Detonation Characteristics of Hydrogen-Oxygen Mixtures

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Detonation velocities were measured in mixtures of hydrogen and oxygen containing 25 to 75 mole % hydrogen at initial temperatures from 160° to 580°K. and initial pressures from ½ to 2 atm. The measurements were made in a number of tubes of different diameter to permit extrapolation to a tube of infinite diameter. Theoretical detonation characteristics were computed for the same range of conditions. The measured and computed velocities are in good agreement except in rich mixtures and at subatmospheric pressures. Schlieren photographs reveal that the detonation wave front is very thin for a stoichiometric mixture but degenerates to a complicated zone of interacting shock waves and turbulent combustion as the percentage of hydrogen is reduced. The detonation velocity is found to depend only slightly on initial temperature and pressure. The computed pressures behind the detonation and reflected waves are roughly proportional to initial pressure and to the reciprocal of the initial temperature.

The elementary theory of detonation was initiated by Riemann (21) with his work on sound waves and essentially completed by Chapman (5) and Jouguet (7). This elementary theory postulates a planar discontinuity in pressure, temperature, and composition moving at sonic velocity with respect to the burned gases (the Chapman-Jouguet condition); chemical equilibrium in the burned gases; no energy, component, or momentum transfer to the surroundings; and ideal gas behavior. Subsequent refinements in the theory have been concerned primarily with the structure of the wave. The details of both the classical and the current theoretical work are presented in modern books such as Hirschfelder, Curtiss, and Bird (10) and Courant and Friedricks (6) and therefore will not be repeated herein.

Experimental work on detonation has been well reviewed by Lewis and von Elbe (16), and only the immediately pertinent work will be mentioned. The effect of composition on the detonation velocity of hydrogen-oxygen mixtures has been investigated extensively, but the effects of initial temperature and initial pressure have received little attention. In 1893 Dixon (7) measured the detonation velocity in stoichiometric mixtures at 283° and 373°K. over a range of pressures from 200 to 1,500 mm. Hg. More recently Bennett and Wedaa (2) reported detonation velocities over a pressure range from 10 to 400 mm. Hg and Hoelzer and Stobaugh (11) over a range from 1 to 10 atm.

Lewis and Friauf (15) in 1930 and Berets, Greene, and Kistiakowsky (3) in 1950 found good agreement between velocities computed from the elementary theory and experimental values in hydrogen-oxygen mixtures at atmospheric pressure and near-ambient temperatures. The objective of this investigation was to test the predictions of the elementary theory over a much wider range of initial conditions.

EXPERIMENTAL WORK

The experimental equipment for the measurement of detonation velocities consisted of six different detonation tubes, a mixing and charging system, an ignition system, and a timing system.

The characteristics of the detonation tubes are given in Table 1. The five round, straight tubes (A, B, C, D, and E) were used to determine the effect of tube diameter on detonation velocity. Tube F was a 10-in. coil for convenience in temperature control for the high- and low-temperature experiments. The effect of coiling was evaluated by comparison of the velocities measured in tubes F and B. Rectangular tube G was used only to obtain schlieren photographs. All seven tubes were closed at both ends.

The velocity of the detonation wave was measured with ionization probes. The probes were made by drilling a no. 76 drill through a Teflon insert in a stainless steel sleeve. The probes were threaded into the detonation tubes and adjusted so that the tip was flush with the wall. Each probe was connected as a shorting switch in the grid of an 884-thyratron tube. The grid bias of the thyratron tube was adjusted almost to the firing point to obtain maximum sensitivity. When the ionized gases behind the detonation front reached a probe, the resistance between the probe electrode (the drill) and ground (the tube wall) fell, and the thyratron fired. One probe and thyratron started a timer, and another probe and thyratron stopped it. The time interval was indicated to the nearest microsecond. The distances between the probes and the distance from the ignitor to the first probe are given in Table 1. The probe locations on tube F were on the outside of the coil and were determined before coiling. The distance between the probes was corrected for thermal expansion and contraction of the tube in computing the detonation velocity at nonambient temperatures. This correction was about 0.1% at the extreme temperatures. The starting distance for all the tubes was greater than the distance

indicated by Laffitte (14) and Greene (9) as necessary to attain stable detonation in hydrogen-oxygen mixtures. The probes required replacement after 20 to 30 runs.

