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On the Theory of Flame Propagation[1]

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A new theory of flame propagation in slow inflammation is proposed which considers that the highly energized atoms or radicals formed in the flame front play a more important rôle than heat conductivity in bringing the unburned gas to the reacting state. A small number of atoms or radicals diffuse over into the unburned phase, there initiating the chemical reaction. This and other considerations allow one to propose that the sum of thermal and chemical energy per unit mass of gas in all layers from the burned phase to the unburned phase is constant. The fundamental equation for the velocity V of the flame is derived simply from the fact that the number of molecules of combustible gas entering the reaction zone (flame front) in unit time equals the number reacting in the zone in the same time. If the flame front extends from xu to xb and the unburned gas enters it at a rate just sufficient to maintain the flame front stationary, then for 1 $\overline{\text{cm}}^2$ cross section the equation reads:

$$VN_{c(u)} = \int_{Tu}^{Tb} -\frac{\partial Nc}{\partial t}\frac{dx}{dT}\,dT$$

where V is the flame speed which is identical with the volume of unburned gaseous mixture (under initial conditions) entering the reaction zone per sec.; $N_{c(u)}$ is the concentration of combustible gas in molecules/cc in the unburned phase; and Tb and Tu are temperatures of the completely burned and unburned gases at xb and xu, respectively. This equation, in addition to the postulates that the sum of thermal and chemical energy per unit mass remains constant and that the rate of change of concentration of the various gas constituents in an elementary layer due to mass flow, diffusion and chemical reaction is zero, allows a solution of the problem. The theory is applied to explosions of mixtures of ozone gas and oxygen. Ozone decomposes to oxygen, with evolution of heat. With the help of the postulate that the total energy per unit mass is constant, the terms $\partial Nc/\partial t$ and dx/dT can be expressed as functions of temperature alone, and the above equation can be solved. In view of certain simplifications the calculated velocities are considered to be in satisfactory agreement with the experimental velocities. *The theory furnishes knowledge of the structure of the flame front.* A particular explosion is analyzed. The width of its flame front is shown to be about 10^{-3} cm. The temperature distribution, the distribution of the concentrations of various molecular and atomic species, and the rate of reaction throughout the flame front are given. The authors add an appendix, which includes a critical analysis of the essential differences between the present theory and previous theories of other investigators.

THERE are two general types of flame movement through mixtures of combustible gases. One is known as slow combustion or inflammation and moves with speeds of the order 10^2 to 10^3 cm per second, while the other is the phenomenon of the detonation wave, which travels with speeds of the order 10^5 cm per second. Treatments of the latter which account for the high velocities are to be found in the hydrodynamic theory of Chapman[4] and Jouguet,[5] and the chain-reaction theory of Lewis.[6]

The phenomenon of inflammation, with which the present paper is concerned, has been treated by several investigators[7] on the assumption that before any reaction occurs the unburned gas preceding the flame front is raised to its *"ignition temperature"* by heat conduction from the burning gases. In the light of modern chemistry we believe this conception is inadequate, since it omits all consideration of the rôle played by the active atoms and radicals known to exist in the flame front. It is quite conceivable that flame

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[4] Chapman, Phil. Mag. **47**, 90 (1899).

[5] Jouguet, J. de Mathématique 347 (1905); 6 (1906). *Mécanique des Explosifs*, Paris, 1917.

[6] Lewis, J. Am. Chem. Soc. **52**, 3120 (1930).

[7] Mallard and LeChatelier, Ann. de Mines 4, 274 (1883). (See also Mason and Wheeler, J. Chem. Soc. (London) **111**, 1044 (1917).)

Jouguet, Compt. Rend. **156**, 872 (1913); **179**, 454 (1924); *Mécanique des Explosifs*, Paris, 1917.

Jouguet and Crussard, ibid. **168**, 820 (1919).

Nusselt, Z. des Vereins Deutscher Ingenieure **59**, 872 (1915).

Daniell, Proc. Roy. Soc. **A126**, 393 (1930).

propagation is governed by diffusion of these active radicals into the unburned mixture, which gives rise to chemical reaction there in a far more efficient way than would be possible purely by heat transfer. An enormous amount of experimentation[8] in reaction kinetics, especially in recent years, has shown that chemical reaction can be initiated at ordinary temperatures by introducing a few active radicals into a gas which ordinarily would require the attainment of higher temperatures to initiate combustion. The question may therefore be raised as to the utility of the conception of ignition temperature in the neighborhood of the flame front, with its high concentration of active radicals.

By the earlier heat-conductivity theory, thermal energy is conducted into the layer of unburned gas which already contains its original thermal plus chemical energy per unit mass. This introduces an energy "hump" into the unburned phase adjacent to the flame front.

