

DETONATION OF HYDROGEN PEROXIDE VAPOUR

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SYNOPSIS

Stable vapour phase detonation has been obtained in hydrogen peroxide/oxygen/water vapour mixtures containing between 30 and 90 mole % hydrogen peroxide at pressures from 20 to 200 mm Hg. The conditions under which vapour phase deflagration will transform to detonation have been determined in 9, 15 and 25 mm diameter tubes and it has been shown that packing the tube facilitates the transformation.

The detonation limits of hydrogen peroxide/oxygen/water vapour mixtures have been determined in a 25 mm tube at pressures from 20 to 200 mm Hg and vapour concentrations from 30 to 55 mole %. The limiting conditions were established by applying a detonation initiated shock wave and measuring the resulting wave velocity in the test mixture.

Detonation velocities have been measured for vapour concentrations between 30 and 90 mole % and close agreement obtained between the calculated and measured values.

Introduction

Hydrogen peroxide in its mixtures with water is a material of commercial interest manufactured on a tonnage basis. Scientifically it is an example of an unstable substance capable of high rates of decomposition to water and oxygen.

In the course of work designed to increase our knowledge of the hazards of hydrogen peroxide we carried out an investigation into the detonability of the vapour. This work was of technical interest since the production of High Test Peroxide involves the distillation of aqueous mixtures.

The limits of ignitability and flammability for hydrogen peroxide/water vapour mixtures have been studied over a wide range of pressures.¹⁻⁴ A limited investigation has been carried out of the quenching distances and ignition energies for mixtures of hydrogen peroxide and water vapour.⁵ It has been shown that hydrogen peroxide/water vapour mixtures are capable of steady state detonation at concentrations over 30 mole %.⁴

As all previous investigators have pointed out, the study of hydrogen peroxide vapour under conditions of high pressure and concentration is fraught with experimental difficulty. Hydrogen peroxide will decompose rapidly even on carefully cleaned glass surfaces thus making the determination of the concentration a particularly difficult problem. All previous investigators have used a dynamic method for the continuous vaporisation and condensation of vapour. They also found that this method of vapour generation was subject to spontaneous explosions which frequently caused equipment damage.

For the work reported here it was decided to use flash vaporisation with automatic operation of the ignition and detection equipment. This method enabled investigation of regions of high pressures and high peroxide concentrations which would not have been possible using a dynamic system.

Preliminary experimental work had shown that:

- (a) Hydrogen peroxide vapour flames are easily accelerated to velocities of 500 m/s.
- (b) On ignition in a narrow bore coiled tube a flame of 60 mole % hydrogen peroxide vapour would transform from deflagration to detonation.
- (c) The detonation velocity was of the order of 1600 m/s.

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From considerations of manufacturing it was necessary to determine the limiting pressures and mixture compositions of hydrogen peroxide and water vapour which could sustain detonation. It was also of interest to determine whether decomposition flames could be accelerated to detonation in tubes of different diameters and the effect of packing on flame acceleration.

Experimental

Hydrogen peroxide vapour, because of the readiness with which it will decompose on any dry surface—even clean glass—will rapidly change in composition and pressure. Ignition of vapour at initial pressures of over 200 mm Hg can cause damage to glass equipment.

Experience with continuous evaporators had shown that they suffered from the major drawback that re-establishment of equilibrium after changing the conditions being studied was time-consuming.

Experiments with a flash vaporiser showed that the required quantity of vapour could be generated in 15 to 30 seconds. This vapour could then be stored in a glass storage vessel until required for the experiments. The maximum pressure that could be achieved in the experiments was 200 mm Hg. Higher pressures could not be obtained because of limitation on the quantity of liquid peroxide which could be vaporised rapidly.

A block diagram showing the layout of the equipment is shown in Fig. 1. The basic unit of the apparatus was a glass detonation tube, 5.2 m long, which could be filled with a mixture of hydrogen peroxide and water vapour of known concentration and pressure. Three groups of ancillary equipment were necessary for the investigation. These were for:

- (a) The production and storage of hydrogen peroxide vapour.
- (b) The determination of vapour composition and pressure.
- (c) The ignition of the mixture and detection of the wave front.

The detonation tubes had internal diameters of 9, 15, 25, and 35 mm. Each tube consisted of a number of sections of Pyrex glass tubing connected by ball-and-socket joints.

