Pressure and velocity measurements on detonation waves in hydrogen-oxygen mixtures

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Measurements are described of the static pressures and velocities of detonation waves in hydrogen-oxygen mixtures, together with the pressures arising on their normal reflexion at the closed end of the explosion tube. Two explosion tubes, of diameter 10 and 1·6 cm, were employed to study the diameter effect on the wave pressures. The experimental results are compared with calculated values of the wave properties for a range of hydrogen-oxygen mixtures initially at atmospheric pressure. In the 10 cm tube the static pressures and velocities are found to agree well with theory for mixtures with hydrogen content in the approximate range 50–75 %; the evidence from pressure profiles and wave velocities indicates that mixtures outside this range may not be able to support ideal C–J waves. Detonation waves in all the mixtures studied in the 1·6 cm tube are found to be subideal. A possible explanation, in terms of energy loss to the tube wall, of the discrepancy between experiment and theory is discussed. Spinning occurs in mixtures near the limits of detonation in the smaller tube; the measured frequencies are found to be in reasonable agreement with the values predicted by the theories of Manson (1947) and Fay (1952).

1. Introduction

Of the various properties of gaseous detonation waves, the velocities have been studied experimentally far more extensively than any other. Early investigators in this field were able to obtain tolerably good values for the wave velocities by means of chronoelectric methods (e.g. Berthelot & Vieille 1882) or from the records of the waves on moving photographic plates or film (e.g. Mallard & Le Chatelier 1900). Since then, the considerable advancements which have been made in high-speed photography and in the application of electronic techniques to the measurement of time intervals enable wave velocities to be measured to a high degree of precision. An example of such measurements is the study of the wave velocities in hydrogen-oxygen mixtures made by Berets, Greene & Kistiakowsky (1950).

In contrast to wave-velocity measurements, pressure measurements have received far less attention; this fact is understandable since it is a more difficult quantity to measure with accuracy. Early work gave no more than a crude and

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uncertain measure of the peak pressures generated in detonation waves. Thus Dixon & Cain (1894) attempted to estimate the pressures generated from the known strengths of glass tubes which were just fractured by the impact of the wave, whilst Campbell, Littler & Whitworth (1932) noted how metal foils of various thickness, placed across the end of an explosion tube, were ruptured. The results of both investigations were very approximate in view of the uncertainties in the mechanisms of fracture or rupture. Similarly, the results of the crusher gauge experiments of Rimarski & Konschak (1934) and Henderson (1941) must be regarded as unreliable.

The most significant measurements reported of detonation pressures in hydrogen-oxygen mixtures appear to be those of Gordon (1949) and Davies, Edwards & Thomas (1950). Gordon employed tourmaline gauges, in which oil or soft wax was used to damp the crystal vibrations, and although the results he presents are few and some of the gauge records are marred by oscillations, quite good agreement is observed between the measured and the theoretical values of pressure for a few compositions. Davies *et al.* used both quartz crystal gauges and the Hopkinson pressure bar method in the electrical form devised by Davies (1948), and in a preliminary investigation obtained results which were promising. It was apparent, however, that a more satisfactory gauge design was required before completely reliable pressure measurement could be achieved.

The need for a study of the pressure distribution in the detonation wave, in addition to a measure of its velocity, may be appreciated from the following considerations. (Contrary to strict usage the term detonation wave will frequently be employed in the present paper to denote the shock front, the reaction zone together with the non-steady regime of the rarefaction wave.) In the case of the ideal detonation wave the Chapman–Jouguet (C–J) plane is identified in the hydrodynamic theory with the plane of complete chemical and thermal equilibrium. Kirkwood & Wood (1954), however, have shown that thermodynamic equilibrium at the C–J plane is not an essential requirement in the generalized theory. Deviations from complete equilibrium at the C–J plane would be expected to give rise to differences between the observed detonation wave parameters and those computed on the assumption of equilibrium. Thus if the rate of release of chemical energy within the reaction zone is lowered, for example by cooling of the reacting gases at the walls of the confining vessel, then the rate of evolution of useful energy may drop below the level required for the propagation of the ideal C–J wave. In this case, the velocity of the wave will be less than the ideal value and the C–J condition, $U_1 = u_1 + c_1$, will now hold for the plane in which the energy required to propagate the wave (i.e. useful energy) is just balanced by the evolution of chemical energy. Berets *et al.* (1950) suggest that the excellent agreement which is usually observed between theoretical and experimental velocities may be due to the stabilizing action on the detonation velocity of the largely dissociated reaction systems, in which exothermic and endothermic reactions, involving both mole increment and decrement, are proceeding simultaneously. This interpretation appears to have been rejected later by Kistiakowsky & Zinman (1955), and agreement between experiment and equilibrium calculations is taken as proof of the attainment of thermodynamic equilibrium in the C–J plane. In the view of the present authors, the original hypothesis of the buffering effect of the reactants on the wave velocity is of some importance, and consequently an examination of the velocity alone does not provide a sufficiently strong criterion to establish whether equilibrium has been achieved in the C–J plane. Moreover, the measurement of any other parameter, such as pressure, density or temperature, for the same reason, would equally be insensitive to small departures from strict equilibrium at the C–J plane. If, however, the pressure-time or density distribution (Kistiakowsky & Kydd 1955) in the wave are known in conjunction with the velocity, then the two parameters give a more complete description of the wave than is obtained from the measurement of the wave velocity alone. Furthermore, a comparison of the detonation pressure with the theoretical value should provide a far more sensitive criterion of the validity of the C–J hypothesis itself than a measure of the velocity. This fact can be verified from an examination of theoretical data (e.g. Manson 1947); for if it is assumed that the end-point of the detonation moves away from the C–J point along the Rankine–Hugoniot curve for complete reaction, the corresponding changes in pressure are, for small deviations, several times as large as the resulting changes in velocity.

In this paper, results are presented of measurements of the static and reflexion pressures in detonation waves in various hydrogen-oxygen mixtures confined in tubes; measurements of the wave velocities were made simultaneously with the pressure measurements. Since no systematic investigation appears to have been carried out previously on the effect of explosion tube diameter on the wave pressures, comparable to the work of Berets *et al.* (1950) on the wave velocity, pressure measurements have been obtained for two explosion tubes of different diameter.

2. The numerical calculations

The best results available of the theoretical properties of detonation waves in hydrogen–oxygen mixtures are those of Berets *et al.* (1950), who employed the most recent thermochemical data given by the National Bureau of Standards (1949). Their calculations were made for an initial gas pressure of 1 atm. at a standard temperature of 25 °C. The ambient temperatures normally found in our laboratories are, however, nearer 18 °C, and whereas wave velocities are comparatively insensitive to small changes in initial gas temperatures, a significant dependence on such changes is found for the values of the wave pressures. Furthermore, to the authors' knowledge, no results have been reported of the properties of the shock wave arising on normal reflexion of a plane detonation wave at a rigid surface. For these reasons, a new series of calculations have been made of the properties of both the detonation wave and normally reflected shock wave.