The theory of flame propagation outlined in this paper allows one to conceive that reaction is initiated in the unburned phase by a relatively small number of active atoms or radicals and that the reaction is initiated faster than could be accomplished by heat transfer in a similar period of time. In this way, the energy "hump" reduces to a minimum and tends to disappear. This leads us to the working hypothesis of the present theory, namely, that the sum of thermal and chemical energy per unit mass in any elementary layer between the unburned and the burned phases remains sensibly constant. This is a very useful relationship. Since the thermal energy per unit mass in any elementary layer is determined by the existing temperature, the corresponding available chemical energy per unit mass in the same layer is fixed and may also be expressed as a function of thermal data alone. Since the chemical energy depends upon the concentration of the reactive gases the concentration distribution throughout the reaction zone is determined by the temperature gradient dT/dx. The latter, therefore, re-

mains the only independent variable along the x axis.

DEVELOPMENT OF EQUATIONS AND APPLICATION TO EXPLOSIONS IN GASEOUS OZONE-OXYGEN MIXTURES

We have developed equations which conform to the conception outlined above and have applied them to the calculation of flame speeds in mixtures of ozone and oxygen for which experimental data are available.[9]

Mixtures of gaseous ozone with inert gases explode when ignited. The resulting flame travels with a definite speed, depending upon the conditions of composition, temperature, and pressure. Such explosions are especially suitable for testing the theory because the net chemical reaction involved is of the simplest type possible in nature, namely,

$$O_3(\text{gas}) = 1\tfrac{1}{2}O_2 + 34{,}220 \text{ calories.}$$
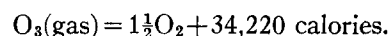
One has no direct knowledge of the intermediate chain mechanism of the reaction. However, the possibilities are very few, and there is rather general agreement among recent investigators that the chief reactions involved are

(a) $O_3 \rightleftharpoons O_2 + O$,

(b) $O + O_3 = 2O_2$.

The relation for the velocity of the flame is derived simply from the fact that the number of molecules of ozone gas entering the reaction zone per unit time equals the number of molecules of ozone reacting in unit time in this zone. The width of the zone extends from xu to xb. The unburned gas enters the zone at the point xu (this direction being positive) with such velocity that the flame front remains stationary. Consider a cross section of 1 $\overline{\text{cm}}^2$; then, since $1O_3$ gives rise to $1.5O_2$,

$$VN_{O_3}(u) = \int_{xu}^{xb} \frac{1}{1.5}\left(\frac{\partial N_{O_2}}{\partial t}\right)_c dx, \qquad (1a)$$

where V is the flame speed sought, which is identical with the volume of unburned gaseous mixture (under initial conditions) entering the reaction zone per sec. at point xu.

$N_{O_3}(u)$ is the initial ozone concentration, in

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[8] For example, the phenomenon of photo-explosions at ordinary or slightly elevated temperatures and the effect of the introduction of atoms and other reactive species into combustible mixtures.

[9] Lewis and von Elbe, J. Chem. Phys. 2, 283 (1934).

molecules per cc, at the temperature Tu and pressure of the unburned gas.

$(\partial No_2/\partial t)_c$ is the rate of formation of oxygen in molecules per cc per sec.

The integral is taken over all elementary volumes dx.

In general, subscripts u and b denote unburned and burned states, respectively.

Since the temperature rises from Tu at xu to the final temperature Tb at xb Eq. (1a) may be rewritten:

$$VNo_3(u) = \int_{Tu}^{Tb} \frac{1}{1.5}\left(\frac{\partial No_2}{\partial t}\right)_c \frac{dx}{dT}dT. \quad (1)$$

Obviously, $(\partial No_2/\partial t)_c$ and dx/dT are functions of the concentrations of O_2, O and O_3, and now the task is to express both these terms as functions of temperature alone.

To maintain a steady state, the rate of change of concentration of each component in an elementary layer at any point x must be zero. The concentration of each component is determined by the mass flow, diffusion and chemical reaction in the elementary layer. In the following, the indices V, D and c denote mass flow, diffusion, and chemical reaction, respectively, of the three components O_2, O and O_3.

The following three equations may therefore be written:

$$\left(\frac{\partial No_2}{\partial t}\right)_V + \left(\frac{\partial No_2}{\partial t}\right)_D + \left(\frac{\partial No_2}{\partial t}\right)_c = 0 \quad (2)$$

$$\left(\frac{\partial No}{\partial t}\right)_V + \left(\frac{\partial No}{\partial t}\right)_D + \left(\frac{\partial No}{\partial t}\right)_c = 0 \quad (3)$$

$$\left(\frac{\partial No_3}{\partial t}\right)_V + \left(\frac{\partial No_3}{\partial t}\right)_D + \left(\frac{\partial No_3}{\partial t}\right)_c = 0. \quad (4)$$

The first terms of Eqs. (2), (3) and (4) are functions of concentration and Vx, where Vx is a volume of gas pushed through the layer at x in unit time by mass flow in the direction of the burned phase. Obviously, for xu, Vx becomes V in Eq. (1). The second terms in Eqs. (2), (3) and (4) are functions of the concentration gradient and Dx, where Dx is the diffusion coefficient corresponding to the layer at x.

Eqs. (1) to (4) contain, therefore, six variables dx/dT, Vx, Dx, No_2, No_3, and No. To express

Eq. (1) as a function of temperature alone, two more equations are required.

