Theory of Burning Velocity. II. The Square Root Law for Burning Velocity

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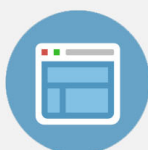
to prepare of sufficient purity by chemical means, notably lithium fluoride[1] and calcium fluoride. This method offers a means of preparing a fairly large amount of purer material in a relatively short time.

Theory of Burning Velocity. II. The Square Root Law for Burning Velocity[1]

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Previous papers by the authors having suggested that the diffusion of active particles (chiefly hydrogen atoms) from the flame front is the controlling factor in combustion in Bunsen-type burners, an equation for burning velocity based on such a concept is derived. This equation shows that the burning velocity should be proportional to the square root of an expression in which the most important factor is the sum of the products p_iD_i for all effective atoms or free radicals, p_i being the concentration of an atom or radical at the flame front, and D_i its coefficient of diffusion into cold, unburnt gas. The burning velocity equation is applied to the combustion of carbon monoxide and hydrogen, and excellent agreement between calculated and experimental values of the burning velocity is obtained. The equation is also used to account for the effect of pressure upon burning velocity.

INTRODUCTION

PREVIOUS papers by the authors on Bunsen-type burner flames (with laminar flow)[3,4] have shown that there exists in moist carbon monoxide flames a close correlation between the calculated equilibrium hydrogen atom concentrations at the flame front and the experimentally determined burning velocity, and have suggested that this correlation can be explained if it is assumed that the diffusion of active particles (chiefly hydrogen atoms) from the flame front into the unburnt gas controls the combustion process. In this paper an equation for burning velocity based on this idea is derived, and is given a number of practical applications.

THE SQUARE ROOT LAW FOR BURNING VELOCITY

As in our Paper I on burning velocity,[4] we consider the simple model of the combustion zone illustrated by Fig. 1. The flame front is defined as the surface where combustion has proceeded to equilibrium, and is used as the origin of a fixed coordinate system. The unburnt gas moves in the direction of the arrow, the flow being taken normal to the flame front, so that in the cold unburnt gas the flow velocity must be the burning velocity as defined in the usual manner. In order to arrive at soluble differential equations, it is necessary to assume that the whole combustion zone is at one constant mean temperature, T_m, which is, in general, taken to be some fraction of the flame temperature, T_1. The effect of this simplification is to give to the density and the flow velocity values ρ_m and u_m, which are constant over the entire combustion zone. It should be pointed out that the actual value chosen for the mean temperature can affect the predicted burning velocity only to a small extent.

We now consider a portion of the flame front of area dS and a cylinder of this same cross-sectional area going from it into the unburnt gas. It is assumed that ignition of unburnt gas can take place at any point in this cylinder by means of active particles (chiefly hydrogen

[1] Abstracted in part from a thesis submitted by Charles Tanford in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Princeton University.
[2] National Research Council Predoctoral Fellow in Chemistry, 1946–47.
[3] C. Tanford and R. N. Pease, J. Chem. Phys. **15**, 431 (1947).
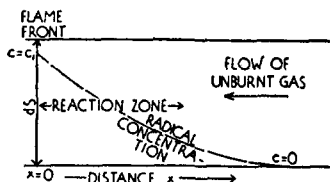[4] C. Tanford, J. Chem. Phys. **15**, 433 (1947).

FIG. 1. Model of flame front and combustion zone.

atoms) present there as a result of diffusion from the flame front. The concentration in molecules per cc of any such active particle at any point has already been obtained in Paper I, and is given by

$$c_i = c_{1i} \exp\left(-\frac{B_i u_m}{D_{mi}} x \right) \qquad (1)$$

where c_{1i} is the equilibrium concentration of the active particle at the flame front, D_{mi} is the diffusion coefficient of the active particle into unburnt gas at the mean temperature T_m, and B_i is a factor, usually close to unity, which corrects for the loss of radicals due to chemical processes. The evaluation of this last factor for hydrogen atoms is discussed in detail in Paper I.

