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# **The Theory of Flammability Limits**

**Natural Convection**

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# THE THEORY OF FLAMMABILITY LIMITS

Natural Convection

by

Martin Hertzberg<sup>1</sup>

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## ABSTRACT

The concept of limit burning velocities is used to formulate a quantitative theory of flammability limits. Competing processes dissipate power from a combustion wave and quench propagation at some characteristically low limit velocity. There are four competing processes and one complication: (a) Free, buoyant convection, (b) conductive-convective wall losses, (c) radiation, (d) selective, diffusional demixing (the complication), and (e) flow gradient effects (flame stretch). These complexities are unraveled by creating an idealization that is initially freed from these competing processes. The ideal serves as a standard, and its burning velocity  $(S_u)_{ideal}$  is a unique function of the initial thermodynamic variables of state. By adding each process individually, it is possible to evaluate their significance, quantitatively, in terms of a limit velocity  $(S_u)_{a, b, c, or e}$ , and to explore the nature of their cooperative interactions. The larger the limit velocity, the more significant the process. The apparently diverse observations of flammability behavior are readily unified within this simple, conceptual framework.

## INTRODUCTION

An accurate knowledge of the flammability behavior of chemical substances is essential for a realistic appraisal of the fire and explosion hazards involved in their manufacture, storage, transportation, and use. This practical concern has motivated numerous experimental studies of the composition limits of flammability of fuel-air mixtures. Thousands of limit determinations have been made for several hundred combinations of fuel-oxidizer systems of practical importance to commerce and manufacturing, to trade and transportation, and to defense and space exploration. The results have been collected, reviewed, and summarized by Coward and Jones (3)<sup>2</sup> and Zabetakis (16).

An understanding of the factors that control the existence of such limits requires a complimentary understanding of the phenomena that control the

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<sup>2</sup>Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

propagation rate of flames. A variety of theories have been proposed to account for these limits in terms of the physical phenomena that compete with the propagation rate processes. These competing processes are effective in dissipating the energy flow density in flames at low propagation rates, and thereby account for the existence of such limits. The problem has challenged the curiosity of many minds. Are the measured limits fundamental ones or do they invariably reflect the interaction of the flame with its cold surroundings? What are the physical phenomena that compete with the propagation processes? Do they act independently or are they coupled? Is there a simple relationship between the limit behavior and the ignition behavior?

A satisfactory theory, according to Egerton (6), "should be able to predict the limit concentration and the burning velocity at the limit." Spalding (15) subsequently presented a quantitative theory based upon the laminarized solutions to the conservation equations that include nonadiabatic heat-loss effects to the surroundings. The problem was surveyed by Linnett and Simpson (12), who showed that the factor which seemed to be most invariant for many fuel-air systems was the limit burning velocity. Linnett and Simpson consider the question of whether the observed limits are fundamental or not, and conclude, in effect, that they are not. This agrees with Levy (9), whose optical studies of limit behavior emphasize the significance of buoyancy effects. Dixon-Lewis (4) concludes, based upon his experimental studies of slow flames stabilized well below their conventional limits (5), that the flammability limits are determined largely by convectional gas velocities.

A combustion wave propagates through a flammable gas mixture of fixed initial composition, temperature, and pressure at a given rate. The mechanism of propagation for even the simplest mixtures is exceedingly complex, involving chemical kinetics, mass diffusion, thermal diffusion, and flow mixing. Nevertheless, these processes are reflected in a simple observable parameter, the ideal burning velocity  $(S_u)_{ideal}$ . This is the velocity of propagation of the combustion wave with respect to the unburned gases in the absence of any complicating or competing effects. This measurable parameter is a unique function of the initial thermodynamic state of the flammable gas mixture.

Now competing processes dissipate power from a combustion wave and quench propagation at some characteristically low limit-velocity. There are four competing processes and one complication:

- a. Natural convective flow or buoyancy effects;
- b. Conductive-convective heat losses to walls;
- c. Radiative heat losses to surroundings;
- d. Selective diffusional demixing;
- e. Nonlaminar flow gradients (flame stretch).

These competing processes not only determine the limits but they complicate burning velocity measurements. Measured values are hopefully the ideal



values obtained from experimental methods that minimize these effects. The ideals serve as standards, and by considering each competing process individually, it is possible to evaluate their significance quantitatively.

