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Flammability of Mixed Gases

By D. S. Burgess, A. L. Furno, J. M. Kuchta,
and K. E. Mura



UNITED STATES DEPARTMENT OF THE INTERIOR

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FLAMMABILITY OF MIXED GASES

By D. S. Burgess,[1] A. L. Furno,[2] J. M. Kuchta,[3] and K. E. Mura[4]

ABSTRACT

About 100 tests of flammability were carried out with H_2, CH_4, and CO in mixtures with air using the Federal Bureau of Mines 12-ft-diameter spherical pressure vessel as an explosion test chamber. The LeChatelier approximation gave slightly conservative estimates of the limits of downward flame propagation (onset of significant pressure rise) using the following measured values for the individual gases, in percent: H_2, 8.5; CH_4, 5.25; CO, 13.0. No justification could be offered for using the LeChatelier law for upward flame propagation limits and indeed reported data suggest that calculated values would not be conservative. The observed upward limit for methane-air mixtures (4.85 pct) was less than the widely accepted lean limit for this fuel; those for lean hydrogen-air mixtures and carbon monoxide-air mixtures did not differ from the lowest accepted values. Diffusional effects on the propagation of single, binary, and ternary fuel mixtures are discussed.

INTRODUCTION

Limits of flammability of multicomponent fuel gas mixtures including those found in mine fires are frequently calculated by applying simple additive laws of mixing. However, such predictions can be misleading particularly when the fuel components differ greatly chemically or when preferential diffusion effects are large. It is important to know not only the difference between predicted limits and experimental values, but also the variation in explosion pressure hazard with the mode of flame propagation, that is, upward or downward. In this research, such information was obtained under *stagnant* initial conditions for single, binary, and ternary component fuels of hydrogen (H_2), methane (CH_4), and carbon monoxide (CO) that were premixed with air and ignited at room temperature and atmospheric pressure; primary emphasis was on the lower or lean limits of flammability, which are of greatest interest in safety applications. The Bureau's large spherical test vessel was utilized in these studies.

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THE 12-FT-DIAMETER SPHERE

In the early 1960's, the Bureau of Mines was continuing flammability research on the many gases and vapors encountered in transportation and in the mineral industry. These studies were typically requested by other Government agencies or by private industry and financed by transfers of funds from these requesting agencies. In furtherance of this research, the Bureau acquired an unusual facility, a 12-ft (3.65-m) diameter spherical pressure vessel with 0.68-in (1.73-cm) thick steel walls that could withstand relatively high explosion pressures. As described in a 1966 publication (*2*)[5] the working pressure of this vessel was calculated to be 300 psig (21.4 atm). Figure 1 shows the present indoor installation of the sphere.

The design of the vessel was taken from patents by Loving (*12-13*) relevant to a facility for use in explosives research. The basic shell consists of six semispherical steel plates, four of which are symmetrically located and welded together about the equator of the sphere. The two remaining plates, top and bottom, are welded to the others in position to complete the shell. A schematic of the sphere is shown in figure 2. There are seven access ports in addition to the major opening of the shell which is equipped with an outer and an inner door. Three of the access ports are 6-in (15.2-cm) diameter nozzles spaced on the same horizontal equator as the door opening. One of these ports (port B) is normally used to monitor flame growth by a high-speed camera. Additional viewing ports are provided by a 6-in nozzle at the bottom (port D) and a 12-in-diameter nozzle at the top (port C). The remaining two openings are for 1-in (2.54-cm) diameter pipes that are used for introducing and sampling gas mixtures and for installing ignition circuits and pressure or temperature monitoring instrumentation.

Design specifications were in accordance with Section VIII of the ASME Boiler and Pressure Vessels Code for Unified Pressure Vessels (*1*). The steel was ASTM type A-212B, that is, of firebox quality. Because of concern for possible brittle fracture of this steel during operations in cold weather, the sphere was installed indoors. The relatively large size of the vessel makes it possible to study propagation of flames over large distances and with minimum wall effects. This capability makes the sphere ideally suited for both practical and fundamental studies of the ignition, propagation, and extinction of flames.

[5] Italic numbers in parentheses refer to the items in the list of references at the end of this report.

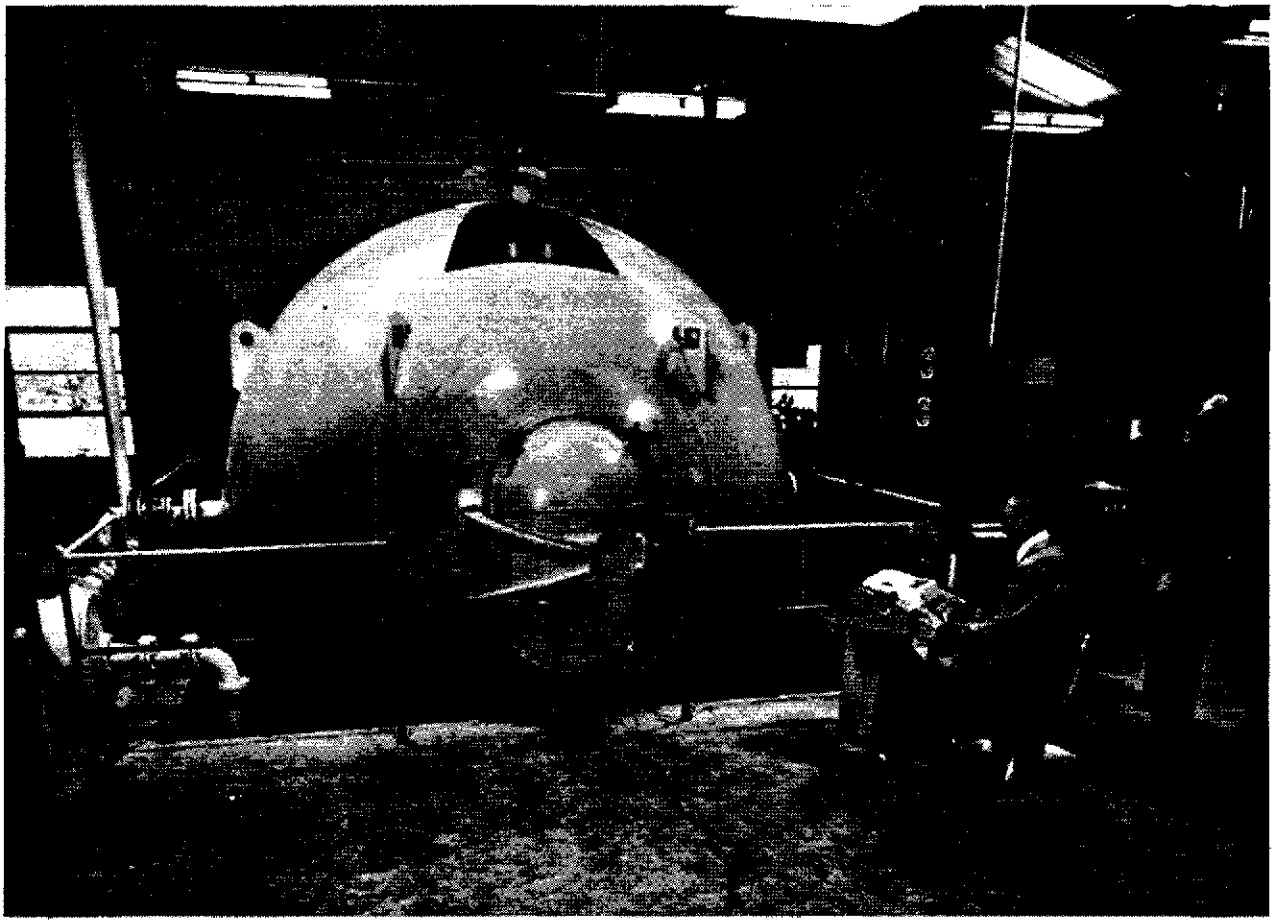


Figure 1.—12-ft-diameter spherical test vessel.

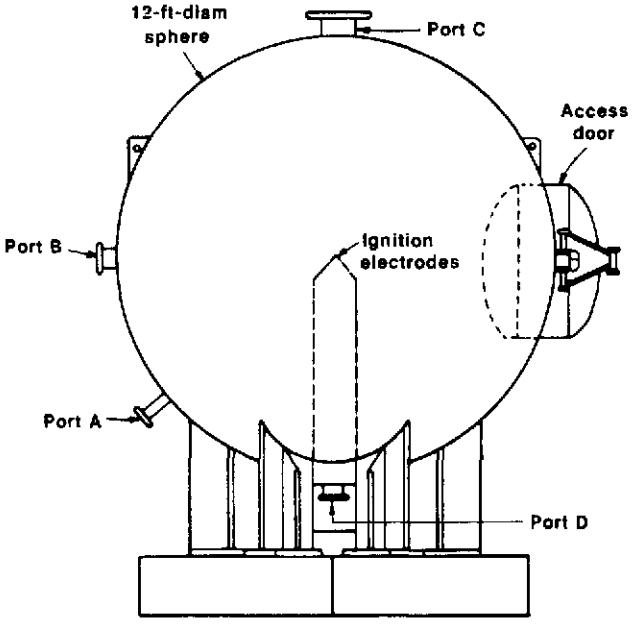


Figure 2.—Schematic of 12-ft-diameter vessel.

SPECIAL CHARACTERISTICS OF THE SPHERE AS A TEST FACILITY

In the work described in this paper, all candidate gas mixtures were initially at 760 torr and approximately 25° C, and ignition was usually attempted with a centrally located spark. Observations of flame propagation or of nonpropagation were affected in the following ways by the size and shape of the vessel:

1. As a flame kernel develops at the spark and does or does not become a propagating flame, the "decision point" for propagation is reached while only a very small fraction of the total gas mixture has been affected. Consequently, flammability is dealt with at essentially *constant pressure.* In the illustrations of this report where calculated flame temperature curves (T_f) are given, the flame temperatures all refer to adiabatic combustion at a pressure of 760 torr.

2. As a flame grows at the ignition source, it is initially free to rise almost as though in free space. The buoyant rise rate of a bubble of burned gas increases with the square root of its diameter; thus, if the gas concentration is at all close to its flammable limit, then the buoyant rise rate quickly exceeds the radial flame speed. In this situation, the observer frequently sees the kind of flame distortion shown in figure 3, which comprises tracings of flame photographs at successive times from ignition in the sphere with quiescent mixtures of 6.9 pct methane-air and added nitrogen. Sapko, Furno, and Kuchta (*16*) have defined the flame speeds and pressure rises of such inerted methane mixtures.

3. As a near-limit flame rises to the top of the vessel, the vessel pressure rises slightly over a period of several seconds (see the curves particularly for 10.0 to 11.5 pct fuel in figure 4, which are from recent work (*10*) with complex gas mixtures). At the top of the vessel the flame spreads into a mushroom cap from which it may or may not propagate downward to complete the burning of the gas mixture. If it does propagate downward the pressure rise rate is rapid because of the large area of flame surface (see the curves for 12.0- and 13.0-pct fuel in figure 4).

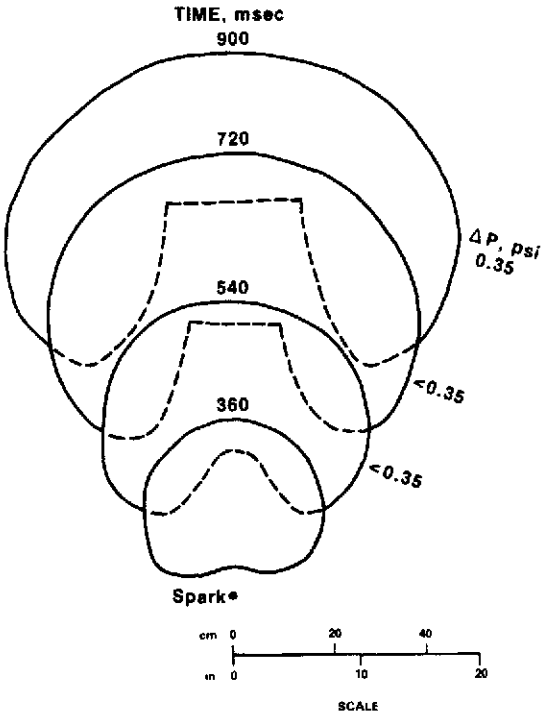


Figure 3.—Side view of flame profile at four time intervals after central ignition of a 6.9-pct CH_4, 65.8-pct air, 27.3-pct N_2 mixture in 12-ft-diameter sphere (*16*).