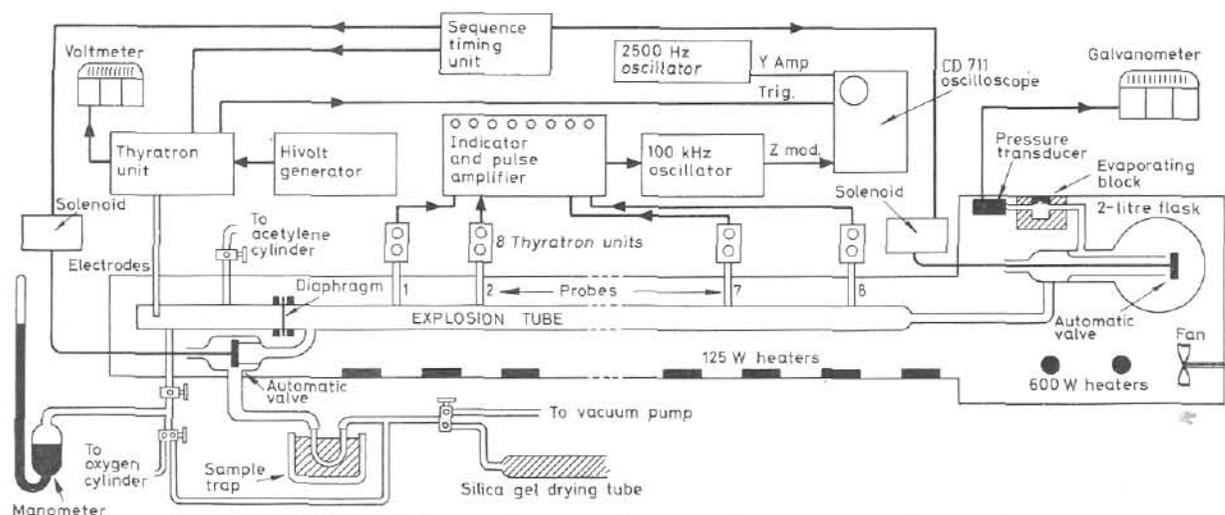


Fig. 1.—Block diagram of apparatus shown set up for experiments on detonation limits

For the studies of transformation from deflagration to detonation, spark electrodes were inserted directly into one end of the detonation tube. For the determination of the limits of hydrogen peroxide concentration and pressure which would sustain detonation the tube was arranged so that a shock wave from a detonating acetylene/oxygen mixture was set up in the vapour.

Production and storage of hydrogen peroxide vapour

The detonation tube was contained in a 10 cm square mild steel conduit, seven feet long thermally insulated with asbestos-aluminium sheet. To prevent vapour condensation, the tube was maintained at a temperature of over 110°C by heater elements inside the conduit.

One end of the detonation tube was connected *via* an electrically operated wide-bore valve to a two litre Pyrex glass storage flask. The other end of the tube was connected through a similar valve to a removable sample cold-trap for complete condensation of water and peroxide. An electrically-heated, hollow, aluminium evaporating block with a silicone-rubber seal provided the means for injecting and vaporising liquid peroxide. A narrow-bore glass tube joined the evaporator to the storage flask.

The flask and evaporator were maintained in a cabinet at 115°C ± 1 degC. All glassware was treated with concentrated nitric acid and washed with demineralised water. Surfaces were re-treated if tests showed decomposition to be excessive. Ground-glass joints were sealed with picein wax or silicone grease.

Vapour was produced and stored by the following procedure:

- (1). The entire apparatus was evacuated with a vacuum pump.
- (2). The storage flask was isolated from the detonation tube and a known quantity of liquid hydrogen peroxide was injected into the evacuated evaporator. The vapour filled the storage flask in about ten seconds.
- (3). To obtain the required vapour concentration, the vapour was held in the storage flask from 15 seconds to five minutes.
- (4). The vapour was shared with the detonation tube and a sample condensed out in a dry-ice trap. The sample was weighed and analysed by standard analytical methods for hydrogen peroxide content.
- (5). The sample valve was closed and after an interval of 0.3 second the ignition spark was fired concurrently with the start of the oscilloscope sweep.

Determination of vapour composition and pressure

The rate of decomposition of hydrogen peroxide vapour in the storage flask was determined by injecting into the vaporiser mixtures of hydrogen peroxide and water of known composition and weight. The change of pressure in the storage flask with time gave directly the rate of peroxide decomposition. The results were checked by condensing the residual vapour and analysing the peroxide content. These calibration experiments showed that hydrogen peroxide decomposed heterogeneously at about 9 mole % per minute. (At the experimental temperature of 115°C the rate of homogeneous decomposition is negligible in comparison.)