It is the prevalent consensus, as indicated by Lewis and von Elbe (10), that the limits as conventionally measured in systems of large size, are determined by the cooperative interaction of processes a and e. It is beyond the scope to consider, in detail, the full range of interactions of all five processes. The author will, however, present some arguments to prove the validity of that consensus view and explore some of its logical consequences.

#### NATURAL CONVECTION LIMIT

The motions induced by a propagating flame originate in the combustion force. This force is contained in the Gibbs chemical potential difference between products and reactants and is obtained from the gradient of the kinetic energy increase per unit volume across a propagating flame zone.

$$\text{Combustion force} = \frac{\Delta(\text{KE})}{\Delta x} = \frac{1/2\rho_b S_b^2 - 1/2\rho_u S_u^2}{\alpha/S_u} = \frac{S_u^3}{2\alpha} \left( \frac{\rho_u}{\rho_b} \right) (\rho_u - \rho_b). \quad (1)$$

Now product gases are less dense than the reactants, and they induce natural convective flows that compete with and dissipate power from the wave. The competing force is--

$$\text{Buoyancy force} = (\rho_u - \rho_b) g. \quad (2)$$

The average convective flow determines the horizontal propagation limit, and this limit is reached when these competing forces are in balance. This defines a limit velocity.

$$(S_u)_a = \left[ 2 \propto g \frac{\rho_b}{\rho_u} \right]^{1/3}. \quad (3)$$

Curves of  $(S_u)_{ideal}$  for several fuel-air mixtures are shown in figure 1. The limit velocity  $(S_u)_a$  is typically 6 to 8 cm sec<sup>-1</sup> and is also shown for each mixture. The predicted limit compositions are defined by the intersection of the limit velocity line with the burning velocity curve. The predictions are compared with the observations, and there is clearly excellent agreement for the cases shown.