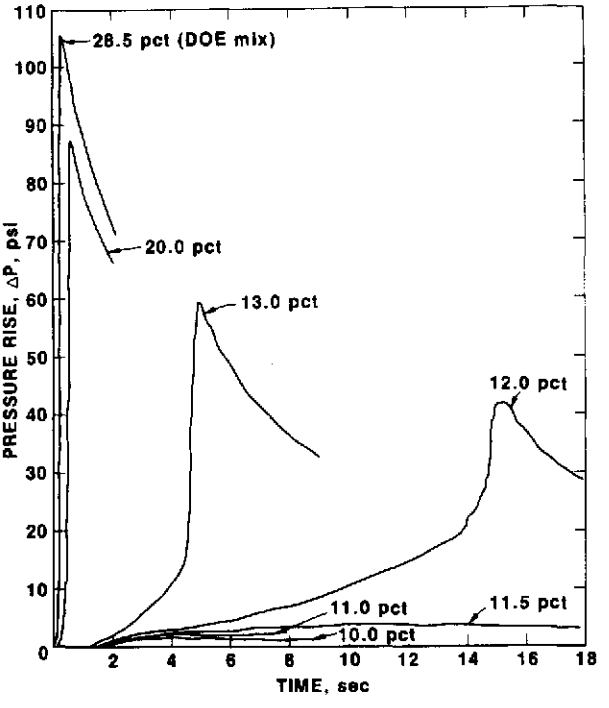


Figure 4.—Pressure rise histories from ignition of various concentrations of Grand Forks (DOE gas mixture (~12 CO:6 H_2:1 CH_4:1 CO_2:0.8 N_2) in air in 12-ft-diameter sphere (*10*).

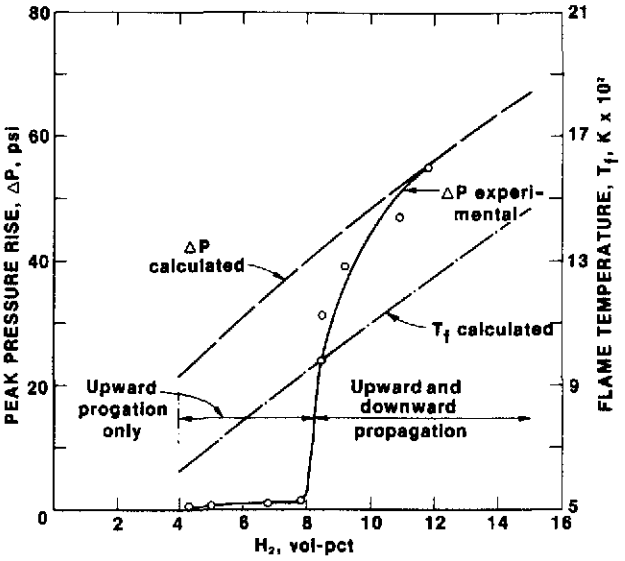


Figure 5.—Peak pressure rises and flame temperatures for ignition of H_2-air mixtures in 12-ft-diameter sphere (after *5*).

4. At the completion of downward propagation, the gas mixture in the sphere should be totally burned. The resultant pressure should be referred to calculated pressure for *constant volume* combustion, curves for which are labeled "ΔP calculated" in figure 5 and subsequent figures. A large deficiency on comparing observed and calculated pressure does not necessarily indicate incomplete combustion; it may be a measure of the heat losses during an upward-downward flame propagation that may require 30 sec or longer to complete. As the gas mixtures depart from limit concentration and approach stoichiometric, flames expand more rapidly relative to rise rate, transient pressures approach a third power dependence on time from ignition (see curves for 20.0- and 28.5-pct fuel in figure 4), and peak pressures approach theoretical as shown in figure 5 and subsequent figures.

USE OF THE SPHERE TO STUDY PREFERENTIAL DIFFUSION IN NEAR-LIMIT FLAMES

In November 1968, the Bureau was invited to participate in a meeting at the Reactor Licensing Division of the Atomic Energy Commission. The topic of discussion was the anticipated hazard of a loss-of-coolant (LOC) accident in reactors under consideration for licensing. It was expected that hydrogen might slowly be released into the containment volume by reaction of water and hot cladding metal, also by radiolytic decomposition of water; unless this hydrogen could be removed, as by catalytic oxidation, its concentration could finally reach the explosive range, that is, above the lower limit of 4 pct in air.

The contribution of the Bureau representative at this discussion was to point out that hazards might be somewhat less than anticipated from the bare statistic of 4 pct as a lower explosive limit for hydrogen in air. The lower limit for *downward* flame propagation had been reported to be about 8 pct hydrogen by Coward and Jones (*4*) who had the following to say about hydrogen flames in the 4- to 8-pct concentration range:

"When a spark was passed near the lower confines of a weak hydrogen-air mixture standing over water in a vessel 6 ft high and 12 in square in section the following observations were made:

"4.0 pct hydrogen—A vortex ring of flame was seen just above the spark gap; it rose, expanded for about 16 in, then broke and disappeared.

"4.2 pct hydrogen—A similar ring of flame was formed. On breaking, it resolved itself into an exceedingly faint cloud or collection of small balls of flame, which traveled steadily to the top of the containing vessel—a distance of more than 5 ft.

"4.4, 4.6, 4.8, 5.2, 5.6 pct hydrogen—In each mixture, a vortex ring of flame rose about 16 in, then broke into segments which subdivided into balls of flame that traveled to the top of the vessel. An increasing fraction of the hydrogen present was burned as the amount of it was increased. . . . (*4*, p. 15)

"The lower-limit mixture of hydrogen in air produces far too little heat to raise the mixture to its ignition temperature, yet flame will travel upward through the limit mixture indefinitely. An explanation of this has been given by F. Goldmann at P. Harteck's suggestion. The flame in the limit mixture rises as a luminous ball or balls, consuming only part of the hydrogen. As the hydrogen is consumed, fresh hydrogen diffuses into the flame more rapidly than the other gases; therefore the mixture that is burning is not the same as that in the rest of the containing vessel." (*4*, p. 11)

The preceding concept of "preferential diffusion" achieved additional respectability subsequent to the Coward and Jones bulletin. In particular, Manton, von Elbe, and Lewis (*14*) invoked the idea to rationalize cellular flames and listed these following necessary conditions for demixing to occur: The deficient component of the gas mixture must be the faster diffusing component; the flame or flamelet must have a small radius of curvature; the flame front must be convex to the unburned gas.

In these circumstances, the flame zone is enriched in the deficient reactant, in this case hydrogen. The mechanism fails if the flamelet grows to assume a large radius of curvature, and flamelets are extinguished in any case when the gross mixture concentration falls below a critical value, that is, 4 pct. Thus, combustioin is necessarily incomplete.

The Bureau was sufficiently confident about preferential diffusion (selective diffusional demixing[6]) in 1968 that it was willing to predict the shape of the explosion pressure versus hydrogen concentration curve that was eventually plotted in figure 5. The actual experimental points in the figure were obtained in 1969 in response to discussions with representatives of the Atomic Energy Commission; each point shows a measured pressure rise in the gas mixture following the application of a 0.2-sec-duration inductance spark at the center of the sphere. These pressure rises refer to ignitions of quiescent mixtures as opposed to turbulent mixtures which generally yield higher explosion pressures (*7*).

SOME APPLICATIONS OF THE CONCEPT OF PREFERENTIAL DIFFUSION

Figure 5 and the comparable figure 6 for rich butane-air (in which oxygen is the faster-diffusing deficient reactant) were

[6] This more descriptive term was was devised by M. Hertzberg of the Bureau's Pittsburgh (Pa.) Research Center.

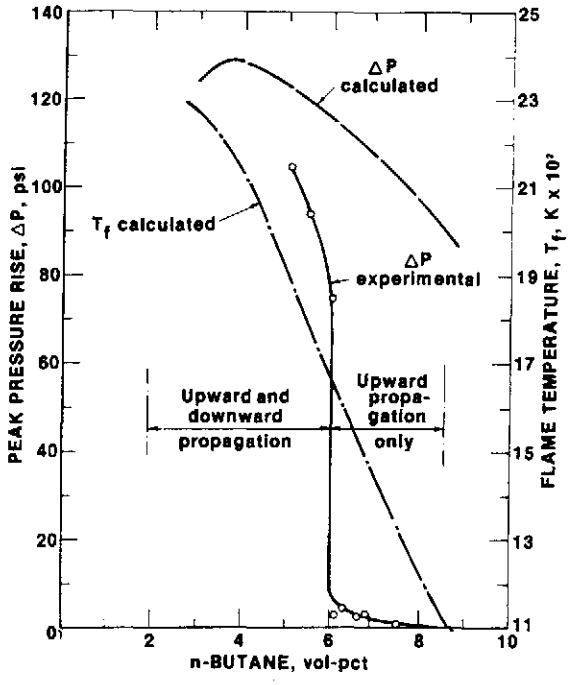


Figure 6.—Peak pressure rises and flame temperatures for ignition of n-C_4H_{10}-air mixtures in 12-ft-diameter sphere (*5*).

presented at an international meeting in 1970 (*5*). Thereafter inquiries were frequently received concerning these following applications of the concept:

1. *The safety of nuclear reactors in LOC accidents.* Figure 5 refers, of course, to explosion initiated at 760 torr and ~25° C with no inerting of fuel-lean hydrogen-air mixtures and under stagnant conditions; the "real world" situation would involve elevated pressure and temperature prior to ignition and large concentrations of water vapor by reason of the elevated temperature; also, turbulence could be an additional important factor. Further studies in the Bureau sphere would have been tempting on technical grounds, but the new demands of the Coal Mine Health and Safety Act of 1969, for mining health and safety research, diminished undertaking the performance of research, in general, for other agencies. Presumably, the desired information was obtained from other sources; however, the authors were not aware of any disclosures of such information in the open literature prior to this study. The current state of knowledge of the flammability limits and pressure development in H_2-air mixtures and ternary mixtures of H_2-air-N_2 and H_2-air-steam, including the effect of turbulence, has been recently summarized by Hertzberg in the proceedings of a meeting sponsored by the U.S. Nuclear Regulatory Commission (*7*).

2. *The detonability of gas mixtures as applied to enclosure safety.* In figure 6, the fuel-rich concentration range of 6 to 9 pct butane is flammable in the sense of upward propagation only. It appears that its flammability is dependent on the slow process of diffusional demixing. If one is designing equipment to withstand the pressure of an explosion in such a gas mixture, there would seem to be little reason to worry about the possibility of gas detonation. Obviously, the Bureau does not take the responsibility for such decisions or recommendations; however, the data shown in figures 5 and 6 were widely disseminated among persons who were interested in enclosure safety.

3. *The inerting requirements of gas mixtures containing hydrogen.* An illustrative example was provided by the Grand Forks (N. Dak.) Energy Research Center of the Department of Energy (*10*). The concern was with a gas mixture containing 57.6 pct CO, 28.8 pct H_2, 4.8 pct CH_4, 4.8 pct CO_2, and 4.0 pct N_2. This gas mixture could conceivably be released from a coal gasification unit so as to ignite within the enclosure building. The basic questions are whether the diffusional demixing concept carries over to complex gas mixtures, whether CO and CH_4 are capable of significant demixing (both have diffusion coefficients slightly larger than oxygen), whether the time-honored LeChatelier law has any applicability in the regime of only upward flame propagation. The answers provided to Grand Forks were derived from figure 4. Figure 4 shows that peak explosion pressure is very modest at all concentrations up to 11.5 pct of the gas mixture. It also shows that the rate of pressure rise is a similar function of gas concentration. Downward flame propagation was seen to occur only at concentrations above 11.5 pct.

The new experimental work which comprises most of the subsequent figures 7 through 19 of the present report was suggested primarily by the explosion hazard problem posed by Grand Forks.

4. *The explosion hazard of gases in a sealed mine.* When a mine is sealed following a fire or explosion, the gases of interest are again H_2, CO, and CH_4 along with CO_2, N_2, and O_2. But the period of observation during which explosion hazard is being considered may extend to months or even years.

During this extended time gas concentrations change dramatically. Thus, following the Scotia Mine disaster (*15*), H_2 disappeared very rapidly from the sealed areas while CO and O_2 decreased more slowly and CH_4 and CO_2 increased, as shown in table 1. The day-zero data are extrapolated values and subject to some uncertainty. However, if ventilation air were to have been mixed with the mine atmosphere at day zero, then the hazard would have involved the flammability of hydrogen and almost certainly the phenomenon of diffusional demixing. By day 117 one is involved mainly with a problem of partially inerted methane. It is not at all clear whether the mine atmosphere was becoming more or less hazardous with time.

One of the more recent and more lucid practical treatments of mine gas flammability (*8*) makes the point that *all* approximation methods for mine recovery work involve the assumption of the LeChatelier law for mixtures containing H_2, CO, and CH_4. This comment pertains to the "simplified graphic method" of Zabetakis, Stahl, and Watson (*21*) which is used in this country and receives comparable treatments in the French and German literature. As shown in the following section, the LeChatelier law provides no discrimination

Table 1.—Change in gas concentrations after mine sealing

	Time after sealing, days		
	0[1]	39	117
Concentration, vol-pct:			
N_2	61.8	57.3	39.4
O_2	12.6	6.2	2.4
CH_4	11.2	29.8	52.5
H_2	7.6	.49	0
CO_2	3.6	4.5	5.3
CO	3.3	1.68	.51
Flammable limits,[2] vol-pct:			
Lower	23.6	16.6	11.4
Upper	88.2	36.2	22.9

[1] Extrapolated.
[2] Limits of complex gas mixture (mine fire atmosphere) when diluted with air.

between gas mixtures which permit preferential diffusion and those which do not. There is a gross oversimplification involved and cause for concern if the resultant errors are not always on the conservative side.

