

425

Correlation of Equilibrium Atom and Free Radical Concentrations in Flames of Carbon Monoxide, Hydrocarbon and Air with Burning Velocities and Flame Stabilities

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A correlation of the equilibrium atom and free radical concentrations with burning velocities and flame stabilities in mixtures of carbon monoxide, propane and air and in mixtures of carbon monoxide, methane and air is found to be lacking. Furthermore, the simplified 'square root law' equation fails to predict the sharp increase in burning velocity of carbon monoxide flames with the addition of small percentages of propane.

IT HAS been known for some time that the burning velocity of carbon monoxide is greatly increased by the addition of small amounts of compounds containing hydrogen. K. BUNTE and E. HARTMANN¹ and later P. L. WALKER and C. C. WRIGHT^{2,3} showed that the addition of a small amount of hydrocarbon to carbon monoxide produced a sharp increase in burning velocity of the latter. A. LEVY and P. F. KURZ⁴ suggested that this marked increase in burning velocity found by Walker and Wright can be attributed to the transformation of the mixture of carbon monoxide and hydrocarbon into a mixture of carbon monoxide and water prior to entering the flame zone. Both for mixtures of carbon monoxide and methane and mixtures of carbon monoxide and propane, the maximum burning velocity and flame stability are found to occur in the range of 5 to 8 per cent water vapour in the transformed mixture. This agrees qualitatively with the experimental results of W. A. BONE⁵, who found that the maximum burning velocity of mixtures of carbon monoxide and water occurs between 5.2 and 8.0 per cent water.

C. TANFORD and R. N. PEASE⁶ successfully correlated the change in burning velocity of mixtures of carbon monoxide (containing 1.35 per cent water and 1.5 per cent hydrogen), oxygen and nitrogen with the change in calculated equilibrium partial pressure of hydrogen atoms in the flame front. This in turn led to the development of the well known 'square root law' of burning velocity⁷. C. TANFORD⁸ has since successfully correlated the changes in burning velocity of hydrogen and methane flames by the above law. Furthermore, D. M. SIMON⁹ showed that changes in the maximum burning velocities of thirty-five hydrocarbons were consistent with this theory.

In the present paper, the author has investigated possible correlations of equilibrium atom and free radical concentrations in mixtures of carbon monoxide, methane and air and mixtures of carbon monoxide, propane and air with variations in burning velocities and flame stabilities. Furthermore,

the agreement between the experimental burning velocities of flames of carbon monoxide, propane and air and those predicted by the simplified 'square root law' equation has been tested.

CALCULATIONS

The 'square root law' equation of Tanford and Pease can be written in the form

$$U_B = \left[\sum_i \frac{k_i p_i D_{i,m}}{B_i} \frac{L_m}{\theta_m^2} \frac{Q'n}{Q} \right]^{1/2} \quad \dots [1]$$

where U_B = burning velocity, k_i = specific rate constant for reaction between i th radical and combustible, p_i = equilibrium partial pressure of i th active particle, $D_{i,m}$ = diffusion coefficient of i th radical at mean combustion zone temperature, B_i = term arising from radical recombination, L_m = total concentration of gas at mean combustion zone temperature, θ_m = ratio of mean combustion zone temperature T_m to initial temperature T_0 , Q' = mole fraction of combustible in unburned gas, Q = mole fraction of potential combustion product in unburned gas, n = total number of molecules of water and carbon dioxide formed per molecule of fuel by stoichiometric relation. As shown by G. L. DUGGER and D. D. GRAAB¹⁰, equation 1 may be modified to the form

$$U_B \propto \left[\sum_i \frac{p_i D_i}{B_i} \frac{\exp\{-5000/T_i\}}{T_i^{0.83}} \right]^{1/2} \quad \dots [2]$$

under the following circumstances:

- (1) $(Q'n/Q)^{1/2}$ is essentially a constant—present calculations indicate that this term does not vary by more than ± 3 per cent in all mixtures investigated and has been assumed a constant
- (2) $k_i \propto (0.7T_i)^{1/2} \exp\{(-7000)/(R)(0.7T_i)\}$: this proportionality depends primarily upon the fact that the activation energies for the reactions between active particles and fuel molecules is 7 kcal/mole; this agrees well with the findings⁹ of Tanford for both carbon monoxide and methane flames and is assumed in the present case
- (3) as is generally accepted, $D_{i,m} \propto D_i \theta_m^{1.07}$.