2.1. *The detonation wave*

In the computation of the properties of the detonation wave, it is assumed that the burnt gases obey the ideal gas law (see Schmidt 1941; Kistiakowsky, Knight & Malin 1952), and the C–J plane is defined as the plane of thermodynamic equilibrium over which the condition $U_1 = u_1 + c_1$ obtains, where U_1, u_1 and c_1 are the wave, mass and sound velocities, respectively. Moreover, Brinkley & Richardson (1953) and Kirkwood & Wood (1954) have shown that the sound velocity, c_1, at the C–J plane must be evaluated at the instantaneous frozen composition (i.e. the total mole number being regarded as independent of pressure and temperature) and not, as had been previously assumed, for mobile equilibrium. Following Berets *et al.* (1950) allowance has been made in the calculations for the following equilibria:

$$\tfrac{1}{2}H_2 \rightleftharpoons H,$$
$$\tfrac{1}{2}O_2 \rightleftharpoons O,$$
$$H_2 + \tfrac{1}{2}O_2 \rightleftharpoons H_2O,$$
$$\tfrac{1}{2}H_2 + \tfrac{1}{2}O_2 \rightleftharpoons OH.$$

Initial composition	Temp. T_1 (°K.)	Pressure (C–J) (atm.)	Density ratio (ρ_1/ρ_0)	Velocity U_1 (m/s)	Velocity c_1 (m/s)	Mass velocity u_1 (m/s)	Final Composition (%)						Total mole number n
							H_2O	H_2	O_2	OH	H	O	
$8H_2+O_2$	2717	14·53	1·74	3802	2186	1615	24·70	73·82	0·00	0·11	1·36	0·00	8·060
$4H_2+O_2$	3439	17·79	1·76	3425	1942	1483	42·74	45·16	0·15	3·37	8·16	0·41	4·270
$3H_2+O_2$	3607	18·44	1·77	3197	1807	1390	48·97	31·68	0·89	7·20	9·78	1·48	3·365
$2H_2+O_2$	3675	18·59	1·77	2853	1610	1243	53·00	16·72	5·13	12·85	8·17	4·13	2·493
H_2+O_2	3467	17·63	1·77	2333	1318	1015	47·59	4·14	26·34	13·45	2·65	5·83	1·673
H_2+2O_2	3029	15·79	1·76	1941	1103	838	34·76	0·62	55·57	6·22	0·34	2·49	2·587
H_2+3O_2	2662	14·14	1·75	1759	1006	752	26·92	0·11	69·77	2·43	0·04	0·72	3·538

TABLE 1. The detonation wave. Initial pressure, 1 atm.; initial temperature, 18 °C.

The method adopted for the solution of the detonation wave and reflected shock wave equations closely follows that used by Huff, Gordon & Morrell (1951) for the computation of the equilibrium composition and temperature of chemical reactions. This method, when applied to the detonation and reflected shock wave equations arranged in a suitable form, gives a rapidly convergent solution and has been found suitable for use with a desk calculator and for programming on an electronic digital computer. The calculated values of the parameters at the C–J plane and their values behind the leading shock of the detonation wave, termed the 'von Neumann' peak, are given in tables 1 and 2. In addition to the symbols already defined, p, ρ and T denote the pressure, density and temperature respectively, and the subscripts 0, 1 and 2 are used to define their values in the unburnt gases, behind the incident detonation front, and behind the reflected shock front, respectively; the peak values of the parameters are designated by a circumflex accent.

2.2. *The reflected shock wave*

The computation of the reflected shock wave properties has been divided into two parts:

(*a*) The computation of the properties of the shock wave obtained on reflexion of the von Neumann peak, in which it is assumed that, immediately on reflexion, the shock wave moves into a medium which is at the conditions prevailing at the von Neumann peak of the incident detonation wave, and for which the boundary condition at the reflecting wall is $\hat{u}_2 = 0$.

(*b*) A similar computation to the above has been made for the C–J plane in which it is assumed that the boundary condition for the reflexion is $u_2 = 0$.

Initial composition	Temp. $\hat{T}_1$ (°K.)	Pressure $\hat{p}_1$ (atm.)	Density ratio ρ_1/ρ_0	Velocity U_1 (m/s)	Mass velocity $\hat{u}_1$ (m/s)
$8H_2+O_2$	1505	26·68	5·16	3802	3065
$4H_2+O_2$	1739	32·69	5·47	3425	2799
$3H_2+O_2$	1778	33·89	5·55	3197	2621
$2H_2+O_2$	1774	34·16	5·61	2853	2344
H_2+O_2	1678	32·43	5·63	2333	1919
H_2+2O_2	1521	29·10	5·57	1941	1593
H_2+3O_2	1391	26·06	5·45	1759	1437

TABLE 2. The von Neumann peak in the detonation wave.
Initial pressure, 1 atm.; initial temperature, 18 °C.

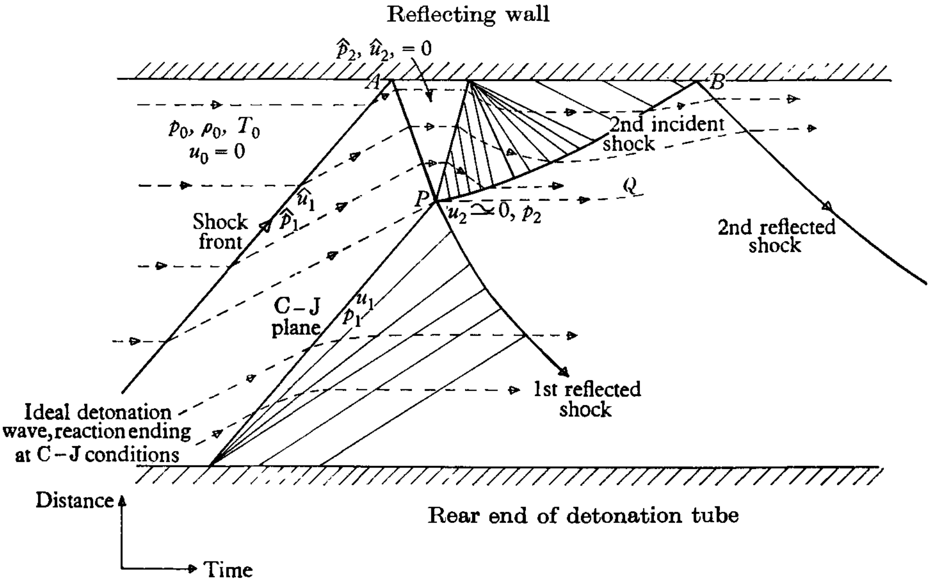

FIGURE 1. Diagram of the proposed construction of the reflexion of an ideal detonation wave at a rigid surface. Particle paths, — ▹ —.

A possible construction of the reflexion process of an ideal detonation wave at a rigid surface has been suggested to the authors by Mr C. K. Thornhill. In order to simplify the geometry the device is adopted of compressing the reaction into an instantaneous event, a short finite time after the passage of the causal shock; i.e. the detonation wave is replaced by an initial shock followed by a short period of steady state at peak conditions and ending in a 'reaction shock' running into the C–J state. This construction is shown, in a qualitative fashion, in the diagram of figure 1.