THE FLAMMABILITY LIMIT APPROXIMATION OF LECHATELIER

According to Coward and Jones (*4*, p. 5) if one postulates that "lower-limit mixtures, when mixed in any proportions, give rise to mixtures that are also at their lower limits," one can derive

$$L = \frac{100}{\frac{P_1}{L_1} + \frac{P_2}{L_2} + \frac{P_3}{L_3} + \cdots}, \qquad (1)$$

in which L is the lower limit (volume percentage) of a complex fuel gas mixture and P_1, P_2, P_3, . . . are the proportions (percentage) of each fuel gas in the mixture, free from air and inerts, so that $P_1 + P_2 + P_3 + \ldots = 100$, and L_1, L_2, L_3, . . . are the lower flammable limits of the individual components. Equation 1 is the usual statement of the so-called LeChatelier law.

Consider for illustration a gas mixture containing 12 parts CO per 6 parts H_2 per 1 part CH_4. This corresponds to 63.1 pct CO, 31.6 pct H_2, and 5.3 pct CH_4. By equation 1, the lower limit of the mixture is given by

$$L = \frac{100}{\frac{63.1}{12} + \frac{31.6}{4.0} + \frac{5.3}{5.0}} = 7.0 \text{ pct}, \qquad (2)$$

where 12, 4.0, and 5.0 pct are the accepted lower limits for upward flame propagation. To accommodate a real situation in which the candidate flammable mixture also includes inert gases, one invokes the inerting curves provided by Jones (*9*) which are reproduced in figure 12. Thus the mixture from the Grand Forks gasifier can be described as 57.6 pct CO, 32.8 pct (H_2 + 0.13 N_2), and 9.6 pct (CH_4 + CO_2). Then equation 1 becomes

$$L = \frac{100}{\frac{57.6}{12} + \frac{32.8}{4.7} + \frac{9.6}{11}} = 7.9 \text{ pct}, \qquad (3)$$

where 12, 4.7, and 11.0 pct are lower limits taken from figure 12.

Either figure 4 or figure 14 shows that 8.0 pct of the coal gasifier mixture is a very conservative estimate of explosion hazard; significant pressure rises are encountered only at gas concentrations above 11.5 pct. This conservatism arises from use of the limits of upward propagation, particularly for hydrogen-air, in equations 2 and 3. Suppose that the limits for downward propagation, particularly for hydrogen-air, had been used in equations 2 and 3. Also, suppose that the observed limits for downward propagation, 13 pct CO, 8.5 pct H_2, and 5.3 pct CH_4, as inferred from figures 5, 7, and 8, had been used; then equation 2 changes to

$$L = \frac{100}{\frac{63.1}{13} + \frac{31.6}{8.5} + \frac{5.3}{5.3}} = 10.4 \text{ pct}. \qquad (4)$$

If the effects of inerts on the individual downward limits were known, accurate prediction of the onset of pressure rises at 11.5 to 12.0 pct could be expected.

The 12-ft-diameter sphere would normally be a clumsy instrument for measuring a new limit of upward flame propagation. Furthermore, Jones (*9*, p. 32) has listed the upward limits observed in a 2-in-diameter vertical tube for 20 gas mixtures that are interesting in transportation and in industry. Table 2 of this report comprises selected data from the Jones paper and shows how remarkedly well the LeChatelier law fits the observations of limits in a standard flammability tube (see last four columns of table).

It is the major objective of the present study to observe the limits of downward flame propagation (onset of significant pressure rises in the sphere) for comparison with calculated limits.

Table 2.—Variations between calculated and determined flammable limits of 20 typical gas mixtures (*9*)[1]

Mixture	Composition of test mixture, vol-pct					Lower limit, vol-pct		Upper limit, vol-pct	
	CO_2	CO	CH_4	H_2	N_2	Calculated	Determined	Calculated	Determined
1	0.0	0.0	25.20	25.30	49.50	9.2	9.2	34.5	33.5
2	.0	.0	16.70	16.60	66.70	14.0	14.0	41.5	40.0
3	.0	.0	10.90	10.90	78.20	21.5	19.5	48.5	45.5
4	.0	9.50	10.30	9.30	70.90	20.5	19.0	48.5	47.5
5	.0	6.10	6.70	6.30	80.90	31.5	30.0	56.5	55.0
6	10.0	5.25	6.0	6.30	72.45	34.0	32.0	56.5	55.5
7	23.65	4.60	4.95	5.20	61.60	42.5	39.5	57.0	52.0
8	16.05	9.50	3.55	3.65	67.25	48.5	47.0	63.5	61.0
9	12.05	6.65	8.95	2.4	69.95	40.0	40.5	50.0	50.5
10	4.90	2.40	3.55	7.55	81.60	39.5	37.0	63.5	62.0
11	2.20	13.80	1.95	3.55	78.50	46.0	45.0	67.0	67.5
12	.45	3.70	36.70	.95	58.20	13.0	14.0	27.0	27.
13	6.75	4.00	13.75	2.10	73.40	30.0	31.0	43.5	42.0
14	18.0	11.30	9.70	9.0	52.00	21.5	21.0	49.5	47.5
15	15.0	9.95	7.80	7.25	60.00	26.0	26.0	51.5	51.0
16	6.30	12.05	2.40	6.25	73.00	36.5	36.5	66.0	65.0
17	7.75	7.60	1.35	4.10	79.20	58.0	55.5	68.0	67.0
18	11.95	8.50	.40	5.40	73.75	52.5	50.5	71.5	71.0
19	15.90	23.70	.20	4.30	55.90	36.0	36.0	71.5	72.0
20	8.30	30.65	.10	3.00	57.95	31.0	35.0	72.0	73.5

[1] All measurements are of upward flame propagation in a 6-ft-high by 2-in-diameter vertical glass tube.

EXPERIMENTAL RESULTS

Both upward and downward limits of flame propagation were determined for the combustible gas-air mixtures investigated in this work. The gases were mixed in the 12-ft sphere by an electric fan to insure homogeneous mixtures and were *centrally* ignited, unless noted otherwise, under stagnant conditions; ignition was generally effected by an electrical spark across a ¼-in (0.64-cm) gap, which was produced by use of a 15,000-v, 30-ma luminous tube transformer. Mixture composition was determined by the partial pressure method and gas chromatographic analysis; for binary and ternary fuel mixtures, the *nominal* total fuel concentrations listed in the tables of this report generally are based upon partial pressure measurements. Extent of flame propagation by any mixture was determined by visual observation, pressure development and photographic records; product gas analyses were also made to verify the extent of combustion. The pressure data were obtained by use of millisecond response transducers whose outputs were fed to a galvanometer oscillograph recorder and a digital computer. The photographic records were obtained by high-speed, motion picture cameras using various light-sensitive films; in some cases, trivial concentrations of coal dust were dispersed prior to ignition in order to increase the luminosity of the flames. All tests were made at *atmospheric pressure* and an ambient temperature of *approximately 25° C.*

SINGLE COMPONENT FUEL GASES—HYDROGEN, METHANE AND CARBON MONOXIDE

Figure 5, showing experimental data for *hydrogen-air*, was taken directly from reference 5. The data seem to fit, in all particulars, the concepts and observations of Harteck and Goldmann (*6*), of Coward and Jones (*4*), and of Manton, von Elbe, and Lewis (*14*). One shortcoming in this study was that no observation was made of the small diameter flamelets described by Coward and Jones with which diffusional demixing is said to occur. For this reason, two additional tests were carried out and added to the series of observations in table 3. The hydrogen concentrations in these tests were a nominal 7.1 and 8.0 pct and the gas mixtures were loaded with 0.7 mg/liter of coal dust to aid in the visualization of the flames. In both cases, flame propagated upward but not downward; at 8.0 pct hydrogen one could see an orange fireball which underwent the distortion illustrated in figure 3; this is presumed to correspond to the "vortex" reported by Coward and Jones; however, a "flamelet" is yet to be observed in any gas mixture. Unfortunately, the photographic records for the above cited tests lacked sufficient clarity for reproduction.

Table 3.—Tests with lean hydrogen-air mixtures

Initial hydrogen, vol-pct		Propagation		Pressure rise		Product gas concentration vol-pct	
Partial pressure	Gas analysis	Up	Down	psig	sec	H_2	O_2
PURE GASES, (REFERENCE 5)							
5.0	NA	Yes	No	<0.5	NA	NA	NA
5.8	NA	Yes	No	<.5	5.5	NA	NA
7.1	NA	Yes	No	<.5	4.2	NA	NA
7.6	NA	Yes	No	<.5	3.4	NA	NA
7.8	NA	Yes	No	1.4	3.7	NA	NA
8.5	NA	Yes	Yes	24.0	30.2	0.8	NA
9.2	NA	Yes	Yes	39.0	7.5	.0	NA
10.9	NA	Yes	Yes	47.0	1.8	.0	NA
11.8	NA	Yes	Yes	55.0	1.3	.0	NA
WITH ADDED COAL DIST (THIS RESEARCH)							
7.0	7.2	Yes	No	0.74	5.0	6.9	19.35
7.8	8.2	Yes	No	.98	6.3	7.8	19.12

NA Not available.

The data provide no information concerning the limit of upward flame propagation. However, the limit of downward propagation must be very close to 8.5 pct hydrogen, at which concentration about 90 pct of the fuel burned and the total pressure rise transient required about 30 sec.

An unusual number of measurements are listed for *methane-air* mixtures (see table 4 and figure 7). Probably the most striking observation is that lower limit concentrations are smaller than those typically reported. For example, the limit of upward propagation is in the 4.8- to 4.9-pct range (table 4) as compared with the value of 5.0 pct given by Zabetakis in 1965 (*19*), the 5.25 pct of Coward and Jones in 1952 (*4*), and the 5.60 pct of Burgess and Wheeler in 1911 (*3*). For downward propagation, the limit suggested by this study is 5.2 to 5.3 pct CH_4 while Coward and Jones report 5.75 pct.

Table 4 comprises experiments related to downward propagation from an ignition source near the top of the sphere. This tests the premise that downward propagation is favored in the experiments of this report by the momentum of the flame which is first buoyed upward from the point of ignition to the top of the sphere. There does seem to be some effect of the location of the ignition source on the flammability limit, as indicated by the pressure rise data.

Again, every upward flame propagation was carefully observed so as to detect any appearance of flamelets in the concentration range of 4.8 to 5.3 pct methane. Since this was methane-air, not hydrogen-air, there was no problem of flame visibility, in fact it was even possible to photograph the rising fireballs in many cases. Cellular flame structures, which are associated with diffusional processes, were observed but no flamelets. Selected film records illustrating the flame growth structure of three methane mixtures with central or top ignition are shown in figure 15.

Only five tests were conducted with *carbon monoxide-air* mixtures (see table 5 and figure 8). The major experimental uncertainty was that CO concentration inferred from the partial pressure method of forming the mixture was never very close to the CO concentration found by gas chromatographic analysis of a sample. The limit for upward propagation is about 12.0 pct (between 11.6 and 12.3 pct) and the limit for downward propagation is about 13.0 pct (between 12.6 and 13.5 pct). Film records of three near-limit mixtures which propagated upward and/or downward are given in figure 16.

No particular effort was made to control the amount of H-containing species in these CO flames. The gas mixtures used ambient air, typically at relative humidity of 30 to 50 pct at laboratory temperature.

BINARY MIXTURES OF HYDROGEN, METHANE, AND CARBON MONOXIDE

Only 50:50 mixtures by volume were used since otherwise the number of candidate gas mixtures would have been prohibitive (table 6 and figure 9).

As listed in table 6, nine lean mixtures in air of 50:50 *methane-hydrogen* were used, ranging in concentration from 4.5 to 7.0 pct of the fuel gases.