Further calculations indicate that for all mixtures studied D_i does not vary by more than 3 per cent and under these circumstances

$$\sum_i \frac{p_i D_i}{B_i} \propto \frac{6.5 p_H}{B_H} + p_{OH} + p_O \quad \dots [3]$$

where the diffusion coefficient for the hydrogen atom is taken as 6.5 times that of the OH radical and O atom¹⁰, and B_{OH} and B_O are taken as being essentially unity⁸. The value of B_H has been calculated in each case using the method of C. TANFORD¹¹.

C. TANFORD and R. N. PEASE⁷ and L. UBBELOHDE and O. DOMMER¹² find that the maximum burning velocity of mixtures of carbon monoxide and air does not tend to zero as the free radical concentration of hydrogen atoms and hydroxyl radical becomes small (mixtures in the complete absence of moisture

and hydrogen) but that the radical-independent contribution to burning velocity is about 17 cm/sec. On the other hand, the maximum burning velocity of hydrocarbon-air mixtures should tend to zero only as their free radical concentrations become small. Therefore, in the calculation of burning

Table 1. Analysis of dry fuels used in both flame stability and burning velocity studies^{2,3}, and present calculations

Mixtures of propane and carbon monoxide				Mixtures of methane and carbon monoxide			
Propane		Carbon monoxide		Methane		Carbon monoxide	
Constituent	%	Constituent	%	Constituent	%	Constituent	%
C ₃ H ₈	73.73	CO	97.60	CH ₄	96.77	CO	98.50
C ₃ H ₆	21.62	CO ₂	0.58	C ₂ H ₆	1.88	CO ₂	0.49
C ₂ H ₆	3.83	H ₂	1.82	C ₂ H ₄	0.11	H ₂	1.01
n-C ₄ H ₁₀	0.69	—	—	O ₂	0.10	—	—
n-C ₄ H ₈	0.13	—	—	N ₂	1.10	—	—
				CO ₂	0.04	—	—

velocities using equation 2, an additive term varying linearly from 17 cm/sec for the 100 per cent carbon monoxide flame to 0 cm/sec for the 100 per cent hydrocarbon flame is used*.

Equilibrium flame temperatures and active particle concentrations have been calculated using the method and charts of V. N. HUFF and C. S. CALVERT¹³. Heat capacity of gases and standard heats of combustion have been taken from data compiled by O. A. HOUGEN and K. M. WATSON¹⁴.

Table 2. Maximum burning velocities and flame stabilities of mixtures of dry carbon monoxide propane and air

Fuel in fuel-air mixtures % _a	Propane in fuel %	Equil. temp. °K	Equil. partial pressure of radicals (calc.) atm × 10 ⁴			Burning velocity cm/sec		Velocity gradient cm/sec/cm exp. ³
			p _H	p _{OH}	p _O	exp. ³	calc.	
45.0	0	2271	3.0	3.3	0.6	38.1	38.1	600
39.0	2.5	2206	4.9	4.0	0.2	58.0	42.1	1300
32.5	4.0	2273	7.5	8.2	0.6	62.5	49.3	1410
23.0	10.0	2323	9.5	17.0	1.7	56.2	53.8	1150
15.2	20.0	2339	9.3	26.0	3.0	50.2	56.2	930
10.0	40.0	2278	10.0	20.0	1.0	43.2	49.2	845
7.1	60.0	2290	9.3	22.0	1.4	40.0	44.3	780
4.0	100	2283	5.4	34.0	3.7	37.1	37.5	700

Maximum velocity gradient for blow-off (called flame stability) and burning velocity data^{2,3} of Walker and Wright on mixtures of hydrocarbon, carbon monoxide and air have been used as a basis of calculation. Burning velocities were evaluated from measured values of flame cone height and burner radius using the relation

$$U_B = \frac{V}{\pi R(R^2 + H^2)^{\frac{1}{2}}}$$

*Unfortunately the true form of the variation of the additive term in going from 100 per cent carbon monoxide to 100 per cent hydrocarbon in the fuel is not clear. This will be discussed briefly later.

where V is the total flow in the burner tube (ml/sec), R is the radius (cm) of the flame cone base (taken as the radius of the burner tube) and H is the measured height of the cone (cm). The compositions of the carbon monoxide and hydrocarbons used in the experimental work and in the calculations are shown in *Table 1*. The temperature and pressure of the inlet fuel mixtures were taken as 18°C and 1 atm respectively.