From the diagram it is seen that the present computation refers to conditions at the point P, on the dividing particle-path PQ, which represents the point of intersection of the reflected shock and incident C–J plane, assuming that the mass flow u_2 is reduced almost to rest at this point. The point P is at a distance of the order of the width of the reaction zone of the incident detonation wave away from the reflecting wall; for gaseous mixtures initially at atmospheric pressure, the reaction time is of the order of 1 μs and the thickness of the reaction zone is ~ 1 mm (Kistiakowsky & Kydd 1956). An important feature of the construction is the hypothesis that a pressure and velocity balance is achieved at the dividing particle-path PQ by the existence of a second shock front which is reflected at the point B in the diagram a finite time after the arrival of the first shock at the reflecting wall; experimental evidence in support of this proposition is discussed later. Calculated values of the parameters at the point P are given in table 3 and their peak values at the wall in table 4.

Initial composition	Temp. T_2 (°K)	Pressure p_2 (atm.)	Density ratio ρ_2/ρ_1	Velocity U_2 (m/s)	Final composition (%)						Total mole number, n
					H_2O	H_2	O_2	OH	H	O	
$8H_2+O_2$	3136	34·31	2·02	1581	24·10	72·08	0·00	0·40	3·40	0·01	8·16
$4H_2+O_2$	3773	42·22	2·10	1343	39·28	44·01	0·27	4·95	10·70	0·78	4·39
$3H_2+O_2$	3915	43·79	2·12	1239	44·20	31·86	1·14	9·00	11·68	2·12	3·47
$2H_2+O_2$	3971	44·18	2·13	1100	47·64	17·89	5·18	14·63	9·63	5·02	2·58
H_2+O_2	3763	41·83	2·12	902	43·37	5·01	24·79	15·91	3·56	7·37	1·72
H_2+2O_2	3345	37·29	2·10	747	32·14	0·98	53·21	8·88	0·66	4·12	2·64
H_2+3O_2	3016	33·31	2·05	715	25·33	0·27	67·94	4·50	0·15	1·81	3·58

TABLE 3. The reflected shock wave. Initial pressure, 1 atm.; initial temperature, 18 °C.

Initial composition	Temp. $\hat{T}_2$ (°K)	Pressure $\hat{p}_2$ (atm.)	Density ratio $\hat{\rho}_2/\hat{\rho}_1$	Velocity $\hat{U}_2$ (m/s)
$8H_2+O_2$	2783	175·4	3·55	1200
$4H_2+O_2$	3243	226·6	3·72	1030
$3H_2+O_2$	3322	237·8	3·76	951
$2H_2+O_2$	3315	241·7	3·79	841
H_2+O_2	3128	229·9	3·80	685
H_2+2O_2	2819	203·7	3·78	573
H_2+3O_2	2559	178·6	3·73	527

TABLE 4. The peak values in the reflected shock wave. Initial pressure, 1 atm.; initial temperature, 18 °C.

2.3. *The effect of initial temperature*

Several calculations were carried out for the stoichiometric mixture assuming different values of initial temperature. In figure 2 graphs are shown of the percentage deviation of the detonation velocities and pressures, from their values calculated for an initial temperature of 18 °C, plotted against temperature. Over the range of temperatures which is likely to occur under laboratory conditions, the variation of the detonation, von Neumann peak, reflected shock and peak reflected shock pressures is sufficiently linear to permit a general correction factor of $-0{\cdot}34\,\%$ per °C rise in temperature to be applied to the values of p_1, $\hat{p}_1$ and p_2, and $-0{\cdot}40\,\%$ per °C to the values of $\hat{p}_2$, given in tables 1–4. The variation of detonation velocity with temperature, shown in the same diagram, is seen to be sufficiently small so as to be negligible for most purposes over moderate ranges of temperature.

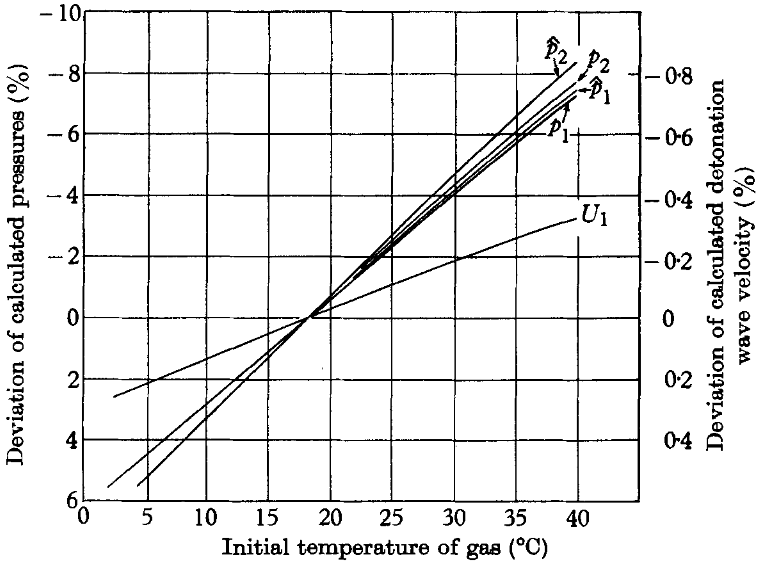

FIGURE 2. Graphs showing the variation with initial gas temperature of the percentage deviation of detonation and shock wave parameters in $2H_2 + O_2$ from their values calculated for an initial temperature of 18 °C. Initial gas pressure 1 atm.

3. Experimental work

3.1. *The explosion tubes*

The two explosion tubes are of circular cross-section, the larger tube is made of mild steel with ½ in. thick wall and internal diameter 10 cm, whilst the smaller tube is of brass of internal diameter 1·6 cm and ⅛ in. wall. Both tubes consist of two sections, termed the 'driving' and 'test' sections, each of the same diameter, which are approximately 1 and 4 m long, respectively. Heavy flanges are welded to the ends of both sections of the 10 cm diameter tube enabling them to be bolted together; by placing a cellophane diaphragm between the flanges the two sections can be isolated from each other. The ends of the tube are closed by means of two steel plates. All the flanges are grooved to accommodate rubber O-rings to ensure vacuum-tight connexions. The smaller tube is similarly designed. The internal wall of the large tube has a slight roughness, whereas the wall of the brass tube is reasonably smooth; no measures were taken to improve these surfaces, the tubes being used as supplied by the manufacturers.

3·2. *The pressure gauges and ionization probes*

A pressure gauge has been developed in this Laboratory which employs an X-cut quartz disk to measure the average stress over the cross-section of a duralumin rod. The construction and behaviour of this gauge is described by Edwards (1958) who has shown that it gives satisfactory records of the pressure profile in gaseous detonation waves. Pressure bars of $\frac{1}{4}$ and $\frac{1}{2}$ in. diameter have been used in the present investigation, the former for the measurement of the reflexion pressures and the latter for the static pressures in the waves. The time interval over which the gauge will record is determined by the length of bar used; in most instances a gauge capable of recording over an interval of 220 μs was adequate, but when recordings were required over longer intervals a gauge of greater length was employed which responded to pressure pulses of approximately 1·1 ms duration. The pressure gauges could be set to measure the static and reflexion pressures by screwing the gauge head into bushes, one is placed in the cylindrical wall of the tube at a distance of 30 cm from the end of the tube and another is placed centrally in the end-plate. In order to reduce the transmission of stress waves propagated in the explosion tube wall to the gauge, these bushes are constructed of polythene. The measuring end of the static pressure gauge is machined to the same radius as the internal wall of the tube so that when the gauge is mounted in position this face is flush with the internal wall surface. Similar care is taken to ensure that the reflexion pressure gauge is flush with the end-plate.