Table 4.—Tests with lean methane-air mixtures

Initial methane, vol-pct		Propagation		Pressure rise		Product gas concentration, vol-pct			
Partial pressure	Gas analysis	Up	Down	psig	sec	CH_4	CO_2	CO	O_2
CENTRAL IGNITION									
5.5	5.5	Yes	Yes	54	10.7	NA	NA	NA	NA
5.4	5.3	Yes	Yes	42	19.6	0.02	5.95	0.003	10.15
5.3	5.3	Yes	Yes	34	27.3	.09	5.83	.042	10.34
5.3	5.1	Yes	Yes	32	29.3	.10	5.65	.070	10.75
5.2	5.2	Yes	Yes	21	20.6	NA	NA	NA	NA
5.2	5.25	Yes	(1)	7.4	12.8	4.25	1.07	.018	18.10
5.2	5.1	Yes	No	1.3	3.7	NA	.16	.002	19.48
5.15	5.1	Yes	No	1.7	4.2	5.40	.17	.001	19.53
5.3	5.1	Yes	No	2.3	4.0	4.85	.25	.002	19.50
5.1	5.1	Yes	No	1.0	5.7	NA	NA	NA	NA
5.2	5.1	Yes	No	2.2	5.3	4.90	.27	.004	19.42
5.0	4.9	Yes	No	0	DT	4.90	.04	NA	19.88
4.9	4.8	Yes	No	.4	3.7	NA	NA	NA	NA
4.9	4.8	No	No	0	DT	NA	.06	NA	19.75
4.85	4.75	Yes	No	0	DT	4.66	.03	0	19.93
4.8	4.3	No	No	0	DT	NA	NA	NA	NA
TOP IGNITION (12 IN FROM TOP OF SPHERE)									
5.6	5.55	Yes	Yes	51	12.5	0.01	6.53	0.001	9.48
5.4	5.5	Yes	Yes	50	12.3	.01	6.50	.001	9.50
5.3	5.2	Yes	No	.8	6.0	5.16	.04	NA	19.81
TOP IGNITION (27 IN FROM TOP OF SPHERE)									
5.6	5.6	Yes	Yes	50	12.0	0.01	6.48	0.001	9.42
5.4	5.35	Yes	No	1.0	6.5	5.25	.18	.001	19.54
5.2	5.15	Yes	No	.2	2.5	5.10	.05	NA	19.92

DT Duration of test, no pressure rise. NA Not available. (1) Partial.

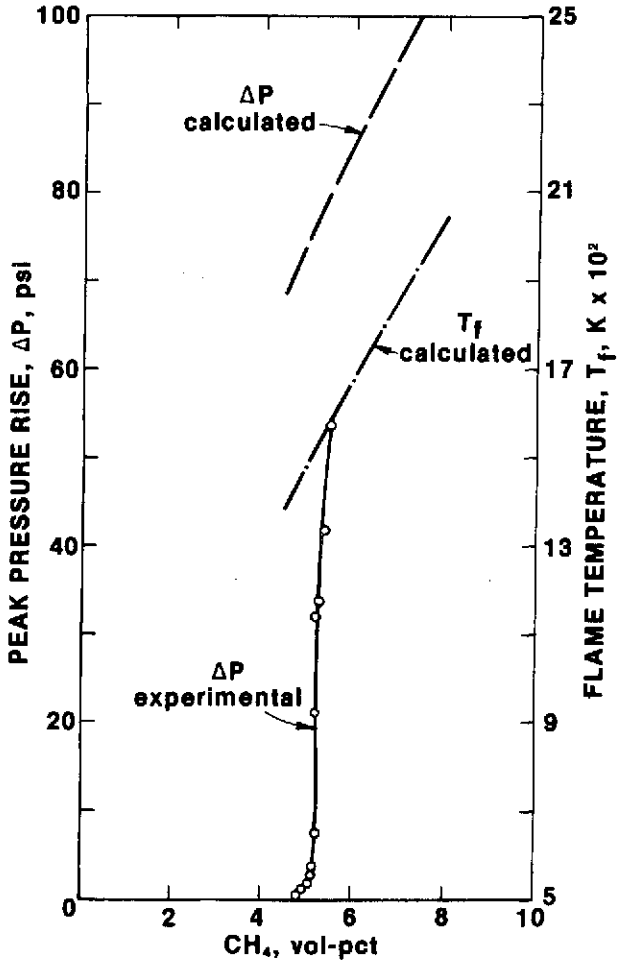


Figure 7.—Peak pressure rises and flame temperatures for ignition of CH_4-air mixtures in 12-ft-diameter sphere.

Table 5.—Tests with lean carbon monoxide-air mixtures

Initial carbon monoxide, vol-pct		Propagation		Pressure rise		Product gas concentration, vol-pct		
Partial pressure	Gas analysis	Up	Down	psig	sec	CO	CO_2	O_2
13.5	12.75	Yes	Yes	39.2	22.9	0.07	14.65	12.1
13.0	12.6	Yes	(1)	4.5	10.3	11.20	1.6	17.7
13.0	12.5	Yes	(1)	3.3	7.6	11.45	.97	17.9
12.0	12.3	Yes	(1)	3.1	8.3	11.47	1.04	17.85
12.0	11.6	No	No	.15	29.4	11.84	.06	18.4

(1) Partial.

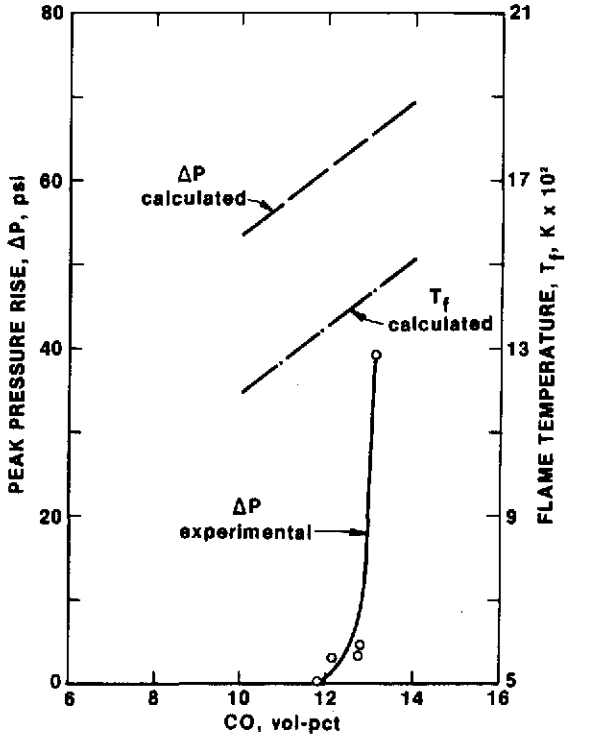


Figure 8.—Peak pressure rises and flame temperatures for ignition of CO-air mixtures in 12-ft-diameter sphere.

Table 6.—Tests with lean mixtures of equimolar hydrogen and methane in air

Nominal mixture	Initial fuel concentration, vol-pct				Propagation		Pressure rise		Product gas concentration, vol-pct				
	Partial pressure		Gas analysis										
	CH_4	H_2	CH_4	H_2	Up	Down	psig	sec	CH_4	H_2	CO_2	CO	O_2
7.0	3.50	3.50	3.4	3.5	Yes	Yes	56.0	9.8	0.00	0.00	4.02	0.004	12.20
6.5	3.25	3.25	3.6	3.2	Yes	No	2.5	5.9	3.06	3.02	.26	.006	19.12
6.5	3.25	3.25	3.2	3.3	Yes	No	2.0	3.9	2.97	3.15	.19	.007	19.26
6.6	3.38	3.38	3.2	3.15	Yes	No	1.7	4.1	3.1	2.95	.18	.016	19.30
6.0	3.0	3.0	2.8	3.0	Yes	No	1.2	4.1	2.92	2.91	.11	.007	19.51
5.0	2.5	2.5	2.3	2.5	Yes	No	.23	6.3	2.25	2.36	.04	.001	19.91
4.7	2.35	2.35	2.25	2.4	(1)	No	.12	5.2	2.22	2.32	.05	.000	19.93
4.5	2.25	2.25	2.15	2.35	No	No	.06	31.0	2.13	2.24	.05	.000	19.96
4.5	2.25	2.25	2.3	2.2	No	No	.06	25.6	2.26	2.22	.04	.000	19.96

[1] Partial.

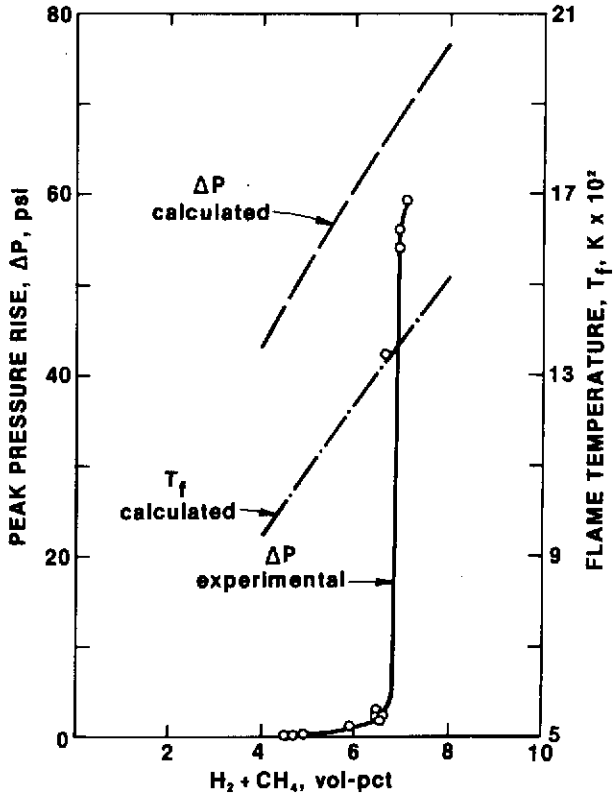


Figure 9.—Peak pressure rises and flame temperatures for ignition of equimolar H_2-CH_4 mixtures in air in 12-ft-diameter sphere.

By the LeChatelier law, the lean limit for upward propagation of this mixture is

$$L_u = \frac{100}{\frac{50}{4.0} + \frac{50}{4.85}} = 4.4 \text{ pct}, \quad (5)$$

and the lean limit for downward propagation is

$$L_d = \frac{100}{\frac{50}{8.5} + \frac{50}{5.25}} = 6.5 \text{ pct}. \quad (6)$$

At 7.0 pct combustible gas, (top line of table 6), the mixture does support both upward and downward flame propagation; the pressure rise is 56.0 psig, all methane and hydrogen is removed from the gas phase, and both CO_2 and oxygen concentrations in the product gas are suggestive of complete combustion of the lean mixture. At 6.5 to 6.6 pct of fuel gas, there are clear-cut observations of upward propagation only, as shown in lines 2 through 4 of the table; pressure rises are about 2 psig and CO_2 concentrations in the product gas about 0.2 pct. Therefore the limit of downward propagation is in the 6.5- to 7.0-pct range as compared to the calculated 6.5 pct. Figure 17 shows some film records of the propagations obtained with two of the near limit mixutes.

Upward propagation persists to 6.0 pct fuel gas. At 5.0 pct the observer recorded a visual observation of upward propagation; however, the pressure rise was only 0.23 psig and both the CO_2 and the O_2 concentration of the product gas were within the normal range of values for the initial, unburned mixture. At 4.7 pct gas, the observer was unsure whether flame propagation had persisted beyond the ignition stage and neither the pressure rise nor the product gas analysis was suggestive of flame propagation. At 4.5 pct gas, all indications were negative. Therefore, the lean limit for upward propagation should be taken as 4.5 to 5.0 pct for comparison with the calculated 4.4 pct.

As shown in table 7, 11 tests were conducted using lean mixtures in air of 50:50 *hydrogen-carbon monoxide;* figure 10 gives the pressure rise data. By the LeChatelier law, the lean limit of upward propagation is

$$L_u = \frac{100}{\frac{50}{4.0} + \frac{50}{12.0}} = 6.0 \text{ pct}, \quad (7)$$

while the lean limit for downward propagation is

$$L_d = \frac{100}{\frac{50}{8.5} + \frac{50}{13.0}} = 10.3 \text{ pct}. \quad (8)$$

The first two lines of data of table 7 show that 12.0- and 11.3-pct mixtures permit fast flame propagation both upward and downward. At 11.0 pct, one is very close to the limit for downward burning as evidenced by the 25.6-sec duration of the pressure transient; both fuel gases are almost completely consumed. At 10.6 pct fuel, downward propagation fails; pressure rise is only 2.6 psig and less than a tenth of the fuel is consumed. Thus the downward limit should be set in the range 10.6 to 11.0 pct fuel as contrasted to the calculated 10.3 pct. Film records of the flames for two of the mixtures which propagated upward and/or downward are shown in figure 18.

At lower concentrations from 10.5 to 7.6 pct fuel, one sees a continued lessening of the pressure rise along with progressively smaller concentrations of CO_2 in the product gases. Finally, at 7.0 pct, one comes to the point where the observer is unsure that flame has propagated to the top of the vessel and neither the pressure rise instrumentation nor

Table 7.—Tests with lean mixtures of equimolar hydrogen and carbon monoxide in air

Nominal mixture	Initial fuel concentration, vol-pct				Propagation		Pressure rise		Product gas concentration, vol-pct			
	Partial pressure		Gas analysis									
	H_2	CO	H_2	CO	Up	Down	psig	sec	H_2	CO_2	CO	O_2
12.0	6.0	6.0	6.0	5.9	Yes	Yes	51.1	4.0	0.0	6.9	0.01	13.97
11.3	5.75	5.75	5.5	5.5	Yes	Yes	48.8	5.5	.08	6.30	.00	14.40
11.0	5.5	5.5	5.3	5.6	Yes	Yes	40.2	25.6	.0	5.70	.02	15.0
10.6	5.4	5.4	5.2	5.2	Yes	No	2.6	8.2	4.6	.48	4.6	18.48
10.5	5.25	5.25	5.1	5.3	Yes	No	1.9	5.5	4.9	.32	4.80	18.53
9.5	4.75	4.75	4.65	4.85	Yes	No	1.0	4.2	4.7	.15	4.55	18.82
8.9	4.5	4.5	4.3	4.5	Yes	No	.73	4.7	4.4	.09	4.20	19.0
8.5	4.25	4.25	4.2	4.3	Yes	No	.6	5.3	4.2	.09	4.08	19.07
8.0	4.0	4.0	3.8	4.2	Yes	No	.6	5.4	4.0	.08	3.74	19.2
7.6	3.75	3.75	3.6	4.0	Yes	No	.4	6.3	3.8	.06	3.64	19.3
7.0	3.5	3.5	3.3	3.7	Yes	No	.0	DT	3.6	.05	3.28	19.45

DT Duration of test, no pressure rise.