The fifth equation is given by the gas law:

$$No_2 + No_3 + No = No_2(b)Tb/T \quad (5)$$

where $No_2(b)$ is the number of oxygen molecules in 1 cc at the end of the reaction zone, namely, where $T = Tb$. Thermal dissociation of oxygen in the completely burned gas is neglected, and therefore the burned phase consists of oxygen molecules only.

The sixth equation is derived from the fundamental hypothesis that the total thermal and chemical energy per unit mass in any elementary layer is constant. (See Appendix for further discussion.) It follows that the chemical energy still available in any layer at temperature T would be just sufficient, if released, to raise the temperature of the gases in the layer from T to Tb. Thus,

$$E_{O_3T}No_3 + E_{OT}No$$
$$= (No_2 + 1.5No_3 + 0.5No)C_{pT}{}^{Tb}(Tb - T) \quad (6)$$

where $C_{pT}{}^{Tb}$ is the mean molar heat capacity of O_2 at constant pressure between the temperatures indicated; E_{O_3T} is the heat of decomposition of 1 mol of ozone at the temperature T, and E_{OT} is the heat of recombination of 1 mol of oxygen atoms at the temperature T.

We shall not attempt an exact solution of the above six equations. In the first place, we have no knowledge of the problem of diffusion of three gases into each other; and, in the second place, information regarding the rate of reversible reaction (a) is not available. We propose to approximate the entire solution by introducing certain simplifications. In the diffusion term of Eq. (2) we shall employ the following equation for the diffusion coefficient D

$$D = \Omega_{O_2}\lambda_{O_2}/3, \quad (7)$$

where Ω_{O_2} is the average velocity of the oxygen molecules at temperature T, and λ_{O_2} is the mean free path in a gas consisting of oxygen molecules. We believe this approximation introduces only secondary changes in the final result.

Furthermore, the third terms in Eqs. (2), (3) and (4) and also the term $(\partial No_2/\partial t)_c$ in Eq. (1) are really each composed of three parts. The first and second parts represent the rates of the reversible reaction (a) and the third part the

rate of the reaction (b). As mentioned above, no kinetic data are available for the first two parts, while the third part can be evaluated easily from the collision frequency and the heat of activation. To dissolve this difficulty, we shall assume that the equilibrium represented by Eq. (a) exists throughout the reaction zone. It is realized that this condition is not fulfilled at lower temperatures near the unburned side of the flame front, but as the temperature increases toward the burned side it approximates actual conditions more and more. The assumption becomes more nearly true for the higher temperature explosions. This approximation, which will tend to increase the calculated flame speeds, introduces perhaps the most serious error into the calculations and will receive further discussion later.

By introducing Eq. (7) for the diffusion coefficient and the condition of equilibrium, namely,

$$K_c = N_O N_{O_2}/N_{O_3}, \tag{8}$$

one may dispense with Eqs. (3) and (4). K_c is the equilibrium constant when the concentrations are measured in molecules per cc.

Using Tolman's[10] numerical factor for Ω_{O_2} and placing $\sigma_{O_2} = 3 \times 10^{-8}$ cm, one obtains

$$D = \frac{14,500 T^{\frac{1}{2}} (1/M_{O_2})^{\frac{1}{2}} \times 0.707}{3\pi \times (3 \times 10^{-8})^2 \times N_{O_2}(b) T b/T}, \tag{9}$$

$$N_{O_2}(b) = 2.71 \times 10^{19} (273/Tb)(P/760), \tag{10}$$

where P is the total pressure in mm Hg.

$$N_{O_2}(b) Tb/T = 2.71 \times 10^{19} (273/T)(P/760) \tag{11}$$

and

$$D = \frac{2.2 \times 10^{-2} T^{\frac{3}{2}}}{P}. \tag{12}$$

K_c is evaluated as follows:

$$K_p = \frac{p_O p_{O_2}}{p_{O_3}}, \tag{13}$$

where p_O, p_{O_2}, and p_{O_3} are the partial pressures of the constituent gases.

Since

$$p_O = \frac{P N_O}{N_{O_2}(b) Tb/T}; \quad p_{O_2} = \frac{P N_{O_2}}{N_{O_2}(b) Tb/T};$$

$$p_{O_3} = \frac{P N_{O_3}}{N_{O_2}(b) Tb/T} \tag{14}$$

$$K_c = (K_p/P) N_{O_2}(b) Tb/T. \tag{15}$$

Furthermore, $\log K_p$ obeys the equation

$$\log K_p = -\Delta H_T/4.573 T + \text{constant}, \tag{16}$$

where ΔH_T is the heat of the reaction $O + O_2 = O_3$ at temperature T and constant pressure and has a mean numerical value of 24,400 calories. From the data of Kassel,[11] the constant is 9.48 if P is measured in mm Hg.

Therefore

$$K_c = 3.03 \times 10^9 \frac{N_{O_2}(b)}{P} \frac{Tb}{T} e^{-12,300/T}. \tag{17}$$

Eqs. (5), (6) and (8) may be used to express the concentrations of O, O_2, and O_3 as functions of temperature.