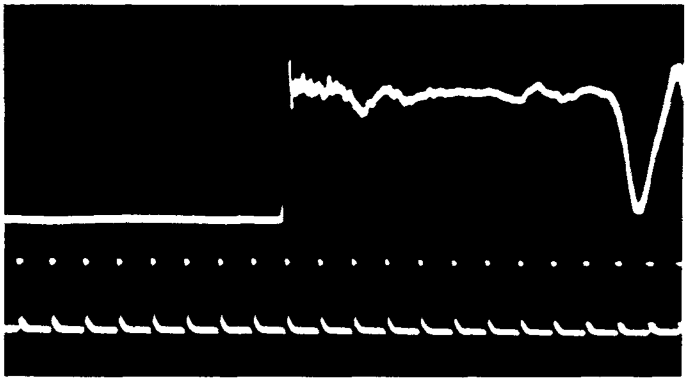

FIGURE 3. Oscillogram obtained with $\frac{1}{4}$ in. gauge when set to measure the reflexion pressure due to a shock wave in air. Shock Mach number: 1·75. Timing marks: 20 μs.

The manner in which the gauges are calibrated by a ball impact method has been described by Edwards (1958). In addition to this method, the gauges were calibrated by the impact of shock waves in air, generated in a 5 cm diameter shock tube. A typical record obtained when a $\frac{1}{4}$ in. diameter gauge is set to measure the reflected shock pressure is shown in figure 3. It is seen that oscillations due to dispersion of the stress waves in the gauge bar occur immediately after the initial rise. The average voltage level, however, remains constant over an interval of $\sim$ 220 μs before the return of the pulse of tension from the free end of the pressure bar. Values of the gauge constant can be determined from these records to an accuracy of within 1 %.

Velocity measurements on the detonation waves are made by the ionization probe technique. The design of the probes and of the associated electrical circuitry used in the 10 cm diameter tube closely resemble those described by Knight & Duff (1955). Twelve probes are fitted into the tube wall in two groups of six, the probes in each group being placed at intervals of 10 and 20 cm, respectively. In the 1·6 cm tube 10 mm sparking plugs are used as probes, their ends having been slightly modified so that no part protrudes into the tube and interferes with the gas flow.

3.3. *The recording apparatus*

Any circuit external to the pressure gauge must possess a sufficiently high input impedance if leakage of charge from the gauge is to be kept low during the time in which the gauge signal is being recorded. For this purpose, a cathode-follower is used which has an input impedance of 20 MΩ and whose frequency characteristics are constant up to 2 Mc/s. The signal from the cathode-follower is fed by a coaxial cable into a recording room where it is amplified and displayed on a c.r.o., a Solarscope Type CD 513, and recorded on a stationary plate camera. The time-base of the c.r.o. is initiated at a predetermined interval before the arrival of the pressure gauge signal by a pulse from an ionization probe.

Two methods are available for recording the ionization probe signals. In the first, when it is desired to follow the variation of the wave velocity along the length of the tube, the voltage pulses, after appropriate shaping, are displayed on a c.r.o. and recorded photographically. Alternatively, if only the average velocity over a particular length of tube is desired, the pulses from two selected probes are employed to trigger a 'Cintel' microsecond chronometer. The accuracy obtainable by these methods in the measurement of velocity is generally $\sim \frac{1}{2}\%$.

3.4. *Preparation of the gas mixtures*

The driving and test sections of the explosion tube are evacuated simultaneously, the pressure in the tube being measured by a mercury manometer and a 'Vacustat' gauge; a residual pressure of 0·1 mm of mercury is considered satisfactory. After evacuation the tube is isolated from the vacuum pump and each section is filled in turn, the constituent gases being obtained from commercial cylinders. The partial pressure of each component gas is measured by means of the mercury manometer, which can be read to the nearest 0·05 cm. The test section of each tube is filled first and in the case of the 10 cm diameter tube a coarse grid, fixed near the end of the driving section, provides support for the diaphragm during this operation. A minimum time of 12 h is allowed for the gases to mix. Facilities are available for pre-mixing the gases in large cylinders before admitting them into the 1·6 cm tube; in this way errors in metering small volumes of gas are avoided.

4. Results

4.1. *The* 10 *cm diameter tube*

In all the experiments performed in this tube, the gaseous mixture was initially at atmospheric pressure and at room temperature which was within a degree or two of 18 °C. In the preliminary work, the cellophane diaphragm separating the driving and test sections was absent, the detonation being initiated by electrically firing copper acetylide matchheads. The pressures obtained, however, even with the more strongly detonating mixtures, were substantially higher than the theoretical values and the measured velocities in all mixtures were between 3 and 4 % below those calculated. After carefully checking the recording apparatus it was concluded that even after a run of approximately 5 m in mixtures near the stoichiometric composition, a stable wave was not established by this method of initiation. It was, therefore, abandoned in favour of the shock wave method of initiation, the shock waves being generated by detonating a stoichiometric acetylene-oxygen mixture, at an initial pressure of 1 atm., contained in the driving section.

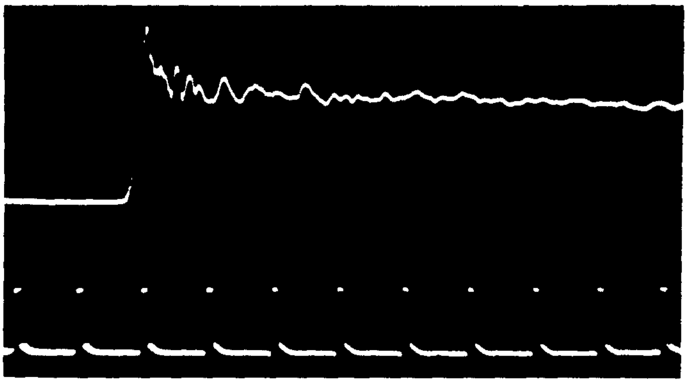

FIGURE 4. Oscillogram of the response of the ½ in. gauge to the static pressure in a detonation wave in $2H_2+O_2$ in the 10 cm diameter tube. Timing marks: 20 μs.

A typical oscillogram, obtained with the ½ in. pressure gauge, of the static pressure in $2H_2+O_2$ is shown in figure 4 and the pressure-time distributions derived from three such records are given in figure 5. The oscillations appearing have been smoothed out so that the general trend of the profile can be appreciated more readily. It will be observed that the rise time of the pressure to the peak value is 7·0 μs, which exceeds the time of traverse of the wave across the end of the pressure gauge of 4·45 μs. This discrepancy in the two values arises from the distortion of the pulse due to the dispersion of the stress pulse as it travels along the pressure-bar; this has the effect of rounding-off sharp pressure variations and lengthening the rise-times (see Davies 1948). The peak pressure observed in the records is attributed to the partial response of the gauge to the von Neumann peak pressure within the detonation wave. That this peak is not due to a gauge effect may be verified by comparing the records with the record of figure 3 obtained for the shock waves in air, in which the characteristic overshoot of the pressure bar signal due to dispersion is seen to be markedly different to the response for the detonation wave. The average value obtained from four records for this peak pressure is 27·1 atm. compared with the theoretical value of 34·16 atm. An exact response to the peak pressure is not to be expected since the reaction zone of the wave is extremely narrow and is obviously outside the limit of resolution obtainable with the gauge; the significance of this peak will be discussed later. Following the peak value the pressure on the records falls rapidly, until after an interval of ~ 5 μs the pressure begins to level out and remains sensibly constant for the next 80–90 μs, and thereafter it begins to decay slowly under the influence of the following rarefaction wave. The average pressure over the period 20–80 μs has been measured for comparison with the theoretical value, and the mean value found from four records for this mixture is 18·6 atm. which is in excellent agreement with the computed C–J value of 18·59 atm. To illustrate the reproducibility of the static pressure records, values for the four records obtained with the stoichiometric mixture are given in table 5.

