velocity, V; Static Pressure, P_s; and Reflected Pressure, P_r, Developed by a Detonation Wave Propagating Through Hydrogen-Oxygen Mixtures in a Cylindrical Tube at Atmospheric Pressure and 18° C.

that even reinforced concrete structures have been completely demolished by explosions of near-limit flammable mixtures.

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*)

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

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 overpressure-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 cinder-block 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

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

and

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

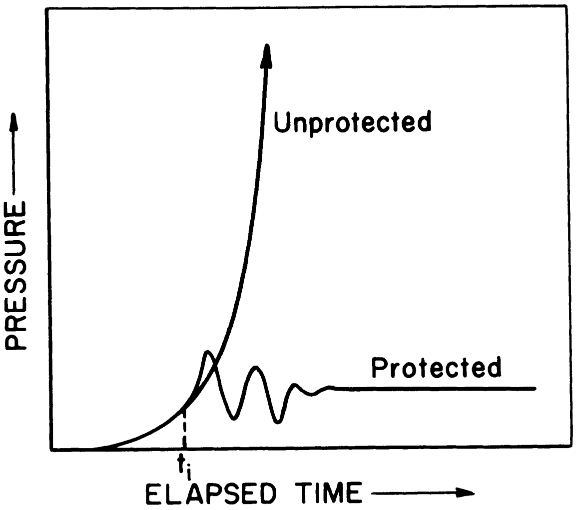

FIGURE 17.—Pressure Variation Following Ignition of a Flammable Mixture in Unprotected and Protected Enclosures.

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*).

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 ft^2 is:

$$P_M=0.07\frac{L}{D}, \text{ and } 6\leq\frac{L}{D}\leq48, \tag{14}$$

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

$$0.8K\leq P_M\leq1.8K, \tag{15}$$

where $2\leq K\leq32$, and $6\leq\frac{L}{D}\leq30$. 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 gas [3]-air mixture:

$$P_1V^{1/3}=1.18kw+1.57. \tag{16}$$

More generally,

$$P_1V^{1/3}=S_o(0.3Kw+0.4), \tag{17}$$

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

$$P_2=K. \tag{18}$$

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

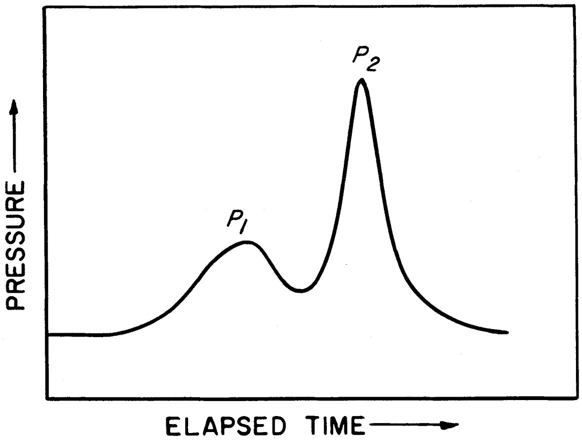

FIGURE 18.—Pressure Produced by Ignition of a Flammable Mixture in a Vented Oven.

In designing explosion reliefs for ovens, Simmonds and Cubbage 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*).

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

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:

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

specific volume being volume of combustible vapor per milligram of combustible. At standard conditions (0° C and 760 mm Hg) this is about 22.414/1,000M, where M is the molecular

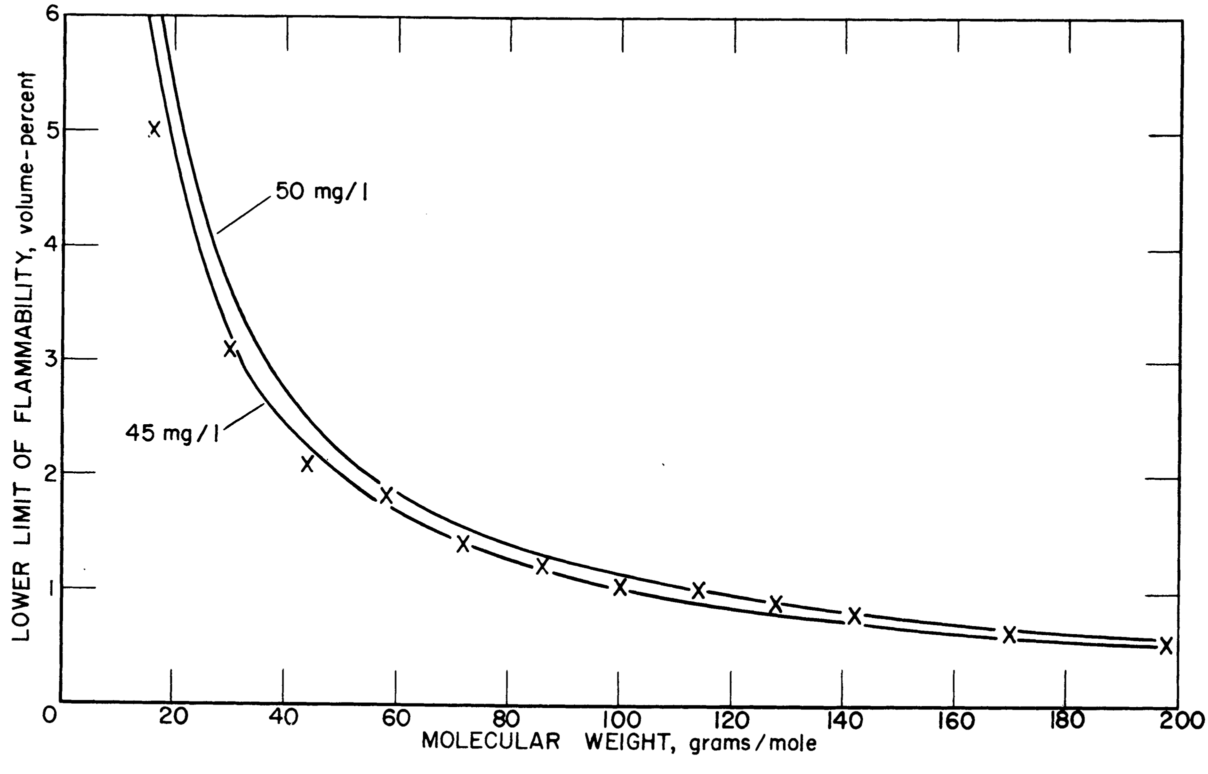

FIGURE 19.—Effect of Molecular Weight on Lower Limits of Flammability of Paraffin Hydrocarbons at 25° C.

TABLE 2.—*Properties of paraffin hydrocarbons*

Combustible	Formula	M	Sp gr (Air=1)	C_{st} in air (vol pct)	Net ΔH_c $\left(\frac{\text{Kcal}}{\text{mole}}\right)$	Lower limit in air				Upper limit in air			
						L_{25} (vol pct)	$\frac{L_{25}}{C_{st}}$	L $\left(\frac{\text{mg}}{1}\right)$	Ref.	U_{25} (vol pct)	$\frac{U_{25}}{C_{st}}$	U $\left(\frac{\text{mg}}{1}\right)$	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_2H_6	30.07	1.04	5.65	341.3	3.0	.53	41	(*40*)	12.4	2.2	190	(*41*)
Propane	C_3H_8	44.09	1.52	4.02	488.5	2.1	.52	42	(*115*)	9.5	2.4	210	(*41*)
n-Butane	C_4H_{10}	58.12	2.01	3.12	635.4	1.8	.58	48	(*113*)	8.4	2.7	240	(*41*)
n-Pentane	C_5H_{12}	72.15	2.49	2.55	782.0	1.4	.55	46	(*40*)	7.8	3.1	270	(*40*)
n-Hexane	C_6H_{14}	86.17	2.98	2.16	928.9	1.2	.56	47	(*246*)	7.4	3.4	310	(*40*)
n-Heptane	C_7H_{16}	100.20	3.46	1.87	1075.8	1.05	.56	47	(*246*)	6.7	3.6	320	(*40*)
n-Octane	C_8H_{18}	114.23	3.94	1.65	1222.8	.95	.58	49	(*246*)				
n-Nonane	C_9H_{20}	128.25	4.43	1.47	1369.7	[1] .85	.58	49	(*246*)				
n-Decane	$C_{10}H_{22}$	142.28	4.91	1.33	1516.6	[2] .75	.56	48	(*246*)	[3] 5.6	4.2	380	
n-Undecane	$C_{11}H_{24}$	156.30	5.40	1.22	1663.6	.68	.56	48	(4)				
n-Dodecane	$C_{12}H_{26}$	170.33	5.88	1.12	1810.5	.60	.54	46	(4)				
n-Tridecane	$C_{13}H_{28}$	184.36	6.37	1.04	1957.4	.55	.53	46	(4)				
n-Tetradecane	$C_{14}H_{30}$	198.38	6.85	.97	2104.3	.50	.52	44	(4)				
n-Pentadecane	$C_{15}H_{32}$	212.41	7.33	.90	2251.2	.46	.51	46	(4)				
n-Hexadecane	$C_{16}H_{34}$	226.44	7.82	.85	2398.2	.43	.51	44	(4)				

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

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

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

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,

$$L_{25°}\approx 0.55C_{st}. \qquad (21)$$

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

$$C_nH_{2n+2}+(1.5n+0.5)O_2\rightarrow nCO_2+(n+1)H_2O, \qquad (22)$$

so that in air

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

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

$$C_{st}=\frac{1{,}000[12.01n+1.008(2n+2)]}{22.414\times 4.773(1.5n+0.5)}\frac{\text{mg}}{1}, \qquad (24)$$

or

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

Thus,

$$C_{st}\approx 87 \text{ mg/1}, \qquad n\geq 4. \qquad (26)$$

Combining this equation with equation (21), we have

$$L_{25°}(\text{mg/1})\approx 48 \text{ mg/1}, \qquad (27)$$

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

$$L_{25°}(\text{vol pct})\approx\frac{107}{M}. \qquad (28)$$

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

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

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

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

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

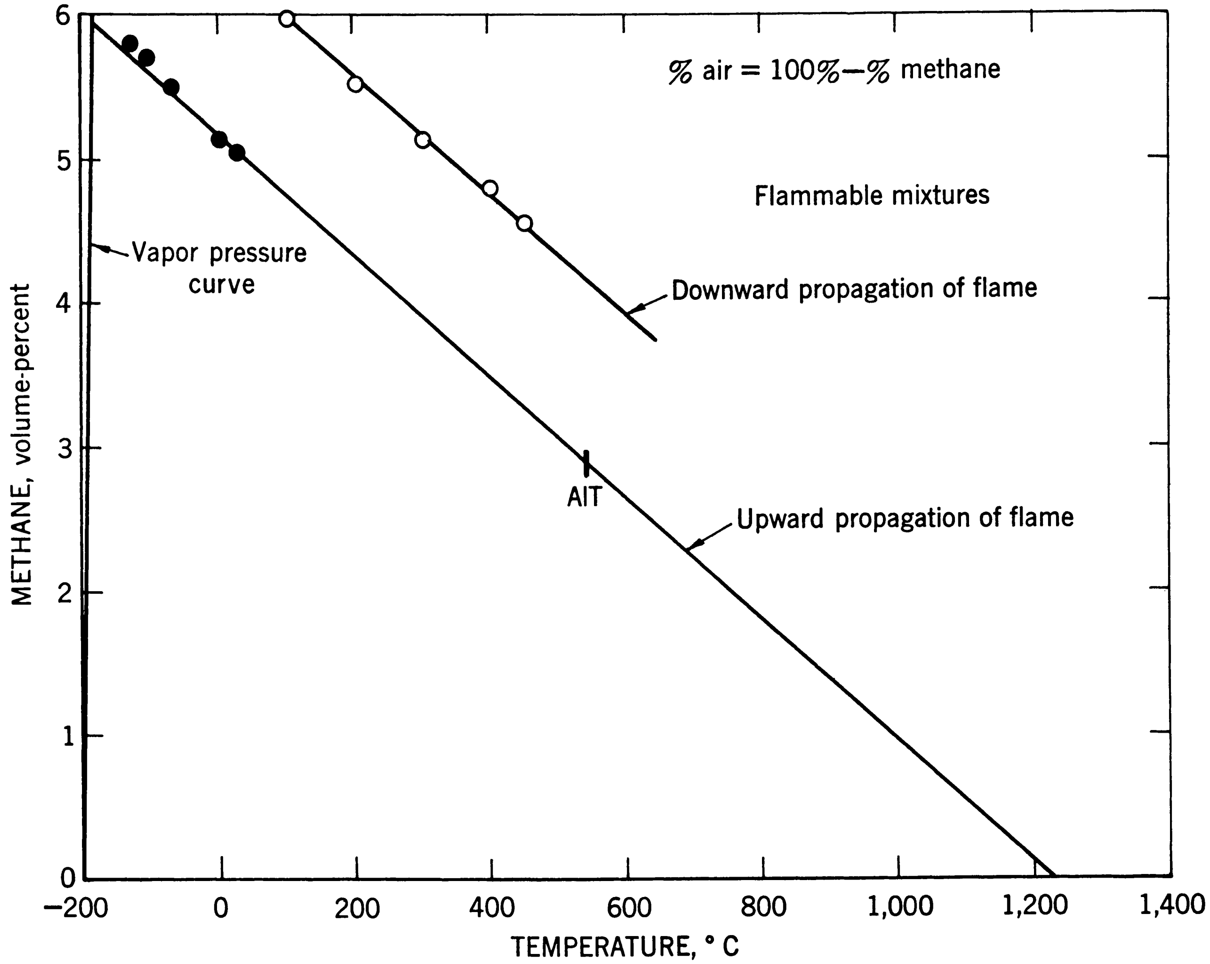

FIGURE 20.—Effect of Temperature on Lower Limit of Flammability of Methane in Air at Atmospheric Pressure.

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:

$$L_t = L_{25^\circ} - \frac{L_{25^\circ}}{(1{,}300^\circ - 25^\circ)}(t - 25^\circ), \qquad (31)$$

or

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

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

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

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

where t is the temperature in °C and ΔH_c is the net heat of combustion in kilocalories per mole. Then,

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

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

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

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

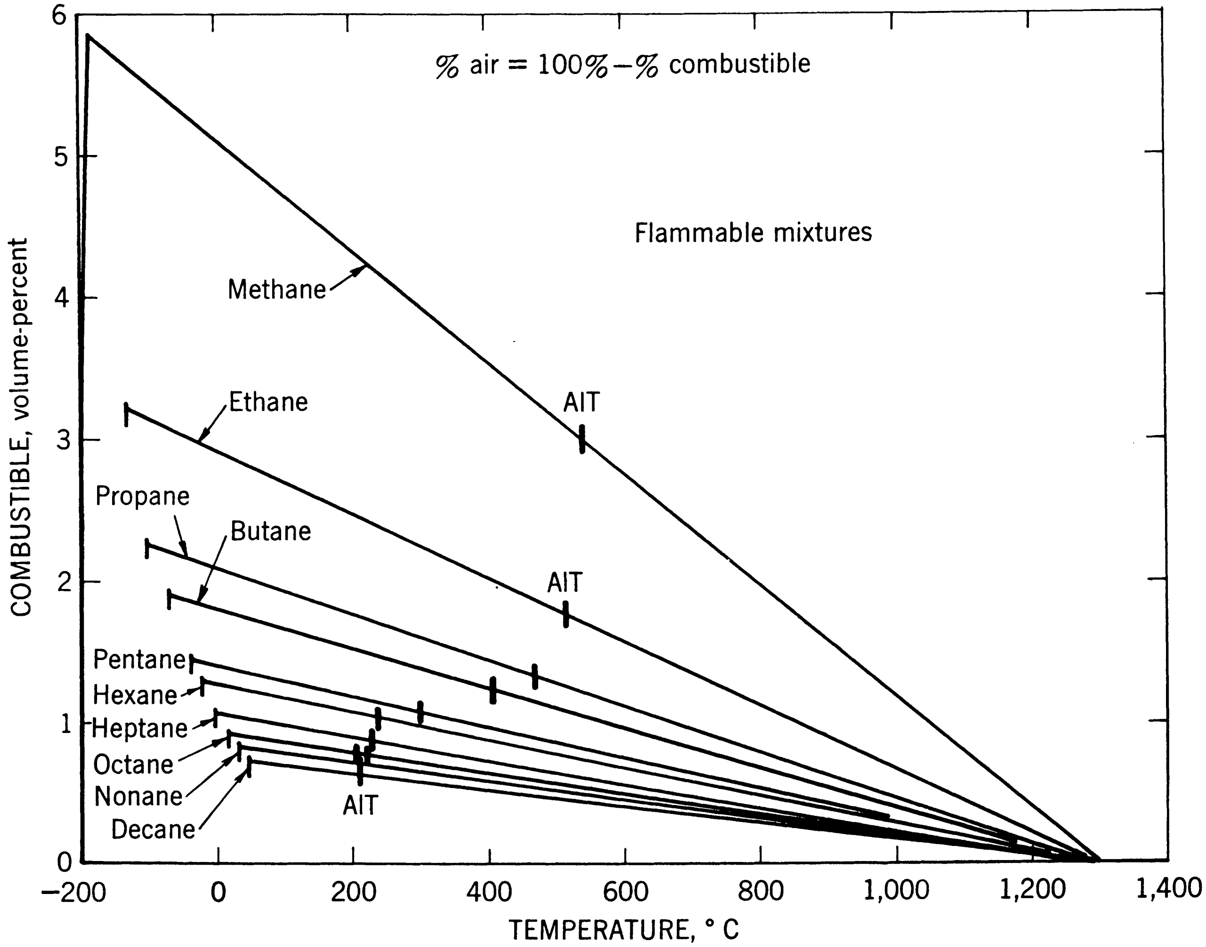

FIGURE 21.—Effect of Temperature on Lower Limits of Flammability of 10 Paraffin Hydrocarbons in Air at Atmospheric Pressure.

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 5.0×0.55, or 2.75 volume-percent. The same value can be obtained directly from figure 21. From the modified Burgess-Wheeler Law curve, $L_t/L_{25°}=0.585$ at 600° C, so that $L_{600°}=2.92$ volume-percent.

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:

$$U_t=U_{25°}+\frac{0.75}{\Delta H_c}(t-25°). \qquad (36)$$

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

$$\frac{U_t}{U_{25°}}=1+0.000721(t-25°). \qquad (37)$$

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, $U_{calc}-U_{exper}$. In each case, the difference is less than

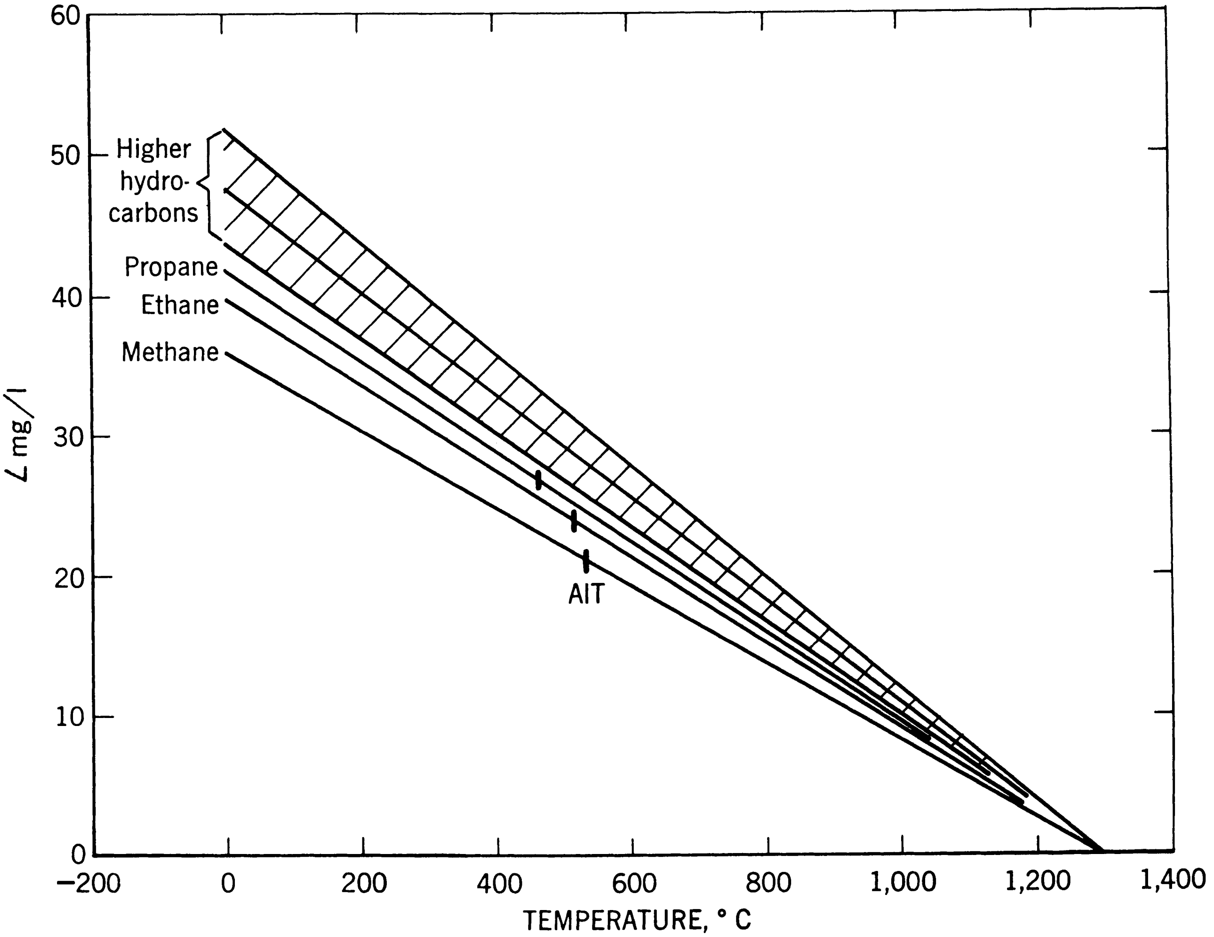

FIGURE 22.—Effect of Temperature on Lower Limits of Flammability of 10 Paraffin Hydrocarbons in Air at Atmospheric Pressure by Weight.

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 $U_{300°}/U_{25°} \approx 1.20$ obtained from figure 24.

Given the vapor pressure curve and the lower limit of flammability, the lower temperature limit or approximate flash point of a combustible can be calculated from either equation (32) or (35) (*218*). Approximate flash points were obtained previously, using only the vapor pressure curve and the lower limit at ordinary or elevated temperatures (*154*). The values obtained with this procedure are somewhat low because the lower limit at any temperature above the flash point is less than at the flash point. The lower temperature limits of paraffin hydrocarbon at atmospheric pressure are given in table 4.

TABLE 3.—*Upper flammability limits, U, of methane-air mixtures at 15 psig*

Temperature (° C)	U_{exper}[1] (vol percent)	U_{calc} (vol percent)	U_{calc}-U_{exper} (vol percent)
25	15. 5	15. 5	0
100	16. 3	16. 4	. 1
200	17. 0	17. 5	. 5
300	17. 9	18. 6	. 7

[1] (*182*).

Moderate changes in pressure do not ordinarily affect the limits of flammability of the paraffins in air, as shown in figure 25 for pentane, hexane, and heptane in air (*241*) in a range from 75 to 760 mm Hg. The lower limits

TABLE 4.—*Lower temperature limits and autoignition temperatures of paraffin hydrocarbons at atmospheric pressure*

	Lower temperature limit In air			Autoignition temperature					
				In air			In oxygen		
	° C	° F	Ref.	° C	° F	Ref.	° C	° F	Ref.
Methane	−187	−305	(1)	537	999	(*158*)			
Ethane	−130	−202	(1)	515	959	(*237*)	506	943	(*94*)
Propane	−102	−152	(1)	466	871	(*158*)			
n-Butane	−72	−96	(1)	405	761	(*237*)	283	542	(*191*)
Isobutane	−81	−114	(1)	462	864	(*158*)	319	606	(*94*)
n-Pentane	−48	−54	(1)	258	496	(*194*)	258	496	(*144*)
n-Hexane	−26	−15	(*159*)	223	433	(*194*)	225	437	(*94*)
n-Heptane	−4	25	(*159*)	223	433	(*237*)	209	408	(*94*)
n-Octane	13	56	(*159*)	220	428	(*237*)	208	406	(*191*)
n-Nonane	31	88	(*159*)	206	403	(*237*)			
n-Decane	46	115	(*159*)	208	406	(*237*)	202	396	(*94*)
n-Dodecane	74	165	(*159*)	204	399	(*237*)			
n-Hexadecane	126	259	(1)	205	401	(*237*)			

[1] Caculated value.

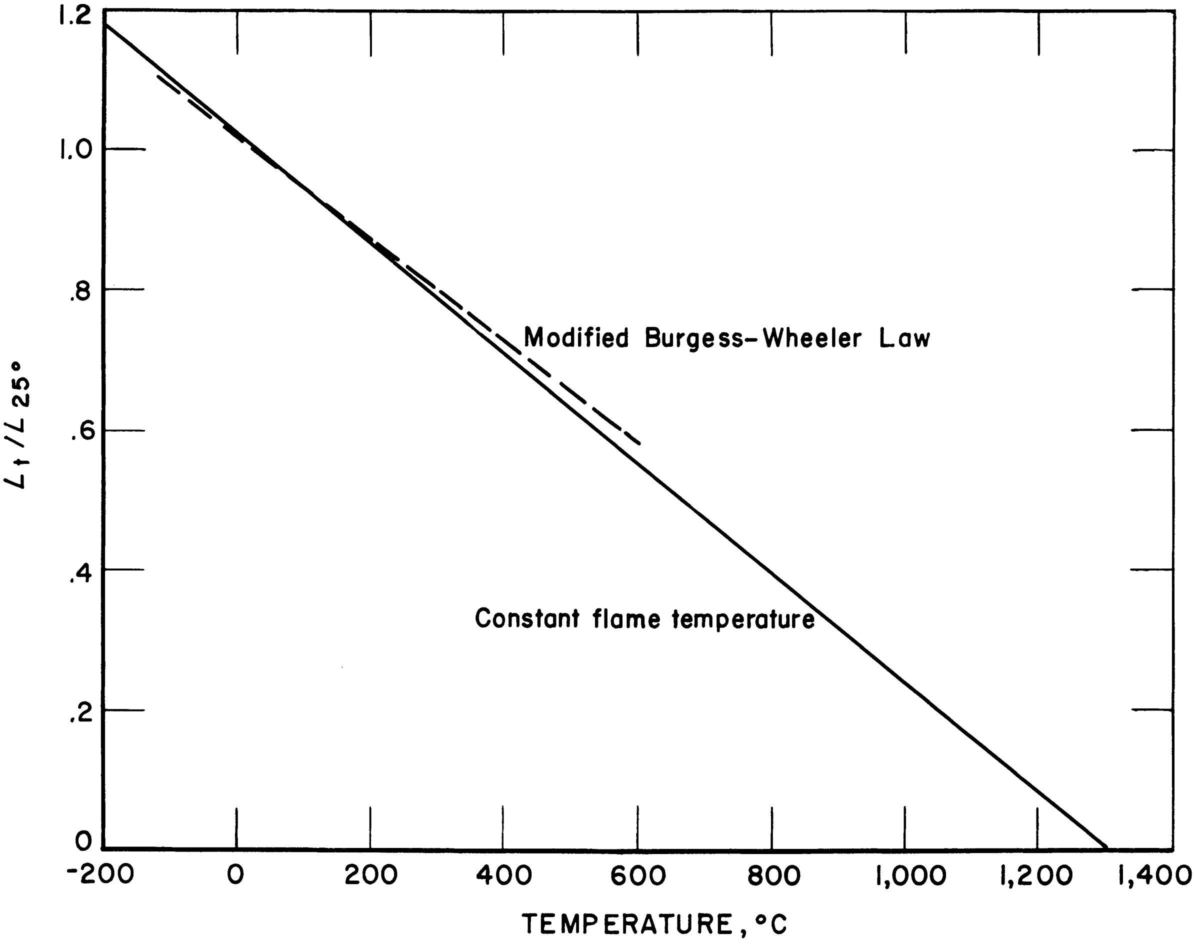

FIGURE 23.—Effect of Temperature on $L_t/L_{25°}$ Ratio of Paraffin Hydrocarbons in Air at Atmospheric Pressure.

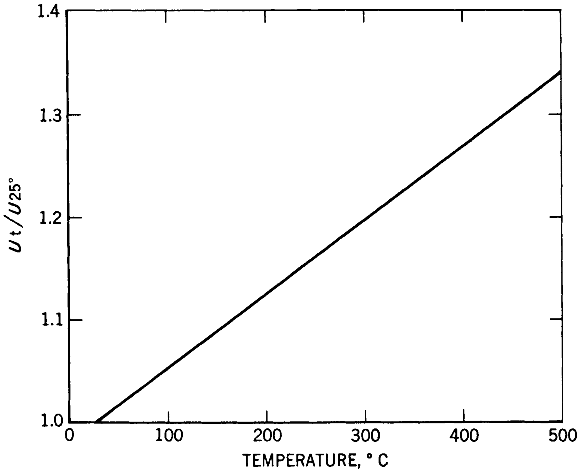

FIGURE 24.—Effect of Temperature on $U_t/U_{25°}$ Ratio of Paraffin Hydrocarbons in Air at Atmospheric Pressure in the Absence of Cool Flames.

coincide, but the upper limits, by weight, increase with increasing molecular weight.

By volume, at atmospheric pressure and 25° C, Spakowski (*201*) found that the upper and lower limits were related by the expression:

$$U_{25°}=7.1L_{25°}^{0.56}. \tag{38}$$

However, the data presented here are correlated more precisely by a somewhat simpler expression:

$$U_{25°}=6.5\sqrt{L_{25°}}. \tag{39}$$

Neither expression is applicable when cool flames are obtained. Substitution of equation (21) for $L_{25°}$ into equation (39) gives

$$U_{25°}=4.8\sqrt{C_{st}}. \tag{40}$$

The limits of flammability of natural gas (85–95 pct methane and 15–5 pct ethane) have been determined over an extended pressure range by Jones and coworkers (*78*, *105*). They are given in figure 26 for pressures from 1 to 680 atmospheres (10,000 psig). An analysis of these data shows the limits vary linearly with the logarithm of the initial pressure. That is,

$$L\text{ (vol pct)}=4.9-0.71\log P\text{ (atm)}, \tag{41}$$

and

$$U\text{ (vol pct)}=14.1+20.4\log P\text{ (atm)}, \tag{42}$$

with a standard error of estimate of 0.53 vol pct for L and 1.51 vol pct for U.

Although the limits of flammability are not affected significantly by moderate changes in pressure, the temperature limits are pressure dependent. As the total pressure is lowered, the partial pressure of the combustible must also be lowered to maintain a constant combustible concentration. The effect of pressure on the lower temperature limit of the normal paraffins pentane, hexane, heptane, and octane in air, for pressures from 0.2 to 2 atmospheres,

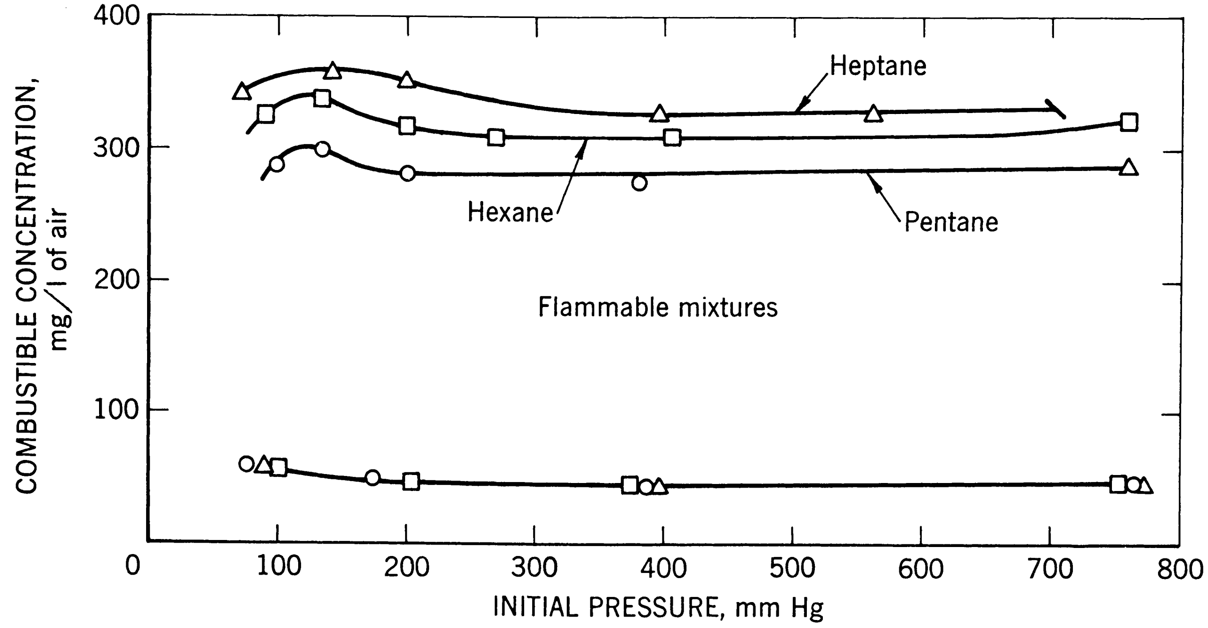

FIGURE 25.—Effect of Pressure on Limits of Flammability of Pentane, Hexane, and Heptane in Air at 26° C.

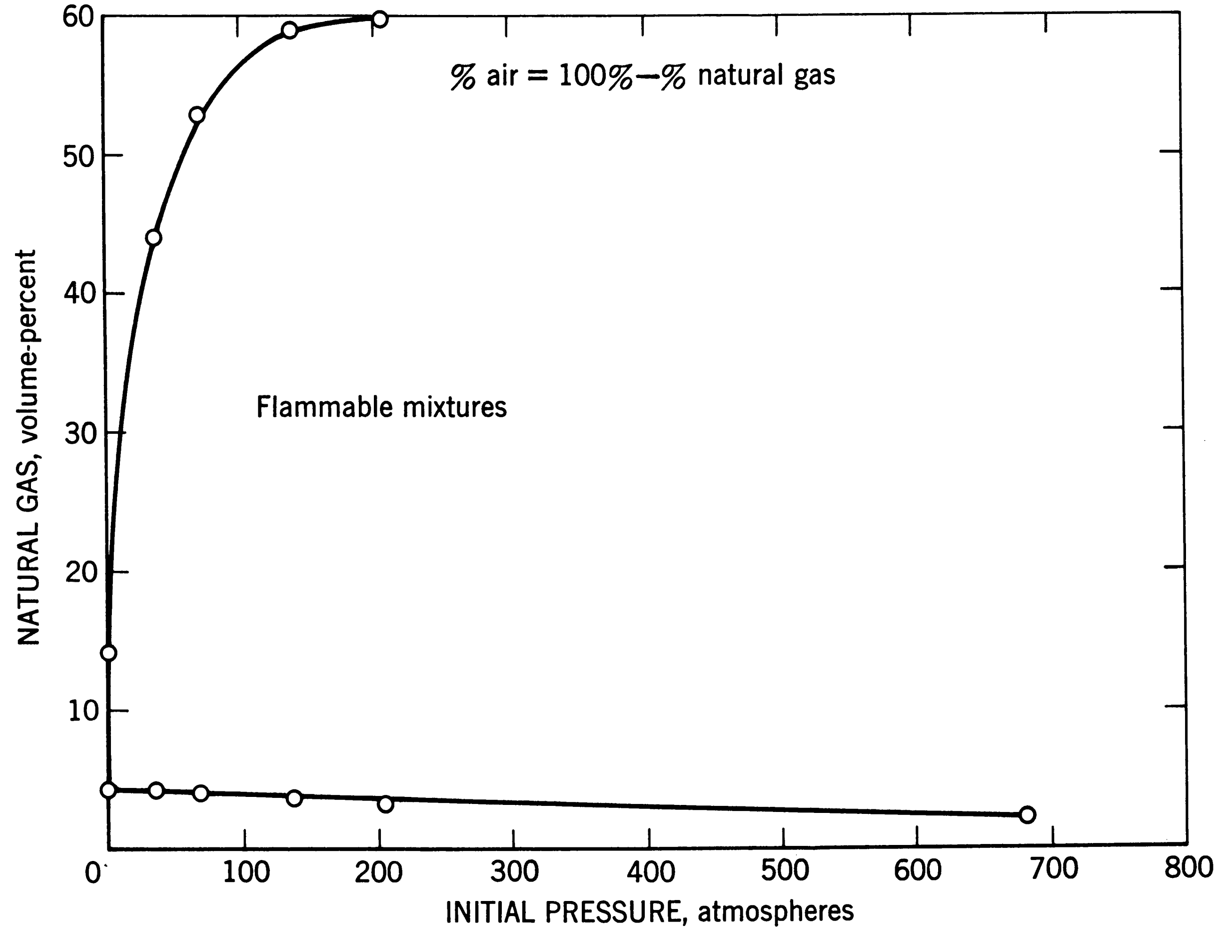

FIGURE 26.—Effect of Pressure on Limits of Flammability of Natural Gas in Air at 28° C.

is shown in figure 27. The temperature limits were calculated from the $L_{25°}$ values, the vapor pressure curves, and the data of figure 23.

Limits in Other Atmospheres

Limits of flammability of some paraffin hydrocarbons have been determined in oxygen, chlorine, and oxides of nitrogen, as well as in mixtures of air and various inerts. The lower limits in oxygen and in a wide variety of oxygen-nitrogen mixtures are essentially the same as those in air at the same temperature and pressure (fig. 10). Limit-of-flammability measurements by Bartkowiak and Zabetakis for methane and ethane in chlorine at 1, 7.8, and 14.6 atmospheres, ranging from 25° to 200° C, are summarized in tables 5 and 6 (*8*).

Coward and Jones (*40*) have presented graphically the limits of flammability of the first six members of the paraffin series in air containing various inerts, based on a representation found useful in some mining applications and treating inert gas or vapor as part of the atmosphere with which the combustible is mixed. The composition of a point on such a diagram, except one that represents only combustible and air, cannot be read directly. Instead, one must determine the composition of the atmosphere, add the combustible content, and then compute the total mixture com-

TABLE 5.—*Limits of flammability of methane in chlorine*

(volume-percent)

Pressure, psig	Limits	Temperature, ° C		
		25	100	200
0	Lower	5.6	3.6	0.6
	Upper	70	66	--------
100	Lower	--------	2.4	.6
	Upper	72	76	77
200	Lower	--------	--------	--------
	Upper	73	72	75

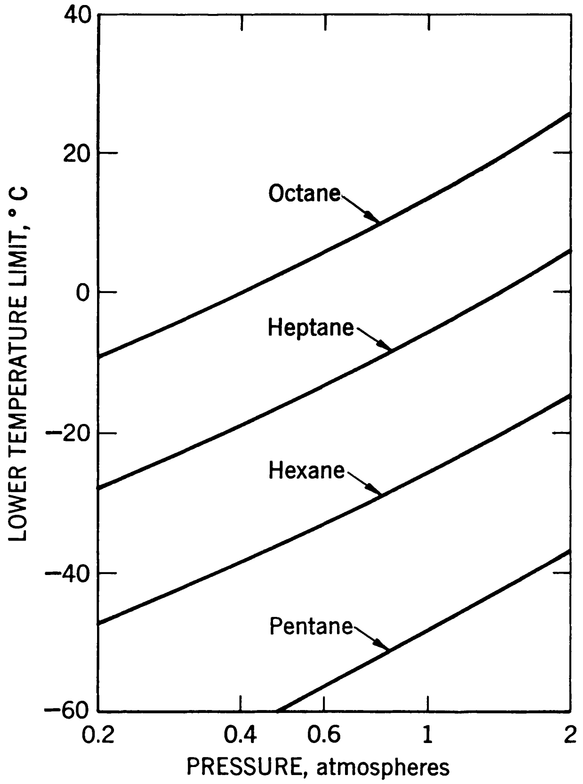

FIGURE 27.—Effect of Pressure on Lower Temperature Limits of Flammability of Pentane, Hexane, Heptane, and Octane in Air.

TABLE 6.—*Limits of flammability of ethane in chlorine*

(volume-percent)

Pressure, psig	Limits	Temperature, ° C		
		25	100	200
0	Lower	6. 1	2. 5	2. 5
	Upper	58	58	--------
100	Lower	3. 5	1. 0	1. 0
	Upper	63	75	82
200	Lower	--------	--------	--------
	Upper	66	73	76

position. This has been done for methane through hexane (figs. 28–33). Compositions are determined directly from the abscissas (inert concentration) and ordinates (combustible concentration); the air in any mixture is the difference between 100 percent and the sum of inert and combustible. Data of Burgoyne and Williams-Leir for methane-methyl bromide (MeBr)-air and methane-carbon tetrachloride-air mixtures are included in figure 28 (*29*). Unfortunately, the methane-methyl bromide-air data were obtained in a 1⅞-inch tube. Although satisfactory for methane and other hydrocarbons, this tube is apparently not satisfactory for many of the halogenated hydrocarbons. Thus a recent industrial explosion involving methyl bromide prompted Hill to reconsider the flammability of methyl bromide in air (*84*). He found that methyl bromide was not only flammable in air but that it formed flammable mixtures at 1 atmosphere with a wider variety of concentrations than Jones had reported (*96*). This would suggest that there is no justification for the assumption that Jones' flammability data for methyl bromide were influenced by the presence of mercury vapor (*196*). Hill's limit values at atmospheric pressure are included in figure 28 and are used to form the approximate, broken, flammability curves for the methane-methyl bromide-air system.

Data of Moran and Bertschy for pentane-perfluoropropane-air, pentane-sulfur hexafluoride-air and pentane-perfluoromethane-air mixtures are included in figure 32 (*147*). Data by Burgoyne and Williams-Leir for hexane-methyl bromide-air and hexane-Freon-12[4] (F–12; CF_2Cl_2)-air mixtures have been included in figure 33. These data were all obtained in 1⅞-inch-diameter tubes. An investigation of flammability of hexane-methyl bromide-air mixtures in a 4-inch tube indicated that an increase in tube size (from 1⅞-inches to 4-inches-ID) resulted in a narrowing of the flammable range; the upper limit decreased from 7.5 to 5.7 volume-percent *n*-hexane vapor in air while the lower limit remained constant. The amount of methyl bromide required for extinction decreased from 7.05 volume-percent in the 1⅞-inch tube to 6.0 volume-percent in the 4-inch tube. However, again this is not in line with the results obtained by Hill with methyl bromide-air mixtures (*84*). Accordingly, while the data obtained in approximately 2-inch tubes were used to construct figure 33, the Hill data, obtained in a larger apparatus, are also used to form the approximate, broken, flammability curves for the hexane-methyl bromide-air system.

The limits of flammability diagrams for the system *n*-heptane-water vapor-air at 100° and 200° C (fig. 34) show the effects of temperature on a system that produces both normal and cool flames at atmospheric pressure (*192*). Interestingly enough, the minimum oxygen requirement for flame propagation (Min O_2) at 200° C is the same for the cool and normal flame regions in this instance. Further, the decrease in minimum oxygen requirements

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[4] Trade names are used for identification only; this does not imply endorsement by the Bureau of Mines.

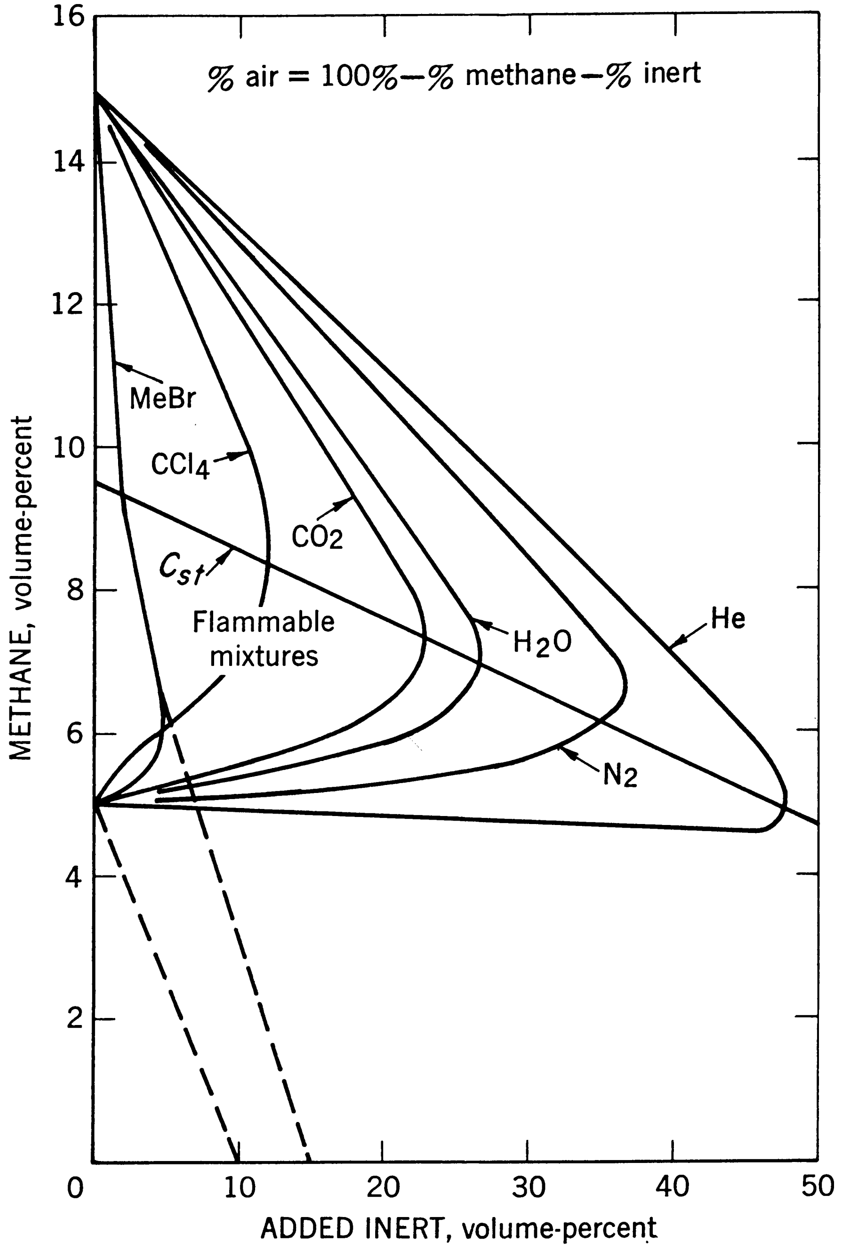

Figure 28.—Limits of Flammability of Various Methane-Inert Gas-Air Mixtures at 25° C and Atmospheric Pressure.

(from 13.5±0.3 volume-percent at 100° C to 12.8±0.3 volume-percent at 200° C) is within the range predicted by the modified Burgess-Wheeler law (equation 35 and fig. 23). However, the available data are too meager at present to permit a realistic evaluation of the validity of this law.

Inspection of the limit-of-flammability curves in figures 28 to 33 reveals that except for methane and ethane, the minimum amounts of carbon dioxide and nitrogen required for flame extinction (peak values) at 25° C and atmospheric pressure are about 28 and 42 volume-percent, respectively. The ratio of these values is approximately inversely proportional to the ratio of their heat capacities at the temperature at which combustion occurs. Accordingly, generalized flammability diagrams of the type given in figure 35 can be constructed for the higher hydrocarbons, ignoring the presence of cool flames. Such diagrams do not appear to be applicable to the halogenated hydrocarbons

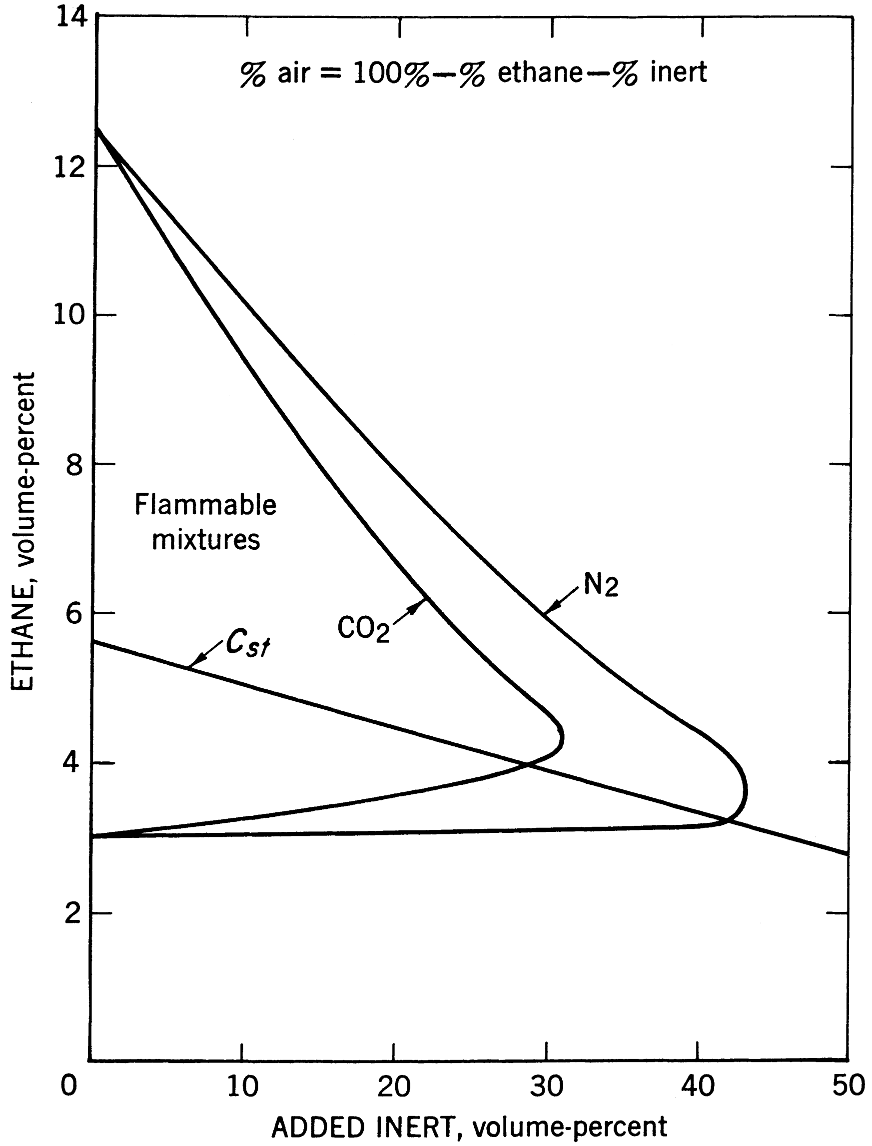

Figure 29.—Limits of Flammability of Ethane-Carbon Dioxide-Air and Ethane-Nitrogen-Air Mixtures at 25° C and Atmospheric Pressure.

since these materials tend to decompose even in flames of limit-mixture composition and, as noted, may themselves propagate flame. Coleman (*37*) has found that the ratios of the peak values of a halogenated hydrocarbon are not constant but are proportional to the heats of combustion of the combustibles to which the halogenated hydrocarbon is added.