Table 8.—Tests with lean mixtures of equimolar methane and carbon monoxide in air

Nominal mixture	Initial fuel concentration, vol-pct				Flame Propagation		Pressure rise		Product gas concentration, vol-pct			
	pressure Partial		Gas analysis									
	CH_4	CO	CH_4	CO	Up	Down	psig	sec	CH_4	CO_2	CO	O_2
8.0	4.0	4.0	4.2	3.8	Yes	Yes	52.2	9.3	0.00	8.85	0.01	10.26
7.8	3.9	3.9	3.9	3.8	Yes	Yes	38.4	16.9	.02	8.45	.08	10.72
7.4	3.75	3.75	3.7	3.6	Yes	No	6.6	12.6	3.00	1.40	2.95	17.96
7.0	3.5	3.5	3.6	3.3	No	No	.1	19.1	3.40	.04	3.30	19.48

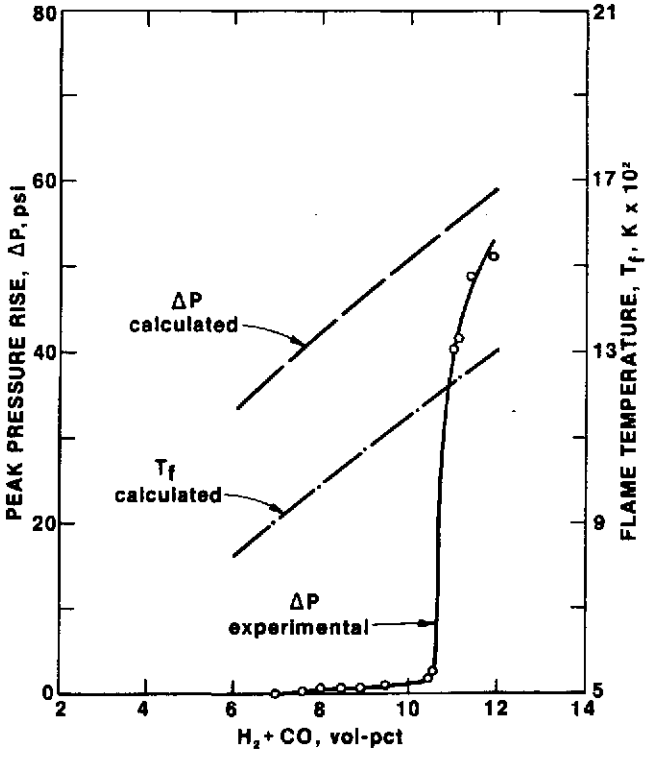


Figure 10.—Peak pressure rises and flame temperatures for ignition of equimolar H_2-CO mixtures in air in 12-ft-diameter sphere.

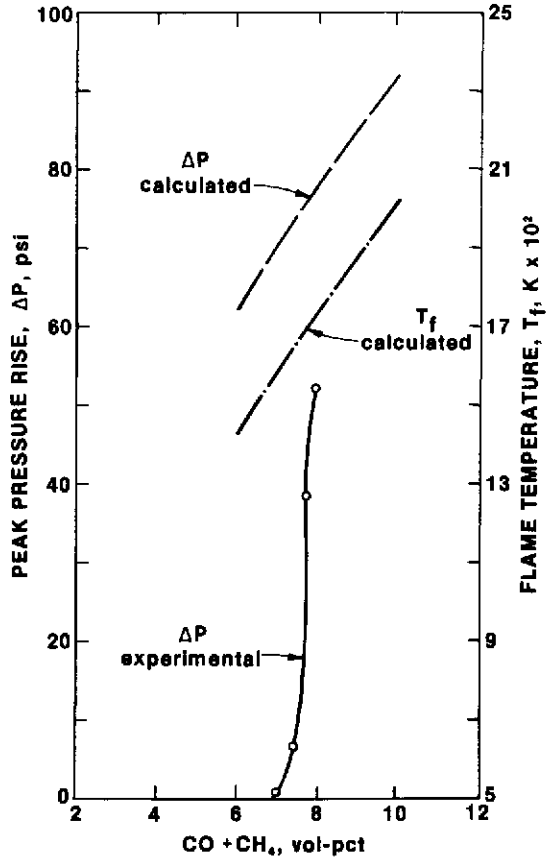


Figure 11.—Peak pressure rises and flame temperatures for ignition of equimolar CO-CH_4 mixtures in air in 12-ft-diameter sphere.

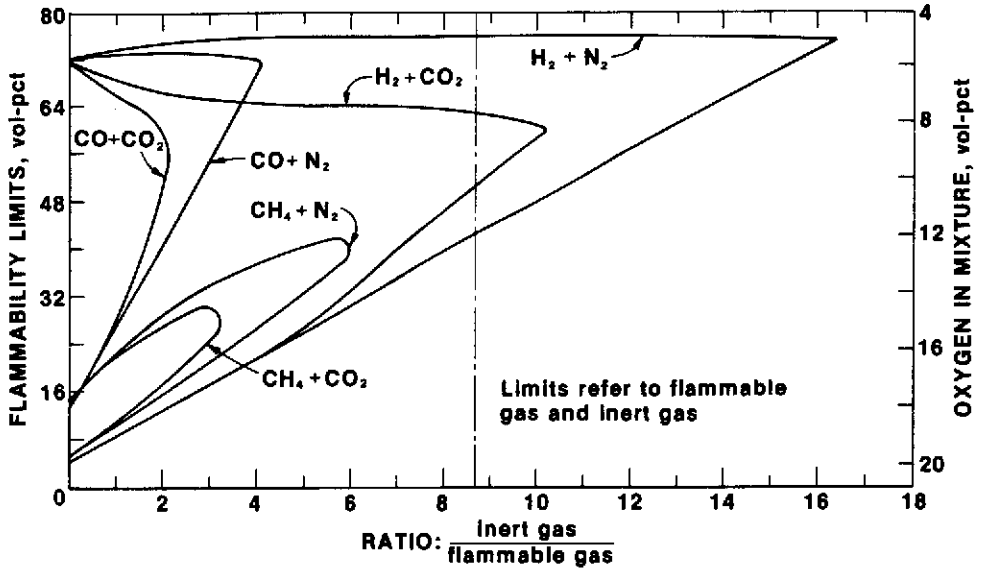


Figure 12.—Limits of flammability of H_2, CO, and CH_4 in air with various amounts of CO_2 and N_2 (*9*).

the product gas analysis is indicative. It was considered useless to go to lower concentrations even though the calculated lean limit is 6.0 pct.

Only five tests were made with *methane-carbon monoxide* since little evidence was found for preferential diffusion, either in the individual gases or in the 50:50 mixture (see table 8 and figure 11). The limit for upward propagation is calculated to be

$$L_u = \frac{100}{\frac{50}{12.0} + \frac{50}{4.85}} = 6.9 \text{ pct}, \qquad (9)$$

and the limit for downward propagation should be

$$L_d = \frac{100}{\frac{50}{13.0} + \frac{50}{5.25}} = 7.5 \text{ pct}. \qquad (10)$$

Table 8 (top line) shows that an 8.0-pct mixture supports fast flame propagation upward and downward, giving a 52.2 psig pressure rise and essentially complete combustion. At 7.8 pct fuel, the downward propagation has slowed considerably and a small fraction of the mixture escapes burning. The limit for downward propagation must actually be very close to 7.4 pct (approximately that calculated above) since the flame was seen to persist for some seconds at the top of the sphere and a pressure rise of 6.6 psig was recorded. At 7.0 pct, upward flame propagation was observed to fail about 12 in above the spark source and both the pressure rise and product gas analysis confirmed that there had been no great amount of combustion. Film records for any of these mixtures are not given particularly because of the poor quality of the records for mixtures only capable of upward prcpagation.

TERNARY MIXTURES OF HYDROGEN, METHANE, AND CARBON MONOXIDE

Two sets of data were accumulated for ternary mixtures. In the one (see table 9 and figure 13), the fuel gases were in equimolar proportions with no inert. In the other (table 10 and figure 14), the gases were in the proportions given by the Department of Energy, that is, 12 CO:6 H_2:1 CH_4:1 CO_2:0.8 N_2.

For equal concentrations of H_2, CH_4, and CO, the LeChatelier law predicts upward propagation at concentrations above

$$L_u = \frac{100}{\frac{33.3}{4.0} + \frac{33.3}{4.85} + \frac{33.3}{12.0}} = 5.6 \text{ pct}. \qquad (11)$$

Downward propagation should occur at concentrations above

$$L_d = \frac{100}{\frac{33.3}{8.5} + \frac{33.3}{5.25} + \frac{33.3}{13.0}} = 7.8 \text{ pct}. \qquad (12)$$

Table 9 shows that upward and downward flame propagation occurred with only one mixture, that containing a nominal 9.2 pct fuel. This mixture propagated flame at a rather high velocity, as indicated by the film records in figure 19. The limit of downward propagation occurs somewhere in the range 8.0 to 9.0 pct fuel as compared with the calculated 7.8 pct. The limit of upward propagation is between 5.5 and 6.0 pct as compared with the calculated 5.6 pct.

The behavior of coal gasifier mixtures, for which table 10 and figure 14 were prepared, is rather more complicated because of the presence of inert. As described in the previous section, one must invoke the curves of figure 12 in order to calculate the limit of upward flame propagation, which turns out to be approximately 8.0 pct. Flame propagation has not been observed in any mixture that approaches such a low concentration. As shown in table 10 and in figures 4 and 14, pressure rises are consistent with upward propagation at 11.0 and 10.0 pct; it is not certain whether the flame persisted from the ignition source at 9.0 pct fuel. The film records in figure 19 show the upward propagation that resulted with an 11.2-pct mixture.

Table 9.—Tests with lean mixtures of equimolar hydrogen, methane, and carbon monoxide in air

Initial fuel concentration, vol-pct												
Nominal mixture	Gas analysis			Propagation		Pressure rise		Product gas concentration, vol-pct				
	H_2	CH_4	CO	Up	Down	psig	sec	H_2	CH_4	CO	CO_2	O_2
9.2	3.2	3.2	3.0	Yes	Yes	65.2	2.6	0.0	0.00	0.00	7.5	10.36
8.1	2.70	2.6	2.6	Yes	(1)	3.8	10.1	2.4	2.33	2.34	.63	18.56
7.0	2.40	2.25	2.3	Yes	No	1.2	4.4	2.4	2.20	2.3	.17	19.25
5.9	2.10	1.80	1.90	Yes	No	.2	13.8	2.10	1.80	1.93	.04	19.65
5.5	1.85	1.75	1.80	No	No	.0	DT	1.85	1.75	1.80	.04	19.72

DT Duration of test, no pressure rise. [1] Partial.

Table 10.—Tests with lean mixtures of Grand Forks fuel gases (DOE mix)[1] in air

Initial gas concentration, vol-pct												
Nominal mixture[2]	Gas analysis			Propagation		Pressure rise		Product gas concentration, vol-pct				
	H_2	CH_4	CO	Up	Down	psig	sec	H_2	CH_4	CO	CO_2	O_2
DATA FROM REFERENCE 9												
28.5	8.9	1.37	15.9	Yes	Yes	106.0	0.3	NA	NA	NA	NA	NA
20.0	5.7	.99	11.2	Yes	Yes	87.5	.6	NA	NA	NA	NA	NA
13.0	3.6	.69	7.3	Yes	Yes	59.5	4.9	NA	NA	NA	NA	NA
11.0	3.1	.56	6.3	Yes	No	2.6	4.2	NA	NA	NA	NA	NA
10.0	3.2	.53	6.0	Yes	No	2.0	3.8	NA	NA	NA	NA	NA
9.0	2.8	.51	5.2	No	No	.0	DT	NA	NA	NA	NA	NA
DATA FROM THIS RESEARCH												
12.0	3.6	0.58	6.73	Yes	Yes	47.7	9.8	0.09	0.00	0.00	8.9	13.15
12.0	3.5	.53	6.7	Yes	Yes	42.1	15.1	.04	.00	.01	8.9	13.36
11.6	3.5	.52	6.6	Yes	No	4.0	11.8	2.95	.48	5.70	1.6	17.84
11.5	3.4	.54	6.4	Yes	(3)	3.8	12.2	2.90	.47	5.6	1.5	17.92
11.2	3.4	.53	6.3	Yes	No	1.6	5.0	3.05	.50	6.0	.9	18.35

DT Duration of test, no pressure rise. NA Not available.
[1] Defined as (12 CO:6 H_2:1 CH_4:1 CO_2:0.8 N_2).
[2] Includes CO_2 and N_2 in DOE mix.
[3] Partial.