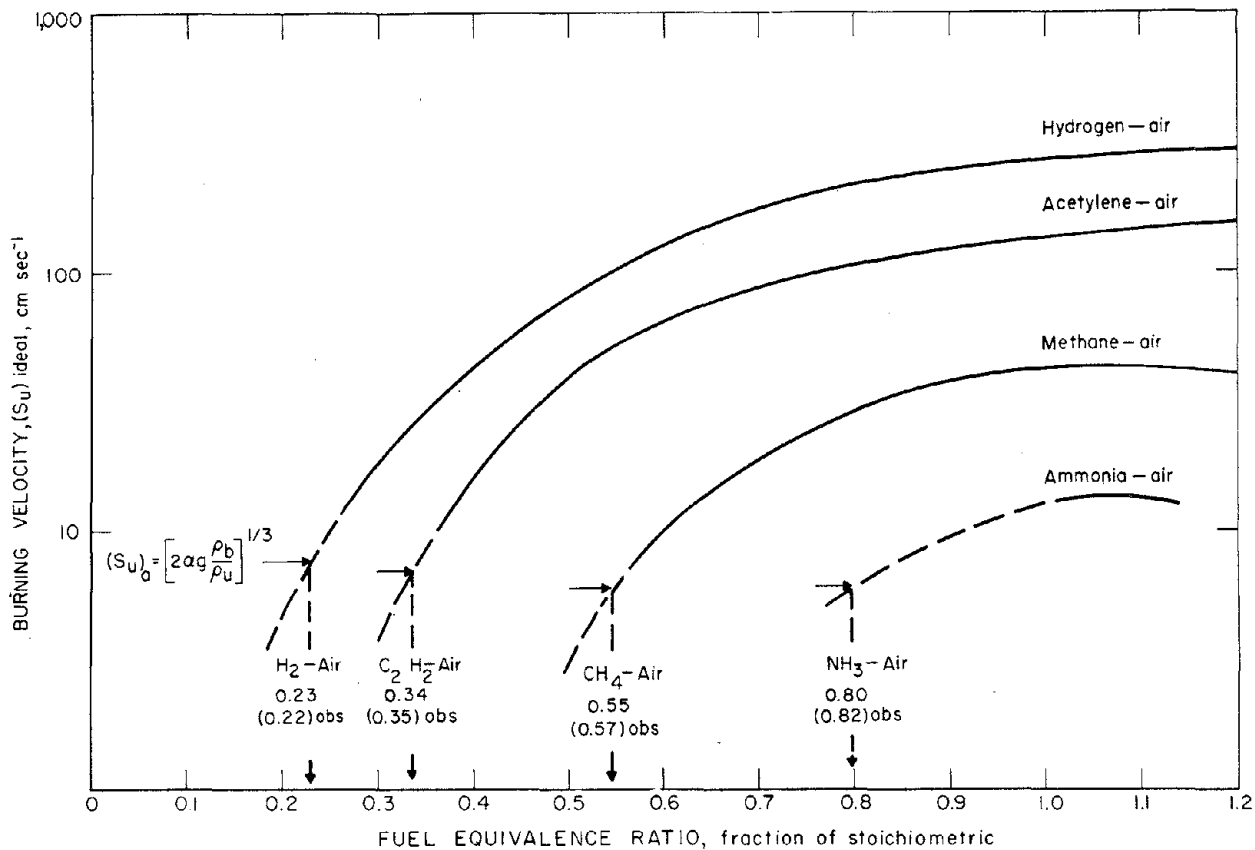


FIGURE 1. - Burning velocities and lean limit equivalence ratios for horizontal propagation from the natural convective limit velocity  $(S_u)_0$ . Comparison theory with experiment.

#### UPWARD AND DOWNWARD LIMITS

For upward propagation, the buoyant acceleration of a burned gas sphere is in the direction of propagation, and hence the buoyant velocity adds to the rate of advance of the flame front. For horizontal propagation, the buoyant acceleration is perpendicular to the direction of propagation. For downward propagation, the buoyant acceleration is opposed to the direction of propagation, and hence the buoyant velocity reduces the rate of advance of the flame front. For the downward case, a point is reached where the intrinsic (gravity-free) flame speed is just balanced by the buoyant retardation velocity. This defines a downward limit burning velocity, where the absence of flow leads to a stagnation limit in the laboratory reference frame. To understand the extinguishment mechanism for upward propagation, the details of the flow field around the rising and expanding flame must be studied. Subtracting away the combustion-force flow expansion, the motion of unburned gas around the propagating sphere is approximated by that of denser gas around a rising balloon. Thus, in the coordinate frame of the rising sphere,

the top of the sphere propagates into diverging or parting cold gas, but the equatorial regions propagate toward cold gas flowing across the propagating direction. The flame is thus constrained to propagate into a velocity gradient that stretches it. The upward limit becomes, in effect, a blow-off limit. The initially spherical flame propagates upward into a nonlaminar velocity gradient of diverging cold gas of increasing magnitude and is thus blown off by the buoyant flows.

A precise consideration of the problem of flame stretch for flows induced by the simultaneous interaction of buoyancy and spherical propagation awaits a more accurate description of the real flow field than has heretofore been available in the literature. It is nevertheless possible to make some realistic estimates based upon a limiting solution for the buoyant rise of a spherically expanding flame.

For early times and small dimensions where the drag force is negligible compared with the increasing inertial mass of the rising burned gases, the buoyant rise velocity is--

$$v_b = \left[ \frac{1}{1+3 \left( \frac{\rho_u}{\rho_u + \rho_b} \right)} \right] \left[ \frac{\rho_u - \rho_b}{\rho_u + \rho_b} \right] g t \simeq \frac{1}{4} \left( \frac{\rho_u - \rho_b}{\rho_u + \rho_b} \right) \frac{g r}{S_b} . \quad (4)$$

The limit burning velocity for quenching by flame stretch is obtained by comparing the heat feedback flux for the ideal laminar flame with the excess advective cooling flux in a cold gas flow gradient, and is

$$(S_u)_e = \left[ \alpha \left( \frac{\partial v}{\partial x} \right) \right]^{1/2} . \quad (5)$$

Now for a rising sphere, the maximum velocity gradient in cold gas flow (8) is approximated by--

$$\frac{\partial v}{\partial x} = \frac{3}{2} \frac{v_b}{r} . \quad (6)$$

Combining equations 4, 5, and 6 gives--

$$\begin{aligned} (S_u)_{a, \uparrow} &= \left[ \frac{3}{8} \left( \frac{\rho_u - \rho_b}{\rho_u + \rho_b} \right) \alpha g \frac{\rho_b}{\rho_u} \right]^{1/3} \\ &= \left[ \frac{3}{16} \left( \frac{\rho_u - \rho_b}{\rho_u + \rho_b} \right) \right]^{1/3} (S_u)_a \simeq \frac{1}{2} (S_u)_a . \end{aligned} \quad (7)$$

This is the identical functional form to that previously obtained by the independent, force-balance argument. It gives a limit burning velocity for upward propagation that is approximately half the value for horizontal propagation.