The surface/volume ratio of the 25 mm detonation tube was four times that of the storage flask. The decomposition rate in the tube was therefore assumed to be about four times that in the flask, that is about 0.6 mole %/s.

In order to minimize decomposition in the detonation tube, vapour was admitted to the tube from the storage flask, a sample of the vapour was condensed out, and the vapour was ignited in less than 1.1s. These operations were performed automatically by a sequence timer.

The concentration of vapour was calculated from the concentration of the injected liquid and the sample collected. Account was taken of the oxygen formed during decomposition in the storage flask. The amount of oxygen in the vapour was between 2 and 20 mole %. No evidence was obtained in the course of the work that there was any difference between water vapour and oxygen as diluents for hydrogen peroxide vapour within the limits of experimental accuracy. The standard deviation of the vapour strength determination was 2.5 mole % for experiments involving transition from deflagration to detonation. For the detonation limit experiments the deviation was higher, about 6 mole %, because of contamination of the detonation tube by fragments from the diaphragms.

The pressure in the storage flask was measured by a pressure transducer which was accurate to ± 1 mm Hg. The method of determining the pressure in the detonation tube at the moment of ignition depended on the mode of initiation. In the experiments on transition from deflagration to detonation the initial pressure was calculated from the final pressure assuming complete decomposition of the hydrogen peroxide. The calculated values were estimated correct to within ± 2% except at pressures below 50 mm Hg where the error was greater.

In the experiments where an acetylene/oxygen driver mixture was used to establish a shock wave the initial pressure was deduced from the measured pressure in the storage vessel and the sharing ratio between storage vessel and detonation tube. Allowance was made for the sample of

vapour collected in the cold sample trap. It is estimated that the accuracy in pressure determination was better than $\pm 7\%$.

Ignition of the mixture and detection of the flame wave front

The automatic sequence of operations was initiated by a switch on the oscilloscope camera. The ignition spark was fired as well as operation of the automatic valve.

The passage of the wave front down the detonation tube was detected by eight ionisation probes situated along the tube. Probe No. 1 was approximately 50 cm from the ignition end, probes 2 to 8 were situated from 120 cm to 520 cm from the ignition end, the spacing between the probes increasing from probe 2 onwards.

They were supplied *via* 1 M Ω resistors with 170 V from a stabilised supply. The outputs from the probes were amplified by single-stage amplifiers and fed to the grids of eight thyratrons. The pulse from a probe triggered the associated thyratron which "fired" a neon tube. Output pulses from the thyratrons were mixed, amplified, and shaped before being fed to the brilliance modulation input of a Solartron CD 711 oscilloscope. Each pulse was arranged to give a 50 μ s black-out on the sweep. If a probe failed to fire or triggered prematurely the fault could easily be detected by plotting a distance/time curve for the wave from the remaining signals.

To permit accurate measurement of the time intervals between the output pulses from the ionisation probes an extended zig-zag sweep was produced on the oscilloscope screen. A 2500 Hz triangular waveform was applied to the Y amplifier of the oscilloscope and in conjunction with a 2 ms/cm sweep from the oscilloscope time base gave a zig-zag trace with a total length of 200 cm. Accurate time-markers were added to the trace by 1 μ s long blanking pulses at 10 μ s intervals. These markers were obtained from an accurate 100 kHz crystal oscillator. The velocity measurements were accurate to better than 1%.

Shock-initiated detonation

The apparatus was modified for the work so that a detonation in a driver mixture of acetylene and oxygen was used to test the hydrogen peroxide vapour for detonability.

A 30 cm length of 25 mm diameter stainless steel tubing was connected to the end of the 25 mm detonation tube. A metal-to-glass mounting was prepared which allowed easy insertion of an 0.002 inch aluminium diaphragm between the two tubes. When required for test the stainless steel section was filled with a mixture of 25 mole % acetylene/oxygen. This mixture was chosen because of its extremely short run-up distance. Ignition was effected by a spark. Tests showed that it was detonating at about 2300 m/s on reaching the diaphragm.

An excess of oxygen in the driver-mixture prevented the formation of carbon in the detonation tube. However, the apparatus had to be cleaned at frequent intervals to remove aluminium and aluminium oxide deposits from the burst diaphragms.

