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# **Flammability Limits: Thermodynamics and Kinetics**

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Andrej Maček

Center for Fire Research  
Institute for Applied Technology  
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Final Report



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**U. S. DEPARTMENT OF COMMERCE  
NATIONAL BUREAU OF STANDARDS**



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**U.S. DEPARTMENT OF COMMERCE, Elliot L. Richardson, Secretary**  
**Dr. Betsy Ancker-Johnson, Assistant Secretary for Science and Technology**  
**NATIONAL BUREAU OF STANDARDS, Ernest Ambler, Acting Director**



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# FLAMMABILITY LIMITS: THERMODYNAMICS AND KINETICS

Andrej Maček

## Abstract

Extinction limits for both premixed and diffusion flames for n-alkanes and n-alcohols found in the literature are assembled. Several sets of theoretical flame temperatures corresponding to the limits are defined and presented. The implications of the view that flames fail to propagate at temperatures at which reaction rates become too low to overcome the dissipation processes are discussed. Equilibrium flame temperatures indicate that at lean limits the excess oxygen does not act merely as a diluent but takes an active part in promoting the kinetics of flame reactions. The burning-rate data and the results of ignition experiments are shown to be pertinent to the interpretation of flammability limits. Extinction characteristics of methane are shown to be atypical (compared to other alkanes and alcohols) and demand a special explanation. It is also shown that the assumption of thermodynamic equilibrium at the limits is unrealistic, so there is need for experimental temperature and concentration measurements in both premixed and diffusion flames. When the assumption of equilibrium is removed, the chemical kinetic considerations suggest a simple qualitative explanation of the limit phenomenon, based on the stipulation of incomplete combustion. Quantitative data are presented in support of this view.

Key words: Chemical kinetics; diffusion flames; flame extinction; flame temperature; flame velocity; flammability; flammability limits; Oxygen Index Test; thermodynamics.

## 1. INTRODUCTION

The question of flame extinction and flammability limits has been recognized for a long time as one of great interest, both theoretical and practical. In particular, measurements have been made over many years on flammability limits in premixed gaseous systems because of obvious applications to the explosion safety problem. While measurements of flammability limits for various diffusion flames are of more recent date, they are even more broadly applicable to fire safety problems, because they can be made with gaseous, liquid, or solid fuels. The common feature of diffusion flames for all fuels is that the principal source of energy is the gas-phase combustion. The distinguishing feature of flames and fires fueled by condensed materials is the existence of a vaporization process, probably endothermic and often involving pyrolysis, which precedes the gas-phase mixing and combustion.

However, once the gaseous pyrolysis product is generated, it forms an analogue to the fuel source in gaseous diffusion flames.

This paper deals with the fundamental phenomena of flammability limits in both premixed and diffusion-controlled systems. While the underlying principles no doubt apply more generally, the discussion is restricted to limits (a) at atmospheric pressure, (b) with oxygen gas ( $O_2$ ) as the only oxidant, and (c) with nitrogen ( $N_2$ ) as the diluent. Furthermore, for the sake of simplicity, all quantitative data used for illustration purposes are drawn from experiments with two homologous series of fuels: n-alkanes and n-alcohols. Thus the discussion is limited to simple systems, the elemental composition of which is restricted to carbon, hydrogen, oxygen and nitrogen. Under these restrictive conditions, a complete set of experimental data needed for our purposes is available.

Flammability limits in premixed gaseous systems have been discussed extensively in the combustion literature. A recent critical review of the subject was published by Lovachev et al. [1]<sup>1</sup>. An even more recent paper by Burgess and Hertzberg [2] summarizes the dissipation processes which convene to determine the limiting conditions; these include both heat loss and several aerodynamic effects. However, while causes of extinction at limits are complex, Burgess and Hertzberg [2] emphasize that at least one experimental parameter, burning velocity at the lean limit, tends to about the same value for many fuels. It has also been common knowledge for a long time that the computed (equilibrium) adiabatic flame temperatures for lean-limit mixtures in air cluster near 1500 or 1600 K for many hydrocarbon-type fuels. Since burning velocities are determined by a combination of chemical kinetics and of transport processes, and since transport properties do not vary much in these fuel systems, a frequently accepted view is that flames fail to propagate at temperatures at which reaction rates become too low to maintain the burning velocity required to overcome the dissipation processes; see the historical outline by Burgess [3]. The fact that addition of small amounts of chemical inhibitors (e.g., halogens), which affect primarily the chemical kinetics of the flame, raises the lean limits — i.e., increases the theoretical flame temperature at the limit — supports that view. The main purpose of this paper is to bring out some fundamental implications of that view. It will be shown that a re-examination of experimental flammability-limit data for simple hydrocarbon fuels (without chemical inhibitors), and the theoretical computations of flame temperatures corresponding to these data, can clarify the thermodynamic and chemical-kinetic aspects of near-limit systems for both premixed flames and diffusion flames.

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<sup>1</sup>Numbers in brackets refer to the literature references listed at the end of this paper.

Flammability-limit data for gaseous diffusion flames are not quite so extensive as in the case of premixed systems, but they are also entirely adequate for our purposes. The best developed and standardized experimental procedure for diffusion flames is the Oxygen Index Test, which was developed for gases and liquids by Wolfhard and coworkers [4, 5,6], and for solids by Fenimore and Martin [7]. In all cases the Oxygen Index is defined as the limiting mole fraction of oxygen in an oxygen/nitrogen mixture necessary to maintain a diffusion flame. In the recent years, many solids have been rated by the test, but these data will not be discussed. The discussion will be restricted to thermodynamic aspects of the results obtained for gases and liquids, and will center around the comparison of these with the results obtained with premixed gaseous systems. A natural limitation imposes itself immediately on the extent to which such a comparison can be made: While in premixed systems one can obtain a set of flammability-limit data for each fuel, corresponding to a wide range of fuel/oxidant/diluent proportions, this is not true of diffusion flames each of which determines its own unique stoichiometry.

In addition to results of these standardized tests, it will be shown that useful information toward a better understanding of thermodynamics and chemical kinetics of flammability limits can be drawn from ignition and burning rate data.

To prevent confusion in the mind of the reader, we must emphasize at the outset that the discussion will be on two distinct levels. Firstly, quantitative calculations and reasoning will be presented based on the assumption that thermodynamic equilibrium obtains in all flames. This is the usual assumption. Secondly, we shall give qualitative conclusions based on the realization that we are dealing with processes where attainment of full equilibrium should not be expected. The distinction is important, because the conclusions differ depending on whether one does or does not assume attainment of full thermodynamic equilibrium.