RESULTS

Table 2 shows both the calculated and experimental data for the mixtures of carbon monoxide, propane and air. *Figure 1*, a graph of maximum experimental burning velocity versus the equilibrium partial pressure of hydrogen atoms, indicates the absence of a correlation. Equally poor correlations are found for the oxygen atoms and hydroxyl radical concentrations. Furthermore, since the changes of experimental velocity gradient values with fuel

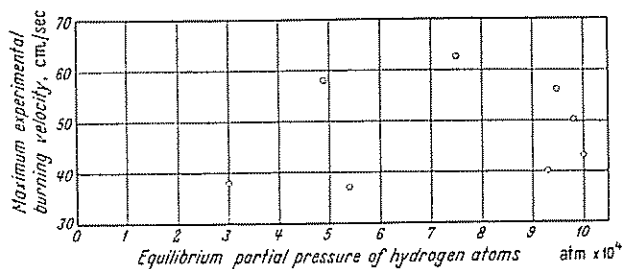


Figure 1. Correlation between maximum experimental burning velocity and equilibrium hydrogen atom concentrations for mixtures of carbon monoxide, propane and air

composition qualitatively agree with the change in burning velocity, no correlation between the equilibrium radical concentrations and the former is found. *Figure 2* presents the experimental and calculated maximum burning velocities for the mixtures of carbon monoxide and propane. It is seen that the

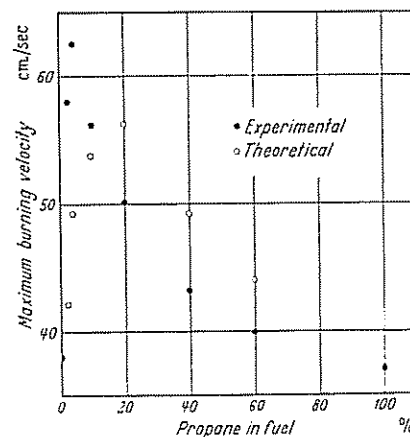


Figure 2. Maximum burning velocity of mixtures of dry carbon monoxide, propane and air

addition of up to 10 per cent propane to the carbon monoxide has a considerably greater effect on increasing burning velocity than that predicted by the simplified 'square root law'. It is also noted that, whereas the experimental

burning velocity reaches a maximum at about 4 per cent propane* in carbon monoxide, the calculated burning velocity continues to increase with increasing propane additions to about 20 per cent.

Table 3 presents experimental and calculated data for the mixtures of dry carbon monoxide, methane and air. Figure 3, a graph of maximum velocity

Table 3. Maximum flame stabilities of mixtures of dry carbon monoxide, methane and air

Fuel in fuel-air mixture %	Methane in fuel %	Equil. flame temp. °K	Equil. partial pressure of radicals (calc.) atm × 10 ⁴			Velocity gradient cm/sec/cm exp.
			p _H	p _{OH}	p _O	
47.0	0	2176	1.5	1.0	0.1	390
45.0	2.5	2149	2.8	1.9	0.1	1230
40.0	5.0	2213	5.1	4.2	0.2	1460
37.0	7.5	2231	6.1	5.9	0.4	1600
34.0	10.0	2271	7.9	9.4	0.6	1550
25.0	20.0	2309	8.8	18.4	1.7	1320
14.0	60.0	2259	6.8	21.0	1.5	630
9.5	100.0	2243	5.0	28.0	2.5	430

gradient for flash-back *versus* the partial pressure of hydrogen atoms, shows no correlation. A similar lack of correlation is found with the hydroxyl radical and oxygen atom. Unfortunately, burning velocities were not determined on these mixtures. However, a similar lack of correlation with burning velocity would be predicted.

