

Fundamental Principles of Flammability and Ignition

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No theoretical criterion for flammability limits is obtained from the steady-state equation of the combustion wave. On the basis of a model of the thermally propagating combustion wave it is shown that the limit is due to instability of the wave toward perturbation of the temperature profile. Such perturbation causes a transient increase of the volume of the medium reacting per unit wave area and decrease of the temperature levels throughout the wave. If the gain in over-all reaction rate due to this increase in volume exceeds the decrease in over-all reaction rate due to temperature decrease, the wave is stable; otherwise, it degenerates to a temperature wave. Above some critical dilution of the mixture, the latter condition is always fulfilled. It is concluded that the existence of excess enthalpy in the wave is a prerequisite of all aspects of combustion wave propagation.

Despite intensive theoretical and experimental research on the combustion wave over the past decade, a universally accepted concept of the phenomenon has not been achieved. This is particularly true with respect to the nonsteady state phenomena of limits of inflammability and ignition.

Frequently in theoretical work on the subject, whether dealing with the steady or nonsteady state, the mathematical development of an adopted model is followed by a descriptive summary of the results which is rarely traced back clearly to the assumptions inherent in the model. This has often resulted in extravagant identification of the model with the actual phenomenon and has been an obstacle in the task of reconciling conflicting views. There is need, therefore, of a purely descriptive exposition, stripped as completely as possible of mathematical language, to clarify the physical concepts of the combustion wave phenomenon.

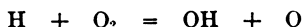
General Description

A combustion wave is established in an explosive medium by application of a local source of ignition. As heat and, possibly, chain carriers of various kinds flow from the source into the adjacent medium, reaction is initiated in the layer next to the source which in turn becomes a source for igniting the next layer, and so on. Let us consider a mass element of the unburned mixture being overrun by the combustion wave. The reaction rate is virtually zero at the initial temperature but increases with temperature at

a high order. Therefore, the mass element at first absorbs heat as a heat sink until at some point inside the wave it becomes a heat source by virtue of the chemical reaction initiated by the temperature rise. From this instant and until the temperature crest of the wave has passed, the mass element remains a heat source. Its source strength at first increases because the rising temperature accelerates the chemical reaction; but because the trend is reversed as the explosive reactant is exhausted, the source strength in time passes through a maximum and then decreases steadily even though the temperature is still rising. When heat liberation has substantially subsided, the mass element has arrived at the crest of the wave. During the period of heat liberation the element loses heat to the adjacent cooler regions of the medium upstream—that is, toward the unburned side—in an amount equal to that which it had received while it was a heat sink. In this way heat is continuously borrowed and repaid in the wave out of what may be called a revolving heat fund which travels with the wave and is referred to as the excess enthalpy (δ , 10), h , of the wave.

The above description is of a thermally propagating steady-state wave. It must be emphasized, however, that the basic feature of a thermal mechanism is not altered by the superposition of molecular diffusion onto the diffusional transport of heat. This applies not only to interdiffusion of reactants and products but also to the diffusion of chain carriers participating in the chemical reaction, provided that the chains are unbranched. The reason for this is that in a wave driven by a diffusion process, the source strength of an entering mass element must continue to grow despite the drain by the adjacent sink region. This growth can occur only if the reaction rate is increased by a product of the reaction, which may be temperature as well as a material product.

In the case of both nonchain and unbranched chain reactions, temperature is the only product that produces this result. Therefore, combustion waves depending on such reactions are all thermal in the sense that the temperature dependence of the reaction rate and thermal diffusivity control the propagation. A different class of waves is encountered in case of a branched-chain reaction. In this case the principal reaction product responsible for wave propagation is a chain carrier which diffuses into the sink region, and causes the growth of source strength (represented by its own concentration) as it multiplies. Because all such reactions are exothermic, this case is never entirely separated from the simultaneous rise of temperature. However, it appears that the so-called cool flames are driven principally by chain branching, examples of which are the cool flames in hydrocarbons and carbon disulfide. The flames normally encountered with flame temperatures exceeding about 1000°C . are thermally driven. This includes flames of hydrogen even though hydrogen and oxygen are capable of chain branching by the reaction