## 2. PREMIXED SYSTEMS

The comprehensive compilation by Zabetakis [8], which presents detailed data on flammability limits in premixed systems obtained from upward flame propagation experiments will be used in all tabulations and calculations. Since it is known that upward limits are broader than for the downward case, they are certainly appropriate for fire and explosion safety purposes, but one may question whether they are entirely so for the purpose of basic correlations. Burgess and Hertzberg [2] point out that buoyancy helps the upward and impedes the downward flame propagation; hence, horizontal propagation, or perhaps an average of upward and downward limits, may be a more logical basis for a fundamental discussion. However, while the numerical flame temperature values derived from such alternative experiments (downward or horizontal) would be somewhat different, it appears probable that our general conclusions would remain

substantially unchanged, especially for heavier fuels, because the spread between upward and downward lean limits decreases with increased molecular weight of the fuel. The case of methane is something of an exception, and will be discussed in section 5.

The flammability-limit diagram for propane [8] is reproduced in figure 1. Propane is chosen for illustration purposes here and in subsequent discussion. The choice is arbitrary, but convenient. Propane is a very common fuel, for which many data are available and, since its molecular weight is higher than that of oxygen, complications associated with selective diffusional demixing are not prominent in lean mixtures — see the article by Burgess and Hertzberg [2] and section 5 of this paper. Plots analogous to figure 1 are available for most fuels which will be discussed. The nomenclature for three key points on the flammability limit curve — lean limit (LL), upper limit (UL), and nitrogen peak (NP) — is conventional and self-explanatory. The term "stoichiometric" is also used in the conventional sense: it refers to mixtures containing just enough oxygen to be able to oxidize all of the carbon to  $\text{CO}_2$  and all of the hydrogen to  $\text{H}_2\text{O}$ . The intersection of the stoichiometric line with the limit curve is denoted SL. In thermodynamic equilibrium the enthalpy release per unit mass of the mixture is maximized along the stoichiometric line, so if an adiabatic flame temperature coordinate were added perpendicular to the plane of figure 1, the stoichiometric line would appear as a high ridge with downward slopes toward both the upper and the lower flammability-limit branches.

A point concerning the distribution of combustion products should be emphasized. Generally, the term "stoichiometric" refers merely to a simple way of specifying the oxygen/fuel ratio necessary for complete oxidation of the fuel; it should not be taken to imply that such complete oxidation actually takes place or is even predicted by thermodynamics. However, along the stoichiometric line in the region of interest to us thermodynamic computations show that the equilibrium combustion products (at the adiabatic flame temperature) do consist largely of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{N}_2$ . Disproportionations of  $\text{CO}_2$  to  $\text{CO}$  and  $\text{O}_2$ , etc., occur to some extent at relatively high temperatures near the ordinate, but are negligible near the flammability limit. A fortiori, thermodynamics predicts virtually full formation of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  everywhere below the stoichiometric line, the excess oxygen remaining as free  $\text{O}_2$ ; thus the thermodynamically-predicted reaction is in fact stoichiometric not only at, but also everywhere below the line. The only consideration of importance is whether the dilution is entirely by nitrogen (along the line), or also partly by excess oxygen (below the line).

### 3. THE OXYGEN INDEX TEST

Oxygen-index (OI) data have been reported for two different experimental test arrangements. The simpler and more commonly used geometry is that of a cylindrical column of fuel (solid stick or cup filled with liquid) having a diameter of the order of 1 cm, and surrounded by an oxygen-nitrogen mixture flowing upward at a velocity of a few centimeters

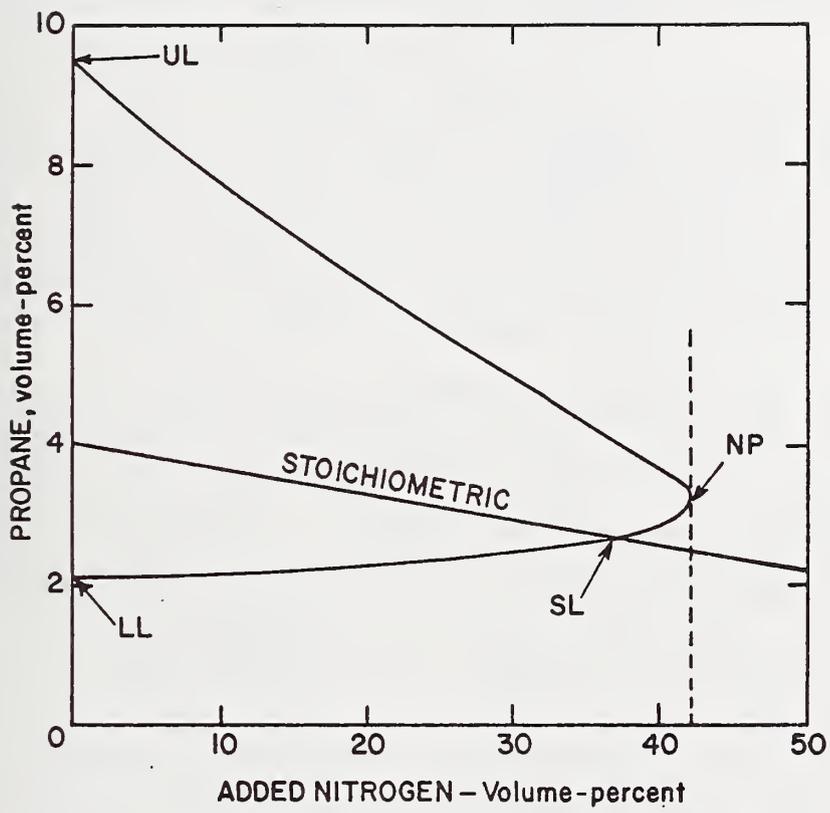


Figure 1. Flammability Limits of Propane-Nitrogen-Air Mixtures at 25 °C and Atmosphere Pressure (from reference [8]).

per second [7]. While, in principle, one can use this geometry also with gaseous fuels, Simmons and Wolfhard [5] report having obtained more reproducible data both for gases and for liquids by a somewhat different geometric arrangement, utilizing an inverted porous-hemisphere burner. For internal consistency, we shall use the Simmons-Wolfhard data for all numerical illustrations of diffusion flames.