DISCUSSION OF RESULTS

The simplified 'square root law' equation is found not to predict the marked rise in burning velocity or flame stability of carbon monoxide flames with the addition of small amounts of methane or propane. On the other hand, for propane additions to carbon monoxide greater than approximately 15 per cent, the simplified 'square root law' equation is seen to predict burning velocities greater than those found experimentally. Other assumed variations in the additive term to burning velocity with variations in fuel composition (than linear) could conceivably result in agreement of theoretical and experimental burning velocities past 15 per cent propane addition. Such assumed, more complicated variations in the additive term are, however, not clear nor justifiable at the moment. Of utmost importance is the fact that the predicted burning velocity at the fuel composition (4 per cent propane in fuel) corresponding to the maximum experimental value of burning velocity—67.5 cm/sec—is 21 per cent low even if an additive term of 17 cm/sec were used. Looking at it another way, for the 4 per cent propane in fuel mixture, the predicted increase in burning velocity accounts at best for only 46 per cent of the experimental increase.

Of course, the calculated burning velocities are strongly dependent upon the calculated equilibrium flame temperatures and it could be that combustion in each case proceeded to different degrees of thermodynamic equilibrium. There is, however, no reason to believe that the addition of small amounts of a

*A 5 per cent propane-95 per cent carbon monoxide mixture was run, and its maximum value of burning velocity was less than that found for the 4 per cent propane-96 per cent carbon monoxide mixture.

hydrocarbon to carbon monoxide would vary significantly the approach of the reaction to equilibrium over that of the pure carbon monoxide flame. For example, for the calculated burning velocity of the 4 per cent propane-96 per cent carbon monoxide mixture to agree with the experimental value, the flame temperature would have to be over 100°K higher than the calculated temperature.

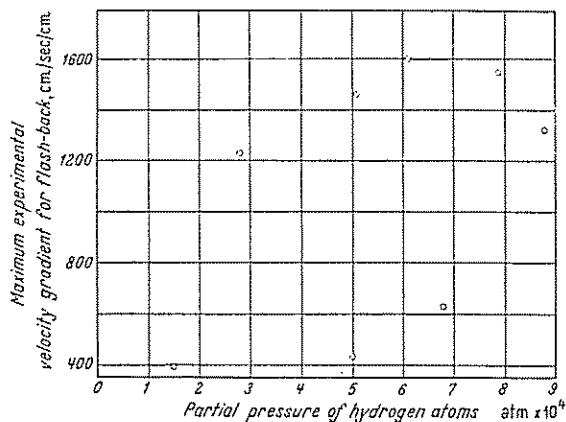
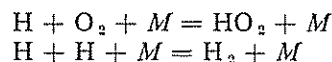


Figure 3. Correlation between maximum experimental velocity gradient for flash-back and hydrogen atom concentration for mixtures of carbon monoxide, methane and air

It might be argued that the rate constant k , for the interaction of the active particles with the combustible material changes appreciably with the addition of a hydrocarbon. Results of Tanford, where he determined the rate constants for the combustion of carbon monoxide and methane to be 1.0×10^{11} and 1.9×10^{11} ml/mole/sec respectively, however, appear to refute this reasoning⁸. The close agreement of these values, particularly in light of the pronounced effect which a small amount of hydrocarbon has on the carbon monoxide combustion, cannot account for the experimental facts.

The only other factor in the general 'square root law' equation which appears to have a possibility of explaining the inconsistencies is the radical recombination term. However, the only two reactions thought fast enough to have an appreciable effect upon the hydrogen atom concentration, according to Tanford, are¹¹



It is difficult to believe that a small addition of hydrocarbon would decrease the rates of these reactions sufficiently to account for the higher burning velocity. As a matter of fact, methane has a molecular weight lower than the third bodies originally present—carbon monoxide, oxygen and nitrogen—whereas propane has a higher molecular weight; even though the rate of the three-body collisions is known to be a function of molecular weights and diameters, the same trend of flame stability and burning velocity is found for small additions of both hydrocarbons.

It has been pointed out by B. LEWIS⁸ that the 'square root law' equation ignores the possibility of the occurrence of chain branching reactions between

the completely burned side to the unburned side of the combustion wave. That chain branching in low percentage hydrocarbon mixtures increases the active particle concentration considerably beyond that calculated would, however, seem to be a remote possibility. This is particularly true if it is remembered that for propane additions above 15 per cent the predicted burning velocity exceeds the experimental value: it would be difficult to explain excessive chain branching for low hydrocarbon additions and little or no chain branching for higher additions.

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