Few data are available for the effects of pressure on the limits of flammability of combustible-inert-air mixtures. One such set of data is summarized in figure 36, which gives the limits of flammability of natural gas (85 pct methane+15 pct ethane) nitrogen-air at 26° C and 0, 500, 1,000 and 2,000 psig (*105*). Similar data are given for ethane-carbon dioxide-air (fig. 37) and ethane-nitrogen-air (fig. 38) (*121*), and for propane-carbon dioxide-air (fig. 39) and propane-nitrogen-air (fig. 40) (*122*). Minimum oxygen requirements for flame propagation (min O_2) through natural gas-nitrogen-air, ethane-nitrogen-air, and propane-nitrogen-air at atmospheric and elevated pressures and 26° C are summarized in figure 41. The minimum O_2 values in volume-percent are related to pressure as follows:

for natural gas:

$$\text{Min. } O_2 = 13.98 - 1.68 \log P; \qquad (43)$$

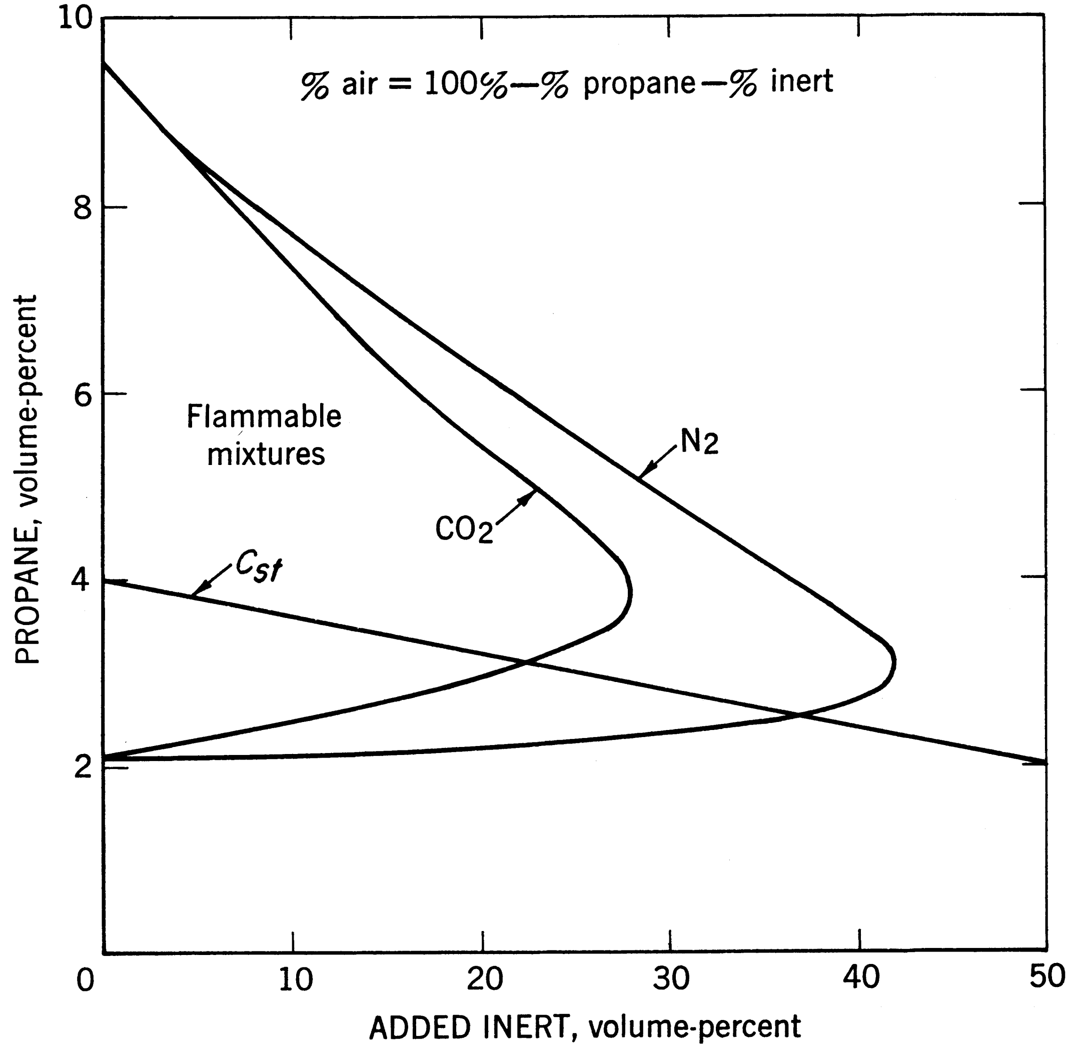

FIGURE 30.—Limits of Flammability of Propane-Carbon Dioxide-Air and Propane-Nitrogen-Air Mixtures at 25° C and Atmospheric Pressure.

for ethane:

$$\text{Min. } O_2 = 12.60 - 1.36 \log P; \text{ and} \qquad (44)$$

for propane:

$$\text{Min. } O_2 = 13.29 - 1.52 \log P; \qquad (45)$$

where P is the initial pressure in psia.

The lower limit of flammability of any mixture of the paraffin hydrocarbons can be calculated by Le Chatelier's law (*40*, *129*, *235*):

$$L = \frac{100}{\sum_{i=1}^{n} \frac{C_i}{L_i}}, \quad \sum_{i=1}^{n} C_i = 100 \qquad (46)$$

where C_i and L_i are the percentage composition and lower limit, respectively, of the i^{th} combustible in the mixture. For example, a mixture containing 80 volume-percent methane, 15 volume-percent ethane and 5 volume-percent propane has a lower limit in air at 25° C and atmospheric pressure of:

$$L_{25°} = \frac{100}{\frac{80}{5.0} + \frac{15}{3.0} + \frac{5}{2.1}} = 4.3 \text{ vol pct.} \qquad (47)$$

Liquid mixtures can be treated in the same way if the relative escaping tendencies of the various components are known. Since the paraffin hydrocarbons obey Raoult's law (*143*), the partial pressure of each component can be calculated as follows:

$$p_i = p_o N_i \qquad (48)$$

where p_i is the vapor pressure of the i^{th} com-

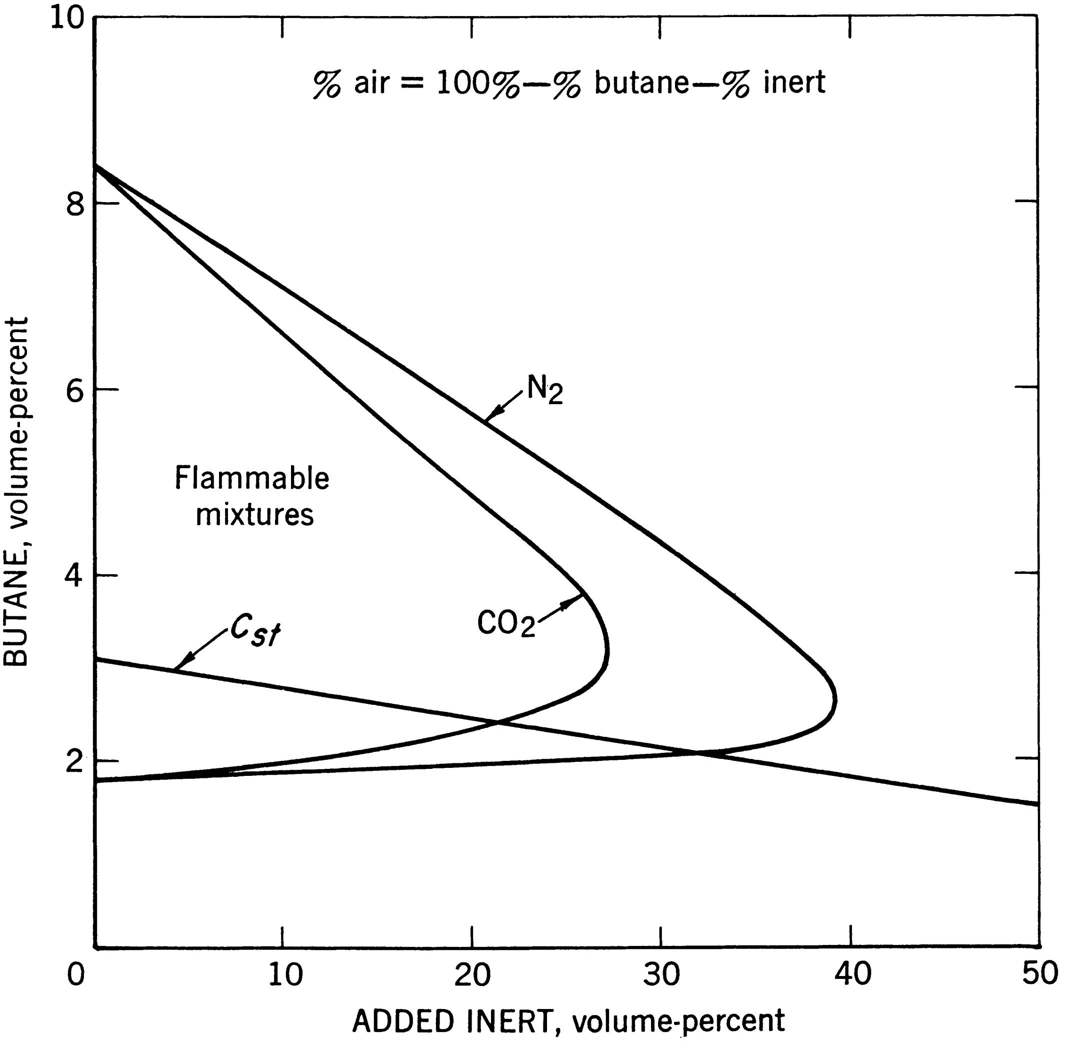

FIGURE 31.—Limits of Flammability of Butane-Carbon Dioxide-Air and Butane-Nitrogen-Air Mixtures at 25° C and Atmospheric Pressure.

ponent in the blend, p_0 is the vapor pressure of the pure component and N_i is its mole fraction in the solution. This procedure has been used to calculate the lower temperature limits of decane-dodecane blends in air (fig. 42). The vapor pressures of decane and dodecane and the calculated low temperature limits are given by solid lines and four experimental values by circles.

Autoignition

Two types of autoignition data are obtained depending upon whether the objective is to cause or to prevent the ignition of a combustible in air. The first type are usually obtained at high temperatures, where the ignition delay is relatively short. Typical of these are the data of Mullins (*153*), Brokaw and Jackson (*15, 90*), Ashman and Büchler (*6*), and Kuchta, Lambiris, and Zabetakis (*127*). These are not normally used for safety purposes, unless there is some assurance that the contact time of combustible and air is less than the ignition delay at the temperature of the hot zone. The minimum autoignition temperature (AIT) is usually the quantity of interest in safety work, especially when combustible and air can remain in contact for an indefinite period.

Some AIT values for paraffin hydrocarbons in air obtained by Setchkin in a 1-liter spherical Pyrex flask (*194*) and by Zabetakis, Furno, and Jones in a 200 cc Pyrex Erlenmeyer flask (*237*) are given in table 4. Interestingly enough, experiments conducted in these and other flasks generally indicate that flask shape and size are important in determining the AIT. The AIT data obtained in the 200 cc flask may

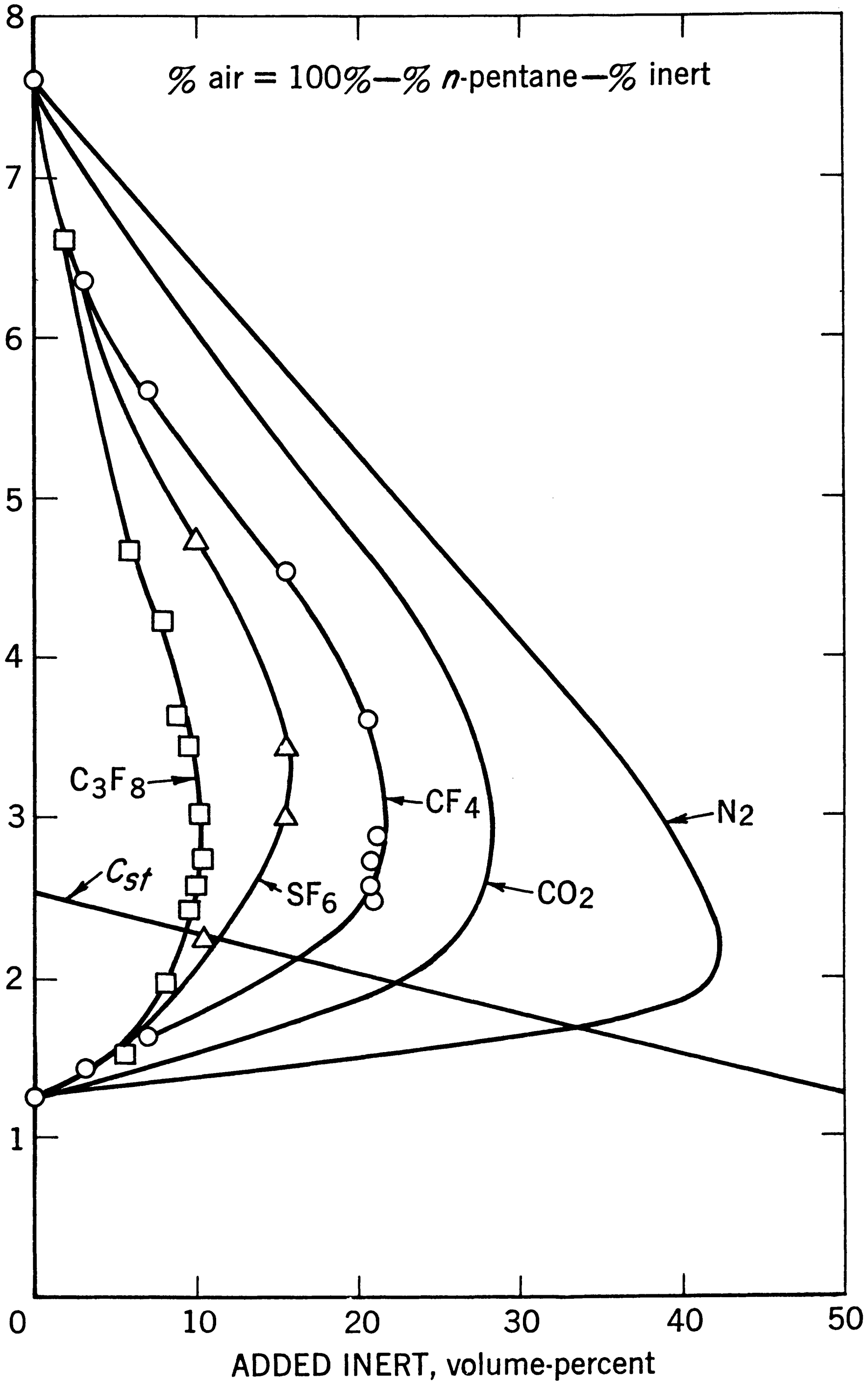

FIGURE 32.—Limits of Flammability of Various *n*-Pentane-Inert Gas-Air Mixtures at 25° C and Atmospheric Pressure.

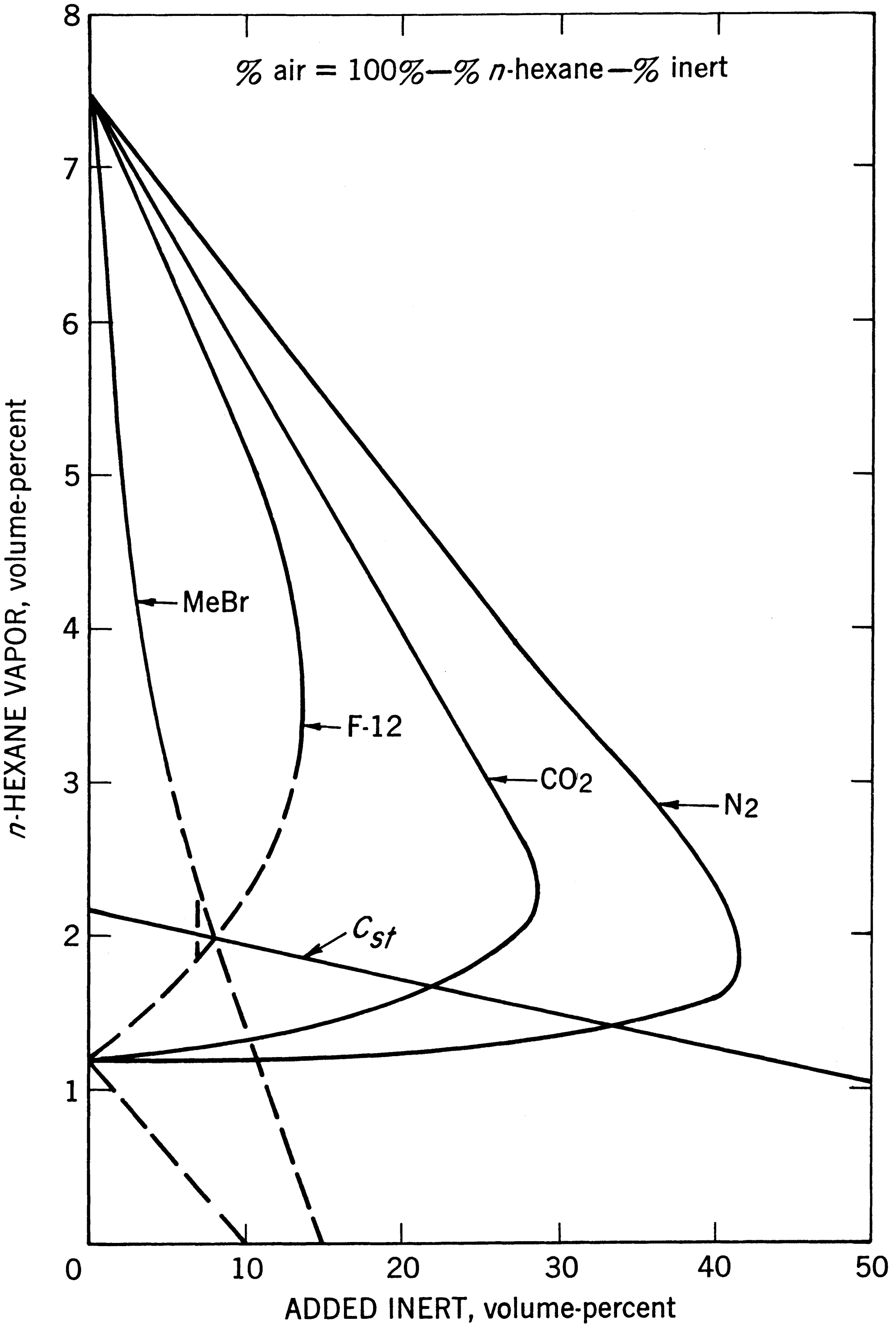

FIGURE 33.—Limits of Flammability of Various *n*-Hexane-Inert Gas-Air Mixtures at 25° C and Atmospheric Pressure.

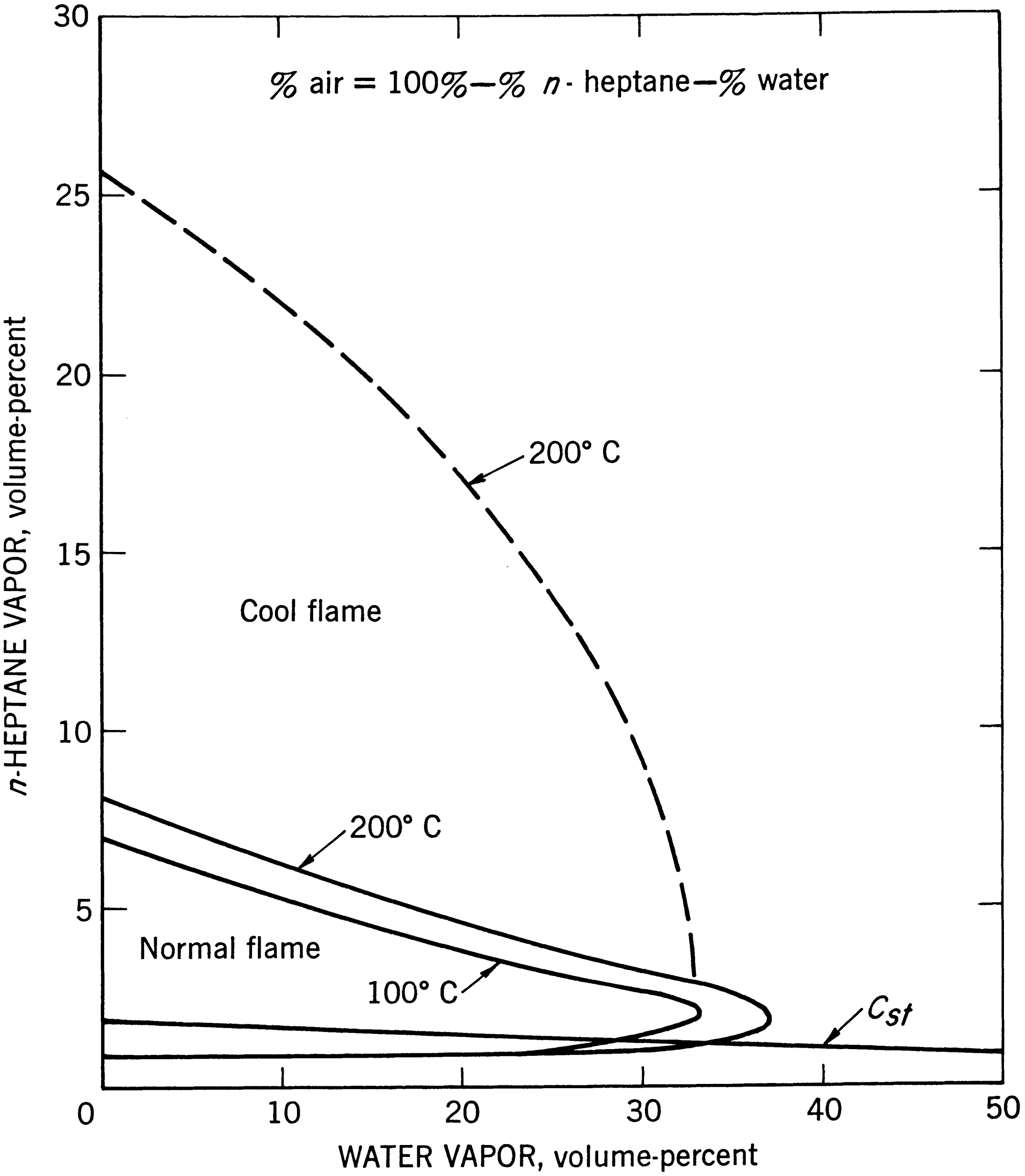

FIGURE 34.—Limits of Flammability of *n*-Heptane-Water Vapor-Air Mixtures at 100° and 200° C and Atmospheric Pressure.

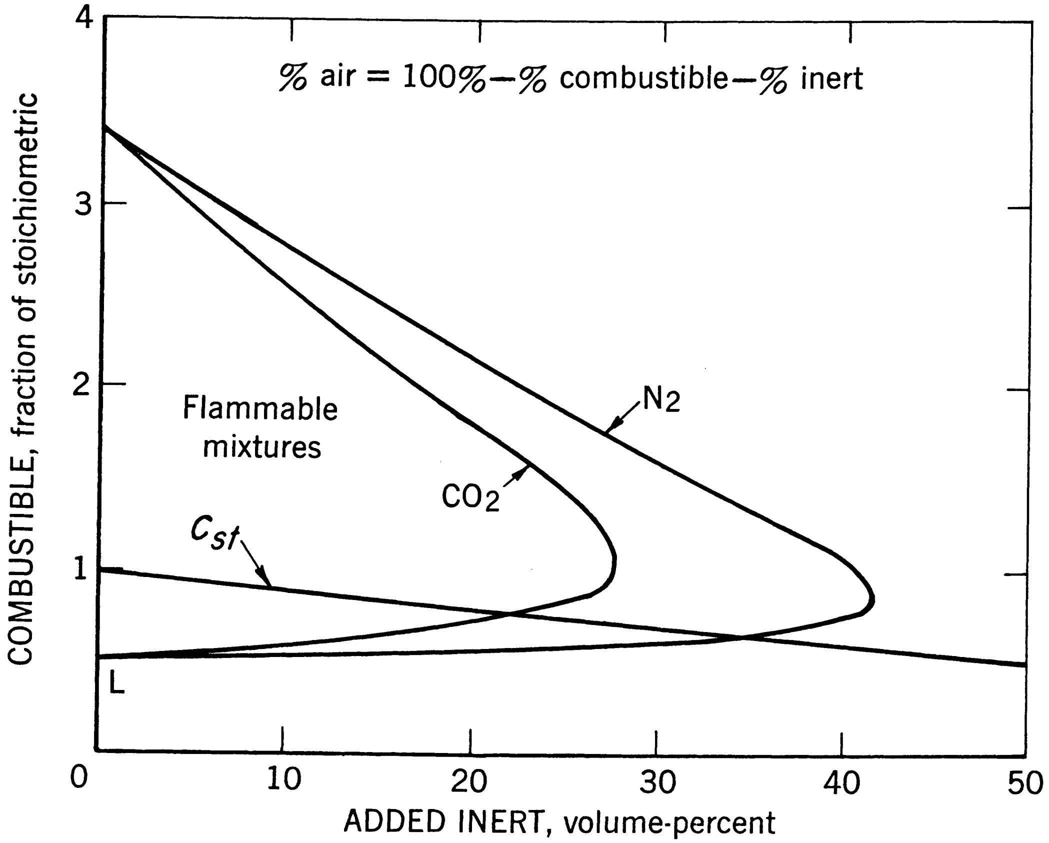

FIGURE 35.—Approximate Limits of Flammability of Higher Paraffin Hydrocarbons (C_nH_{2n+2}, $n \geq 5$) in Carbon Dioxide-Air and Nitrogen-Air Mixtures at 25° C and Atmospheric Pressure.

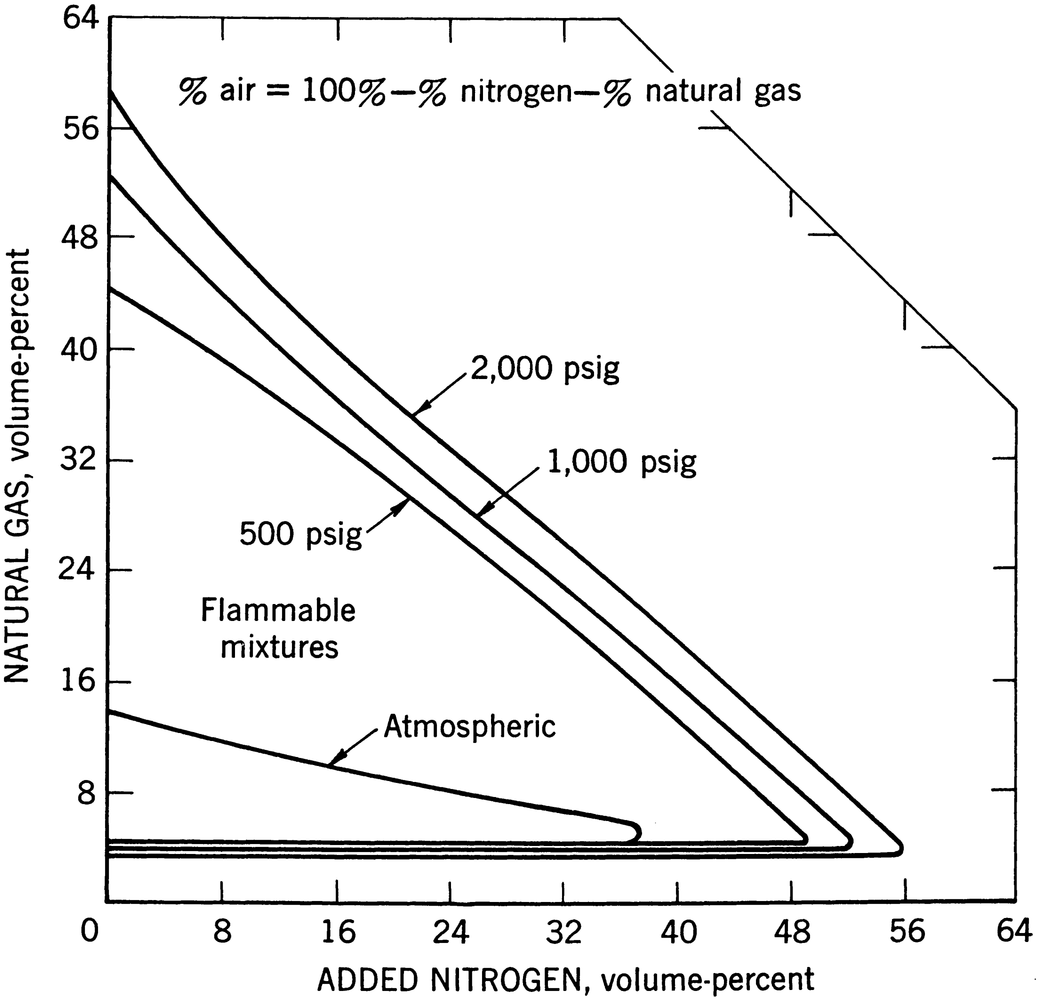

Figure 36.—Effect of Pressure on Limits of Flammability of Natural Gas-Nitrogen-Air Mixtures at 26° C.

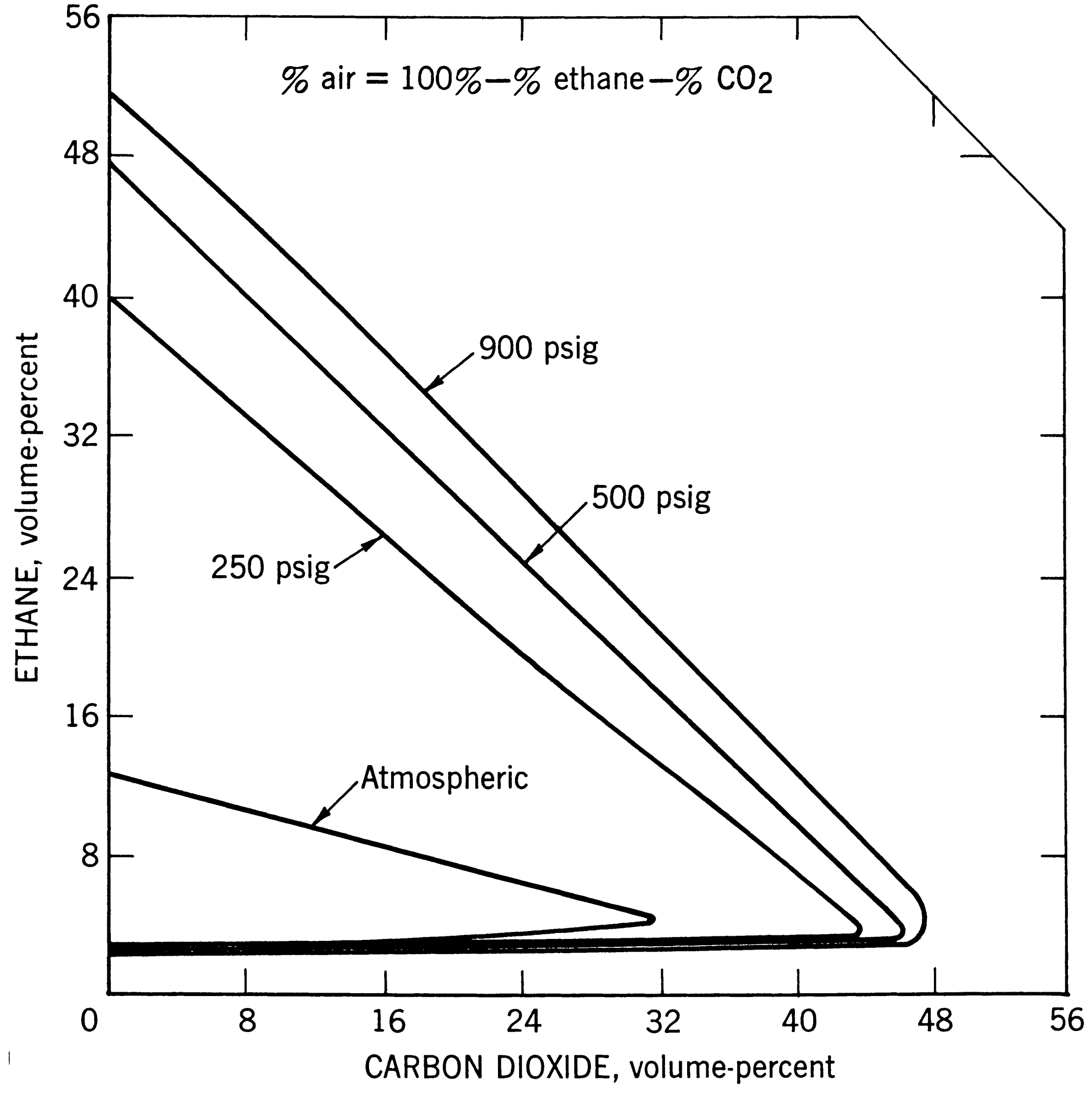

Figure 37.—Effect of Pressure on Limits of Flammability of Ethane-Carbon Dioxide-Air Mixtures at 26° C.

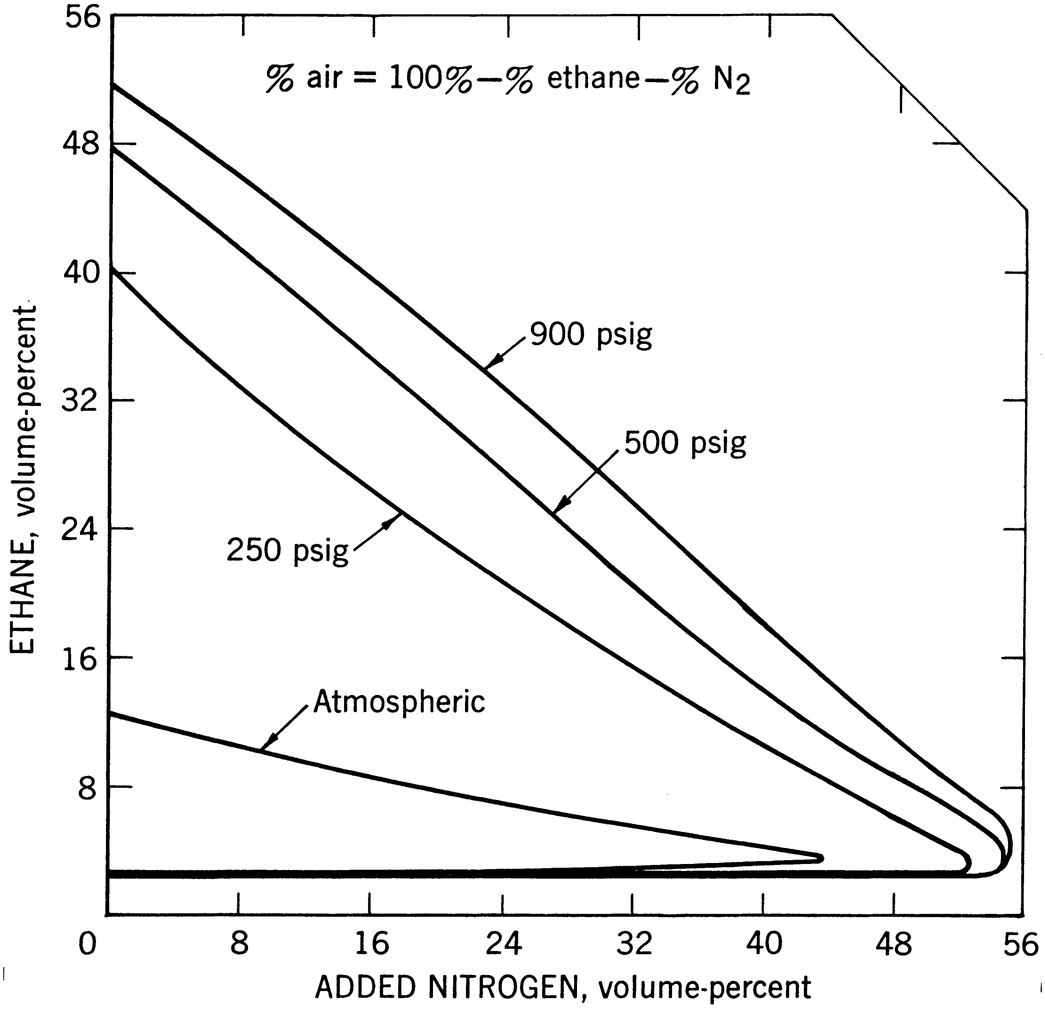

FIGURE 38.—Effect of Pressure on Limits of Flammability of Ethane-Nitrogen-Air Mixtures at 26° C.

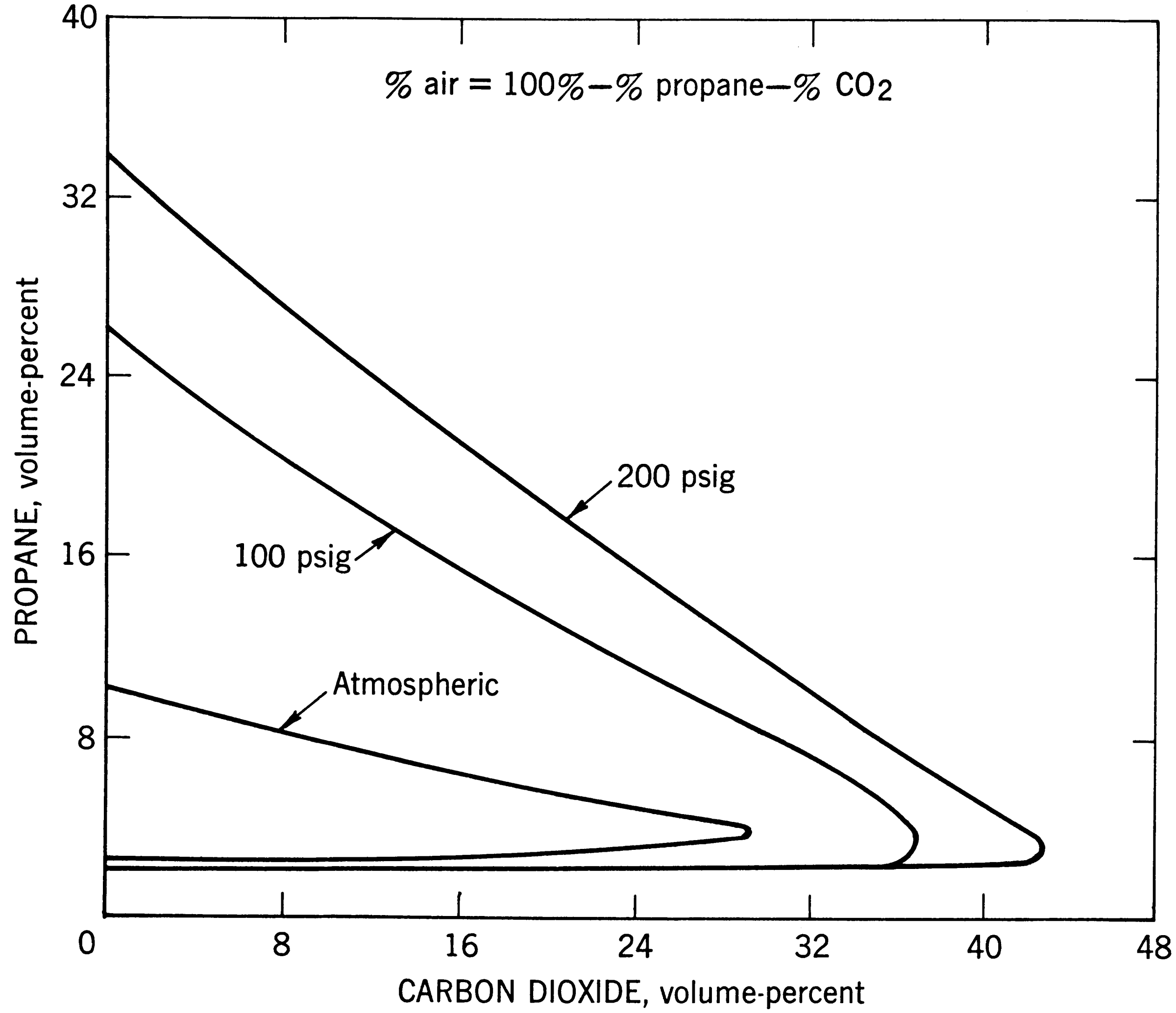

Figure 39.—Effect of Pressure on Limits of Flammability of Propane-Carbon Dioxide-Air Mixtures.

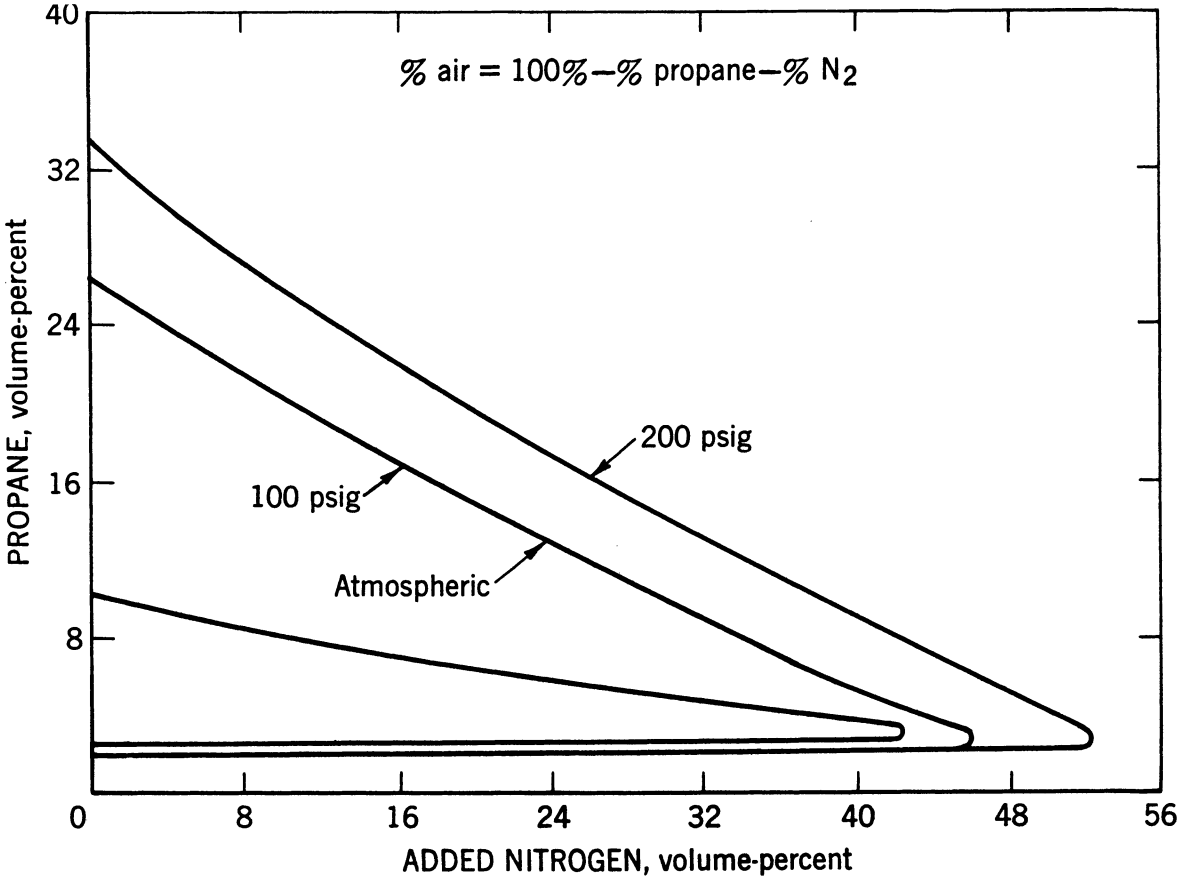

Figure 40.—Effect of Pressure on Limits of Flammability of Propane-Nitrogen-Air Mixtures.

be correlated with molecular structure by plotting them against the average carbon chain length defined as

$$L_{ave}=\frac{2\sum_{i}^{n} g_i N_i}{M(M-1)}, \qquad (49)$$

where g_i is the number of possible chains each containing N_i carbon atoms and M is the number of methyl (—CH_3) groups. For example, n-nonane and 2,2,3,3-tetramethyl pentane each have 9 carbon atoms, but the former has 2 methyl groups and the latter has 6. The former has only one chain of 9 carbon atoms with a methyl group on each end, and the latter has a maximum of 4 chains with 3 carbon atoms, 8 chains with 4 carbon atoms, and 3 chains with 5 carbon atoms. Thus, *n*-nonane has an average chain length of 9 and 2,2,3,3-tetramethyl pentane has an average of 3.9. The more highly branched a combustible is, the higher its ignition temperature will be. Minimum autoignition temperatures of 20 paraffins were plotted as ordinate against the average chain length as abscissa (fig. 43). The data fall into two regions—a high-temperature region in which the AIT is greater than 400° C and a low temperature region in which the AIT is less than 300° C. These regions coincide with those of Mulcahy who found that oxidation proceeds by one of two different mechanisms (*152*), and by Frank, Blackham, and Swarts (*60*). The AIT values of combustibles in the first region are normally much more sensitive to the oxygen concentration of the oxidizing atmosphere and to the spray injection pressure than are the combustibles in the second region. Unfortunately, the available consistent AIT data about the effects of oxygen concentration and injection pressure are too meager to permit a detailed comparison.

The physical processes (*206*) and reactions that lead to autoignition are of interest in any detailed study of this ignition process. Salooja (*184*), Terao (*207*), Affens, Johnson and Carhart (*1*, *2*), and others have studied the autoignition of various hydrocarbons in an effort to determine the mechanisms that lead to the ignition reaction.

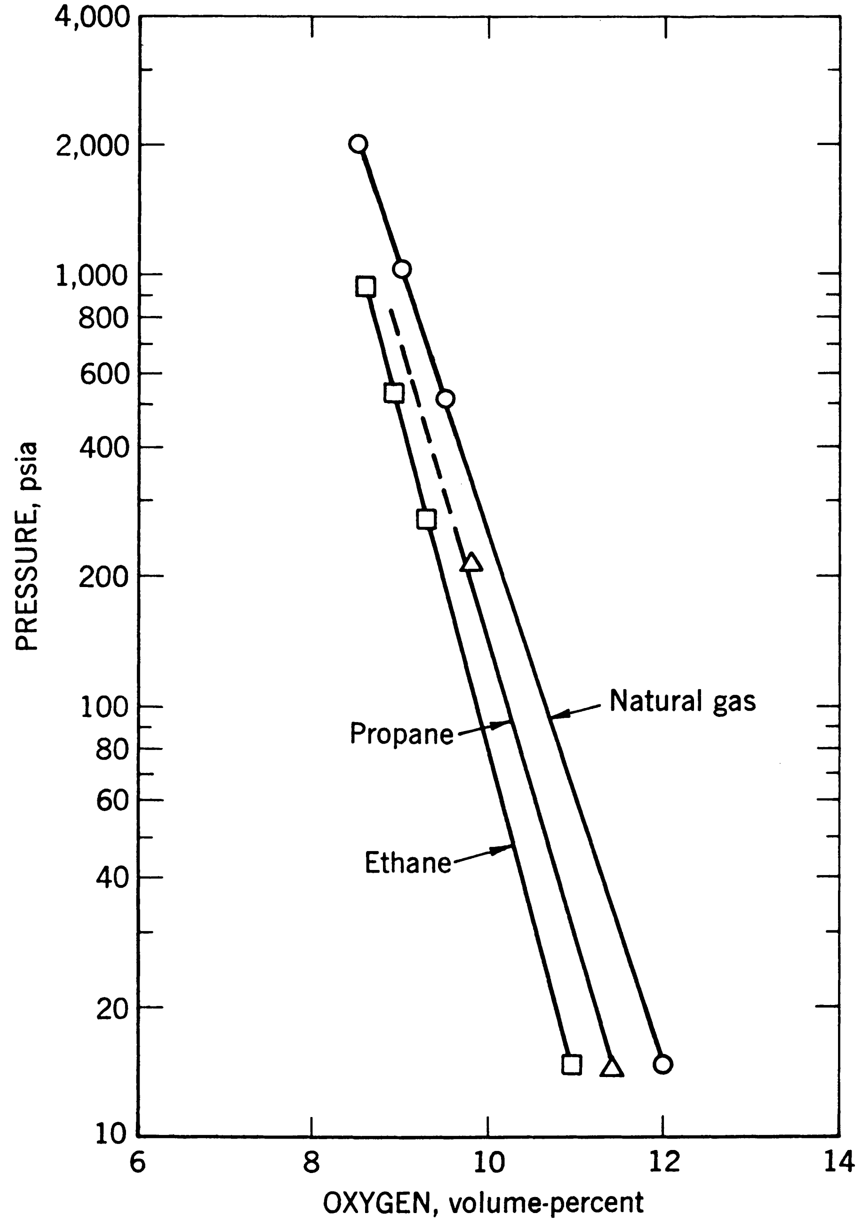

FIGURE 41.—Effect of Pressure on Minimum Oxygen Requirements for Flame Propagation Through Natural Gas-Nitrogen-Air, Ethane-Nitrogen-Air, and Propane-Nitrogen-Air Mixtures at 26° C.

An increase in pressure generally decreases the AIT of a combustible in a given oxidant. For example, the AIT of a natural gas in air decreased from 530° C at 1 atmosphere to 240° C at 610 atmospheres (9,000 psig) (*78*). The AIT's of several hydrocarbons were found to obey Semenov's equation over a limited pressure range (*248*):

$$\log \frac{P}{T} = \frac{A}{T} + B \qquad (50)$$

where T is the AIT at an initial pressure P, and A and B are constants. Accordingly, the AIT values obtained at atmospheric pressure should not be used to assess ignition hazards at high pressures.