Adiabatic flame temperatures corresponding to the OI (i.e. extinction) conditions were calculated by Simmons and Wolfhard [5], but it must be recognized that they rest on two assumptions. The first assumption is that flame products come to thermodynamic equilibrium. In a diffusion flame this means that the reactants fully consume each other, i.e., that they enter the flame in very nearly stoichiometric proportions (providing the temperature is so low that dissociation is negligible — see section 2. While the assumption of thermodynamic equilibrium, hence of complete reaction, is probably not realistic near flammability limits, it must be pointed out that the same assumption is made also in conventional computations of premixed flame temperatures. The second assumption is that the  $N_2/O_2$  ratio in the flame is the same as at the cold boundary. Again, this may not be quite true, because in diffusion flames one generally expects to find concentration gradients of all species, including diluents, but the assumption is probably good in cases where the inert gas is present in very large amounts (over 80% at OI for alkanes and alcohols). These two assumptions suffice for a complete thermodynamic definition of the experimental OI; furthermore, the thermodynamic state so defined corresponds to a point along the stoichiometric line in the flammability-limit diagram for premixed systems, discussed in section 2. Indeed, Simmons and Wolfhard [5] call the ratio  $O_2/(O_2 + N_2)$  at premixed flammability limits also "oxygen index from limits of inflammability," with the implication that one can define an infinite set of oxygen indices along a single flammability-limit curve, such as the one for propane shown in figure 1; the relation between the two oxygen indices so defined — by diffusion and by flammability — presumably offers a measure of similarity, or differences, in flammability requirements for premixed and diffusion flames. Since in the recent years the term Oxygen Index has become firmly associated with diffusion experiments, it will not be applied to premixed systems in this discussion. However, we shall proceed along the path indicated by Wolfhard and coworkers [4,5,6] and examine closely the relation of calculated flame temperatures corresponding to experimental OI data,  $T(OI)$ , and temperatures calculated along the premixed flammability-limit curves, e.g.,  $T(LL)$ ,  $T(SL)$ , or  $T(NP)$ .

#### 4. THERMODYNAMIC EQUILIBRIUM — ADIABATIC FLAME TEMPERATURES

This section explores the implications of the assumption that thermodynamic equilibrium is attained in flammability-limit experiments.

Table 1 lists values of LL, SL, and NP for premixed systems from Zabetakis [8], OI from diffusion experiments of Simmons and Wolfhard [5], and the respective computed adiabatic flame temperatures for each. LL is given as the mole percent of fuel, a standard practice in the combustion literature. SL and NP are given in terms of oxygen mole fractions, Y, which is convenient for the subsequent discussion. Note that OI, being defined as the mole fraction of oxygen in oxygen/nitrogen mixtures without fuel, is always slightly higher than the mole fraction Y(OI) in the corresponding premixed system used for calculations of T(OI). Note also that, in the Oxygen Index experiment, only  $OI \equiv [O_2/(O_2 + N_2)]_{lim}$  is an experimental quantity; the values of both Y(OI) and T(OI) depend on the thermodynamic assumptions stated in section 3. Thermodynamic data for temperature computations were taken from JANAF Tables [9] and from Stull et al. [10].

Consider first the series of alkanes. As pointed out originally by Simmons and Wolfhard [5], the states OI and SL coincide quite closely; furthermore, all temperatures pertaining to these two sets of data — T(OI) and T(SL) — cluster in the same range, except for ethane, the values for which are somewhat low. The apparent implication is that in the OI test, and in the premixed limit test at the stoichiometric point, ethane is somehow more flammable than other alkanes. This matter will now be pursued somewhat beyond the extent of earlier discussions.

Figure 2 shows the plots of T(OI) and T(LL) for alkanes versus the number of carbon atoms in the fuel molecule. Two aspects of these plots deserve attention. Note first that both T(OI) and T(LL) decrease smoothly with decreasing molecular weight of the fuel, T(OI) for methane being the only gross exception. Following the T(OI) curve down the rungs of carbon atoms, one would perhaps expect to find methane in the familiar region around 1500 K; instead, it appears about 300 K higher. Thus the suggestion of the T(OI) curve is not so much that the OI test rates ethane as unusually flammable, but that it rates methane as anomalously nonflammable. This problem will be discussed in section 5.

The second point of interest is a quantitative comparison of the two curves in figure 2. Note that the T(OI) values are on the average about 150 K higher than T(LL) — less than average for ethane, much more so for methane. One may be tempted to ascribe the temperature difference to the fact that the upper curve relates to diffusion experiments and the lower to premixed flames. Surely, this would be incorrect. One need not go at all to diffusion experiments to demonstrate the difference between T(LL) and temperatures of limiting mixtures at or near the stoichiometric, as an inspection of table 1 will show: the T(SL) values, while somewhat more scattered than their T(OI) counterpart, are clearly in the domain of the upper curve of figure 2 and substantially above the lean-limit data. Yet, these SL temperatures are derived from the same source of premixed flammability data as T(LL). The difference, then, is not one between premixing and diffusion, but one of stoichiometry: it is the difference between excess oxygen (at LL) and the bare sufficiency thereof (OI and SL). In figure 1, as one proceeds from LL along the limit curve, the equilibrium flame temperature necessary to maintain the

Table 1. Thermodynamic Equilibrium Properties at Extinction  
(See Text for Notation)

Fuel	LL	T(LL) (°K)	Y(SL)	T(SL) (°K)	Y(NP)	T(NP) (°K)	OI	Y(OI)	T(OI) (°K)
CH <sub>4</sub>	5.0	1480	0.123	1720	0.117	1610	0.139	0.130	1780
C <sub>2</sub> H <sub>6</sub>	3.0	1530	0.114	1620	0.111	1540	0.118	0.114	1630
C <sub>3</sub> H <sub>8</sub>	2.1	1540	0.125	1730	0.114	1470	0.127	0.124	1720
n-C <sub>4</sub> H <sub>10</sub>	1.8	1640	0.134	1830	0.121	1490	—	—	—
n-C <sub>5</sub> H <sub>12</sub>	1.4	1590	0.135	1810	0.115	1410	0.1325	0.130	1760
n-C <sub>6</sub> H <sub>14</sub>	1.2	1610	0.135	1800	0.117	1420	0.1335	0.132	1770
n-C <sub>7</sub> H <sub>16</sub>	1.05	1620	0.134	1770	0.118	1430	—	—	—
n-C <sub>8</sub> H <sub>18</sub>	0.90	1650	0.134	1770	0.118	1440	0.134	0.133	1780
∞ n-C <sub>10</sub> H <sub>22</sub>							0.1345	0.133	1780
CH <sub>3</sub> OH	6.7	1550	0.112	1690	0.085	1430	0.111	0.103	1530
C <sub>2</sub> H <sub>5</sub> OH	3.3	1490	0.118	1700	0.106	1430	0.126	0.121	1670
n-C <sub>3</sub> H <sub>7</sub> OH	2.2	1490					0.128		1700
n-C <sub>4</sub> H <sub>9</sub> OH	1.7	1510					0.129		1710
n-C <sub>5</sub> H <sub>11</sub> OH	1.4	1550					0.130		1730
n-C <sub>6</sub> H <sub>13</sub> OH	1.2	1490					0.1315		1740
n-C <sub>8</sub> H <sub>17</sub> OH							0.1315		1750
CH <sub>4</sub>	5.75*	1630							
C <sub>2</sub> H <sub>6</sub>	3.2*	1580							

\* Downward propagation (ref. [2]). Other premixed data are for upward propagation (ref. [8]).

