

THEORY OF FLAME PROPAGATION¹

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The purpose of this paper is to discuss the mechanism of the propagation of flame through a combustible mixture relative to the unburnt gas. This rate of flame propagation is sometimes referred to as the fundamental speed of flame or transformation velocity or burning velocity. The considerations will be confined to burning velocities that are far below the velocity of sound, as distinct from detonations that travel with speeds greater than the velocity of sound. The problem of the burning velocity is obviously very complex, the process of flame propagation being dependent on heat flow, on diffusion of many species, particularly active ones such as atoms and radicals, and on kinetics of complex reactions. Therefore at present any theory must necessarily involve hypotheses and approximations.

The study of chemical kinetics is a comparatively recent development. It was natural, therefore, that in the first attempts (10) the problem should have been regarded as one involving primarily the conduction of heat from the burnt to the unburnt gas. To illustrate, let us consider the reaction zone stationary with respect to the coördinate system $x-T$ in figure 1. The unburnt gas at the temperature T_u moves in the direction of the arrow against the heat flow along the temperature gradient between the final temperature T_b (after complete combustion) and T_u . When its temperature has risen to the ignition temperature T_{ig} , reaction commences and continues until T_b is established. Taken as it is, no serious objections could be raised against this picture even today, provided the proper limitation is placed on the interpretation of T_{ig} . It was widely supposed that

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this temperature was something of the nature of a physical constant of the gas mixture that could be determined in independent experiments. As was perhaps evident in the first section of this symposium on the kinetics of ignition, the ignition temperature is not a physical constant of the gas mixture but is a function of the system as a whole in which ignition occurs and of time (ignition lag). For the case of flame movement it is almost certain that no experiment could be performed that would ensure conditions that simulate those that define T_{ig} . This is quite apart from the consideration that T_{ig} , even according to older views of reaction kinetics, would not be a sharply defined temperature but would comprise a certain, possibly small, temperature range within which the reaction becomes so fast that during the further travel of a gas element from T_{ig} to T_b the percentage of heat evolution is commensurate with the percentage of distance traveled.

Several attempts have been made to derive an expression for the burning velocity from the foregoing picture. While such derivations cannot lead

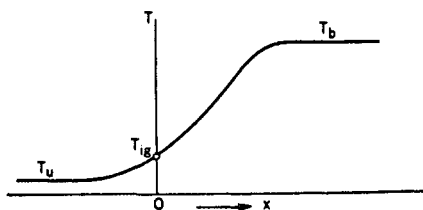


FIG. 1

to a quantitative description, owing to uncertainties in the conception of T_{ig} and the general lack of knowledge of the reaction rate, they lead to some qualitative conclusions that are not without interest. For this purpose a crude mathematical development will suffice.

The zero point of the x -axis is placed at the point where the temperature of the gas has risen to T_{ig} . Consider a stream of combustible mixture of unit area cross section. The unburnt gas at this point is receiving per unit time an amount of thermal energy (required for ignition)

$$H_{ig} = S_u \rho_u \bar{c}_p (T_{ig} - T_u) \quad (1)$$

where S_u is the burning velocity, ρ_u the density of the unburnt gas, \bar{c}_p the average specific heat of the mixture at constant pressure, T_{ig} the ignition temperature, and T_u the temperature of the unburnt gas.

Since this heat is transferred by conduction it must be equal to

$$H_{ig} = \mu \left(\frac{dT}{dx} \right)_{x=0} \quad (2)$$

where μ is the coefficient of heat conductivity. If it is assumed as a first approximation that $\left(\frac{dT}{dx}\right)_{x=0}$ is proportional to $T_b - T_{ig}$, i.e., the temperature gradient between T_b and T_{ig} is substantially linear, then

$$H_{ig} = \mu(T_b - T_{ig}) \frac{1}{x_b} \quad (3)$$

x_b represents the thickness of the reaction zone between T_{ig} and T_b and is a function of the reaction rate. It becomes smaller the faster the reaction.

