[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Burning Velocities of Hydrogen–Air Flames[1]

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Burning velocities of hydrogen–air mixtures were measured by the bunsen burner method. A modified angle technique applied to the dark outer edge of the shadow cone was used in calculating the burning velocities. An attempt was made to correlate the experimental result with approximate diffusion and thermal theories of flame propagation. It was found that diffusion theory predicts a maximum in burning velocity at a much leaner hydrogen composition than is observed experimentally, whereas thermal theory produces the opposite situation by predicting a maximum at a richer composition (29 *vs.* 42 *vs.* 55% H_2). Possible explanations of these discrepancies are discussed briefly.

In correlating experimental burning velocity measurements with the current theories of flame propagation, the values most frequently used for hydrogen–oxgyen–nitrogen mixtures have been those reported by Jahn.[2] As there has been some uncertainty regarding the accuracy of those measurements, it was proposed to obtain additional data for the hydrogen–air system and to relate these new results to diffusion and thermal theories of burning velocity. In particular, it was desired to confirm Jahn's observation that maximum burning velocity corresponds to very rich fuel–air mixtures.

Experimental

The apparatus and procedure used in this work were essentially the same as described by Clingman,[3] with certain modifications to be given below.

The copper burner used had an inside diameter of 0.317 cm., and was held at 25° by means of a water-jacket. The burner assembly was placed in a mantle to prevent the flames from entraining air. The windows on the mantle were made of optically clear Pyrex glass.

Because of the low light intensity of the hydrogen flame, direct photography was ineffective without extended exposure times. Measurements were therefore made on photographs of the shadow cone. The following optical arrangement was used. Light from a 10-watt concentrated-arc lamp (Sylvania) was collimated by means of a lens, both the source and the lens being mounted in a metal tube which was lined up with the burner at a distance of about 12 feet. The parallel beam was roughly 7 cm. in diameter at the site of the flame, which itself never measured more than about 1 cm. in height. Shadow photographs were taken with a Speed Graphic camera (4 × 5 in.) on Kodak Super XX, high-speed, panchromatic film at exposures of 1–3 milliseconds. The camera (with bellows extended) was mounted on a support rod along which it could be moved for focusing purposes.

The camera was first focused on the burner rim, whose outside diameter (1.11 cm.) provided the scale of measurement. In this position the shadow cone was not visible on the ground glass, but could be brought into view by moving the camera back a small distance. A photograph was then taken, and an enlargement was made giving a positive image 10–12 cm. in height. The dark, outer edge of this image was utilized in evaluating the burning velocity.[4]

The calculation was based on the modified angle method developed by Clingman.[5] In brief the method involves an analytical procedure for determining a mid-region of the cone over which burning velocity is constant. Values so calculated for methane–air mixtures were shown by Clingman to be independent of flow rate and burner diameter, when the visible cone was examined.

Application of this method to the shadow cone of the hydrogen–air flame produced acceptable results within 2–3%. The data shown in Fig. 1 are averages of analyses of 2 or more separate photographs. Values were independent of variations in flame-to-camera distance. They were also independent of flow rate insofar as could be determined. However, the limits imposed by blow-off and flash-back at Reynolds number below 2000 (*i.e.*, in the laminar region) severely restricted variations in flow rate, and also in burner diameter.

Hydrogen was obtained from the American Oxygen Co. Air was taken from the laboratory supply lines, and was dried by passing through calcium chloride.

Results and Discussion

Experimental burning velocities are shown graphically in Fig. 1. Jahn's[2] data are included as a dotted curve, in conjunction with some other data represented by points only. As can be seen, our results are substantially higher than those given by Jahn. This is not inconsistent with the fact that Jahn's measurements were made on the visible cone, using a total area method based on cone height measurement. However, it should be noted that the burning velocity maximum occurs at approximately the same composition in each case.

Bartholomé,[6] using a nozzle burner and the angle method on the visible flame, reported values on the rich side very similar to those reported by us. On the other hand Smith and Pickering,[7] using an angle method on the visible flame (exposure times of 4 minutes) reported points closer to Jahn's data. All agree that the maximum velocity occurs at well in excess of the stoichiometric mixture (42 *vs.* 28%).