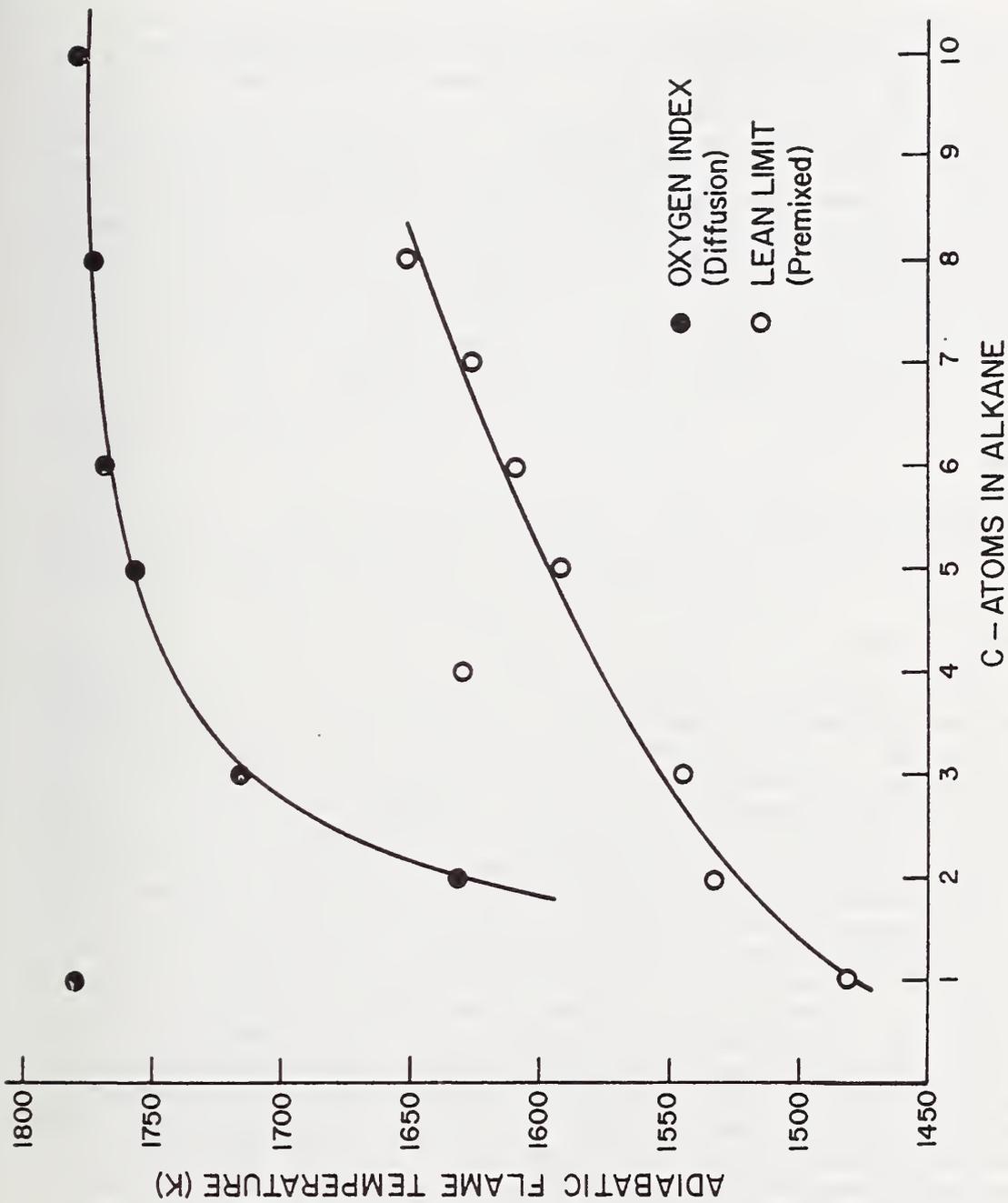


Figure 2. Computed (Equilibrium) Flame Temperatures at Flammability Limits for n-Alkanes.

flame increases. Now, if one accepts the general explanation of the role of chemical kinetics near flammability limits, as stated in the introduction, the clear implication is that SL conditions are kinetically less favorable than at the LL, and therefore demand higher temperatures for viability of the flame.

An attempt to use the data in table 1 to reach a conclusion also about differences in flammability requirements between premixed and diffusion flames creates something of a dilemma. On one hand, a comparison of  $T(OI)$  and  $T(SL)$ , or of the respective oxygen mole fractions  $Y(OI)$  and  $Y(SL)$  — which is entirely appropriate in the light of the foregoing discussion — shows virtually no differences. If anything, the indication is that in some cases the diffusion flames have slightly lower thermal and oxygen requirements (see the entries in table 1 for pentane, hexane, and methyl alcohol), which in itself is somewhat puzzling; one would rather expect the opposite. On the other hand, there is the experimental fact, unencumbered by the thermodynamic assumptions used to calculate  $Y(OI)$ ,  $T(OI)$ , and  $T(SL)$ , that the maximum dilution which a diffusion flame can tolerate is less than for premixed flames: a comparison of OI with NP appears to give a more reasonable idea of the differences in flammability requirements, than the comparison of OI with SL. This was recognized by Simmons and Wolfhard [5] who, after establishing a close correspondence of OI and SL, still used the dilution effect, i.e. a comparison of OI with NP, to reach their conclusion: it is the fact that a premixed flame can be diluted with more nitrogen than a diffusion flame that points to fundamental differences between the two types of flames. A resolution of this dilemma will be given at the end of the paper, after a discussion of non-equilibrium effects.

An additional comment regarding the flammability limits in premixed systems, having practical consequences, is in order here. To wit, the effect of oxygen in shifting the limiting equilibrium flame temperature in these systems, although qualitatively understandable, appears surprisingly large; for example, in the case of propane there is a 190 K temperature increase upon a modest decrease of oxygen mole fraction from 0.204 at LL to 0.125 at SL. This means that the assumption of thermodynamic equilibrium strongly indicates that practical explosion and fire safety problems must be approached with care. In particular, even if the hazard occurs because of rising mole fraction of the fuel (i.e., if there is threat of crossing the lower branch of the flammability-limit curve, which is a common practical case), one should be careful not to identify potential problems of gas-phase explosion and flammability indiscriminately and exclusively with lean limits, because the oxygen/nitrogen ratio also matters. Lean-limit thermodynamics will indeed be applicable if the  $O_2/N_2$  ratio is that of air, but the thermodynamics may be significantly different if that ratio is lower. It is obviously different in OI experiments. Oxygen depletion may occur also in practical fire and explosion situations. In such cases, increase of mole fraction of oxygen (without change in mole fraction of the fuel) may be hazardous: as the above discussion shows, oxygen in excess of the stoichiometric does not merely act as a diluent but takes an active part

in promoting flame reactions and thus lowering the thermodynamic requirement for establishment of a flame. However, it should be mentioned here that non-equilibrium considerations admit the possibility that the effect of oxygen is somewhat less than indicated by the discussion so far; this is an important matter, and it will be taken up in section 6.