Combining equations 1 and 3 one obtains

$$S_u = \frac{\mu}{\rho_u \bar{c}_p} \frac{T_b - T_{ig}}{T_{ig} - T_u} \frac{1}{x_b} \quad (4)$$

This is substantially the equation originally proposed by Mallard and Le Chatelier (10).

Equation 4 predicts the existence of limits of inflammability. With sufficiently lean or rich mixtures T_b will decrease, and, although T_{ig} is presumably a complicated function of mixture composition and other factors, it is evident that $T_b - T_{ig}$ must vanish while $T_{ig} - T_u$ remains positive and finite. If in lean mixtures the nitrogen of the air is replaced by oxygen, \bar{c}_p , μ , and T_b will not change very much. Neither will the diffusion characteristics of the mixture and the reaction velocity change very much, so that it is not unreasonable to consider T_{ig} and x_b substantially unchanged. Thus it can be understood that the lower limit of inflammability is little different in air and in oxygen, as was also pointed out by Jost (5) and as table 1 shows.

For the same reason it is understandable that in sufficiently lean mixtures the substitution of oxygen for nitrogen has little effect on the burning velocity. This is shown in table 2.

If T_{ig} is reasonably constant over a range of mixture composition near the stoichiometric, the ratio $\frac{T_b - T_{ig}}{T_{ig} - T_u}$ goes through a maximum for the maximum T_b ; furthermore, x_b presumably goes through a minimum at the maximum T_b . Therefore one can understand the near coincidence of the maximum burning velocity mixture and the maximum flame temperature mixture, both being slightly on the rich side.

The nature of an inert component of the gas mixture will affect principally \bar{c}_p , μ , and T_b . If nitrogen is replaced by carbon dioxide, whose specific heat is larger and heat conductivity smaller, the burning velocity should decrease. This is found experimentally (4). If nitrogen is replaced by argon, whose specific heat is much lower, the burning velocity should increase, which is confirmed experimentally (13). Replacing the

argon by helium increases the burning velocity still further (3, 8), which is in qualitative agreement with the larger heat conductivity of helium.² The data show, however, that the increase in burning velocity is by no means as large as the increase in the heat conductivity of the mixture. Therefore one would have to postulate a higher T_{ig} or larger x_b or both in

TABLE 1

Lower limits of inflammability of combustibles in air and oxygen under comparable conditions (1)

COMBUSTIBLE	LOWER LIMIT	
	In air	In oxygen
Hydrogen.....	9.4	9 to 10
Carbon monoxide.....	16.3	16.7
Methane.....	6.1	6.4
Ethylene.....	3.13	3.1
Propylene.....	2.00	2.10
Acetylene.....	3.45	3.1
Diethyl ether.....	1.85	2.10
Divinyl ether.....	1.70	1.85
Cyclopropane.....	2.40	2.45

TABLE 2

Burning velocities of combustibles in mixtures of oxygen and nitrogen (4)

MIXTURES	BURNING VELOCITY	
	cm. per second	
30% of (97.15% CO + 1.5% H ₂ + 1.35% H ₂ O).....	{ in (70% N ₂ + 30% O ₂)	31
	{ in (60% N ₂ + 40% O ₂)	34
	{ in (40% N ₂ + 60% O ₂)	37
	{ in (1.5% N ₂ + 98.5% O ₂)	39
30% H ₂	{ in (60% N ₂ + 40% O ₂)	240
	{ in (50% N ₂ + 50% O ₂)	250
	{ in (30% N ₂ + 70% O ₂)	260
	{ in (1.5% N ₂ + 98.5% O ₂)	300
10% CH ₄	{ in (60% N ₂ + 40% O ₂)	60
	{ in (1.5% N ₂ + 98.5% O ₂)	75

helium mixtures. This is not unreasonable from kinetic experience, since T_{ig} would be higher the lower the local concentration of chain carriers, that is, the larger the diffusion coefficient of the mixture. For the same reason the reaction velocity in any layer dx would be retarded and the

² See also Jost (5) for such comparisons.

thickness of the flame front increased. Thus one begins to recognize the importance of diffusion phenomena in the flame front.

