# PROBLEMS IN FLAME PROPAGATION

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We suggest that the outstanding problem in flame propagation is to ascertain the mechanism by which flame travels through an inflammable gas mixture, i.e., to correlate the speed of movement of flame with the various chemical and physical factors involved by means of an equation with no empirical constant. It may be expected that when this has been accomplished the solution of most of the other problems in flame propagation will follow immediately or will have been found incidentally. Such a correlation has been made for detonation in gaseous mixtures, on the theory that in this mode of burning the zone of reaction is propagated by a mechanical shock wave maintained by the chemical reaction. In this communication we propose, therefore, to consider only the more usual mode of propagation, in which the pressure of the gas in the flame is not sensibly greater than that of the rest of the gas.

## OBSERVED SPEEDS OF FLAME

At comparatively low rates the speed of flame relative to an observer is a function of three factors: (*a*) the movement of the medium in which the flame is travelling, (*b*) the area of flame relative to the area of cross section of gaseous mixture to which it is exposed, and (*c*) the speed of flame relative to the gas mixture itself. It has been shown that the observed speed of flame in a moving medium, whose motion may be imposed from without or may be caused by the expansion due to the heat of the flame itself (13), is equal to the speed in a still mixture plus the speed of movement of the medium (5), and also that the amount of mixture burned is proportional to the area of flame in it (11, 6).

The fundamental speed of flame (*c*) is the linear speed of the flame, in a direction at right angles to its surface, through a mixture at rest and at constant temperature and pressure just ahead of the flame. The observed speed of flame travelling in a tube is, therefore,

$$\text{Fundamental speed} \times \frac{\text{area of flame}}{\text{area of cross section of tube}} + \text{speed of movement of medium}$$

At higher speeds, during what has been termed the predetonation period, compression factors, which attain their maximum effect in detonation, may also exert a pronounced influence (17).

### FUNDAMENTAL SPEED OF FLAME

The conception just defined as the fundamental speed of flame may be what Mallard and Le Chatelier (13) had in mind when they wrote of "la vitesse normale," which was characteristic of "deflagration" (as distinct from detonation) and was, they thought, observable in the propagation of flames, not accelerated by turbulence or by expansion of the burning gases, in tubes wide enough to eliminate the effect of cooling by the walls of the tubes. The term of Mallard and Le Chatelier is as ambiguous in French as in English, we have been informed, in that the word "normale" may mean either "ordinary" or "at right angles to its surface." The term "fundamental" is suggested as preferable (6).

The fundamental speed of flame is the most difficult of all factors to analyze, the others, as has just been shown, being of an obvious mechanical nature. The mode of transfer of energy from the flame front to the neighboring unburnt layers remains to be established, and when physicochemical hypotheses on this process are formulated, they must be tested by measurements of the fundamental speed. What measurements of this are available?

### MEASUREMENTS OF THE FUNDAMENTAL SPEED OF FLAME

Le Chatelier's attempt to determine the "vitesse normale" from measurements of the speed of flame in tubes was based on the assumption that the flame front was plane and normal to the axis of the tube; the attempt failed because, as was shown later, the flame front is strongly curved (4). Three methods have subsequently been used with success. They may be called (*a*) the Bunsen cone method, (*b*) the soap-bubble method, and (*c*) the method based on measurements of the shape of the flame front and its speed of translation during the uniform movement of flame in a tube.

From the dimensions of the inner cone of a Bunsen flame, burning a known mixture at a known rate, can be calculated the component of the linear speed at which the mixture meets the stationary flame, normal to its surface (11). This is reasonably assumed to be equal to the speed of flame in a stationary mixture, but experimental difficulties make some of the results unreliable; for example, flame speeds have been deduced by this method for mixtures containing from 14 to 17 per cent of methane, although these mixtures do not propagate flame, and mixtures containing less than about 7.3 per cent of methane do not burn on the Bunsen burner, although the lower limit of inflammability of methane is about 5 per cent.