It is perhaps intuitively understandable that the steady state, characterized by the well known property of the combustion wave to propagate at constant velocity in a homogeneous explosive medium, results from the fact that there is a ceiling on the source strength imposed by exhaustion of the reactants. Mathematical treatments of the steady state, of which there are many, involve integration of the various wave parameters between suitably formulated boundaries representing the unburned and burned states, and yield the value of burning velocity as an eigen-value solution. Some perplexity connected with the formulation of the boundary conditions for the unburned state has arisen occasionally as a result of the assumption of an ideal steady state, in the sense that the wave was thought to travel *ad infinitum* in an infinite volume of explosive medium. Evidently, if such assumption is not supplemented by the further assumption that the reaction rate is absolutely zero throughout the medium untouched by the wave and becomes finite only as the wave approaches, the system mathematically “explodes.” The relation of such boundary conditions to reality lies merely in the fact that an explosive medium is always so recently prepared that it has not reacted appreciably prior to the instant it is consumed by the wave.

Flammability Limits

It is found experimentally that limit mixtures, incapable of supporting combustion waves, nevertheless have theoretical thermodynamic flame temperatures of the order of 1000° C. or more. It is, therefore, not immediately clear why combustion waves, albeit slowly propagating, should not develop in mixtures possessing such substantial chemical enthalpy. The question arises whether the observed limits of flammability are true limits or whether such mixtures are actually capable of supporting combustion waves but are prevented from doing so by experimental limitations. Experimentalists believe that the limits are true. On the other hand, no theoretical criterion for the limit is obtained from the steady-state equations of the combustion wave. That is, the equations describe combustion waves without differentiating between mixtures that are known to be flammable and mixtures that are known to be nonflammable. Therefore, for nonflammable mixtures the combustion wave becomes unstable to perturbations and thus disappears (?). Conversely, for flammable mixtures the combustion wave can overcome perturbations—i.e., it returns to the steady state after being perturbed.

This may be understood as follows. Suppose that a steady-state combustion wave is established with a temperature profile as shown by the solid line in Figure 1, *A*. If some small volume of unburned medium, on entering the source zone, would receive a slightly stronger-than-average stimulus so that it would liberate heat at a rate slightly in excess of the statistical kinetic average, the temperature in that volume would increase above the steady-state profile. The flow of heat from the perturbed volume to the cooler wave regions would accelerate and the flow of heat from the hotter wave regions into the perturbed volume would decelerate. Because the temperature gradient is steeper on the cool side of the volume than on the hot side, more heat would flow during the perturbation to the cooler regions than would be retained by the hotter regions. Consequently, the enthalpy in the perturbed volume would decrease but in the adjacent volume elements it would increase, the increase being larger on the cool side than on the hot side. As the wave continues to propagate, the temperature adjacent to the perturbed volume would increase above the steady-state profile, and within the perturbed volume it would drop below, so that a ripple would develop in the profile as shown by the dotted line in Figure 1, *A*. The boundary of the source zone is extended toward the unburned side so that the width of the source zone is increased beyond that of the steady state.

In the higher temperature region of the source zone the rate of heat liberation decreases because here the temperatures drop below the steady-state profile. This is illustrated in Figure 1, *B*, where the solid line represents the distribution of the rate of heat liberation per unit volume, q , in the unperturbed wave, and the dotted line represents the distribution of q as modified by the temperature ripple. The area comprising the qdx -integral gains in width but loses in height, the former representing the advance of the source zone front beyond the steady-state position, and the latter representing the decrease of the rates q in the source zone. Depending upon which effect predominates, the total source strength (represented by the qdx -integral) either increases or decreases. In the former case, the wave momentarily accelerates and then returns to the steady state as the temperature ripple passes over the wave crest into the burned medium. In the latter case, the heat transferred to the sink zone plus the heat retained by the combustion products as they leave the source zone, momentarily exceeds the heat generated in the source zone, so that the temperatures drop still further. This results in further decrease of the source strength, and so on. Consequently, the wave does not return to the steady state but deteriorates.