Now, the rate of formation of combustion product at any point must certainly depend upon this active particle concentration. It can be expected to be the sum of a number of terms, one for each effective atom or free radical. The concentrations of species other than these active particles can also be expected to enter into the expression. For the sake of simplicity we shall assume here that of the latter only the concentration of combustible, C, is of importance, and that the rate of formation of combustion product in molecules per cc per sec. at any point can be represented by

$$d(\text{product})/dt = \sum_i k_i c_i C$$

where k_i is a rate constant appropriate to the ith active species. Then the total rate of formation of product molecules in the cylinder of Fig. 1 in molecules/sec. is

$$\int_{x=0}^{\infty} \sum_i k_i c_i C dS dx.$$

Now, from the initial composition of the combustion mixture it is possible to compute the total rate of formation of combustion product which is required to bring about complete combustion, and this rate must be equated to the above expression. To calculate this rate we consider the volume of gas (measured at 298°K) which crosses the section dS of the flame front per second. This volume is given by the product of the burning velocity (u_0) and the cross-sectional area (dS). If Q is the mole fraction of potential combustion product in this gas,[5] then, where L is the number of molecules in one cc of gas at 298°K, the number of molecules of product required to be formed per second over the cross-sectional area dS for complete combustion must be $LQu_0 dS$. Since, by definition, combustion must be complete at the flame front, we then have

$$LQu_0 dS = \int_{x=0}^{\infty} \sum_i k_i c_i C dS dx.$$

We now substitute for c_i from Eq. 1, and assume a mean value independent of x for the concentration of combustible, so that we obtain

$$LQ_0 u dS = \sum_i k_i C c_{1i} dS \int_0^{\infty} \exp\left(-\frac{B_i u_m}{D_{mi}} x \right) dx$$

$$= \sum_i k_i C c_{1i} dS \frac{D_{mi}}{B_i u_m}. \qquad (2)$$

The equilibrium composition of the burnt mixture is usually in terms of partial pressures or mole fractions,[5] so that we replace c_{1i} by Lp_i/θ_m where θ_m is T_m/T_0, the ratio of the mean temperature of the combustion zone to the temperature of the unburnt gas (usually 298°K), and L/θ_m therefore the number of molecules in one cc of gas at the mean temperature. Furthermore, the diffusion coefficient varies approximately as the square of the temperature,[6] so that we can replace D_{mi} by $D_i \theta_m^2$, where D_i is the diffusion coefficient of the ith active species into cold,

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[5] The compositions of the unburnt gas and of the final equilibrium mixture at the flame front are most conveniently expressed as volumes percent, or, better as mole fractions. We shall use the symbols q_k to represent mole fractions in the unburnt gas, and the symbols p_k to represent calculated equilibrium mole fractions at the flame front. If the flame is at a pressure of one atmosphere, these mole fractions are, of course, equivalent to partial pressures.

[6] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, 1939), p. 248.

unburnt gas. Finally, the flow velocity, u_m, can be related to the burning velocity, i.e. the flow velocity in cold, unburnt gas, by the relation $u_m = u_0 \theta_m$.

Making these substitutions in Eq. 2, we find that L, θ_m, and dS drop out, and we obtain the square root law for burning velocity,

$$u_0 = \left(\sum_i \frac{k_i C p_i D_i}{Q B_i} \right)^{\frac{1}{2}}. \tag{3}$$

Since the existence of combustion limits imposes a relatively narrow range of variability upon the concentration of combustible, C, and upon the mole fraction of potential combustion product, Q, and since the factors B_i vary but little from mixture to mixture, we can say that, for the purpose of comparing the burning velocities of different mixtures in which the same kinetics (i.e., the same k_i) are likely to be involved, the burning velocity must be roughly proportional to $(\sum_i p_i D_i)^{\frac{1}{2}}$. This immediately explains the correlation between burning velocity and hydrogen atom concentration found for mixtures containing carbon monoxide.[3]