Burning Rate

The burning velocities, S_u, of various hydrocarbons have been measured by numerous investigators in air and other oxidants (*68, 131*). At one atmosphere and 26° C, the burning

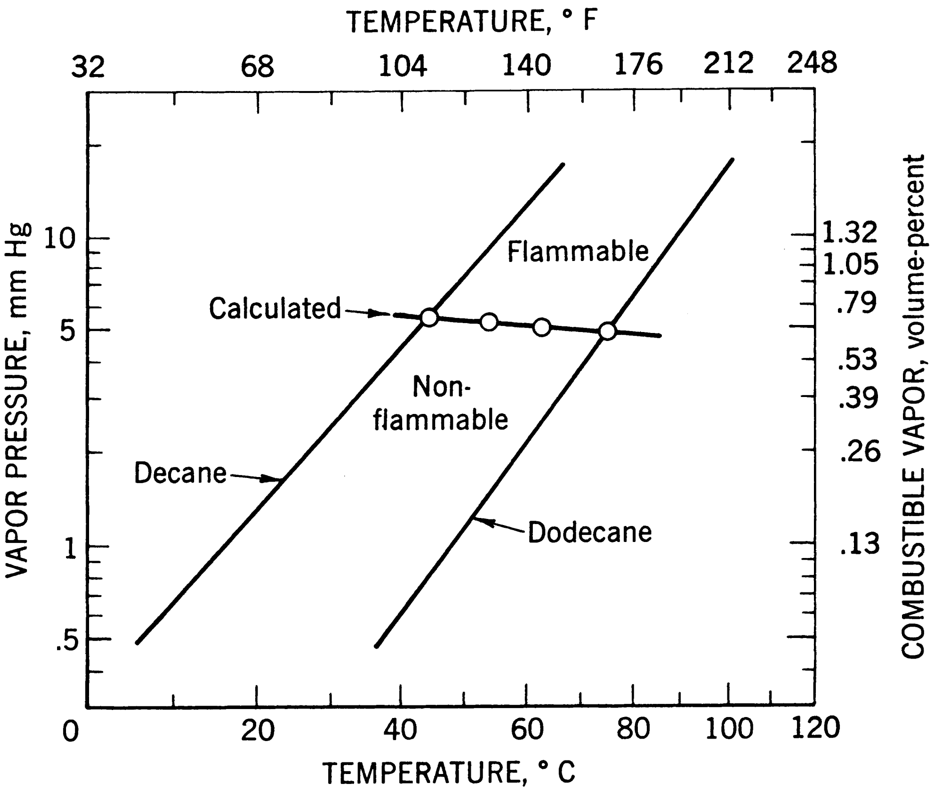

FIGURE 42.—Low-Temperature Limit of Flammability of Decane-Air, Dodecane-Air and Decane-Dodecane-Air Mixtures (Experimental Points 0).

velocities of paraffin hydrocarbons in air range from a few centimeters a second near the limits to about 45 cm/sec near the stoichiometric mixture composition; much higher values are obtained with paraffin hydrocarbon-oxygen mixtures. Figure 44 gives results obtained by Gibbs and Calcote for four paraffin hydrocarbon-air mixtures at atmospheric pressure and room temperature (*68*). The data are expressed in terms of the stoichiometric composition, C_{st}; burning velocities are given for the composition range from 0.7 to 1.4 C_{st}. These authors have presented similar data for combustibles at 25° and 100° C. Figure 45 gives results obtained by Singer, Grumer, and Cook for three paraffin hydrocarbon-oxygen mixtures at atmospheric pressure and room temperature in the range from 0.3 to 1.4 C_{st} (*198*). Burning velocities range from a low of 125 cm/sec to a high of 425 cm/sec; these values are considerably greater than those obtained in air. A change in either temperature or pressure will alter S_u for a particular mixture. For example, Agnew and Graiff (*3*) found that an increase in pressure causes S_u of stoichiometric methane-air and propane-air mixtures to decrease in the pressure range from 0.5 to 20 atmospheres (fig. 46); S_u of stoichiometric methane-oxygen mixtures, however, increased in the pressure range from 0.2 to 2 atmospheres (fig. 47). The effect of temperature is more consistent. For a given pressure and mixture composition, an increase in temperature raises S_u. In general:

$$S_u = A + BT^n \qquad (51)$$

where A and B are constants, T is the temperature and n is a constant for a particular mixture composition. Dugger, Heimel, and Weast (*50, 51, 81*) obtained a value of 2.0 for n for some of the paraffin hydrocarbons (fig. 48). The burning velocity of the stoichiometric methane-air and methane-oxygen mixtures given in figures 44 and 45 do not agree with the values given in figures 46 to 48 but, in each case, the burning velocity data are internally consistent.

The actual flame speed relative to a fixed observer may be much greater than S_u since the burned gases, if not vented, will expand and impart a motion to the flame zone. If detonation occurs, the reaction speed increases markedly. For example, figure 49 gives the Kogarko data on velocities with which a detonation wave propagates through various methane-air mixtures at atmospheric pressure in a 30.5 cm-diameter pipe (*125*). Similar results have been obtained by Gerstein, Carlson, and Hill at low pressures with natural gas-air mixtures (*67*).

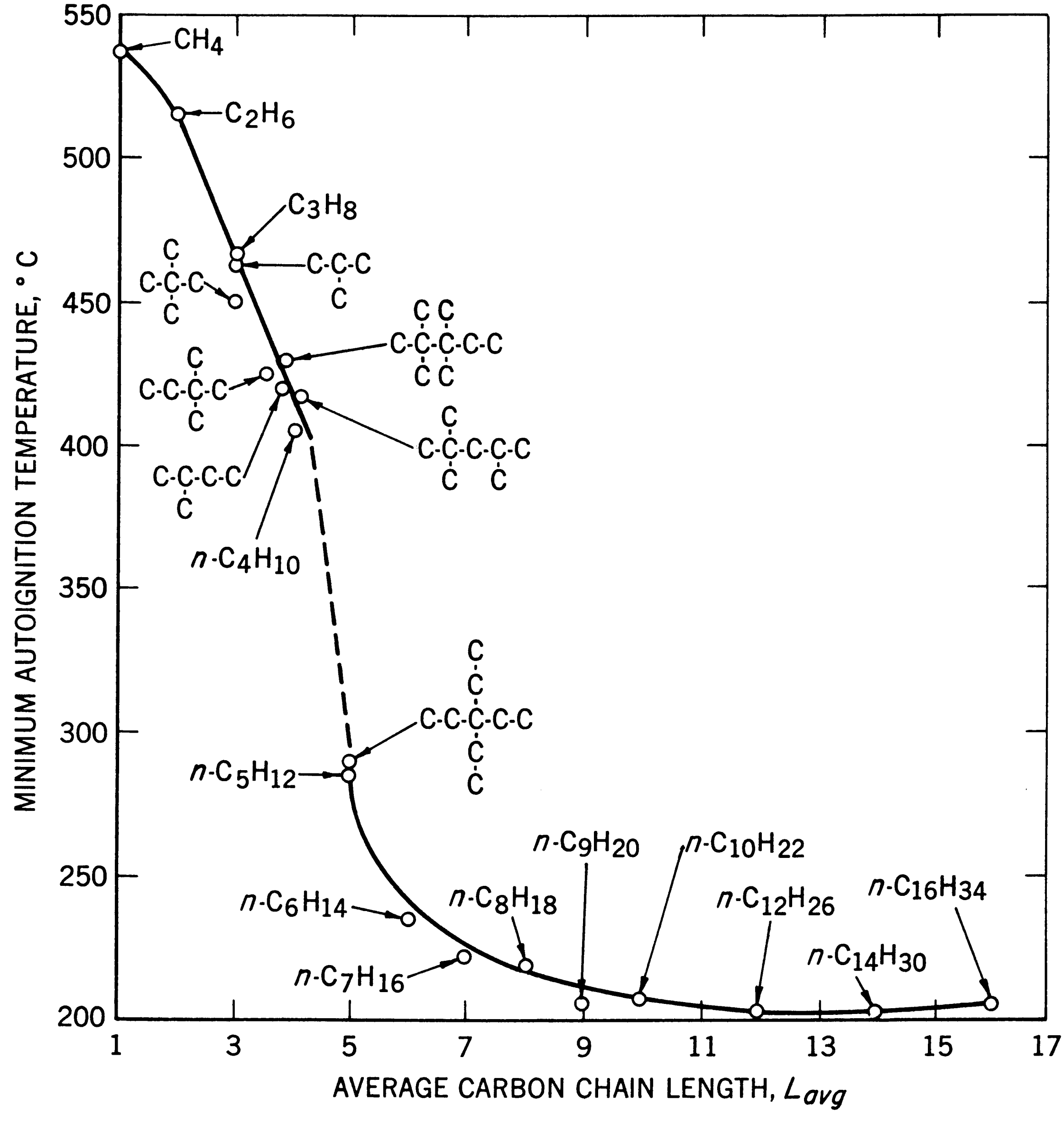

FIGURE 43.—Minimum Autoignition Temperatures of Paraffin Hydrocarbons in Air as a Function of Average Carbon Chain Length.

In each case, powerful initiators were required to obtain a detonation in relatively large pipes. The energy requirements for ignition are reduced if oxygen is used as the oxidant in place of air. Further, the detonation velocity increases as the oxygen content of the atmosphere is increased. Detonation velocities obtained by Morrison for methane, ethane, propane, butane, and hexane in oxygen are given in figure 50 (*150*); similar data obtained by Wayman and Potter are given in figure 51 for n-heptane-nitrogen-white fuming nitric acid vapors (*219*). Of principal interest here is the magnitude of the detonation velocity; even in air, this velocity is so great that pressure waves are not sent out ahead of the detonation front. Thus, pressure detectors that are useful in explosion prevention with deflagration waves are useless with detonations.

With liquid fuels, the burning rate depends in part on the rate of vaporization and on the pool size. Burgess, Strasser, and Grumer (*20*) have shown that the liquid regression rate v is given by

$$v=v_{\infty}(1-e^{-Kd}), \qquad (52)$$

where v_{∞} is the value of v in large pools, K is a constant, and d is the pool diameter. They

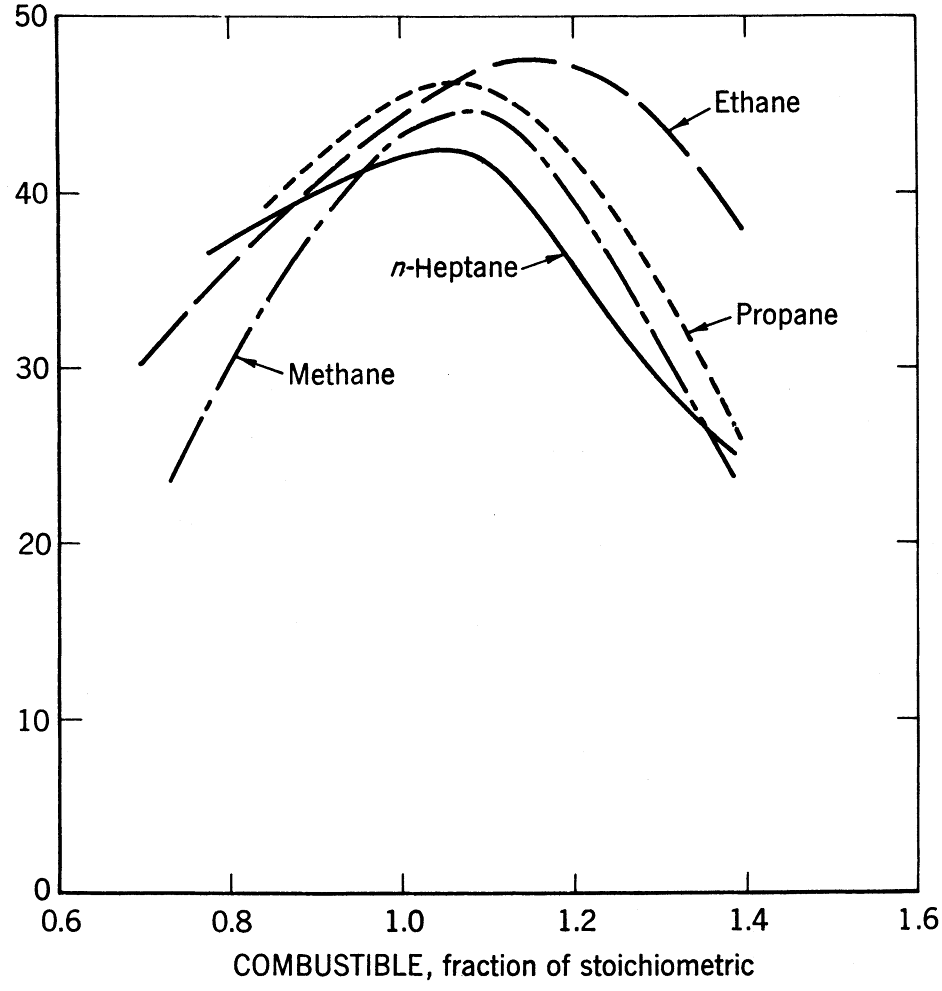

FIGURE 44.—Burning Velocities of Methane-, Ethane-, Propane-, and *n*-Heptane Vapor-Air Mixtures at Atmospheric Pressure and Room Temperature.

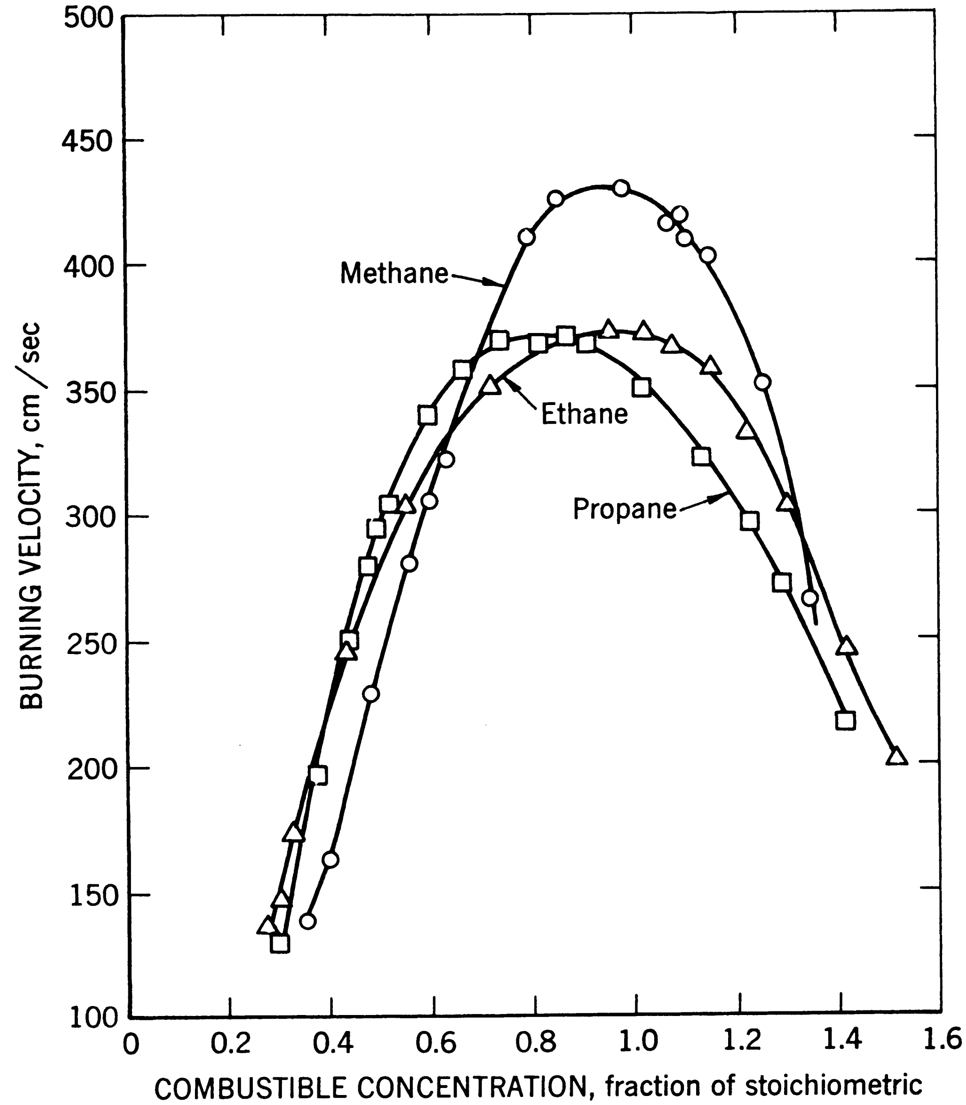

FIGURE 45.—Burning Velocities of Methane-, Ethane-, and Propane-Oxygen Mixtures at Atmospheric Pressure and Room Temperature.

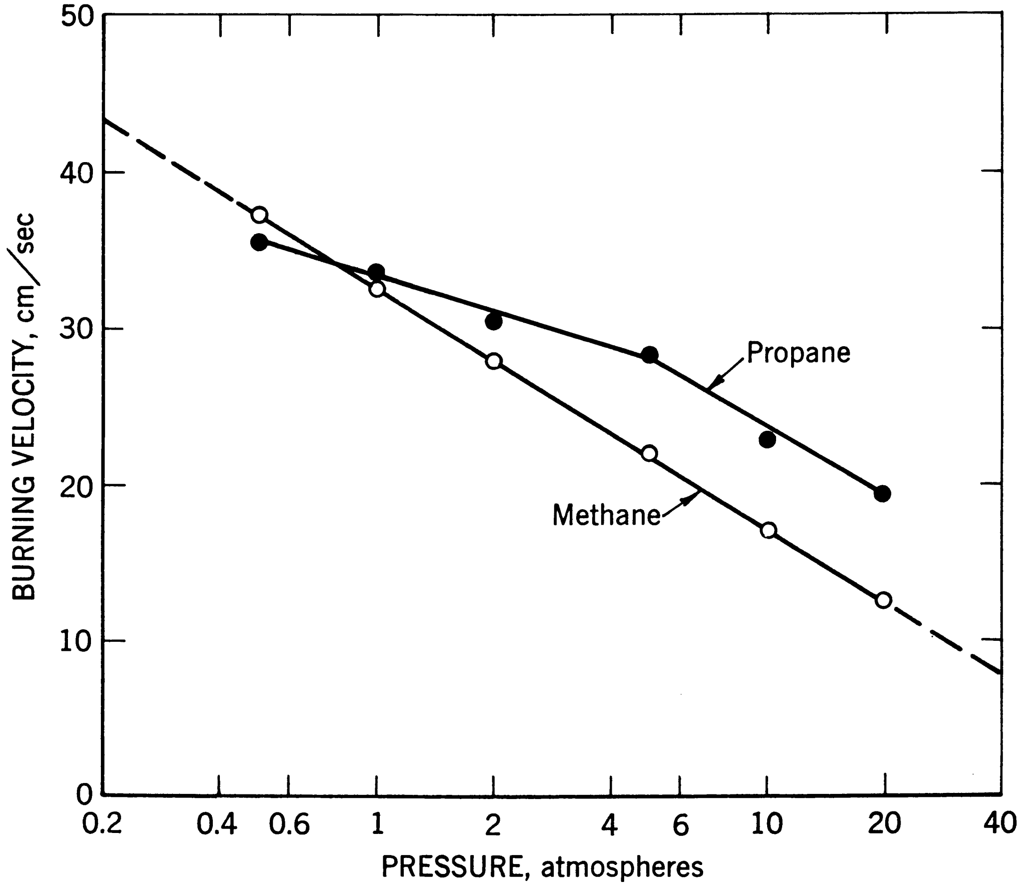

FIGURE 46.—Variation in Burning Velocity of Stoichiometric Methane-Air and Propane-Air Mixtures With Pressure at 26° C.

expressed v_∞ as:

$$v_\infty = 0.0076 \left(\frac{\text{net heat of combustion, } \Delta H_c}{\text{sensible heat of vaporization, } \Delta H_v} \right) \text{ cm/min.} \quad (53)$$

Figure 52 gives a summary of the v_∞ values for a number of combustibles, including several paraffin hydrocarbons (*21*). Of special significance here is that $\Delta H_c/\Delta H_v$ is nearly constant (about 100) for the paraffin hydrocarbons, so that their linear burning rates in large pools are all about ¾ cm per minute.

UNSATURATED HYDROCARBONS

(C_nH_{2n}, C_nH_{2n-2})

Limits in Air

The molecular weight, specific gravity, and other properties of the hydrocarbons considered here are included in table 7. At room temperature and atmospheric pressure, the lower limits of flammability of the olefins (C_nH_{2n}) excluding ethylene fall in the range from 46 to 48 mg combustible vapor per liter of air (0.046 to 0.048 oz combustible vapor per cubic foot of air).

The effect of temperature on the lower limit of flammability of ethylene in air at atmospheric pressure, assuming a constant limit flame temperature, is shown by the curve labeled "Upward propagation of flame" in figure 53. Unfortunately, only downward flame propagation data are available over an extended temperature range (*222*); these are included in figure 53. As in the case of similar data obtained with methane, these define a straight line parallel to the "Constant flame temperature," "Upward propagation of flame" line. Again, the modified Burgess-Wheeler law, equation (33), gives a variation in lower limit with temperature that is close to that given by the "Constant flame temperature" line, so that either could be used at temperatures below the AIT of ethylene (490° C). Moreover, as the limit flame temperatures of olefins are not too

TABLE 7.—*Properties of unsaturated hydrocarbons*

Combustible	Formula	M	Sp gr (Air=1)	C_{st} in air (vol pct)	Net ΔH_c $\left(\frac{\text{Kcal}}{\text{mole}}\right)$	Lower limit in air				Upper limit in air			
						L_{25} (vol pct)	$\frac{L_{25}}{C_{st}}$	L $\left(\frac{\text{mg}}{1}\right)$	Ref.	U_{25} (vol pct)	$\frac{U_{25}}{C_{st}}$	U $\left(\frac{\text{mg}}{1}\right)$	Ref.
Ethylene	C_2H_4	28.05	0.97	6.53	316.2	2.7	0.41	35	(*115*)	36	5.5	700	(*26*)
Propylene	C_3H_6	42.08	1.45	4.45	460.4	2.4	.54	46	(*101*)	11	2.5	210	(*40*)
Butene-1	C_4H_8	56.10	1.94	3.37	607.7	1.7	.50	44	(1)	9.7	2.9	270	(1)
cis-Butene-2	C_4H_8	56.10	1.94	3.37	606.0	1.8	.53	46	(*40*)	9.7	2.9	270	(*40*)
Isobutylene	C_4H_8	56.10	1.94	3.37	604.1	1.8	.53	46	(*40*)	9.6	2.8	260	(*26*)
3-Methyl-butene-1	C_5H_{10}	70.13	2.42	2.72	752.3	1.5	.55	48	(*40*)	9.1	3.3	310	(*40*)
Propadiene	C_3H_4	40.06	1.38	4.97	443.7	2.6	.53	48	(2)	------	------	------	------
1,3-Butadiene	C_4H_6	54.09	1.87	3.67	576.3	2.0	.54	49	(*102*)	12	3.3	320	(*26*)

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[1] Figures compiled at Explosive Res. Center, Federal Bureau of Mines.

[2] Calculated value.

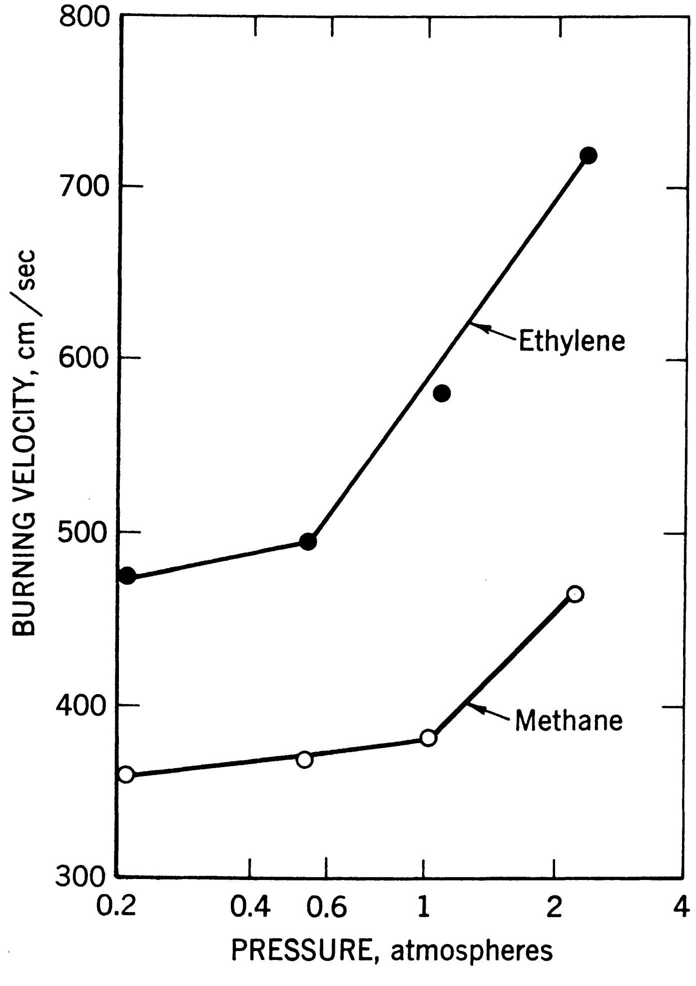

FIGURE 47.—Variation in Burning Velocity of Stoichiometric Methane- and Ethylene-Oxygen Mixtures With Pressure at 26°C.

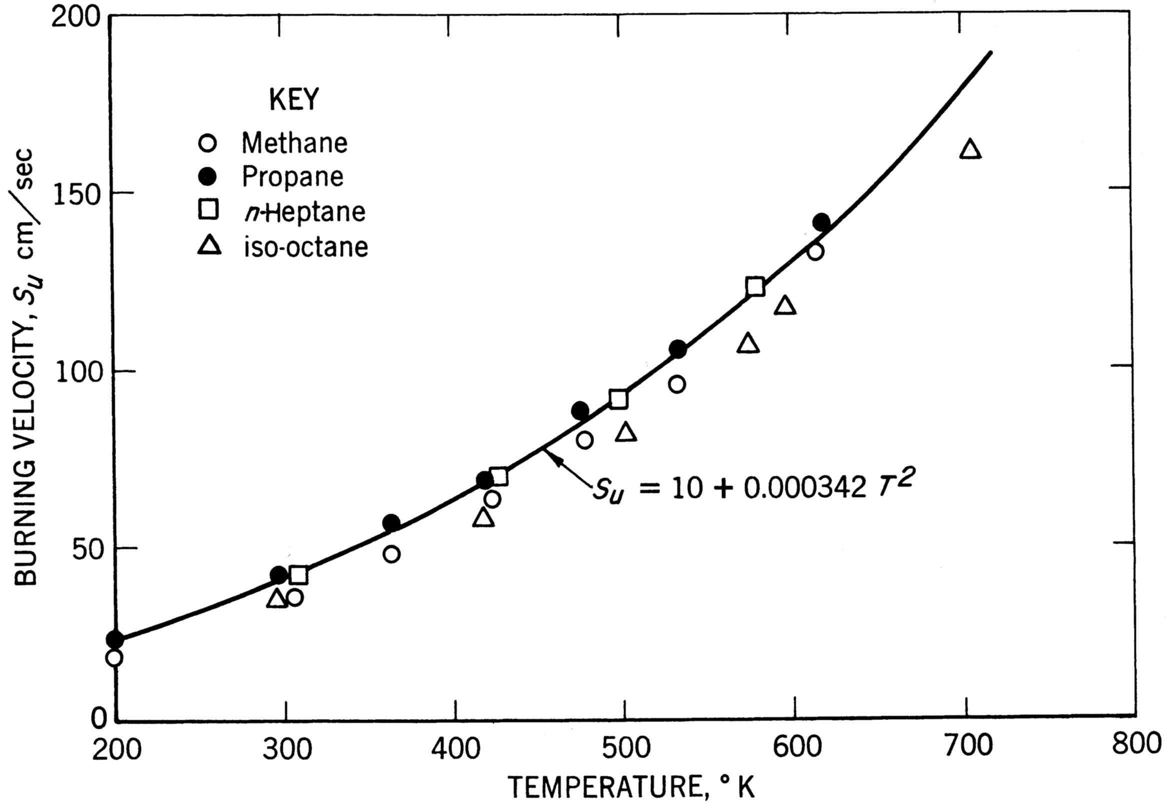

FIGURE 48.—Effect of Temperature on Burning Velocities of Four Paraffin Hydrocarbons in Air at Atmospheric Pressure.

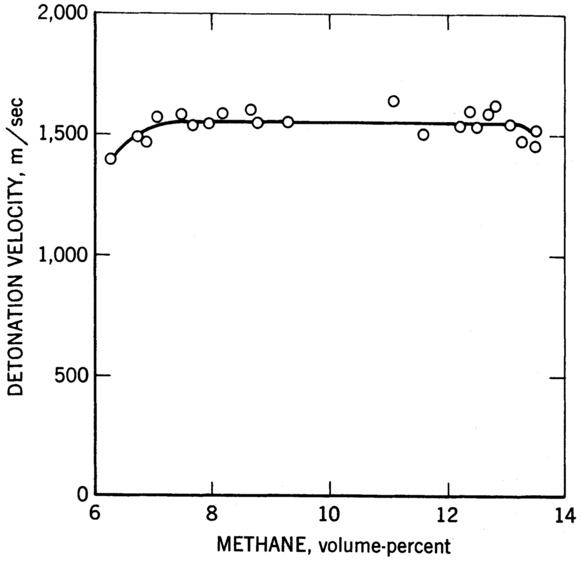

FIGURE 49.—Detonation Velocities of Methane-Air Mixtures at Atmospheric Pressure. (Initiator: 50–70 grams of amatol explosive. Pipe diameter: 30.5 cm.)

different from those of paraffin hydrocarbons, the generalized graph for $L_t/L_{25°}$ (fig. 23) can be used for these unsaturated hydrocarbons.

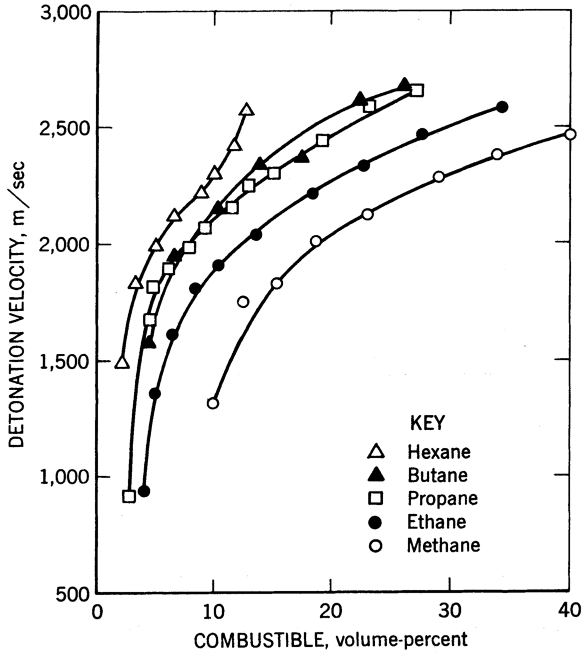

FIGURE 50.—Detonation Velocities of Methane-, Ethane-, Propane-, Butane-, and Hexane-Oxygen Mixtures at Atmospheric Pressure.

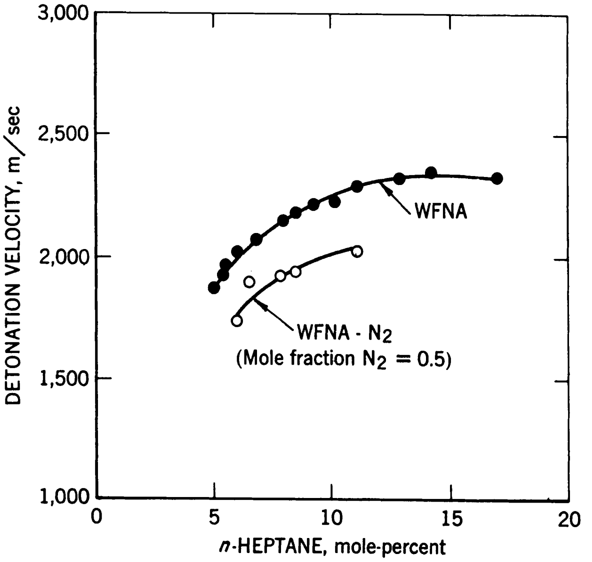

Figure 51.—Detonation Velocities of *n*-Heptane Vapor in WFNA (White Fuming Nitric Acid)-Nitrogen Gas Mixtures at Atmospheric Pressure and 400° K.

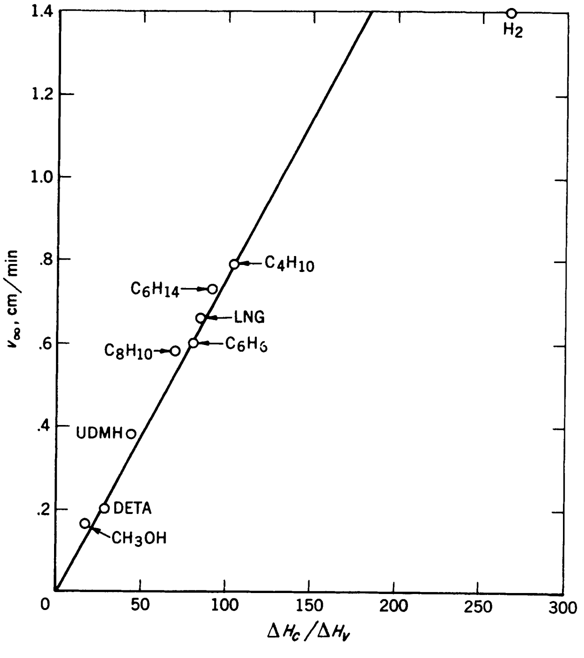

Figure 52.—Relation Between Liquid-Burning Rate (Large-Pool Diameter) and Ratio of Net Heat of Combustion to Sensible Heat of Vaporization.

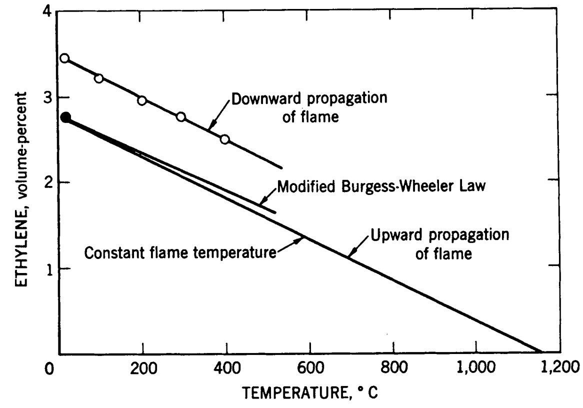

Figure 53.—Effect of Temperature on Lower Limit of Flammability of Ethylene in Air at Atmospheric Pressure.

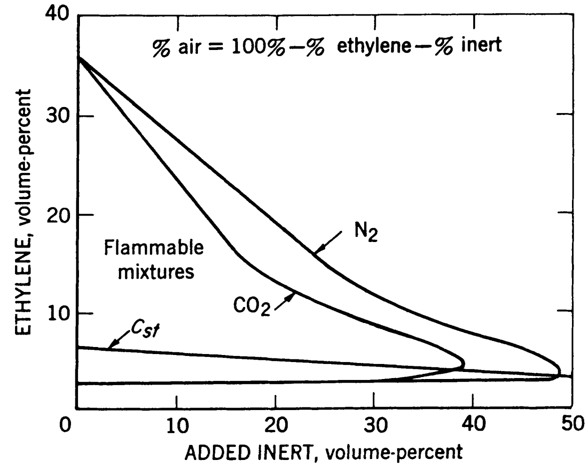

Figure 54.—Limits of Flammability of Ethylene-Carbon Dioxide-Air and Ethylene-Nitrogen-Air Mixtures at Atmospheric Pressure and 26° C.

Limits in Other Atmospheres

The limits of flammability of ethylene, propylene, isobutylene, butene-1, 3 methyl butene-1, and butadiene in various inert-air atmospheres have been determined by Jones and coworkers (*100, 101, 103*), (figs. 54–60). The first two figures are modifications of the limit-of-flammability diagrams given in (*40*); the third is essentially the same as that given in the earlier publication but includes the experimental points. The other curves were constructed from original, unpublished data obtained at the Explosives Res. Center, Federal Bureau of Mines.

Other limit-of-flammability determinations have been made in oxygen and nitrous oxide. These data are included in table 8 (*40, 100, 106*).

Autoignition

There have been few determinations of AIT's of the unsaturated hydrocarbons in air or other oxidants; the available data (*94, 116, 191*) are summarized in table 9.

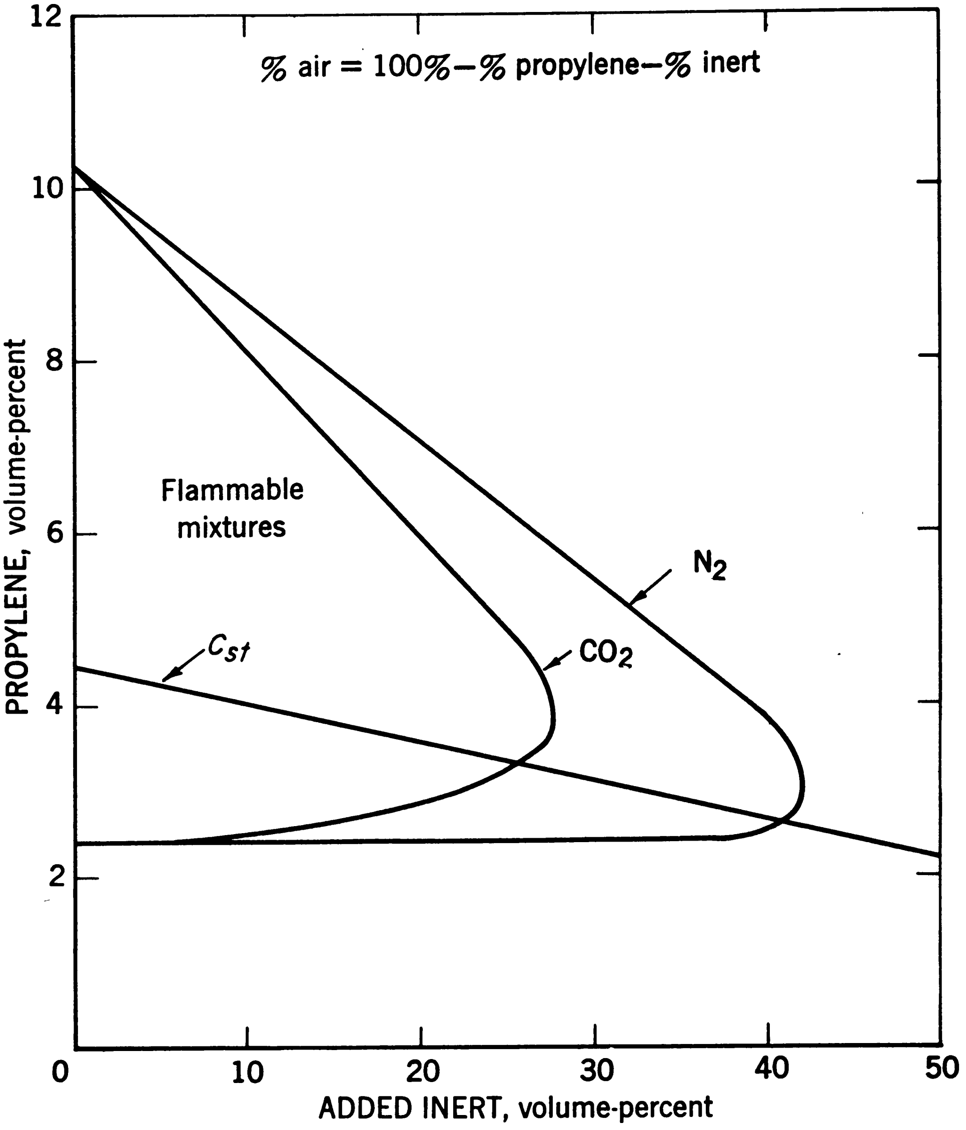

FIGURE 55.—Limits of Flammability of Propylene-Carbon Dioxide-Air and Propylene-Nitrogen-Air Mixtures at Atmospheric Pressure and 26° C.

Burning Rate

The burning velocity of ethylene has been determined in air, oxygen, and oxygen-nitrogen atmospheres by numerous investigators (*3*, *47*, *49*, *68*, *131*). In general, it is higher than the burning velocities of the paraffin hydrocarbons under the same conditions (fig. 47). Similar results are to be expected for other unsaturated hydrocarbons, although the available data are rather meager.

Stability

Many unsaturated hydrocarbon vapors can propagate flame in the absence of air at elevated temperatures and pressures; that is, they have no upper limit of flammability. These combustibles have positive heats of formation, ΔH_f (table 10) and would therefore liberate heat if decomposed to the elements carbon and hydrogen. Even more heat would be liberated if gases with a negative heat of formation—for example, methane—form from the elements. In practice, a mixture of products results upon decomposition of such combustibles. For example, a propagating decomposition reaction can be initiated in pure ethylene in a 2-inch-ID tube at 23° C and pressures as low as 750 psig, using 2 grams of guncotton. A reaction can be initiated at 21° C and pressures as low as 975 psig with 1 gram of guncotton. The decomposition products are

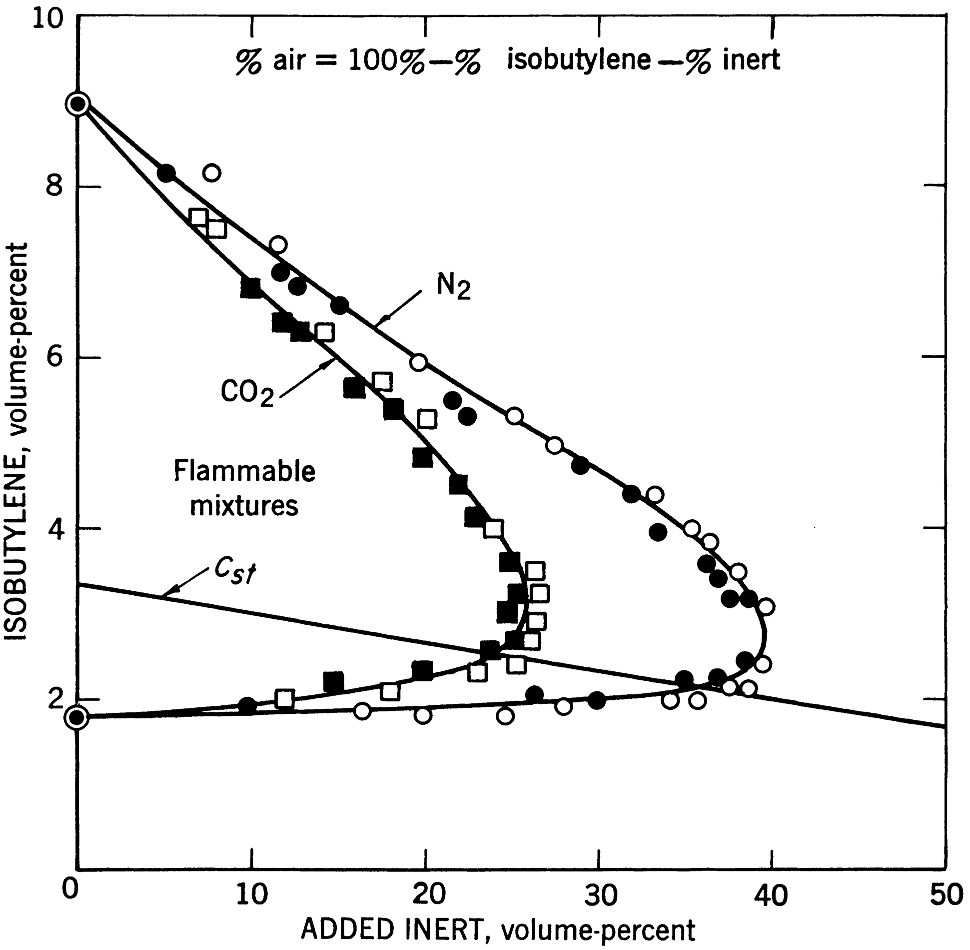

FIGURE 56.—Limits of Flammability of Isobutylene-Carbon Dioxide-Air and Isobutylene-Nitrogen-Air Mixtures at Atmospheric Pressure and 26° C.

TABLE 8.—*Limits of flammability of unsaturated hydrocarbons at atmospheric pressure and room temperature, in volume-percent combustible vapor*

(L=lower limit; U=upper limit)

Combustible	In air		In oxygen		In nitrous oxide	
	L	*U*	*L*	*U*	*L*	*U*
Ethylene	2. 7	36	2. 9	80	1. 9	40
Propylene	2. 0	11	2. 1	53	1. 4	29
Butene-1	1. 6	10	1. 7	58	-----	-----
Butene-2	1. 7	9. 7	1. 7	55	-----	-----

primarily carbon, methane, and hydrogen; approximately 30 Kcal are released per mole of ethylene decomposed. Propylene yielded similar products following explosive decomposition during compression to 4,860 atmospheres (*34*).

TABLE 9.—*Minimum autoignition temperatures of unsaturated hydrocarbons at atmospheric pressure*

Combustible	Autoignition temperature					
	In air			In oxygen		
	° C	° F	Ref.	° C	° F	Ref.
Ethylene	490	914	(*116*)	485	905	(*116*)
Propylene	458	856	(*94*)	423	793	(1)
Butene-1	384	723	(1)	310	590	(1)
Butene-2	324	615	(1)	-----	-----	-----
1,3-Butadiene	418	784	(*191*)	335	635	(*191*)

[1] Figures compiled by Explosives Res. Center, Federal Bureau of Mines.

Propadiene and butadiene also decompose readily under the action of powerful ignitors. Propadiene vapor has been decomposed in a

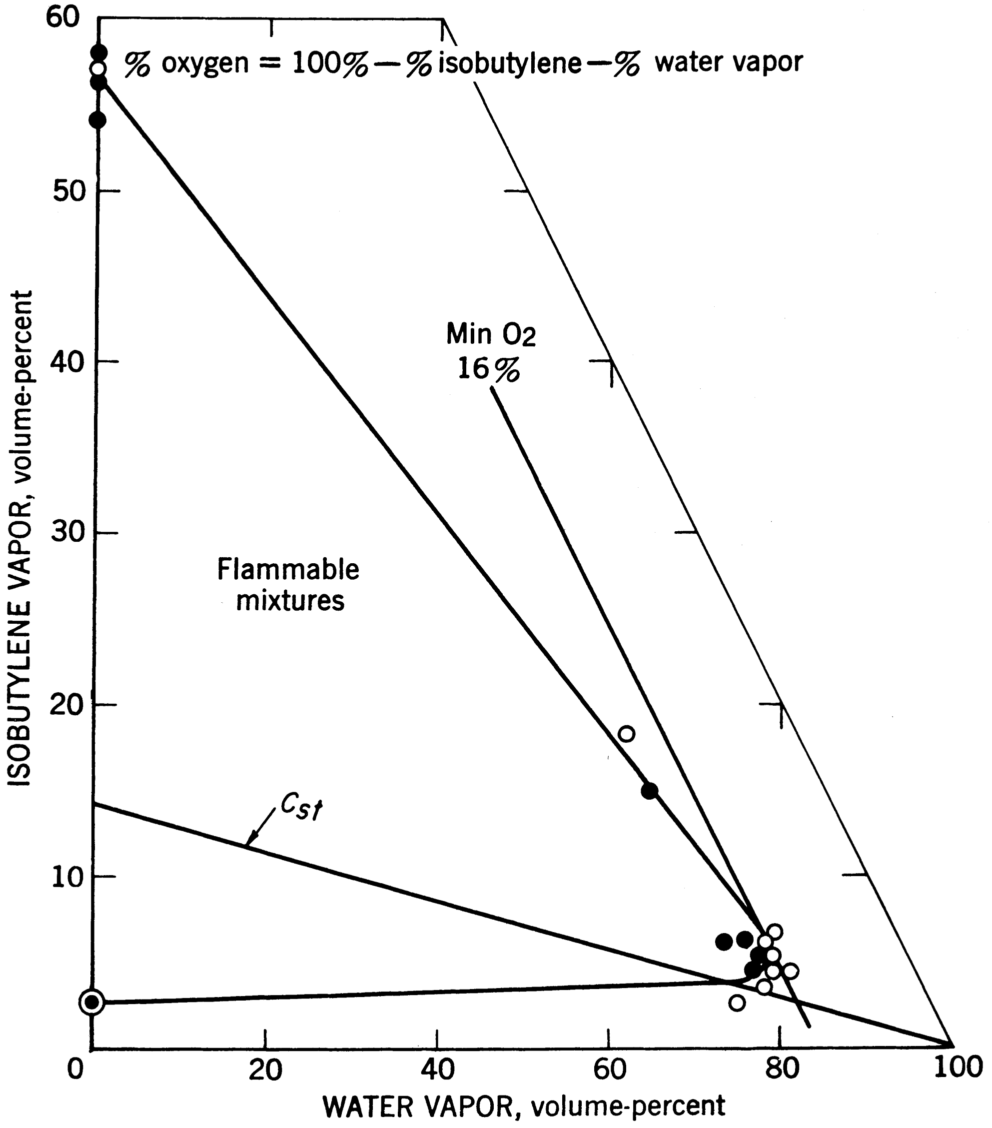

FIGURE 57.—Limits of Flammability of Isobutylene-Water Vapor-Oxygen Mixtures at 150° C and Atmosperic Pressure.

2-inch tube at 120° C and 50 psig using a platinum wire ignitor. Decomposition of butadiene in an industrial accident resulted in a "popcorn" polymer; the reaction was apparently initiated by an unstable peroxide (*4*).

TABLE 10.—*Heats of formation (Kcal/mole) of unsaturated hydrocarbons at 25° C.*

Combustible:	ΔH_f[1]
Acetylene	54. 2
Propadiene	45. 9
Methylacetylene	44, 3
1-3, Butadiene	26. 8
Ethylene	12. 5
Propylene	4. 9
1-Butene	. 3

[1] Refs. (*124, 183*).

ACETYLENIC HYDROCARBONS

(C_nH_{2n-2})

Limits in Air

Acetylene forms flammable mixtures in air at atmospheric pressure and 25° C, in a range from 2.5 to 100 volume-percent acetylene. Quenched and apparatus limited upper limits have been obtained in 1-, and 2-, and 3-inch-diameter tubes (*40*), but pure acetylene can propagate flame at atmospheric pressure in tubes with diameters of at least 5 inches. Sargent has summarized available data on initial pressure requirements for deflagration and

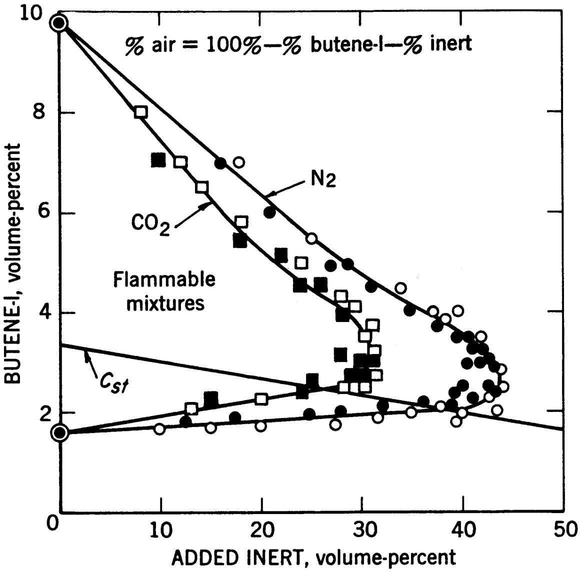

FIGURE 58.—Limits of Flammability of Butene-1-Carbon Dioxide-Air and Butene-1-Nitrogen-Air Mixtures at Atmospheric Pressure and 26° C.

detonation through acetylene in horizontal tubes of about .02 to 6 inches ID at 60° F. (*89*, *185*). His curves are given in figure 61, which also includes an experimental point from the data of Jones and coworkers obtained in a vertical 2-inch-diameter tube. The existence of this point, at a pressure below that given by Sargent's curve for a 2-inch tube, indicates that this curve should be used only for horizontal systems. The point labeled "Industrial explosion" was reported by Miller and Penny (*144*) and presumably refers to a deflagration. The third experimental point is discussed, along with the detonation curve, in the section on stability.