Equation 4 can be derived in a different way. The differential equation expressing that in any layer dx of the stationary reaction zone the rate of change of temperature is zero, is given by

$$\mu \frac{\partial^2 T}{\partial x^2} - \bar{c}_p \rho_u S_u \frac{\partial T}{\partial x} + \frac{\partial H}{\partial t} = 0 \quad (5)$$

The terms in this equation represent the rate of change of thermal energy due to conduction, mass flow, and chemical reaction, respectively. According to the approximation of Mallard and Le Chatelier, $\frac{\partial T}{\partial x}$ is a constant between 0 and x_b , and since $\frac{\partial H}{\partial t} = 0$ for $x < 0$, equation 5 is easily integrated to give equation 4.

The Mallard-Le Chatelier equation is sometimes given in another form. The rate of heat liberation for constant $\frac{\partial T}{\partial x}$ between 0 and x_b is, from equation 5,

$$\frac{\partial H}{\partial t} = \rho_u S_u \bar{c}_p \frac{(T_b - T_{i_0})}{x_b} \quad (6)$$

If f denotes the reaction rate, defined as the mass of gas that is reacting in the time dt as the gas passes through the layer dx , then

$$\frac{\partial H}{\partial t} = f \bar{c}_p (T_b - T_u) \quad (7)$$

Combining equations 6 and 7 and eliminating x_b in equation 4, one obtains

$$S_u^2 = \frac{\mu}{\rho_u^2 \bar{c}_p} \frac{T_b - T_u}{T_{i_0} - T_u} f \quad (8)$$

For the purpose of drawing qualitative conclusions this form has little advantage over the original Mallard and Le Chatelier equation.

Further refinements of the treatment were made by Jouguet (6), Nusselt (11), and Daniell (2). In these treatments the temperature gradient between T_b and T_{i_0} and the reaction rate were considered to vary along the x -axis. It will be noted from equation 5 that the assumption of some temperature distribution along the x -axis automatically fixes the rate of heat liberation, and thus, after introduction of the proper boundary conditions, allows a solution of the problem; this was the procedure chosen by Mallard and Le Chatelier. On the other hand, an assumption concerning the rate of heat liberation along the x -axis does not alone determine the

temperature distribution. The refinements mentioned consist of introducing some assumption concerning the progress of the reaction along the x -axis. In order to solve the problem, another equation must be introduced. Since the mass of gas that enters the reaction zone in unit time equals the mass of gas that undergoes chemical reaction within the zone in unit time, this is easily found to be

$$\rho_u S_u = \frac{1}{c_p(T_b - T_{ig})} \int_{T_{ig}}^{T_b} \frac{\partial H}{\partial t} \frac{dx}{dT} dT \quad (9)$$

Considering the extreme difficulty of proposing a satisfactory hypothesis concerning the progress of the reaction along the x -axis, it is evident that these investigations could not have led any further than the Mallard-Le Chatelier treatment. Little has been gained by these attempts beyond a more fully developed mathematical formalism. The incorporation of the cooling effect of the walls in Daniell's treatment of the propagation of flame in tubes may be noted, which demonstrates the existence of a lower critical diameter below which propagation is impossible.

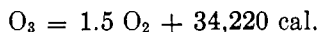
The weakness in all of the above treatments is the concept of ignition temperature as a true physical constant of the gas mixture. In any attempt to develop the theory beyond the stage in which it was left by Mallard and Le Chatelier, it would seem appropriate also to eliminate ignition temperature as an assumed given quantity. In view of the development of reaction kinetics, one must assume that the layer in the unburnt gas in which the reaction becomes fast will be determined not only by a temperature condition but to a large degree by the concentration of active particles or chain carriers. The reaction zone itself may be considered to be abnormally rich in active particles which must diffuse in both directions, toward the burnt and the unburnt gases. The combined effect of diffusion of active particles and heat flow will carry the reaction zone forward into the unburnt gas. It is at once evident that the problem has become considerably more complicated, and it is only by daring approximations that a solution along these lines is at all possible.