## 5. THE METHANE ANOMALY, BURNING VELOCITIES, AND REACTION RATES

As seen in table 1 and figure 2, the OI test gives methane a relatively low flammability rating, compared to other alkanes and alcohols. In particular, its flammability is substantially lower than those of its neighbor alkanes, ethane and propane, and very much lower than that of methyl alcohol. Other combustion experiments indicate that this low rating by the OI test is in fact realistic. For example, Vanpée and Wolfhard [6] report ignition temperatures for a hot air jet into fuel as 1310 K for methane, but only 1110 K for ethane, 1160 K for propane, and 1180 K for butane. We shall now discuss some burning velocity ( $S_u$ ) experiments which indicate the same relative ranking and, moreover, give additional insight into reactivity and kinetics of hydrocarbon oxidation at high temperatures.

The data of Gibbs and Calcote [11] show that lean methane-air mixtures generally have  $S_u$  values lower than other alkanes; only high homologues on the rich side show  $S_u$  values somewhat below that of methane. Ethane and propane always burn faster than methane.

Kaskan [12] made an especially interesting study of burning velocities as functions of flame temperature by means of a quenched-flame technique which allows controlled flame temperature variation for a fixed stoichiometry. He found that methane-air mixtures not only burn more slowly than either ethane or propane, but that  $S_u$  for methane has a higher temperature coefficient, hence a higher "overall activation energy." According to Kaskan's own interpretation [12], which is most useful for the purposes of this discussion, the differences among the burning velocities of various hydrocarbons must be sought in the differences of primary oxidation rates to CO and H<sub>2</sub>O. This is so because the final stage of flame reactions, which is known to be oxidation of CO to CO<sub>2</sub> [13], must be common to all hydrocarbons. The interpretation is bolstered by the fact that CO/H<sub>2</sub> mixtures, in which the primary oxidation of carbon is eliminated, burn very rapidly: burning velocities of all hydrocarbons which Kaskan [12] studied — ethane, propane, ethylene, and acetylene — were found to be intermediate between those of methane (slow) and carbon monoxide/hydrogen mixtures (fast). Thus, hydrocarbons which burn slowly do so because their primary oxidation rates to CO are relatively slow. Kaskan's activation energies (from burning velocities in air, stoichiometric ratios), which must relate in some fashion to the kinetics of primary oxidation to CO and H<sub>2</sub>O, rank the five fuels in the following increasing order: C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, CH<sub>4</sub>. This is also the order of increasing T(OI) values.

Thus, several independent combustion measurements agree with the flammability-limit ranking of the OI test. For alkanes, this means that fuels become progressively more flammable with decreasing molecular weight, with sudden reversal of the trend in the case of methane. The key to low flammability of methane must be in the fundamental kinetic mechanism of oxidation of methane, more specifically in differences between oxidation mechanisms of methane and ethane. This problem has not been resolved, but two points may be mentioned indicating that it is reasonable to expect methane oxidation to be relatively slow. First, methane is a very stable molecule, so the initial attack upon it (by hydrogen abstraction) will be relatively slow. Second, despite much work, no kinetically easy route has been found for subsequent oxidation of the  $\text{CH}_3$  radical in flames. Recent studies by Peeters and Mahnen [14] indicate that oxidation of  $\text{CH}_3$  by oxygen atoms is the key step — a radical-radical reaction, hence necessarily relatively slow. Attachment of oxygen to the C-C bond in higher hydrocarbons may be kinetically easier. If this reasoning is correct, one should expect that fuel molecules containing a single carbon atom which is already oxidized will be substantially more flammable than methane. Two such molecules are formaldehyde, which in fact is usually assumed to be an intermediate in the oxidation of methane, and methyl alcohol. Rough high-temperature OI data for formaldehyde [4] indeed indicate it to be much more flammable than methane, but the data cannot be quantitatively compared to the results of Simmons and Wolfhard [5]. Methyl alcohol, on the other hand, does provide the comparison and it fulfills the expectation: as shown in table 1, the  $T(\text{OI})$  value for methyl alcohol, 1530 K, is substantially lower than for ethyl alcohol, and very much lower than for methane.  $T(\text{OI})$  values for alcohols higher than methyl are aligned along the upper curve in figure 2 showing that, with the sole exception of methane, alkanes have about the same thermal requirements for flammability as the corresponding alcohols.

In view of the considerable weight of evidence that methane is a gas of unusually low flammability, it is surprising that the lean-limit data indicate the opposite to be true: the lower curve in figure 2 descends uniformly down to methane, indicating it to be the most flammable of alkanes. We believe this apparent behavior to be caused by the phenomenon of selective diffusional demixing, which has been known for a long time to influence the flammability-limit behavior of hydrogen because of its low molecular weight. Alone among the alkanes (and alcohols), methane has the molecular weight only half that of  $\text{O}_2$ . Thus, it must be expected that the actual mole fraction of methane in the flame, hence also the flame temperature, is higher than that calculated on the basis of complete mixedness. It has been pointed out by Burgess and Hertzberg [2] that the phenomenon has less of an effect on downward than on upward propagation of the flame. Indeed, a comparison of  $T(\text{LL})$  for downward propagation, listed in table 1, shows methane to be slightly less flammable than ethane. Thus, while the lean limits for methane given in the literature [8,15] no doubt give a good measure of flammability for safety purposes, they are not representative for the purpose of thermodynamic comparisons.

## 6. DEVIATIONS FROM THERMODYNAMIC EQUILIBRIUM

The preceding pages have discussed some implications of the assumption of thermodynamic equilibrium at flammability limits, both for premixed and for diffusion flames. We now return to a subject, first brought up in section 4, which pertains to premixed limits only; to wit, the role of oxygen along the lower branch of the flammability-limit curve (fig. 1). We pointed out that as the mole fraction of oxygen decreases, the equilibrium flame temperature at the limit increases quite substantially; and following earlier thoughts, we interpreted this to mean that the decreasing availability of oxygen chemical kinetic conditions for oxidation becomes less favorable, demanding increasing temperatures for viability of the flame. The reader will have noted, however, that the word so far has been only about the segment of the limit curve between the lean limit and the stoichiometric point. An attempt to extend this reasoning over the short, but extremely important, segment to the nitrogen peak, at once, reveals an apparent failure of the interpretation and gives a clue as to what can and what cannot be expected from thermodynamic equilibrium calculations.