These errors are due to the entrainment of air at the orifice of the burner. The measurements of speeds of the more explosive mixtures, containing from 8 to 12 per cent of methane, may be made fairly reliable by careful attention to experimental conditions (6).

The soap-bubble method, first used by Stevens (19), depends on measurement of the speed of a spherical flame front travelling in a medium which is put in motion by the flame. From this measurement is deduced the speed in a stationary mixture, on the assumption that the observed speed is equal to the fundamental speed plus the speed of movement of the medium due to thermal expansion. This method is applicable to mixtures which burn at a sufficient rate to make negligible the effects of convection. Its results agree with those of the Bunsen flame method, so far as experiments have been made with the same mixtures (20).

The third method is more laborious than the others, and requires more special apparatus. Its results are claimed to be more accurate for the only mixtures to which it has been applied, namely, those of methane and air (6).

It seems clear that all three methods of measurement lead to the same constant, the fundamental speed of flame, and that one or another method is preferable, according to the nature of the flame. The first is simplest, but reliable only with mixtures of composition near to that of the mixture for complete combustion; the second is successful only with fast burning mixtures; the third is the only accurate method for slow burning mixtures.

## THEORETICAL ANALYSIS OF FUNDAMENTAL SPEEDS

Mallard and Le Chatelier regarded the "vitesse normale" (fundamental speed) as governed by the transfer of heat by conduction from the flame to the nearest unburnt layer of gas, and deduced the formula:

$$v = \text{const.}\,\frac{k}{c}\cdot\frac{T_f - T_i}{T_i - T_0}$$

in which $k$ = thermal conductivity,
$c$ = mean specific heat,
$T_f$ = temperature of the flame,
$T_i$ = ignition temperature, and
$T_0$ = temperature of the unburnt mixture at some distance from the flame.

Crussard (8) gave a modified formula, introducing the rate of chemical reaction as a factor:

$$v = \sqrt{kF\frac{v_0}{c}\cdot\frac{T_0}{T_i}\cdot\frac{T_f - T_i}{T_i - T_0}}$$

in which $F$ = rate of reaction and $v_0$ = initial specific volume.

Nusselt (15) gave a somewhat similar formula, but the factor for reaction rate was represented by the concentrations of the reactants. For mixtures of hydrogen and air his equation was

$$v = \text{const.} \sqrt{k \cdot \frac{p_0 T_0^2}{c} \cdot \frac{T_f - T_i}{T_i - T_0} \cdot [\mathrm{H_2}][\mathrm{O_2}]}$$

in which $p_0$ = pressure and $[H_2]$, $[O_2]$ are the concentrations of hydrogen and oxygen.

Daniell (9) gave the formula

$$v = \sqrt{kF \cdot \frac{v_0}{c} \cdot \frac{T_0}{T_m} \cdot \frac{T_f - T_0}{T_i - T_0}}$$

in which $T_m$ is a (harmonic) mean temperature which is probably nearer to $T_f$ than to $T_i$.

All the foregoing formulas are based on the theory that flame is propagated by conduction of heat (except in the detonation wave) and all contain the independent variable $k$, the thermal conductivity of the mixture, either as $k$ or $\sqrt{k}$. Their validity can readily be tested, for it is easy to prepare series of mixtures which differ greatly in thermal conductivity and very little in any other property which affects the speed of flame. Such mixtures are those of an inflammable mixture with two or more of the inert gases, severally, in the same ratio. The speeds of uniform movement of flame in a series of mixtures of methane and atmospheres approximately $O_2 + 4A$ and $O_2 + 4He$ were measured some time ago; in mixtures of equal percentages of methane, the speeds with the helium atmospheres were somewhat higher than with the argon atmospheres, but not nearly in proportion to the thermal conductivities of the mixtures (7). Some hitherto unpublished observations of a similar character, in which the inflammable gas is hydrogen, are shown in figure 1 (12). Moreover, the various mixtures of hydrogen and oxygen propagate flame at speeds which are nearly equal for each pair of mixtures $2H_2 + O_2 + n(H_2 \text{ or } O_2)$, in spite of the great difference in thermal conductivity according as the one gas or the other is in excess (figure 2, drawn from results in reference 3).