One may leave the problem thus unsolved mathematically or attempt a solution with the introduction of approximations. It has, however, become sufficiently clear that diffusion plays an important rôle in the propagation of flame and that this diffusion concerns the migration of chain carriers into the unburnt gas where it renders the latter reactive. A solution has been attempted here, and the results will be given for a particular case.

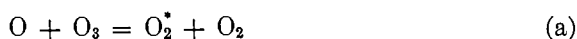
In order to overcome the difficulties inherent in the simultaneous treatment of heat conduction and diffusion, Lewis and von Elbe (9) proposed the following hypothesis. The sum of thermal and chemical energy per unit

mass in any layer dx between the unburnt and burnt gases is sensibly constant. To consider the consequences of this hypothesis, it will be noted that the chemical energy in the unburnt gas at the temperature T_u is equal to the thermal energy needed to raise the temperature of the burnt gas from T_u to T_b , neglecting the generally inappreciable loss due to radiation. Any layer of gas between the unburnt and burnt gases if allowed to complete its reaction adiabatically would acquire a temperature T_b . The hypothesis may be understood to be based on the following considerations. Since thermal energy flows from the burnt to the unburnt side and chemical energy predominantly in the opposite direction, there is a tendency to equalize deviations from the average total energy content. There will, of course, be an excess of energy in the unburnt gas, formerly denoted by H_{ig} ; this energy "hump" is conceivably much smaller than would correspond to earlier ideas concerning ignition temperature values. The latter may be very low, owing to the presence of active particles which, of course, represent a form of chemical energy imparted to the unburnt gas in excess of its original chemical energy content. However, owing to the property of active particles to promote a reaction efficiently, this excess energy is conceivably very small and the energy hump on the unburnt side is therefore flat.

This hypothesis allows one to confine the analysis to the flow of chemical energy which is transported through the reaction zone by mass flow. Lewis and von Elbe have attempted to develop a theory of the propagation of flames traveling through ozone-oxygen mixtures, the decomposition of ozone being a reaction of comparative simplicity. The overall reaction



is presumed to proceed by the following steps:



where O_2^* is an energy-rich molecule. One should also take into consideration the reaction



It will be necessary to simplify this mechanism further. It will be assumed that both reactions b and c proceed fast compared to reaction a, so that thermodynamic equilibrium between O and O_3 is sensibly established in any layer. This assumption will be in error, particularly on the unburnt side where the concentration of oxygen atoms which have arrived by diffusion will exceed the equilibrium concentration. At higher temperatures, that is, toward the burnt side, it is quite possible that the assumption is not

very much in error. Therefore, we shall consider the mechanism to consist only of reaction a and reaction d,



Denoting by N_{O} , N_{O_2} , etc. the number per cubic centimeter of the atoms or molecules indicated by the subscripts, the relation

$$\frac{N_{\text{O}} N_{\text{O}_2}}{N_{\text{O}_3}} = K \quad (10)$$

is thus assumed to hold in any elementary layer dx . K is the equilibrium constant and is a function of temperature. According to published data (7)

$$K = 3.03 \times 10^9 \frac{N_{\text{O}_2(b)}}{P} \frac{T_b}{T} e^{-12,300/T} \quad (11)$$

where P is the pressure in millimeters of mercury and $N_{\text{O}_2(b)}$ is the number of molecules in 1 cc. at the end of the reaction zone, namely where the temperature is T_b .

The hypothesis that the sum of thermal and chemical energy per unit mass is constant in any layer within the reaction zone may be expressed by the equation

$$N_{\text{O}_3} E_{\text{O}_3(T)} + N_{\text{O}} E_{\text{O}(T)} = (N_{\text{O}_2} + 1.5 N_{\text{O}} + 0.5 N_{\text{O}}) C_{p,T}^{T_b} (T_b - T) \quad (12)$$

where $E_{\text{O}_3(T)}$ is the heat of decomposition of 1 mole of ozone at the temperature T ; $E_{\text{O}(T)}$ is the heat of recombination of 1 mole of oxygen atoms at the temperature T and is approximately equal to 59,000 cal.; $C_{p,T}^{T_b}$ is the mean molar heat capacity of oxygen at constant pressure between the temperatures indicated.