The upper curve in figure 3 shows the equilibrium temperature variation along the entire lower branch of the limit curve for propane, from LL to NP plotted against added nitrogen as in figure 1 (fig. 3 should be inspected in conjunction with fig. 1); the mole fraction of oxygen in the unburnt mixture is also indicated on the abscissae. Similar temperature curves are obtained from flammability limits of other hydrocarbons. The precipitous temperature drop from SL to NP, amounting to 260 K for propane and as much as 400 K for pentane, is striking — and unrealistic. It does not appear reasonable that gradual deprivation of oxygen, without an identifiable discontinuity, should suddenly benefit the flame to the point where it becomes viable even at temperatures below those at the lean limit where oxygen abounds. The opposite should be expected, namely an increase of limit temperatures beyond SL, where oxygen becomes deficient. We conclude that the negative slope, and hence the entire stoichiometric hump in figure 3, cannot have the kinetic-thermodynamic significance postulated in the discussion thus far, and may not arise in reality at all.

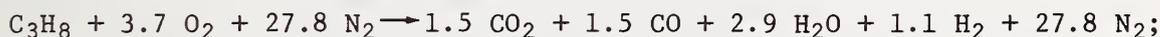
The cause of the sharp rise in equilibrium temperature from NP to SL is easily seen by inspection of the two respective stoichiometries:

At SL:



$T(\text{SL}) = 1730 \text{ K}.$

At NP:



$T(\text{NP}) = 1470 \text{ K}.$

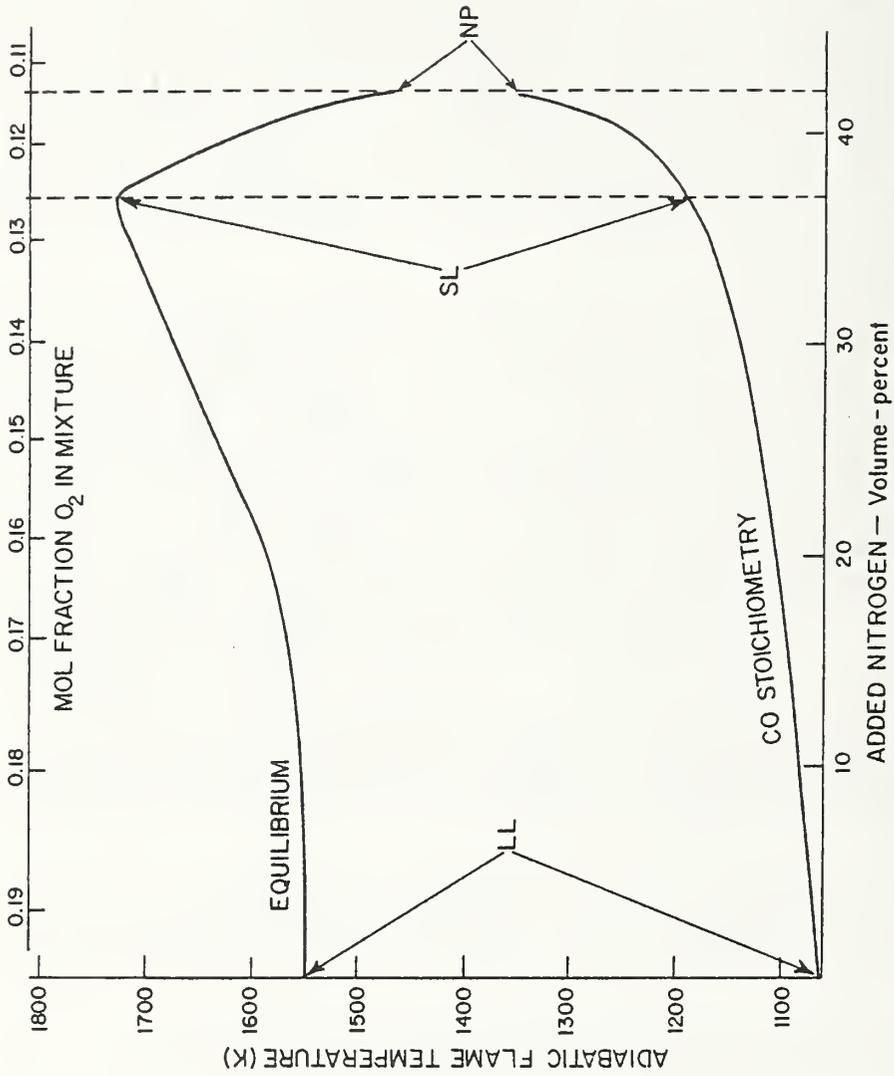


Figure 3. Computed Flame Temperature Along the Lower Branch of the Flammability Limits of Propane (see fig. 1).

The enthalpy responsible for the temperature difference  $T(\text{SL}) - T(\text{NP})$  comes largely from oxidation of CO, present at NP, to  $\text{CO}_2$ , with a smaller contribution from oxidation of  $\text{H}_2$ . However, if chemical kinetics becomes limiting near extinction, it is precisely the oxidation of CO to  $\text{CO}_2$ , the final stage of the flame reaction requiring a relatively long time at high temperatures, which will be affected. Therefore, one can certainly not assume that equilibrium amounts of  $\text{CO}_2$  (which would mean complete oxidation of carbon at all points to the left of SL in figures 1 and 3) will form at extinction. Rather, one should expect incomplete reaction.

Since it appears that, at least in the region between SL and NP, the equilibrium thermodynamics does not give a realistic representation, one must turn to the experiment for information about the chemical composition and temperature of combustion products near limits; the available reaction rate data, of course, are totally inadequate to be of quantitative use. Unfortunately, the experimental information is also extremely limited. We are aware of no temperature measurement or chemical analysis in premixed flammability-limit tests. Since the flame front in these tests is moving, and the reaction tube has to be open on both ends, such measurements would be difficult to make. As far as the OI test is concerned, Fenimore and Jones [16] made both analytical and temperature measurements for polymers at reduced pressures, and concluded that, even significantly above the extinction (OI) values, formation of CO and  $\text{CO}_2$  in equal amounts — i.e., substantially incomplete combustion — is a reasonable assumption for estimates of heat release. At limits, one should probably expect even less complete combustion. Evidently, much more experimental information is needed on both the composition and temperature of the flame reaction products as flammability limits are approached.

Besides the meager data from flammability-limit tests, more extensive and detailed experimental data from burner experiments are on record, and some of these may be of indirect use for our purposes. Such, for example, are the early findings of Friedman and Cyphers [13] that the  $\text{CO}/\text{H}_2$  ratio in low-pressure lean propane flames is much in excess of the equilibrium value, indicating that the formation of  $\text{H}_2$  in the water-gas equilibrium,



cannot keep up with generation rates of  $\text{H}_2\text{O}$  and CO. Relative rates of formation for these and other species in low-pressure methane flames have also been reported by several workers [14,17].