Flame temperatures and compositions were computed in conventional manner, the method being described by Gaydon and Wolfhard.[8] Equilibrium constants, enthalpies, heats of formation and other necessary thermodynamic quantities were obtained from N.B.S. tables[9] except for the hydroxyl radical. The equilibrium constants for the reaction $H_2O \rightleftarrows {}^1/_2 H_2 + OH$ were calculated using the value for the

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(2) G. Jahn, "Der Zundvorgang in Gasgemischen," Oldenburg, Berlin, 1934.

(3) W. H. Clingman, R. S. Brokaw and R. N. Pease, "Fourth Symposium on Combustion," The Williams and Williams Co., Baltimore, Md., 1953, p. 310.

(4) For a discussion of shadow cone formation, see J. R. Grove, M. F. Hoare and J. W. Linnett, *Trans. Faraday Soc.*, **46**, 745 (1950).

(5) W. H. Clingman, Ph.D. Thesis, Princeton University, Sept., 1954.

(6) E. Bartholomé, *Z. Elektrochem.*, **54**, 169 (1950).

(7) F. A. Smith and S. F. Pickering, *J. Research Natl. Bur. Standards*, **17**, 7 (1936).

(8) A. G. Gaydon and H. G. Wolfhard, "Flames, Their Structure, Radiation and Temperature," Chapman and Hall, Ltd., London, 1953, p. 264.

(9) "Selected Values of Chem. Thermod. Props," Natl. Bur. of Standards, Series III, 1948 (Loose-Leaf).

dissociation energy of the hydroxyl radical as reported by Hornbeck.[10]

Diffusion coefficients for the active species into the unburned gas mixtures were estimated assuming that the reciprocal of the average diffusion coefficient for a multicomponent mixture may be taken as the molal average of the reciprocals of the binary coefficients, as suggested by Hirschfelder and Curtiss.[11] The binary coefficients were calculated by the first approximation for rigid elastic spheres.[12] Values for collision radii for N_2, O_2 and H_2 were obtained from ref. 12, p. 229. The values for H, OH and O radii were the ones used by Clingman.[3]

As no experimental data on thermal conductivities, λ, for the hydrogen–air mixtures were available, and methods of calculation were of questionable validity, those for hydrogen–nitrogen mixtures were used, as reported by Ibbs and Hirst.[13] The thermal conductivities of nitrogen and air are sufficiently similar to make this substitution reasonable. Thermal conductivities were corrected to flame temperature by assuming direct proportionality ($\lambda \propto T$).

Pertinent data are summarized in Table I. The ratio $[\lambda/C_p\rho]_f$ in the last column was used as an index for evaluating thermal theory. Here C_p is the molar heat capacity and ρ is the density at flame temperature.

TABLE I

HYDROGEN–AIR FLAMES

H_2, vol. %	Burning velocity, cm./sec.	Flame temp., °K.	Concn.,[b] atm. × 10^4		Diffusion coeff.,[b] cm.^{2} sec.$^{-1}$ at 298°K.		Thermal cond., cal. cm.$^{-1}$ sec.$^{-1}$ °C.$^{-1}$ × 10^5 at 298°K.	$\left[\frac{\lambda}{C_p\rho}\right]$
			H	OH	H	OH		
25.0	180[a]	2140	1.5	153	..	...	..	..
28.6	225	2315	12.0	165	1.11	0.306	10.3	1.13
31.6	246	2300	20.0	77.7	1.13	.314	..	..
37.5	298	2200	21.0	23.0	1.16	.332	12.2	1.36
40.0	312[a]	2130	15.9	12.1	1.18	.340	..	..
44.4	310	2020	9.2	4.2	1.20	.356	13.8	1.44
49.0	294	1900	4.3	1.3	1.23	.373	14.9	1.48
52.5	280	1800	..	...	..	...	15.8	1.51
55.0	270	1740	..	...	..	...	16.4	1.55
57.5	258[a]	1660	..	...	..	...	17.0	1.53
63.0	235	1500	..	...	..	...	18.4	1.51

[a] Interpolated values from Fig. 1. [b] The calculated concentration of oxygen atoms was negligible, and values of concentration and diffusion coefficients are therefore omitted.