Now for the downward stagnation limit we set  $v_b = (S_u)_{ideal} \rho_u / \rho_b$  and obtain

$$(S_u)_{a_1} \simeq \frac{1}{2} \rho_b / \rho_u \left[ \left( \frac{\rho_u - \rho_b}{\rho_u + \rho_b} \right) g r \right]^{1/2}. \quad (8)$$

Interestingly, equation 8 implies that a downward stagnation limit is always observable for free space propagation in a system of large enough size, regardless of the initial value of  $(S_u)_{ideal}$ . For tubular propagation,  $r$  becomes the tube radius  $r_0$ , and the consideration of drag forces alters the proportionality constant somewhat.

For methane-air, equations 7, 3, and 8 predict limit velocities of 3.0, 6.0, and 9.1 cm sec<sup>-1</sup> for upward, horizontal, and downward propagation, respectively (the last for a 15-cm-radius tube). Using the author's best estimate for  $(S_u)_{ideal}$  (fig. 1), the predicted lean limits are 4.8%, 5.3%, and 5.6% for upward, horizontal, and downward propagation, respectively. These compare favorably with the corresponding observed values of 5.0%, 5.4%, and 5.8% and are systematically leaner because of the neglect of the other competing processes.

A word of caution is necessary in applying equation 8 to very small tubes. It predicts wider limits in narrower tubes, whereas the observations generally show the opposite: narrower limits in narrower tubes. For small tubes, thermal losses to the initially cold walls (process b) becomes more significant. This process interacts with the buoyancy effect, and complicates the  $r_0$ -dependence. The limit velocity for process b varies as  $1/r_0$ . The limit behavior in tubes of decreasing diameter clearly shows that the inverse  $1/r_0$  dependence is approximately the correct dependence for small tubes where wall losses dominate. For the larger size tubes, one expects eventually to reach a condition of independence of  $r_0$  as wall losses become less significant and the  $1/r_0$  dependence is canceled by the  $r_0^{1/2}$  dependence of buoyancy (equation 8). This is the region where most downward limits are measured. In this transition region (10 to 20 cm) the dependence would involve a fractional power increasing dependence on  $r_0$ , and eventually, as equation 8 indicates, in a system of large enough size, a downward stagnation limit should always be observable for any composition.

#### HIGH- AND LOW-G LIMITS

Some new limit phenomena are now considered that the theory is capable of predicting. Equation 3 predicts a limit velocity that varies as the cube root of the local gravitational acceleration. The  $g$ -dependence of equation 3 is thus capable of verification by performing experiments in low-gravity environments such as are obtained in free fall, in space, or in the moon's gravitational field. Alternatively, experiments can be performed in high- $g$  environments by using rotating systems where the centrifugal acceleration can be several orders of magnitude higher than that of the earth's gravity.