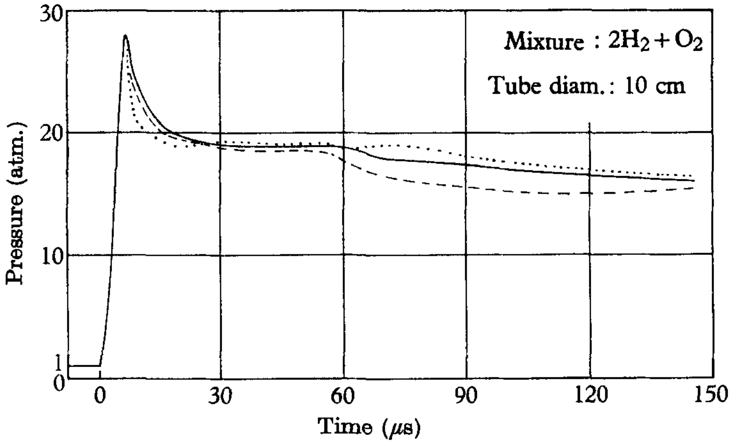

FIGURE 5. Pressure-time distributions obtained from three recordings with a ½ in. gauge set to measure the static pressure in $2H_2 + O_2$. Tube diameter: 10 cm.

Peak pressure (obs.) (atm.)	Average pressure 20–80 μs (obs.) (atm.)	Average pressure 100–200 μs (atm.)	Rise time (obs.) (μs)
26·8	19·0	16·7	7·2
26·7	18·4	15·2	7·2
27·9	18·6	16·7	6·8
27·1	18·6	17·5	7·1

TABLE 5. Reproducibility of the static pressures in $2H_2 + O_2$ in 10 cm diameter tube. Peak pressure (theor.), 34·16 atm.; C–J pressure (theor.), 18·59 atm.

Pressure–time curves for the non-stoichiometric mixtures investigated are shown in figure 6. As before, the small amplitude irregular oscillations appearing on the records have been smoothed out. The general shapes of the curves for all the mixtures are very similar except for H_2+3O_2 which does not exhibit the sharp initial rise found in the others. The values of the observed and theoretical peak and C–J pressures are given for each mixture in table 6, and the corresponding wave velocities in Table 7.

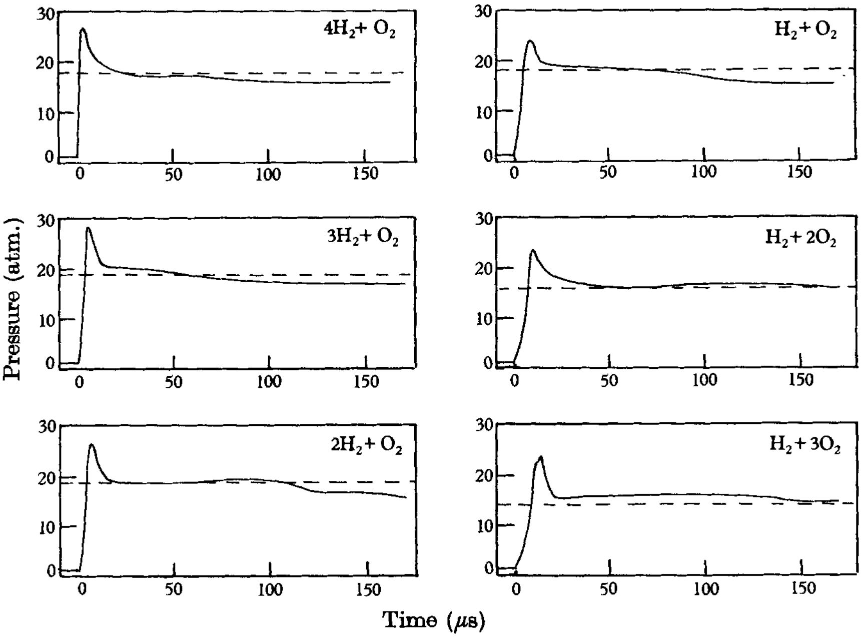

Figure 6. Static pressure–time curves for various mixture compositions in the 10 cm diameter tube. Broken lines represent the calculated C–J pressures.

Mixture	Peak pressure (obs.) (atm.)	Peak pressure (theor.) (atm.)	Average pressure 20–80 μs (obs.) (atm.)	C–J pressure (theor.) (atm.)
$4H_2+O_2$	27·3	32·69	18·0	17·78
$3H_2+O_2$	28·1	33·89	18·4	18·44
$2H_2+O_2$	27·1	34·16	18·6	18·59
H_2+O_2	26·1	32·43	18·3	17·63
H_2+2O_2	25·0	29·10	16·7	15·79
H_2+3O_2	24·9	26·06	15·1	14·14

Table 6. Static pressures in the 10 cm diameter tube.

The pressure–time relationship obtained when the ¼ in. gauge is set to measure the pressure due to the normal reflexion of a detonation wave in $2H_2+O_2$ at the plate closing the end of the tube is shown in figure 7. As would be expected the initial rise-time of 3·2 μs is shorter than the corresponding times on the static records. Following the initial peak, the pressure drops rapidly and after a further interval, ranging between 11 and 19 μs, depending on the composition of the mixture, a second very sharp peak occurs which again rapidly decays; thereafter, the pressure remains reasonably constant for the next 100 μs or so before beginning to rise slowly. Similar features are observed for the reflexion records in all the mixtures and consequently they are not reproduced; numerical values are given in table 8.

Mixture	Velocity (obs.) (m/s)	Velocity (theor.) (m/s)	Standard deviation (%)	Deviation from theory (%)
$4H_2+O_2$	3344	3425	0·7	−2·3
$3H_2+O_2$	3156	3197	0·2	−1·3
$2H_2+O_2$	2825	2853	0·5	−1·0
H_2+O_2	2320	2333	0·5	−0·6
H_2+2O_2	1909	1941	0·3	−1·6
H_2+3O_2	1691	1759	0·3	−3·8

TABLE 7. Detonation velocities in the 10 cm diameter tube

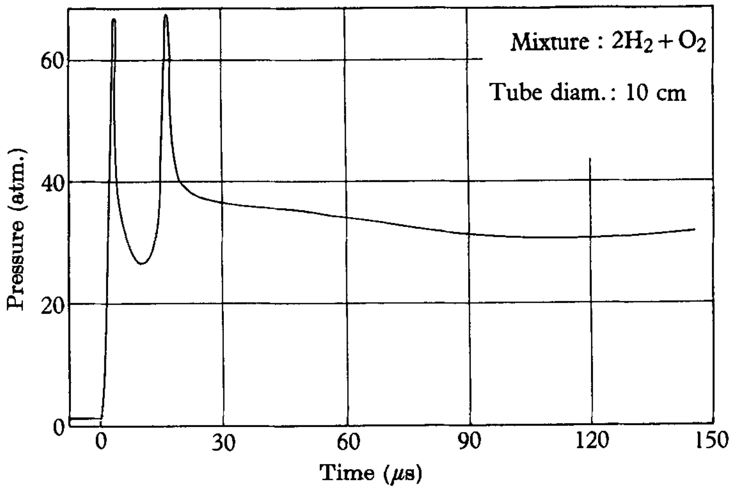

FIGURE 7. Pressure–time curves of the reflexion pressure for a detonation wave in $2H_2+O_2$ in the 10 cm diameter tube.