APPLICATION TO CARBON MONOXIDE COMBUSTION

In the combustion of carbon monoxide the mole fraction of potential combustion product in the initial mixture is the mole fraction of carbon monoxide, or (since one mole of oxygen can oxidize two moles of carbon monoxide) twice the mole fraction of oxygen, whichever of these is smaller. This is conveniently represented by the symbol $(q_{CO}, 2q_{O_2})_<$. If the average mole fraction of carbon monoxide over the combustion zone is, say, 0.7 of that present initially, the average concentration of combustible, C, can be expressed in terms of that initial concentration. For, since the number of molecules in one cc of gas at the temperature T_m is L/θ_m, we then have

$$C = 0.7 L q_{CO} / \theta_m.$$

Considerable evidence exists which suggests that oxygen atoms are not of importance in initiating carbon monoxide combustion (for example, combustion in the absence of moisture, even with an excess of oxygen, proceeds only with the greatest difficulty), so that it appears reasonable to suppose that only hydrogen atoms and hydroxyl radicals of the available active particles are of interest to us. Of these, the contribution of hydroxyl is usually small, because D_{OH} is small. In a few of the mixtures for which calculations have been made, however, the concentration of hydroxyl is very much larger than that of hydrogen atoms, and in those cases good agreement of experimental burning velocities with those predicted by Eq. 3 can be obtained only by inclusion of the part played by hydroxyl. Thus the special form of this equation for carbon monoxide combustion becomes

$$u_0 = \left\{ \frac{0.7L}{\theta_m} \frac{q_{CO}}{(q_{CO} \cdot 2q_{O_2})_<} \times \left(\frac{k_H p_H D_H}{B_H} + \frac{k_{OH} p_{OH} D_{OH}}{B_{OH}} \right) \right\}^{\frac{1}{2}}. \tag{4}$$

This equation can be simplified to some extent. The correction term B_{OH} is found to be always within one or two percent of unity, and can therefore be neglected. Further, in all mixtures containing chiefly carbon monoxide, oxygen and nitrogen, in any proportion whatsoever, diffusion coefficients have about the same value. At 298°K D_H is 1.95 cm²/sec. (see paper I) and D_{OH} is 0.29 cm²/sec. Finally, we can assume that the rate constant k has about the same value for H as for OH. Placing the mean temperature, T_m, equal to, say, 0.7 of the equilibrium flame temperature, and substituting for L its numerical value, 2.48×10^{19} (298°K, one atmosphere pres-

TABLE I. Burning velocities in carbon monoxide flames.

Composition	θ_1 $= T_1/T_0$	P_H ×10⁴ atmos.	P_{OH} ×10⁴ atmos.	B_H	u_0, cm/sec. calc.	u_0, cm/sec. obs.[c]
35%CO,[a] 8.5%O₂, 56.5%N₂	5.8	0.1	—	1.08	22	25
26.5%CO,[a] 44.1%O₂, 29.4%N₂	7.8	0.7	20.6	1.23	36	30
40%CO,[b] 12.6%O₂, 47.4%N₂	7.8	2.5	3.4	1.32	37	30
40%CO,[a] 12.6%O₂, 47.4%N₂	7.8	3.8	4.9	1.28	41	40
40%CO,[a] 59.1%O₂, 0.9%N₂	9.1	5.6	56	1.25	51	48
40%CO,[a] 24%O₂, 36%N₂	8.9	11.6	56	1.39	56	51
45%CO,[a] 22%O₂, 33%N₂	9.1	16	58	1.38	59	57
40%CO,[a] 59.1%O₂, 0.9%N₂	9.1	9.2	88	1.25	59	60
60%CO,[b] 39.4%O₂, 0.6%N₂	9.8	24	86	1.35	67	68
50%CO,[a] 30%O₂, 20%N₂	9.4	24	91	1.35	69	72
80%CO,[b] 19.7%O₂, 0.3%N₂	9.6	29	39	1.39	84	72
60%CO,[a] 24%O₂, 16%N₂	9.6	38	90	1.39	81	83
60%CO,[a] 39.4%O₂, 0.6%N₂	9.8	39	134	1.32	81	93
70%CO,[a] 24%O₂, 6%N₂	9.7	52	102	1.37	96	98
80%CO,[a] 19.7%O₂, 0.3%N₂	9.6	59	78	1.37	112	106

[a] CO contains 1.35% H₂O and 1.5% H₂.
[b] CO contains 1.35% H₂O.
[c] G. Jahn, Der Zündvorgang in Gasgemischen (Oldenbourg, Berlin, 1934).