The effect of temperature on the lower limit of flammability was determined by White in a 2.5-cm tube with downward propagation of flame (*222*). Although the actual limit values are not satisfactory for our purposes, they can be used to check the applicability of the $L_t/L_{25°}$ ratio data presented in figure 23. The White ratio of lower limits at 300° and 20° C. is 2.19/2.90=0.76; the corresponding ratio from

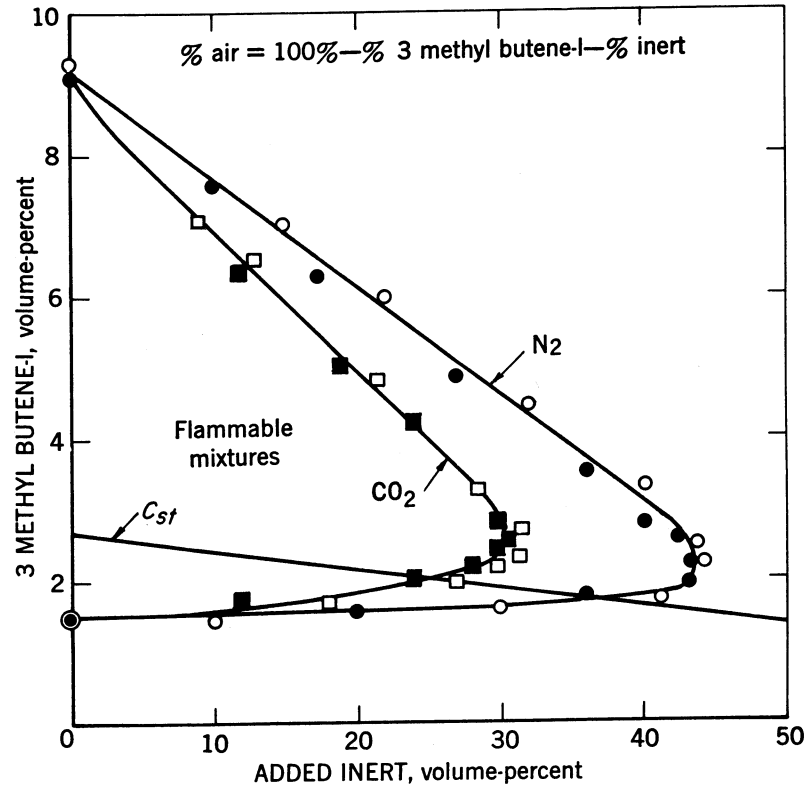

FIGURE 59.—Limits of Flammability of 3 Methyl Butene-1-Carbon Dioxide-Air and 3 Methyl-Butene-1-Nitrogen-Air Mixtures at Atmospheric Pressure and 26° C.

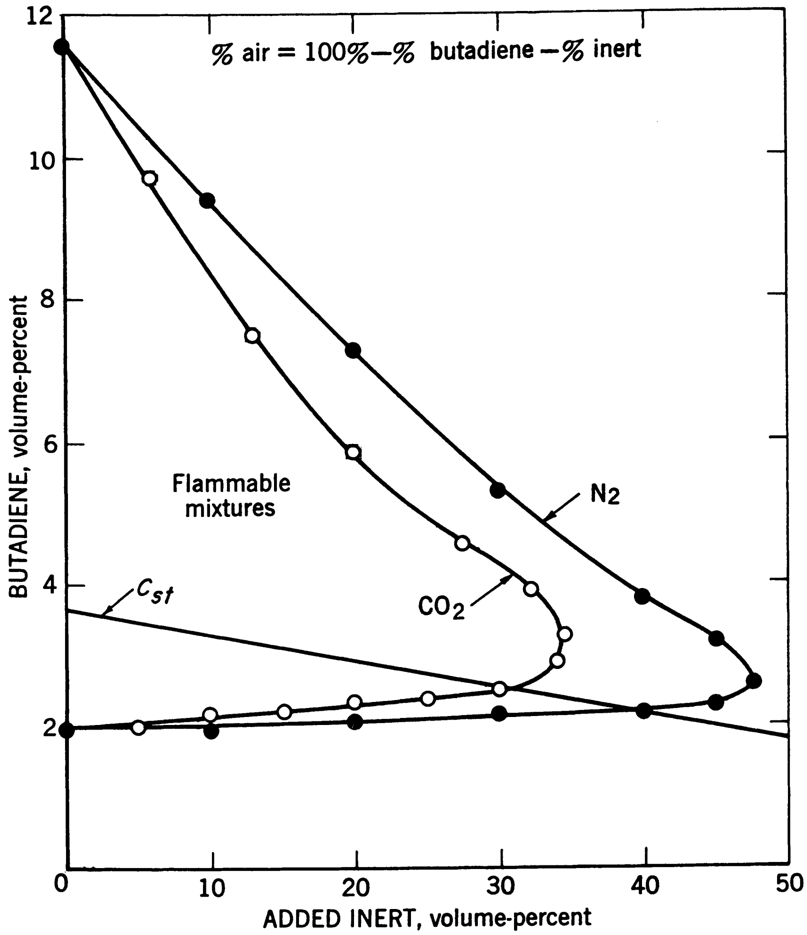

Figure 60.—Limits of Flammability of Butadiene-Carbon Dioxide-Air and Butadiene-Nitrogen-Air Mixtures at Atmospheric Pressure and 26° C.

"Constant flame temperature" curve in figure 23 is 0.78. Accordingly, this figure should be satisfactory for use with acetylene at temperatures in the range from 20° to 300° C.

The lower limit of flammability of methylacetylene (propyne) in air at atmospheric pressure is 1.7 volume-percent, equal to 0.34 C_{st} which compares favorably with the value for acetylene (0.32 C_{st}). Upper limit investigations have been conducted by Fitzgerald (*59*) in a 2-inch tube at 20° and 120° C to determine the low-pressure limits or lowest pressures at which a flame will propagate through methylacetylene vapor at these temperatures. He found these to be 50 and 30 psig at 20° and 120° C, respectively. In a 4-inch tube, Hall and Straker (*77*) obtained a low-pressure limit of 43 psig at 20° C. This indicates that the upper limit of flammability of methylacetylene in air is probably less than 100 percent at 20° C and 1 atmosphere.

The quantities of propylene required to prevent flame propagation through methylacetylene-propadiene-propylene mixtures at 120° C and 50 and 100 psig have been determined in 1-, 2-, 4-, and 12-inch tubes (fig. 62), and at 120° C and 100 psig in a 24-inch sphere. As noted, the propylene requirements are strongly affected by temperature, pressure, and container size. As the tube diameter increases, the quantity of propylene required to prevent flame propagation increases; this effect is less pronounced in the larger vessels (diameter greater than 4 inches) than in the smaller vessels (diameter less than 4 inches). The results obtained in the 24-inch sphere were similar to those in the 12-inch tube.

Limits in Other Atmospheres

Gliwitzky (*71*), and Jones and coworkers determined the effects of carbon dioxide and

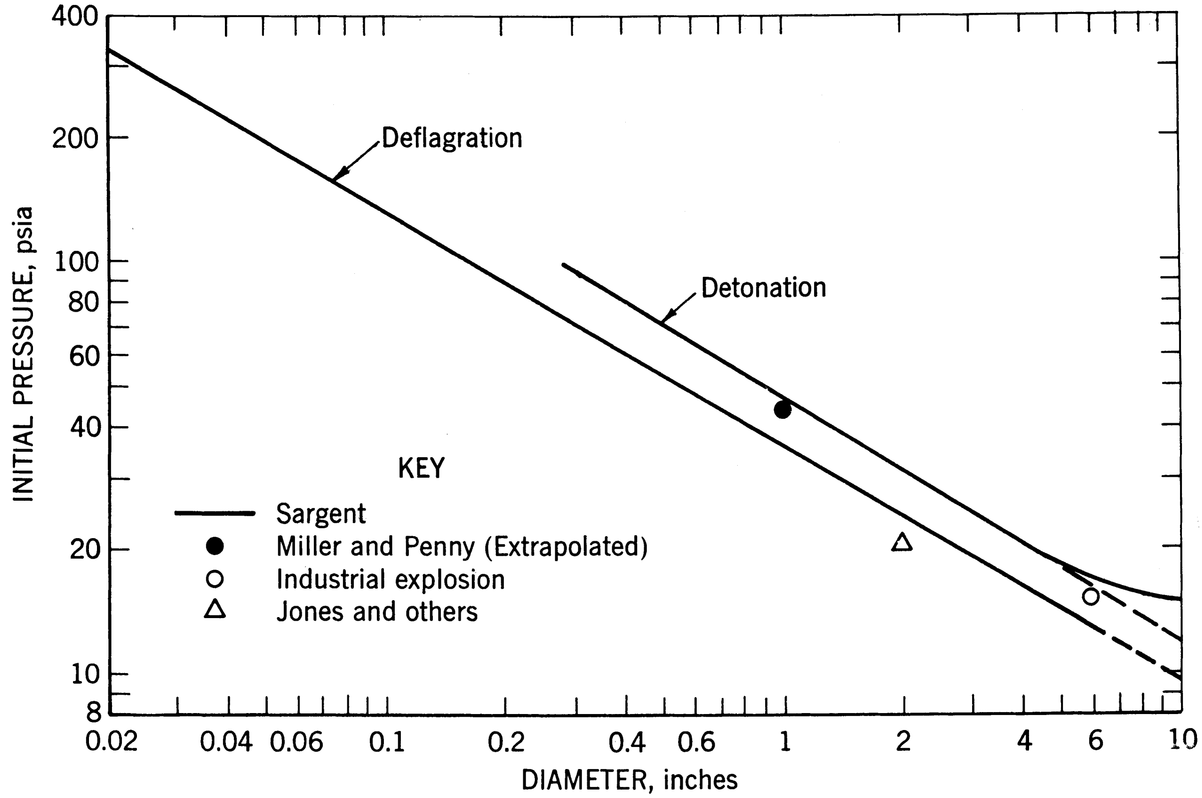

Figure 61.—Effect of Tube Diameter on Initial Pressure Requirements for Propagation of Deflagration and Detonation Through Acetylene Gas.

nitrogen on the limits of acetylene in air at atmospheric pressure and room temperature. Unfortunately, all measurements were made in tubes that were too narrow to give actual upper limit data. Nevertheless, the resulting quenched-limit data are summarized in figure 63, because they show the relative effects of adding two inert diluents to acetylene-air mixtures in a 2-inch-ID tube.

Autoignition

A summary of available autoignition temperature data for acetylene, acetylene-air, and acetylene-oxygen mixtures in clean systems is given in figure 64. They are based on measurements by Jones and Miller (*110*), by Jones and Kennedy in quartz tubes (*99*), and by Miller and Penny in a 0.5-inch steel pipe, 15 inches long (*144*). Jones and Miller found minimum autoignition temperatures of 305° and 296° C for a variety of acetylene-air and acetylene-oxygen mixtures, respectively, at atmospheric pressure. Miller and Penny report little variation in the autoignition temperature of acetylene in a clean pipe at 4 to 26 atmospheres initial pressure. However, the presence of 1 gram of powdered rust, scale, kieselguhr, alumina, silica gel, or charcoal lowered the pipe temperature required for ignition to a 280° to 300° C range. The presence of 1 gram of potassium hydroxide lowered the pipe temperature still further to 170° C. The impact of a 0.25-inch steel ball falling from a height of 15 inches against a fragment of copper acetylide produced a hot spot that ignited the surrounding gaseous acetylene at room temperature and 3 atmospheres.

Burning Rate

The burning velocity data for acetylene in air obtained by Manton and Milliken at 1 atmosphere and room temperature are given in figure 65 (*138*). The burning velocity ranges from a low of a few centimeters per second near the lower limit to a high of about 160 cm/sec on the rich side of the stoichiometric composition. Parker and Wolfhard (*164*) have found considerable variation in the burning velocity of acetylene in various oxidants. The burning velocities in stoichiometric mixtures with oxygen, nitrous oxide, nitric oxide, and nitrogen tetroxide were found to be 900, 160, 87, and 135 cm/sec, respectively; for comparison, the burning velocity in a stoichiometric acetylene-air mixture (fig. 65) is 130 cm/sec.

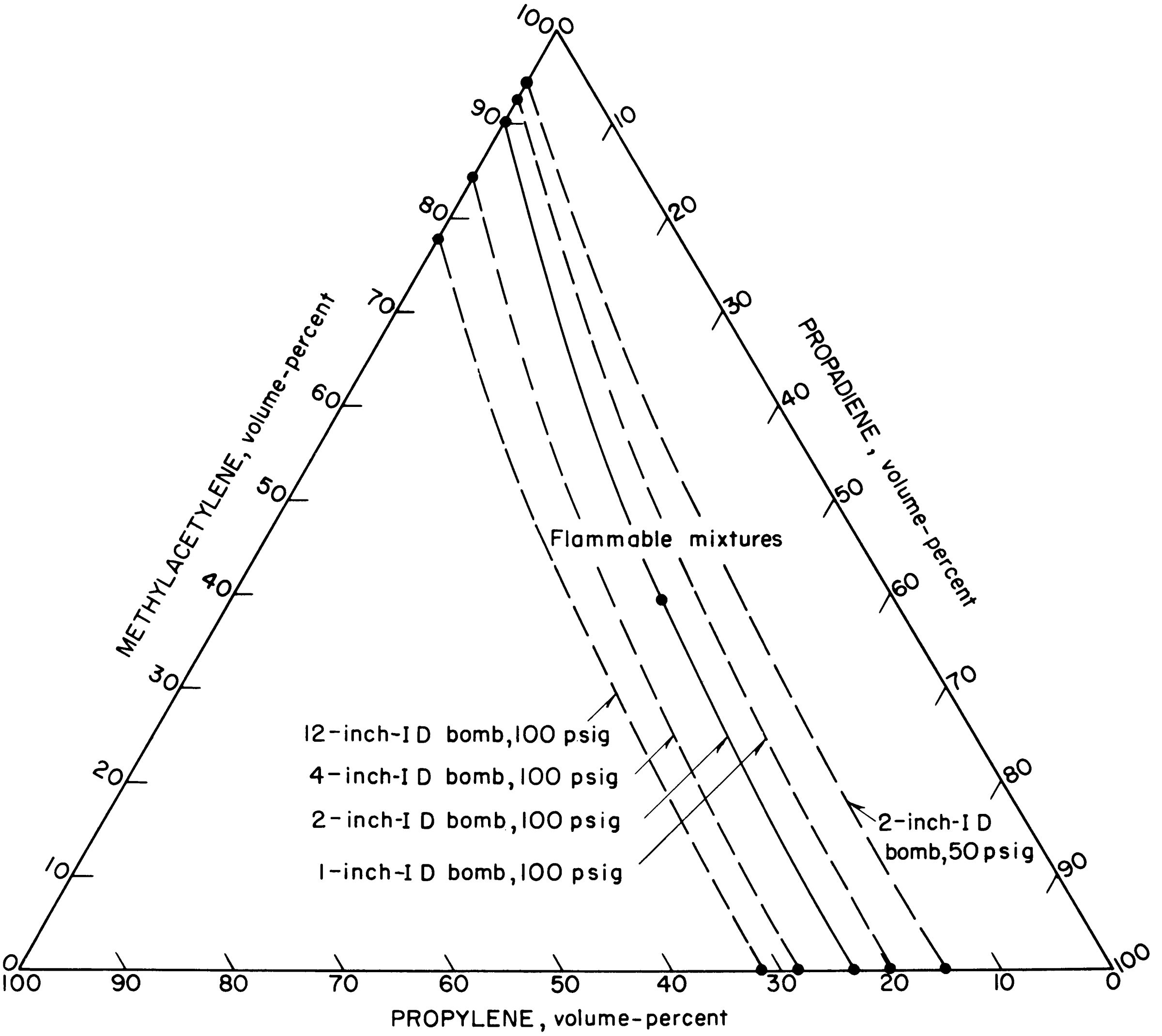

FIGURE 62.—Range of Flammable Mixtures for Methylacetylene-Propadiene-Propylene System at 120° C and at 50 and 100 Psig.

The burning velocities of acetylene-air mixtures were found to be independent of pressure between 0.1 and 1.0 atmosphere (*138*). Similarly, Agnew and Graiff (*3*) and Parker and Wolfhard (*164*) found the burning velocities of stoichiometric acetylene-oxygen and acetylene-nitrous oxide mixtures were independent of pressure between approximately 0.5 and 2 atmospheres and 0.03 and 1 atmosphere, respectively. The burning velocities of stoichiometric acetylene-nitric oxide and acetylene-nitrogen tetroxide mixtures increased slightly over this pressure range 0.03 to 1 atmosphere (*164*).

Stability

As noted, acetylene can propagate flame in the absence of air (*39*, *165*). The pressures required for propagation at subsonic (deflagration) and supersonic rates (detonation) into the unburned gas are given for a range of pipe diameters in figure 61 (*185*). Deflagration is discussed briefly under Limits of Flammability; detonation is discussed in this section.

The curve labeled "Detonation" in figure 61 gives the minimum pressure required for propagation of a detonation, once initiated, in tubes of 0.3 to 10 inches diameter. In practice, a detonation may be initiated directly from a deflagration that has propagated through a rather ill-defined distance, known as the predetonation or run-up distance. This distance depends on temperature, pressure, tube diameter, condition of tube walls, and on ignition-source strength. For example, using a fused platinum wire ignitor, Miller and Penny

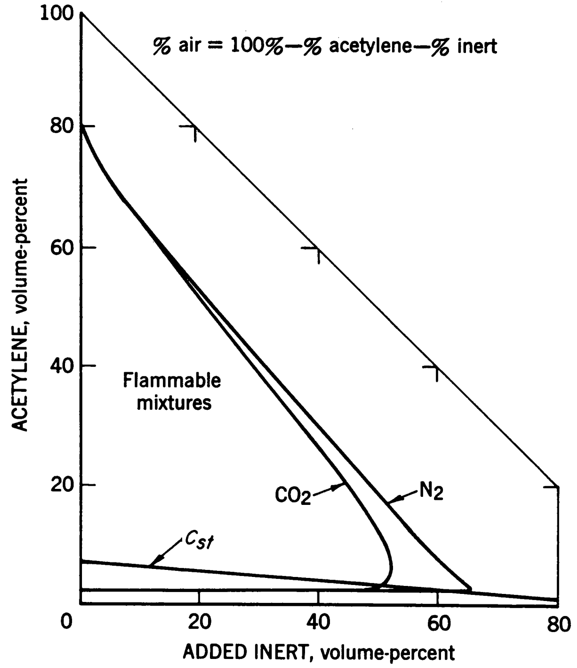

Figure 63.—Quenched Limits of Flammability of Acetylene-Carbon Dioxide-Air and Acetylene-Nitrogen-Air Mixtures at Atmospheric Pressure and 26° C, Obtained in a 2-Inch Tube.

(*144*) found the predetonation distance for acetylene in a 1-inch tube to be 30 feet at 51.4 psia, 22 feet at 55.9 psia, 12 feet at 73.5 psia, and 2.8 to 3.2 feet at 294 psia initial pressure. Extrapolation of these data yields the point in figure 61 for a very large predetonation distance. This point (44 psia and 1-inch diameter) lies fairly close to the detonation curve established by Sargent (*185*). The maximum lenth-to-diameter ratios (L/D) given by Sargent for establishing detonation in acetylene is plotted against intial pressure in figure 66. In tubes, having a diameter greater than those given along the top of the figure and having powerful ignitors, the L/D ratio will be less than that given by the curve. Nevertheless, this figure should be of use in giving the outer bound of L/D and the approximate quenching diameter; a better value for the quenching diameter can be obtained directly from figure 61.

Although predetonation distances are difficult to measure and experimental data often exhibit much scatter, they are of interest in safety work because they can be used to evaluate the maximum pressures likely to occur in a system due to cascading or pressure piling. This phenomenon presents a special problem because the final pressure achieved in a detona-

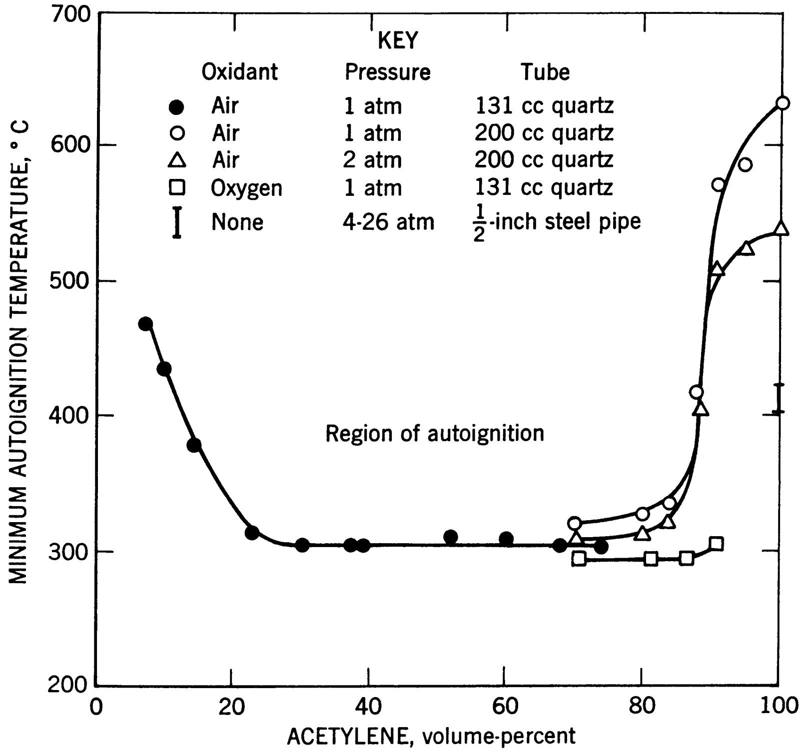

Figure 64—Minimum Autoignition Temperatures of Acetylene-Air and Acetylene-oxygen mixtures at atmospheric and elevated pressures.

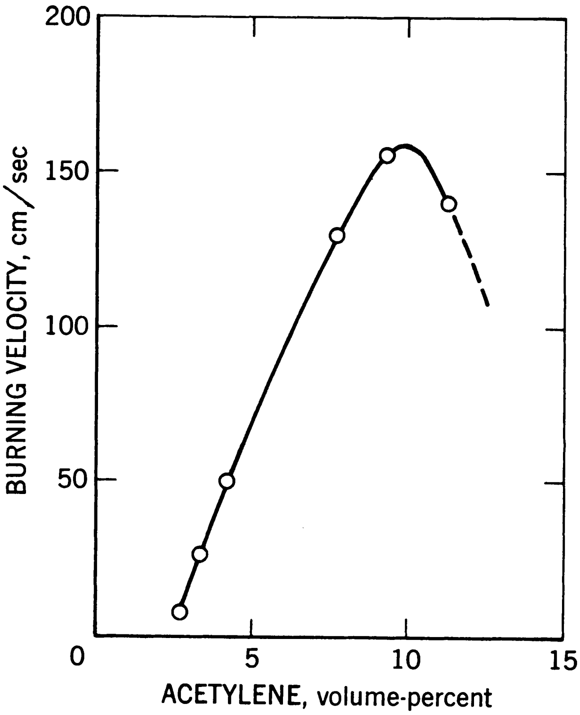

FIGURE 65.—Burning Velocity of Acetylene-Air Mixtures at Atmospheric Pressure and Room Temperature.

tion depends on the initial pressure at the onset of detonation. For example, the maximum pressure to be expected from the deflagration of acetylene at moderate pressures is about 11 times the initial pressure (*144*); the maximum to be expected from a detonation is about 50 times the initial pressure. As the pressure equalizes at the speed of sound in a deflagration, the maximum initial pressure to be expected upon transition from deflagration to a detonation is approximately 11 times the fraction of acetylene that has been burned times the initial precombustion pressure. Fifty times this pressure is the approximate maximum pressure that would be obtained when a detonation occurs. To illustrate this, Sargent has plotted the final-to-initial pressure ratio (P_f/P_i) against the predetonation distance-to-tube length for acetylene. A similar graph is given in figure 67. To use this graph, the maximum predetonation distance to be expected must first be determined from figure 66. This distance divided by the tube length gives the maximum final-to-initial pressure ratio.

AROMATIC HYDROCARBONS
(C_nH_{2n-6})

Limits in Air

The combustibles considered in this section are listed in table 11, with pertinent properties. At atmospheric pressure and room temperature, the lower limits of flammability of the aromatic hydrocarbons are approximately 50±2 mg/l (0.050±0.002 oz combustible vapor per cubic foot of air).

The lower limit of toluene was determined by Zabetakis and coworkers in air at 30°,

FIGURE 66.—Maximum *L/D* ratio Required for Transition of a Deflagration to a Detonation in Acetylene Vapor at 60° F and from 10 to 70 Psia.

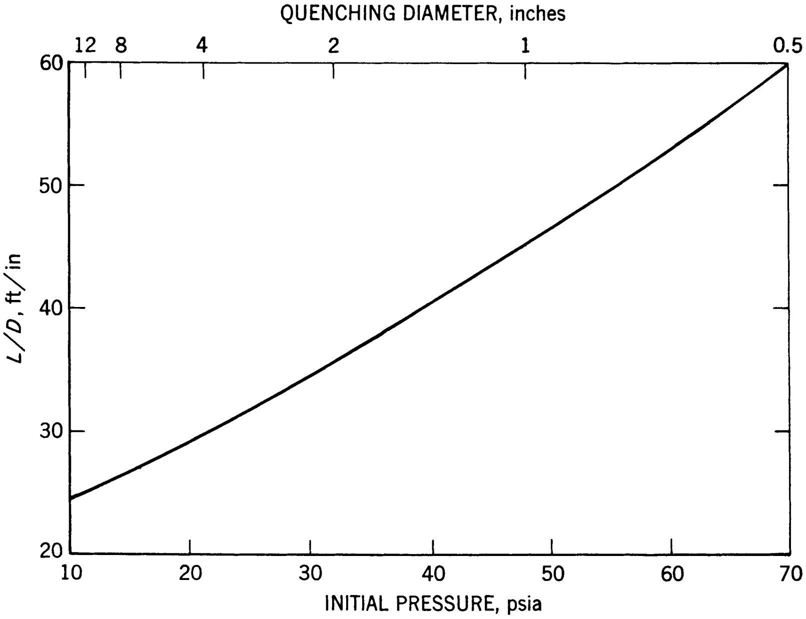

TABLE 11.—*Properties of selected aromatic hydrocarbons*

Combustible	Formula	M	Sp gr (Air=1)	C_{st} in air (vol pct)	net ΔH_c $\left(\frac{\text{Kcal}}{\text{mole}}\right)$	Lower limit in air[1]			Upper limit in air[1]		
						L_{100} (vol pct)	$\frac{L_{100}}{C_{st}}$	L $\left(\frac{\text{mg}}{\text{l}}\right)$	U_{100} (vol pct)	$\frac{U_{100}}{C_{st}}$	U $\left(\frac{\text{mg}}{\text{l}}\right)$
Benzene	C_6H_6	78.11	2.69	2.72	757.5	1.3	0.48	47	7.9	2.9	300
Toluene	C_7H_8	92.13	3.18	2.27	901.5	1.2	.53	50	7.1	3.1	310
Ethyl benzene	C_8H_{10}	106.16	3.67	1.96	1048.5	1.0	.51	48	6.7	3.4	340
o-Xylene	C_8H_{10}	106.16	3.67	1.96	1045.9	1.1	.56	53	6.4	3.3	320
m-Xylene	C_8H_{10}	106.16	3.67	1.96	1045.5	1.1	.56	53	6.4	3.3	320
p-Xylene	C_8H_{10}	106.16	3.67	1.96	1045.7	1.1	.56	53	6.6	3.4	340
Cumene	C_9H_{12}	120.19	4.15	1.72	1194.2	.88	.51	48	6.5	3.8	370
p-Cymene	$C_{10}H_{14}$	134.21	4.63	1.53	1341.8	.85	.56	51	6.5	3.6	350

[1] Ref. (*247*).

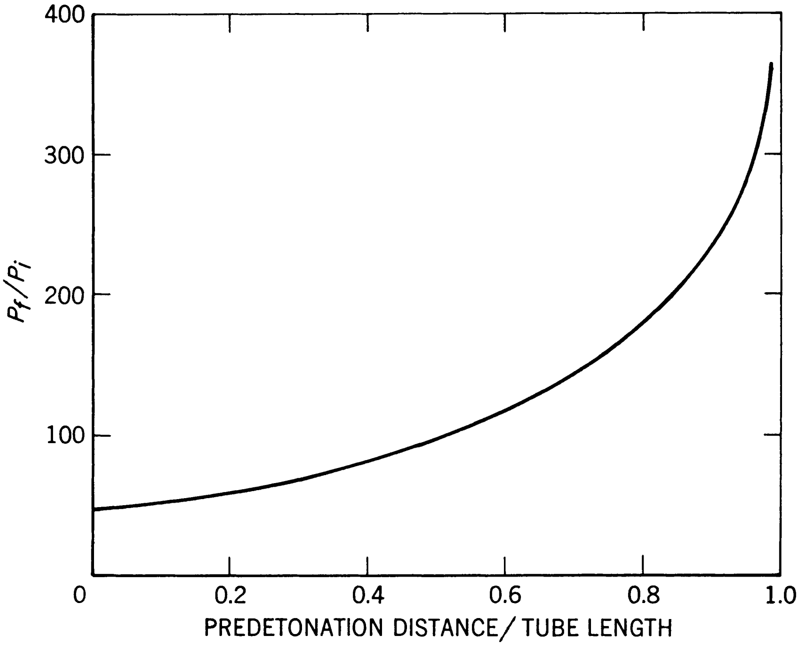

FIGURE 67.—Final-to-Initial Pressure Ratios Developed by Acetylene With Detonation Initiation at Various Points Along a Tube.

100°, and 200° C (*235*, *247*); the variation in lower limit with temperature is given by equations (31) and (33) derived for paraffin hydrocarbons, and the corresponding curves of figure 23. For example, $L_{200^\circ\,C}/L_{30^\circ\,C}$ was found to be 1.07/1.24 or 0.86; the ratio predicted by the curve in figure 23 is 0.87.

The upper limits of the aromatics considered here at 100° C are included in table 11 (*247*). These were obtained at atmospheric pressure in a 2-inch-diameter tube, open at one end. Butler and Webb obtained upper limit data on a commercial grade cumene (93.3 pct cumene) in air at elevated temperatures and atmospheric and elevated pressures in a closed bomb (*31*). Their values range from 8.8 percent cumene (80° C and atmospheric pressure) to 10.8 percent cumene (146° C and 100 psig pressure).

Limits in Other Atmospheres

The limits of flammability obtained by Burgoyne (*29*) and by Jones (*40*) for benzene-carbon dioxide-air and benzene-nitrogen-air mixtures at atmospheric pressure and 25° C are given in figure 68; similar data are given for the last two mixtures at atmospheric pressure and 150° C. The inerting requirements at 25° C are approximately the same as those of *n*-hexane (fig. 33). Again, it should be noted

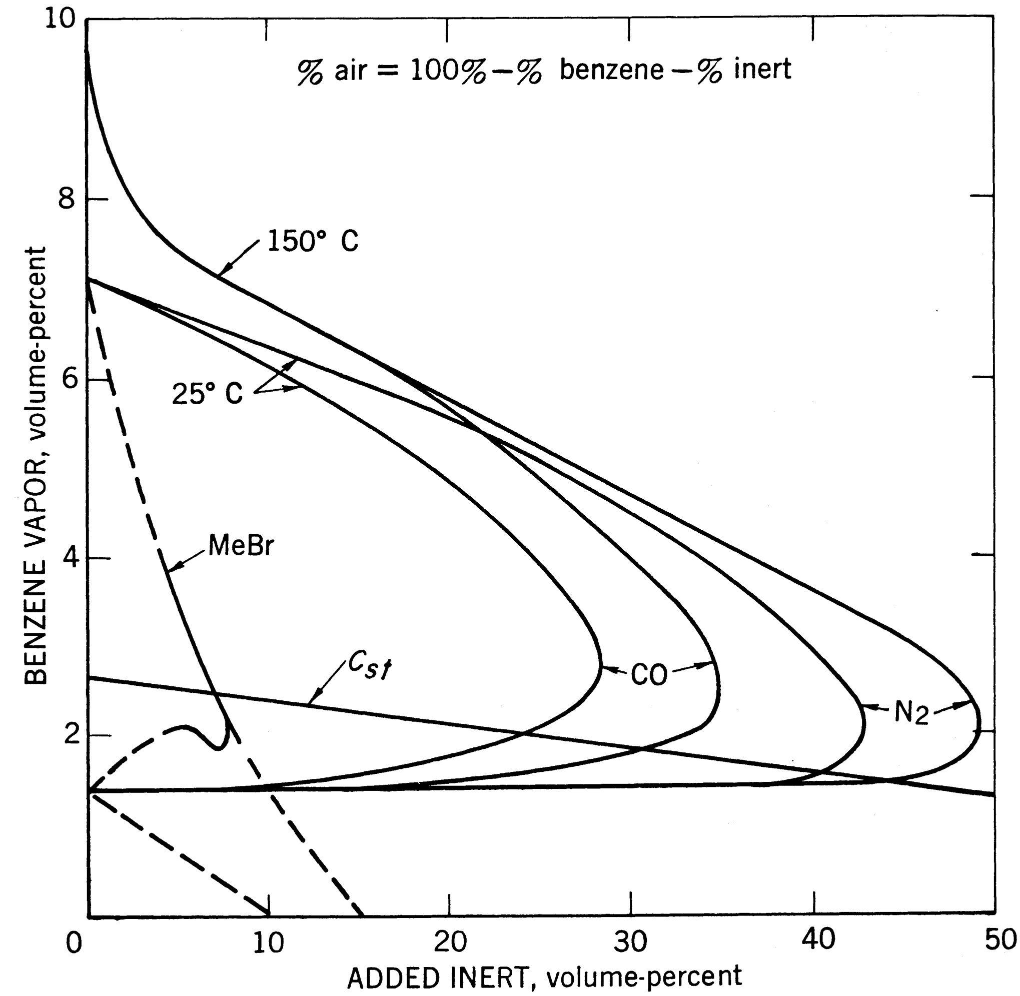

FIGURE 68.—Limits of Flammability of Benzene-Methyl Bromide-Air Mixtures at 25° C and Benzene-Carbon Dioxide-Air and Benzene-Nitrogen-Air Mixtures at 25° and 150° C and Atmospheric Pressure.

that the methyl bromide data are not consistent with those obtained by Hill (compare figs. 28 and 33). These latter data (*84*) were used to construct the approximate (broken) flammability curves for the benzene-methyl bromide-air system.

The decrease in the minimum oxygen requirements for flame propagation (from 14.2±0.3 volume-percent at 25° C to 13.1±0.3 volume-percent at 150° in a carbon dioxide-air atmosphere; from 11.4±0.3 volume-percent at 25° C to 10.1±0.3 volume-percent at 150° in a nitrogen-air atmosphere) is within the range predicted by the modified Burgess-Wheeler law (equation (35), fig. 23).

The limits of flammability of orthoxylene ($C_6H_4 \cdot (CH_3)_2$)-water-hydrogen peroxide mixtures were determined at 154° C and 1 atmosphere presssure by Martindill, Lang, and Zabetakis (*140*). The data are presented in a triangular plot in figure 69; compositions are expressed in mole-percent as in the original presentation. This system has no lower limit mixtures, as a flame can be initiated in hydrogen peroxide vapors (*186*). As a 90-weight-percent hydrogen peroxide was actually used to obtain these flammability data, all compositions were calculated to yield values based on a 100-percent hydrogen peroxide content. This could be done here because only three components are considered. Where four components are considered, the flammability data can be presented in a three-dimensional plot; if two of the components appear in fixed proportions, a triangular plot can be used with the two components (for example, 90-weight-percent hydrogen peroxide) considered as a single component. Such a plot is presented in figure 70 for 90-weight-percent hydrogen peroxide-orthoxylene-formic acid (HCOOH) at 154° C and 1 atmosphere. This was considered to be a plane in a regular tetrahedron in the original article and is there-

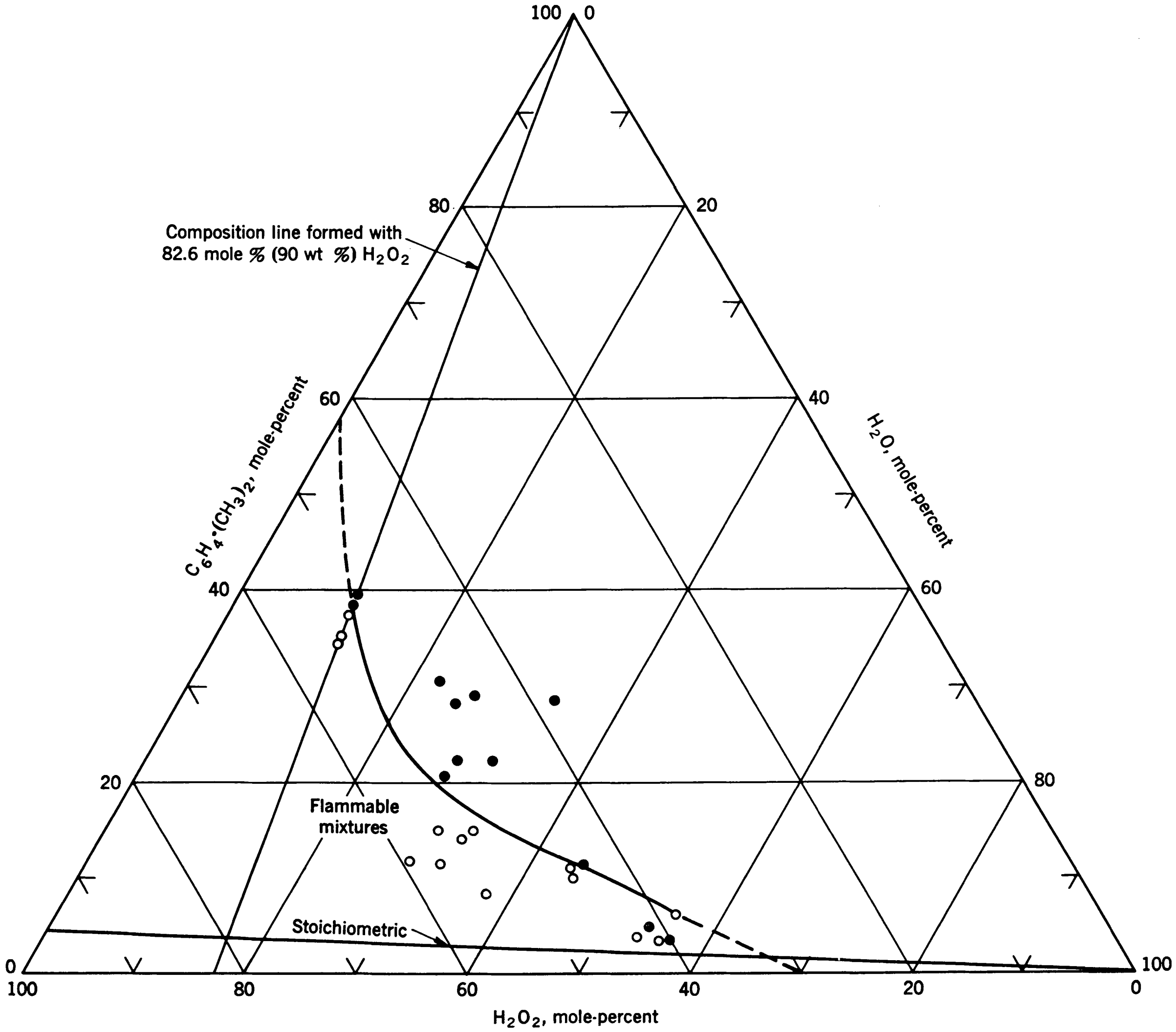

FIGURE 69.—Limits of Flammability of H_2O_2-$C_6H_4 \cdot (CH_3)_2$-H_2O at 154° C and 1 Atmosphere Pressure.

fore not a regular triangle. As before, only an upper limit curve is given because 90-weight-percent hydrogen peroxide is flammable. In addition, a calculated curve based on Le Chatelier's rule is given, as is the upper limit curve obtained with decomposed hydrogen peroxide. Decomposition of the peroxide lowers the upper limit appreciably and yields a system which has a lower limit of flammability (not determined in this study).

Autoignition

The minimum autoignition temperatures of a series of aromatic hydrocarbons in air at atmospheric pressure are given in figure 71 as a function of the correlation parameter L_{ave}. This parameter was determined by use of equation (*49*), treating the benzene ring as a $-CH_3$ group (*241*). When the benzene ring contains two side groups, L_{ave} is determined first for the side group that yields the largest average value and to this is added ½, ⅓, or ¼ of the average chain length of the second side group; (½, ⅓, and ¼ correspond to the ortho-, meta-, and para-positions, respectively). The data again fall into high- and low-temperature regions (fig. 43).

Burning Rate

Burning rates and detonation velocities of benzene in air and oxygen appear to be approximately the same as those of the higher paraffin hydrocarbons. For example, the results of Golovina and Fyodorov (*211*) show that the maximum burning velocities of benzene in nitrogen-oxygen mixtures range from about

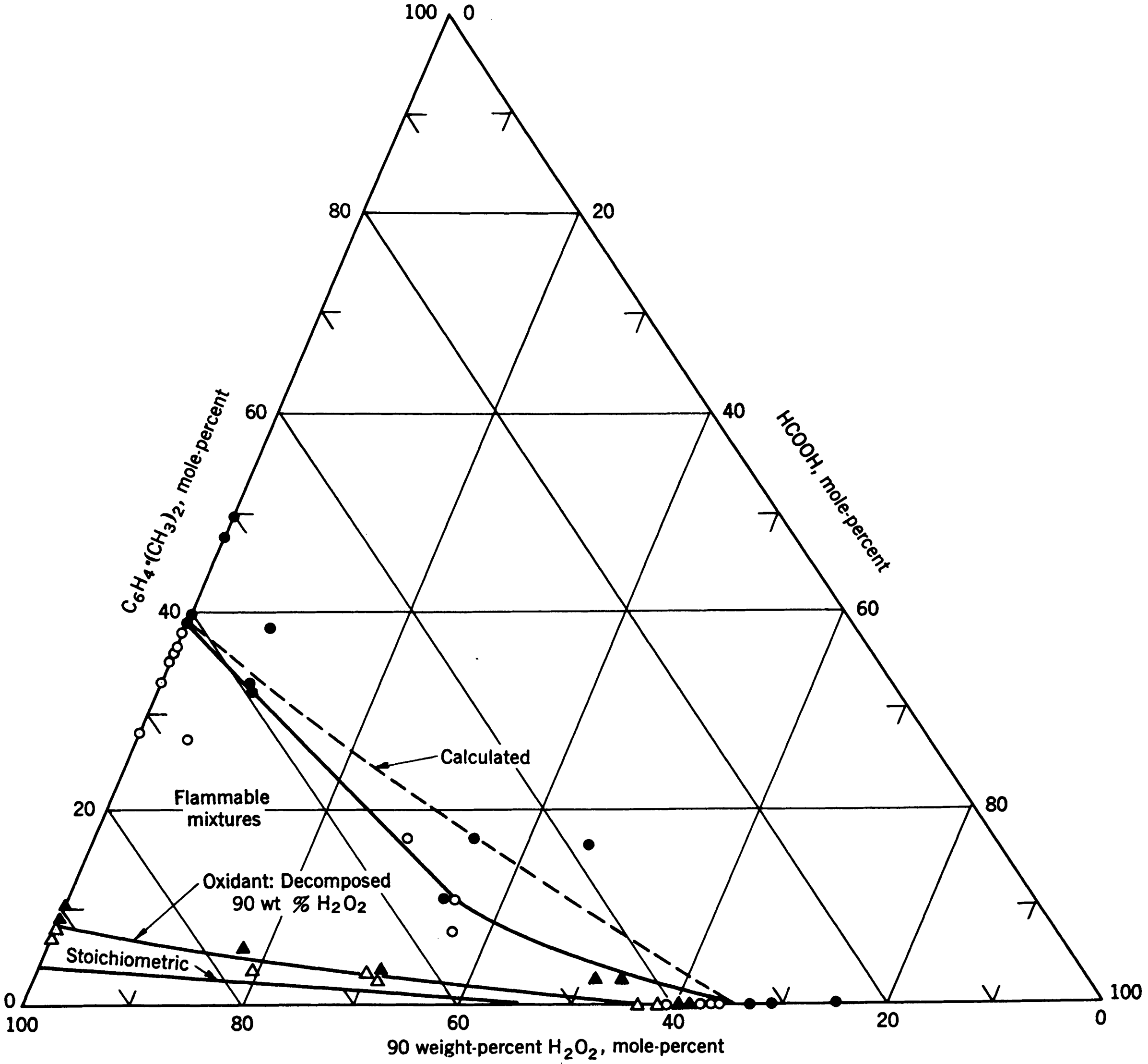

FIGURE 70.—Limits of Flammability of 90-Weight-Percent H_2O_2-$C_6H_4 \cdot (CH_3)_2$-HCOOH at 154° C and 1 Atmosphere Pressure.

295 cm/sec in oxygen to 45 cm/sec in air; the maximum burning velocities of hexane in various nitrogen-oxygen mixtures range from about 260 cm/sec in oxygen to 40 cm/sec in air. Similarly, Fraser (*61*) found the maximum detonation velocities of benzene and *n*-octane in oxygen to be 2,510 and 2,540 m/sec, respectively.

ALICYCLIC HYDROCARBONS (C_nH_{2n})

Limits in Air

A summary of the pertinent properties of some of the members of the series is given in table 12. The lower limits of flammability in air at atmospheric pressure and room temperature fall in the range from 48±3mg/l (.048 ±.003 oz combustible per cubic foot of air). By volume, this is equivalent to approximately 0.55 C_{st}, which is the same as for paraffin hydrocarbons. The ratio of the upper limit to C_{st} appears to increase with molecular weight.

According to Jones (*40*), the lower limit of cyclohexane in air at atmospheric pressure and 26° C determined in a 2.0-inch tube is 1.26 volume-percent. Under the same conditions, Burgoyne and Neale (*26*) found the lower limit to be 1.34 volume-percent, using a 2.5-inch tube. Matson and Dufour (*141*) found the

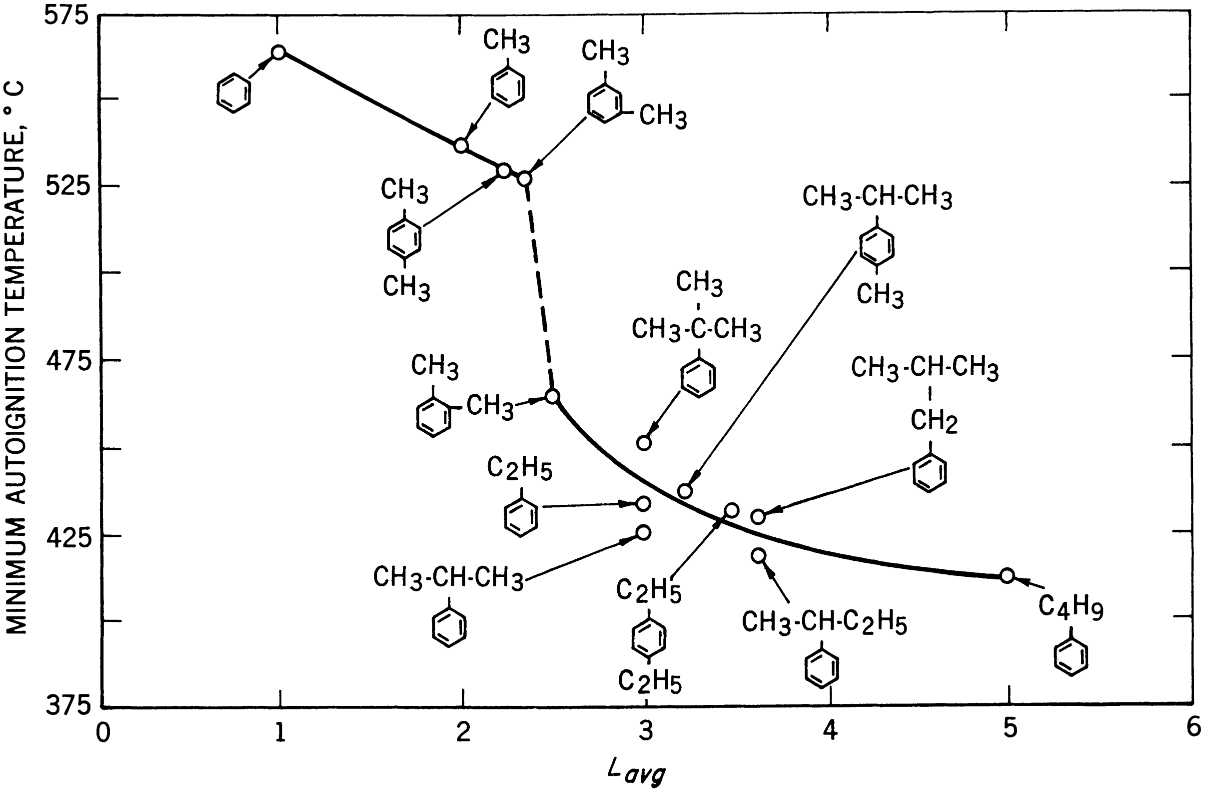

FIGURE 71.—Minimum Autoignition Temperatures of Aromatic Hydrocarbons in Air as a Function of Correlation Parameter L_{ave}.