In the absence of adequate experimental information, one must resort to conjecture. If, as appears to be the case, both  $\text{CO}_2$  and  $\text{H}_2$  are late products, their concentrations will tend to remain low as the late reaction stages are affected at extinction. Therefore, we shall attempt to use the simple CO stoichiometry — i.e., oxidation of hydrogen to  $\text{H}_2\text{O}$ , but carbon to CO only — as a rough first approximation to the distribution of products formed at limits. The implied assumption is that

oxidation of CO to CO<sub>2</sub>, if any, will take place sufficiently downstream of the main reaction zone not to affect extinction (or the processes determining the flame velocity). The extent of such oxidation will depend on the residence time of partly oxidized products at high temperatures, i.e., on the geometry of a particular burner. In the case of experiments discussed in this paper it is probable that the extent of oxidation to CO<sub>2</sub> near extinction is always low, and especially for stoichiometries near NP.

Several consequences of the assumption of partial combustion can be made evident easily. Adiabatic flame temperatures calculated on the assumption of the CO stoichiometry are plotted in figure 3 (lower curve) along with the equilibrium temperatures. As expected, these temperatures increase monotonically with decreasing availability of oxygen. In particular, the very steep temperature increase as the ultimate dilution by nitrogen is approached, appears qualitatively reasonable. Figure 4 is even more interesting. It shows the flammability-limit curves for several higher hydrocarbons from the literature [8], in which, however, we have indicated not only the conventional full-combustion stoichiometry, but also the deficient CO stoichiometry. It is most instructive to see that the CO-stoichiometry lines intersect the limit curves near NP in all four cases, showing that the maximum allowable dilution by nitrogen is attained when there is just enough oxygen for oxidation to H<sub>2</sub>O and CO; beyond that point a truly fuel-rich situation obtains, corresponding to the upper branch of the flammability-limit curve.

Thus, the fact that nitrogen peaks usually lie well to the fuel-rich side of "stoichiometric" mixtures does not necessarily imply a peculiar preference by flames for fuel-rich conditions, occasionally hinted at in the literature. Rather, the a priori expectation that maximum allowable dilution by nitrogen will coincide with the stoichiometry corresponding to the maximum heat release may well be true, after all. It is just that the choice of this stoichiometry should be based on estimates of realistic flame reactions, not simply on the assumption of complete oxidation. As our discussion shows, both the experimental flammability-limit data (see especially fig. 4) and the conjecture about chemical kinetics suggest that for many fuels the CO stoichiometry may be a more realistic first guess.

It is doubtful whether any special significance should be attached to the fact that some nitrogen peaks (fig. 4) are a little on the lean and others on the rich side of the CO-stoichiometry. It is generally agreed that the flammability limit is not a sharply defined fundamental phenomenon. Thus even at LL the definition of the limit composition may be a bit diffuse. At NP the uncertainty is apt to be more, because the definition of the peak is very sensitive to the exact shape of the curve. This causes a problem in calculation of flame temperatures around NP, especially in cases where NP corresponds to a composition even richer than the CO stoichiometry: in the case of pentane, for example, the construction of curves analogous to those given in figure 3 becomes well nigh impossible, because both curves become virtually

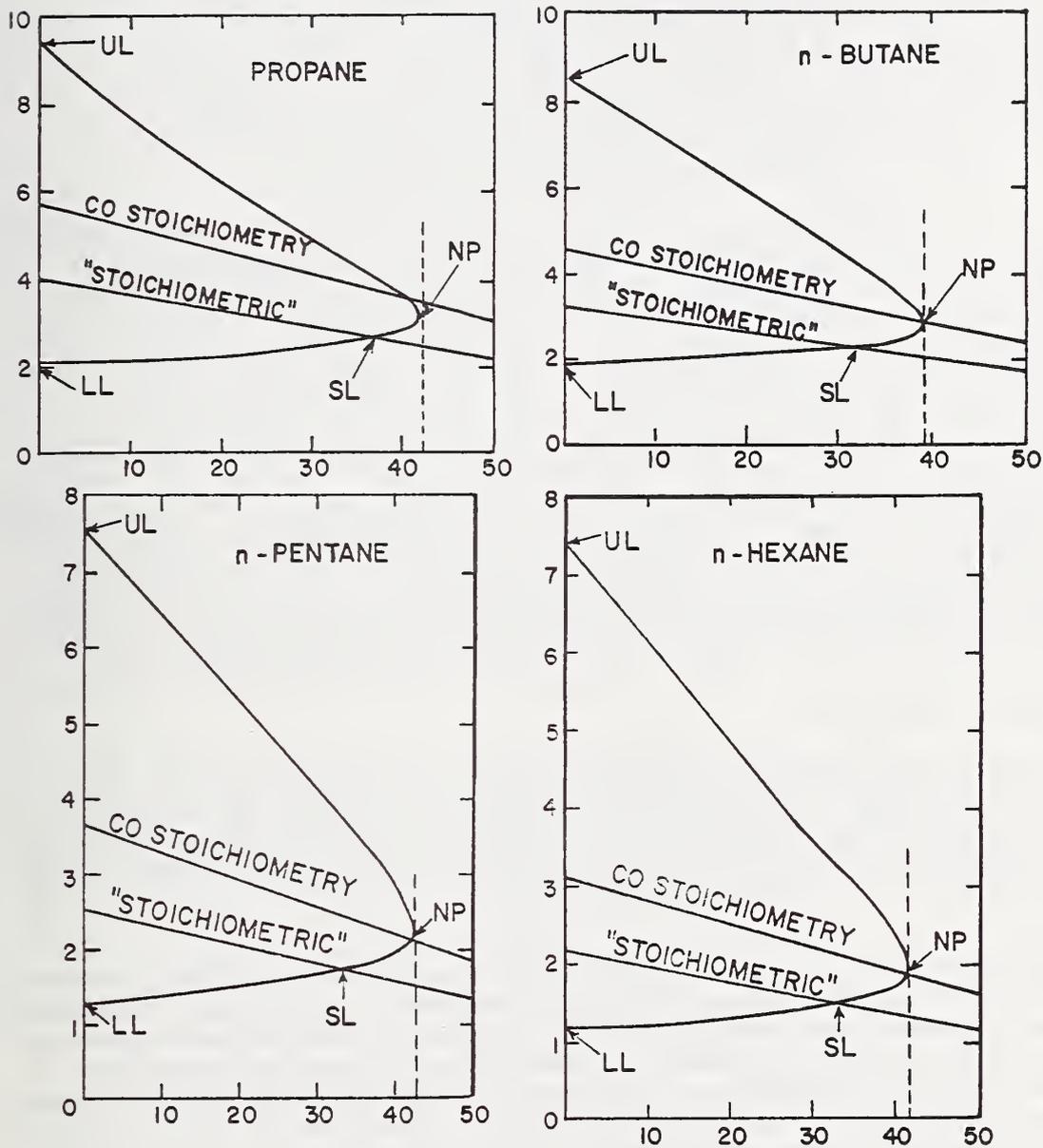


Figure 4. Flammability Limits of Fuel/Nitrogen/Air Mixtures. Percent Fuel vs Percent Nitrogen Added to Air (from ref. [8]).

vertical as NP is approached, tending to meet around 1400 K. In fact, all adiabatic flame temperatures calculated on the basis of the CO stoichiometries approach values near 1400 K as nitrogen peaks are approached.