TABLE II. Burning velocities in hydrogen flames.

Composition			$\theta_1 = \dfrac{T_1}{T_0}$	$P_H \times 10^4$ atmos.	$P_{OH} \times 10^4$ atmos.	B_H	u_0, cm/sec.	
							calc.	obs.[a]
40%H₂,	7.5%O₂,	52.5%N₂	5.0	0.1	—	1.02	120	100
60%H₂,	8.4%O₂,	31.6%N₂	5.5	0.6	—	1.04	140	175
40%H₂,	10.5%O₂,	49.5%N₂	6.5	5.6	0.4	1.16	180	200
40%H₂,	15%O₂,	45%N₂	8.3	85	46	1.10	330	300
60%H₂,	12%O₂,	28%N₂	7.3	32	2.5	1.15	320	350
40%H₂,	24%O₂,	36%N₂	9.2	135	380	1.01	390	360
40%H₂,	36%O₂,	24%N₂	9.2	96	520	1.06	390	380
60%H₂,	16%O₂,	24%N₂	8.7	214	50	1.15	530	485
60%H₂,	24%O₂,	16%N₂	9.9	590	400	1.02	700	660
60%H₂,	32%O₂,	8%N₂	10.1	590	890	1.02	690	730

[a] G. Jahn, *Der Zündvorgang in Gasgemischen* (Oldenbourg, Berlin, 1934).

sure), we then obtain

$$u_0 = \left\{ \frac{4.84 \times 10^{19} k}{\theta_1} \frac{q_{CO}}{(q_{CO} \cdot 2q_{O_2})_<} \right.$$

$$\left. \times \left(\frac{p_H}{B_H} + 0.15 p_{OH} \right) \right\}^{\frac{1}{2}}. \quad (5)$$

Before this equation is applied, it must be remembered that the burning velocity of carbon monoxide mixtures does not tend to zero as the free radical concentration becomes zero,[7] i.e., there appears to be a small, probably fairly constant contribution to the burning velocity which is not dependent upon the free radical concentration. A plot of burning velocity against the square root of the free radical concentration shows that this radical-independent contribution is about 17 cm/sec. This value agrees closely with burning velocities observed by Ubbelohde and Dommer[8] for carbon monoxide—air mixtures in the complete absence of moisture or hydrogen, i.e., under conditions where H and OH could not be formed. This contribution to the burning velocity must be added to Eq. 5, so that we obtain

$$u_0 = 17 + \left\{ \frac{4.84 \times 10^{19} k}{\theta_1} \frac{q_{CO}}{(q_{CO} \cdot 2q_{O_2})_<} \right.$$

$$\left. \times \left(\frac{p_H}{B_H} + 0.15 p_{OH} \right) \right\}^{\frac{1}{2}}. \quad (6)$$

Equation 6 has been used to compute burning velocities of a number of mixtures containing

[7] Reference 3, Fig. 1.
[8] L. Ubbelohde and O. Dommer, J. Gasbel. **57**, 757 (1914).

carbon monoxide. The constant k is, of course, arbitrary, best fit of the experimental data being obtained with the value 1.64×10^{-13}. Methods for the calculation of the free radical concentrations at the flame front and of the term B_H have been described in previous papers. The results of the calculations are shown in Table I, and it is seen that excellent agreement exists between the calculated burning velocities and experimental values determined by Jahn.[9] It was found that somewhat less good agreement is obtained for extremely rich mixtures (ratio of CO and O_2 greater than 4), and such mixtures have not been included in Table I.