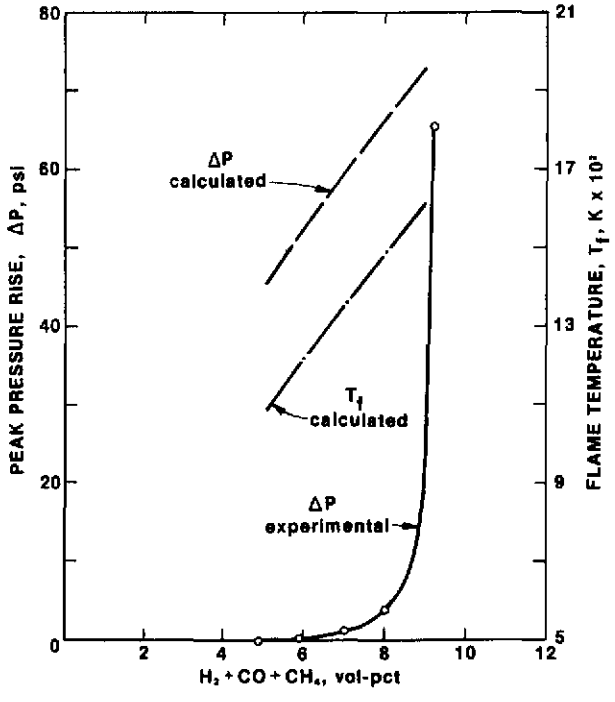


Figure 13.—Peak pressure rises and flame temperatures for ignition of equimolar H_2-CO-CH_4 mixtures in air in 12-ft-diameter sphere.

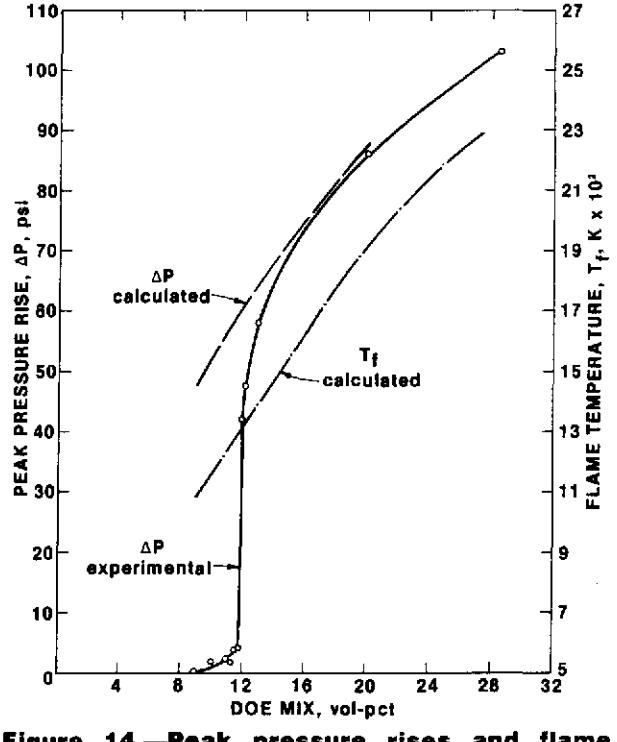


Figure 14.—Peak pressure rises and flame temperatures for ignition of DOE fuel gas (~12 CO:6 H_2:1 CH_4:1 CO_2:0.8 N_2)-air mixtures in 12-ft-diameter sphere.

The LeChatelier law suggests that the limit of downward propagation should be 10.4 pct of a mixture containing 12 CO:6 H_2:1 CH_4 with no inert. No information is available as to how inert gases affect a downward limit. However, the CO_2 and N_2 add very nearly 10 pct to the volume of the gas without contributing to its heating value; therefore it is safe to assume that the calculated limit for the total mixture must be at least 11.4 pct. According to the first six lines of data in table 10 (measurements made in 1978) the experimental limit was between 11.0 and 13.0 pct of gasifier mixture. The last five lines of data (from this research) further pin this down to 11.6 to 12.0 pct. Film records for the 12.0-pct mixture are included in figure 19.

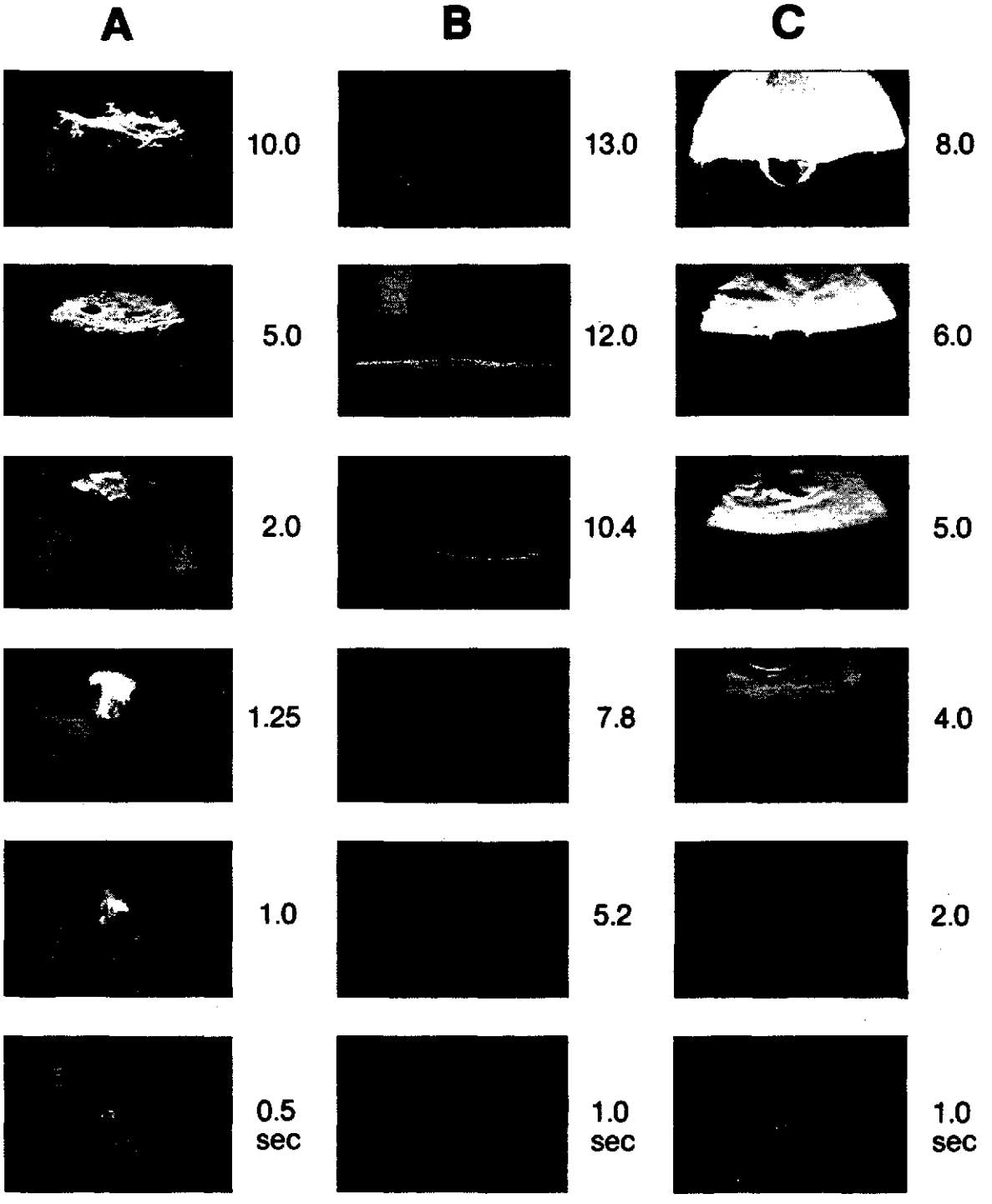


Figure 15.—Film records showing flame propagation after central (A and B) and top ignition (C) of CH_4-air mixtures in 12-ft-diameter sphere. A, 5.1 vol-pct CH_4; B, 5.3 vol-pct CH_4; C, 5.4 vol-pct Ch_4.

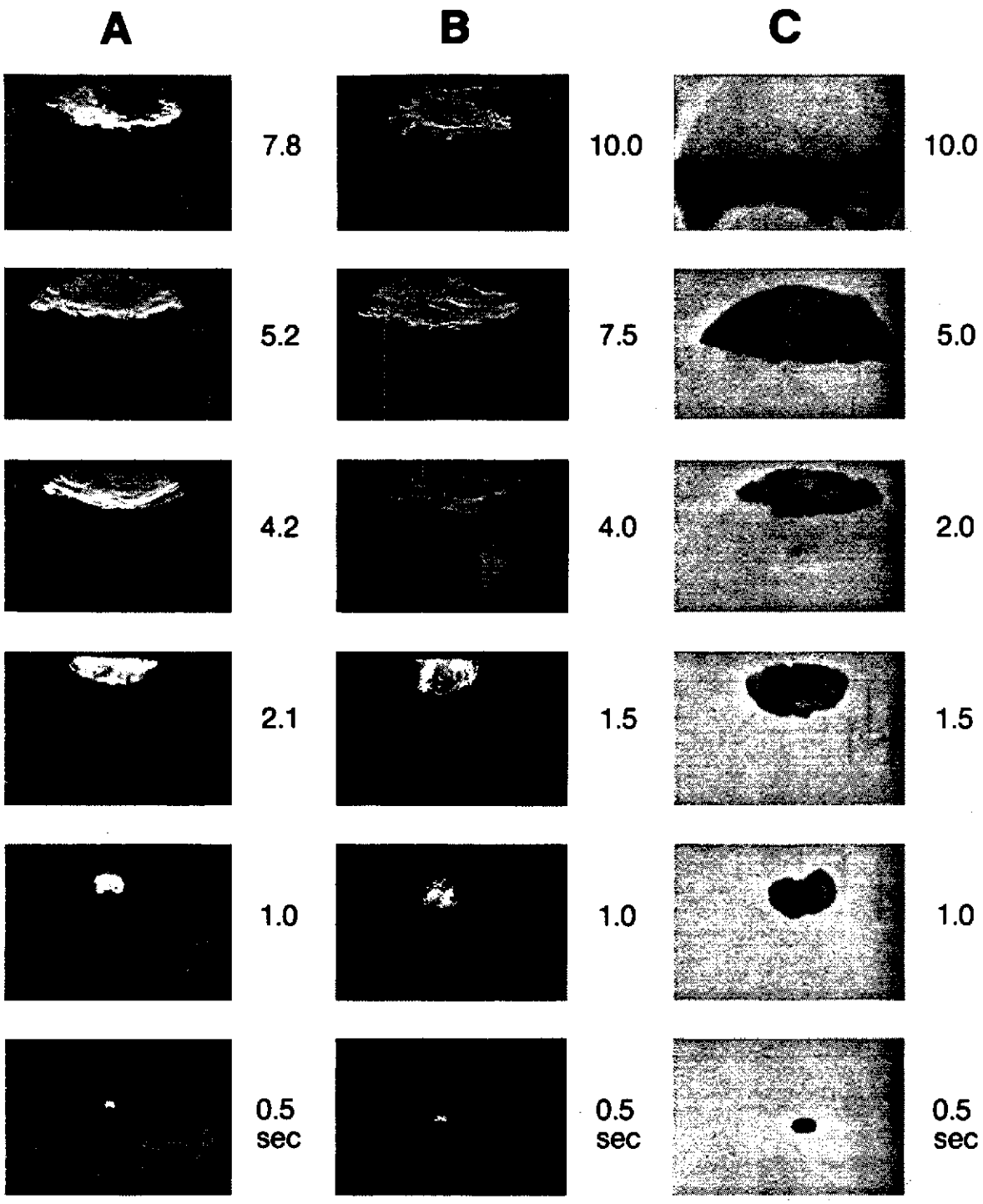


Figure 16.—Film records showing flame propagation after central ignition of CO-air mixtures in 12-ft-diameter sphere. A, 12.5 vol-pct CO; B, 13.0 vol-pct CO; C, 13.5 vol-pct CO.