In another description of the flammability condition, the authors (?) introduced the average rate of heat liberation, \bar{q} , defined by

$$\bar{q}s = \int_{-\infty}^{+\infty} q'x \quad (1)$$

where s is a measure of the width of the source zone. If the width is increased by an element, ds , due to an advance of the source zone front beyond the steady-state position,

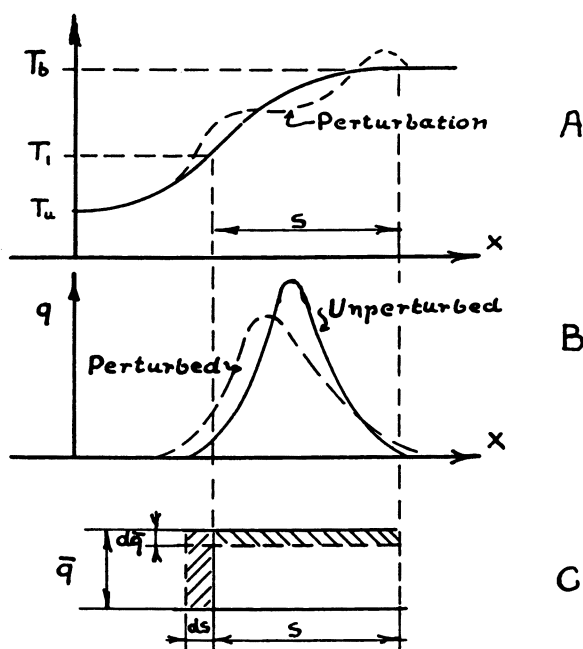


Figure 1. Temperature profile of steady-state combustion wave

A—Temp. profile of combustion wave in steady state. (T_u , T_i , T_b , denote temps. of unburned medium, inflection point, and burned, medium, resp.)—Temp. perturbation.

B—Profile of source strength $\int_{-\infty}^{+\infty} q dx$. Source strength corresponding to temp. perturbation (q denotes rate of heat liberation per unit volume).

C—Same as B, showing source strength in the form

$$\bar{q}s = \int_{-\infty}^{+\infty} q dx,$$

and perturbed source strength as $\bar{q}s + \bar{q}ds - s d\bar{q}$.

the source strength, $\bar{q}s$, is changed by addition of the element, $\bar{q}ds$, and by subtraction of the element, $s d\bar{q}$, as shown in Figure 1, C. Depending upon which of the two differentials is larger the total source strength either increases or decreases, so that the flammable region is defined by

$$\bar{q}ds > s |d\bar{q}| \quad (2)$$

and the nonflammable region by

$$\bar{q}ds < s |d\bar{q}| \quad (3)$$

the symbol $| |$ indicating that $d\bar{q}$ is a negative quantity. This is in substance the relation given in the authors' treatise (8).

Writing Inequality 2 in the form, $ds/s > |d\bar{q}|/\bar{q}$, the condition for wave stability demands that the percentage increase of source zone width, resulting from a temperature ripple, be larger than the percentage decrease of the average reaction rate. The two sides of the inequality are related by the temperature decrease that results from the distribution of the sensible heat of the source zone over the enlarged zone width. To illustrate the type of relationship that may be expected to govern the stability condition, we shall assume for simplicity that the difference between the flame temperature, T_b , and the average source-zone temperature, T_{av} , increases proportionate to the source zone width,