TABLE 12.—*Properties of selected alicyclic hydrocarbons*

Combustible	Formula	M	Sp gr (Air=1)	C_{st} in air (vol pct)	Net ΔH_c $\left(\frac{\text{kcal}}{\text{mole}}\right)$	Lower limit in air				Upper limit in air			
						L_{25} (vol pct)	$\frac{L_{25}}{C_{st}}$	L $\left(\frac{\text{mg}}{\text{l}}\right)$	Ref.	U_{25} (vol pct)	$\frac{U_{25}}{C_{st}}$	U $\left(\frac{\text{mg}}{\text{l}}\right)$	Ref.
Cyclopropane	C_3H_6	42.08	1.45	4.45	465	2.4	0.54	46	(*107*)	10.4	2.3	220	(*107*)
Cyclobutane	C_4H_8	56.10	1.94	3.37	[1] 600	1.8	.56	46	(1)	------	------	------	------
Cyclopentane	C_5H_{10}	70.13	2.42	2.72	740.8	1.5	.55	48	(1)	------	------	------	------
Cyclohexane	C_6H_{12}	84.16	2.91	2.27	881.7	1.3	.57	49	(*40*)	7.8	3.4	320	(*40*)
Ethylcyclobutane	C_6H_{12}	84.16	2.91	2.27	[1] 880	1.2	.53	46	(*40*)	7.7	3.4	310	(*40*)
Cycloheptane	C_7H_{14}	98.18	3.39	1.96	[1] 1024	1.1	.56	49	(1)	6.7	3.4	310	(1)
Methylchcylhexane	C_7H_{14}	98.18	3.39	1.96	1026.0	1.1	.56	49	(*40*)	6.7	3.4	310	(1)
Ethylcyclopentane	C_7H_{14}	98.18	3.39	1.96	1032.6	1.1	.56	49	(*40*)	[2] 6.7	3.4	310	(*40*)
Ethylcylcohexane	C_8H_{16}	112.21	1.71	1.71	1173.7	[3] .95	.56	48	(*40*)	[3] 6.6	3.9	350	(*40*)

[1] Calculated value.
[2] P=0.5 atm.
[3] t=130° C.

lower limit to be 1.12 volume-percent at 21° C in a 12-inch diameter chamber about 15 inches long; however, there is evidence that they did not use the same criteria of flammability as did the other authors; only one observation window was provided at the top of a rather squatty chamber, whereas with the glass tubes used by Jones and by Burgoyne and Neale the flame could be observed along the entire tube. Accordingly, the data of Jones and of Burgoyne and Neale are used here.

Limits in Other Atmospheres

The limits of flammability of cyclopropane-carbon dioxide-air, cyclopropane-nitrogen-air, and cyclopropane-helium-air mixtures at 25° C and atmospheric pressure are given in figure

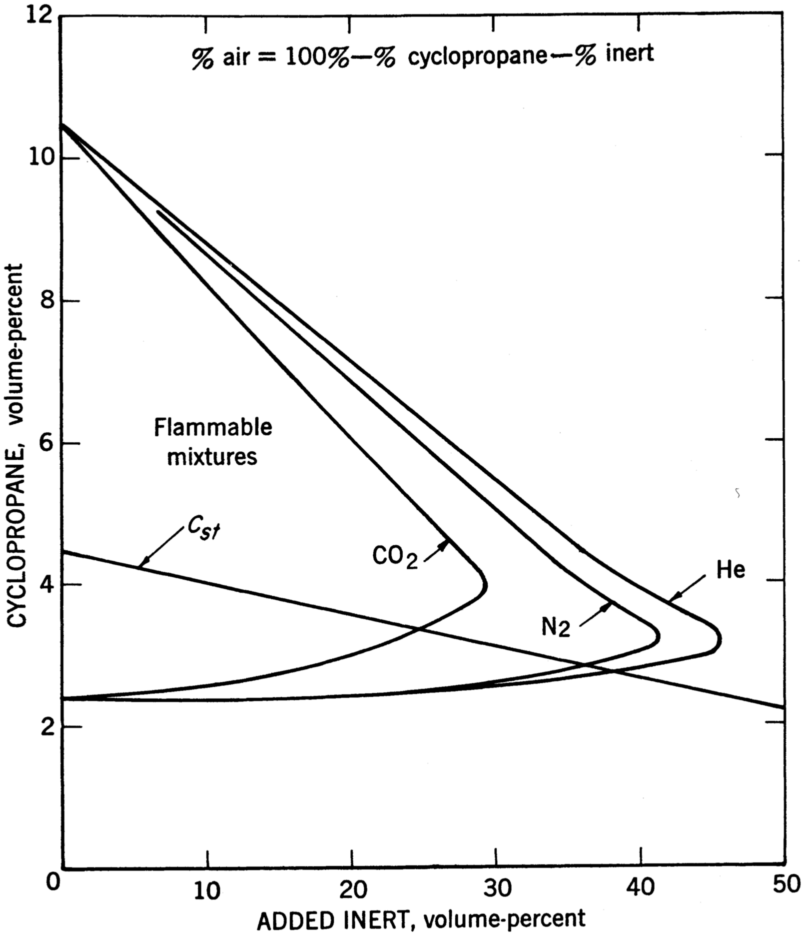

FIGURE 72.—Limits of Flammability of Cyclopropane-Carbon Dioxide-Air, Cyclopropane-Nitrogen-Air, and Cyclopropane-Helium-Air Mixtures at 25° C and Atmospheric Pressure.

72 (*106*). The first two curves are similar to those obtained with paraffin hydrocarbons (fig. 35).

The limits of flammability of cyclopropane-helium-oxygen and cyclopropane-nitrous oxide-oxygen mixtures at 25° C and atmospheric pressure are given in figure 73 (*106*). The latter curve differs from the former, as both additives are oxidants (oxygen and nitrous oxide).

The limits of flammability of cyclopropane-helium-nitrous oxide mixtures at 25° C and atmospheric pressure are given in figure 74 (*106*). Here the minimum oxidant concentration (nitrous oxide) required for flame propagation is approximately twice the corresponding concentration of oxygen in the systems cyclopropane-helium-air (fig. 72) and cyclopropane-helium-oxygen (fig. 73).

ALCOHOLS ($C_nH_{2n+1}OH$)

Limits in Air

The alcohols considered here are listed in table 13 together with $L_{25°}$ and $U_{25°}$. The ratios $L_{25°}/C_{st}$ are approximately 0.5. However, the L (mg/l) values decrease with increase in molecular weight. If L^* is taken to be the weight of combustible material (exclusive of the oxygen in the molecule) per liter of air, then for the simple alcohols:

$$L^* = L\,\frac{M-16}{M}. \qquad (54)$$

This equation gives the values listed in parentheses in the mg/l column; these are in fair agreement with the values obtained for the

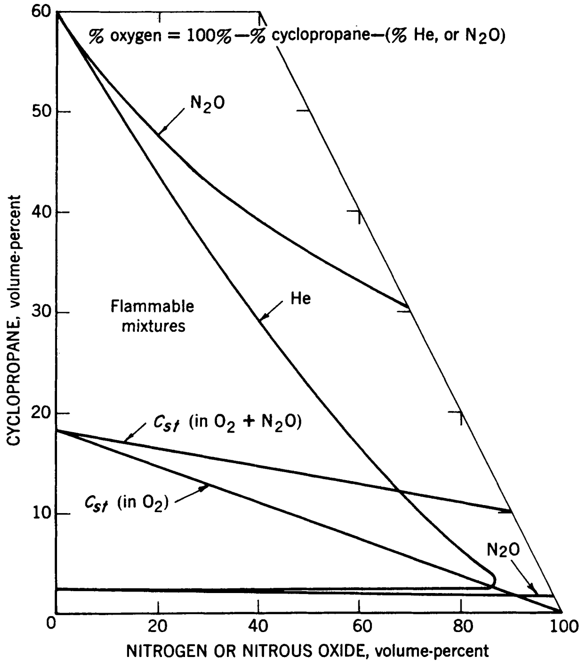

Figure 73.—Limits of Flammability of Cyclopropane-Helium-Oxygen and Cyclopropane-Nitrous Oxide-Oxygen Mixtures at 25° C and Atmospheric Pressure.

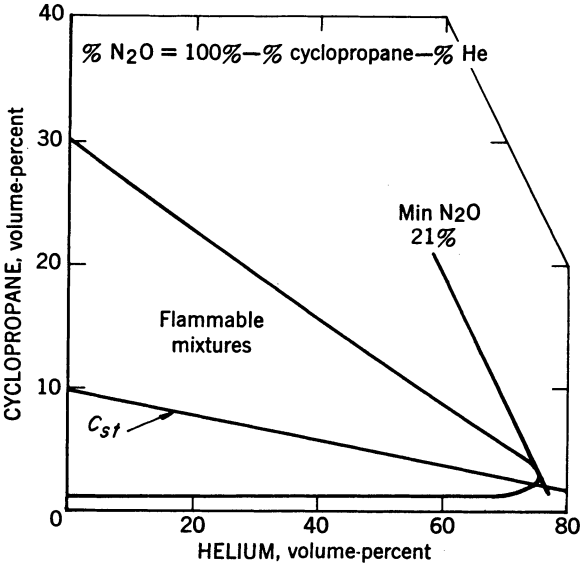

Figure 74.—Limits of Flammability of Cyclopropane-Helium-Nitrous Oxide Mixtures at 25° C and Atmospheric Pressure.

saturated hydrocarbons. Approximate L (mg/l) values can be obtained from the higher hydrocarbon values given in figure 22 by multiplying these by the ratio $M/(M-16)$. Further, figure 19 can be used to obtain L^* and L values in volume-percent. For example, at 25° C, L^* is about 47 mg/l from figure 22; the corresponding $L^*_{25^\circ}$ from figure 19 for ethyl alcohol ($M=46$) is 2.2 volume-percent. Then, from equation (54), L is 3.4 volume-percent; the measured value is 3.3 volume-percent.

The lower limits of methyl alcohol have been determined by Scott and coworkers at 25°, 100°, and 200° C (*192*). The values at these three temperatures are 6.7, 6.5, and 5.9 volume-percent, respectively. The calculated values obtained from the modified Burgess-Wheeler law (fig. 23) at 100° and 200° C are 6.4 and 5.8 volume-percent, respectively.

Limits in Other Atmospheres

The limits of flammability of methyl alcohol-carbon dioxide-air and methyl alcohol-nitrogen-air mixtures at atmospheric pressure and 25° and 50° C are given in figure 75; flammability determinations on mixtures containing more than 15 percent methyl alcohol vapor were conducted at 50° C. The maximum amounts of carbon dioxide and nitrogen required to prevent flame propagation in these mixtures

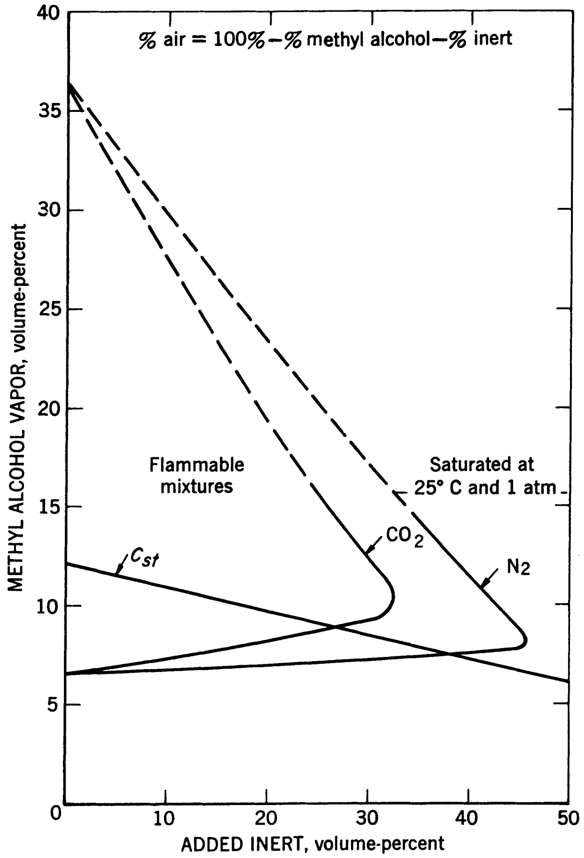

Figure 75.—Limits of Flammability of Methyl Alcohol-Carbon Dioxide-Air and Methyl Alcohol-Nitrogen-Air Mixtures at 25° C and Atmospheric Pressure. (Broken curve at 50° C and atmospheric pressure.)

TABLE 13.—*Properties of selected simple alcohols*

Combustible	Formula	M	Sp gr (Air=1)	C_{st} in air (vol pct)	Net ΔH_c $\left(\frac{Kcal}{mole}\right)$	Lower limit in air				Upper limit in air			
						L_{25} (vol pct)	$\frac{L_{25}}{C_{st}}$	L $\left(\frac{mg}{1}\right)$	Ref.	U_{25} (vol pct)	$\frac{U_{25}}{C_{st}}$	U $\left(\frac{mg}{1}\right)$	Ref.
Methyl alcohol	CH_3OH	32.04	1.11	12.25	159	6.7	0.55	103 [1] 52	(*40*)	[2] 36	2.9	810 [1] 405	(*225*)
Ethyl alcohol	C_2H_5OH	46.07	1.59	6.53	306	3.3	.50	70 [1] 46	(*40*)	[2] 19	2.9	480 [1] 310	(*226*)
n-Propyl alcohol	C_3H_7OH	60.09	2.07	4.45	448	[3] 2.2	.49	60 [1] 44	(*40*)	[3] 14	3.2	420 [1] 310	(*40*)
n-Butyl alcohol	C_4H_9OH	74.12	2.56	3.37	596	[4] 1.7	.50	57 [1] 45	([5])	[4] 12			([5])
pri-n-Amyl alcohol	$C_5H_{11}OH$	88.15	3.04	2.72	742	[4] 1.4	.51	56 [1] 46	([5])	[4] 10			
n-Hexyl alcohol	$C_6H_{13}OH$	102.17	3.53	2.27	[6] 888	1.2	.53	55 [1] 46	([4])				

[1] $L^* = L\frac{M-16}{M}$.

[2] $t=60°$.

[3] At saturation temperature.

[4] $t=100°$ C.

[5] Figures compiled by Explosives Res. Center, Federal Bureau of Mines.

[6] Calculated value.

were compared with the corresponding maxima for paraffin hydrocarbons (figs. 28–35); it was found that appreciably more inert is required to make mixtures containing methyl alcohol nonflammable. Conversely, methyl alcohol requires less oxygen to form flammable mixtures, at a given temperature and pressure, than paraffin hydrocarbons do. This may be due in part to the oxygen of the alcohol molecule. For the simple alcohols, we have:

$$C_nH_{2n+1}OH + 1.5nO_2 \rightarrow nCO_2 + (n+1)H_2O. \quad (55)$$

Thus, the ratio of oxygen required for complete combustion of an alcohol to that for complete combustion of the corresponding paraffin, equation (22), is:

$$R_{O_2} = \frac{3n}{3n+1}. \quad (56)$$

When $n=1$, this ratio is 0.75. The corresponding ratios of the experimental minimum oxygen values from figures 75 and 28 are 0.82 with carbon dioxide and 0.85 with nitrogen as inert.

The limits of flammability of methyl alcohol-water vapor-air were obtained by Scott (*192*) in a 2-inch-ID cylindrical tube at 100° and 200° C and in a 4.9-liter cylindrical bomb at 400° C and 1 atmosphere (fig. 76). Similar data were obtained by Dvorak and Reiser in a 2.2-liter apparatus at 100° C (*53*).

The limits of flammability of ethyl alcohol-carbon dioxide-air and ethyl alcohol-nitrogen-air mixtures were obtained at 25° C and atmospheric, or one-half atmosphere, pressure as noted (fig. 77). Additional flammability data obtained for ethyl alcohol at 100° C and 1 atmosphere are given in figure 78. Flammability data for the systems *tert*-butyl alcohol-carbon dioxide-oxygen and 2-ethylbutanol-nitrogen-oxygen are given in figures 79–81.

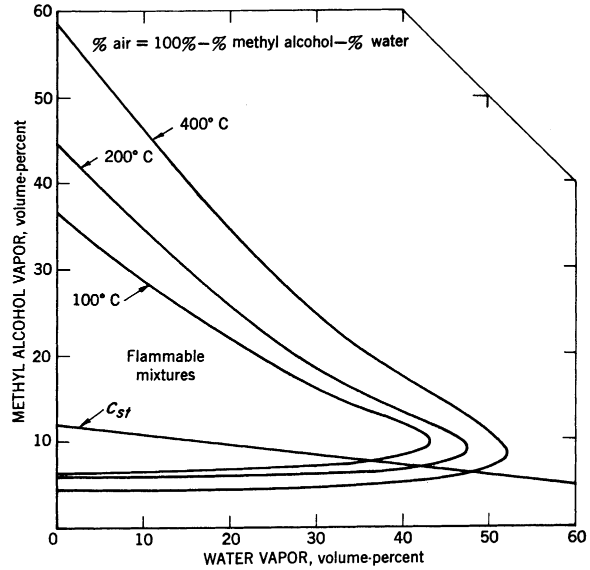

FIGURE 76.—Limits of Flammability of Methyl Alcohol-Water Vapor-Air Mixtures at 100°, 200°, and 400° C and Atmospheric Pressure.

Autoignition

The minimum autoignition temperatures in air and oxygen of a number of alcohols at atmospheric pressure are given in appendix A. Comparison of these values with those of the corresponding paraffins (methyl alcohol and methane; ethyl alcohol and ethane, etc.), shows that the AIT values of the alcohols are generally lower.

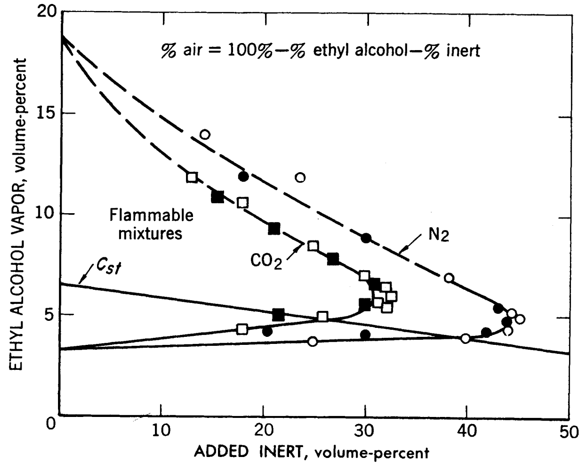

FIGURE 77.—Limits of Flammability of Ethyl Alcohol-Carbon Dioxide-Air and Ethyl Alcohol-Nitrogen-Air Mixtures at 25° C and Atmospheric Pressure. (Broken curves at one-half atmosphere.)

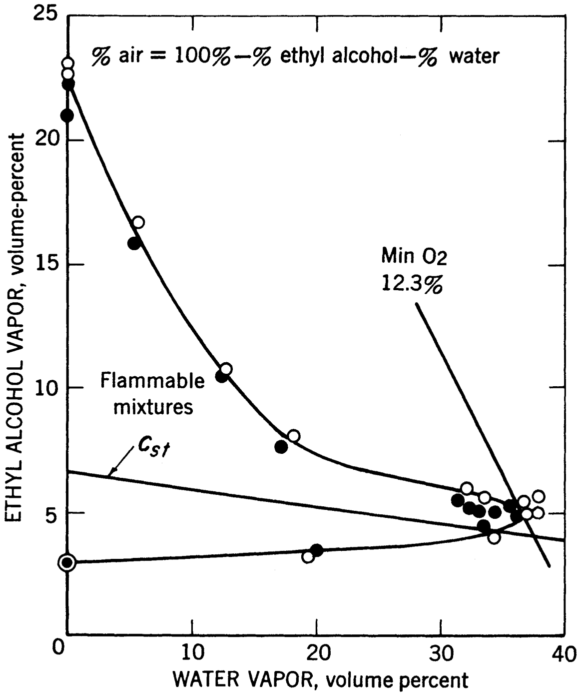

FIGURE 78.—Limits of Flammability of Ethyl Alcohol-Water Vapor-Air Mixtures at 100° C and Atmospheric Pressure.

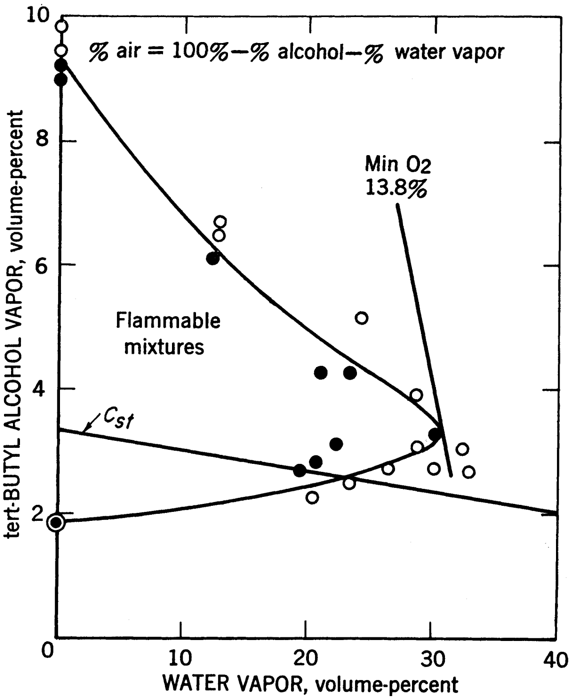

FIGURE 79.—Limits of Flammability of *tert*-Butyl Alcohol-Water Vapor-Air Mixtures at 150° C and Atmospheric Pressure.

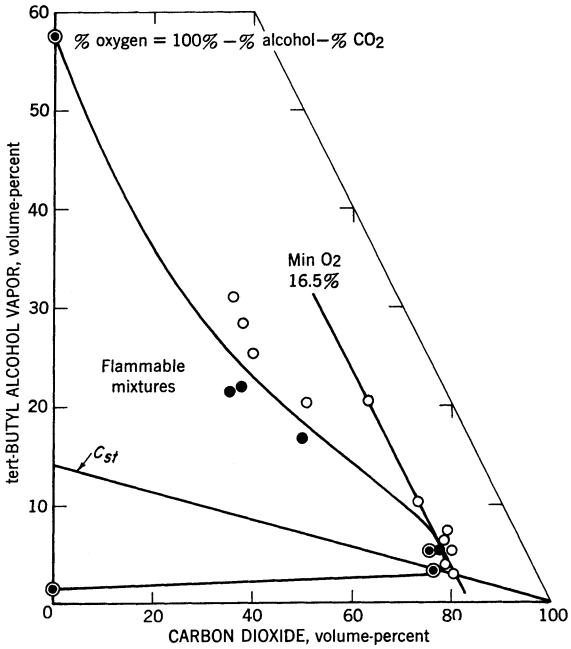

FIGURE 80.—Limits of Flammability of *tert*-Butyl Alcohol-Carbon Dioxide-Oxygen Mixtures at 150° C and Atmospheric Pressure.

Burning Rate

The burning velocities of methyl and isopropyl alcohol in air were determined by Gibbs and Calcote for a range of mixture compositions at 25° C; the maximum burning velocities were found to be 50.4 and 41.4 cm/sec, respectively (*68*). These investigators also obtained the burning velocities of methyl and *n*-propyl alcohol at 100° C; the maximum values were 72.2 and 64.8 cm/sec, respectively. These values

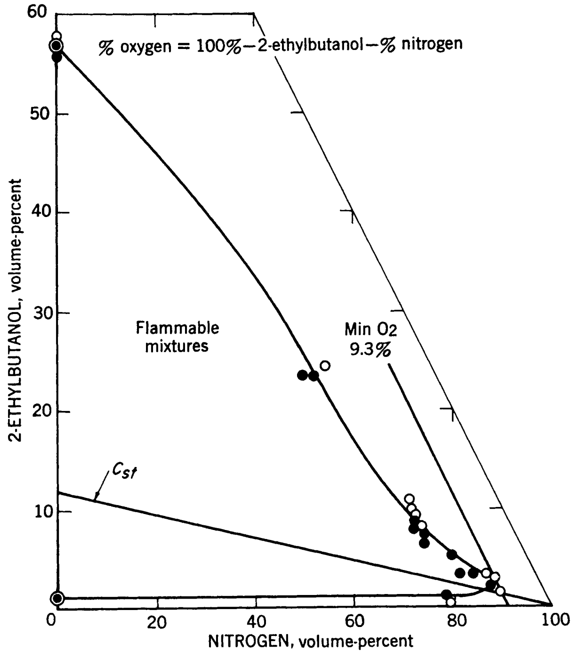

Figure 81.—Limits of Flammability of 2-Ethylbutanol-Nitrogen-Oxygen Mixtures at 150° C and Atmospheric Pressure.

are in fair agreement with the corresponding values of the paraffin hydrocarbons.

The methyl alcohol liquid-burning rate obtained from equation (53) is in fair agreement with that obtained experimentally (fig. 52). The relatively low $\Delta H_c/\Delta H_v$ ratios for the alcohols indicates that they should be characterized by low-burning rates in large pools.

ETHERS ($C_nH_{2n+1}OC_mH_{2m+1}$)

Limits in Air

The properties of a few common ethers are listed in table 14. Unfortunately, the limits data show appreciable scatter, so it is difficult to establish any general rules with the given data. However, as a first approximation, the L_{25}/C_{st} is about 0.5 for the simple ethers.

Limits in Other Atmospheres

Because of the importance of ethers as anesthetics, limits of flammability were determined in several atmospheres. The limits of the systems dimethyl ether-Freon-12 (CCl_2F_2)-air, dimethyl ether-carbon dioxide-air, and dimethyl ether-nitrogen-air obtained by Jones and coworkers are given in figure 82 (*114*); the limits of the systems diethyl ether-carbon dioxide-air and diethyl ether-nitrogen-air are given in figure 83 (*26*, *106*, *108*), Cool flames exist above the upper limit as noted; the upper limit of the cool flame region in air is 48.4 volume-percent, according to Burgoyne and Neale (*26*). The limits of the systems diethyl ether-helium-oxygen and diethyl ether-nitrous oxide-oxygen are given in figure 84 and the limits of diethyl ether-helium-nitrous oxide are given in figure 85 (*106*). Again, as with the alcohols, more inert is needed to assure the formation of nonflammable mixtures than is needed for the corresponding paraffin hydrocarbons. Also, cool flames are encountered at lower temperatures and pressures.

Comparison of curves in figures 84 and 85 shows that the minimum oxidant requirement for the formation of flammable diethyl ether-helium-oxidant mixtures is approximately twice

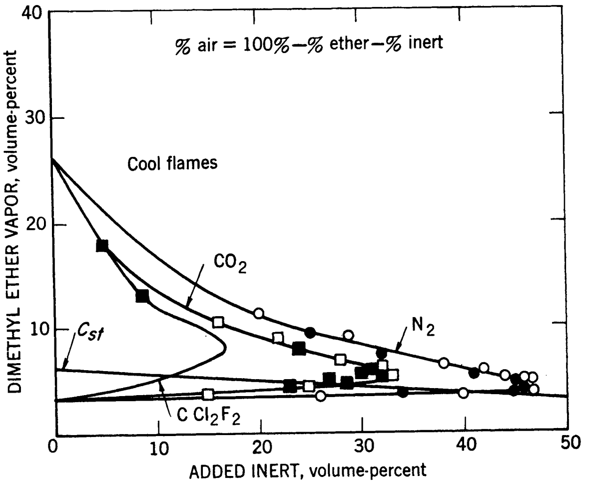

Figure 82.—Limits of Flammability of Dimethyl Ether-Carbon Dioxide-Air and Dimethyl Ether-Nitrogen-Air Mixtures at 25° C and Atmospheric Pressure.

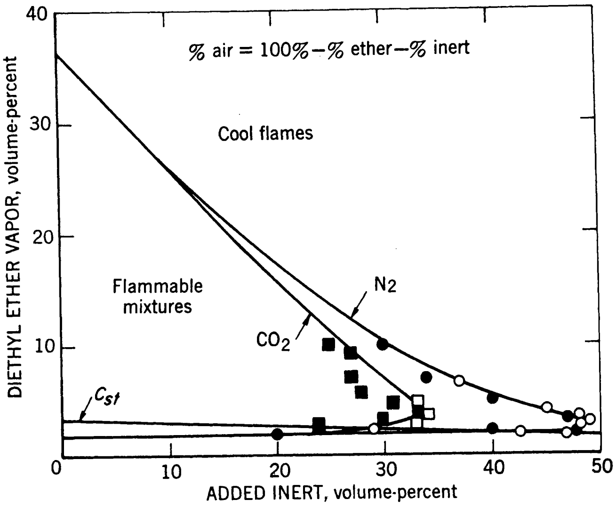

Figure 83.—Limits of Flammability of Diethyl Ether-Carbon Dioxide-Air and Diethyl Ether-Nitrogen-Air Mixtures at 25° C and Atmospheric Pressure.

TABLE 14.—*Properties of selected ethers*

Combustible	Formula	M	Sp gr (Air=1)	C_{st} in air (vol pct)	Net ΔH_c $\left(\frac{\text{Kcal}}{\text{mole}}\right)$	Lower limit in air				Upper limit in air			
						L_{25} (vol pct)	$\frac{L_{25}}{C_{st}}$	L $\left(\frac{\text{mg}}{\text{l}}\right)$	Ref.	U_{25} (vol pct)	$\frac{U_{25}}{C_{st}}$	U $\left(\frac{\text{mg}}{\text{l}}\right)$	Ref.
Dimethyl ether	CH_3OCH_3	46.07	1.59	6.53	316	3.4	0.52	72 [1] 47	*114*	27	4.1	760	(*114*)
Diethyl ether	$C_2H_5OC_2H_5$	74.12	2.56	3.37	605	1.9	.56	64 [1] 50	(*40*)	[2] 36	11	1,880	(*40*)
Ethyl propyl ether	$C_2H_5OC_3H_7$	88.15	3.28	2.72	[3] 750	1.7	.62	68 [1] 56	(*26*)	[4] 9	3.3	390	(*26*)
Di-i-propyl ether	$C_3H_7OC_3H_7$	102.17	3.53	2.27	[5] 900	1.4	.57	60 [1] 51	(*40*)	7.9	3.5	290	(*40*)
Divinyl ether	$C_2H_3OC_2H_3$	70.09	2.42	4.02	[3] 1,770	1.7	.42	54 [1] 42	(*97*)	27	6.7	1,160	(*97*)

[1] $L^* = L\frac{M-16}{M}$.

[2] Cool flames: $U_{25}=53$ vol pct.

[3] Calculated value.

[4] Cool flames: $U_{25}>16$ vol pct.

[5] Ref. (*155*).

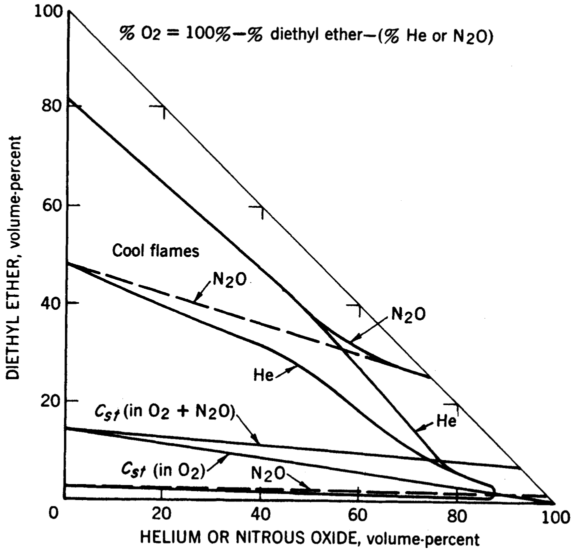

FIGURE 84.—Limits of Flammability of Diethyl Ether-Helium-Oxygen and Diethyl Ether-Nitrous Oxide-Oxygen Mixtures at 25° C and Atmospheric Pressure.

as great with nitrous oxide as with oxygen. However, if 1 mole of nitrous oxide furnishes one-half mole of oxygen during combustion, then the minimum oxygen contents in the two cases are nearly equal. Unfortunately, the available data are too meager to permit a more detailed comparison.

Autoignition

In general, ethers are readily ignited by hot surfaces. These combustibles usually have a lower ignition temperature in air and in oxygen than do the corresponding paraffins and alcohols. The available autoignition temperature data are included in appendix A.

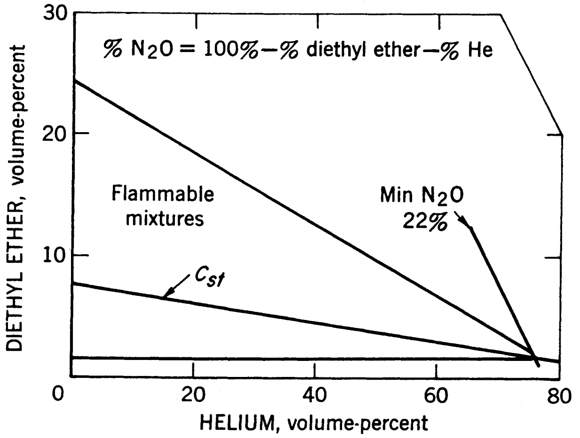

FIGURE 85.—Limits of Flammability of Diethyl Ether-Nitrous Oxide-Helium Mixtures at 25° C and Atmospheric Pressure.

Since the ethers tend to form peroxides under a variety of conditions, they may appear to be unstable at room temperature (*233*).

ESTERS ($C_nH_{2n-1}OOC_mH_{2m+1}$)

The properties of several esters are listed in table 15. The ratio of the lower limit at 25° C to the stoichiometric concentration is about 0.55 for many of these compounds. This is the same ratio as in equation (21) for paraffin hydrocarbons. The lower limit values expressed in terms of the weight of combustible per liter of air (see section about alcohols) are listed in parentheses under L(mg/l). These are larger than the corresponding values for the hydrocarbons and alcohols. The inert requirements and minimum oxygen requirements for the first member of the series, methyl formate, are nearly the same as for methyl alcohol and dimethyl ether (figs. 76, 82, 86). This is not

TABLE 15.—*Properties of selected esters*

Combustible	Formula	M	Sp. gr. (Air=1)	C_{st} in air (vol pct)	Net ΔH_c $\left(\frac{\text{Kcal}}{\text{mole}}\right)$	Lower limit in air				Upper limit in air			
						L_{25} (vol pct)	$\frac{L_{25}}{C_{st}}$	L $\left(\frac{\text{mg}}{1}\right)$	Ref.	U_{25} (vol pct)	$\frac{U_{25}}{C_{st}}$	U $\left(\frac{\text{mg}}{1}\right)$	Ref.
Methyl formate	$HCOOCH_3$	60.05	2.07	9.48	219	5.0	0.53	142 [1] 66	*(111)*	23.0	2.4	800	*(111)*
Ethyl formate	$HCOOC_2H_5$	74.08	2.56	5.65	367	2.8	.50	95 [1] 54	*(40)*	16.0	2.8	630	*(40)*
n-Butyl formate	$HCOOC_4H_9$	102.13	3.53	3.12	[2] 650	1.7	.54	79 [1] 50	*(40)*	8.2	2.6	410	*(40)*
Methyl acetate	CH_3COOCH_3	74.08	2.56	5.65	358	3.2	.57	106 [1] 60	*(40)*	16.0	2.8	630	*(40)*
Ethyl acetate	$CH_3COOC_2H_5$	88.10	3.04	4.02	504	2.2	.55	88 [1] 56	*(40)*	11.0	2.7	510	*(175)*
n-Propyl acetate	$CH_3COOC_3H_7$	102.13	3.53	3.12	[2] 650	1.8	.58	83 [1] 57	*(40)*	[3] 8.0	2.6	400	*(40)*
n-Butyl acetate	$CH_3COOC_4H_9$	116.16	4.01	2.55	----------	[4] 1.4	.55	73 [1] 53	(5)	[4] 8.0	3.1	450	(5)
n-Amyl acetate	$CH_3COOC_5H_{11}$	130.18	4.50	2.16	----------	[4] 1.0	.51	65 [1] 49	(5)	[4] 7.1	3.3	440	(5)
Methyl propionate	$C_2H_5COOCH_3$	88.10	3.04	4.02	----------	2.4	.60	97 [1] 62	*(40)*	13.0	[6] 3.2	580	*(40)*
Ethyl propionate	$C_2H_5COOC_2H_5$	102.13	3.53	3.12	[2] 650	1.8	.58	83 [1] 57	*(40)*	11.0	[6] 3.5	510	*(40)*

[1] $L^* = L\frac{M-32}{M}$.

[2] Calculated value.

[3] $t=90°$ C.

[4] $t=100°$ C.

[5] Figures compiled by Explosives Res. Center, Federal Bureau of Mines.

[6] $P=0.5$ atm.

true of the other members for which data compiled at the Explosives Research Center are available—isobutyl formate and methyl acetate (figs. 87, 88). Accordingly, it is rather difficult to make additional generalizations for this series.

The autoignition temperatures of many esters in air and oxygen at atmospheric pressure are given in appendix A. In general, the AIT values of the esters are lower than are those of the corresponding paraffins.

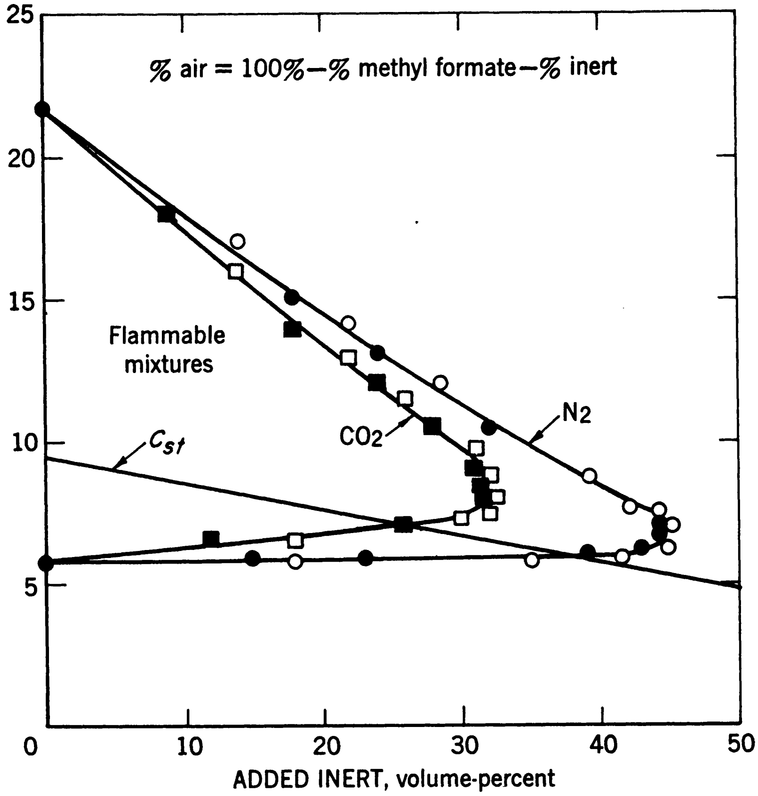

FIGURE 86.—Limits of Flammability of Methyl Formate-Carbon Dioxide-Air and Methyl Formate-Nitrogen-Air Mixtures.

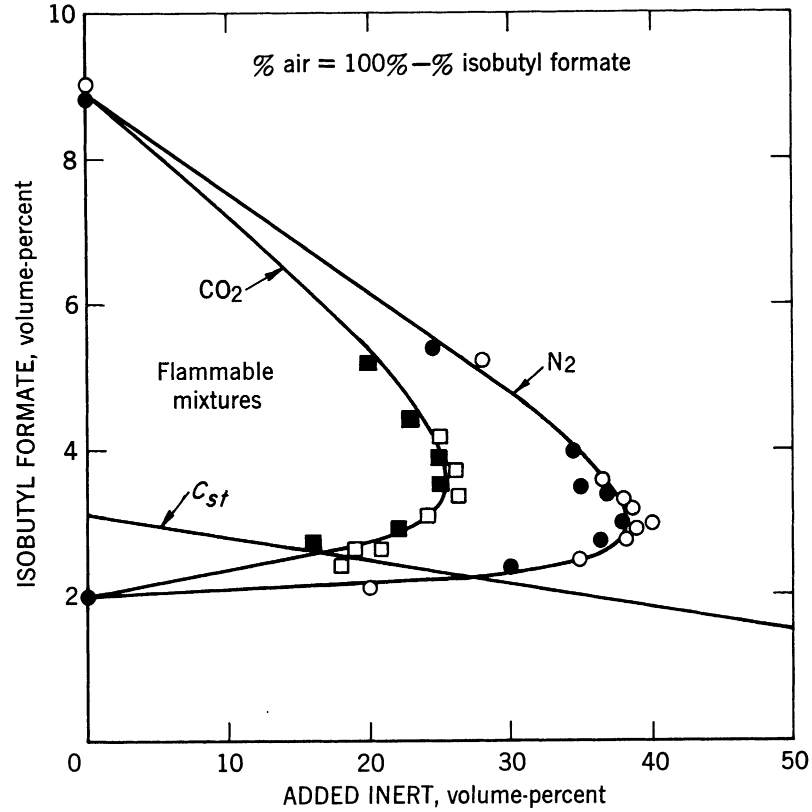

FIGURE 87.—Limits of Flammability of Isobutyl Formate-Carbon Dioxide-Air and Isobutyl Formate-Nitrogen-Air Mixtures.

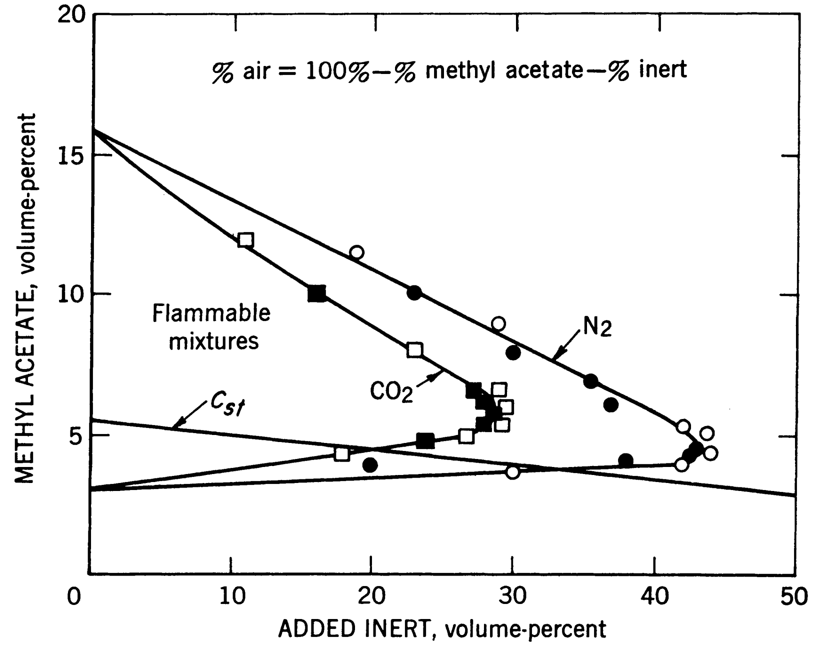

FIGURE 88.—Limits of Flammability of Methyl Acetate-Carbon Dioxide-Air and Methyl Acetate-Nitrogen-Air Mixtures.

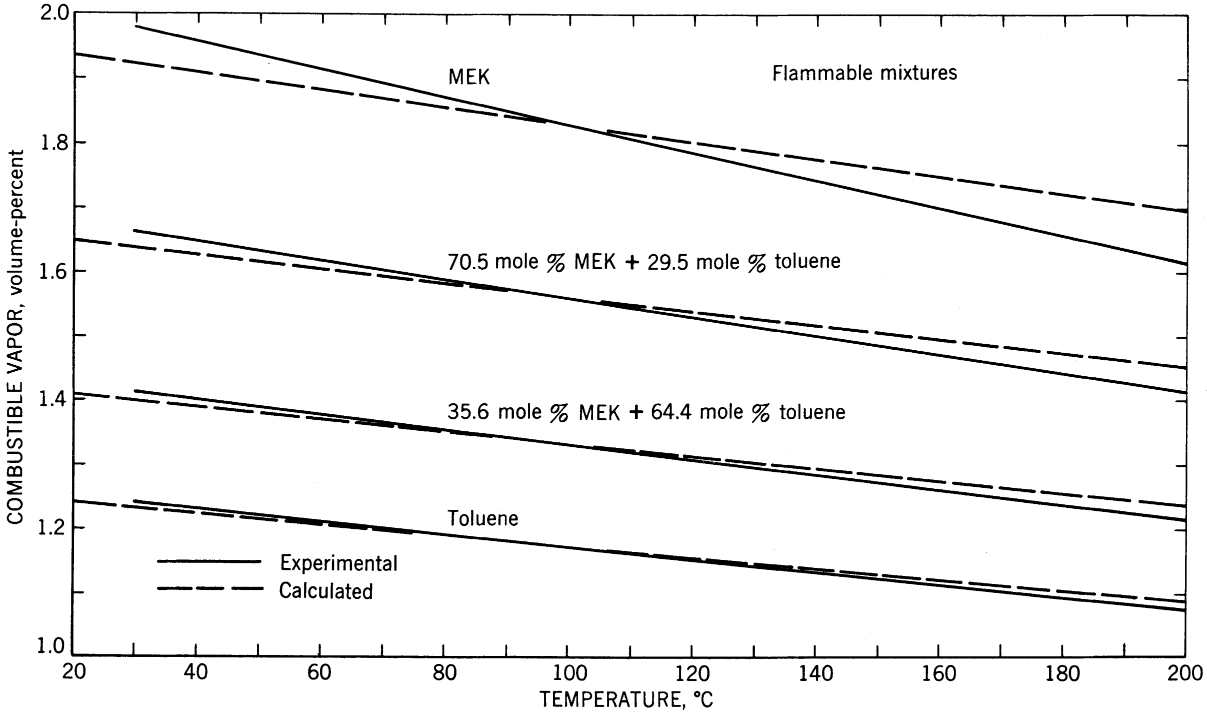

FIGURE 89.—Effect of Temperature on Lower Limits of Flammability of MEK-Toluene Mixtures in Air at Atmospheric Pressure.

ALDEHYDES AND KETONES ($C_n H_{2n}O$)

Properties of some aldehydes and ketones are given in table 16. The ratio of the lower limit at 25° C in air to the stoichiometric composition is approximately 0.5.

Zabetakis, Cooper, and Furno found that the lower limits of methyl ethyl ketone (MEK) and MEK-toluene mixtures vary linearly with temperature between room temperature and 200° C (*235*). A summary of these data is given in figure 89; broken curves in this figure were obtained from the modified Burgess-Wheeler law, equation (33), taking the lower limit at 100° C as the reference value. Similar data were obtained for tetrahydrofuran (THF) and THF-toluene mixtures (fig. 90). In addition, it was shown that the systems MEK-toluene and THF-toluene obey Le Chatelier's law, equation (46). Calculated and experimental values for the preceding systems in air are given in figures 91 and 92.

The limits of the systems acetone-carbon dioxide-air, acetone-nitrogen-air, MEK-chlorobromomethane (CBM)-air, MEK-carbon dioxide-air, and MEK-nitrogen-air are given in figures 93 and 94. The data in these figures were obtained by Jones and coworkers (*238*).

TABLE 16.—*Properties of selected aldehydes and ketones*

Combustible	Formula	M	Sp gr (Air=1)	C_{st} in air (vol pct)	Net ΔH_c $\left(\frac{\text{Kcal}}{\text{mole}}\right)$	Lower limit in air				Upper limit in air			
						L_{25} (vol pct)	$\frac{L_{25}}{C_{st}}$	L $\left(\frac{\text{mg}}{1}\right)$	Ref.	U_{25} (vol pct)	$\frac{U_{25}}{C_{st}}$	U $\left(\frac{\text{mg}}{1}\right)$	Ref.
Acetaldehyde	CH_3CHO	44.05	1.52	7.73	264	4.0	0.52	82	(*223*)	[1] 36	4.7	1,100	(*26*)
Propionaldehyde	C_2H_5CHO	58.08	2.01	4.97	409	2.9	.59	77	(*26*)	[2] 14	2.8	420	(*26*)
Paraldehyde	$(CH_3CHO)_3$	132.16	4.56	2.72	----	1.3	.48	78	(*40*)	----	----	----	----
Acetone	CH_3COCH_3	58.08	2.01	4.97	403	2.6	.52	70	(*98*)	13	2.6	390	(*98*)
Methyl ethyl ketone	$CH_3COC_2H_5$	72.10	2.49	3.67	548	1.9	.52	62	(*235*)	10	2.7	350	(*223*)
Methyl propyl ketone	$CH_3COC_3H_7$	86.13	2.97	2.90	692	1.6	.55	63	(*40*)	8.2	2.8	340	(*40*)
Diethyl ketone	$C_2H_5COC_2H_5$	86.13	2.97	2.90	692	1.6	.55	63	(3)	----	----	----	----
Methyl butyl ketone	$CH_3COC_4H_9$	100.16	3.46	2.40	840	[4] 1.4	.58	64	(*40*)	[5] 8.0	3.3	390	(*40*)

[1] Cool flames: U_{25}=60 vol pct.
[2] Cool flames: U_{25}=17 vol pct.
[3] Calculated value.
[4] t=50° C.
[5] t=100° C.

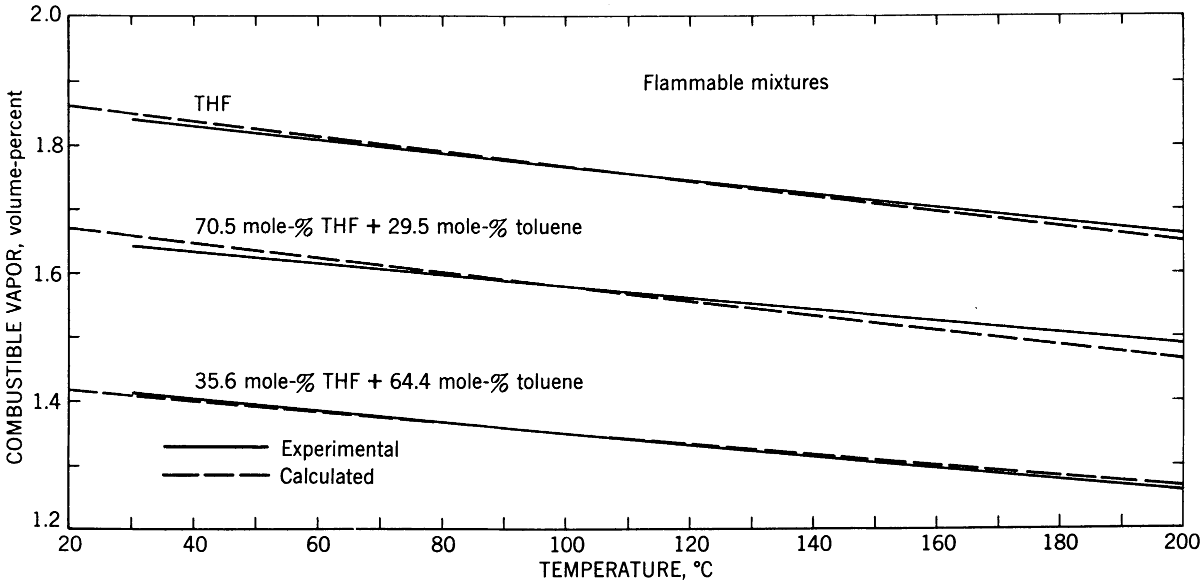

FIGURE 90.—Effect of Temperature on Lower Limits of Flammability of THF-Toluene Mixtures in Air at Atmospheric Pressure.