The high-temperature runs were made with the coiled tube in an oven, and the low-temperature runs with the coiled tube immersed in 5 gal. of normal propanol in an insulated tank. Dry ice was added to the propanol to cool to 200°K. and liquid nitrogen to reach lower temperatures. As the result of vigorous stirring, the temperature variation within the bath was held within ±2°K.

The detonation tube was evacuated and then filled with premixed oxygen and hydrogen through a manifold and switch system that kept the ignition circuit open while the filling valve was open. In the low-temperature runs the tube was evacuated at room temperature before cooling to avoid condensation. In both the high- and low-temperature runs the mixture was not ignited until the pressure indicated on a manometer had remained constant for at least 5 min. Analyses of the hydrogen and oxygen on a mass spectrograph indicated purities greater than 99.5%. The composition of the mixtures were regularly determined by the partial-pressure method but were periodically checked with a mass spectrograph.

The schlieren measurements were made by the Töpler method (1) in a ⅜- by ½-in. rectangular tube with a test section containing ⅜- by 14-in. windows ½-in. thick on two opposite sides. Additional details concerning the equipment and experimental procedures are given in reference 18.

Measurements of detonation velocity were repeated five or more times at the same conditions to check reproducibility. All in all over 600 runs were carried out at over 100 conditions encompassing a range of compositions from 25 to 76 mole % hydrogen for an initial temperature of 298°K. and an initial pressure of 1 atm., a range of initial pressures from ½ to 2 atm. for an initial temperature of 298°K. and compositions from 40 to 76% hydrogen and a range of initial temperatures from 160° to 477°K. for an initial pressure of 1 atm. and compositions from 41 to 73% hydrogen. The detailed data are given in reference 18. The averages of the repeated runs are presented herein. The maximum deviation of any individual velocity from the average was less than 1.0% except for a few runs at subatmospheric pressures.

When the velocities measured at atmospheric pressure and 298°K. in the 0.125-, 0.250-, 0.375-, 0.909-, and 3.250-in. straight tubes were plotted as a function of initial gas composition, a small but
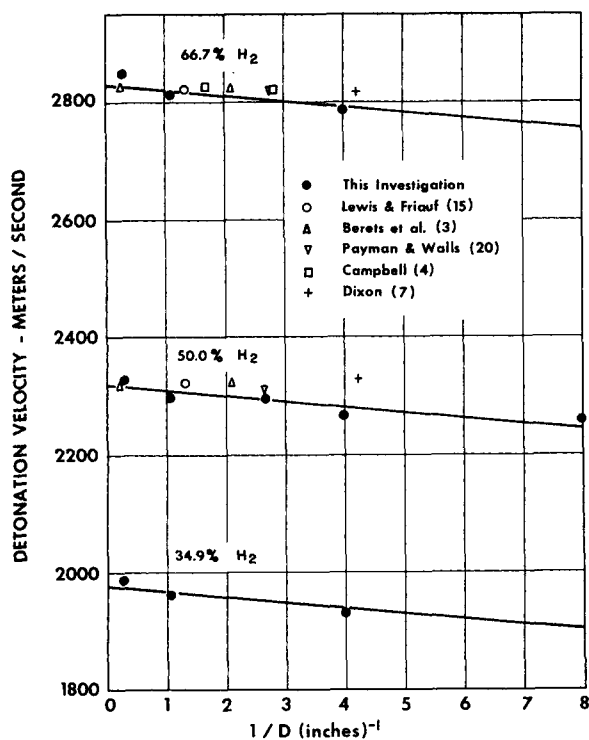
Fig. 1. Effect of tube diameter on detonation velocity.

Fig. 2. Detonation velocities at atmospheric pressure and ambient temperature.

definite dependence on tube diameter was apparent. Therefore the velocities measured in mixtures containing 34.9, 50.0, and 66.7% hydrogen were plotted vs. reciprocal tube diameter in Figure 1 as suggested by Kistiakowsky and Zinman (9). The data of several previous investigators (3, 4, 7, 15, 20) for atmospheric pressure and temperatures near 298°K. are also included. The data appear to lie in parallel straight lines indicating that the wall effect is independent of composition in this range. The best set of parallel lines through the data of this investigation only was determined by least squares by the use of the method of Ergun (8). These lines are included in Figure 1. The slope of the lines was computed to be 9.04 (in.) (m.)/sec.; therefore the velocities measured in this and previous investigations at all conditions were extrapolated to the equivalent velocity in a tube of infinite diameter by means of the equation