From Eq. (5)

$$N_{O_2} = N_{O_2}(b) \frac{Tb}{T} - N_{O_3} - N_O. \tag{18}$$

The calculations will be simplified enormously by making

$$N_{O_2} \simeq N_{O_2}(b) Tb/T. \tag{19}$$

This approximation can be made without serious error, especially at intermediate and higher temperatures, because the concentrations of O_3 and O, which are required to fulfill Eq. (6), become very small. It should be mentioned also in this connection that the experiments with which the calculated flame speeds will be compared were made with mixtures especially rich in oxygen.

By combining Eqs. (6) and (8) and using the simplified symbol C_p for $C_p{}_T{}^{Tb}$,

$$N_{O_3} = \frac{N_{O_2} + 1.5 N_{O_3} + 0.5 N_O}{(K_c/N_{O_2}) E_{O_T} + E_{O_3 T}} C_p (Tb - T), \tag{20}$$

which from Eq. (19) resolves to

$$N_{O_3} = \frac{N_{O_2}(b)(Tb/T) C_p (Tb - T)}{K_c E_{O_T}/N_{O_2}(b)(Tb/T) + E_{O_3 T}}. \tag{21}$$

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[10] Tolman, *Statistical Mechanics*, p. 63, Eq. (95), 1927.

[11] Kassel, J. Chem. Phys. **1**, 414 (1933).

By combining Eq. (21) with (8) and (19)

$$No = \frac{KcCp(Tb - T)}{KcE_{0T}/No_2(b)(Tb/T) + E_{03T}}. \quad (22)$$

EVALUATION OF dx/dT

dx/dT will be evaluated by a consideration and development of Eq. (2), which may be written:

$$-\frac{\partial}{\partial x}(No_2 V_x)dx + \frac{\partial}{\partial x}D\left(\frac{\partial No_2}{\partial x}\right)dx$$
$$+ \left(\frac{\partial No_2}{\partial t}\right)_c dx = 0, \quad (23)$$

where dx is the thickness of the elementary layer of 1 $\overline{cm}^2$ cross section.

Since the mixture becomes richer in oxygen molecules in the direction unburned phase to burned phase, more oxygen molecules are pushed out of the layer than are pushed in by mass flow. The first term is therefore negative. Since chemical reaction leads to formation of oxygen molecules the third term is positive. Since the O_2 concentration decreases with increasing temperature (Eq. 19) and the positive direction of the x-axis is the direction of increasing temperature, the sign of the diffusion term is positive.
Then

$$-V_x\frac{\partial No_2}{\partial x} - No_2\frac{\partial V_x}{\partial x} + \frac{\partial}{\partial x}\left(D\frac{\partial No_2}{\partial x}\right)$$
$$+ \left(\frac{\partial No_2}{\partial t}\right)_c = 0. \quad (24)$$

If we let $w = \partial T/\partial x$ this may be written as,

$$-wV_x\frac{\partial No_2}{\partial T} - wNo_2\frac{\partial V_x}{\partial T}$$
$$+ w\frac{\partial}{\partial T}\left(wD\frac{\partial No_2}{\partial T}\right) + \left(\frac{\partial No_2}{\partial t}\right)_c = 0. \quad (25)$$

Using Eq. (19) and substituting $\partial No_2/\partial T$ and No_2 in Eq. (26) and dividing by $No_2(b)Tb$ we obtain

$$+\frac{wV_x}{T^2} - \frac{w}{T}\frac{\partial V_x}{\partial T} - w\frac{\partial}{\partial T}\left(\frac{wD}{T^2}\right)$$
$$+ \frac{1}{No_2(b)Tb}\left(\frac{\partial No_2}{\partial t}\right)_c = 0. \quad (26)$$

Volumes Vx contain equal masses and therefore, strictly speaking,

$$V_x = \frac{VT}{Tu}\frac{1 + 0.5a + m}{1 + m}, \quad (27)$$

where m is the ratio mols O_2/mols O_3 in the original mixture and $0 \leq a \leq 1$. However, in line with the approximation made in Eq. (19), it is essentially correct, especially for intermediate and higher temperatures, to write

$$V_x \cong const. \times T. \quad (28)$$

Eq. (26) becomes,

$$-w\frac{\partial}{\partial T}\left(\frac{Dw}{T^2}\right) + \frac{1}{No_2(b)Tb}\left(\frac{\partial No_2}{\partial t}\right)_c = 0. \quad (29)$$

As will be shown later, $(\partial No_2/\partial t)_c$ can be expressed as a function of temperature. Placing

$$\frac{1}{No_2(b)Tb}\left(\frac{\partial No_2}{\partial t}\right)_c = f(T),$$

$$-\frac{wD}{T^2}\frac{\partial}{\partial T}\left(\frac{wD}{T^2}\right) + \frac{D}{T^2}f(T) = 0. \quad (30)$$