The comparative measurements just quoted were made on the uniform movement of flame. This is an imperfect basis for comparison unless the areas of the flames are equal, because if, for example, the area of one were $n$ times the area of the other and the speeds of uniform movement were equal, the fundamental speed of the first would be but $1/n$ of that of the other. A series of comparative experiments in which the fundamental speeds of flame were measured has therefore been made (12), the results of which are shown in table 1.

Although the thermal conductivities of these mixtures at flame temperatures have not been measured, it must surely be that their ratio, or even the square root of their ratio, is much higher than the ratio of the fundamental speeds of flame. Hence the speed of propagation of flame is not correctly expressed by any of the formulas quoted.

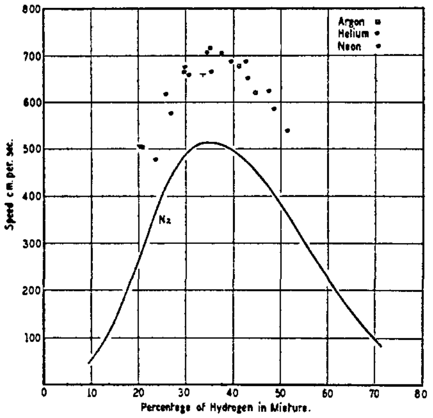

FIG. 1

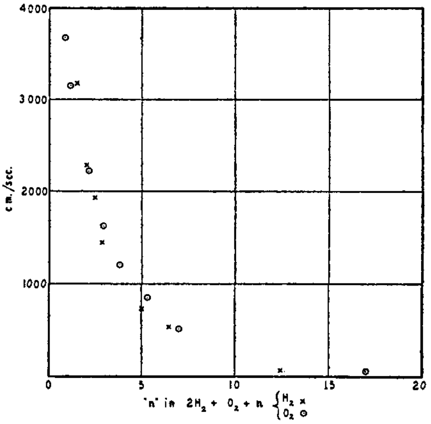

FIG. 2

FIG. 1. Speed of uniform movement of flame in mixtures of hydrogen with air (curve $N_2$) or air in which the nitrogen was replaced by an equal volume of argon or neon or helium. Observations in a tube having a diameter of 2.5 cm.

FIG. 2. Speed of uniform movement of flame in mixtures of hydrogen and oxygen. Observations in a tube having a diameter of 2.5 cm.

TABLE 1

*Speed of flame in a tube, 2.5 cm. in diameter, in mixtures of 10 per cent of methane with 90 per cent of an atmosphere containing argon or helium*

| COMPOSITION OF ATMOSPHERE | SHAPE OF FLAME FRONT | SPEED OF UNIFORM MOVEMENT | AREA OF FLAME FRONT | FUNDAMENTAL SPEED OF FLAME |
|---|---|---|---|---|
| *per cent* | | *cm. per second* | *cm.²* | *cm. per second* |
| Oxygen:20.9<br>Helium:79.1 | Symmetrical | 206 | 12.3 | 82 |
| Oxygen:20.9<br>Argon: 79.1 | Symmetrical | 138 | 11.4 | 59 |

The conclusion just reached does not mean that the propagation of flame is not governed by conduction of heat from the burning to the neighboring unburnt layer, for the slow factor in the succession of events may be the chemical reaction itself, and the speed of flame may measure mainly the speed of chemical reaction. Without making any attempt at finality we may now refer briefly to some of the outstanding experimental observations that must guide future theoretical developments.

1. The calorific value of the mixture mainly determines the relative speed of flame in a series of mixtures, in various proportions, of the same constituents. Figure 2 shows this; dilution of the mixture $2H_2 + O_2$ with equal quantities of hydrogen or oxygen caused the same reduction in the speed of "uniform movement" of flame.