$$V_\infty = V + \frac{9.0}{D} \quad (1)$$

Data at high and low temperatures were obtained only in the 0.250-in. coiled tube and only at atmospheric pressure. Comparison of data obtained in the coiled and straight 0.250-in. tubes at atmospheric pressure and 298°K. indicated that the coiled tube yielded velocities 1% lower than those measured in the straight tube. Accordingly, the velocities measured in the coiled tube at all conditions were corrected by this amount as well as by Equation (1), that is

$$V_\infty = \frac{V_c}{0.99} + \frac{9.0}{D} \quad (2)$$

Scorah (22) maintains that the detonation

velocity is unaffected by coiling or even zigzagging the tube, and the observed correction is probably due to stretching the tube in the coiling process rather than to fundamental effects.

Corrected velocities are presented in all subsequent plots.*

THEORETICAL COMPUTATIONS

The detonation characteristics of hydrogen-oxygen mixtures were computed from the elementary theory on an IBM-650 computer over essentially the same range of initial temperatures, pressures, and compositions as in the experimental work. The only species assumed to be present were water, hydrogen, oxygen, hydroxyl, atomic hydrogen and atomic oxygen. Equilibrium constants, heat capacities, and heats of formation from

* A tabulation of the average and corrected experimental velocities and of the computed theoretical detonation characteristics has been filed as document 6124 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 photoprints or 35-mm. microfilm.
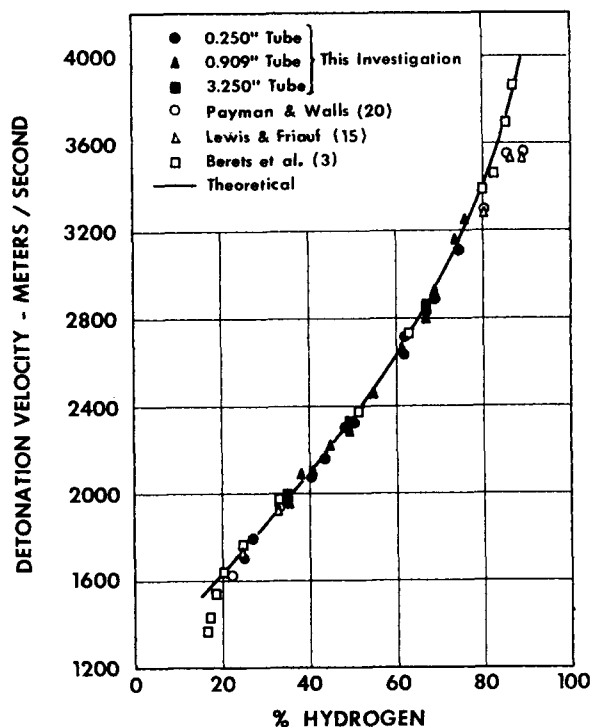
the National Bureau of Standards tables (23) were utilized.

The pressure, temperature, and equilibrium composition behind the detonation wave as well as the wave velocity were obtained from the computer. The further increase in pressure obtained by reflection of the detonation wave off a solid wall was also computed with no further change assumed in composition.

The experimental velocities were not measured at exactly the same temperatures, pressures, and compositions as those selected for computation. Therefore it was necessary to plot and interpolate the experimental data. Since the theoretical detonation velocity is a near linear function of initial pressure, temperature, and composition, very little uncertainty was introduced by this interpolation.

DETONATION VELOCITIES

The corrected experimental velocities of this and previous investigations for

TABLE 1. DETONATION TUBES

Tube	Material	I. D., in.	Form	Ignitor to 1st probe, ft.	Probe separation, ft.	Total length, ft.
A	Stainless steel	0.125	Straight	7.0	3.0007	11.5
B	Stainless steel	0.250	Straight	9.0	2.999	13.5
C	Stainless steel	0.375	Straight	7.5	2.0003	12.0
D	Stainless steel	0.909	Straight	7.0	3.9944	12.0
E	Carbon steel	3.250	Straight	10.0	3.000	14.0
F	Stainless steel	0.250	10-in. Coil	8.0	12.00	24.0
G	Carbon steel	(0.375 × 0.5)	Straight	6.0	—	7.5