The pressure of the driver mixture used initially was 280 mm Hg. When the hydrogen peroxide vapour pressure was 150 mm Hg or more it was necessary to increase the pressure of the driver mixture to 380 mm Hg to obtain consistent results. However, in view of the length-to-diameter ratio of the detonation tube (200 diameters), there is no reason to suppose that the higher pressure driver mixture led to overdriven detonation waves.

Results

Transition from deflagration to detonation

Transition from deflagration to detonation was studied in 9, 15, and 25 mm dia. glass tubes 5.2 m long. Some

results were also obtained in a 35 mm tube packed with 13 mm \times 13 mm Raschig rings for a distance of 30 cm. This packed section was situated 20 cm from the spark gap.

The wave velocity/distance curves were plotted for each experiment. The criterion for detonation was taken as a steady wave velocity beyond probe 5 situated at about 300 cm from the ignition point. (Probe 1 was at the ignition end). This represents 330, 200, and 120 tube diameters for the 9, 15, and 25 mm tubes respectively. Steady velocities could not be obtained in the unpacked 35 mm tube which, because of its large volume, meant that only low pressures could be studied. For this tube 300 cm was at 85 tube diameters. For many lower-energy gas-phase systems (that is, using fuel/air as opposed to fuel/oxygen) run-up distances of 100 tube diameters are often necessary in smooth-walled pipe with quiescent gas and no obstructions.

The limiting conditions of hydrogen peroxide concentration and pressure in which detonation could be obtained in tubes of 9, 15, and 25 mm diameter as well as a partly packed 35 mm diameter tube are shown in Fig. 2. For a given hydrogen peroxide vapour concentration in unpacked tubes the run-up distance in tube diameters varies inversely as the square root (approximately) of the pressure. Examination of the literature shows that run-up distances decrease with increasing pressure but the published data is, in general, insufficiently consistent to determine the relationship with any accuracy.

It is apparent that the reason for the difficulty experienced by previous workers⁶ in obtaining stable detonation waves in hydrogen peroxide vapour from point source ignition was due to the use of a wide bore (50 mm) tube only three metres (60 diameters) in length. The authors report that in experiments at atmospheric pressure the velocities were increasing rapidly towards the end of the tube.

In the present work it was frequently observed that the wave velocity in the 15 mm tube exceeded the steady state velocity during the transition from deflagration to detonation. This subject has been well treated by Craven and Greig⁷ and will not be pursued here.

Figure 2 shows that the introduction of a packed section close to the ignition source greatly facilitates the onset of detonation. This effect is well known in relation to obstacles of various kinds and can be attributed to the effect of induced turbulence on the pre-detonation flame speed. The effect of a relatively coarse packing reduces the run-up distance by a factor of at least two.

Shock-initiated detonation

One of the primary objects of the investigation was to determine the limiting conditions of hydrogen peroxide concentration and pressure which would support stable detonations. To do this a shock wave from an acetylene/oxygen detonation was sent into the test mixture.

Since the transition to detonation work had shown that detonations could be obtained in a nine millimetre tube it was decided to use a 25 mm tube for the limit work. It was hoped that quenching effects would thus be minimised since the quenching diameters for detonation in hydrogen peroxide vapour are not known.

The wave-velocity/distance curves were plotted for each experiment. The driver velocity was always in excess of the hydrogen peroxide detonation velocity. The velocity was either attenuated all along the tube length giving a negative result or the velocity steadied out from probe 5 (at 120 diameters from initiating end) onwards. This was taken as the criterion of a positive result.

It was found that fading detonation waves obtained with below limit mixtures sometimes accelerated again towards the end of the tube. Mooradian and Gordon⁸ have reported