The speeds of flame in a series of mixtures of various combustible gases, individually, and air reach a maximum at a composition somewhat on the rich side of the mixture of maximum calorific value. The displacement has been interpreted as an effect of mass action (16).

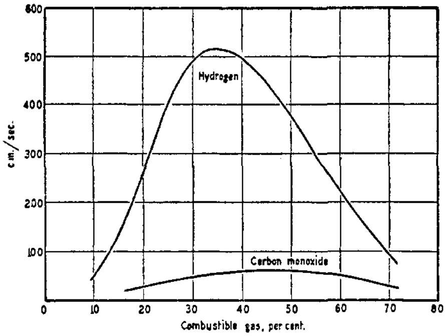

FIG. 3. Speed of uniform movement of flame in mixtures of hydrogen and air, and of carbon monoxide and air. Observations in a tube having a diameter of 2.5 cm.

2. The speeds of flame in various mixtures of equal calorific value may be greatly different; for example, the speeds of uniform movement of flame in mixtures of hydrogen and air on the one hand and carbon monoxide and air on the other, which are shown in figure 3. The differences are too great to be due to differences in thermal conductivity, and must be explained by differences in the rates of reaction or in the production of active radicals, or both.

3. Ignition temperatures, corresponding with the very short lags (in time) available in the propagation of flame, have not been determined except perhaps for mixtures of methane and air. It is, therefore, not yet possible to correlate ignition temperatures with the speeds of flame, but in any case an ignition temperature is a function of simpler properties, and so any connection discovered between ignition temperature and flame speed would only be one step towards a final solution of the problem.

4. The propagation of flame is obviously a continuous succession of ignitions of unburnt gas next to the flame front. It might therefore be expected that the most easily ignited mixtures would be those which would propagate flame most rapidly. This is not so, as the following table will show.

| | | |
|---|---|---|
| Mixture in which the speed of flame is a maximum | | 10 per cent methane |
| Most readily ignitible mixture | by heated silica surface | 5 to 6 per cent (14) |
| | by adiabatic compression | 7 to 7.5 per cent (10) |
| | by impulsive electric spark | 8.2 to 8.3 per cent (21) |
| | by the detonation of a solid explosive | 8.7 to 9.3 per cent (18) |

5. The relative rates of isothermal reaction of a series of mixtures at temperatures below those of ignition are not parallel to the speeds of flame in the same mixtures. Thus at 250–400°C. the most reactive mixtures of each of the simple paraffin hydrocarbons with oxygen are those containing hydrocarbon and oxygen in the molecular proportion 2:1 (2). Far from these mixtures giving the maximum speed of flame, none of them, at room temperature, can propagate flame.

6. There is evidence that, with hydrocarbons, the course of the chemical reactions is the same in flames as at lower temperatures (2, 1), but there exist various rival theories of these and other oxidations.

7. Of much significance is the smallness of the effect of large differences in thermal conductivity on the speed of certain flames, other conditions being the same. There must be a less steep temperature gradient in front of the flame in the mixtures of higher thermal conductivity, and preflame reaction must start correspondingly sooner. But the layer of gas just in front of the flame does not ignite any sooner. What is it waiting for? The indication is that the "bursting into flame" is a consequence of the arrival not so much of sufficient heat as of a sufficient concentration of active particles which, provided that they do not lose their activity to or share it with the inert gas, would diffuse at equal rates from the flame front of such mixtures as we are comparing (combustible + oxygen + argon or helium), whereas the diffusion rate of the heat would be different. Hence the active particles owe their efficiency, as propagators of flame, to their chemical nature rather than to their kinetic energy. The conclusion is, therefore, that they belong to some species of radical or atom.

If, however, such an interpretation is to be given to the equality of flame speeds for each pair of mixtures with equal values of $n$ in the series $2H_2 + O_2 + nH_2$ and $2H_2 + O_2 + nO_2$ (figure 2), then the concentration of active particles must be the same in each pair, whether the hydrogen or the oxygen be in excess. More direct evidence that this is so is to be sought.

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