Fig. 3. Detonation velocities at several initial pressures and 298°K.
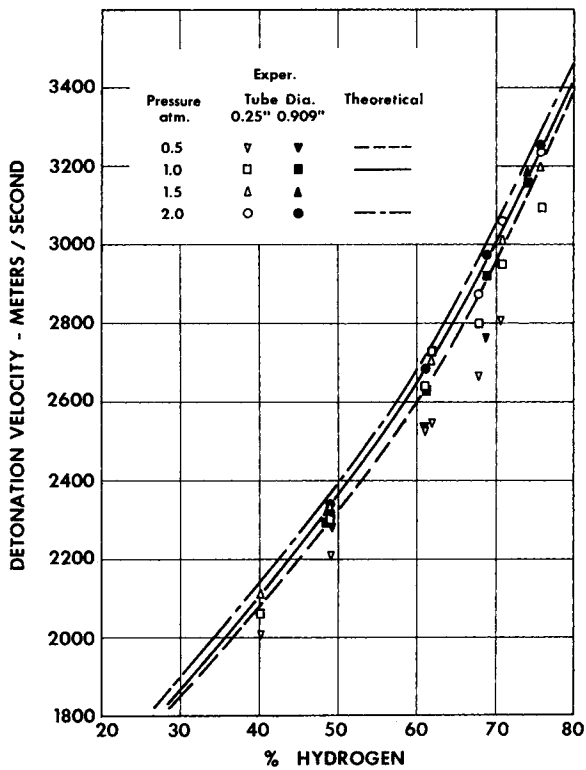

Fig. 5. Detonation velocities at several initial temperatures and 1 atm.

an initial pressure of 1 atm. and initial temperatures of approximately 298°K. are plotted as a function of initial composition in Figure 2. Excellent agreement is demonstrated with the curve representing the computed theoretical velocities over the range of composition from 20 to 80% hydrogen.
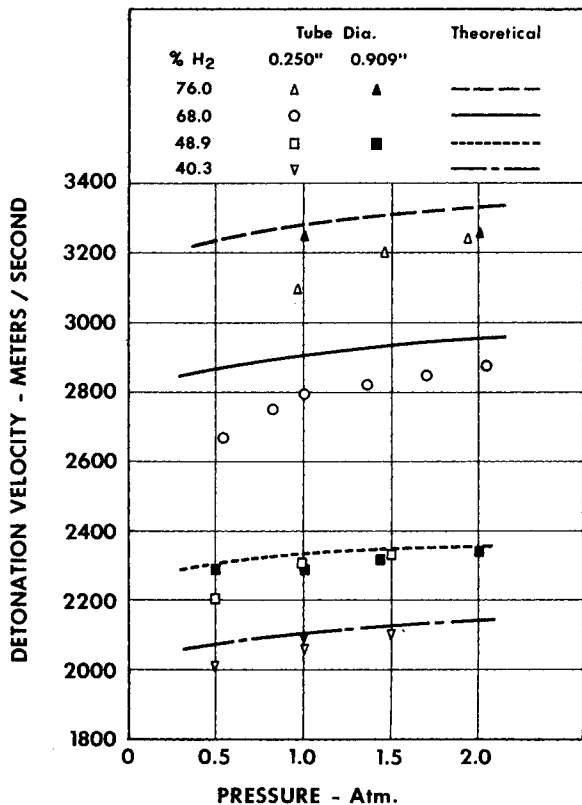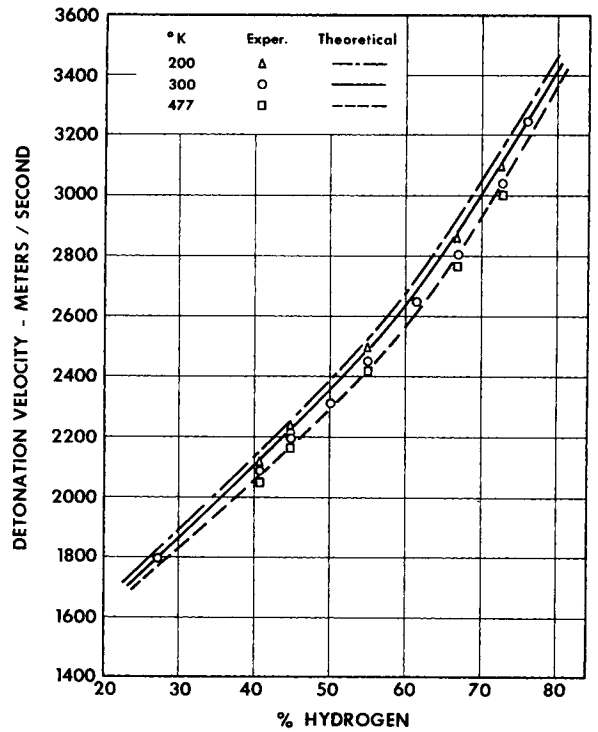
The effect of initial pressure on detonation velocity was investigated at ambient temperature only for a wide range of compositions in the straight 0.250- and 0.909-in. tubes. Difficulty was encountered in obtaining reproducible data at subatmospheric pressures in the 0.909-in. tube. Velocities