Let $wD/T^2 = y$. Then,

$$-y\frac{\partial y}{\partial T} + \frac{D}{T^2}f(T) = -\frac{1}{2}\frac{\partial y^2}{\partial T} + \frac{D}{T^2}f(T) = 0. \quad (31)$$

To integrate Eq. (31) it becomes necessary to introduce a limiting condition. We shall choose $w = 0$ when $T = Tu$, an assumption which implies that there is no temperature discontinuity between the unburned phase and the reaction zone. Considering the mode of activation of the unburned gas this probably is not far from the truth. (See Appendix.) Then

$$y^2 = \frac{D^2w^2}{T^4} = 2\int_{Tu}^{T}\frac{D}{T^2}f(T)dT. \quad (32)$$

From Eq. (1)

$$VNo_3(u) = \int_{Tu}^{Tb} \frac{1}{1.5}\left(\frac{\partial No_2}{\partial t}\right)_c dx$$

$$= \frac{1}{1.5}No_2(b)Tb \int_{Tu}^{Tb} (fT)\frac{dx}{dT}dT$$

$$= \frac{1}{1.5}No_2(b)Tb \int_{Tu}^{Tb} \frac{f(T)dT}{w}. \quad (33)$$

Then

$$\frac{1.5\,VNo_3(u)}{No_2(b)Tb} = \int_{Tu}^{Tb} \frac{f(T)dT}{w} \quad (34)$$

$$= \int_{Tu}^{Tb} \frac{\dfrac{D}{T^2}f(T)dT}{\left(2\displaystyle\int_{Tu}^{T}\dfrac{D}{T^2}f(T)dT\right)^{\frac{1}{2}}} \quad (35)$$

$$= \left(2\int_{Tu}^{T}\frac{D}{T^2}f(T)dT\right)^{\frac{1}{2}}\Bigg|_{Tu}^{Tb.} \quad (36)$$

$$= \sqrt{2}\left(\int_{Tu}^{Tb}\frac{D}{T^2}f(T)dT\right)^{\frac{1}{2}} \quad (37)$$

$$= \sqrt{2}\left(\frac{1}{No_2(b)Tb}\int_{Tu}^{Tb}\frac{D}{T^2}\left(\frac{\partial No_2}{\partial t}\right)_c dT\right)^{\frac{1}{2}}. \quad (38)$$

Since

$$No_3(u) = \frac{No_2(b)}{1+m}\frac{Tb}{Tu}. \quad (39)$$

Eq. (38) becomes

$$V = \frac{1.41(1+m)Tu}{1.5(No_2(b)Tb)^{\frac{1}{2}}}\left(\int_{Tu}^{Tb}\frac{D}{T^2}\left(\frac{\partial No_2}{\partial t}\right)_c dT\right)^{\frac{1}{2}}. \quad (40)$$

$(\partial No_2/\partial t)_c$ is evaluated as follows. As mentioned above, only reaction (b) will be considered because of the assumption of equilibrium by reaction (a). The rate of reaction (b) is determined by the collision frequency between oxygen atoms and ozone molecules and by the probability that reaction will take place on collision. The number of collisions per sec. per cc between O and O_3 is given by the expression.[12]

$$Z = 2NoNo_3(\sigma_{0,0_3})^2\left(2\pi RT\frac{Mo+Mo_3}{MoMo_3}\right)^{\frac{1}{2}}, \quad (41)$$

where R is the gas constant, and Mo and Mo_3 are the molecular weights of the oxygen atom and the ozone molecule, respectively.

The probability that reaction (b) takes place, or the ratio of the number of successful collisions to the total number of collisions is given by the expression $ke^{-E/RT}$, where E is the energy of activation. In the simpler bimolecular reactions k is of the order unity. An accurate value of E is not known, but the best available value[13] seems to be about 6000 calories per mol.

Every successful collision produces 2 molecules of oxygen, and therefore

$$(\partial No_2/\partial t)_c = 2Ze^{-E/RT}. \quad (42)$$

Introducing the expressions for No_3 and No of Eqs. (21) and (22) in the expression for Z, and substituting Eq. (42) and D of Eq. (12) in Eq. (40), one obtains:

$$V = \frac{1.41(1+m)Tu}{1.5(No_2(b)Tb)^{\frac{1}{2}}}$$

$$\times\left(\int_{Tu}^{Tb}\frac{2.2\times10^{-2}}{PT}\times\frac{4Kc(Cp)^2(Tb-T)^2No_2(b)Tb}{(KcEo_T/No_2(b)(Tb/T)+Eo_{3T})^2}e^{-6000/RT}\times(\sigma_{0,\,0_3})^2\sqrt{2\pi R\frac{Mo+Mo_3}{MoMo_3}}dT\right)^{\frac{1}{2}} \quad (43)$$

With the following numerical values $Eo_T = 58{,}000$ calories/mol; $Eo_{3T} = 34{,}000$ calories/mol; $Mo = 16$; $Mo_3 = 48$; $\sigma_{0,\,0_3} = 3\times10^{-8}$ cm; and substituting the value of Kc in Eq. (17) and combining the numerical factors one obtains:

$$V = 1.05\times10^8 Cp(1+m)TuP^{\frac{1}{2}}\left(\int_{Tu}^{Tb}\frac{[(Tb/T)-1]^2e^{-15,300/T}}{(1.76\times10^{14}e^{-12,300/T}+3.4\times10^4P)^2}dT\right)^{\frac{1}{2}}, \text{ cm/sec.,} \quad (44)$$

[12] Tolman, *Statistical Mechanics*, p. 242, 1927.