Mixture	Peak pressure (obs.) (atm.)	Peak pressure (theor.) (atm.)	Average pressure 20–100 μs (atm.)	C–J reflexion pressure (theor.) (atm.)
$4H_2+O_2$	59·4	226·6	37·0	42·22
$3H_2+O_2$	59·7	237·8	37·5	43·79
$2H_2+O_2$	62·5	241·7	33·8	44·18
H_2+O_2	60·6	229·9	38·0	41·82
H_2+2O_2	—	203·7	34·3	37·29
H_2+3O_2	75·4	178·5	37·9	33·31

TABLE 8. Reflexion pressures in the 10 cm diameter tube.

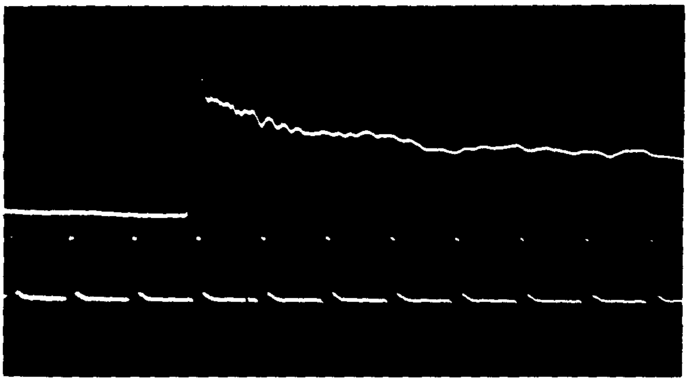

FIGURE 8. Oscillogram of static pressure in $2H_2 + O_2$ in the 1·6 cm diameter tube. Timing marks: 20 μs.

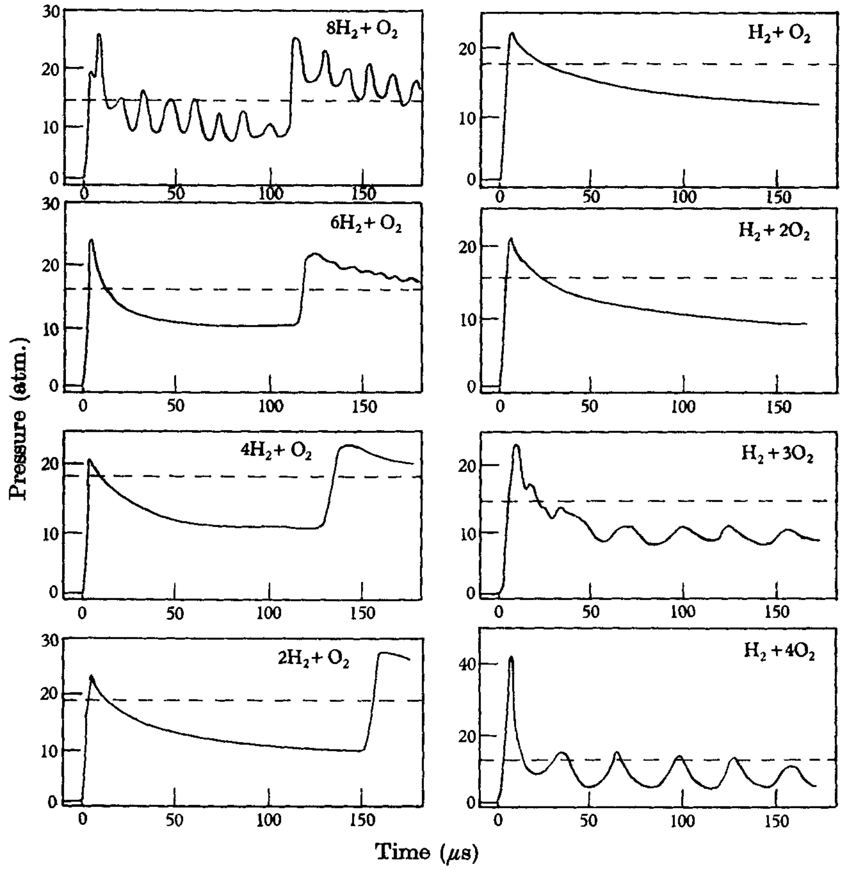

FIGURE 9. Static pressure–time curves for various mixture compositions in the 1·6 cm diameter tube. Broken lines represent the calculated C–J pressures.

4.2. *The* 1·6 *cm diameter explosion tube*

An oscillogram obtained in the 1·6 cm diameter tube for the detonation wave in $2H_2 + O_2$ is shown in figure 8; the initiating mixture again is $C_2H_2 + O_2$ at an initial pressure of 1 atm. Pressure–time curves for each of the mixtures examined in this tube are given in figure 10; on the first four of these records the shock wave reflected from the closed end of the tube has been recorded. The compositions

Mixture	Peak pressure (obs.) (atm.)	Peak pressure (theor.) (atm.)	Average pressure 20–80 μs (obs.) (atm.)	C–J pressure (theor.) (atm.)
$8H_2+O_2$	33·2	26·7	11·6	14·53
$6H_2+O_2$	24·2	29·4	12·3	15·85
$4H_2+O_2$	23·3	32·7	13·5	17·78
$2H_2+O_2$	24·3	34·2	14·6	18·59
H_2+O_2	21·7	32·4	14·4	17·63
H_2+2O_2	21·3	29·1	13·4	15·79
H_2+3O_2	23·4	26·1	11·2	14·14
H_2+4O_2	43·4	24·2	10·2	12·60

TABLE 9. Static pressure in the 1·6 cm diameter tube.

Mixture	Velocity (obs.) (m/s)	Velocity (theor.) (m/s)	Standard deviation (%)	Deviation from theory (%)
$8H_2+O_2$	3542	3802	0·5	−6·8
$6H_2+O_2$	3550	3750	0·4	−5·3
$4H_2+O_2$	3268	3425	0·3	−4·6
$2H_2+O_2$	2769	2853	1·0	−3·0
H_2+O_2	2315	2333	0·2	−0·8
H_2+2O_2	1901	1941	0·2	−2·1
H_2+3O_2	1683	1759	0·2	−4·3
H_2+4O_2	1522	1680	0·2	−9·4

TABLE 10. Detonation velocities in the 1·6 cm diameter tube.