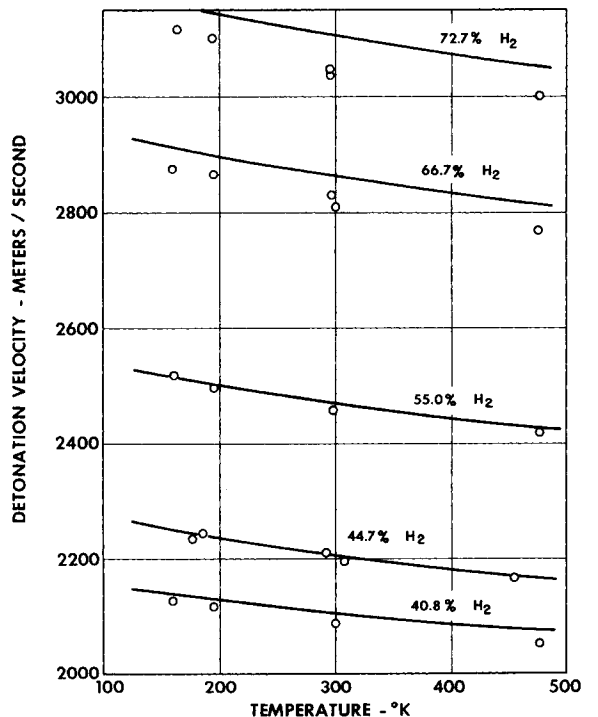Fig. 4. The effect of initial pressure on detonation velocity at 298°K.

Fig. 6. The effect of temperature on detonation velocity at 1 atm.

corrected to infinite diameter by Equation (1) are plotted as a function of composition at initial pressures of 0.5, 1.0, 1.5, and 2.0 atm. in Figure 3. The data fall somewhat below but indicate the same trend with pressure as the theoretical curves. The corrected experimental velocities for several mixtures are plotted directly vs. pressure in Figure 4. This plot includes data at pressures intermediate to those in Figure 3. The limited range of the ordinate of Figure 4 exaggerates the slight effect of initial pressure on the detonation velocity and emphasizes the deviations. The experimental data are no more than 7% below the theoretical curves even at 0.5 atm. in rich mixtures.

The corrected velocities equivalent to those obtainable in an infinite straight tube are plotted as a function of gas composition in Figure 5 for temperatures of 200°, 300°, and 477°K. Although the data fall slightly below the theoretical curves, the agreement is generally good. The data for a number of mixtures are plotted directly as a function of temperature in Figure 6. Again the limited range of the ordinate exaggerates the slight variation of the velocity with initial temperatures and emphasizes the deviations from the computed velocities which are less than 2.5% even in the rich mixtures.

Schlieren photographs of detonation waves in 28.75, 39.00, and 52.50% hydrogen at ambient conditions are shown in Figure 7. The detonation wave is moving from left to right in the photographs. In Figure 7a (52.5% hydrogen) small-scale turbulence can be noted behind a sharp wave front. In Figure 7b (39.0% hydrogen) the wave front is thicker and the scale of the turbulence is greater. In Figure 7c (28.75% hydrogen) the wave front has degenerated into a complicated shock pattern followed by an irregular combustion zone. In view of these photographs, it is surprising that a theory which assumes

TABLE 2. COMPARISON OF COMPUTED AND EXPERIMENTAL PRESSURE RATIOS

	Computed	Experimental (19)
Detonation/initial pressure	17.5	20.4
Reflected/detonation pressure	2.45	3.0
Reflected/initial pressure	43.0	61.2

chemical equilibrium in a planar wave and neglects heat, component, and momentum transfer predicts detonation velocities in reasonable agreement with the experimental values.