s, and that \bar{q} follows a simple Arrhenius law—viz., $\bar{q} \sim \exp. (-E/RT_{av})$. Thus, ds/s , becomes $|dT_{av}|/(T_b - T_{av})$, $|dq|/\bar{q}$ becomes $(E/RT_{av}^2)|dT_{av}|$, and the stability condition may be written in the form

$$T_{av} > \left(\frac{T_b}{T_{av}} - 1 \right) \frac{E}{R} \quad (4)$$

It is reasonable to assume that T_b/T_{av} changes comparatively little with change of T_b as long as the latter is well above T_{av} . Consequently, as T_b is decreased by adding a diluent to an explosive medium, a critical concentration of the diluent is eventually reached at which inequality 4 is reversed. This depends upon the nature of the diluent and constitutes the limit of flammability.

To obtain the flammability criterion from a more formal development of the combustion wave equations, it is necessary to retain the idea of perturbed heat transfer within the wave independent of the distribution of concentrations of reactants and reaction products. Such treatment has been given by Rosen (12), whose result expresses the described physical concept in other form. Layzer (3) has investigated a wave model in which no change of total enthalpy (thermal and chemical) is allowed to occur in any wave layer (4, 5). Richardson (11) has investigated a wave model in which the reaction rate term is a function of only one parameter—e.g., concentration. Neither of these models yields a flammability criterion in terms of instability to perturbations. Both models possess, in addition to a stable solution of the steady-state equation, unstable solutions whose physical meaning constitutes unlimited extensibility of the reaction zone into the unburned medium, that is, unlimited rate of propagation of the source zone. It would seem, therefore, that a realistic description of the combustion wave, including a limit condition, is obtainable only by retaining excess enthalpy in the model.

Ignition

Concerning the origin of the excess enthalpy in a combustion wave, it is obvious that it derives from either the heat furnished to the explosive medium by an independent source or from the heat of the combustion products behind the wave. In the example of a spherically growing flame, the wave area, and hence the total amount of excess enthalpy continuously increase. Evidently, the ignition source can furnish only an initial amount of this energy, and after the flame has grown to some size the additional demand is met at the expense of the heat content of the burned gas—that is, some of the chemically liberated heat is retained in the wave, so that the temperature T_b behind the wave is somewhat lower than the adiabatic flame temperature T_b° . As the flame radius increases from r to $r + dr$, the increase of wave surface per unit area is $2dr/r$, and in first-order approximation the increment of excess enthalpy is $dh = h \times 2dr/r$. It is seen that the differential quotient, $dh/dr = 2h/r$, vanishes for large radii but is very large near the origin, so that a critical flame radius should exist below which the excess enthalpy cannot be furnished by the heat liberated in the wave but must be furnished, instead, by the ignition source.

On this basis, it is seen that the source must supply a minimum energy, H , which enables the flame to grow to a critical diameter, d , beyond which the wave can propagate under its own power.

Minimum ignition energy may be written

$$H = \pi d^2 h \quad (5)$$

where πd^2 is the area of the combustion wave at the surface of the critical flame volume and h being the excess of enthalpy per unit area.

For physical realization of ignition by the minimum amount of energy, it is necessary that the energy, H , be imparted to a volume that is small compared to the volume of diameter, d , and that the energy release occur in a time that is short compared to the time required for the flame to develop to the critical diameter, d . Electric sparks are the most likely means to realize these conditions. Furthermore, it is clear that no heat sink must touch the flame before it has grown to diameter, d ; hence, the metallic spark

Table I. Comparison of Experimental and Calculated Minimum Ignition Energies H Atmospheric Pressure and Room Temperature