Mixture	Peak pressure (obs.) (atm.)	Peak pressure (theor.) (atm.)	Average pressure 20–100 μs (obs.) (atm.)	C–J reflexion pressure (theor.) (atm.)
$8H_2+O_2$	81·4	175·4	21·9	34·31
$6H_2+O_2$	67·0	201·0	22·8	38·26
$4H_2+O_2$	66·9	226·6	28·5	42·22
$2H_2+O_2$	60·5	241·7	30·9	44·18
H_2+O_2	51·5	229·9	30·4	41·83
H_2+2O_2	56·6	203·7	26·6	37·29
H_2+3O_2	104·9	178·5	28·2	33·31
H_2+4O_2	118·0	153·3	23·3	29·33

TABLE 11. Reflexion pressures in the 1·6 cm diameter tube.

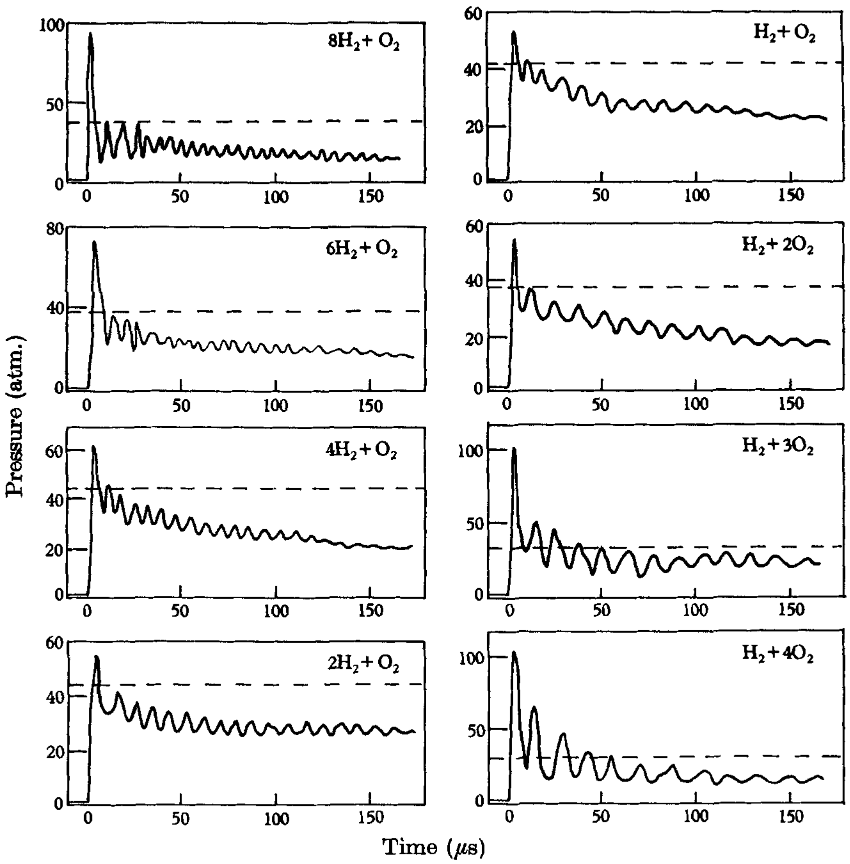

FIGURE 10. Pressure–time curves of the reflexion pressures for various mixture compositions in the 1·6 cm diameter tube. Broken lines represent the calculated reflexion pressures.

Mixture	Fundamental mode spin frequency (Kc/s)	Frequency observed on static gauge (Kc/s)	Frequency observed behind reflected shock on static gauge (Kc/s)	Frequency observed on reflexion gauge (Kc/s)
$8H_2+O_2$	80·7	76	79·9	154·9
$6H_2+O_2$	76·2	—	138·0	143·5
$4H_2+O_2$	71·7	—	—	129·8
$2H_2+O_2$	59·4	—	—	110·2
H_2+O_2	48·6	—	—	93·3
H_2+2O_2	40·7	—	—	76·5
H_2+3O_3	37·1	36·3	—	74·3
H_2+4O_2	33·6	32·9	—	66·3

TABLE 12. Frequencies of vibrations observed on the static and reflexion pressure records in 1·6 cm diameter tube.

$8H_2+O_2$, H_2+3O_2 and H_2+4O_2 show pronounced regular oscillations; the periods of these oscillations have been measured and they will be discussed later in connexion with the theory of spinning detonation. In all the records no pressure plateau occurs after the initial peak; the pressure drops relatively rapidly after the peak value and continues to do so throughout the duration of the record. However, since it is useful to compare the pressures of the detonation waves in the two tubes, the mean pressures over the interval 20–80 μs on the records are quoted in Table 9. Values of the velocities for the various mixtures are given in table 10.

Pronounced oscillations are found on all the reflexion pressure–time curves in the 1·6 cm tube which are given in figure 10. The curves show an initial sharp pressure peak followed by a slow decay in pressure, but after approximately 80 μs the pressure remains fairly constant for the remainder of the record. Observed and calculated values for the reflexion pressures are given in table 11, and the frequencies of the oscillations in both the static and reflexion records in table 12.

5. Discussion

5.1. *The* 10 *cm diameter tube*

The static pressures observed in this tube (table 6) are in general agreement with the theoretical C–J pressures and for some of the mixtures the agreement is well within the experimental error. Most of the observed values, however, are somewhat higher than the theoretical values; the discrepancies, which are more pronounced for mixtures containing excess oxygen, cannot be accounted for by systematic errors in measurement. Furthermore, the observed detonation velocities are all lower than the calculated values, the lack of agreement becoming more serious the further the gas composition is removed from stoichiometric. Berets *et al.* (1950), in their investigation of the velocities of detonation waves in hydrogen-oxygen in a 10 cm tube, obtained good agreement with theory in the middle composition range, lower velocities in mixtures with excess hydrogen, and higher velocities in mixtures with excess oxygen. During the course of later investigations Kistiakowsky & Zinman (1955) report that the high velocities observed in the excess oxygen mixtures were due entirely to overdriving of the mixture by the initiator. This interpretation would seem to imply that the low velocities, when excess hydrogen is present, are genuine and since in these mixtures the effects of overdrive would presumably have been present, it can only be inferred that the effect of its removal would be to yield even lower values than were originally observed. Even after allowing for the spread in the present measurements the conclusion cannot be escaped that, for the extreme composition, the velocities are significantly lower than those computed. At first it was thought that these low values could be attributed to the imperfections in the explosion tube wall; in view of the work of Kistiakowsky & Zinman on acetylene-oxygen mixtures however, this hypothesis would appear to be untenable since the 'wall-effect' is independent of the mixture composition.