THEORETICAL COMPOSITIONS, TEMPERATURES, AND PRESSURES

The temperature, pressure, and equilibrium composition behind the detonation wave and the pressure behind the reflected wave are tabulated for all the computed conditions in reference 18 and also are on file with the American Documentation Institute.[*]

The equilibrium compostion behind the detonation wave is illustrated in Figure 8 for an initial temperature of 298°K. and an initial pressure of 1 atm. Dissociation is observed to be significant for the entire range of initial compositions.

The detonation and reflected pressure ratios are plotted as a function of initial pressure for several initial compositions in Figure 9 and as a function of initial temperature for several initial compositions in Figure 10. These pressure ratios are observed to increase steeply as the initial temperature decreases but to be relatively independent of the initial pressure. A plot (not shown) of the pressure ratios vs. reciprocal tempera-

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[*] See footnote, p. 93.

ture demonstrates near proportionality. Thus for a given composition the developed pressures are roughly proportional to the initial density.

The temperature, pressure, and composition behind the detonation and reflected waves are extremely difficult to measure because of their brief existence, and only fragmentary experimental values are available for comparison with the computed values. The average of the detonation and reflected pressures measured by Ordin (19) for 55% hydrogen at 1 atm. and 298°K. are compared with the theoretical values for the same conditions in Table 2. The agreement is only fair but is probably within the range of uncertainty of these experimental values.

The absence of firm and extensive experimental confirmation of the computed temperatures, pressures, and compositions makes their validity uncertain but at the same time necessitates their use for design or other engineering purposes. The impact pressure, that is the pressure behind the reflected wave, is of particular practical interest as a possible criterion for the design of process equipment subject to detonation. Indeed, Luker and Leibson (17) have recently reported that the computed impact pressure for conditions under which a rupture disk just fails under detonation bears a constant ratio slightly greater than unity to the rated static bursting pressure of the disk.

CONCLUSIONS

The detonation velocity in hydrogen-oxygen mixtures depends slightly upon tube diameter. Correlation of the data for tubes of different diameter in terms of a linear relationship between velocity and the reciprocal of the tube diameter as suggested by Kistiakowsky and Zinman (9) permits correction of the velocities to their equivalent in a tube of infinite diameter.

After this correction the experimental detonation velocities agree reasonably

a   25.5% hydrogen
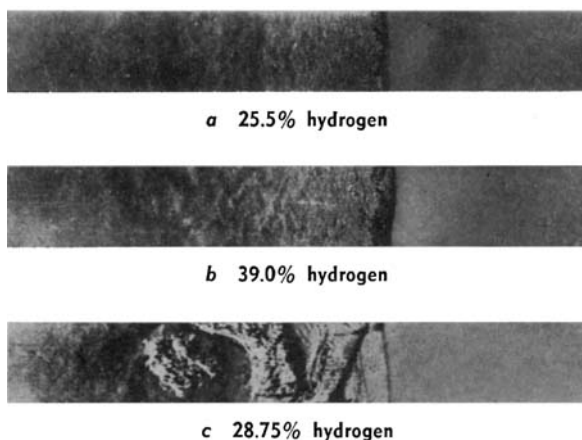
b   39.0% hydrogen

c   28.75% hydrogen

Fig. 7. Schlieren photographs of detonation waves in hydrogen-oxygen mixtures at atmospheric pressure and 298°K.
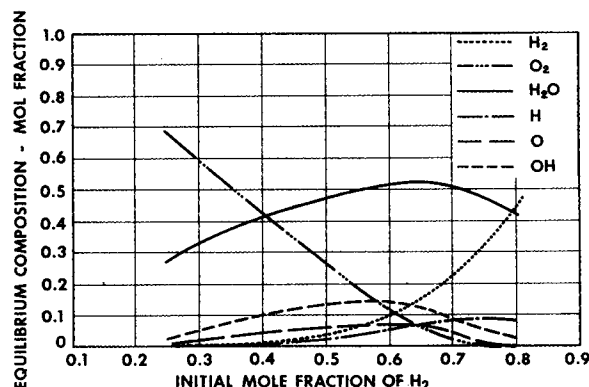