Fuel Content, Fraction of Stoichiometric	S_u , Cm./Sec.	$T_b - T_u$, ° C.	$\frac{\mu \times 10^4}{\text{Cal./Cm.}^2 \cdot \text{Sec.}},$ ° C.	d , Cm.	Min. Ign. Energy Cal. $\times 10^6$ $H_{\text{calcd.}}$ $H_{\text{exp.}}$		Ratio, $\frac{H_{\text{calcd.}}}{H_{\text{exp.}}}$
CH ₄ -O ₂							
0.3	80	1900	6.3	0.072	24	10	2.4
0.45	175	2350	6.4	0.050	6.7	3.1	2
0.75	304	2700	6.5	0.027	1.4	1.4	1
1.2	305	2700	6.7	0.058	4.9	5.0	1
1.5	122	2350	6.9	0.165	109	110	1
1.58	87	2200	6.9	0.38	790	430	2
C ₃ H ₈ -O ₂							
0.4	240	2200	6.1	0.038	2.5	1.7	1.5
0.6	335	2550	6.0	0.028	1.1	0.68	1.6
0.8	382	2700	5.9	0.024	0.77	0.50	1.5
0.8	382	2700	5.9	0.024	0.77	0.50	1.5
1.0	375	2750	5.9	0.022	0.65	0.48	1.3
1.2	320	2700	5.8	0.024	0.88	0.63	1.4
1.4	235	2500	5.7	0.028	1.5	1.0	1.5
1.9	30	1300	5.6	0.045	15	6	2.5
1.1 CH ₄ + O ₂ , Nitrogen Added							
N ₂ /O ₂ = 0.5	240	2640	6.3	0.045	4.5	5.3	0.9
1.0	170	2510	6.4	0.053	8.4	9	0.9
1.86	110	2320	6.5	0.079	2.6	20	1.3
air	42	1900	6.5	0.25	590	110	5
H ₂ -Air							
0.67	100	1610	7.2	0.071	18	6.2	3
1.01	195	2000	8.0	0.064	10	4.5	2
1.35	265	1940	9.0	0.076	12	6.6	1.8
1.92	190	1550	9.0	0.165	63	49	1.3
C ₃ H ₈ -Air							
0.7	28	1570	6.5	0.42	2000	530	4
0.9	35	1870	6.5	0.24	630	140	4
1.0	40	1940	6.5	0.19	360	92	4
1.28	27	1820	6.5	0.17	400	59	7
1.40	17	1730	6.5	0.20	820	62	13
1.50	12	1530	6.5	0.25	1620	70	23
CH ₄ -Air							
0.7	15	1600	6.5	0.29	1800	180	10
0.8	27	1700	6.5	0.22	610	100	6
0.9	35	1850	6.5	0.20	430	72	6
1.0	43	1950	6.5	0.21	410	72	6
1.1	42	1900	6.5	0.25	590	110	5
1.25	25	1800	6.5	0.45	2900	400	7

electrodes must be separated beyond a critical distance—the quenching distance. In the first approximation, the latter may be identified with diameter, d , and its experimental determination is possible by variation of the electrode distance.

The quantity, h , in Equation 5 is not likely to be greatly different from its value in a plane adiabatic combustion wave. Taking x as the coordinate normal to such wave, h becomes the integral of the excess enthalpy per unit volume along the x -axis, so that the differential quotient, dh/dx , represents the excess enthalpy per unit volume in any layer, dx . Assuming the layer to be fixed with respect to a reference point on the x -axis, the mass flow passes through the layer in the direction from the unburned, u , to the burned, b , side at a velocity, S , transporting enthalpy at the rate Sdh/dx . Because the wave is in the steady state, heat flows by conduction at the same rate in the opposite direction, so that

$$\mu dT/dx = Sdh/dx \quad (6)$$

where μ is the coefficient of heat conductivity. For order-of-magnitude calculations consider the ratio μ/S to be constant and equal to its values on the unburned side. This is suggested both by the fact that the increase of μ with temperature is partly compensated by the corresponding increase of S and that the enthalpy excess may be expected to exist predominantly at relatively low temperature levels on the unburned side. The velocity S is taken to be S_u , the burning velocity, and Equation 6 on integration yields the equation originally derived by the authors (9)

$$h = \frac{\mu}{S_u} (T_b - T_u) \quad (7)$$

Values of μ are available for numerous gases and gas mixtures. Burning velocities have been measured on burner flames, and flame temperatures, T_b , can be computed thermodynamically. It is thus possible to put Equation 5 to a test by comparing experimental values of minimum spark-ignition energies with values calculated from data on quenching distances, burning velocities, heat conductivities, and flame temperatures.