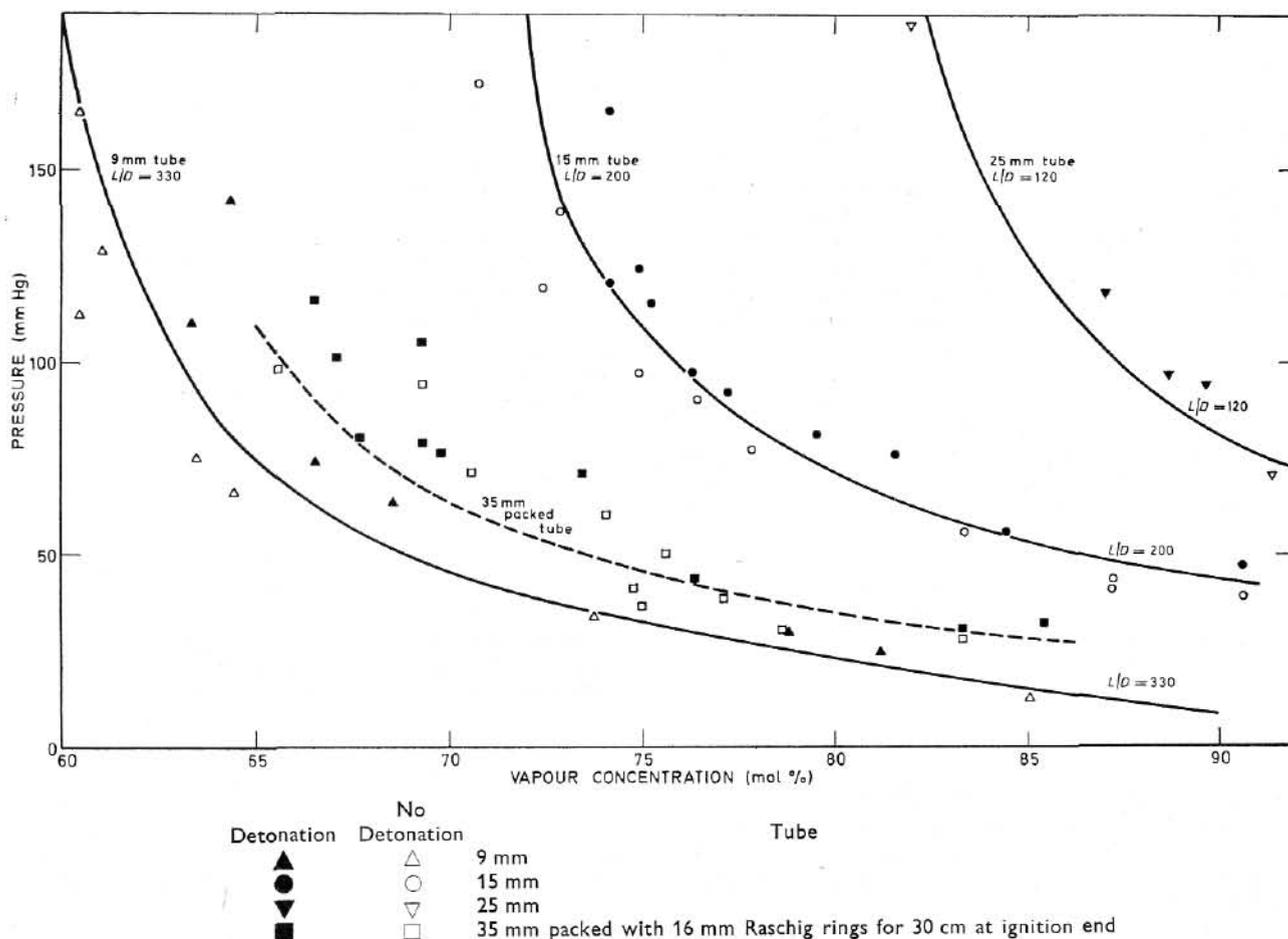


Fig. 2.—Graph of limiting conditions of concentration and pressure of hydrogen peroxide which will support the transformation to detonation in tubes 5.2 m long and of different diameter

a similar effect with mixtures of hydrogen and oxygen which was attributed to separation of the detonation shock from the combustion zone. However a reflected shock from the end of the tube could produce similar effects.

The limiting conditions of hydrogen peroxide concentration and pressure which would support steady detonations in a 25 mm diameter tube are shown in Fig. 3. Because of the potential errors in the vapour concentration, and to a lesser extent the pressure measurement, the limiting line cannot be defined accurately. All points appearing to represent detonable compositions on the non-flammable side of the line are less than one standard deviation from the limiting vapour concentration. Although of less consequence the points representing failure to detonate inside the detonable region are, with one exception, no more than one standard deviation inside the limiting concentration.

Comparison of the detonability limit with Laporte's unpublished data on the ignitability of hydrogen peroxide water vapour mixtures shows that the two limits are nearly parallel and lie close together. Work on the detonability of mixtures of fuel and air at the U.S. Bureau of Mines has recently shown that the flammability and detonability limits can coincide at large diameters.

Detonation velocity

The steady detonation velocity was measured in all experiments (transition to detonation or shock initiated) in which the hydrogen peroxide concentration and pressure were known within the prescribed limits.