Since the burning velocity is small compared to sound velocity, the pressure will be practically constant throughout the reaction zone, and one obtains from the gas law

$$N_{\text{O}_2} + N_{\text{O}_3} + N_{\text{O}} = N_{\text{O}_2(b)} \frac{T_b}{T} \quad (13)$$

Since the mixtures whose experimental burning velocities will be compared with the theory contain considerably more oxygen than ozone, no serious error is introduced by the approximation

$$N_{\text{O}_2} \simeq N_{\text{O}_2(b)} \frac{T_b}{T} \quad (14)$$

This approximation is particularly allowable at intermediate and higher temperatures because the concentrations of O_3 and O that are required to fulfill equation 12 become very small.

From the concentration of O_2 in any layer, the concentrations of O_3 and O and the temperature T in the layer are determined by the foregoing system of equations. The condition for the stationary state is now simply that the rate of change of concentration of O_2 in any layer due to diffusion, mass flow, and chemical reaction is zero. This leads to

$$D \frac{\partial^2 N_{O_2}}{\partial x^2} - \frac{\partial}{\partial x} (N_{O_2} S_x) + \left(\frac{\partial N_{O_2}}{\partial t} \right)_c = 0 \quad (15)$$

D is the diffusion coefficient. Since the O_2 concentration decreases with increasing temperature (equation 14) and the positive direction of the x -axis is the direction of increasing temperature, the sign of the diffusion term is positive. S_x is the flow velocity through any layer x . Since the percentage of O_2 in the mixture increases in the direction of unburnt to burnt gas, more oxygen molecules are pushed out of the layer dx than are pushed in by mass flow. The second term is therefore negative. The third term is the rate of formation of oxygen molecules by chemical reaction.

S_x can also be interpreted to mean the volume of gas passing unit area per second. Since all volumes S_x contain equal masses, then from the gas law and the increased number of moles due to reaction

$$S_x = S_u \frac{T}{T_u} \frac{1 + 0.5a + m}{1 + m} \quad (16)$$

where m is the ratio of moles of O_2 to moles of O_3 in the original mixture, and $0 \leq a \leq 1$. However, in conformity with the approximations made in equation 14, it is essentially correct, especially for intermediate and higher temperatures, to write

$$S_x = S_u \frac{T}{T_u} \quad (17)$$

The diffusion coefficient is given by

$$D = \frac{\bar{v}\lambda}{3} \quad (18)$$

where \bar{v} is the average molecular velocity and λ the mean free path. For this purpose the gas may be considered to consist entirely of oxygen molecules. Using numerical values (14)

$$D = 2.2 \times 10^{-2} \frac{T^{3/2}}{P} \quad (19)$$

The rate of formation of O_2 by the chemical reaction is given by the number of successful collisions between O and O_3 per second per cubic centimeter, viz.,

$$\left(\frac{\partial N_{O_2}}{\partial t}\right)_c = 2Ze^{-E/RT} \quad (20)$$

where Z is the collision frequency which is given by

$$Z = 2N_O N_{O_3} \sigma_{O, O_3}^2 \left(2\pi RT \frac{M_O + M_{O_3}}{M_O M_{O_3}}\right)^{1/2} \quad (21)$$

where M_O and M_{O_3} are the molecular weights of O and O_3 . E is the energy of activation, the best available value being about 6000 cal. per mole (12, 15).

TABLE 3

Comparison of calculated and experimental burning velocities of ozone-oxygen mixtures

P	T_u	T_b	m	S_u	
				Experimental	Calculated
<i>mm. Hg</i>	$^{\circ}K.$	$^{\circ}K.$		<i>cm. per second</i>	<i>cm. per second</i>
624	300	1239	3.054	55	253
2560	427	1343	3.054	158	451
595	302	1922	1.016	160	333
3760	468	2044	1.016	747	664

It will be recalled that in equation 5 the choice of a function for $\frac{\partial H}{\partial t}$ did not suffice to arrive at a solution until equation 9 was introduced. Similarly, in the present case, it is necessary to introduce an equation analogous to equation 9, which may be written

$$S_u N_{O_3(u)} = \frac{1}{1.5} \int_{T_u}^{T_b} \left(\frac{\partial N_{O_2}}{\partial t}\right)_c \frac{dx}{dT} dT \quad (22)$$

where $N_{O_3(u)}$ is the concentration of O_3 in the unburnt gas. All equations necessary for the solution of the problem have now been given.