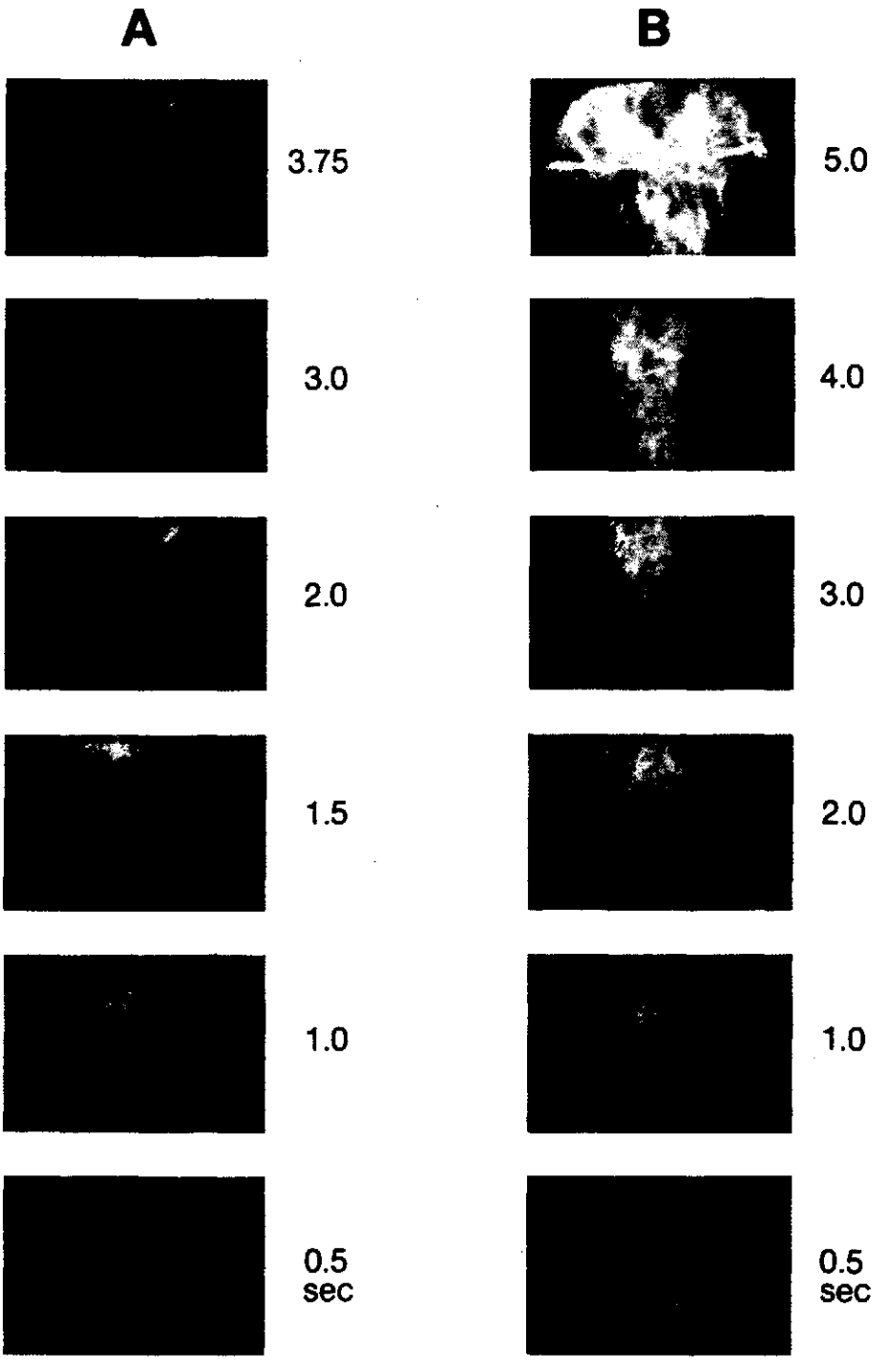


Figure 17.—Film records showing flame propagation after central ignition of equimolar H_2-CH_4 mixtures in air in 12-ft-diameter sphere. A, 6.5 vol-pct (H_2 + CH_4); B, 7.0 vol-pct (H_2 + CH_4).

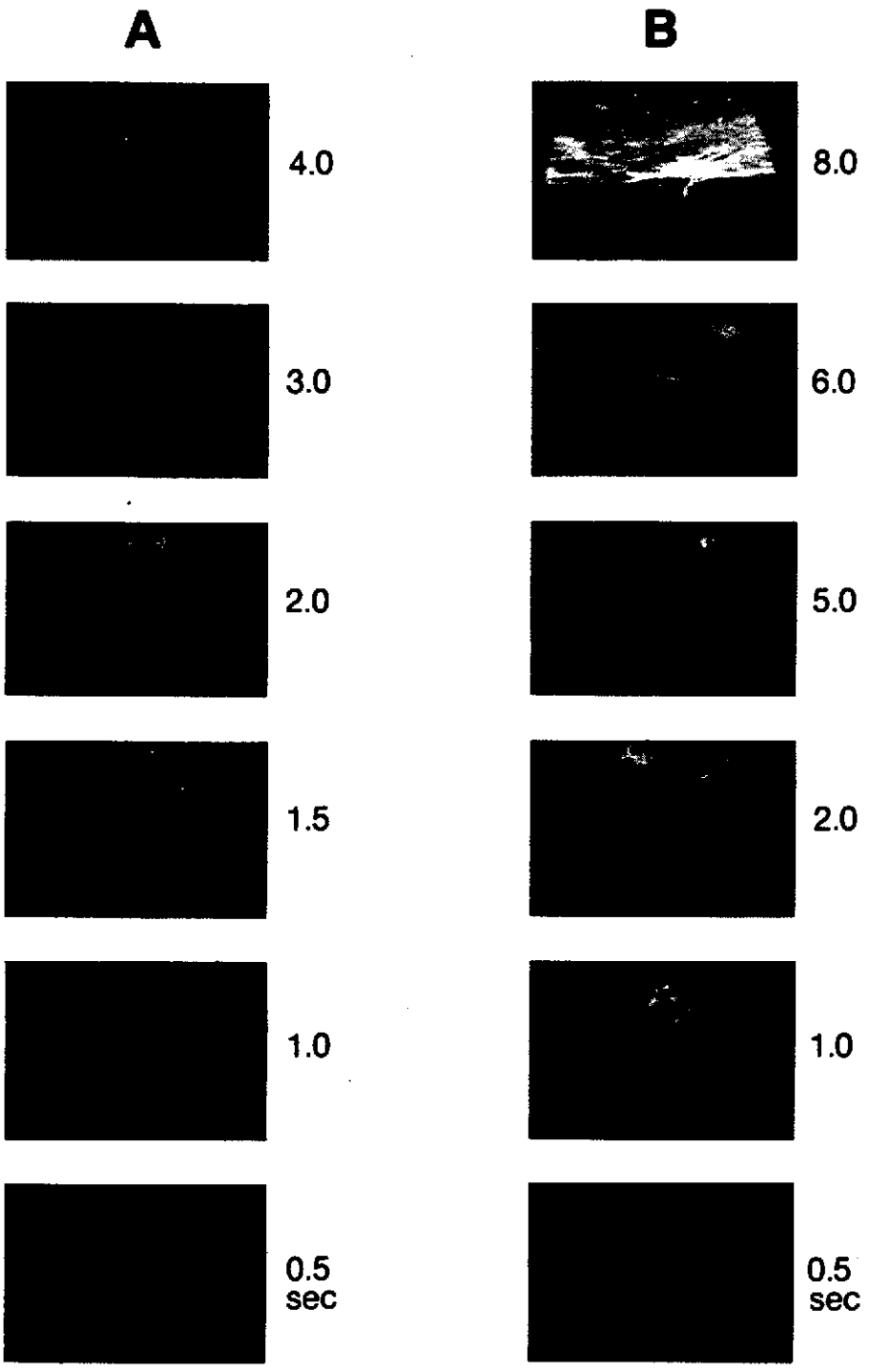


Figure 18.—Film records showing flame propagation after central ignition of equimolar H_2-CO mixtures in air in 12-ft-diameter sphere. A, 10.5 vol-pct (H_2 + CO); B, 11.0 vol-pct (H_2 + CO).

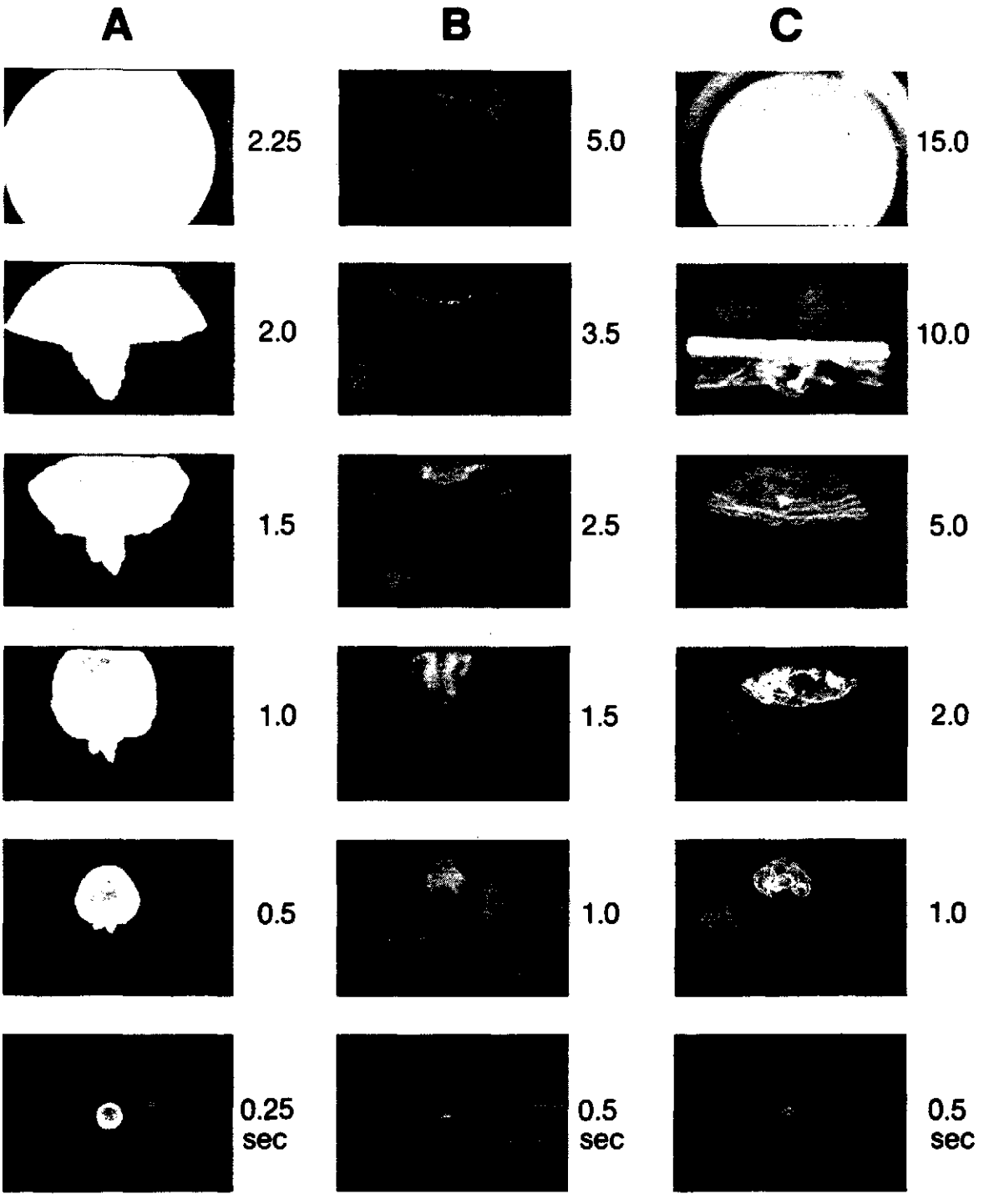


Figure 19.—Film records showing flame propagation after central ignition of equimolar H_2-CO-CH_4 mixture and DOE fuel gas mixtures (~12 CO:6 H_2:1 CH_4:1 CO_2:0.8 N_2) in air in 12-ft-diamter sphere. A, 9.2 vol-pct (H + CO + CH_4); B, 11.2 vol-pct DOE mix; C, 12.0 vol-pct DOE mix.

DISCUSSION

Observations that were described in the previous section are summarized in table 11.

With respect to the lean limits of upward flame propagation the few measurements of this study are in fair agreement with the voluminous data of Jones (*9*) which are collected in table 2. One significant difference is that all observed limits in table 11 are higher than calculated by use of the LeChatelier law, that is, the calculations are made to appear conservative. But Jones was able, in 11 mixtures out of 20, to observe flame propagation at lower concentrations than calculated. It is assumed he had a more sensitive methodology for observing upward propagation. Also, he was able to make many more repetitive measurements, which can only lead to observing propagation at equal or at lower concentrations. As admitted below, there is no compelling reason why the LeChatelier law should apply to upward propagation in hydrogen mixtures; therefore it should be no affront that the calculated lean limits are not always conservative.

With respect to the lean limits of downward flame propagation, the data given in table 11 are again consistently higher than calculated. In this case, there is no body of reported data available for reference. Therefore the question arises as to whether the small number of measurements of this study are really sufficient to establish lean limits of flame propagation. In defense of the numbers in table 11, note the relatively large number of independent observations that occur with each downward flame propagation in the 12-ft-diameter sphere: visual and photographic observations of flame movement; pressure rise rate and peak pressure; and gas analytical measurements of reactant and product concentration. Also, since each occurrence of downward propagation begins from a mushroom-shaped zone of burned gas at the top of the sphere, there are no questions of ignitor intensity or duration.