It was often found that the measured detonation velocity

was not absolutely constant towards the end of the detonation tube. The fluctuations observed were greater than the experimental error and often followed a definite pattern for a given tube diameter. For example, in the nine millimetre tube the velocity between probes 5 and 6 (probe 1 was at the initiating end of the tube) was always slightly lower than between probes 3 and 4 or probes 6 and 7. The reason for this is not known.

Velocities in the first part of the tube which differed by more than 3% from the final steady velocity were ignored in calculating the average detonation velocity for a given experiment. The average standard deviation for the experiments in the 9 mm and 15 mm tubes was about 12 m/s or 0.75% corresponding to an interval in time interval measurement of 3 μ s.

Since detonation velocity depended on tube diameter and pressure all results were corrected for variations in these parameters. Zeldovich and Kompaneets¹⁰ suggest that the relationship between measured detonation velocity, pressure and tube diameter is of the form:

$$U_{\infty} - U = \frac{k}{pd}$$

where U is the detonation velocity for pressure, p , and tube diameter, d . The term U_{∞} is the detonation velocity at infinite tube diameter and pressure and k is a constant.

To obtain a value for k the initial conditions of 100 mm Hg pressure and the nine millimetre diameter tube were chosen as an arbitrary reference for which a large number of measurements of velocity were available. The difference

between the measured velocity under these conditions and the velocity at any other pressure and tube diameter was plotted against $1/pd$. A straight line plot was obtained, the slope of which gave k as 9.1×10^4 m/s/mm Hg mm. This value of k was used to calculate U from the measured detonation velocity at any pressure and tube diameter.

Detonation velocities of hydrogen peroxide/water vapour mixtures and mixtures of hydrogen peroxide/water vapour/oxygen were calculated by the method given by Edse.¹¹ The oxygen content of the three-component mixtures was fixed at 10 mole %. Dissociation of the detonation products was taken into account at higher peroxide concentrations. The results of the calculations are plotted in Fig. 4 for hydrogen peroxide diluted with water vapour and with water vapour/oxygen.

Selected values are given in Table I with additional details. In calculating the dissociation the final pressure was taken as one atmosphere, corresponding to an initial pressure of about

TABLE I.—Calculated Detonation Pressures, Temperatures and Velocities for Mixtures of Hydrogen Peroxide and Water Vapour

Hydrogen peroxide (mol %)	Detonation Temperature (K)	P_a/P_b Pressure ratio	U_D Detonation Velocity (m/s)‡	Dissociation		
				%OH	%H ₂	%O
100	2490	16.90	1885	3.5	0.7	0.9
75	2261	13.83	1805	1.6	0.2	0.2
40	1689	8.76	1585	—	—	—
40†	1721	8.90	1515	—	—	—

†Containing 10 mol % oxygen.

‡Velocities rounded to nearest 5 m/s.

50 mm Hg. Since the dissociation is only a correction the error in this procedure is small. The initial temperature was taken as 400 K.

Figure 4 shows the variation in velocity with concentration for corrected values of the measured velocity together with the calculated values. In general the measured velocities are slightly lower than the theoretical velocities. This may be due to the presence of oxygen which is a slightly more effective diluent than water vapour. In view of the difficulty of dealing with such an unstable vapour and the consequent inaccuracy in the determination of the vapour strength the agreement between calculated and measured values is good.

Discussion and Conclusions

The investigational work just described may not appear, at first sight, to have much practical value to those concerned with hydrogen peroxide. It does however present a study of the determination of some of the limiting explosion hazard conditions for a particular material. This should of course be seen against a background for other materials, particularly those which explode by decomposition. Data for some of these materials is given below.

Those concerned in chemical plant operations should know the limiting hazardous conditions for the materials being processed. They should know the readiness with which detonable compositions can be formed and initiated. Detonation is a phenomenon which can be particularly destructive. It is therefore most important that the factors which could facilitate or prevent the onset of detonation are appreciated.