Fig. 8. Equilibrium composition behind detonation wave in hydrogen-oxygen mixtures at atmospheric pressure and 298°K.
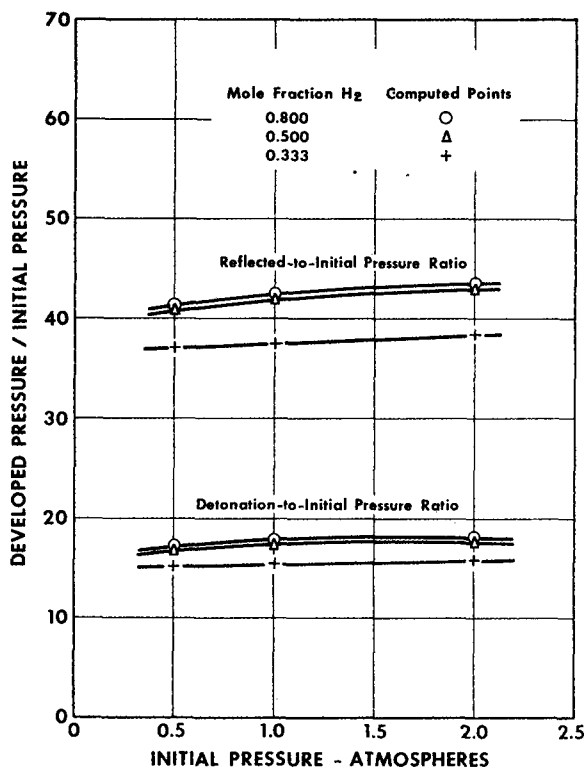
Fig. 9. Effect of initial pressure on developed pressure ratios in hydrogen-oxygen mixtures at 298°K.
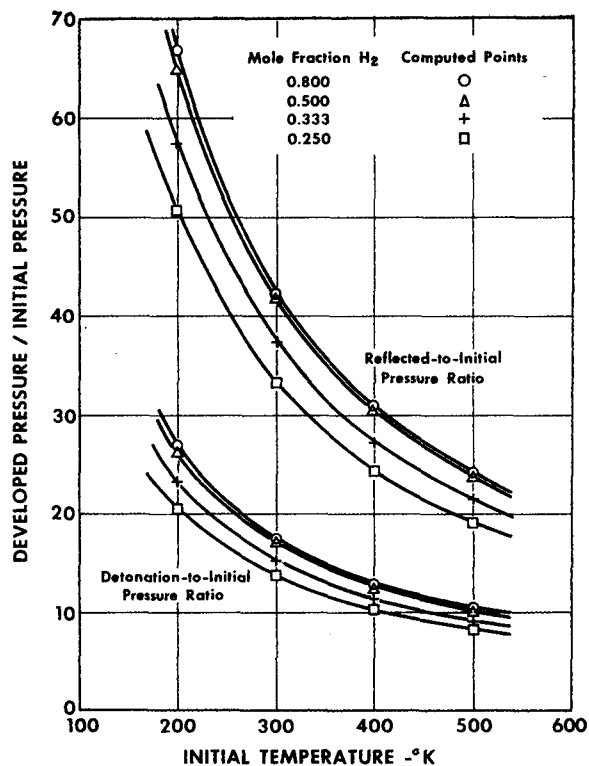

Fig. 10. Effect of initial temperature on developed pressure ratios in hydrogen-oxygen mixtures at atmospheric pressure.

well with values computed from the elementary theory of detonation over a range of compositions from 20 to 80% hydrogen, temperatures from 160° to 477°K., and pressures from ½ to 2 atm. Within this range of conditions the agreement between theory and experiment is poorest, and further investigation is warranted for rich mixtures and subatmospheric pressures. Below 20 and above 80% hydrogen the experimental velocities fall below the predicted values. The general agreement between theory and experimental velocities is surprising in view of the significant deterioration of the structure of the detonation wave front indicated by schlieren photographs for 39% and less hydrogen.

Experimental data to test the computed temperatures, pressures, and compositions are difficult to obtain and are not generally available. However recent work indicates that the computed impact pressure may be a suitable criterion for design.

The detonation velocity depends only slightly on the initial pressure and temperature but critically on the initial composition. The pressures behind the detonation and reflected waves depend only moderately on initial composition but increase linearly with initial pressure and with the reciprocal of the initial temperature.

NOTATION

D = tube diameter, in.

V = measured velocity in straight tube, m./sec.

V_c = measured velocity in coiled tube, m./sec.

V_∞ = equivalent velocity in infinite tube, m./sec.

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