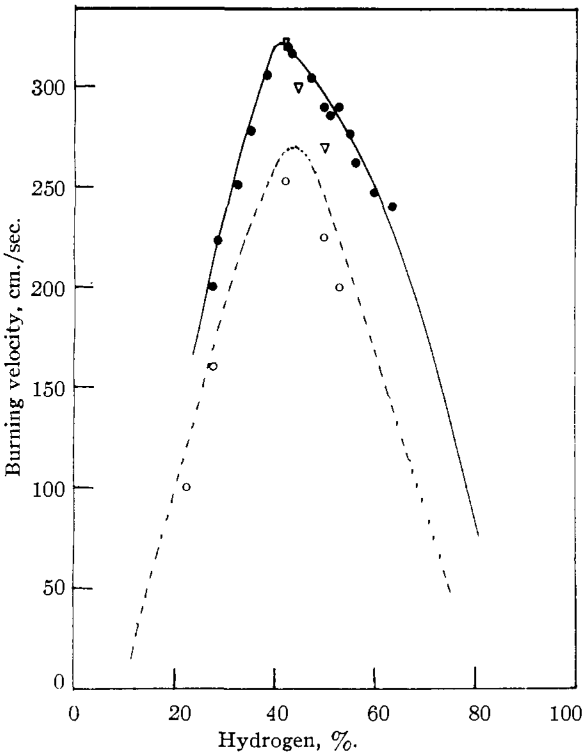

Fig. 1.—A plot of burning velocities for H_2-air flames: broken curve, John; ▽, Bartholome; ○, Smith and Pickering.

In a preliminary attempt to investigate the role of atoms and radicals in flame propagation, Tanford and Pease[14] have developed a theory which assumes that the rate of flame propagation is controlled by the diffusion of atoms and radicals from the flame front into the unburned gas, and subsequent reaction of these species with the fuel. The mathematical consequences of the theory can be expressed in the form

$$S^2 \propto \sum_i (k_i p_i D_i) \qquad (1)$$

where S represents the burning velocity, p_i, the equilibrium partial pressures of the radicals or atoms, and D_i the diffusion coefficients of the active species at the flame temperature (assuming $D \propto T^{3/2}$). Rate constants for the assumed primary reactions between radicals and reactants are represented by k_i. As the latter cannot be evaluated with any degree of accuracy, an absolute calculation of burning velocity, based on this theory, cannot be made. However, certain qualitative relations can be derived from equation 1 by comparing $[\sum_i (p_i D_i)]^{1/2}$ with S.

These relations were tested in the following manner. In Fig. 2, curve A is a plot of $[\sum_i (p_i D_i)]^{1/2}$ against percentage hydrogen in the initial mixture, while curve B is a corresponding plot of experimental burning velocities. If the Tanford equation were precisely applicable, these two curves would bear a close resemblance to one another. However, it is evident that curve B maximizes less sharply, and at a substantially higher percentage hydrogen (42 *vs.* 29% H_2). This situation would be somewhat improved if the term for OH-radical were omitted, but the discordance would still be considerable (see Table I). It is seen, therefore, that the Tanford equation in its present form is not quantitatively applicable in this case, although the greater importance of the H atom concentration

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[10] G. A. Hornbeck, "Fifth Symposium on Combustion" (International), Reinhold Pub. Corp., New York, N. Y., 1955, p. 790.

[11] C. F. Curtiss and J. D. Hirschfelder, *J. Chem. Phys.*, **17**, 552 (1949).

[12] J. Chapman and T. G. Cowling, "The Mathematical Theory of Non-Uniform Gases," Cambridge University Press, 1939, p. 245.

[13] T. L. Ibbs and A. A. Hirst, *Proc. Roy. Soc. (London)*, **A123**, 134 (1929).

[14] C. Tanford and R. N. Pease, *J. Chem. Phys.*, **15**, 861 (1947).

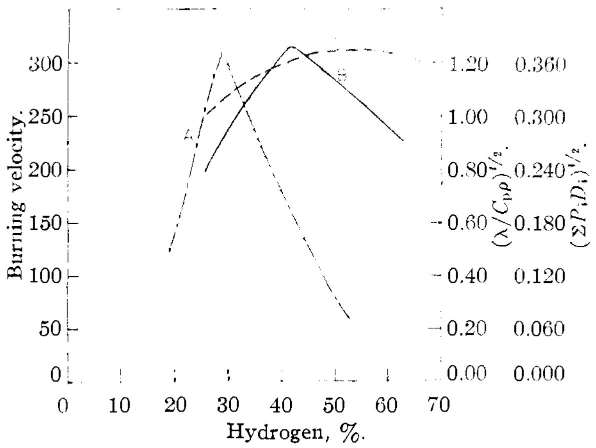

Fig. 2.—A plot of mixture strength (volume % hydrogen) *vs.* A, $[\Sigma(P_iD_i)]^{1/2}$; B, burning velocities, cm./sec.; C, $(\lambda/C_p\rho)^{1/2}$.