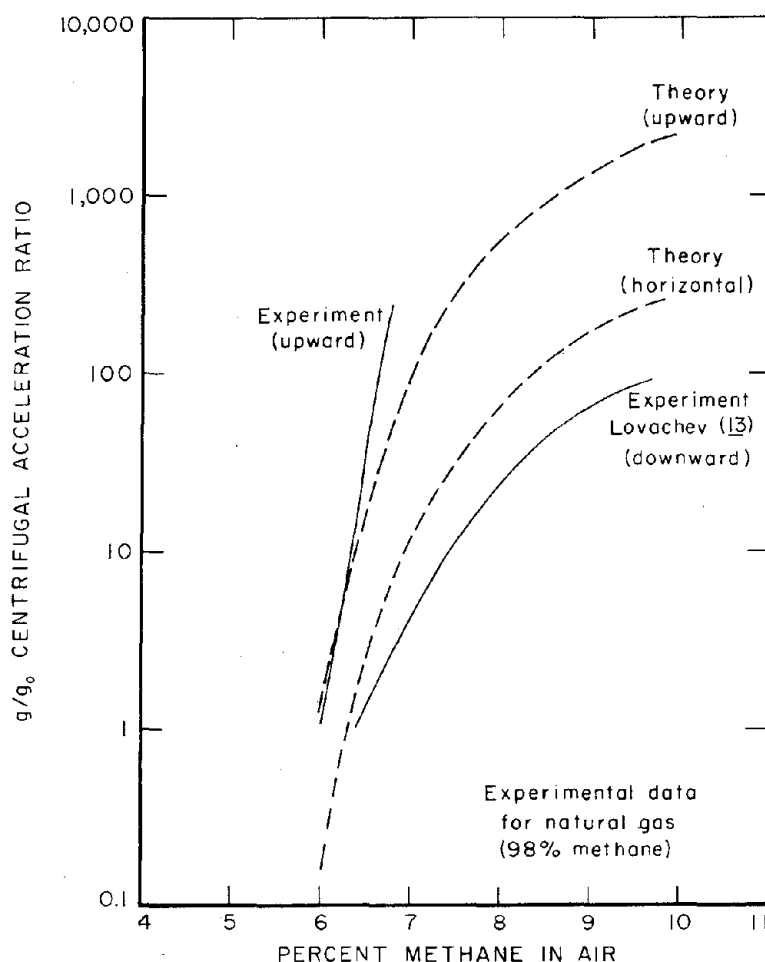


FIGURE 2. - High-g flammability limits. Comparison of theory with experiment.

upward limit, we use equation 7 and set  $(S_u)_{ideal} = (S_u)_{a, \uparrow} + (S_u)_b$ . This yields a high-g limit that is a factor of 8 higher, and is also shown. This prediction for the upward limit extends to  $g$ -values that are much higher than the data obtained. It predicts that the upward curve will reach a high- $g$  limit of 2,180  $g_0$  for a stoichiometric mixture in their apparatus (assuming wall losses are independent of  $g$ ). In a system of infinite volume, the predicted high- $g$  limit is 4,300  $g_0$ .

This prediction is in good agreement with recent data by Lewis and Smith (11) for the turbulent inward propagation limit of a near-stoichiometric propane-air mixture (essentially the same  $(S_u)_{ideal}$  as for methane). Their value is 3,500 to 4,000  $g_0$  for a 6.7-cm tube. Realistic predictions for downward limits are difficult to make for the narrower tubes because of wall drag and its complex interaction with process b. But clearly the magnitude and trends of the theory's predictions are in good agreement with Lovachev's data. There may be differences at low  $g$ 's (for lean or rich mixtures) because of the presence of earth's gravity, which becomes significant at low  $g$ 's.

Recently, Lovachev, Babkin, Bunev, V'yun, Krivulin, and Baratov (13) have reported the results of some rather definitive experiments. The high- $g$  limit was measured for both upward (inward) and downward (outward) propagation in a centrifugal force field. Their data are shown in figure 2. The data can be used to test the validity of equation 3, which predicts the high- $g$  limit. The comparison is complicated by the fact that their tube diameters were 3.6 cm (ID); hence, one cannot neglect the limit velocity for wall quenching,  $(S_u)_b$ , which is a significant 9.25 cm sec<sup>-1</sup>. We set  $(S_u)_{ideal} = (S_u)_a + (S_u)_b$ , at the limit, and solve for  $g$ . Using ideal burning velocities, near-equilibrium values for  $\rho_b/\rho_u$  and  $\alpha = 0.55$  cm<sup>2</sup> sec<sup>-1</sup>, gives the theoretically predicted curve (fig. 2). The curve is the average limit for buoyant convection; that is, the horizontal limit. For a prediction of the

Several flammability studies have been reported in free fall experiments at low g's and in aircraft flying low-g trajectories (1, 7). However, these experiments have been performed on mixing limited flames. A zero g environment quenches the normal steady-state burning of such "candle" flames. They are convectively mixed, and in the absence of convection, they become spherical diffusion flames and propagation is soon quenched by the accumulation of combustion products. These combustion products are normally convected upward, but at zero g, they surround the fuel reservoir and prevent air from reaching the fuel space.

In a premixed system on the other hand, the fuel and air are initially predistributed in space. Combustion products merely accumulate behind the propagating wave and generally do not mix with the bulk of the unburned gas into which the combustion wave propagates. The absence of convection currents should in this case enhance flammability. Equation 3 predicts that  $(S_u)_a \rightarrow 0$  as  $g \rightarrow 0$ . The flammability limit of methane-air mixtures in free space should thus be much lower than the 1-g limit of 5%. If a large volume system is considered,  $(S_u)_b \rightarrow 0$ , and the limit would be determined by the other processes, c, d, and e. Since generally  $(S_u)_e \gg (S_u)_c$ , and since process e is sensitive to the ignition geometry, the zero g flammability limit should be more sensitive to the details of ignition than is normally the case. For example, for an ignition system the geometry and power input of which generates a flame volume of initial radius of 10 cm,  $(S_u)_e$  is  $1.1 \text{ cm sec}^{-1}$ . This would give a zero g flammability limit below 4% methane. For truly planar ignition (and planar propagation)  $(S_u)_e \rightarrow 0$ , and the limit would presumably be determined entirely by radiative losses. Typically  $(S_u)_c \simeq 0.1 \text{ cm sec}^{-1}$ , and the zero g limit would be about 2% to 3% or lower.