It can be seen at once that the value found for k is of the right order of magnitude. For, converting from the units of cc molecule^{-1} sec.$^{-1}$ to the more familiar units of cc mole^{-1} sec.$^{-1}$ by multiplication by Avogadro's number, we obtain $k = 1.00 \times 10^{11}$ cc mole^{-1} sec.$^{-1}$. This value is entirely reasonable for the high temperatures obtaining in the combustion zone,[10] and suggests that the activation energy of the rate-determining step in the combustion mechanism is about 7 or 8 kcal./mole. The fact that the same value for the rate constant can be used throughout, despite the fact that there is variation in the mean temperature, also requires that the activation be of this order or lower.

APPLICATION TO THE COMBUSTION OF HYDROGEN

Assuming that the mechanism of hydrogen combustion is similar to that of carbon monoxide combustion, we obtain for the burning velocity an equation similar to Eq. 4. Again it is found that there is a contribution independent of the concentration of active particles, this time of about 110 cm/sec., so that the burning velocity equation becomes

$$u_0 = 110 + \left\{ \frac{2.48 \times 10^{19} k D_H}{\theta_1} \frac{q_{H_2}}{(q_{H_2} \cdot 2q_{O_2})_<} \right.$$

$$\left. \times \left(\frac{p_H}{B_H} + 0.21 p_{OH} \right) \right\}^{\frac{1}{2}}. \quad (7)$$

[9] G. Jahn, *Der Zündvorgang in Gasgemischen* (Oldenbourg, Berlin, 1934).
[10] For reaction at every collision and zero entropy of activation, the bimolecular rate constant is about 10^{14} cc mole^{-1} sec.$^{-1}$.

It should be noted that while the ratio D_{OH}/D_H remains about constant, the value of D_H now depends upon the composition, being 2.35 for mixtures containing 40 percent hydrogen, and 2.6 for mixtures containing 60 percent hydrogen.

Equation 7 has been used to compute the burning velocities of a number of mixtures containing hydrogen, with the best value of k now 6.5×10^{-13} (corresponding to a value of 3.9×10^{11} cc mole^{-1} sec.$^{-1}$), i.e., slightly higher than for carbon monoxide. The computations are shown in Table II, and again good agreement is found between calculated burning velocities and those observed experimentally by Jahn.[9]

THE EFFECT OF PRESSURE ON BURNING VELOCITY

Equation 3 should prove to be very useful in predicting the effect of a number of variables, such as pressure, preheating, nature of diluent gas, etc., upon burning velocity. As an example we shall give here a semi-quantitative estimation of the effect of pressure upon burning velocities in general.

We observe at once that only three of the factors of Eq. 3 depend upon pressure, these being C, p_i, and D_i. Moreover, for a mixture of given initial percentage composition, the concentration of combustible, C, in molecules per cc, is directly proportional to the pressure, while the diffusion coefficients, D_i, are inversely proportional to the pressure. These two effects therefore cancel, and it remains to consider only the pressure-dependence of the free radical mole fractions, p_i. Since these free radicals are products of dissociation, their mole fractions will decrease with increasing pressure, in general roughly as the square root of the pressure. (Slight changes in flame temperature and molecular concentrations always occur, so that an analytical expression is not feasible.) Since the burning velocity itself is proportional to the square root of the p_i, therefore, it should vary inversely, roughly as the fourth root of the pressure. Such an effect has indeed been observed for a number of hydrocarbon flames, as well as for carbon monoxide.[11]

CONCLUSION

It should perhaps be pointed out in conclusion that the very simple treatment of burning velocity given in this paper is successful only because the effects of the motion of the gas stream and of diffusion upon local free radical concentrations are relatively much greater than the effects of chemical processes. In other words, the concentration of active particles at any point depends very little upon the chemical reactions occurring in the gas. Of the latter, we have taken into account only the recombination of hydrogen atoms and the formation of HO$_2$, and it is very likely that the accuracy of the burning velocity equation could be improved if full consideration could be given to chain branching and other chemical processes which in this simple treatment have been ignored.

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[11] L. Ubbelohde and coworkers, J. Gasbel. **59**, 49 (1916), **60**, 225 (1917); L. Khitrin, Tech. Phys. U.S.S.R. **3**, 926 (1936).