The mathematical development of the equations was carried out by Lewis and von Elbe (9) and calculations of burning velocities were made for certain mixtures for which experimental values were available. The results are given in table 3.

An agreement exists in the order of magnitude, which, considering the assumptions that had to be introduced, would not seem to be unsatisfactory. This indicates that an analysis of the structure of the

reaction zone by the foregoing theory would also lead to agreement in the order of magnitude in the temperature and concentration gradients. Such an analysis is given in figure 2. It is seen that the thickness of the flame front is of the order of 10^{-3} to 10^{-4} cm. The distributions of the reaction rate and of the concentration of the chain carriers (oxygen atoms) are of interest. The latter are seen to reach a high local concentration in a zone of a thickness of the order of one hundred mean free paths. One may perhaps generalize this result by stating that high concentrations of chain carriers are needed in order to produce the fast chemical reaction required for the propagation of flames.

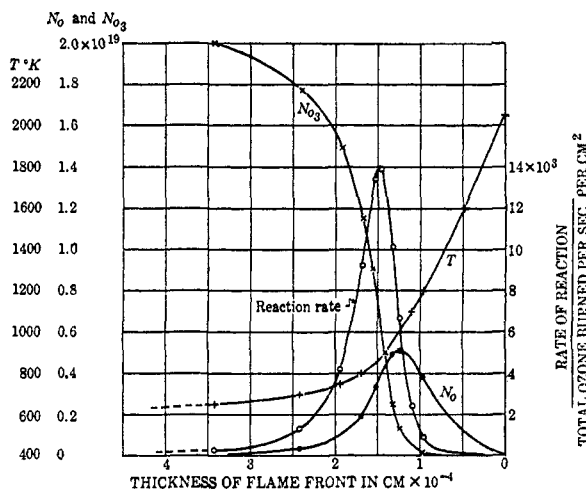


FIG. 2. Structure of reaction zone of ozone flame, showing temperature gradient, distribution of ozone and oxygen atoms, and the reaction rate throughout the zone. 49.6 per cent ozone in oxygen; pressure = 3760 mm. Hg; $T_u = 468^\circ\text{K}$.; $T_b = 2044^\circ\text{K}$.

Substances that accelerate or retard chemical reaction must also exert a similar influence on the burning velocity. The area under the rate curve in figure 2 would be either increased or decreased. Since the activation energy is of less importance at high temperatures, one may suggest that the increase or decrease of the area occurs mainly on the low-temperature side of the rate curve.

SUMMARY

In Mallard and Le Chatelier's treatment of flame propagation the problem is considered simply one of heat flow in which the unburnt gas is raised to its ignition temperature. Although crude, this treatment is able to explain a number of observations: limits of inflammability, effect of

diluent gases on the latter and on rate of flame propagation, and near coincidence of maximum flame temperature mixture and maximum speed mixture. Later elaborations of Mallard and Le Chatelier's treatment have not advanced the problem appreciably, owing to the indefiniteness of the term "ignition temperature." Certain observations show the importance of diffusion in the treatment of flame propagation. A solution of the problem without the use of ignition temperature has been attempted for the propagation of ozone-oxygen flames, using simplifying assumptions concerning the reaction mechanism and the combined effects of heat flow and diffusion. Agreement in the order of magnitude is found between calculated flame speeds and experimental values. In the flame front there is a steep temperature gradient and also a high local concentration of active species. The width of the flame front is calculated to be of the order of 10^{-3} cm. Some consideration is given to the effect of activators and inhibitors on flame speed.

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