Berets *et al.* (1950) attribute the differences between experimental and theoretical velocities to energy losses to the explosion tube wall. Such losses could arise in two ways: (1) by the instantaneous cooling of a layer of gas in contact with the wall, and (2) by friction at the wall causing a reduction in mass velocity in the proximity of the wall. Both effects would give rise to a rarefaction wave which is propagated into the interior of the tube. If this occurs within the reaction zone, the resulting lowering of the temperature reduces the rate of chemical reaction thereby causing a lowering of the detonation velocity. At the same time, this hypothesis necessarily implies a lowering of the pressure which is contrary to the experimental evidence. Thus although cooling and frictional effects are almost certainly present, they are alone insufficient to explain the observed deviations of pressure, so that some further mechanism must be present which maintains the pressure at a higher value. On close examination of the pressure profiles of figure 6, it is seen that the further the mixture composition is removed from the stoichiometric, the longer the pressure takes to decay from its peak to the C–J equilibrium value. Even though the gauge is incapable of reproducing faithfully the pressure variations which occur in times of a few microseconds, a comparison of the width of the peak in various mixtures provides a relative measure of the duration of the reaction zone. It appears reasonable to assume that although the greater part of the chemical reaction is completed within the first few microseconds, complete equilibrium is not attained in some mixtures until $\sim 80\,\mu s$ after the onset of the detonation wave. This effect is more marked in mixtures away from stoichiometric composition where the rate of chemical reaction is much lower owing to the lower temperature. Thus mixtures away from stoichiometric may not be able to support an ideal C–J wave at all; the detonation waves in these mixtures corresponding to the subideal waves of Brinkley & Richardson (1953). These waves have been shown to propagate with velocities which are less than the ideal C–J values and since the rate of chemical reaction is low the pressure in the wave will not decay as quickly as in the ideal wave. From the present pressure and velocity measurements it may be concluded that the hydrodynamic theory gives a correct description of the detonation wave in hydrogen-oxygen mixtures having a hydrogen content in the range of approximately 50–75 %. The agreement between experiment and theory, however, does not imply that the assumption of chemical equilibrium at the C–J plane has been rigorously established.

The first peak on the reflexion pressure records corresponds to the reflexion of the von Neumann peak of the incident wave; the magnitude of the peak pressures recorded bears no resemblance to the calculated values due to the inadequacy of the gauge response. The interesting feature of these records is the second sharp peak, which occurs in all the mixtures studied in this tube, and which appears to present strong evidence for the second reflected shock front predicted by the construction shown in figure 1 for the normal reflexion of a detonation wave. It is certain that the second peak is not attributable to a property of the gauge, and the time interval between its occurrence and the first peak shows a corresponding variation with the acoustic velocity of the burnt gases of the mixtures. Further elucidation of the reflexion process, however, must await a photographic investigation of waves in this tube. Moreover, the values of the properties calculated on the assumption stated in

§ 2.2(*b*) are essentially the values obtaining at a plane a distance of the order of the width of the reaction zone in front of the reflecting wall; consequently there is no strict basis for comparison between the calculated pressures and the pressures measured at the wall. It is to be expected, however, that they would be of the same order of magnitude as the comparison, given in table 8, between the calculated and observed average pressures in the interval 20–100 μs shows.

5.2. *The* 1·6 *cm diameter tube*

The main features of the static pressure records obtained in this tube are the relatively rapid decay of the pressure following the initial peak and the pronounced oscillations occurring in the mixtures H_2+3O_2, H_2+4O_2 and $8H_2+O_2$. Furthermore, the measured velocities are all less than the ideal values, the deviations being greater for extreme compositions. To account for these low velocities and the observed pressure profiles it must be assumed that all the waves in the 1·6 cm tube are subideal. It has been noted above that the effect of the rarefaction wave, which originates at the wall of the tube due to cooling of the gas, is to lower the pressure and the rate of chemical reaction which in turn tends to maintain the pressure at a higher value. Whereas it was concluded that in the 10 cm tube the latter effect is dominant, in the small diameter tube it is reasonable to expect the lowering of the pressure due to cooling of the burnt gas to have the greater effect on the pressure profile of the wave. Consequently, the low values of pressure found in the 1·6 cm tube are probably due to the encroachment of the rarefaction wave into the reaction zone. If this were so, a large part of the energy released by the chemical reaction is lost to the walls of the tube since the reaction zone is spread out down the tube; this would lead to wave velocities less than the theoretical values, which is borne out by experiment.

The large amplitude oscillations occurring on the records of three of the mixtures are attributed to spinning of the wave. Measured values of the spin frequencies are compared in table 12 with values derived from the theories of Manson (1947) and Fay (1952), in which the frequency ν of the fundamental mode of transverse vibration is related to the acoustic velocity in the burnt gas c_1 and the tube radius r_0 by $\nu = c_1\, 1{\cdot}841/2\pi r_0$. The agreement between the observed and calculated frequencies leaves no doubt as to the nature of these vibrations; the observed values are, however, slightly lower due to the value of c_1 being lower than the ideal value assumed. It is seen that these vibrations persist behind the reflected shock wave in $8H_2+O_2$ (figure 9), but their frequency has increased slightly compared with the detonation wave. A similar effect has been observed by Knight & Duff (1952), by means of light emission photographs, where the frequency of the transverse vibrations increased as the burnt gas flowed through the reflected shock front. This fact may be accounted for by the higher temperature behind the reflected wave giving a higher sound velocity.

The reflexion pressure records for all the mixtures examined in this tube exhibit very regular non-sinusoidal pressure undulations whose recurrence frequency given in table 12 are approximately twice the measured spin frequencies on the static pressure records. However, no evidence of a second mode spin frequency is found on any of the static pressure records of the detonation wave. In the record obtained with $6H_2+O_2$ (figure 10), where the reflected shock wave has also been recorded by the static pressure gauge, the higher frequency oscillations are present although their amplitude is small. Schlieren streak photographs taken in this Laboratory of the reflexion of spinning waves at a rigid wall reveal that the pressure undulations recorded on the end pressure gauge are caused by the reflexion of longitudinal compression waves behind the detonation front. The recurrence frequency of the pressure crests of the longitudinal mode of vibration measured from these photographs agrees very well with the results obtained from the pressure records. The pressures set up by this mode of vibration are very small, but after reflexion they are sufficiently great to be detected not only on the end gauge but also on the side gauge. These vibrations probably correspond to the passage of pressure pulses upstream due to the chemical reaction proceeding in the rarefaction wave; this mechanism is essentially the same as that proposed by Brinkley & Richardson (1953) to explain the build up of an ideal C–J wave.

6. Conclusions

The low velocities observed in mixtures near the limits of detonation and with decreasing tube diameter are in general agreement with the results of previous investigators. Decreasing the tube diameter also decreases the wave pressures; the pressure profile is found to be much more dependent on tube diameter than velocity. The hypothesis that energy is abstracted from the wave through the formation of a rarefaction wave at the wall of the tube is capable not only of explaining the low velocities observed but also the slightly high pressures in the 10 cm tube and the rapid decay of the pressure in the 1·6 cm tube. From a consideration of the pressure and velocity data in the 10 cm tube together it is concluded that mixtures with hydrogen content in approximately the range 50–75 % are able to support ideal waves; waves in mixtures outside these limits are subideal in the sense the term is defined by Brinkley & Richardson (1953). All the detonation waves examined in the 1·6 cm diameter tube are subideal and energy losses to the wall are sufficiently great to cause certain mixtures near the detonation limits to spin; these same mixtures showed no evidence of spin in the 10 cm tube. Further support for the subideal nature of the waves in the 1·6 cm tube is deduced from the vibrations, whose frequency is about twice the fundamental mode spin frequency, recorded on the reflexion gauge in all mixtures; these are attributed to the reflexion of pressure pulses which are delivered upstream by the chemical reaction taking place in the rarefaction wave.

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