[13] O. R. Wulf, J. Am. Chem. Soc. **54**, 156 (1932); H. J. Schumacher, ibid. **52**, 2377 (1930).

w may be determined from Eq. (32).

$$\frac{D^2w^2}{T^4} = \frac{2}{No_2(b)Tb} \int_{Tu}^{T} \frac{D}{T^2} \left(\frac{\partial No_2}{\partial t} \right)_c dT \tag{45}$$

$$= 2.48 \times 10^{16} (Cp)^2 P \int_{Tu}^{T} \frac{[(Tb/T) - 1]^2 e^{-15,300/T}}{(1.76 \times 10^{14} e^{-12,300/T} + 3.4 \times 10^4 P)^2} dT \tag{46}$$

$$w = 7.17 \times 10^9 Cp P^{\frac{3}{2}} T^{\frac{1}{2}} \left(\int_{Tu}^{T} \frac{[(Tb/T) - 1]^2 e^{-15,300/T}}{(1.76 \times 10^{14} e^{-12,300/T} + 3.4 \times 10^4 P)^2} dT \right)^{\frac{1}{2}} \text{deg./cm.} \tag{47}$$

The reaction rate is determined from Eq. (42) by using the numerical factors of the above equations.

$$\left(\frac{\partial No_2}{\partial t} \right)_c = 5.52 \times 10^{36} (Cp)^2 P^3 T^{\frac{1}{2}} \frac{[(Tb/T) - 1]^2 e^{-15,300/T}}{(1.76 \times 10^{14} e^{-12,300/T} + 3.4 \times 10^4 P)^2} \text{molecules } O_2/\text{sec. cc.} \tag{48}$$

Numerical values of speeds of flames were determined for specific explosions by graphical integration. The calculation has been carried out for several experiments, and the results are given in Table I.

TABLE I.

Experiment	P, mm Hg	T_u, °K	T_b, °K	m	V, cm/sec. exptl.	V, cm/sec. calc.
3.13	624	300	1239	3.054	55	253
3.13	2560	427	1343	3.054	158	451
3.32	495	302	1922	1.016	160	333
3.32	3760	468	2044	1.016	747	664

It will be recalled that certain approximations and assumptions had to be made, either because of insufficient available knowledge of the details of the reaction or because of mathematical complexities. The assumption that reaction (a) reaches equilibrium results in calculated values which are too large. In reality, equilibrium is not approached, except perhaps at high temperatures. The oxygen atoms which diffuse over into the colder side of the reaction zone do not disappear there as fast as they would if equilibrium were established. The reaction, therefore, actually goes slower than the assumption of equilibrium would predict. This effect would be more pronounced for lower than for higher initial temperatures. For this reason, one should expect a gradual improvement in the differences between the observed and calculated speeds as the temperature increases. It is noteworthy that

in the higher temperature region where, because of approximations, the theory is expected to apply best in this particular reaction, the observed and calculated speeds do approach one another.

We wish to emphasize that, although the theory proposed may be essentially correct, its universal application, even in the seemingly simple present case, is hampered by lack of quantitative knowledge of the reactions involved.

STRUCTURE OF FLAME FRONT

The structure of the reaction zone has been worked out for experiment 3.32 and is presented in Fig. 1. It contains the temperature, the concentrations of oxygen atoms and ozone molecules, and the rate of chemical reaction plotted against the distance from the Tb side of the reaction zone. Toward the unburned side the temperature drops very slowly to Tu because the atom concentration and therefore the rate of reaction is too small on account of the necessity for neglecting the atom diffusion. Therefore it is practical to measure distances from the Tb side and to extend the curve toward the Tu side only to the point at which the reaction becomes very small. The width of the reaction zone for this explosion is of the order 10^{-3} cm.

The curve T versus x is obtained by first integrating Eq. (47) graphically, plotting $1/w = dx/dT$ against T and again integrating graphically.
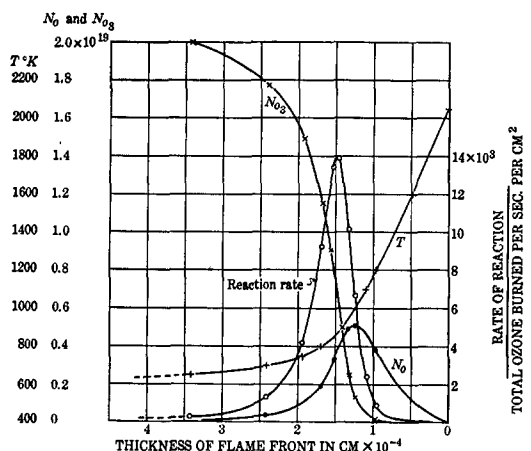
FIG. 1. Structure of flame front: showing temperature gradient, distribution of ozone and oxygen atoms and the reaction rate throughout the flame front. Experiment 3:32—pressure=3760 mm Hg, $T_u=468°K$, $T_b=2044°K$, $m=1.016$.