The autoignition temperatures of various aldehydes and ketones in oxygen and air at atmospheric pressure are given in appendix A. In general, the AIT values are lower than those of the corresponding paraffins.

SULFUR COMPOUNDS

The pertinent properties of sulfur compounds are given in table 17. In general, they have wide flammable ranges and relatively low ignition temperatures (appendix A).

Flammability diagrams are given for carbon disulfide mixed with carbon dioxide-air, water vapor-air (*239*) and nitrogen-air (fig. 95); hydrogen sulfide-carbon dioxide-air (fig. 96); and ethyl mercaptan with chlorodifluoromethane and dichlorodifluoromethane in air (*117*) (fig. 97). Figure 95 is interesting in that it shows not only the wide flammable range of carbon disulfide in air but also the large quantities of inert required to prevent the formation of flammable mixtures.

FUELS AND FUEL BLENDS

Fuels used for propulsion, not covered in other sections, are considered here (table 18).

Ammonia and Related Compounds

This series includes ammonia (NH_3), hydrazine (N_2H_4), monomethylhydrazine ($N_2H_3{\cdot}CH_3$) and unsymmetrical dimethylhydrazine ($N_2H_2{\cdot}(CH_3)_2$).

Ammonia forms flammable mixtures with air and other oxidants in a variety of concentrations, as noted in table 19. White (*225*) and more recently, Buckley and Husa, (*19*) reported that, as with hydrocarbons, an increase in either temperature or pressure tends to widen the flammable range. Further, White found that the lower limit flame temperature remains essentially constant with increase in initial temperature.

TABLE 17.—*Properties of selected sulfur compounds*

Combustible	Formula	M	Sp gr (Air=1)	C_{st} in air (vol pct)	Net ΔH_c $\left(\frac{\text{Kcal}}{\text{mole}}\right)$	Lower limit in air				Upper limit in air			
						L_{25} (vol pct)	$\frac{L_{25}}{C_{st}}$	L $\left(\frac{\text{mg}}{1}\right)$	Ref.	U_{25} (vol pct)	$\frac{U_{25}}{C_{st}}$	U $\left(\frac{\text{mg}}{1}\right)$	Ref.
Hydrogen sulfide	H_2S	34.08	1.18	12.25	145	4.0	0.33	63	(1)	44	3.6	1,190	(1)
Carbon disulfide	CS_2	76.13	2.63	6.53	252	1.3	.20	45	(*239*)	50	7.7	3,400	(*223*)
Methyl mercaptan	CH_3SH	48.10	1.66	6.53	276	3.9	.60	87	(1)	22	3.4	600	(1)
Ethyl mercaptan	C_2H_5SH	62.13	2.15	4.45	492	2.8	.63	80	(*104*)	18	4.4	610	(*104*)
Dimethyl sulfide	CH_3SCH_3	62.13	2.15	4.45	----------	2.2	.50	62	(1)	20	4.5	690	(1)

[1] Figures compiled at Explosives Res. Center, Federal Bureau of Mines.

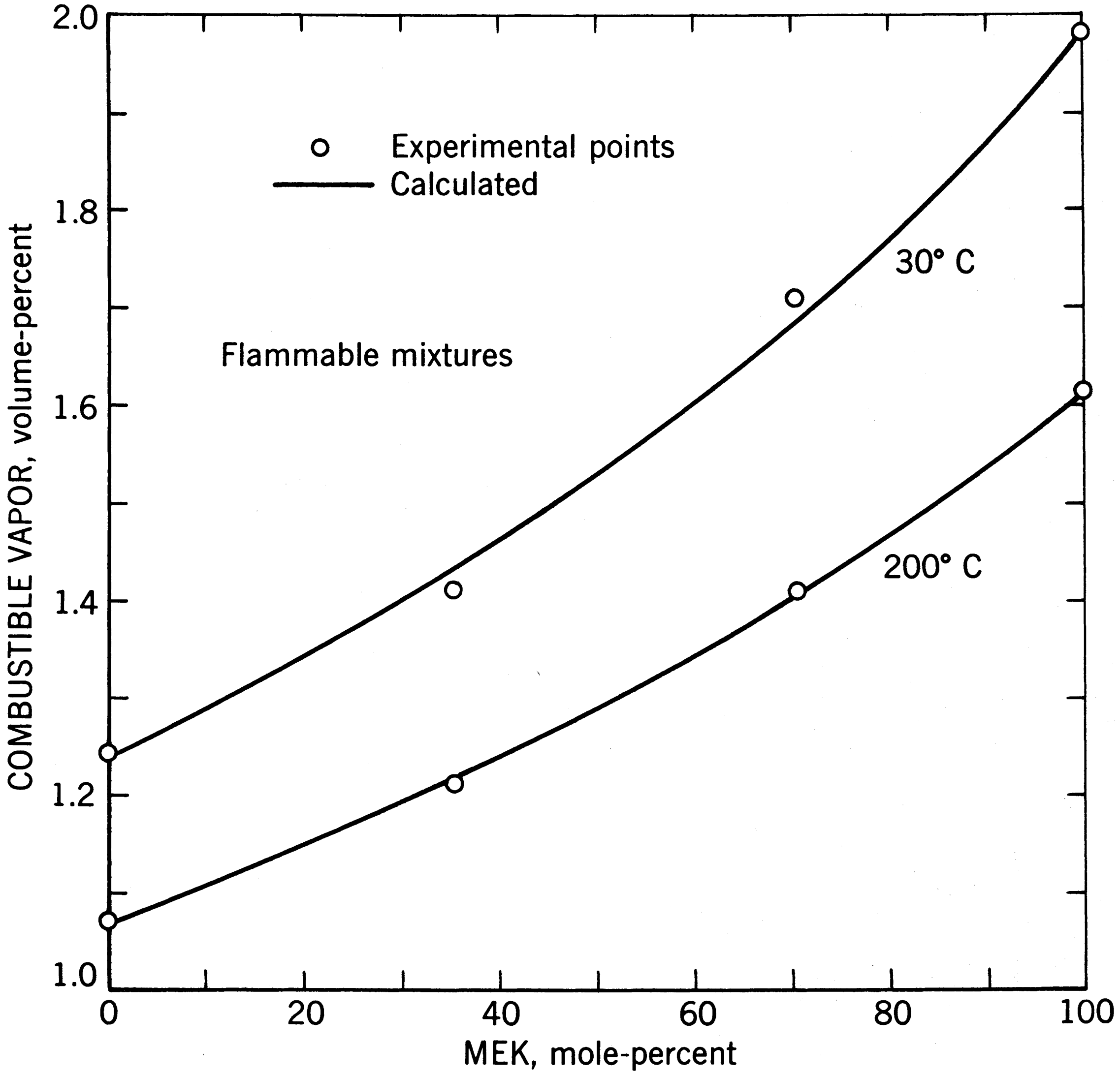

FIGURE 91.—Effect of Liquid Composition on Lower Limits of Flammability of MEK-Toluene Mixtures in Air at 30° and 200° C.

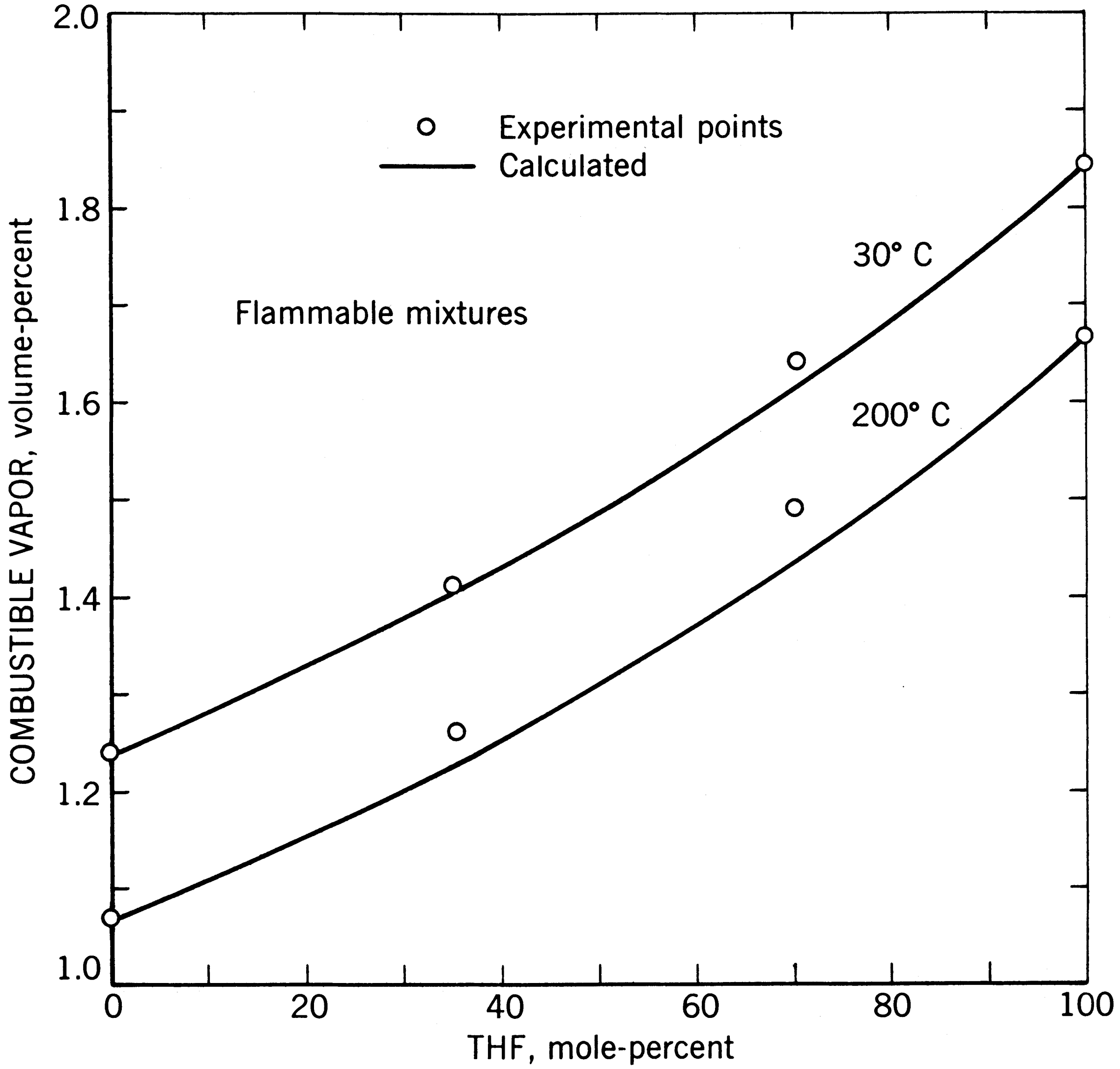

FIGURE 92.—Effect of Liquid Composition on Lower Limits of Flammability of THF-Toluene Mixtures in Air at 30° and 200° C.

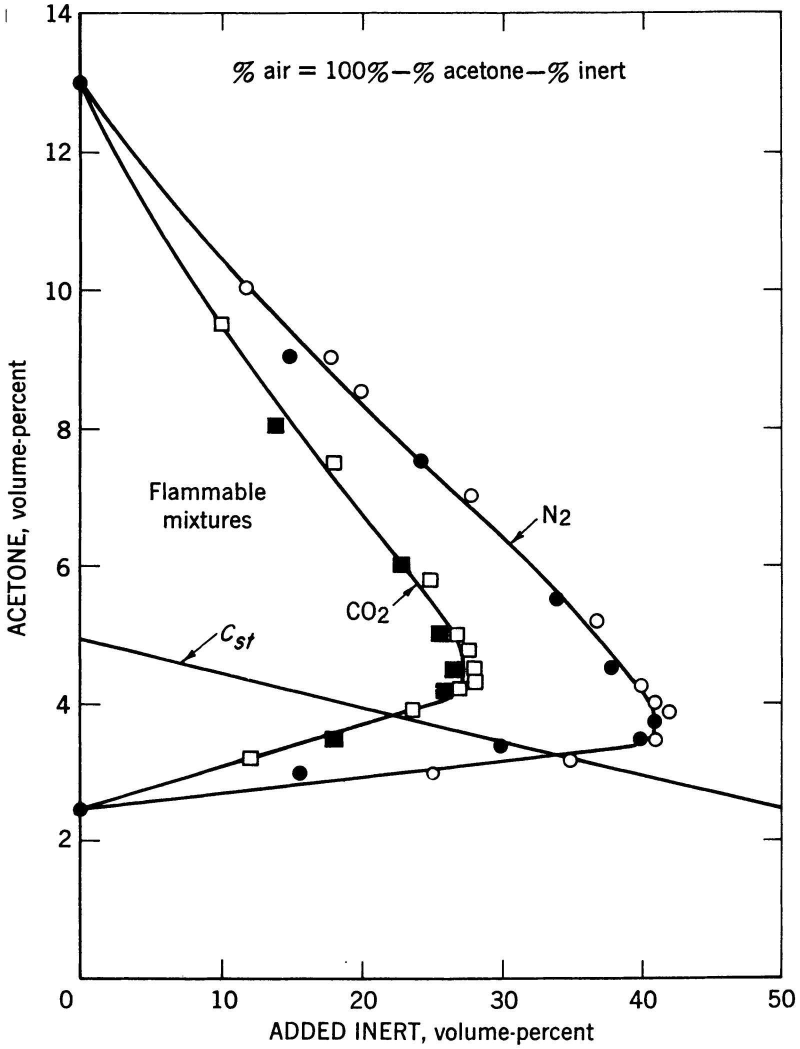

FIGURE 93.—Limits of Flammability of Acetone-Carbon Dioxide-Air and Acetone-Nitrogen-Air Mixtures.

TABLE 18.—*Properties of selected fuels and fuel blends*

Combustible	Formula	M	Sp gr (Air=1)	C_{st} in air (vol pct)	Net ΔH_c $\left(\frac{\text{Kcal}}{\text{mole}}\right)$	Lower limit in air				Upper limit in air			
						L_{25} (vol pct)	$\frac{L_{25}}{C_{st}}$	L $\left(\frac{\text{mg}}{1}\right)$	Ref.	U_{25} (vol pct)	$\frac{U_{25}}{C_{st}}$	U $\left(\frac{\text{mg}}{1}\right)$	Ref.
Ammonia	NH_3	17.03	0.59	21.83	----------	15	0.69	134	(*167*)	28	1.3	300	(*182*)
Hydrazine	N_2H_4	32.05	1.11	17.32	----------	4.7	.27	70	(*188*)	100	5.8	----------	(*218*)
Monomethyl hydrazine	$N_2H_3CH_3$	46.07	1.59	7.73	----------	4	.52	86	(*218*)	----------	----------	----------	----------
Unsymmetrical dimethylhydrazine.	$N_2H_2(CH_3)_2$	60.10	2.08	4.97	----------	2	.40	55	(*166*)	95	19.1	----------	(*218*)
Diborane	B_2H_6	27.69	.96	6.53	478	.8	.12	10	(*163*)	88	13.5	----------	(*163*)
Tetraborane	B_4H_{10}	53.36	1.84	3.67	----------	.4	.11	10	(1)	----------	----------	----------	----------
Pentaborane	B_5H_9	63.17	2.18	3.37	1030	.42	.12	12	----------	----------	----------	----------	----------
Decaborane	$B_{10}H_{14}$	122.31	4.23	1.87	----------	.2	.11	11	(1)	----------	----------	----------	----------
Aviation gasoline 100/130	----------	----------	----------	----------	----------	1.3	----------	----------	(*241*)	7.1	----------	----------	(*241*)
Aviation gasoline 115/145	----------	----------	----------	----------	----------	1.2	----------	----------	(*241*)	7.1	----------	----------	(*241*)
Aviation jet fuel JP-1	----------	----------	----------	----------	----------	----------	----------	[2] 48	(*241*)	----------	----------	[2] 380	(*241*)
Aviation jet fuel JP-3	----------	----------	----------	----------	----------	1.4	----------	----------	(*241*)	8	----------	----------	(*241*)
Aviation jet fuel JP-4	----------	----------	----------	----------	----------	1.3	----------	48	(*241*)	8	----------	330	(*241*)
Aviation jet fuel JP-6	----------	----------	----------	----------	----------	----------	----------	[3] 46	(*127*)	----------	----------	[2] 290	(*127*)
Hydrogen	H_2	2.016	.07	29.53	57.8	4.0	.14	3.7	(*40*)	75	2.54	270	(*224*)

[1] Calculated value.

[2] $t=150°$ C.

[3] $t=100°$ C.

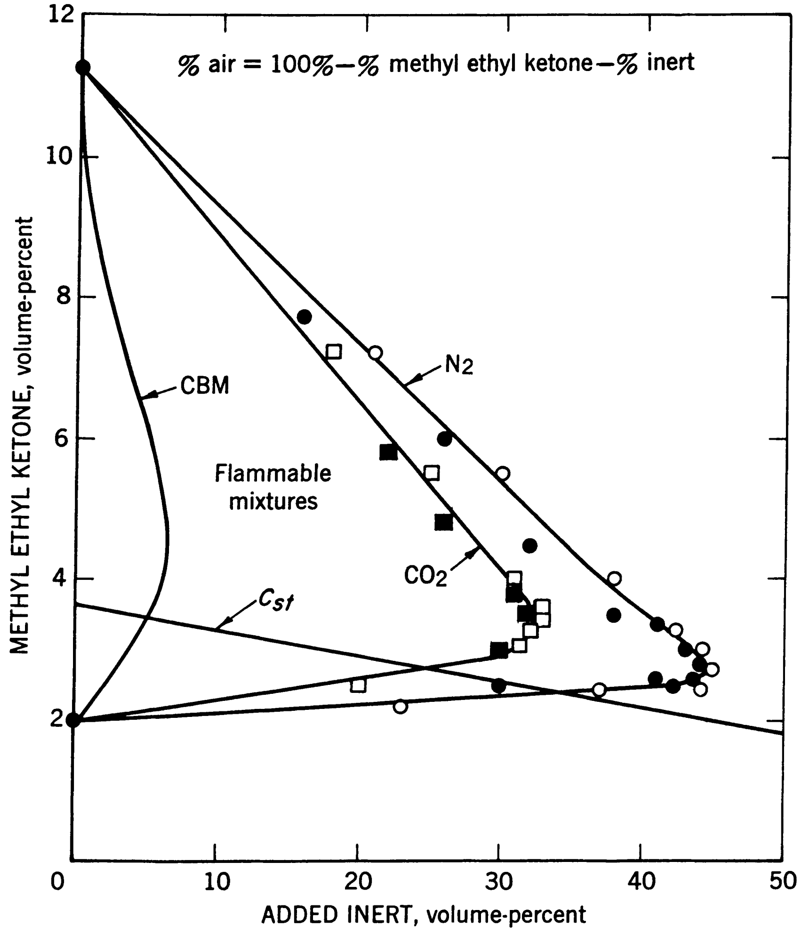

Figure 94.—Limits of Flammability of Methyl Ethyl Ketone (MEK) - Chlorobromemethane (CBM)-Air, MEK-Carbon Dioxide Dioxide-Air and MEK-Nitrogen-Air Mixtures at 25° C and Atmospheric Pressure.

Table 19.—*Limits of flammability of ammonia at room temperature and near atmospheric pressure*

Oxidant	C_{st}	L	U	Ref.
Air	21. 8	15	28	(*167, 182*)
Oxygen	57. 1	15	79	(*225*)
Nitrous oxide	40. 0	2. 2	72	(*109*)

Hydrazine vapor burns in the absence of an oxidizer, so that it has no upper limit and can therefore be used as a monopropellant. The decomposition flame yields hydrogen, nitrogen, and ammonia (*64*, *73*). However, hydrazine vapor can be rendered nonflammable by addition of stable diluents or inhibitors. The amount of diluent required at any temperature and pressure appears to be governed in part by the ignition source strength. With a 0.25-inch spark gap and a 15,000-volt, 60-ma-luminous-tube transformer as the energy source, Furno, Martindill, and Zabetakis (*63*) found that the following quantities of hydrocarbon vapor were needed to inhibit flame propagation in a 1¼-inch glass tube[5] at 125° C and atmospheric pressure: 39.8 pct benzene; 35.0 pct toluene; 27.3 pct *m*-xylene; 23.8 pct cumene; 21.0 pct *n*-heptane. On this same basis, 95.3 pct air is needed to prevent flame propagation (*188*); this corresponds to a lower limit of flammability of 4.7 pct hydrazine vapor. The flammable range in air at atmospheric pressure is presented graphically in figure 98, which also gives the flammable ranges of monomethylhydrazine, unsymmetrical dimethylhydrazine, and ammonia for comparison (*218*). The flammability diagram for the system hydrazine-*n*-heptane-air at 125° C and atmospheric pressure is given in figure 99. These data were also obtained in a 1¼-inch glass tube.

A summary of the autoignition temperature data obtained by Perlee, Imhof, and Zabetakis (*166*) for hydrazine, MMH, and UDMH in air and nitrogen dioxide (actually, the equilibrium

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[5] Comparable results were partially obtained in a 2-inch tube.

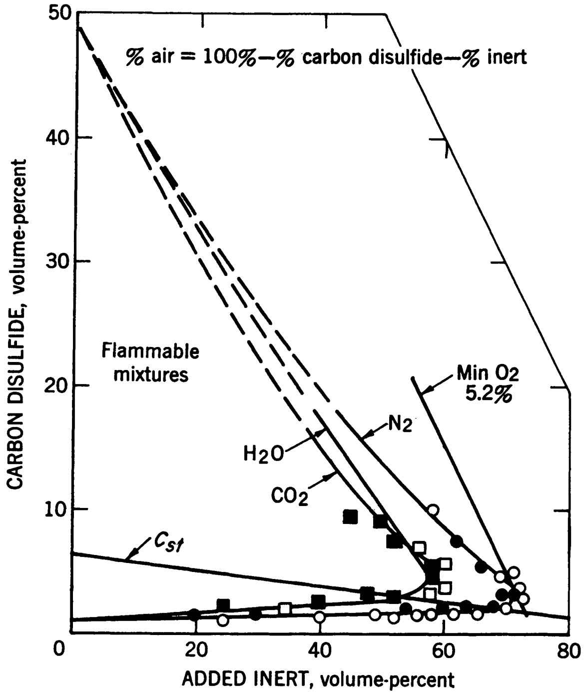


Figure 95.—Limits of Flammability of Carbon Disulfide-Carbon Dioxide-Air, Carbon Dioxide-Nitrogen-Air Mixtures at 25° C and Atmospheric Pressure, and Carbon Disulfide-Water Vapor-Air at 100° C and Atmospheric Pressure.

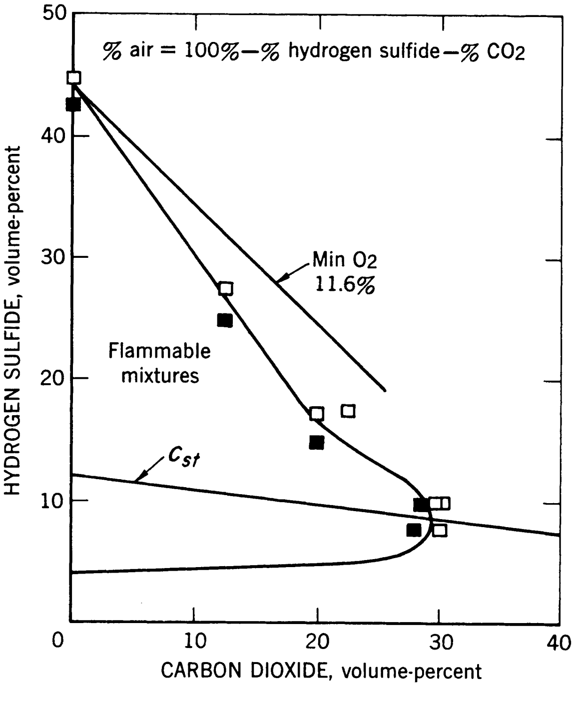


Figure 96.—Limits of Flammability of Hydrogen Sulfide-Carbon Dioxide-Air Mixtures at 25° C and Atmospheric Pressure.

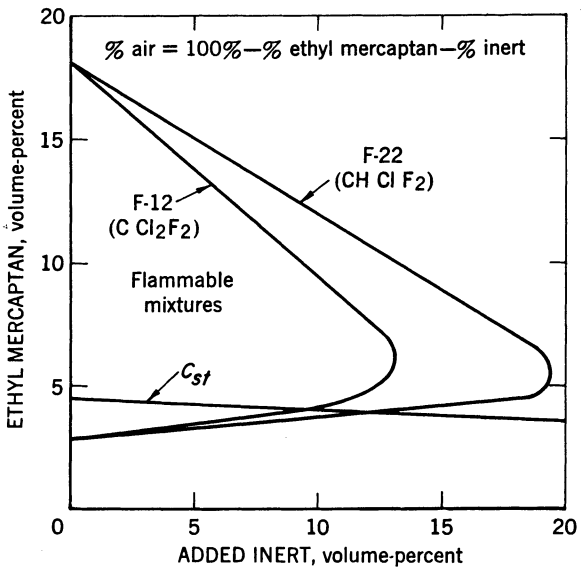


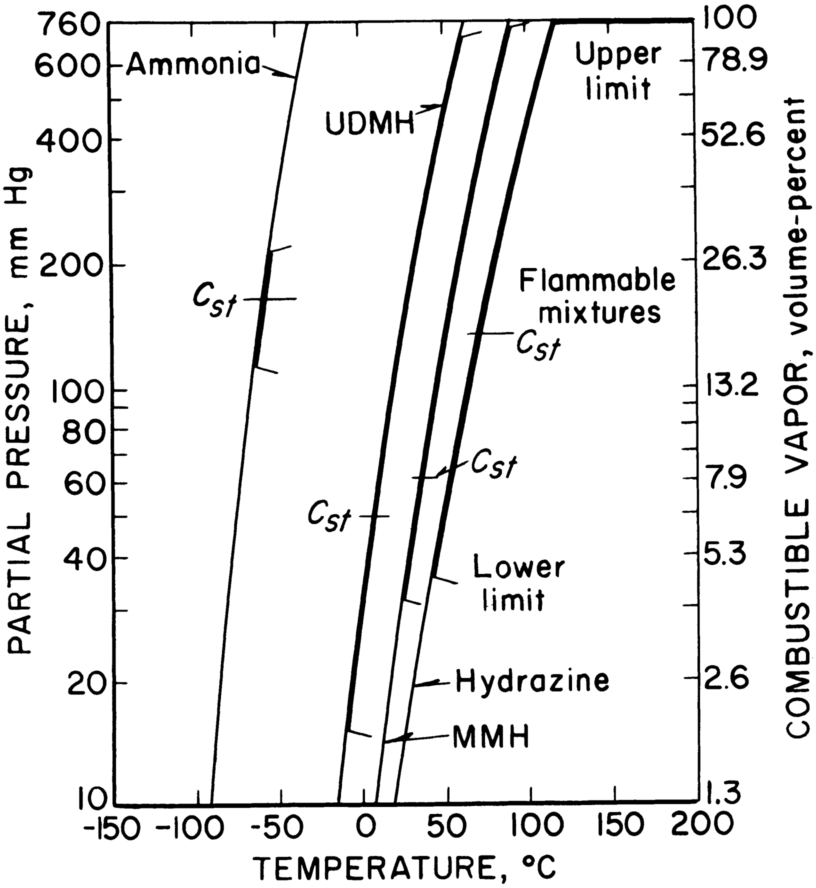
Figure 97.—Limits of Flammability of Ethyl Mercaptan-F-12-Air and Ethyl Mercaptan-F-22-Air Mixtures at Atmospheric Pressure and 27° C.

mixture $NO_2^* \rightleftharpoons NO_2 + N_2O_4$) is given in figure 100; short horizontal lines indicate the uncertainty in NO_2^* concentrations. These materials may ignite spontaneously at room temperature with relatively small NO_2^* concentrations in the air; at 25° C, liquid UDMH ignites in NO_2^*-air atmospheres that contain more than about 8 volume-percent NO_2^*; MMH and hydrazine ignite in atmospheres that contain more than about 11 and 14 volume-percent NO_2^*, respectively. In general, even smaller concentrations of NO_2^* produce spontaneous ignition of these combustibles at higher initial combustible liquid temperatures. The effect of the hydrazine liquid temperature on the spontaneous ignition temperature in NO_2^*-air atmospheres is illustrated in figure 101. Similar data are given in figures 102 and 103 for MMH and UDMH; there is an apparent anomaly in the data obtained with MMH at 36°, 55°, and 67° C.

The use of various helium-oxygen atmospheres in place of air results in the spontaneous ignition temperature curves given in figure 104 for UDMH. Comparison of curve *B* of this set with curve *A* of figure 100 indicates that the spontaneous ignition temperature of UDMH in NO_2^*-He-O_2 atmospheres is the same as that obtained in NO_2^*-air atmospheres.

Ignition temperature data obtained with UDMH in NO_2^*-air mixtures at 15 and 45 psia are summarized in figure 105. These indicate that although the spontaneous ignition temperature of UDMH in air is not affected ap-

FIGURE 98.—Limits of Flammability of Ammonia, UDMH, MMH, and Hydrazine at Atmospheric Pressure in Saturated and Near-Saturated Vapor-Air Mixtures.



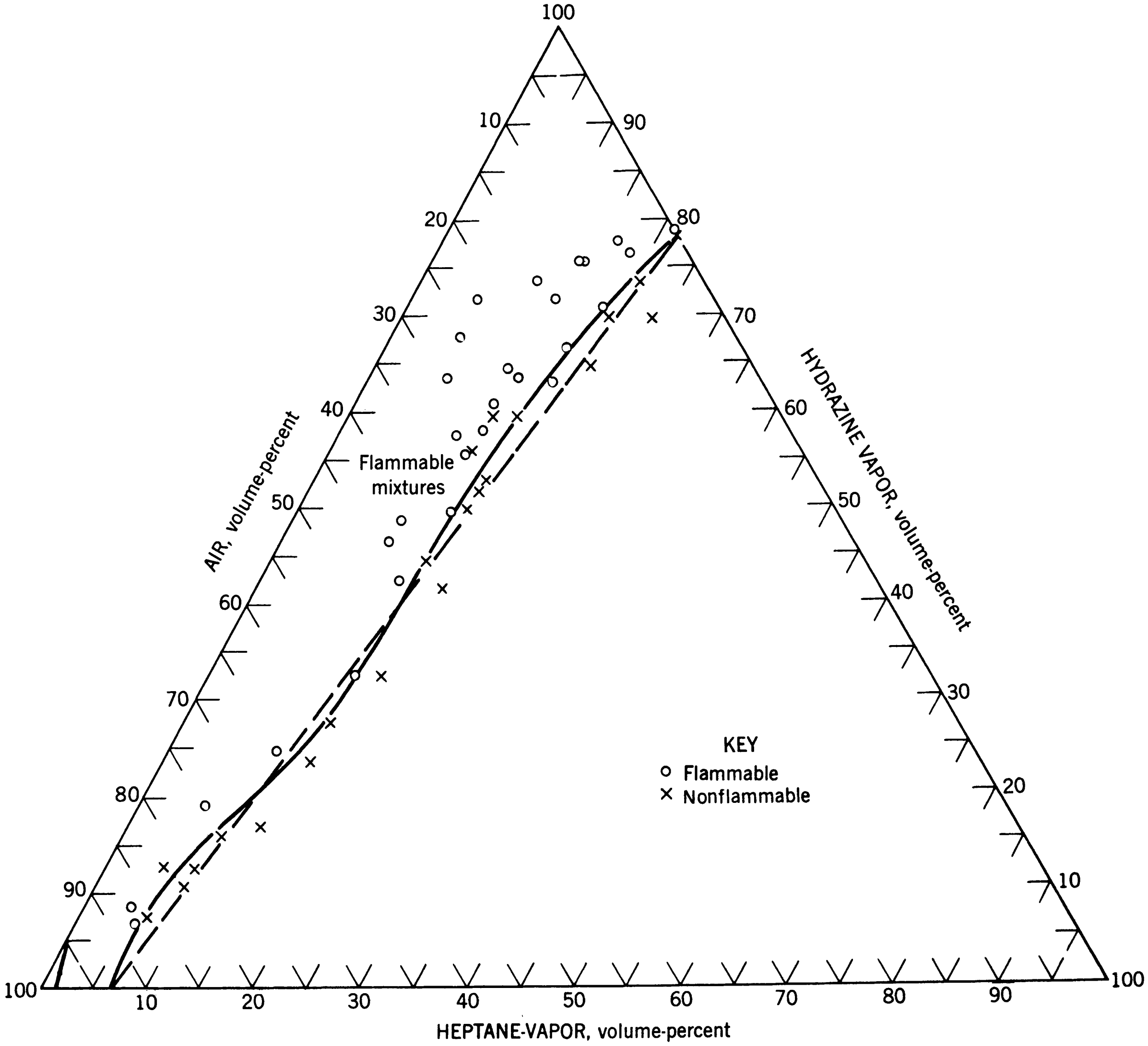


FIGURE 99.—Flammable Mixture Compositions of Hydrazine-Heptane-Air at 125° C and Approximately Atmospheric Pressure.

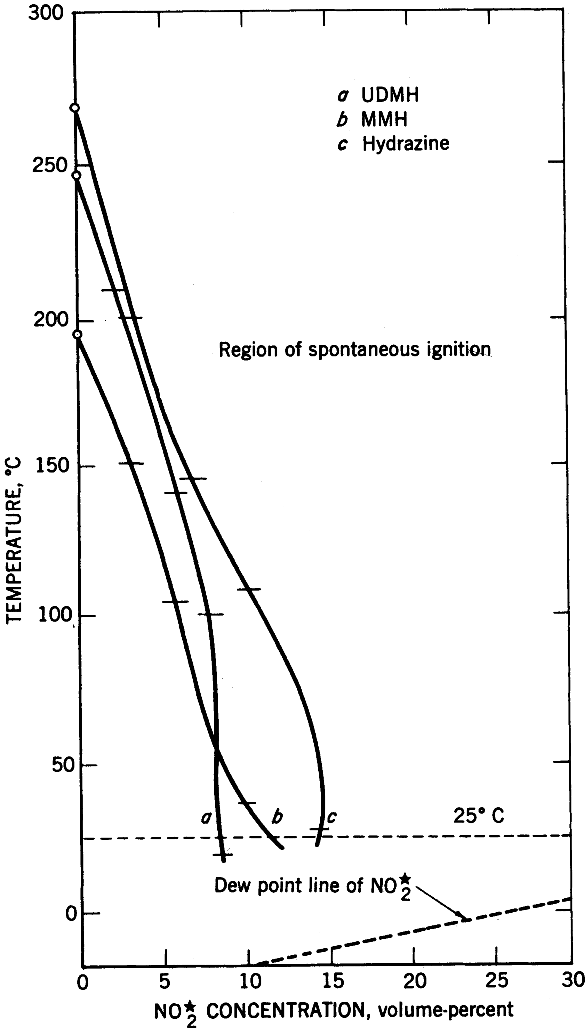


FIGURE 100.—Minimum Spontaneous Ignition Temperatures of Liquid Hydrazine, MMH, and UDMH at an Initial Temperature of 25° C in Contact With NO_2*-Air Mixtures at 740±10 mm Hg as a Function of NO_2* Concentration.

preciably by this pressure change, it is affected in a range of NO_2*-air mixtures.

The data presented in figures 100 to 105 were obtained with liquid fuel in contact with vaporized NO_2^* in air. Similar data obtained with vaporized UDMH-air in contact with NO_2^* are given in figure 106. This figure indicates that UDMH-air mixtures that contain more than 9 volume-percent UDMH will ignite spontaneously on contact with NO_2^*; UDMH-air mixtures that contain more than approximately 2 volume-percent UDMH can be ignited by an ignition source under the same conditions (*166*).

Boron Hydrides

This series includes diborane (B_2H_6), tetraborane (B_4H_{10}), pentaborane (B_5H_9), and decaborane ($B_{10}H_{14}$). However, reliable upper and lower limit data are available only on the first member of this series at the present time. These were obtained by Parker and Wolfhard (*163*) who determined the limits of flammability of diborane in air in a 5-cm-diameter tube at an initial pressure of 300 mm Hg; this combustible forms flammable mixtures in air in the range from 0.8 to 87.5 volume-percent. A pale blue flame propagated throughout the tube at the upper limit; luminous flames were not visible above 79 volume-percent. Limit of flammability curves for the system diborane-ethane-air are presented in rectangular coordinates in figure 107. Except for the slight dip to the ethane-axis (zero diborane) in the area in which ethane forms flammable mixtures in air, these curves are rather similar to those obtained with other combustible-oxidant-inert systems. Burning velocities in excess of 500 cm/sec were measured in this same study for fuel-rich diborane-air mixtures.

Berl and Renich have prepared a summary report about boron hydrides (*9*). It includes data obtained by these and other authors; they found the lower limit of pentaborane in air to be 0.42 volume-percent.

The autoignition temperature of diborane in air is apparently quite low. Price obtained a value of 135° C at 16.1 mm Hg (*169*); that of pentaborane is 30° C at about 8 mm Hg (*9*).

Gasolines, Diesel and Jet Fuels

Fuels considered in this section are blends that contain a wide variety of hydrocarbons and additives. Accordingly, their flammability characteristics are governed by the method used to extract a vapor sample as well as by the history of the liquid. For example, since the lower limit of flammability, expressed in volume-percent, is inversely proportional to the molecular weight of the combustible vapor, equation (28), the first vapors to come from a blend, such as gasoline, give a higher lower limit value than the completely vaporized sample. Conversely, the heavy fractions or residue give a smaller lower limit value. For this reason, there is some disagreement about the limits of flammability of blends such as gasoline and the diesel and jet fuels. These fuels are, in general, characterized by a wide distillation range; the ASTM distillation curves

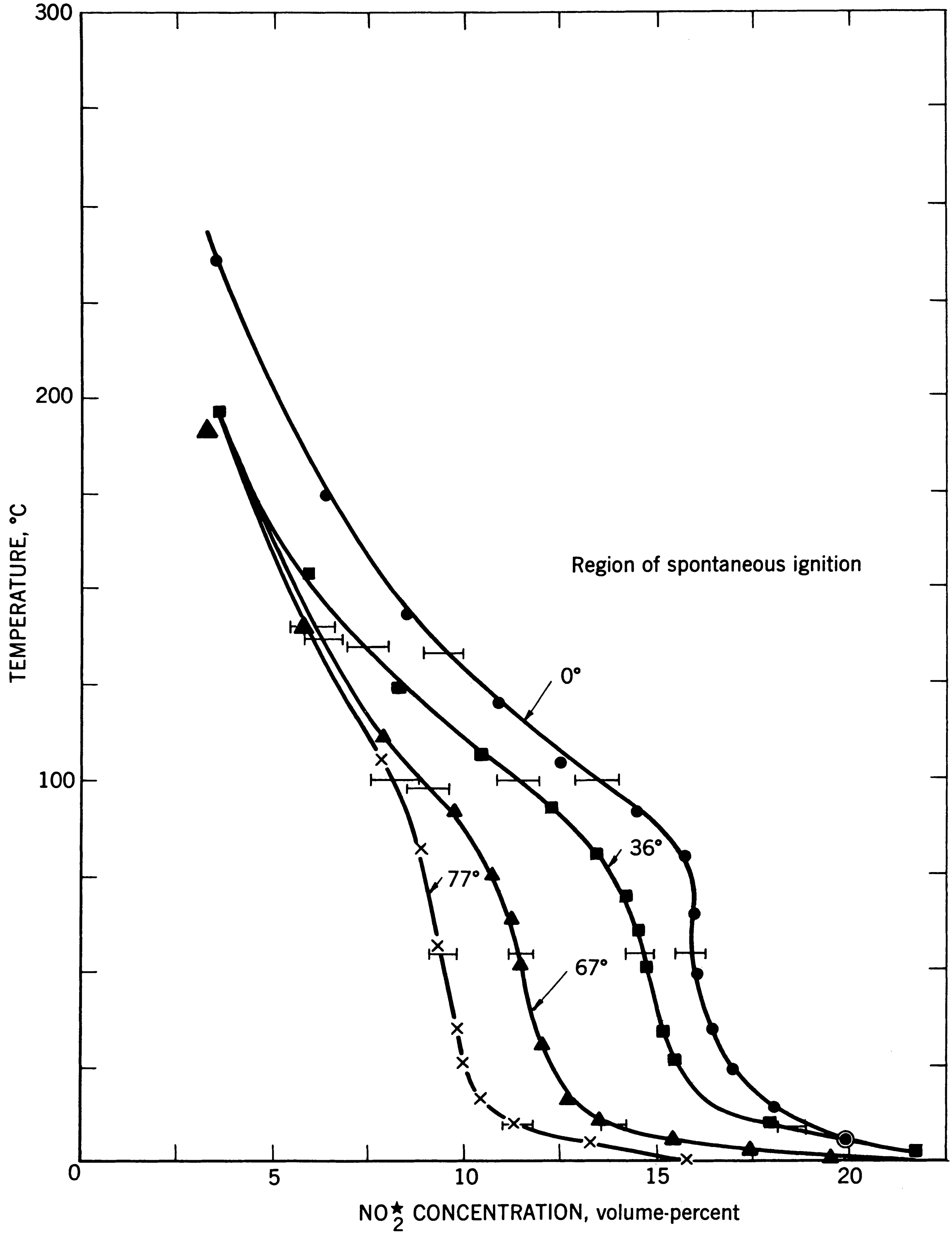


FIGURE 101.—Minimum Spontaneous Ignition Temperatures of Liquid Hydrazine at Various Initial Temperatures in NO_2*-Air Mixtures at 740±10 mm Hg as a Function of NO_2* Concentration.

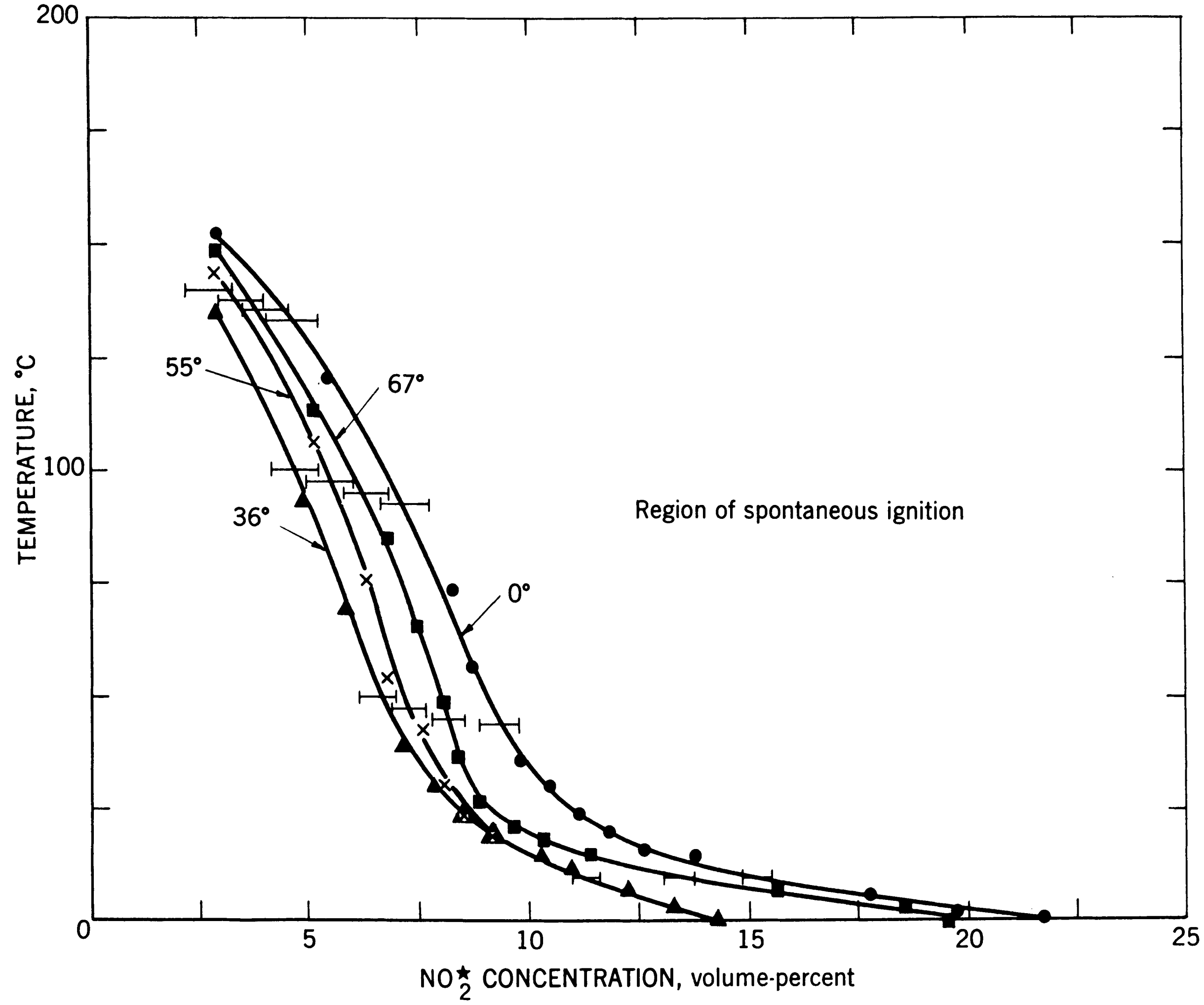


Figure 102.—Minimum Spontaneous Ignition Temperatures of Liquid MMH at Various Initial Temperatures in NO$_2$*-Air Mixtures at 740±10 mm Hg as a Function of NO$_2$* Concentration.

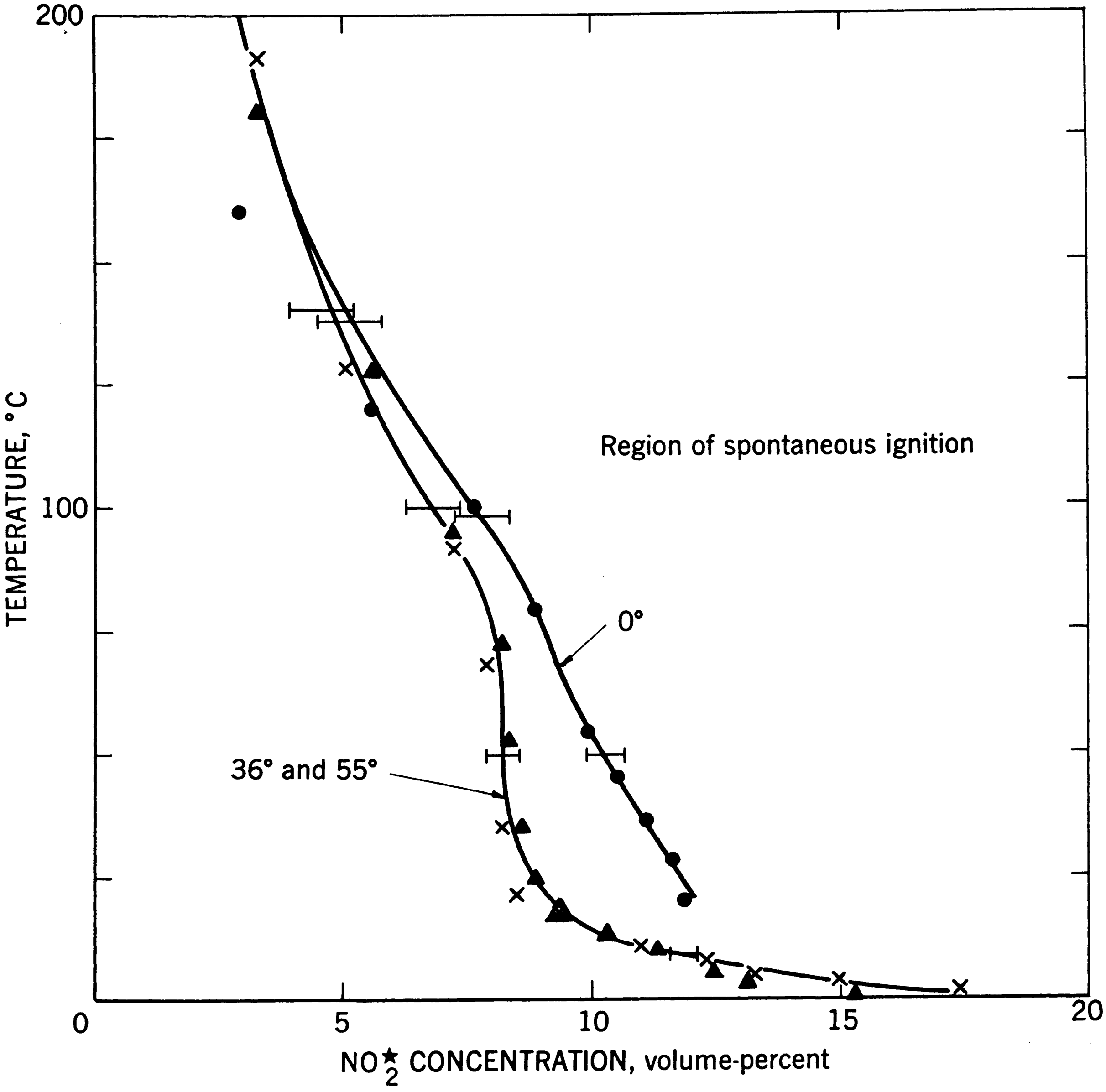


FIGURE 103.—Minimum Spontaneous Ignition Temperatures of Liquid UDMH at Various Initial Temperatures in NO_2*-Air Mixtures at 740±10 mm Hg as a Function of NO_2* Concentration.