Nitrogen peaks of both methane and ethane differ somewhat from those of higher alkanes: they are intermediate between the CO stoichiometry and the fully oxidized CO<sub>2</sub> stoichiometry.<sup>2</sup> While methane displays sufficient anomalous behavior (section 5) to explain the difference between it and the higher alkanes, the explanation for ethane is not obvious. The N-peaks for both methyl and ethyl alcohol are close to, but a little to the lean side of the CO stoichiometry.

It follows that, until adequate experimental data become available, only extremely rough estimates can be made of actual temperatures at extinction. From what was said above, it appears that the adiabatic flame temperature most likely will be somewhere between the two curves in figure 3 (although there is no fundamental reason why it could not fall even below the CO-stoichiometry curve). This means that it is reasonably well bracketed only at the nitrogen peak (about 1400 K). Beyond that, we may surmise that it will decrease monotonically toward the lean limit, and thus fall somewhere below 1400 K at LL. To be sure, it should not be assumed that it will follow the lower curve, even though this curve does predict qualitatively reasonable behavior. Quite apart from the fact that the CO stoichiometry is only a first approximation which can hardly be given quantitative credence at any point, one might guess that increasing availability of oxygen will favor some formation of CO<sub>2</sub> toward the lean limit. Thus, the quantitative value of the temperature difference between LL and NP remains in question (cf. discussion in section 4).

The above estimates concerning adiabatic flame temperatures must, of course, be further modified by a downward correction for the heat loss. Quantitative estimates of heat losses at limits are available in the literature — see for example the text by Mullins and Penner [19] — but this subject will not be pursued here.

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<sup>2</sup>The discussion by Lewis and von Elbe [18] indicates otherwise, because it assumes that the NP composition for methane is fuel-lean, corresponding to an equivalence ratio  $ER = 0.88$ . However, this value of  $ER$  is due to an error in arithmetic. According to the data of Coward and Jones [15], used by Lewis and von Elbe, the NP composition for methane is in fact slightly fuel-rich ( $ER = 1.03$ ). According to the more recent compilation by Zabetakis [8], which we have adopted for all our calculations, the NP compositions for both methane and ethane are substantially fuel-rich having  $ER$  values of 1.12 and 1.14 respectively. The discussion of the N-peak region by Lewis and von Elbe [18], which is partly based on the erroneous value for methane, would have to be amended.

We conclude with a brief and tentative discussion of the applicability of this interpretation to diffusion flames. On the assumption of the CO stoichiometry the OI point will lie somewhere on the line appropriate to that stoichiometry (upper straight lines in figure 4). The relevant data for higher alkanes and the two alcohols for which the flammability-limit curves are available are listed in table 2. It can be seen that both thermal and oxygen requirements are always somewhat higher for diffusion flames than for their premixed counterpart. Graphically, this means that, in all cases, in order to find the extinction limit for a diffusion flame one must move from the premixed limit along the CO stoichiometry line to a point inside the flammability peninsula (see fig. 4). This is entirely reasonable. By contrast, it will be recalled that thermodynamic equilibrium (table 1) would place the OI state either at SL, or even shift it along the "stoichiometric" line to a lower temperature at a point outside the premixed limit. This does not appear reasonable. Thus for diffusion flames, just as for premixed flames, the CO stoichiometry describes behavior which is qualitatively more credible than that predicted by the assumption of equilibrium. Table 2 also allows another quantitative comparison. It can be seen that differences in extinction temperatures among the fuels, within either the premixed or the diffusion column, are larger than the differences between the two columns; compare especially the data for alkanes with those for methyl alcohol. This would indicate that in diffusion flames, just as in premixed flames (see Introduction), the extinction temperature is determined primarily by chemical kinetic requirements. Increments of extinction temperatures in the OI experiment over those found with premixed flames — presumably due to the additional requirements of interdiffusion of the fuel and the oxidant — are noticeable, but small (20 to 100 K).

It should be noted that reasonable comparisons can be made from the data in table 2 because for all fuels listed in that table the CO stoichiometry lines intersect the flammability-limit curves near NP; when this is the case the CO stoichiometry appears to be a useful rule of thumb, and it can be invoked to resolve the dilemma about relative flammability requirements in the two types of flames (see section 4). It shows that it is indeed the location of NP — not of SL — relative to OI that gives a meaningful measure of the difference. No broad generalizations should be made, however, because there is no assurance that any given experimental situation will always be so simple; for example, in the case of ethane neither the full equilibrium stoichiometry nor the CO stoichiometry appears to fit the facts. Only further experiments aimed at elucidating realistic combustion stoichiometries can tell.

Table 2. Oxygen Mole Fractions, Y, and Flame Temperatures at Extinction Computed on the Basis of the CO Stoichiometry

	Premixed Flammability Limits*		Oxygen Index (Diffusion)**	
	Y	T(°K)	Y	T(°K)
C <sub>3</sub> H <sub>8</sub>	0.114	1400	0.123	1470
n-C <sub>4</sub> H <sub>10</sub>	0.120	1420	—	—
n-C <sub>5</sub> H <sub>12</sub>	0.116	1390	0.130	1480
n-C <sub>6</sub> H <sub>14</sub>	0.117	1420	0.131	1480
n-C <sub>8</sub> H <sub>18</sub>	0.119	1380	0.131	1480
n-C <sub>10</sub> H <sub>22</sub>	0.119	1390	0.132	1480
CH <sub>3</sub> OH	0.098	1260	0.100	1280
C <sub>2</sub> H <sub>5</sub> OH	0.107	1330	0.119	1380

\* From experimental data compiled by Zabetakis [8].

\*\* From experimental data of Simmons & Wolfhard [5].

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16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)  Extinction limits for both premixed and diffusion flames for n-alkanes and n-alcohols found in the literature are assembled. Several sets of theoretical flame temperatures corresponding to the limits are defined and presented. The implications of the view that flames fail to propagate at temperatures at which reaction rates become too low to overcome the dissipation processes are discussed. Equilibrium flame temperatures indicate that at lean limits the excess oxygen does not act merely as a diluent but takes an active part in promoting the kinetics of flame reactions. The burning-rate data and the results of ignition experiments are shown to be pertinent to the interpretation of flammability limits. Extinction characteristics of methane are shown to be atypical (compared to other alkanes and alcohols) and demand a special explanation. It is also shown that the assumption of thermodynamic equilibrium at the limits is unrealistic, so there is need for experimental temperature and concentration measurements in both premixed and diffusion flames. When the assumption of equilibrium is removed, the chemical kinetic considerations suggest a simple qualitative explanation of the limit phenomenon, based on the stipulation of incomplete combustion. Quantitative data are presented in support of this view.				
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