seems to be well established. Nevertheless, as Tanford[14] has shown, there is a general correlation over a broad range of compositions in which molecular hydrogen concentration is kept constant, but the flame temperature is varied by varying the O_2/N_2 ratio. It is only when the molecular hydrogen concentration is varied that the discrepancy becomes serious.

The applicability of a thermal theory is now to be considered. In general, most thermal theories deal with a "thermal" parameter such that[15]

$$S^2 \propto \left[\frac{\lambda}{C_p\rho}\right] \qquad (2)$$

where λ is the thermal conductivity, C_p is the average molecular heat capacity, and ρ is the gas density, all calculated for the initial mixture at the flame temperature. The term in equation 2 is given for each mixture in the last column of Table I.

The variation of $[\lambda/C_p\rho]^{1/2}$ with the mixture strength is shown in Fig. 2, curve C. It is obvious that the thermal parameter produces an almost equal but opposite deviation from that of the Tanford diffusion theory, maximizing at substantially higher hydrogen concentrations (~55%).

It appears from this work, therefore, that neither a simple diffusion theory nor a thermal theory applied exclusively can adequately explain the experimental data in this example. It should be possible to set up an empirical relation involving both 1 and 2 that would yield a closer correspondence to observation, but this point was not pursued further. Such a relation would be based on the presumption that the greater conductivity of hydrogen-rich mixtures results in a higher average flame temperature.

It may also be pointed out that neither approximation takes any account of the peculiarities of the reaction kinetics as deduced from observations on the slow (low temperature) reaction.[16] In particular, it will be recalled that there is strong evidence for chain branching, for which no allowance has been made in the above. It is also true that low-temperature rates are substantially greater at high hydrogen concentrations, a result in qualitative agreement with the burning velocity data. In terms such as these, a closer understanding of hydrogen–air flames will doubtless be achieved.

[15] M. Evans, *Chem. Revs.*, **51**, 363 403 (1952); A. G. Gaydon and H. G. Wolfhard, "Flames," Chapman and Hall, Ltd., 1953, p. 117.

[16] B. Lewis and G. von Elbe, "Combustion, Flames and Explosion of Gases," Academic Press, Inc., New York, N. Y., 1950, pp. 27–61.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE PENNSYLVANIA STATE UNIVERSITY]

A Simple Model for Barriers to Internal Rotation

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A number of symmetrical barriers to internal rotation about single bonds in molecules have been calculated on the assumption that the barriers were caused by ordinary van der Waals repulsions between non-bonded atoms or groups of atoms in the molecules. The repulsions have been estimated by analogy with known repulsions between similar atoms or groups of atoms which are not part of a larger molecule, with allowances made for any residual electrical charges on the atoms or groups. The calculations based on this simplified model indicate that in most cases about half the barrier can be attributed to van der Waals repulsion forces. It is suggested that the remainder can perhaps be explained on the basis of the electrostatic interactions between the charge distributions of the chemical bonds, as originally suggested by Lassettre and Dean (ref. 9) and by Oosterhoff (ref. 3). Although it is admittedly rather empirical, the model seems capable of furnishing reasonable estimates of steric repulsions.

The interactions between non-bonded atoms in molecules seem to be responsible for a large number of phenomena in chemistry and physics. These interactions influence the spectra and thermodynamic properties of many substances, are responsible at least in part for the existence of certain rotational isomers, and cause certain configurations of complex molecules to be preferred over others.[2,3] Furthermore, if these interactions change on going from a reactant to a product (or a transition state), the equilibrium constant (or rate constant) for the reaction is affected. Such effects on reactivity are

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[1] Institute of Molecular Physics, University of Maryland, College Park, Maryland.

[2] S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954.

[3] L. J. Oosterhoff, Thesis, Leiden, 1949; *Disc. Faraday Soc.*, **10**, 79, 87 (1951).