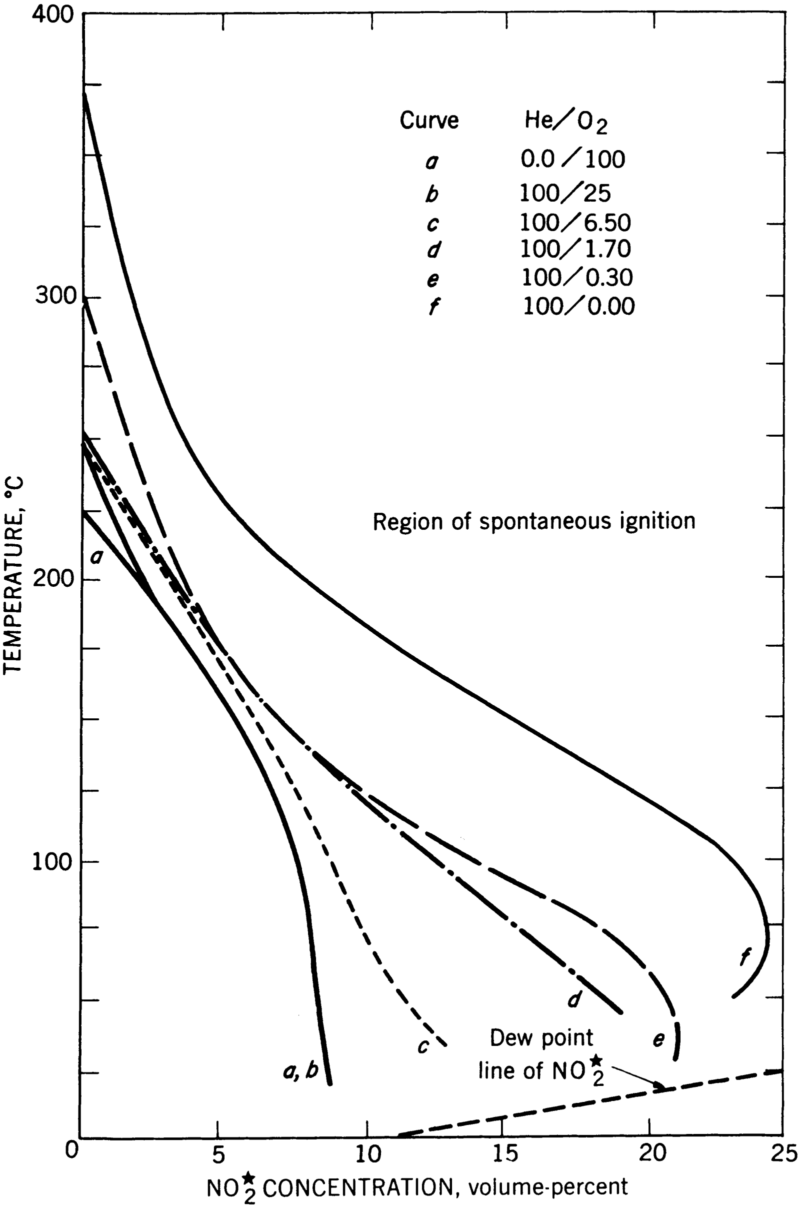


FIGURE 104.—Minimum Spontaneous Ignition Temperatures of 0.05 cc of Liquid UDMH in He-O_2-NO_2* Atmospheres at 1 Atmosphere for Various He/O_2 Ratios.

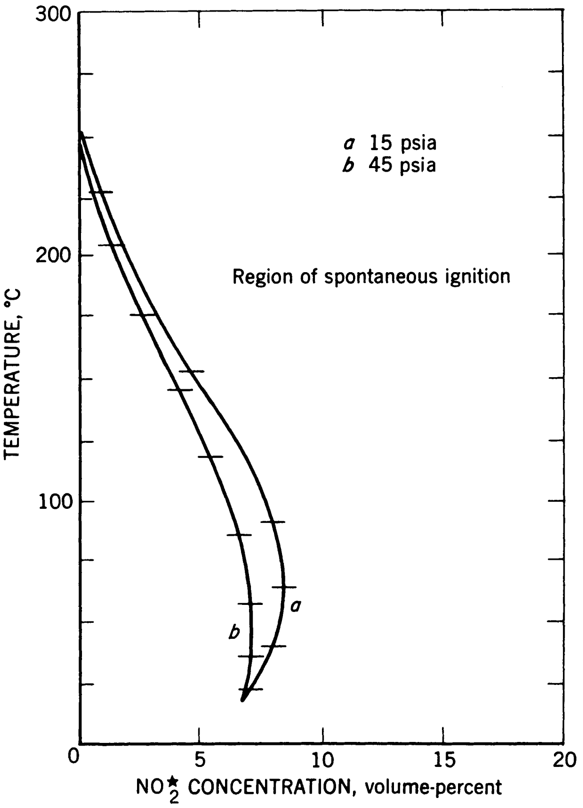


FIGURE 105.—Minimum Spontaneous Ignition Temperatures of 0.05 cc of Liquid UDMH in NO_2*-Air Mixtures at 15 and 45 Psia as a Function of NO_2* Concentration.

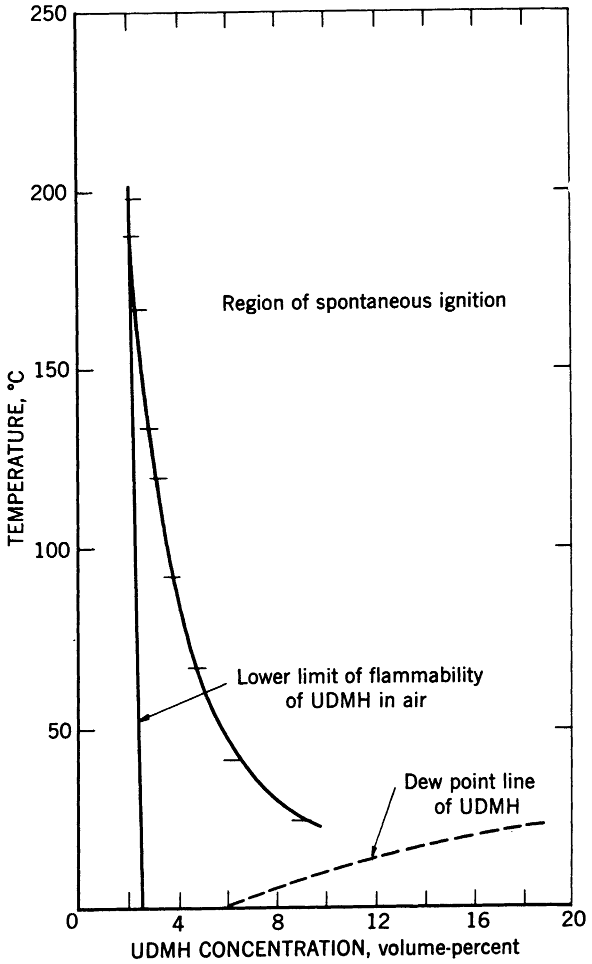


FIGURE 106.—Minimum Spontaneous Ignition Temperatures of Vaporized UDMH-Air Mixtures in Contact With 100 pct NO_2^* at 25° C and 740±10 mm Hg as a Function of UDMH Concentration in Air.

of two gasolines and three jet fuels considered here are given in figure 108. Unfortunately, such curves give only an approximate measure of the volatile constituents in the liquid blend. Even relatively nonvolatile high-flashpoint oils may liberate flammable vapors at such a slow rate that the closed vapor space above the liquid may be made flammable at reduced temperatures. Gasolines can produce flammable saturated vapor-air mixture at temperatures below −65° C (*241*), although the flash points of such fuels are considered to be about −45° C (*158*). An apparent discrepancy thus exists if flashpoint data are used to predict the lowest temperature at which flammable mixtures can be formed in a closed vapor space above a blend in long-term storage.

As noted earlier, the limits of flammability of hydrocarbon fuels are not strongly dependent on molecular weight when the limits are expressed by weight. However, since results measured by a volume are perhaps more widely used than those measured by weight, typical flammability curves are presented by volume for the light fractions from aviation gasoline, grade 115/145 (fig. 109), and aviation jet fuel, grade JP–4 (fig. 110). Combustible vapor-air-carbon dioxide and vapor-air-nitrogen mixtures at about 25° C and atmospheric pressure are considered for each. Similar data are given in figure 14 for the gasoline vapor-air-water vapor system at 21° and 100° C; the effect of pressure on limits of flammability of volatile constituents of JP–4 vapor in air are discussed in connection with figure 12.

Minimum autoignition temperatures of gasolines and jet fuels considered here are given in compilations by Zabetakis, Kuchta, and coworkers (*126*, *237*). These data are included in table 20.

Setchkin (*194*) determined the AIT values of four diesel fuels with cetane numbers of 41, 55, 60 and 68. These data are included in table 20. Johnson, Crellin, and Carhart (*92*, *93*) obtained values that were larger than those obtained by Setchkin, using a smaller apparatus.

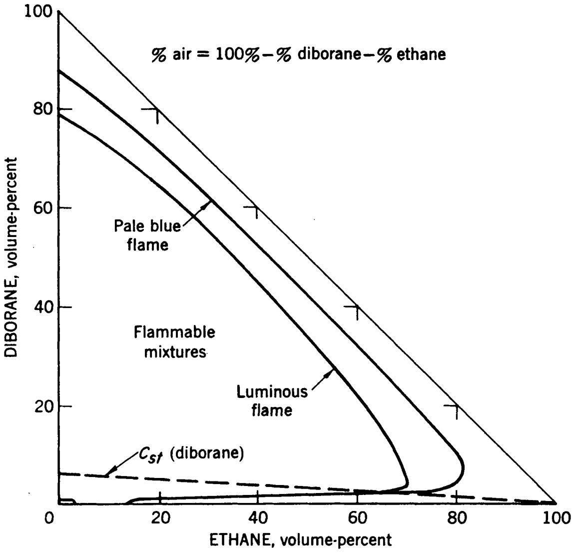


Figure 107.—Limits of Flammability of Diborane-Ethane-Air Mixtures at Laboratory Temperatures and 300 mm Hg Initial Pressure.

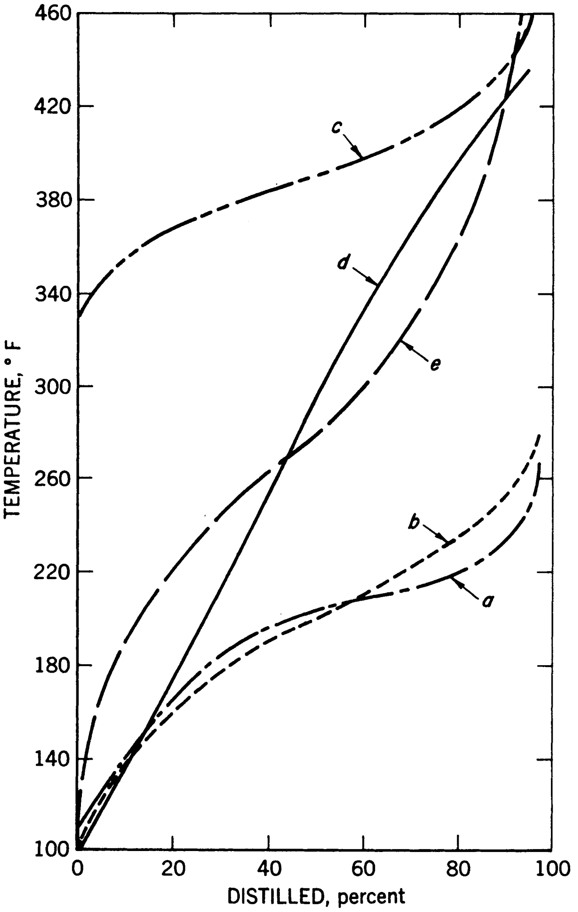


Figure 108.—ASTM Distillation Curves for, A, Aviation Gasoline, Grade 100/130; B, Aviation Gasoline, Grade 115/145; C, Aviation Jet Fuel, Grade JP–1; D, Aviation Jet Fuel, Grade JP–3; and E, Aviation Jet Fuel, Grade JP–4.

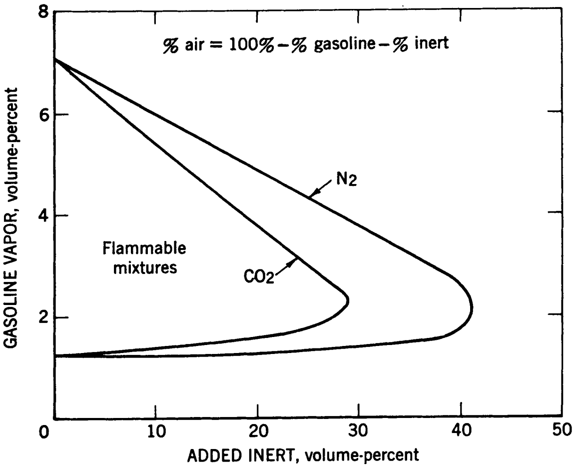


Figure 109.—Limits of Flammability of Aviation Gasoline, Grades 115/145 Vapor-Carbon Dioxide-Air and 115/145 Vapor-Nitrogen-Air, at 27° C and Atmospheric Pressure.

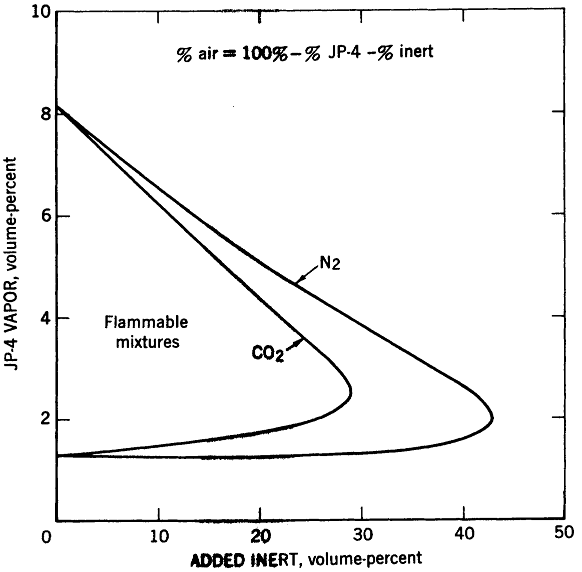


Figure 110.—Limits of Flammability of JP–4 Vapor-Carbon Dioxide-Air and JP–4 Vapor-Nitrogen-Air Mixtures at 27° C and Atmospheric Pressure.

Table 20.—*Autoignition temperature values of various fuels in air at 1 atmosphere*

Fuel:	AIT, °C
Aviation gasoline:	
100/130	440
115/145	471
Aviation jet fuel:	
JP–1	228
JP–3	238
JP–4	242
JP–6	232
Diesel fuel:	
41 cetane	233
55 cetane	230
60 cetane	225
68 cetane	226

Burning velocities of the fuels considered here are in the same range as those of the hydrocarbons considered earlier. Values for various fuels have been tabulated by Barnett and Hibbard (*156*).

Hydrogen

Numerous flammability characteristics studies have been conducted with hydrogen in recent years. Drell and Belles have prepared an excellent survey of these characteristics (*48*). This survey includes all but the most recent work of interest.

The low pressure limits of flame propagation for stoichiometric hydrogen-air mixtures are somewhat lower than those for stoichiometric ethylene-air mixtures (*197*) in cylindrical tubes. In the range from 6 to 130 mm Hg, the limit for stoichiometric hydrogen-air mixtures is given by the expression:

$$\log P = 3.19 - 1.19 \log D, \qquad (57)$$

where P is the low-pressure limit in millimeters of Hg, and D is the tube diameter in millimeters.

Hydrogen forms flammable mixtures at ambient temperatures and pressures with oxygen, air, chlorine, and the oxides of nitrogen. Limits of flammability in these oxidants at approximately 25° C and 1 atmosphere are listed in table 21.

TABLE 21.—*Limits of flammability of hydrogen in various oxidants at 25° C and atmospheric pressure*

Oxidant	L_{25}	U_{25}	Ref.
Oxygen	4. 0	95	(*40*)
Air	4. 0	75	(*40*)
Chlorine	4. 1	89	(*216, 128*)
N_2O	3. 0	84	(*189*)
NO	6. 6	66	(*189*)

Flammability diagrams of the systems hydrogen-air-carbon dioxide and hydrogen-air-nitrogen obtained by Jones and Perrott (*112*) are given in figure 111. Lines that establish minimum oxygen values for each system are also included. Note that although the minimum value occurs near the "nose" of the hydrogen-air-nitrogen curve, the corresponding value occurs at the upper limit of the hydrogen-air-carbon dioxide curve.

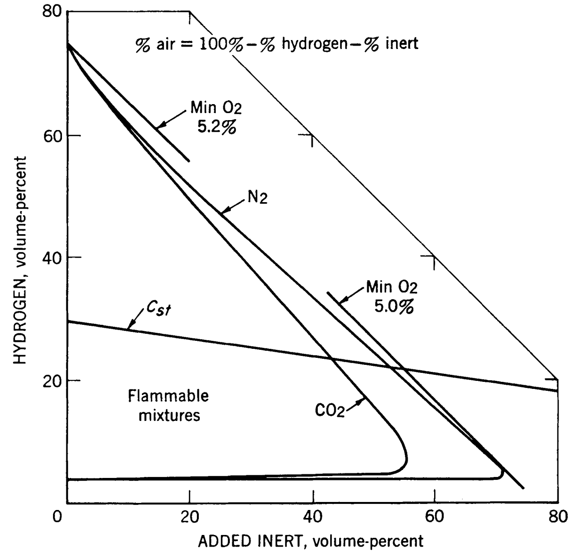


FIGURE 111.—Limits of Flammability of Hydrogen-Carbon Dioxide-Air and Hydrogen-Nitrogen-Air Mixtures at 25° C and Atmospheric Pressure.

Flammability diagrams obtained by Scott, Van Dolah, and Zabetakis for the systems hydrogen-nitric oxide-nitrous oxide, hydrogen-nitrous oxide-air, and hydrogen-nitric oxide-air are given in figures 112–114 (*189*). Upper limit curves were found to deviate from the results obtained from the Le Chatelier law, broken curves; additional data are given in the original article.

The burning velocity of hydrogen in air at 25° C and one atmosphere range from a low of a few centimeters per second to 325 cm/sec (*68*). When liquefied, it vaporizes and burns in air at a rate that is determined by the rate at which heat enters the liquid. Heat is abstracted from the surroundings and, where a flame exists, from the flame itself. Figure 115 gives the results obtained from vaporizing liquid hydrogen from paraffin cast in a Dewar flask; experimental points were obtained from gas evolution measurements. The solid curve (theoretical) was obtained by Zabetakis and Burgess by assuming the heat influx rate to be conduction limited (*234*); the initial flash vaporization rates are probably film- and nucleate boiling-limited. The theoretical liquid regression rates following spillage of liquid hydrogen onto three soils are presented in figure 116, the corresponding decrease in liquid level is given in figure 117. Because of its low temperature, the vaporized hydrogen forms a vapor trail as it leaves the liquid. However, the position of this trail or visible cloud does not necessarily coincide with that of the flammable zones formed above the liquid pool. This is illustrated in figure 118, in which the positions of the flammable zones and visible clouds are defined in a height-elapsed time graph. Two flammable zones are defined here. These are also seen in the motion picture sequence (fig. 119) of the visible clouds and

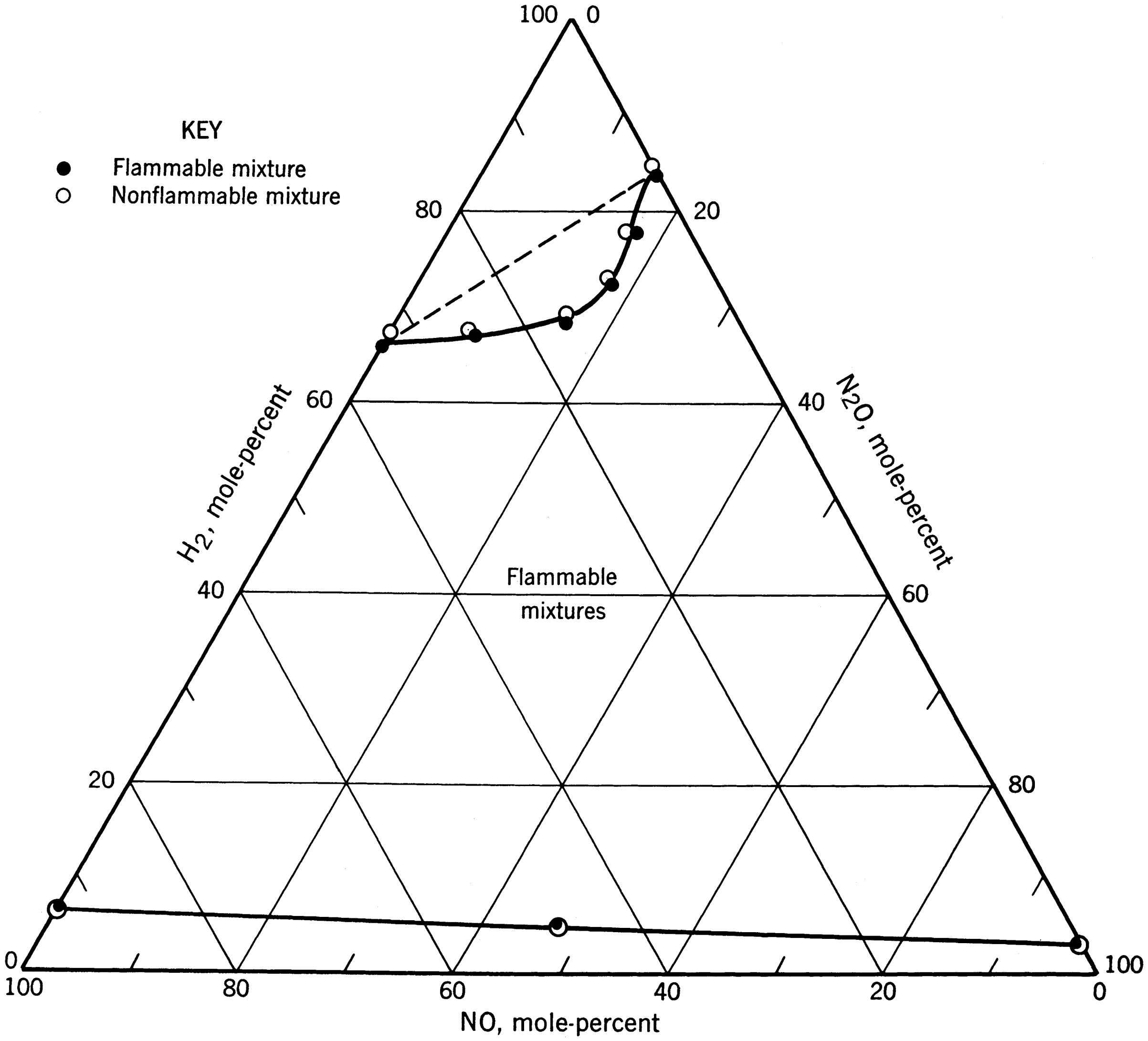


FIGURE 112.—Limits of Flammability of H_2-NO-N_2O at Approximately 28° C and 1 Atmosphere.

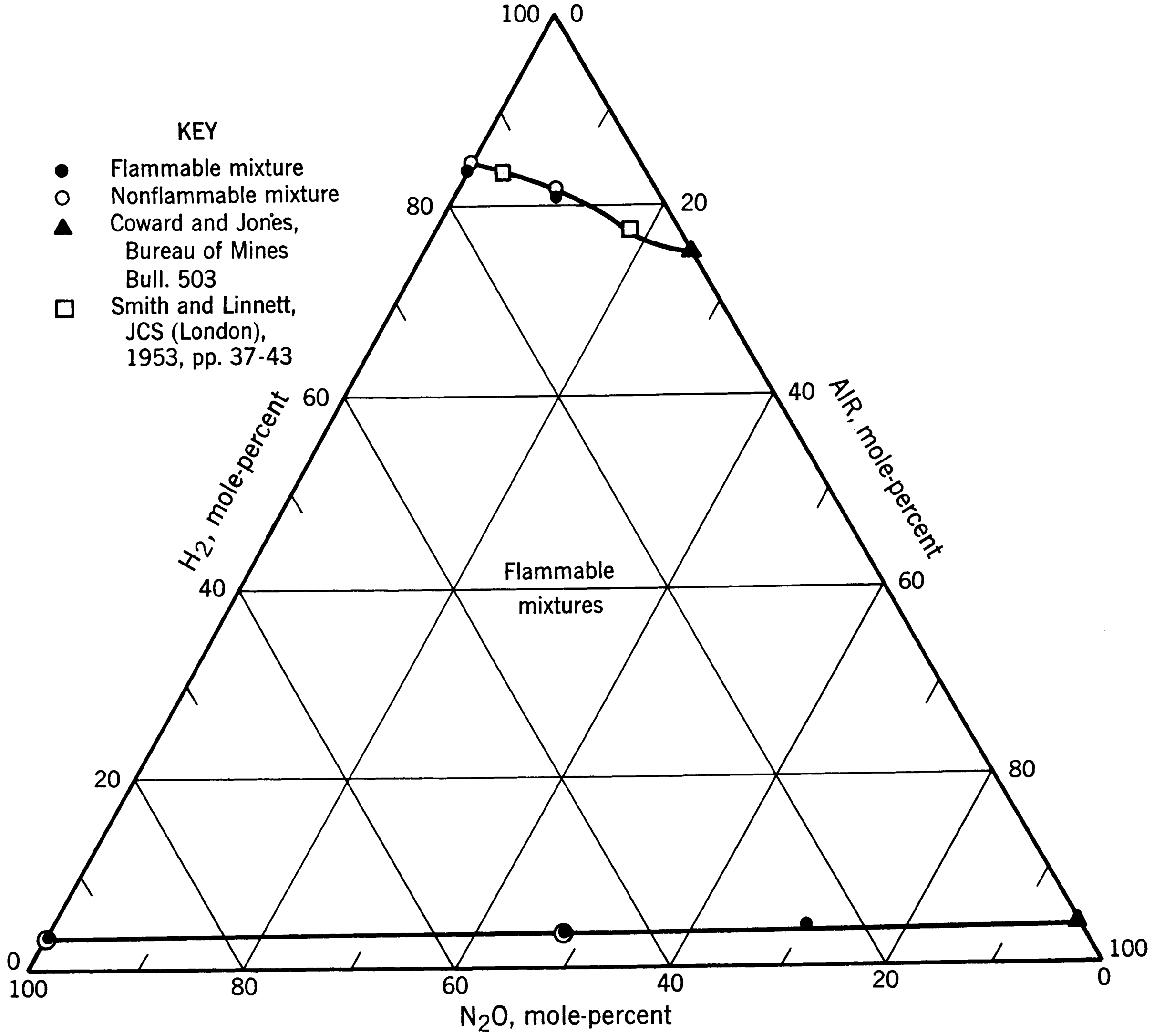


FIGURE 113.—Limits of Flammability of H_2-N_2O-Air at Approximately 28° C and 1 Atmosphere.

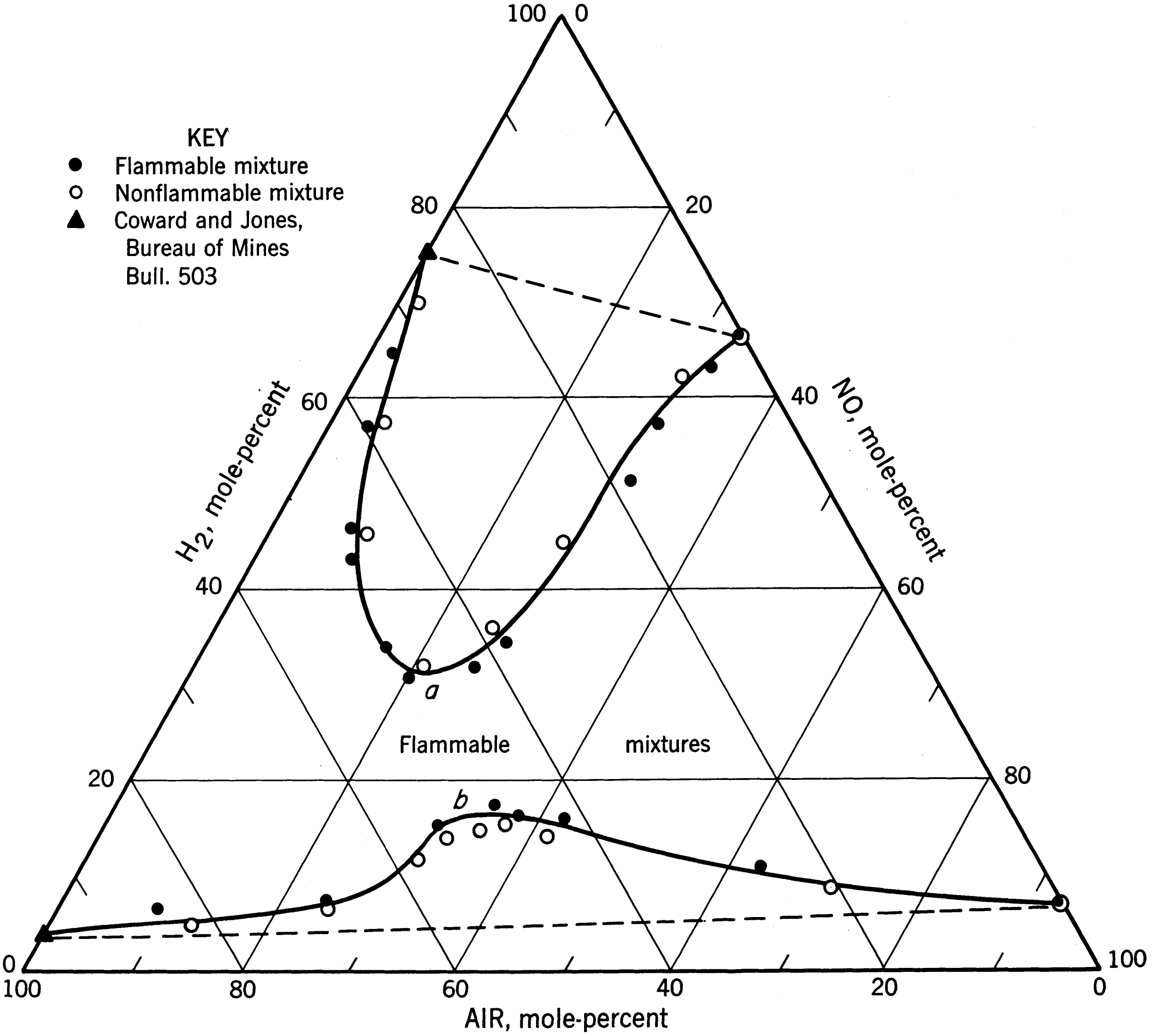


FIGURE 114.—Limits of Flammability of H_2-NO-Air at Approximately 28° C and 1 Atmosphere.

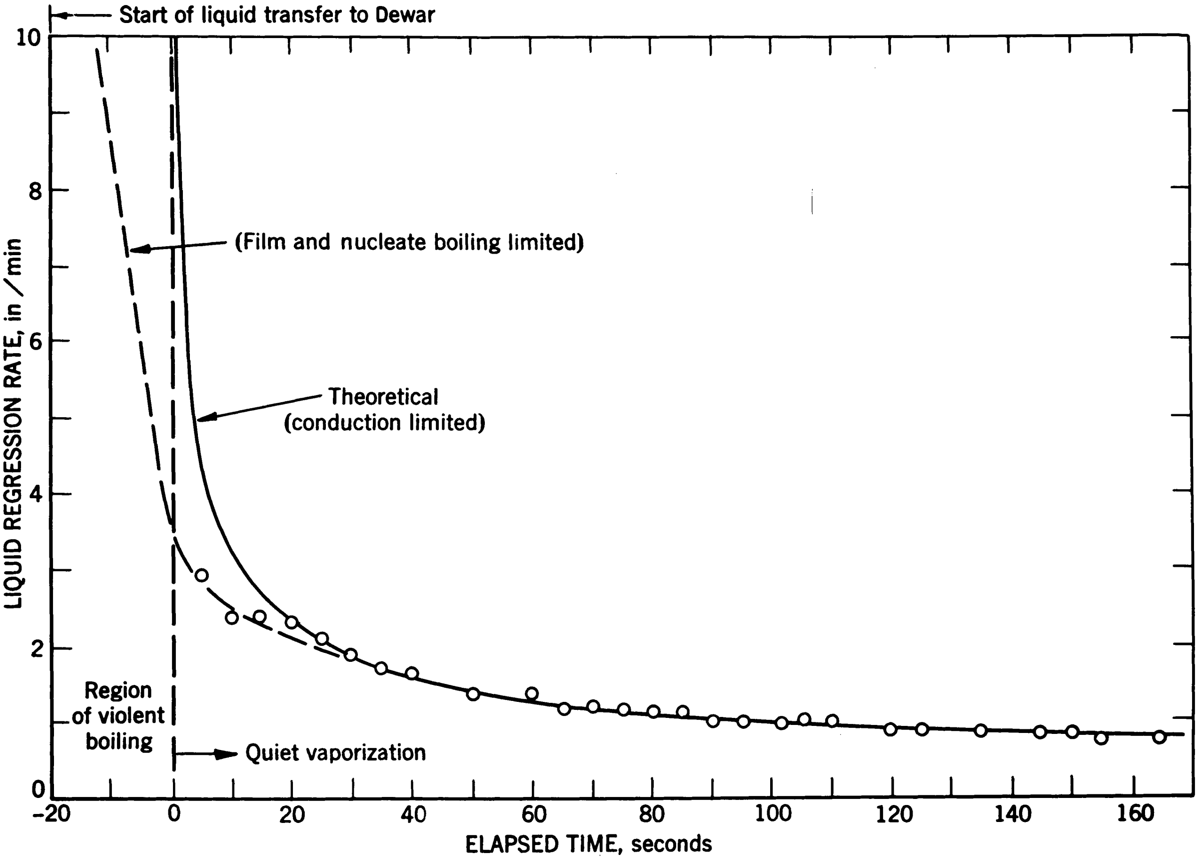


FIGURE 115.—Rate of Vaporization of Liquid Hydrogen From Paraffin in a 2.8-Inch Dewar Flask: Initial Liquid Depth—6.7 Inches.

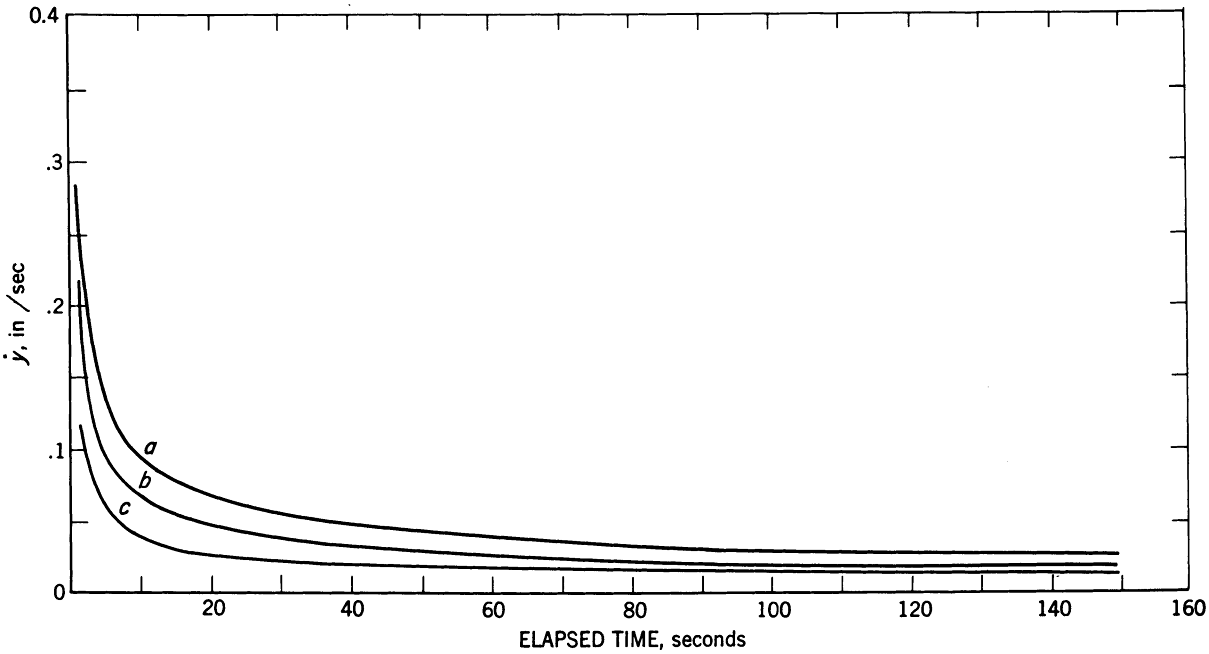


FIGURE 116.—Theoretical Liquid Regression Rates Following Spillage of Liquid Hydrogen Onto, *A*, an Average Soil; *B*, Moist Sandy Soil (8 Pct. Moisture); and *C*, Dry Sandy Soil.

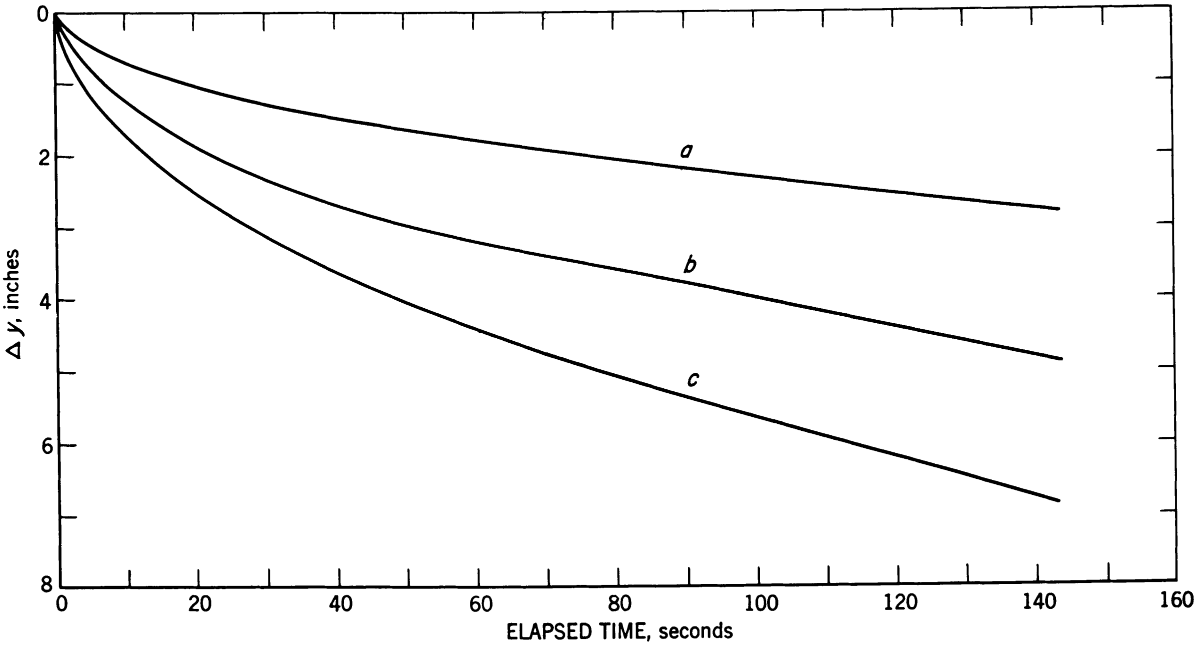


FIGURE 117.—Theoretical Decrease in Liquid Hydrogen Level Following Spillage Onto, *A*, Dry Sandy Soil; *B*, Moist Sandy Soil (8 Pct. Moisture); and *C*, and Average Soil.

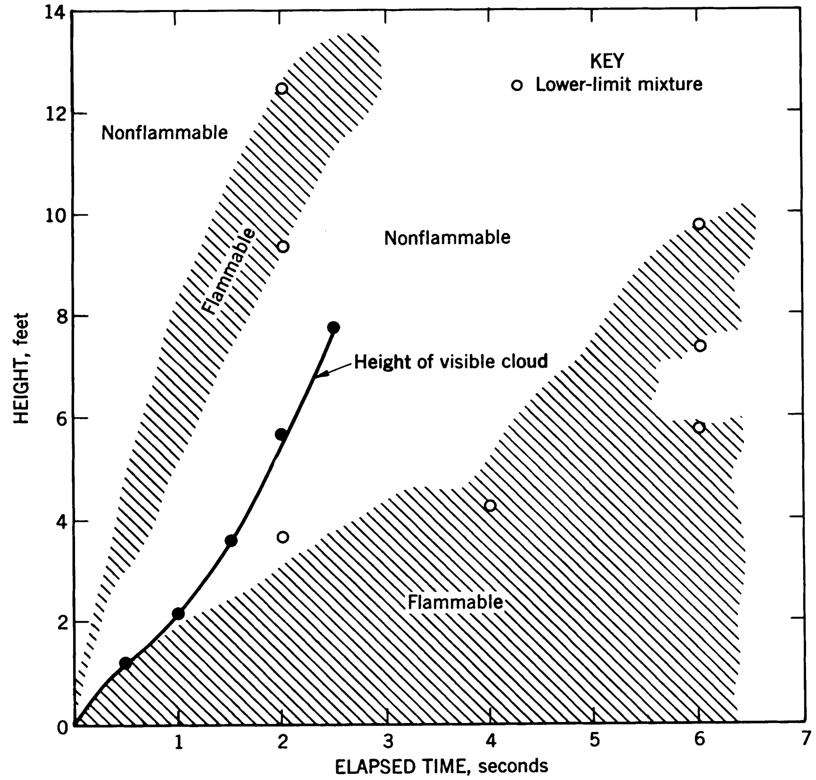


FIGURE 118.—Extent of Flammable Mixtures and Height of Visible Cloud Formed After Rapid Spillage of 3 Liters of Liquid Hydrogen on a Dry Macadam Surface in a Quiescent Air Atmosphere at 15° C.

flames that resulted following spillage of 7.8 liters of liquid hydrogen and subsequent ignition of vapors above the spill area. The height and width of fireballs that resulted from ignition of vapors produced by rapid vaporization of about 3 to 90 liters of liquid hydrogen are given in figure 120. The data are represented fairly well by the equation

$$H_{\max}=W_{\max}=7\sqrt{V_l}\text{ feet}=17.8\sqrt{M}\text{ feet,} \quad (56)$$

where $H_{\max}$ and $W_{\max}$ are the maximum flame height and width, respectively, V_l is the volume of liquid hydrogen in liters, and M is the mass of this volume in pounds.

The burning rate of a 6-inch pool of liquid hydrogen in air is given as the regression of the liquid level in figure 121; burning rate data for liquid methane are included for comparison. An extrapolated value of burning rate for large pools of liquid hydrogen is included in figure 52.

Approximate quantity-distance relationships can be established for the storage of liquid hydrogen near inhabited buildings and other storage sites if certain assumptions are made (*33*, *160*, *234*). Additional work is required to establish such distances for very large quantities of liquid.

The detonation velocity and the static and reflected pressures developed by a detonation wave propagating through hydrogen-oxygen mixtures are given in figure 16. The predetonation distance in horizontal pipes is reportedly proportional to the square root of the pipe diameter (*229*); this is presumably applicable to results obtained with a mild ignition source, since a shock front can establish a detonation at essentially zero runup distance. Numerous investigators have examined this and related problems in recent years (*11–13*, *65*, *135–137*, *151*).

HYDRAULIC FLUIDS AND ENGINE OILS

Both mineral oil derived and synthetic hydraulic fluids and engine oils are presently in common use (*148*). These materials are often used at elevated temperatures and pressures and contain additives designed to improve stability, viscosity, load-bearing characteristics, etc. Such additives affect flammability characteristics of the base fluid. However, the base

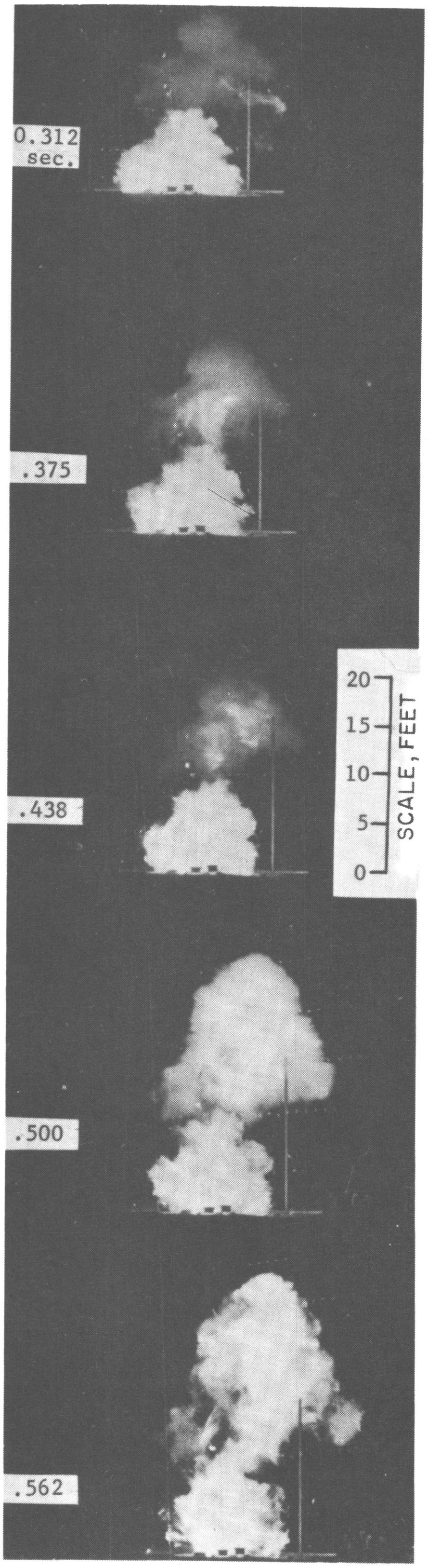


FIGURE 119.—Motion Picture Sequence (16 Frames per Second) of Visible Clouds and Flames Resulting From Rapid Spillage of 7.8 Liters of Liquid Hydrogen on a Gravel Surface at 18° C. Ignition Source: 20 Inches Above Gravel.

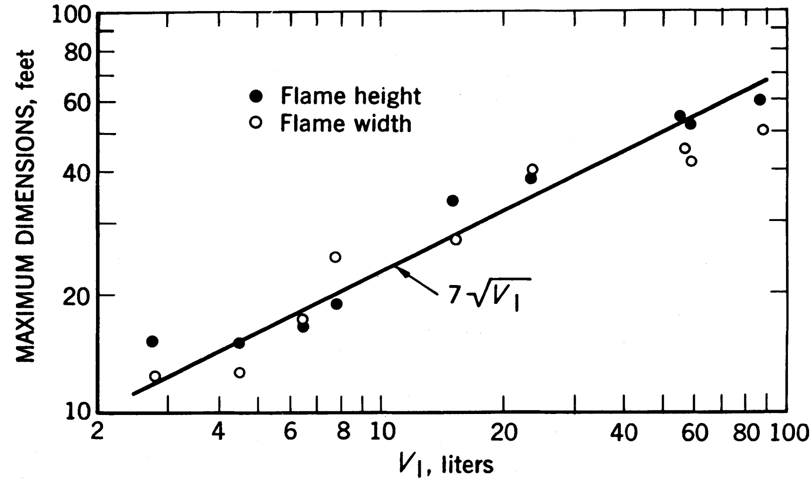


FIGURE 120.—Maximum flame height and width produced by ignition of vapor-air mixtures formed by sudden spillage of 2.8 to 89 liters of liquid hydrogen (V_l).

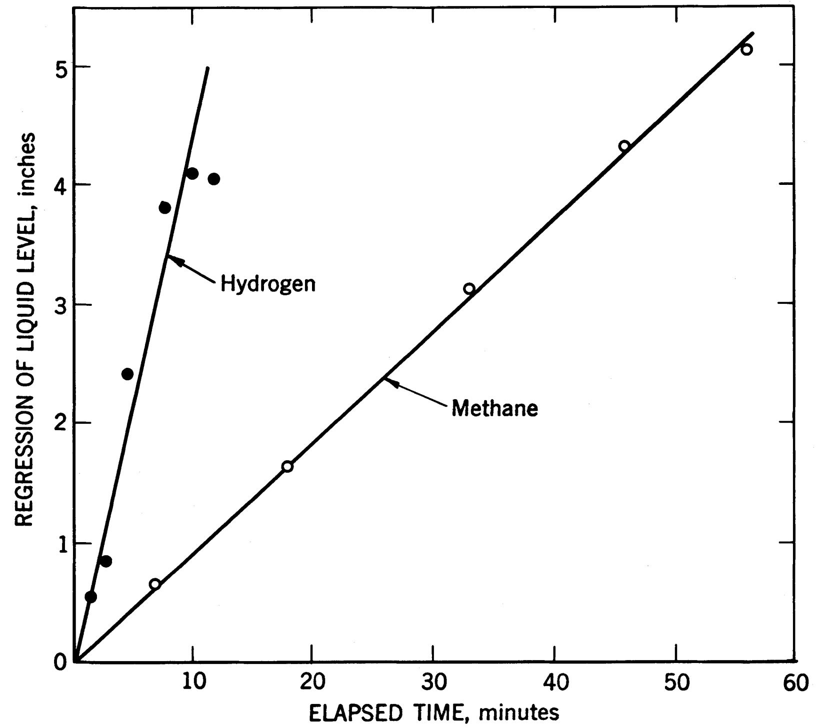


FIGURE 121.—Burning rates of liquid hydrogen and of liquid methane at the boiling points in 6-inch-Pyrex Dewar flasks.

fluid generally plays a predominant role in determining limits of flammability and ignition temperature of a particular fluid. For example, many of the oil-based fluids have lower limits of flammability that fall in the ranges given in figure 22 for paraffin hydrocarbons. Further, those that have minimum autoignition temperatures in the lower temperature ranges considered in fiugres 43 and 71 are not affected appreciably by oxygen concentration of the atmosphere and by ambient and fluid-injection pressures; those that have minimum autoignition temperatures in the higher temperature ranges do not follow these generalizations (*237*). Since these fluids are designed for use at elevated temperatures and pressures, they are normally made up of high-molecular weight matetials. Accordingly, they are flammable at ordinary temperatures and pressures as mists and foams. Burgoyne and his coworkers (*27*) found that lubricating-oil mists were flammable in air but not in carbon dioxide-air mixtures that contained about 28 volume-percent carbon dioxide (fig. 35). At elevated temperatures, the oil vapors cracked and produced acetylene and hydrogen, which affected the flammability of the resultant mixture; the vapors are often unstable at elevated temperatures. Chiantella, Affens, and Johnson have determined the effect of elevated temperatures on the stability and ignition properties of three commercial triaryl phosphate fluids (*36*).

Zabetakis, Scott, and Kennedy have determined the effect of pressure on the autoignition temperatures of commercial lubricants (*248*). Figure 122 gives the minimum autoignition temperatures for four commercial phosphate ester-base fluids (curves 1–4) and three mineral oils (curves 5–7). In each case, the minimum autoignition temperature was found to decrease with increase in pressure over most of the pressure range considered. A plot of the logarithm of the initial pressure to temperature ratio versus the reciprocal of the temperature is given for curves 1 to 7 in figure 123. The resultant curves are linear over a limited temperature range.

The ratio of the final temperature attained by air in an adiabatic compression process to the initial temperature is given in figure 124 as a function of both the final-to-initial pressure ratio and initial-to-final volume ratio. If a lubricating oil is exposed to high temperatures during a compression process, autoignition may occur if the residence or contact time is adequate. Such high temperatures do occur in practice and have been known to cause disastrous explosions (*58*, *146*, *149*, *227*, *231*). The curves in figure 125 show that in the compression pressure range 1 to 10 atmospheres (initial pressure=1 atmosphere), a wide range of ambient temperatures can lead to the autoignition of a mineral oil lubricant (curve 5) if sufficient vapor or mist is in the system. In the same pressure range, only elevated initial temperatures could lead to the autoignition of a phosphate ester (curve 4). If the initial pressure is increased to 10 atmospheres, autoignition can occur at lower air-intake temperatures in every case (*248*).