In lunar gravity, equation 3 predicts an upward flammability limit of about 4.5% methane, measurably below the leanest earthly limit.

Naturally at zero g, there should be no distinction between downward, upward, and horizontal propagation even for the near-limit mixtures. Very slow, very cool, near-limit flames should be able to propagate spherically in premixed gases once the flame-stretch divergence losses are overcome by the ignition energy. Their behavior as they approach a limit at zero g would be markedly different from their normal behavior at 1 g.

#### LIMIT FLAME TEMPERATURES AND MIXTURE HEATS OF COMBUSTION, KINETIC CRITERIA

The fuel-air mixtures considered in figure 1 include the typical range of flammable fuels that can be encountered. Their kinetic reactivities vary widely as shown in table 1. For a reactive fuel such as hydrogen, the limit heat of combustion is low, and this is reflected in a low limit flame temperature. For a much less reactive fuel such as ammonia, both quantities are markedly higher. This fact demonstrates the importance of kinetic factors in determining the limits, and this is predicted by the theory.

TABLE 1. - Limit flame temperatures for horizontal propagation  
and mixture heats of combustion for fuels of  
widely varying kinetic reactivities

Fuel	Lean horizontal limit ( $L_h$ ), %	$\Delta H_c$ , kcal mole <sup>-1</sup> of fuel	$\frac{L_h}{100} \Delta H_c$ , kcal mole <sup>-1</sup> of mixture	$T_{adiabatic}$ , K
Hydrogen.....	6.50	57.8	3.75	828
Acetylene....	2.69	300.1	8.07	1,337
Methane.....	5.38	191.8	10.32	1,561
Ammonia.....	18.0	75.7	13.63	1,845

The ideal burning velocity is generally given by an expression of the form

$$(S_u)_{ideal} = k[\alpha \dot{q}]^{1/2} = k[\alpha(\text{rate}) (\Delta H)]^{1/2}. \quad (9)$$

The diffusivity factor,  $\alpha$ , is related in a complicated way to both mass and thermal diffusivities. The heating rate per unit volume  $\dot{q}$  is the product of a kinetic rate factor and a thermochemical factor  $\Delta H$ . At the limit  $(S_u)_{ideal} = (S_u)_a$  and  $\Delta H = \frac{L}{100} \Delta H_c$ . Hence,

$$\frac{L \Delta H_c}{100} = \frac{(2 g \rho_b / \rho_u)^{2/3}}{k \alpha^{1/3} (\text{rate})_L}. \quad (10)$$

Thus the limit mixture heats of combustion vary inversely with the fuel's reactivity at the limit, and directly as  $g^{2/3}$ .

For the paraffin hydrocarbons, as shown in table 2, the reactivity factors vary only slightly with increasing carbon number, and the limit calorific value levels off to 11.6 kcal mole<sup>-1</sup> of mixture. Higher molecular weight organic fuels all seem to show similar values (2), suggesting similar kinetics for their lean limit mixtures. There are significant differences for the lower molecular weight fuels: Alkenes and alkynes are more reactive, and amines are less reactive; however, the higher the molecular weight of a substituted derivative, the more closely it approaches the heavy hydrocarbon value of 11.6. Branched chain hydrocarbons, especially those with tertiary H-atoms at the branch, are somewhat more reactive than their straight chain isomers. The light alkenes have limit calorific values of between 8.5 and 10 kcal mole<sup>-1</sup>; the lighter acetylenes between 7 and 8.5 kcal mole<sup>-1</sup>. The most reactive fuels such as hydrogen, hydrazine, and diborane have limit calorific values below 5 kcal mole<sup>-1</sup>.