Table 11.—Summary of observed and calculated lean limits of flame propagation at approximately 25° C and 1 atm

Mixture	Upward limits		Downward limits	
	Observed	Calculated	Observed	Calculated
H_2-air	4.0	NAp	8.5	NAp
CH_4-air	4.85	NAp	5.25	NAp
CO-air	12.0	NAp	13.0	NAp
($H_2 + CH_4$)-air	4.5- 5.0	4.4	6.5- 7.0	6.4
(H_2 + CO)-air	~7.0	6.0	10.6-11.0	10.3
(CH_4 + CO)-air	7.0- 7.4	6.8	7.4	7.4
($H_2 + CH_4$ + CO)-air	5.5- 6.0	5.5	8.0- 9.0	7.8
DOE mix[1]-air	~9.0	8.0	11.6-12.0	>11.4

NAp Not applicable.
[1] Defined as (12 CO:6 H_2:1 CH_4:1 CO_2:0.8 N_2).

Various arguments have been offered during the past century as to which of the two measurements—upward or downward propagation—should be regarded as "fundamental." It is obvious from the foregoing sections that the authors regard downward propagation as representative of the gas mixture under study and indicative of its explosion hazard. When diffusional demixing is involved, upward propagation seems to be an almost trivial artifact. Unfortunately it must be given serious consideration in some safety practices because known low gas concentrations, for example, 4.1 pct hydrogen in air, may well be adjacent to unknown higher concentrations such as 10 pct hydrogen. But when one deals with a large system such as a sealed mine or the containment vessel of a nuclear reactor, and if one knows that gas concentrations are changing slowly and uniformly throughout the volume, then the pressure-concentration curves of figures 5 through 11, 13, and 14 are representative of explosion hazard for ignitions under stagnant conditions and may be used to calculate the time that one has to take corrective action. The corresponding times for turbulent mixtures would necessarily be shorter, depending upon the mixture composition and degree of turbulence.

In reference 5, the suggestion of Spalding (*17*) that fuel-oxidant ratio in the flame front could be altered by diffusional demixing to the extent of $(D_o/D_f)^{1/2}$ where D_f and D_o are the diffusivities of fuel and oxygen, respectively, was followed. From this it was argued that the ratios of the limits of flammability for upward and downward flame propagation should also be in the ratio $(D_o/D_f)^{1/2}$. This argument is somewhat loosely supported by table 12 which is taken from reference 5. The second column of data, $(D_o/D_f)^{1/2}$, should be compared with the third column, the optimum stoichiometric ratio for spark ignition, and also with the last column which is the ratio of upward-downward limits of flammability. Only the spark ignition data for hydrogen tend to be inconsistent in such correlations.

In this spirit, the authors presume that a 4.0 pct (gross) concentration of hydrogen is so altered by diffusional

Table 12.—Stoichiometric ratios[1] of the most easily ignited mixtures and of limit mixtures in upward and downward propagation (*5*)

Fuel-oxidant	$(D_o/D_f)^{1/2}$	Optimum stoichiometric ratio, spark ignition	Flammable limit stoichiometric ratio		
			Upward	Downward	Upward-downward
			Rich limits		
Methane-air	0.96	0.9	1.46	1.43	1.02
Ethane-air	1.29	1.2	2.21	1.79	1.24
Propane-air	1.44	1.3	2.37	1.66[2]	1.43
Butane-air	1.55	1.5	2.73	1.94[3]	1.41
Pentane-air	1.63	NA	3.10	1.80	1.72
Hexane-air	1.70	1.7	3.19	NA	NA
Heptane-air	1.78	1.8	3.58	NA	NA
Benzene-air	1.52	NA	2.84	1.94	1.46
			Lean limits		
Hydrogen-air	.54	.95[4]	0.14	0.31[3]	0.46
Methane-air	.96	.9	.56	.61	.92
Benzene-air	NA	NA	NA	.57	NA

NA Not available.
[1] Fuel concentration of mixture-fuel concentration for combustion to CO_2 and H_2O (hydrocarbons) or to H_2O (hydrogen).
[2] Measured in small-diameter tube but supported by extrapolation of values at elevated pressure.
[3] Estimated from measurements reported in reference 5.
[4] Added value to original table based on data reported by Lewis and von Elbe in Combustion, Flames and Explosion of Gases, 2d ed., Academic Press, Inc., N.Y., 1961, 731 pp.

Table 13.—Calculated flame temperatures and pressure rises for adiabatic combustion of hydrogen, methane, and carbon monoxide mixtures in air at 25° C (298 K)

Fuel concentration vol-pct	Pressure rise (ΔP), psig	Flame temperature (T_f), K: Constant volume	Flame temperature (T_f), K: Constant pressure
H_2-air:			
4	21.4	746	628
6	30.9	951	788
8	39.8	1,151	944
12	56.2	1,528	1,249
15	67.2	1,794	1,472
CH_4-air:			
4.5	68.5	1,688	1,382
5	74.6	1,810	1,485
6	86.0	2,040	1,683
7	96.4	2,248	1,870
8	105.4	2,425	2,043
CO-air:			
10	53.2	1,450	1,194
11	57.4	1,547	1,275
12	61.5	1,643	1,355
13	65.4	1,736	1,434
14	69.2	1,828	1,512
(H_2 + CH_4)-air:			
4	43.1	1,184	946
5	52.2	1,373	1,093
6	60.7	1,553	1,237
7	68.8	1,724	1,375
8	76.5	1,887	1,510
(H_2 + CO)-air:			
6	32.9	995	823
8	42.2	1,201	988
10	50.8	1,398	1,148
12	58.9	1,587	1,304
(CH_4 + CO)-air:			
6	62.1	1,580	1,427
7	70.3	1,753	1,587
8	78.0	1,917	1,740
9	85.2	2,072	1,886
10	92.0	2,215	2,023
(H_2 + CH_4 + CO)-air:			
5.1	45.7	1,245	1,090
6	52.4	1,388	1,216
7.2	60.9	1,571	1,378
8.1	67.0	1,702	1,496
9	72.8	1,828	1,611
DOE mix[1]-air:			
9	47.7	1,317	1,083
12	60.3	1,603	1,320
13	64.2	1,694	1,397
15	71.6	1,870	1,547
20	87.6	2,265	1,905

[1] Defined as (12 CO:6 H_2:1 CH_4:1 CO_2:0.8 N_2).

processes that the upward propagating flame burns as though in 8.5 pct hydrogen. Then T_f in a flamelet should not be 628 K as is plotted at 4 pct in figure 5 but close to 1,000 K as shown at 8.5 pct. For comparsion, the reported minimum autoignition temperature for hydrogen-air is 500° C (773 K) (*20*) and the reported minimum temperature for hot gas ignition of hydrogen in air is 655° C (928 K) (*18*). On the basis of these numbers, 1,000 K as a flame temperature in lean H_2/air could be accepted but 628 K seems clearly impossible. By the same token, the temperature of a rich butane-air flamelet, which according to figure 6 propagates upward at concentrations from 6 to 8.6 pct butane, should be 1,600 to 1,700 K.

Table 13 presents computed temperatures (NASA-Lewis code) for constant pressure and constant volume combustion of H_2, CH_4, and CO and of mixtures thereof in air at various concentrations.

It is fashionable in the present generation of research to treat the LeChatelier approximation as a purely empirical observation that is somewhat useful. But LeChatelier surely had more in mind than an empirical law; in his 1898 paper with Boudouard (*11*) he reported that limit mixtures of the paraffin hydrocarbons in air all had about the same heat of combustion. Since limit mixtures in air are comprised almost entirely of air, equal heats of combustion imply equal flame temperatures. Thus the concept of a constant limit flame temperature was very actively pursued in the early decades of this century, leading to the Burgess-Wheeler law and, subsequently, the modified law by Zabetakis (*19*, p. 22) for predicting the limits at different temperatures. As the authors understand the history of combustion, researchers became disillusioned with limit flame temperatures because the concept seemed to fail so badly with heavy hydrocarbons on the rich side of stoichiometric. This is illustrated in figure 6 where the "T_f calculated" curve for n-butane-air mixtures is drawn down to impossibly low values. This report has shown already that the assumption of diffusional demixing provides a rationalization of this low apparent T_f.

Coward and Jones (*4*, pp. 12-14), summarize some of the early investigations that relate the LeChatelier law to the concept of limit flame temperature. They list eight publications in the Japanese literature of Y. Nagai and coworkers and have this to say about their conclusions.

> "Nagai has offered an explanation for certain deviations from LeChatelier's law. He assumes that, if two gases individually have the same calculated temperature for their limit-mixture me, which he calls the theoretical flame-propagation temperature (TFPT) the mixtures of these gases will obey the law. If, however, the TFPT's are not equal, the mixed gases will not obey the law. the gas of higher TFPT does not play the part suggested by LeChatelier's law until the amount of the other gas is increased in lower-limit mixtures or decreased in higher-limit mixtures. Over a greater or smaller middle range of composition the limit mixtures of some pairs of gases have constant TFPT's, therefore these mixtures obey the law over that range."

Among those gases which are most cited as producing deviations from LeChatelier's law are hydrogen sulfide and the extinguishant gases such as ethyl bromide. Another example of irregular behavior is that of H_2-CH_4 mixtures which were said to obey the LeChatelier law far better than one might expect from the dissimilar values of TFPT.

As the attempt is made to tie these loose ends together, the authors find that their opinions are much in agreement with those of Nagai but are cloaked in the technical jargon of five intervening decades of combustion research. The LeChatelier law has served well in the past. This is because the great bulk of the important flammable gases and vapors (Group D of the National Electric Code) are organic compounds whose lean limit mixtures have heats of combustion about 10 to 11 kcal/mole; their lean limit flame temperatures are typically about 1,500 to 1,600 K. Of all these common fuels only methane has a higher diffusivity than oxygen and figure 7 shows that its zone of preferential diffusion is so narrow as to be unimportant in gas mixtures. Fortunately, safety considerations mostly involve *lean* limits of flammability; had the combustion community been much involved with rich limits, then the demixing process reflected in figure 6 would have confused the issue and the LeChatelier law would have lost credibility. One would expect the bromides to give violations of a mixing law because of free radical scavenging which necessarily must increase limit flame temperature and require more nearly stoichiometric gas mixtures for flame propagation. The authors must decline comment on hydrogen sulfide as a component of gas

mixtures, having had no personal experiences with this compound as a flammable material.

When the case of H_2-CH_4 mixtures is reached, no reason is seen to rationalize the applicability of the LeChatelier law because the LeChatelier law does not really apply. In table 11, it is seen that the limits of downward propagation are very conservatively estimated by the LeChatelier method. This would have been explained by Nagai in his terms that the gas of higher TFPT (methane) did not play its appropriate role in flammability of the mixture. Unfortunately, Nagai must have been dealing largely with upward flame propagations; from the dates of their respective publications, he could hardly have been aware of the surmise of Goldmann (*6*) about diffusional effects and surely not of its substantiation which came much later; he could hardly have known that Jones (*9*) had found so many observed limits which were lower than calculated (table 2). Finally, something should be said about the assumption of the LeChatelier law within the shortcut methods that have been offered to the personnel in mine recovery work. This is a case, the authors believe, of compensating errors: If one computes flammability by LeChatelier law using 4 pct as the lean limit of hydrogen, then he obtains an answer that is meaningless; but then if there is an "explosion" underground that is analogous to the explosion of 4 pct hydrogen in air, the chances are that the phenomnon will go unnoticed.

The authors doubt that anyone has ever been injured by a fallacious assumption of the LeChatelier approximation, particularly where the ignitions primarily involved quiescent gas mixtures; however, that should not preclude better dissemination of the story of upward and downward flame propagation.

CONCLUSIONS AND RECOMMENDATIONS

Perhaps the most striking new observation in this work was that of flame propagation in methane-air at concentrations slightly below the accepted lean limit of 5.0 pct. This small lowering of the limit by 0.1 or 0.2 pct is hardly important in itself but it does illustrate that continued study of a flammable mixture brings about continued widening of the known flammable range.

The study showed that neither methane-air nor carbon monoxide-air have a very wide range of lean concentrations that support upward but not downward propagation. Some preferential diffusion apparently exists in methane-air as evidenced by cellular flame structures in upward flame propagations. The flamelets described by Coward and Jones as occurring in lean hydrogen-air mixtures could not be observed in the present experimental system.

The LeChatelier mixture law gave approximations to the limits of downward propagation which were uniformly on the conservative side. The present work was not well adapted to study of upward propagation; however earlier work by Jones has shown that it could be dangerous to apply the LeChatelier law to upward flame propagation in any situation involving preferential diffusion.

It is concluded that there are numerous practical aspects of diffusional demixing and that the combustion community should be provided much more on this subject. It would probably be a more fertile area for further research to study the rich mixtures of high molecular weight hydrocarbons rather than to continue on the lean side with low molecular weight fuels.

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