MISCELLANEOUS

The flammability characteristics of a number of miscellaneous combustibles not considered elsewhere, are discussed in this section. These include carbon monoxide, *n*-propyl nitrate, and the halogenated hydrocarbons. The properties of these and a great variety of other materials are included in Appendix A.

The limits of flammability of the systems carbon monoxide-carbon dioxide-air and carbon monoxide-nitrogen-air are presented in figure 126. These curves were constructed from the flammability data obtained by Jones in a 2-inch vertical glass tube with upward flame propagation (*112*); other representations may be found in the original reference and in the compilation prepared by Coward and Jones (*40*).

Materials that are oxidized or decomposed readily may yield erratic flammability data under certain conditions. This effect is illustrated in figure 127 which summarizes the lower-limits data obtained by Zabetakis, Mason and Van Dolah with *n*-propyl nitrate (NPN) in air at various temperatures and pressures (*243*). An increase in temperature from 75° to 125° C is accompanied by a decrease in the lower-limit values; a further increase in temperature to 150° C results in a further lowering of the lower limit at pressures below 100 psig, but not at the higher pressures. An increase in the temperature to 170° C results in an apparent increase in the lower-limit value because of the slow oxidation of NPN. A complete flammability diagram has been constructed for the NPN vapor system in figure 128; a single lower limit curve and two upper limit curves are given here to show the effect of pressure on the flammable range of a vapor-air system.

The spontaneous ignition of NPN in air was considered earlier at 1,000 psig (figs. 3, 4). The explosion pressures obtained at this initial pressure in air and in a 10-volume-percent oxygen +90-volume-percent nitrogen atmosphere at various NPN concentrations are presented in figure 129. A summary of the minimum spontaneous ignition and decomposition temperatures obtained with NPN in air and nitrogen respectively are given in figure 130. The data given in this figure exhibit a behavior that is typical of that found with other combustibles

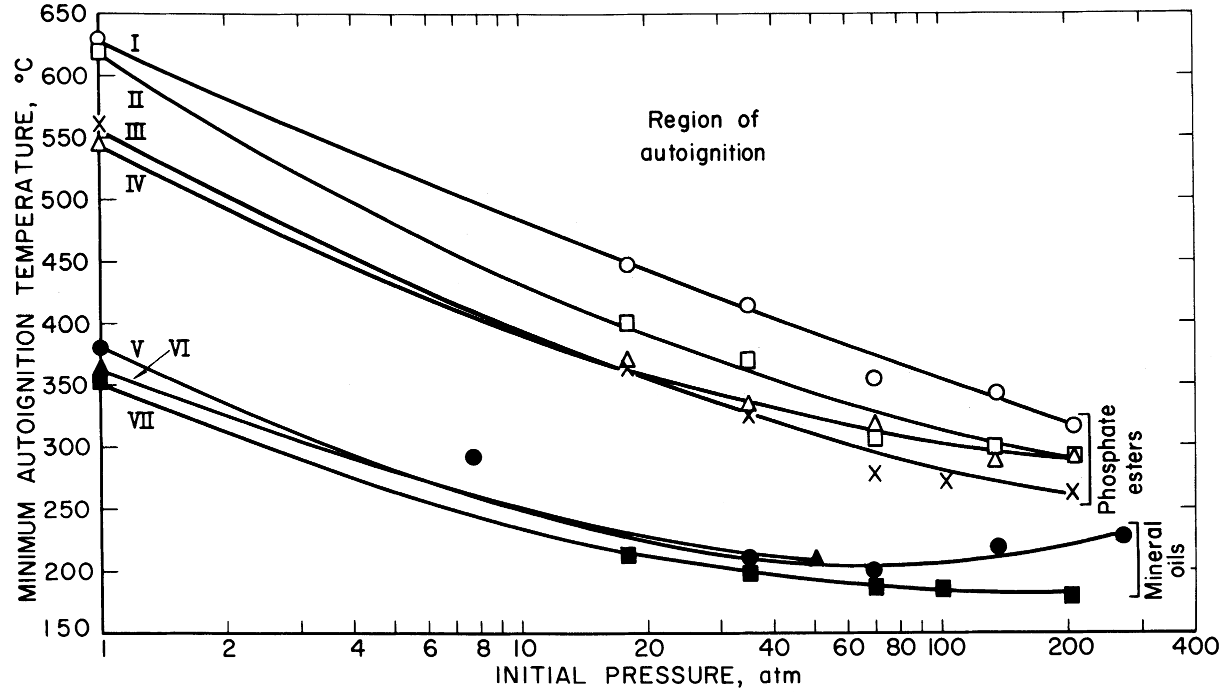


FIGURE 122.—Variation in Minimum Autoignition Temperature With Pressure of Commercial Phosphate Ester and Mineral Oil Lubricants in Air in a 450-cc-Stainless Steel Bomb.

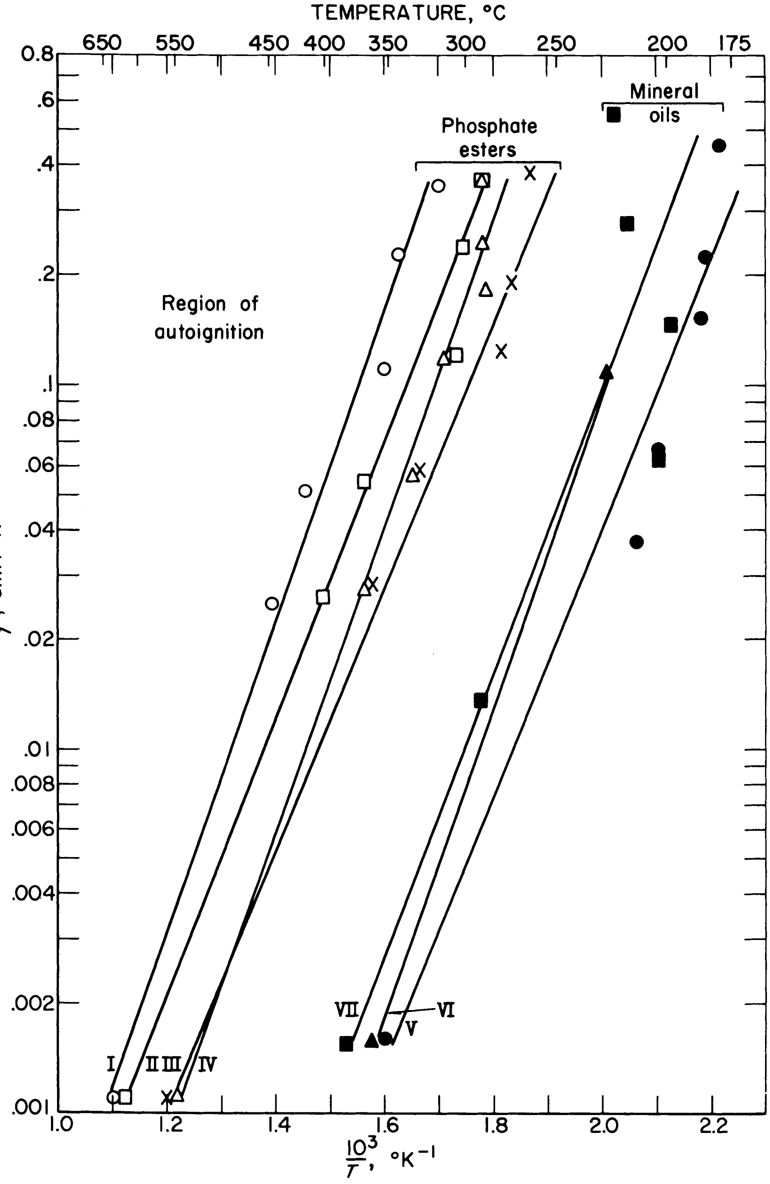
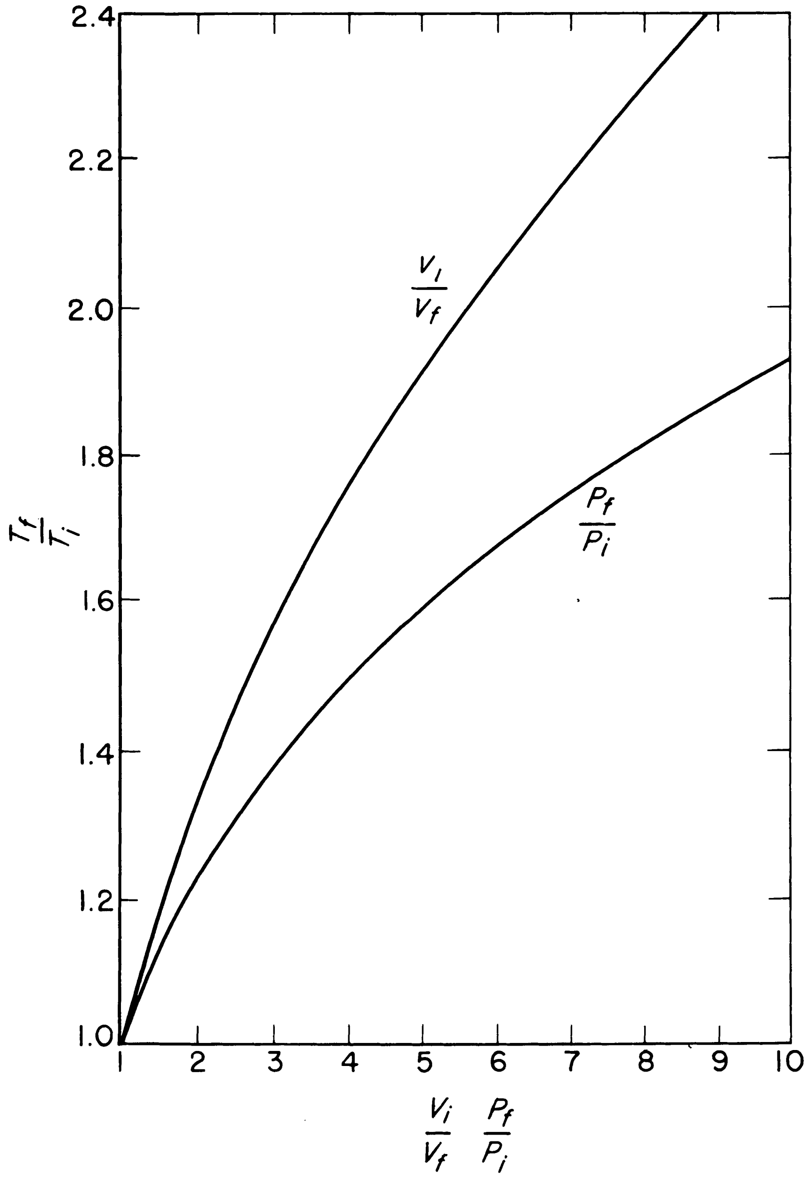


FIGURE 123.—Logarithm of Initial Pressure–AIT Ratio of Seven Fluids in Air for Various Reciprocal Temperatures. Data from Figure 122.

FIGURE 124.—Variation in T_f/T_i of Air With V_i/V_f and With P_f/P_i in an Adiabatic Compression Process.



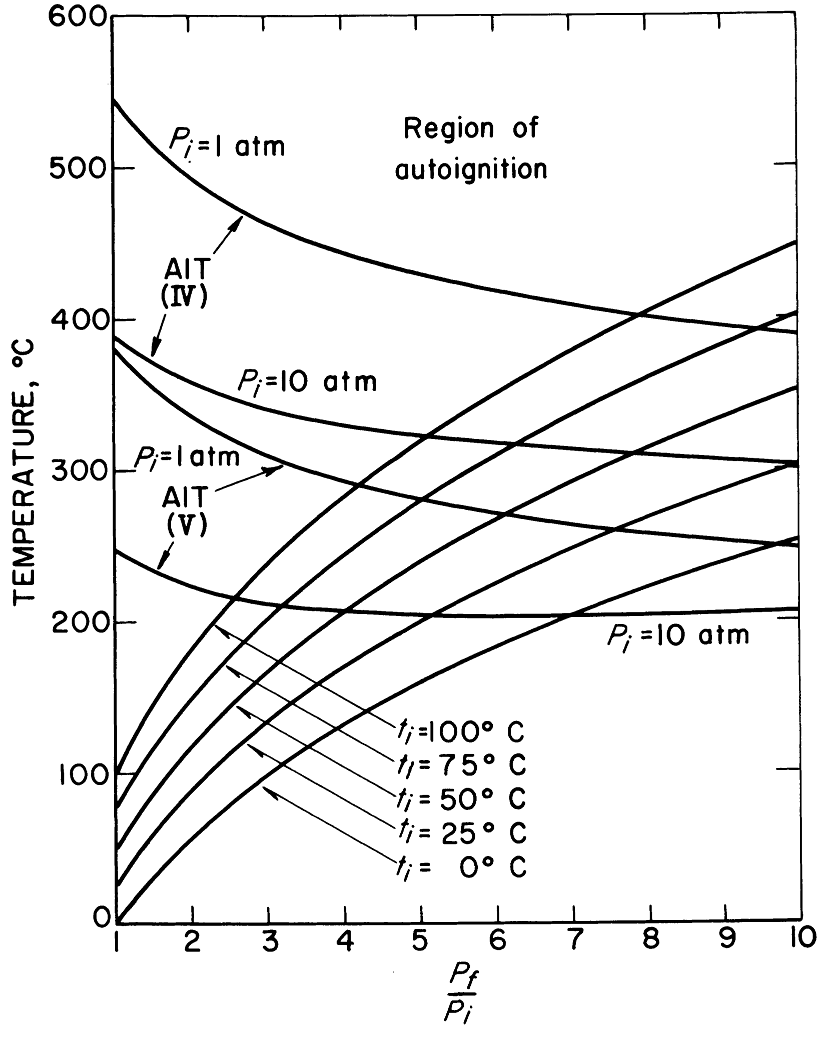


FIGURE 125.—Variation In Air Temperature With P_f/P_i in an Adiabatic Compression Process for Five Initial Air Temperatures (0°, 25°, 50°, 75°, and 100° C). Regions of autoignition for lubricants IV and V at P_f/P_i Between 1 and 10 Atmosphere and P_i of Between 1 and 10 Atmospheres.

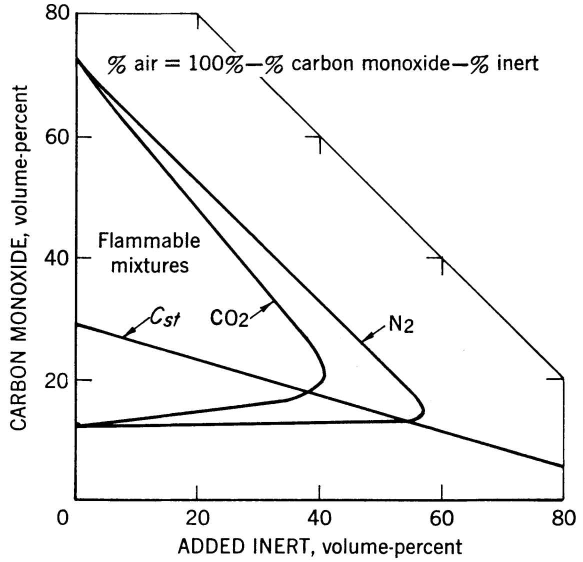


FIGURE 126.—Limits of Flammability of Carbon Monoxide-Carbon Dioxide-Air and Carbon Monoxide-Nitrogen-Air Mixtures at Atmospheric Pressure and 26° C.

at elevated pressures; the minimum spontaneous ignition temperature first decreases with initial increase in pressure and then increases as the pressure is increased still further (*120, 248*).

Burning velocities were found to range from 20 cm/sec to 110 cm/sec in NPN-air mixtures containing 3.0 to 7.2 volume-percent NPN. Detonations were obtained in saturated NPN vapor-air mixtures from 30° to 65° C and 1 atmosphere pressure; the detonation velocity was from 1,500 to 2,000 meters per second. Stable detonations were obtained with liquid NPN at 90° C; the detonation velocity was from 4,700 to 5,100 meters per second.

Although many of the halogenated hydrocarbons are known to be flammable (*40*) still others such as methyl bromide, methylene chloride, and trichloroethylene (TCE) have been considered to be nonflammable or essentially nonflammable in air. As noted in connection with the methyl bromide data given in figure 28, Hill found methyl bromide to be flammable in air at 1 atmosphere pressure (*84*); the reported limits of flammability were from 10 to

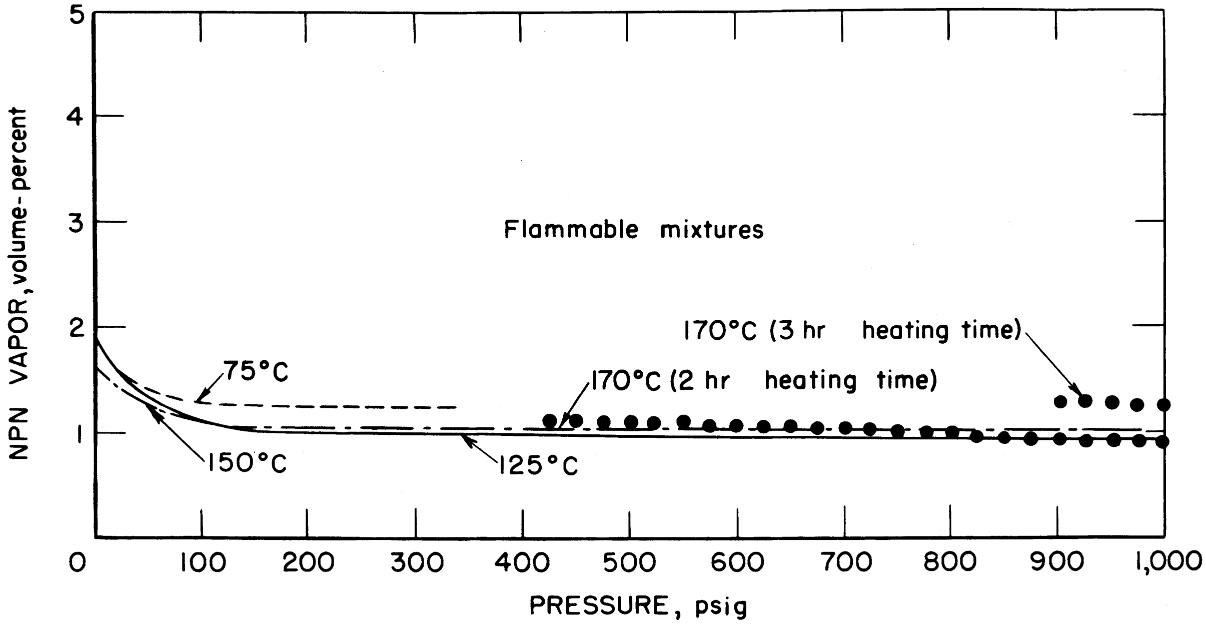


FIGURE 127.—Lower Limits of Flammability of NPN Vapor-Air Mixtures Over the Pressure Range From 0 to 1,000 Psig at 75°, 125°, 150°, and 170° C.

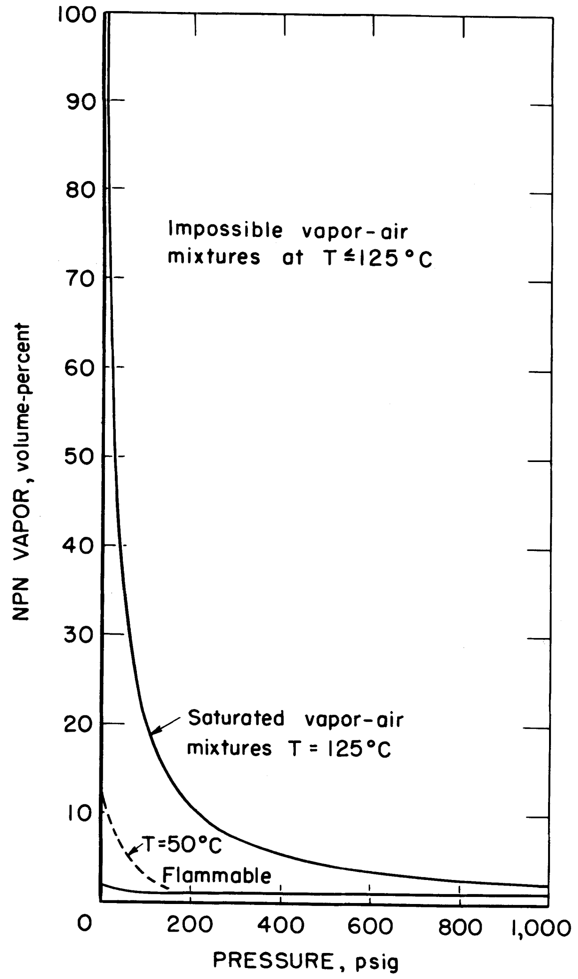


FIGURE 128.—Flammable NPN Vapor-Air Mixtures Formed Over the Pressure Range From 0 to 1,000 Psig at 50° and 125° C.

15 volume-percent methyl bromide. At an initial pressure of 100 psig, the flammable range was found to extend from 6 to 25 volume-percent. Similarly, methylene chloride and trichloroethane were found to be flammable in air at ambient temperatures although the flammable ranges were not determined. In general, much higher source energies are required with these combustibles than are required to ignite methane-air mixtures.

An approximate flammability diagram was prepared by Scott for trichloroethylene-air mixtures (*190*); a modification is reproduced in figure 131. The lower limit data were obtained in a vertical 7-inch-diameter flammability tube and the upper limit data in an 8-inch-diameter glass sphere with upward propagation of flame. Flammable mixtures of TCE and air were also obtained between 10.5 and 41 volume-percent TCE at 1 atmosphere and 100° C in an 8-inch-diameter glass sphere. Under the same conditions, flammable mixtures of TCE and oxygen were obtained between 7.5 and 90 volume-percent TCE. However, additional work must be conducted with this and the other halogenated hydrocarbons to determine the effect of vessel size, ignition source strength, temperature and pressure on their flammability characteristics.

Other useful flammability data may be found for various miscellaneous combustibles in many of the publications listed in the bibliography (*40*, *154*, *200*, *208–214*, *218*). These include data on the gases produced when metals react with water (*56*) and sulfur reacts with various hydrocarbons (*62*). Still other references consider the hazards associated with the production of unstable peroxides (*142*, *157*, *187*, *233*) and other reactive materials (*66*, *74*, *80*, *139*).

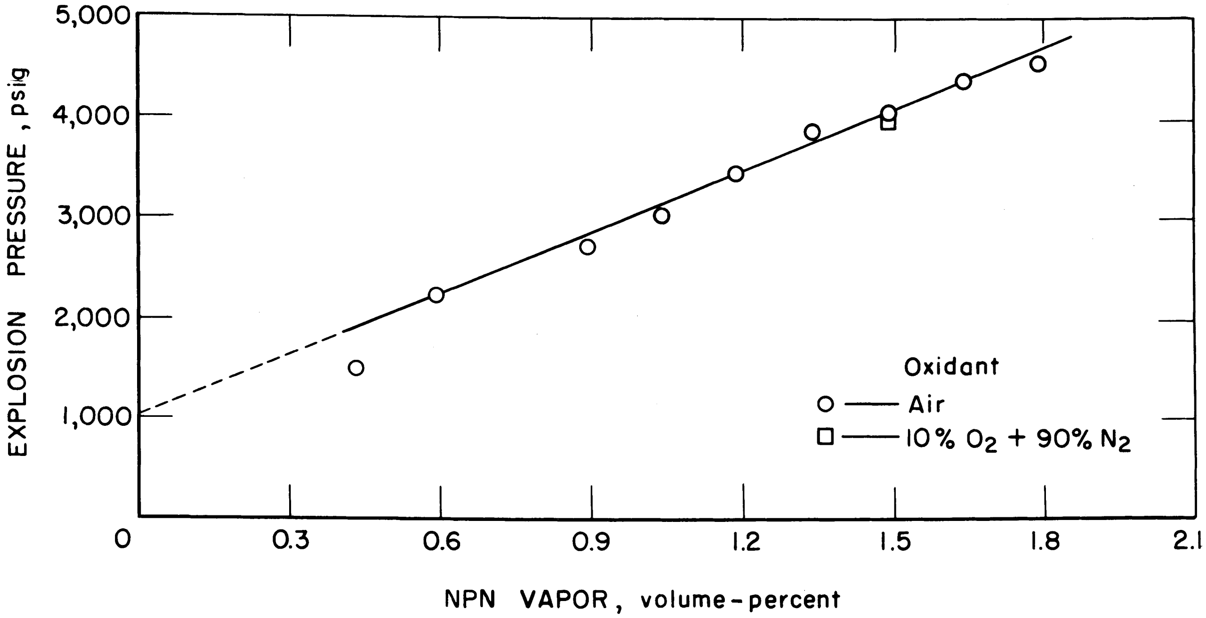


Figure 129.—Variation of Explosion Pressure Following Spontaneous Ignition With NPN Concentration, Initial Pressure 1,000 Psig.

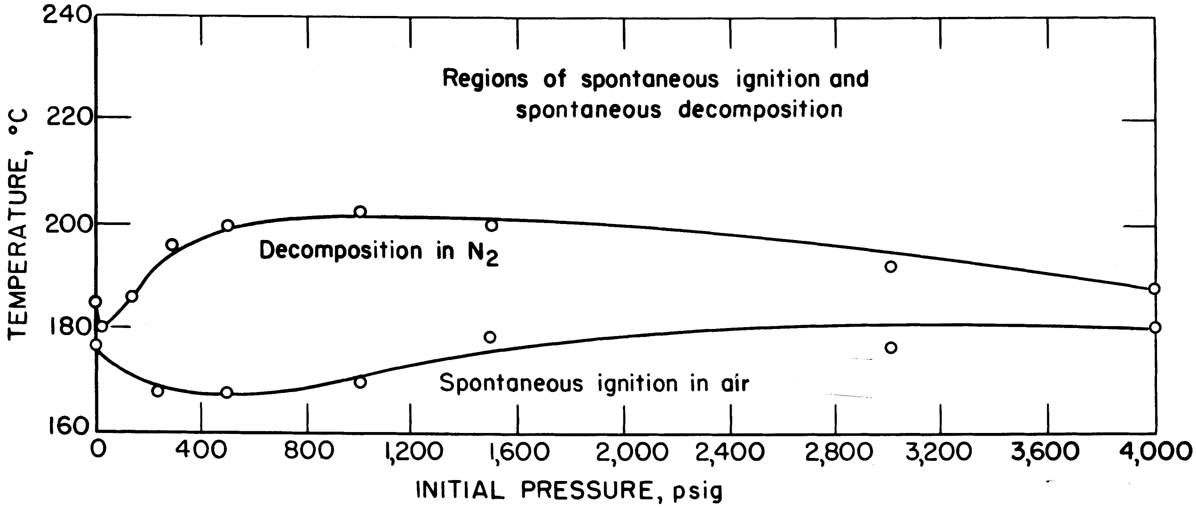


Figure 130.—Minimum Spontaneous Ignition and Decomposition Temperatures of *n*-Propyl Nitrate in Air as a Function of Pressure, Type 347 Stainless Steel Test Chamber.

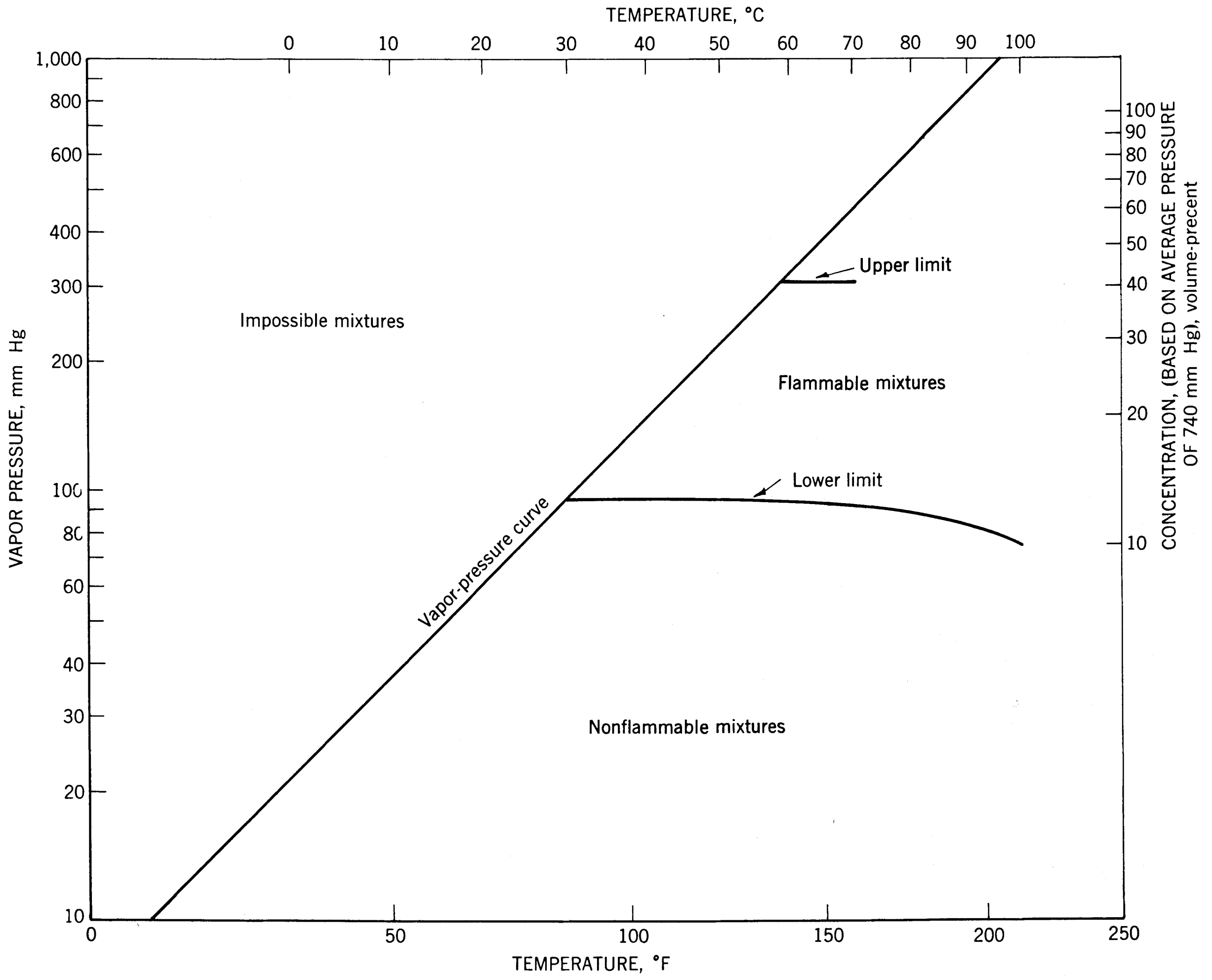


FIGURE 131.—Flammability of Trichloroethylene-Air Mixtures.

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APPENDIX A

TABLE A—1. *Summary of limits of flammability, lower temperature limits (T_L), and minimum autoignition temperatures* (AIT) *of individual gases and vapors in air at atmospheric pressure*

Combustible	Limits of flammability (volume-percent)		T_L (° C)	*AIT* (° C)
	L_{25}	U_{25}		
Acetal	1.6	10	37	230
Acetaldehyde	4.0	60	------	175
Acetic acid	[1] 5.4	------	40	465
Acetic anhydride	[2] 2.7	[3] 10	47	390
Acetanilide	[4] 1.0	------	------	545
Acetone	2.6	13	------	465
Acetophenone	[4] 1.1	------	------	570
Acetylacetone	[4] 1.7	------	------	340
Acetyl chloride	[4] 5.0	------	------	390
Acetylene	2.5	100	------	305
Acrolein	2.8	31	------	235
Acrylonitrile	3.0	------	−6	-----
Acetone Cyanohydrin	2.2	12	------	-----
Adipic acid	[4] 1.6	------	------	420
Aldol	[4] 2.0	------	------	250
Allyl alcohol	2.5	18	22	-----
Allyl amine	2.2	22	------	375
Allyl bromide	[4] 2.7	------	------	295
Allyl chloride	2.9	------	−32	485
o-Aminodiphenyl	.66	4.1	------	450
Ammonia	15	28	------	-----
n-Amyl acetate	[1] 1.0	[1] 7.1	25	360
n-Amyl alcohol	[1] 1.4	[1] 10	38	300
tert-Amyl alcohol	[4] 1.4	------	------	435
n-Amyl chloride	[5] 1.6	[1] 8.6	------	260
tert-Amyl chloride	[6] 1.5	------	−12	345
n-Amyl ether	[4] .7	------	------	170
Amyl nitrite	[4] 1.0	------	------	210
n-Amyl propionate	[4] 1.0	------	------	380
Amylene	1.4	8.7	------	275
Aniline	[7] 1.2	[7] 8.3	------	615
Anthracene	[4] .65	------	------	540
n-Amyl nitrate	1.1	------	------	195
Benzene	[1] 1.3	[1] 7.9	------	560
Benzyl benzoate	[4] .7	------	------	480
Benzyl chloride	[4] 1.2	------	------	585
Bicyclohexyl	[1] .65	[8] 5.1	74	245
Biphenyl	[9] .70	------	110	540
2-Biphenylamine	[4] .8	------	------	450
Bromobenzene	[4] 1.6	------	------	565
Butadiene (1,3)	2.0	12	------	420
n-Butane	1.8	8.4	−72	405
1,3-Butandiol	[4] 1.9	------	------	395
Butene-1	1.6	10	------	385
Butene-2	1.7	9.7	------	325
n-Butyl acetate	[5] 1.4	[1] 8.0	------	425
n-Butyl alcohol	[1] 1.7	[1] 12	------	-----
sec-Butyl alcohol	[1] 1.7	[1] 9.8	21	405
tert-Butyl alcohol	[1] 1.9	[1] 9.0	11	480
tert-Butyl amine	[1] 1.7	[1] 8.9	------	380
n-Butyl benzene	[1] .82	[1] 5.8	------	410
sec-Butyl benzene	[1] 0.77	[1] 5.8	------	420
tert-Butyl benzene	[1] .77	[1] 5.8	------	450
n-Butyl bromide	[1] 2.5	------	------	265
Butyl cellosolve	[8] 1.1	[10] 11	------	245
n-Butyl chloride	1.8	[1] 10	------	-----
n-Butyl formate	1.7	8.2	------	-----
n-Butyl stearate	[4] .3	------	------	355
Butyric acid	[4] 2.1	------	------	450
α-Butryolactone	[8] 2.0	------	------	-----
Carbon disulfide	1.3	50	------	90
Carbon monoxide	12.5	74	------	-----
Chlorobenzene	1.4	------	21	640
m-Cresol	[8] 1.1	------	------	-----
Crotonaldehyde	2.1	[11] 16	------	-----
Cumene	[1] .88	[1] 6.5	------	425
Cyanogen	6.6	------	------	-----
Cycloheptane	1.1	6.7	------	-----
Cyclohexane	1.3	7.8	------	245
Cyclohexanol	[4] 1.2	------	------	300
Cyclohexene	[1] 1.2	------	------	-----
Cyclohexyl acetate	[4] 1.0	------	------	335
Cyclopropane	2.4	10.4	------	500
Cymene	[1] .85	[1] 6.5	------	435
Decaborane	.2	------	------	-----
Decalin	[1] .74	[1] 4.9	57	250
n-Decane	[12] .75	[13] 5.6	46	210
Deuterium	4.9	75	------	-----
Diborane	.8	88	------	-----
Diesel fuel (60 cetane)	------	------	------	225
Diethyl amine	1.8	10	------	-----
Diethyl analine	[4] .8	------	80	630
1,4-Diethyl benzene	[1] .8	------	------	430
Diethyl cyclohexane	.75	------	------	240
Diethyl ether	1.9	36	------	160
3,3-Diethyl pentane	[1] .7	------	------	290
Diethyl ketone	1.6	------	------	450
Diisobutyl carbinol	[1] .82	[10] 6.1	------	-----
Diisobutyl ketone	[1] .79	[1] 6.2	------	-----
2-4, Diisocyanate	------	------	120	-----
Diisopropyl ether	1.4	7.9	------	-----
Dimethyl amine	2.8	------	------	400
2,2-Dimethyl butane	1.2	7.0	------	-----
2,3-Dimethyl butane	1.2	7.0	------	-----
Dimethyl decalin	[1] .69	[9] 5.3	------	235
Dimethyl dichlorosilane	3.4	------	------	-----
Dimethyl ether	3.4	27	------	350
n,n-Dimethyl formamide	[1] 1.8	[1] 14	57	435
2,3-Dimethyl pentane	1.1	6.8	------	335
2,2-Dimethyl propane	1.4	7.5	------	450
Dimethyl sulfide	2.2	20	------	205
Dimethyl sulfoxide	------	------	84	-----
Dioxane	2.0	22	------	265
Dipentene	[8] .75	[8] 6.1	45	237
Diphenylamine	[4] .7	------	------	635

See footnotes at end of table.

Combustible	Limits of flammability (volume-percent)		T_L (° C)	AIT (° C)
	L_{25}	U_{25}		
Diphenyl ether	[4] 0.8	--------	------	620
Diphenyl methane	[4] .7	--------	------	485
Divinyl ether	1.7	27	------	-----
n-Dodecane	[4] .60	--------	74	205
Ethane	3.0	12.4	−130	515
Ethyl acetate	2.2	11	------	-----
Ethyl alcohol	3.3	[11] 19	------	365
Ethyl amine	3.5	--------	------	385
Ethyl benzene	[1] 1.0	[1] 6.7	------	430
Ethyl chloride	3.8	--------	------	-----
Ethyl cyclobutane	1.2	7.7	------	210
Ethyl cyclohexane	[14] 2.0	[14] 6.6	------	260
Ethyl cyclopentane	1.1	6.7	------	260
Ethyl formate	2.8	16	------	455
Ethyl lactate	1.5	--------	------	400
Ethyl mercaptan	2.8	18	------	300
Ethyl nitrate	4.0	--------	------	-----
Ethyl nitrite	3.0	50	------	-----
Ethyl propionate	1.8	11	------	440
Ethyl propyl ether	1.7	9	------	-----
Ethylene	2.7	36	------	490
Ethyleneimine	3.6	46	------	320
Ethylene glycol	[4] 3.5	--------	------	400
Ethylene oxide	3.6	100	------	-----
Furfural alcohol	[15] 1.8	[16] 16	72	390
Gasoline:				
100/130	1.3	7.1	------	440
115/145	1.2	7.1	------	470
Glycerine	--------	--------	------	370
n-Heptane	1.05	6.7	−4	215
n-Hexadecane	[4] .43	--------	126	205
n-Hexane	1.2	7.4	−26	225
n-Hexyl alcohol	[1] 1.2	--------	------	-----
n-Hexyl ether	[4] .6	--------	------	185
Hydrazine	4.7	100	------	-----
Hydrogen	4.0	75	------	400
Hydrogen cyanide	5.6	40	------	-----
Hydrogen sulfide	4.0	44	------	-----
Isoamyl acetate	[1] 1.1	[1] 7.0	25	360
Isoamyl alcohol	[1] 1.4	[1] 9.0	------	350
Isobutane	1.8	8.4	−81	460
Isobutyl alcohol	[1] 1.7	[1] 11	------	-----
Isobutyl benzene	[1] .82	[10] 6.0	------	430
Isobutyl formate	2.0	8.9	------	-----
Isobutylene	1.8	9.6	------	465
Isopentane	1.4	--------	------	-----
Isophorone	.84	--------	------	460
Isopropylacetate	[4] 1.7	--------	------	-----
Isopropyl alcohol	2.2	--------	------	-----
Isopropyl biphenyl	[4] .6	--------	------	440
Jet fuel:				
JP–4	1.3	8	------	240
JP–6	--------	--------	------	230
Kerosine	--------	--------	------	210
Methane	5.0	15.0	−187	540
Methyl acetate	3.2	16	------	-----
Methyl acetylene	1.7	--------	------	-----
Methyl alcohol	6.7	[11] 36	------	385
Methyl amine	[4] 4.2	--------	------	430
Methyl bromide	10	15	------	-----
3-Methyl butene-1	1.5	9.1	------	-----
Methyl butyl ketone	[5] 1.2	[1] 8.0	------	-----
Methyl cellosolve	[17] 2.5	[7] 20	------	380
Methyl cellosolve acetate	[8] 1.7	--------	46	-----
Methyl ethyl ether	[4] 2.2	--------	------	-----
Methyl chloride	[4] 7	--------	------	-----
Methyl cyclohexane	1.1	6.7	------	250
Methyl cyclopentadiene	[1] 1.3	[1] 7.6	49	445
Methyl ethyl ketone	1.9	10	------	-----
Methyl ethyl ketone peroxide	--------	--------	40	390
Methyl formate	5.0	23	------	465
Methyl cyclohexanol	[4] 1.0	--------	------	295
Methyl isobutyl carbinol	[4] 1.2	--------	40	-----
Methyl isopropenyl ketone	[5] 1.8	[5] 9.0	------	-----
Methyl lactate	[1] 2.2	--------	------	-----
α-Methyl naphthalene	[4] .8	--------	------	530
2, Methyl pentane	[4] 1.2	--------	------	-----
Methyl propionate	2.4	13	------	-----
Methyl propyl ketone	1.6	8.2	------	-----
Methyl styrene	[4] 1.0	--------	49	495
Methyl vinyl ether	2.6	39	------	-----
Methylene chloride	--------	--------	------	615
Monoisopropyl bicyclohexyl	.52	[18] 4.1	124	230
2-Monoisopropyl biphenyl	[10] .53	[18] 3.2	141	435
Monomethylhydrazine	4	--------	------	-----
Naphthalene	[19] .88	[20] 5.9	------	526
Nicotine	[1] .75	--------	------	-----
Nitroethane	3.4	--------	30	-----
Nitromethane	7.3	--------	33	-----
1-Nitropropane	2.2	--------	34	-----
2-Nitropropane	2.5	--------	27	-----
n-Nonane	[21] .85	--------	31	205
n-Octane	0.95	--------	13	220
Paraldehyde	1.3	--------	------	-----
Pentaborane	.42	--------	------	-----
n-Pentane	1.4	7.8	−48	260
Pentamethylene glycol	--------	--------	------	335
Phthalic anhydride	[7] 1.2	[22] 9.2	140	570
3-Picoline	[4] 1.4	--------	------	500
Pinane	[23] .74	[23] 7.2	------	-----
Propadiene	2.16	--------	------	-----
Propane	2.1	9.5	−102	450
1,2-Propandiol	[4] 2.5	--------	------	410
β-Propiolactone	[3] 2.9	--------	------	-----
Propionaldehyde	2.9	17	------	-----
n-Propyl acetate	1.8	8	------	-----
n-Propyl alcohol	[12] 2.2	[1] 14	------	440
Propyl amine	2.0	--------	------	-----
Propyl chloride	[4] 2.4	--------	------	-----
n-Propyl nitrate	[17] 1.8	[17] 100	21	175
Propylene	2.4	11	------	460
Propylene dichloride	[4] 3.1	--------	------	-----
Propylene glycol	[24] 2.6	--------	------	-----
Propylene oxide	2.8	37	------	-----
Pyridine	[11] 1.8	[25] 12	------	-----
Propargyl alcohol	[5] 2.4	--------	------	-----
Quinoline	[4] 1.0	--------	------	-----
Styrene	[26] 1.1	--------	------	-----
Sulfur	[27] 2.0	--------	247	-----
p-Terphenyl	[4] .96	--------	------	535
n-Tetradecane	[4] .5	--------	------	200
Tetrahydrofurane	2.0	--------	------	-----
Tetralin	[1] .84	[8] 5.0	71	385

See footnotes at end of table.

TABLE A—*1. Summary of limits of flammability, lower temperature limits* (T_L) *and minimum autoignition temperatures* (AIT) *of individual gases and vapors in air at atmospheric pressure*—Continued

Combustible	Limits of flammability (volume-percent)		T_L (° C)	*AIT* (° C)
	L_{25}	U_{25}		
2,2,3,3-Tetramethyl pentane	0. 8	--------	------	430
Tetramethylene glycol	--------	--------	------	390
Toluene	[1] 1. 2	[1] 7. 1	------	480
Trichloroethane	--------	--------	------	500
Trichloroethylene	[28] 12	[25] 40	30	420
Triethyl amine	1. 2	8. 0	------	-----
Triethylene glycol	[8] . 9	[28] 9. 2	------	-----
2,2,3-Trimethyl butane	1. 0	--------	------	420
Trimethyl amine	2. 0	12	------	-----
2,2,4-Trimethyl pentane	. 95	--------	------	415
Trimethylene glycol	[4] 1. 7	--------	------	400
Trioxane	[4] 3. 2	--------	------	-----
Turpentine	[1] . 7	--------	------	-----
Unsymmetrical dimethylhydrazine	2. 0	95	------	-----
Vinyl acetate	2. 6	--------	------	-----
Vinyl chloride	3. 6	33	------	-----
m-Xylene	[1] 1. 1	[1] 6. 4	------	530
o-Xylene	[1] 1. 1	[1] 6. 4	------	465
p-Xylene	[1] 1. 1	[1] 6. 6	------	530

[1] t=100° C.
[2] t=47° C.
[3] t=75° C.
[4] Calculated.
[5] t=50° C.
[6] t=85° C.
[7] t=140° C.
[8] t=150° C.
[9] t=110° C.
[10] t=175° C.
[11] t=60° C.
[12] t=53° C.
[13] t=86° C.
[14] t=130° C.
[15] t=72° C.
[16] t=117° C.
[17] t=125° C.
[18] t=200° C.
[19] t=78° C.
[20] t=122° C.
[21] t=43° C.
[22] t=195° C.
[23] t=160° C.
[24] t=96° C.
[25] t=70° C.
[26] t=29° C.
[27] t=247° C.
[28] t=30° C.
[29] t=203° C.

APPENDIX B

STOICHIOMETRIC COMPOSITION

The stoichiometric composition (C_{st}) of a combustible vapor $C_nH_mO_\lambda F_k$ in air may be obtained from the equation

$$C_nH_mO_\lambda F_k+\left(n+\frac{m-k-2\lambda}{4}\right)O_2\rightarrow nCO_2$$

$$+\left(\frac{m-k}{2}\right)H_2O+kHF.$$

Thus, $C_{st}=\dfrac{100}{1+4.773\left(n+\dfrac{m-k-2\lambda}{4}\right)}$ volume-percent, where 4.773 is the reciprocal of 0.2095, the molar concentration of oxygen in dry air. The following table lists the values of C_{st} for a range of $\left(n+\dfrac{m-k-2\lambda}{4}\right)$ values from 0.5 to 30.75:

N[1]	0	0.25	0.50	0.75
0	--------	--------	29.53	21.83
1	17.32	14.35	12.25	10.69
2	9.48	8.52	7.73	7.08
3	6.53	6.05	5.65	5.29
4	4.97	4.70	4.45	4.22
5	4.02	3.84	3.67	3.51
6	3.37	3.24	3.12	3.01
7	2.90	2.81	2.72	2.63
8	2.55	2.48	2.40	2.34
9	2.27	2.21	2.16	2.10
10	2.05	2.00	1.96	1.91
11	1.87	1.83	1.79	1.75
12	1.72	1.68	1.65	1.62
13	1.59	1.56	1.53	1.50
14	1.47	1.45	1.42	1.40
15	1.38	1.36	1.33	1.31
16	1.29	1.27	1.25	1.24
17	1.22	1.20	1.18	1.17
18	1.15	1.13	1.12	1.10
19	1.09	1.08	1.06	1.05
20	1.04	1.02	1.01	1.00
21	.99	.98	.97	.95
22	.94	.93	.92	.91
23	.90	.89	.88	.87
24	.87	.86	.85	.84
25	.83	.82	.81	.81
26	.80	.79	.78	.78
27	.77	.76	.76	.75
28	.74	.74	.73	.72
29	.72	.71	.71	.70
30	.69	.69	.68	.68

For example, the stoichiometric mixture composition of acetyl chloride (C_2H_3OCl) in air may be found by noting that

$$N=n+\frac{m-k-2\lambda}{4}=2+\frac{3-1-2}{4}=2.0.$$

The entry for $N=2.0$ in the preceding table is 9.48 volume-percent, which is the value of C_{st} for this combustible in air.

---

[1] $N=n+\dfrac{m-k-2\lambda}{4}$; where n, m, λ, and k are the number of carbon, hydrogen, oxygen, and halogen atoms, respectively, in the combustible.

APPENDIX C

HEAT CONTENTS OF GASES

(Kcal/mole[1])

T, ° K	CO_2	H_2O	O_2	N_2
298.16	0	0	0	0
300	.017	.014	.013	.013
400	.941	.823	.723	.709
500	1.986	1.653	1.4541	1.412
600	3.085	2.508	2.2094	2.125
700	4.244	3.389	2.9873	2.852
800	5.452	4.298	3.7849	3.595
900	6.700	5.238	4.5990	4.354
1,000	7.983	6.208	5.4265	5.129
1,100	9.293	7.208	6.265	5.917
1,200	10.630	8.238	7.114	6.717
1,300	11.987	9.297	7.970	7.529
1,400	13.360	10.382	8.834	8.349
1,500	14.749	11.494	9.705	9.178
1,600	16.150	12.627	10.582	10.014
1,700	17.563	13.785	11.464	10.857
1,800	18.985	14.962	12.353	11.705
1,900	20.416	16.157	13.248	12.559
2,000	21.855	17.372	14.148	13.417
2,100	23.301	18.600	15.053	14.278
2,200	24.753	19.843	15.965	15.144
2,300	26.210	21.101	16.881	16.012
2.400	27.672	22.371	17.803	16.884
2,500	29.140	23.652	18.731	17.758

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[1] Gordon, J. S. Thermodynamics of High Temperature Gas Mixtures and Application to Combustion Problems. WADC Technical Report 57-33, January 1957, 172 pp.

APPENDIX D

DEFINITIONS OF PRINCIPAL SYMBOLS

Symbol:	*Definition*
A	Constant.
A'	Area.
a	Velocity of sound.
B	Constant.
C_{st}	Stoichiometric composition.
ΔH_c	Heat of combustion.
K	Ratio of duct area to vent area.
k	Thermal conductivity.
L	Lower limit of flammability.
L^*	Modified lower limit value.
L_{Ave}	Average carbon chain length for paraffin hydrocarbons and correlation parameter for aromatic hydrocarbons.
L_t	Lower limit of flammability at t° C.
L/D	Length to diameter ratio.
M	Molecular weight.
M_1	Mach number.
NO_2^*	Equilibrium mixture of NO_2 and N_2O_4 at a specified temperature and pressure.
n	Number of moles.
P	Pressure.
P_m	Maximum pressure.
ΔP	Pressure rise.
p	Partial pressure.
S_u	Burning velocity.
T	Absolute temperature.
t	Temperature.
τ	Time delay before ignition.
U	Upper limit of flammability.
U_t	Upper limit of flammability at t° C.
V	Volume.
V'	Critical approach velocity.
v	Liquid regression rate.
γ	Specific heat ratio.

SUBJECT INDEX

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