Instead of plotting $(\partial N_{O_2}/\partial t)_c$ versus x, we plot the expression $(1/1.5)(\partial N_{O_2}/\partial t)_c(1/VN_{O_3}(u))$, which is proportional to it. The total area under this curve is unity. Any fraction of this area represents the percentage reaction occurring up to point x. At the same time, the curve provides a measure of the rate of reaction at any point, x.

The equations for N_{O_3} and N_O are

$$N_{O_3}=\frac{1.215\times10^{27}[(T_b/T)-1]}{1.76\times10^{14}e^{-12,300/T}+1.28\times10^8}, \qquad (49)$$

$$N_O=\frac{9.78\times10^{32}e^{-12,300/T}[(T_b/T)-1]}{1.76\times10^{14}e^{-12,300/T}+1.28\times10^8}. \qquad (50)$$

Incidentally it should be remarked that the three-body collision reaction $O+O+O_2=2O_2$ which has not been mentioned, is negligible compared with the reaction $O+O_3=2O_2$ except in the last portions of the reaction zone. Here, however, its contribution to the speed is inappreciable because most of the reaction is complete.

The slower temperature rise in the first part of the zone compared with the more rapid rise in the last part is due to the preponderance in the first part of the endothermic reaction $O_3=O_2+O$ and the preponderance in the last part of the highly exothermic atom recombination.

ACKNOWLEDGMENT

APPENDIX

The authors feel that the present paper would be incomplete without a critical analysis of the essential differences between the theory herein proposed and previous theories.

To begin with it is to be noted that the theories of Jouguet, Nusselt, and Daniell[7] are fundamentally identical. In the first place, a relationship is introduced explicitly or implicitly which is essentially identical with our Eq. (1). Secondly, since the reaction zone is assumed to be stationary, a relationship is used which states that the rate of change of heat energy in an elementary layer dx due to conduction, mass flow, and chemical reaction equals zero. This equation may be written in the following way, if cooling losses are neglected:

$$k\frac{d^2T}{dx^2}-cm\frac{dT}{dx}+\left(\frac{dH}{dt}\right)_{\text{chem.}}=0,$$

where k is the coefficient of heat conductivity,
m is the mass passing unit area in the time element dt,
c is the specific heat per unit mass,
$(dH/dt)_{\text{chem.}}$ represents the rate of liberation of thermal energy due to chemical reaction within the elementary layer dx.

Both relationships allow complete solution of the problem, provided an assumption is made regarding the progress of the chemical reaction along the x axis, that is, the percentage of the original chemical energy which has been spent up to the point x. Daniell leaves the latter in a general term, dn/du, in his fundamental equation[14] and he shows that by introducing any desirable assumption regarding the progress of the reaction, a solution may be obtained. His equation, moreover, contains another general term, λ, which by his equations (6) and (9) is a

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[14] Reference 7, Eq. (15), page 398.

function of the reaction rate in the usual purely kinetic sense. Nusselt, studying flame propagation in hydrogen-air mixtures, arbitrarily assumes that equal amounts of heat energy are released in unit lengths of the x axis. Furthermore, he assumes a kinetic reaction-rate equation which we now know to be erroneous. By introducing an empirical constant, qualitative agreement is found with experiment, but this may not be accepted as proof for the validity of the underlying conceptions. Jouguet obtains the same fundamental formula[15] as Daniell, but it already includes specific assumptions regarding both the progress of the reaction along the x axis and the kinetic rate of chemical reaction. These assumptions are embodied in the formulae (written in Jouguet's symbols)

$$d\alpha/dt = u \, d\alpha/dx,$$

$$d\alpha/dt = f(T, \alpha),$$

where u is the mass velocity at the point x, α is the fraction of chemical energy which is spent up to the point x, $f(T, \alpha)$ is the rate of chemical reaction in the kinetic sense.

Both the latter equations, taken together, mean that during the time element dt an elementary mass of gas moves a distance dx and an amount of chemical energy corresponding to $d\alpha$ is lost by chemical reaction. It should be noted that in Jouguet's (also Daniell's) conception no allowance is made for the possible flow of chemical energy by diffusion. The underlying physical picture of their conception, therefore, would seem to be that of an elementary mass of gas moving along the x axis, through which the process of heat conduction may take place, but not intermixing by diffusion with neighboring mass elements. Both equations allow a solution for $d\alpha/dx$ (the latter is identical with Daniell's dn/du) in terms of reaction rate and mass velocity.