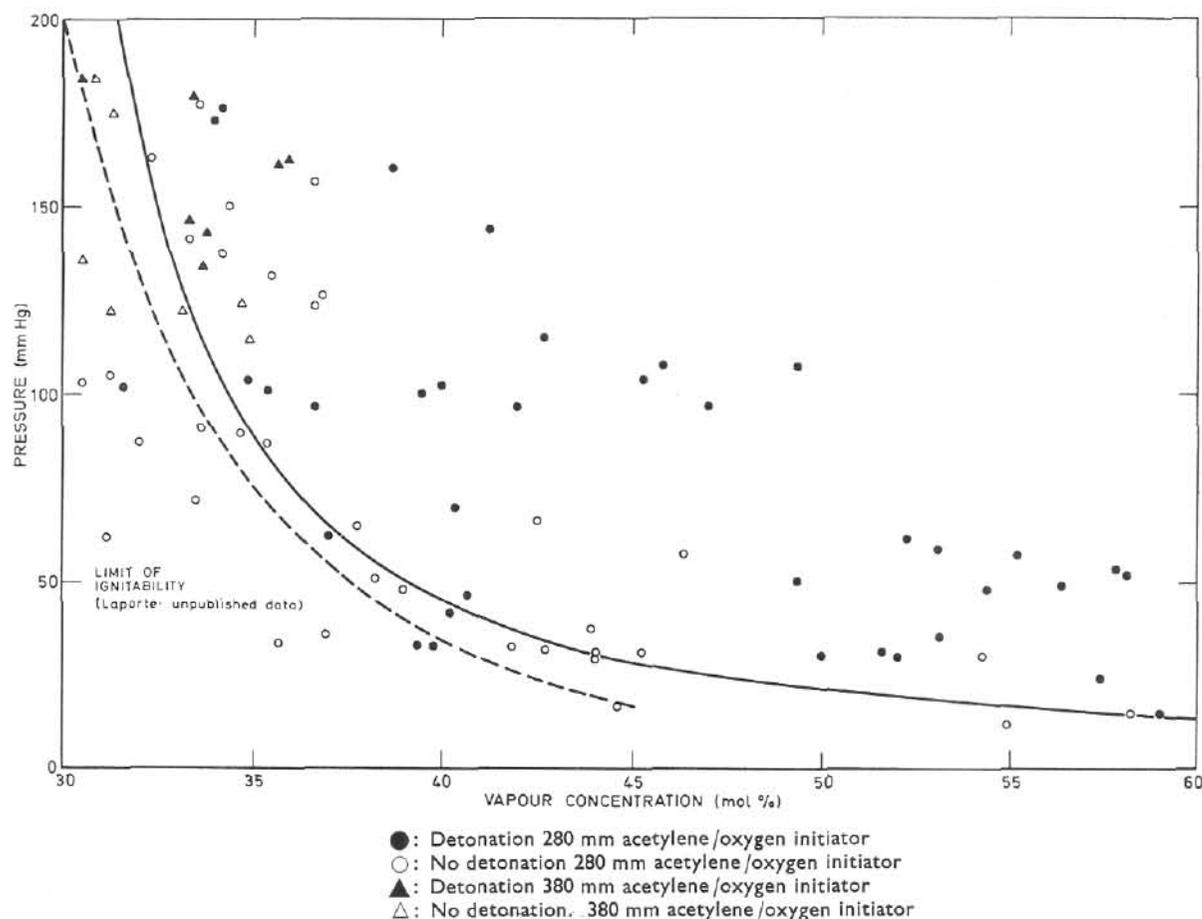
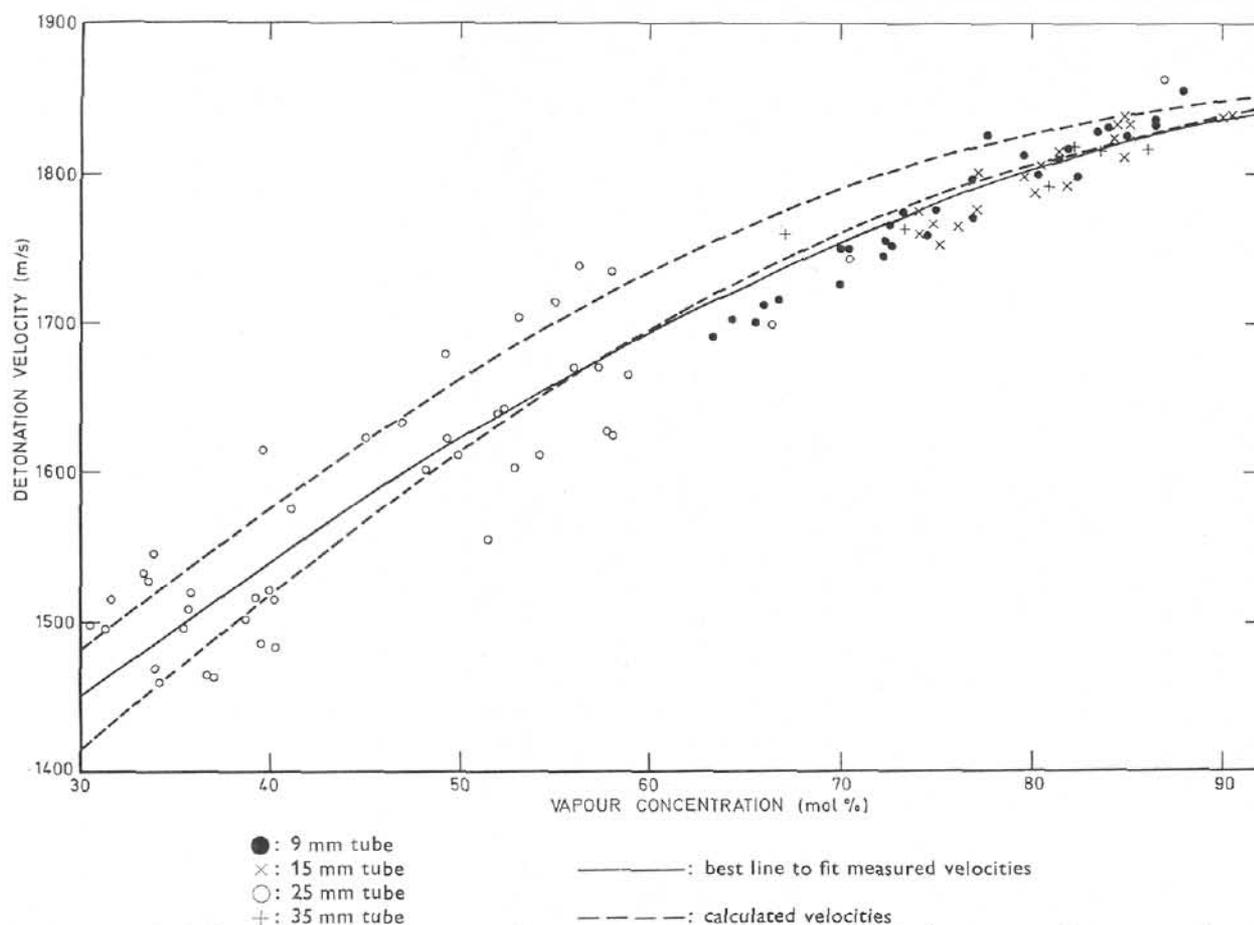