Table I (1) shows a comparison of experimental and calculated minimum ignition energies for several series of fuel-oxygen and fuel-air mixtures. A discussion of these results will be prefaced by a consideration of the limitations of the thermal model in predicting the magnitude of the excess enthalpy h . In gaseous explosive mixtures, enthalpy is transported not only in the form of sensible heat by heat conduction but also in the form of chemical enthalpy by the diffusion of reactants into the reaction products. The transport of heat occurs in the direction, burned to unburned, whereas the net transport of chemical enthalpy occurs in the direction, unburned to burned. The existence of an excess enthalpy in the form of heat is dependent upon the enthalpy flux by heat conduction being larger than the opposing enthalpy flux by diffusion of reactants. If these opposing fluxes were equal then no mass element of the combustion wave would contain more than the initial total enthalpy of the mixture; there would be no excess enthalpy and therefore no minimum of the spark energy required for ignition. This does not occur in nature.

However, it is clear that the calculation of the excess enthalpy from a model in which diffusion is neglected, as in Equation 7, yields values that are larger than those in an actual wave. The discrepancy between the actual value of h and that calculated from the no-diffusion model depends on whether change of mixture composition throughout the wave width is caused essentially by chemical reaction or whether interdiffusion of reactants and reaction products makes a significant contribution. It may be surmised that in rapidly reacting mixtures diffusional change of mixture composition is negligible but that in slowly reacting mixtures it becomes increasingly important. Accordingly, we would expect the computed value of h to be in substantially better agreement with the experimental value in rapidly reacting mixtures than in slowly reacting mixtures. Moreover, the discrepancy would show the calculated values to be always larger than the experimental values and to become increasingly larger as the mixture is diluted either by an excess of one of the reactants or by addition of inert gas. Inspection of the mixture compositions, and the last column of Table I shows that these considerations are borne out. The agreement between the calculated and experimental values of h is surprisingly good for the very rapidly reacting stoichiometric mixtures undiluted with inert gas.

The foregoing demonstrates that the existence of excess enthalpy is a prerequisite for a conceptual understanding of the real combustion wave. The growing awareness of this situation is illustrated in recent discussions (2).

Literature Cited

- (1) Blanc, M. V., Guest, P. G., von Elbe, G., Lewis, B. J., *J. Chem. Phys.* **15**, 798 (1947); "Third Symposium on Combustion, Flame and Combustion Phenomena," p. 363, Williams & Wilkins, Baltimore, 1949; "Fourth Symposium on Combustion," p. 16, Williams & Wilkins, Baltimore, 1953.
- (2) Burgoyne, J. H., Weinberg, F. J., *Fuel* **34**, 351 (1955).
- (3) Layzer, David, *J. Chem. Phys.* **22**, 222, 229 (1954).
- (4) *Ibid.*, Equations 319, 320, p. 224.
- (5) *Ibid.*, p. 227.
- (6) Lewis, B., von Elbe, G., "Combustion, Flames and Explosions of Gases," p. 345 seq., Academic Press, New York, 1951.
- (7) *Ibid.*, pp. 369-71.
- (8) *Ibid.*, Equation 82, p. 370.
- (9) *Ibid.*, p. 374.
- (10) Lewis, B., von Elbe, G., *J. Chem. Phys.* **15**, 803 (1947).
- (11) Richardson, J. M., "Fourth Symposium on Combustion," p. 182, Williams & Wilkins, Baltimore, 1953.
- (12) Rosen, J. B., *J. Chem. Phys.* **22**, 733, 743, 750 (1954).