In our treatment, aside from dismissing the concept of ignition temperature, for reaction may be initiated by active radicals at practically initial temperature, we postulate that the rate of change of *concentration* of the various gas constituents in an elementary layer, due to mass

flow, diffusion, and chemical reaction, is zero. The problem of the progress of the reaction along the x axis is solved by introducing a new working hypothesis, namely, the energy relationship expressed in Eq. (6), which states that the total energy, thermal plus chemical, per unit mass in any elementary layer along the x axis is constant. We believe that this hypothesis, while speculative in character, is more defensible than either of those of Jouguet or Nusselt.

The assumption that flame propagation is determined by heat conductivity and ignition temperature involves the establishment of an energy "hump" in the unburned phase adjacent to the flame front. This must be so, since thermal energy is conducted into the layer of unburned gas which already contains its original thermal plus chemical energy per unit mass. Thus, while the sum of thermal and chemical energy per unit mass in an incompletely burned layer may exceed the total thermal energy per unit mass in the completely burned gas it cannot fall below the value for the completely burned gas if the flame front is to be stable. This can be understood from the following consideration. Suppose a layer in the flame front which is not yet completely burned (near the burned side of the flame front) contains such an amount of energy that the residual chemical energy is insufficient to raise the mass of gas to the final temperature of the completely burned gas. Then energy must flow into this layer if it is to reach the final temperature. In view of the rising temperature gradient from the unburned to the burned phase, thermal energy can flow into it only from the direction of completely burned gas. Since the chemical energy of the latter is spent, such a process would result in a decrease of its own temperature; that is, an energy "valley" of this sort would correspond to an unstable state in the flame front. It follows that the energy per unit mass of the completely burned phase represents the minimum total energy, chemical and thermal, which may be possessed by any unit mass of gas in the reaction zone.

Eq. (6) is therefore the lower limit of the general relationship

$$E_{O_3 T} N_{O_3} + E_{O_T} N_O$$

$$\geqq (N_{O_2} + 1.5 N_{O_3} + 0.5 N_O) C_{P_T}{}^{Tb} (Tb - T)$$

[15] Jouguet, Compt. Rend. **179** (1924), Eq. 4, page 456. Priority belongs to Jouguet.

and therefore possesses definite physical significance. As a matter of fact, we may conceive of Eq. (6) representing rather closely the true conditions, as outlined early in this paper. Eq. (6), with the condition that the rate of change of concentrations in an elementary layer is zero, automatically takes care of the requirement that the rate of change of heat energy shall also be zero. The equations, however, go further in that they also impose conditions as to the flow of chemical energy among the different layers which, as pointed out, the other theories neglect.

In common with other authors our differential equation is solved by imposing a condition regarding the temperature gradient. The type of our equation is such that its solution is imaginary if one assumes that the temperature gradient disappears at point x_b where the gas is completely burned. The solution is obtained by making the temperature gradient disappear toward the unburned side. We believe that this is in harmony with the physical picture of the theory. In their equations, Jouguet and Nusselt impose the condition that the temperature gradient disappears toward the burned side, although for mathematical purposes the same condition may be employed for the unburned side. The latter was utilized by Daniell.
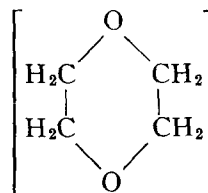

The Electric Moments of Fatty Acids

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A number of investigators have reported moments of fatty acids from dielectric constant and density measurements made upon the solutions of these substances in benzene. As is well known, fatty acids exist as double molecules when dissolved in hydrocarbons and consequently these reported moments have no significance as applied to the single molecules. No detailed reference to this work need be given. From measurements made upon the gaseous substances Zahn[1] reported moments of $1.51-$, $1.73-$ and 1.74×10^{-18} c.g.s.e.s.u. for the simple molecules of formic, acetic and propionic acids, respectively. At the temperatures of measurement the formic acid existed as a mixture of single and double molecules. From a knowledge of the density of the gas the fraction of the molecules in the associated state was calculated and the moments of both the single and double molecules were reported. The latter was given to be 0.99 D. The moments of acetic and propionic acids were obtained from measurements made at temperatures sufficiently high that dissociation of the double molecules into single molecules was sufficiently complete.

Oxygenated solvents have the property of dissociating the double fatty acid molecules into single ones. Nearly all of the common oxygenated solvents are polar and therefore not suited as media for measuring the moments of polar solutes. Recently dioxane

has been used in the determination of electric moments. It is non-polar and miscible with the lower acids and dissolves sufficient amounts of the higher members. The authors measured the moments of formic, acetic and propionic acids in dioxane for the sake of making comparisons with the values obtained for the gaseous substances. In order to determine the effect of greatly increasing the length of the hydrocarbon chain data are also given for stearic acid in Table I.

The polarizations at infinite dilution were calculated by the method of Hedestrand.[2] In Table II are listed the values of the polarization at infinite dilution, the molecular refraction for the sodium line and the electric moment.

The moments of acetic and propionic acids as

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[1] C. T. Zahn, Phys. Rev. **37**, 1516 (1931).

[2] Hedestrand, Zeits. f. physik. Chemie **B2**, 428 (1929).