Fig. 3.—Plot of limiting conditions of concentration and pressure of hydrogen peroxide which will support detonation in a 25 mm tube. Shock wave initiation. Also shown is the limit of ignitability



(The upper curve of calculated velocities is for mixtures of hydrogen peroxide and water vapour; the lower curve is for mixtures of hydrogen peroxide, water vapour, and oxygen)

Fig. 4.—Graph of detonation velocity against concentration of hydrogen peroxide

TABLE II.—Comparison of Detonation Properties of Hydrogen Peroxide, Ozone, and Acetylene

Parameter	Material		
	Hydrogen peroxide	Ozone	Acetylene
Molecular weight:	34	48	26
Energy content at 25°C and 1 atm (cal/mol):	25 260	33 980	54 340
Detonation velocity for pure material (m/s)			
Liquid:	6 500 ^(1,2) at 20°C	6 060 ^(1,3) at -177°C	1 483 ^(1,4) at 32°C
Vapour:	1 885	1 893	2 053
Detonation velocity of vapour when diluted to 80% (m/s)			
H ₂ O ₂ with H ₂ O	1 825		
O ₃ with O ₂		1 793	
C ₂ H ₂ with N ₂			1 675
Limiting pressure at which detonation fails in pure vapour material -	15-20 mm Hg	9 mm Hg	1.5 atm

At the present time the conditions affecting the run-up to detonation, particularly where they concern practical operation in chemical plants, are incompletely understood. The effect of flowing mixtures, pressures, obstructions in the gas stream, the behaviour of accelerating flames in large plant items, together with the effect of externally applied shock waves, are subjects still requiring further study.

Figure 3 presents the limiting conditions of hydrogen peroxide vapour concentration and pressure which will sustain a flame and a detonation wave. Figure 2 presents the conditions of composition and pressure at which detonation can be initiated from a small source in tubes of different diameters. Some data are included on the effect of packing induced turbulence on the run-up to detonation.

It is of interest to compare the system hydrogen peroxide/water vapour with that of ozone/oxygen and acetylene/diluent because all three are examples of substances capable of supporting detonation waves by their self decomposition.

For comparison their detonation parameters are set out in Table II.

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