TABLE 2. - Mixture heats of combustion at the lean limits  
for normal (n) saturated hydrocarbons

Alkane	Upward			Downward	
	Lean limit ( $L_u$ ), %	( $\Delta H_c$ ) kcal mole <sup>-1</sup>	$\frac{L_u}{100} \Delta H_c$ <sup>1</sup>	Lean limit ( $L_d$ ), %	$\frac{L_d}{100} \Delta H_c$
Methane.....	5.00	191.76	9.6	5.75	11.03
Ethane.....	2.95	341.26	10.1	3.22	10.99
Propane.....	2.12	488.53	10.4		
n-Butane.....	1.68	635.05	10.7		
n-Pentane.....	1.41	782.04	11.0	1.47	11.50
n-Hexane.....	1.23	928.93	11.4		
n-Heptane.....	1.08	1,075.85	11.6		
n-Octane.....	.95	1,222.77	11.6		
n-Nonane.....	<sup>2</sup> .84	1,369.70	11.5		
n-Decane.....	<sup>3</sup> .77	1,516.63	11.6		

<sup>1</sup>Heat of combustion per mole of gas mixture at the limit.

<sup>2</sup>Measured at 43° C, corrected to 25° C.

<sup>3</sup>Measured at 53° C, corrected to 25° C.

NOTE.--Limiting value =  $11.6 \pm 0.1$  kcal mole<sup>-1</sup> of mixture.

The aforementioned generalities apply to the normal run-of-the-mill fuels that contain hydrogen atoms in their structure. These fuel molecules generate abundant supplies of H-atoms or OH-radicals, which play key roles as chain carriers in the kinetics of flame propagation. A word of caution is necessary for some fuels that show marked anomalies in their measured limits. These are the nonhydrogen-bearing fuels such as carbon monoxide and cyanogen. Their limit behavior shows an anomalous sensitivity to hydrogen impurities or to hydrogen-bearing impurities such as moisture (3, 14). They are far less reactive in their pure state, and their flame propagation rate is markedly catalyzed by providing H-atom chain carriers. Carbon disulphide also displays anomalies. For such hydrogen-starved fuels, kinetic and/or diffusivity factors seem to far outweigh the thermodynamic ones.

#### CONCLUSION

The limit burning velocity for a system mixed by natural convection is

$$(S_u)_a = [2 \alpha g \rho_b / \rho_u]^{1/3}.$$

The limit condition  $(S_u)_{ideal} = (S_u)_a$ , accurately predicts the lean horizontal limits for a variety of fuel-air mixtures. Markedly different flame-flow interactions are involved for upward versus downward propagation. The upward limit is a blow-off limit involving process e; the downward limit is a stagnation limit. Limit compositions are predicted for several cases that give good agreement with the data, particularly with the recent data for high-g flammability limits.



Limit behavior at zero g should be markedly different, with wider ranges of flammability than those on earth, and increased explosion hazards.

Limit mixture heats of combustion for the n-saturated hydrocarbons converge to a value of  $11.57 \pm 0.10$  kcal mole<sup>-1</sup> of mixture, but vary substantially with reactivity for other fuels. Values for a given fuel should vary as  $g^{2/3}$ .

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## APPENDIX

Symbols and Nomenclature

$g$	The gravitational or centrifugal acceleration.
$g_0$	The earth's value of $g$ .
$\Delta H_c$	Heat of combustion per mole of fuel.
$\Delta H$	Heat of combustion per mole of reacting mixture.
$k$	A proportionality constant.
$L$	The flammability limit in volume percent of fuel.
$\dot{q}$	The heating rate per unit volume of a propagating flame.
$r$	The radius of a spherically expanding flame.
$r_0$	The radius of a tube.
$S_u$	The burning velocity. The velocity of a flame front relative to the unburned gas.
$(S_u)_{a, b, c, \text{ or } e}$	The limit burning velocity for quenching by processes $a, b, c, \text{ or } e$ .
$(S_u)_{ideal}$	The true or ideal laminar burning velocity.
$S_b$	The ideal burned gas velocity relative to the flame front; equal to the outward flame speed relative to the observer for a spherical flame.
$T$	The temperature.
$t$	The time.
$v$	The cold gas flow velocity.
$v_b$	The buoyant rise velocity.
$x$	The propagation direction.
$\Delta x$	The flame zone thickness.
$\alpha$	The spatially average or effective diffusivity.
$\rho_u, \rho_b$	The density of the unburned and burned gases, respectively.

Subscripts

u, ↑	upward
d, ↓	downward
L	limit value
h	horizontal

