Explosive Limits of Hydrogen Peroxide Vapor

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The published vapor phase ignition limit of hydrogen peroxide-water mixtures as a function of temperature, pressure, and concentration was extended both to lower and to higher pressures. The total available data now include the pressure range from 0.1 p.s.i.a. to 1000 p.s.i.a. A correlation was derived which is in good agreement with the experimental data.

THE VAPOR PHASE ignition limit of hydrogen peroxide-water mixtures over the pressure range from 1 p.s.i.a. has been reported by Satterfield and coworkers (*3-6*). The limit was experimentally determined at both lower and higher pressures so that data are now available over the pressure range, 0.1 to 1000 p.s.i.a. A semitheoretical correlation was developed which gives good agreement with the data. Additional information concerning detonation characteristics are given in a subsequent paper (*2*).

EXPERIMENTAL

Superatmospheric Vapor Phase Explosive Limit. The apparatus used to investigate the superatmospheric pressure vapor phase explosion limit is shown schematically in Figure 1. The entire system of 304 stainless steel was thoroughly cleaned and passivated with caustic, nitric acid, and 90% w. hydrogen peroxide before use.

Liquid 90% hydrogen peroxide was fed to a continuous flow system under nitrogen pressure. The flow rate of 0.1 to 0.5 gallon/per minute was measured by a turbine-type flowmeter and controlled by a motor valve operated manually. The pressure in the system was maintained by a back pressure regulator and read visually with a gage. A pressure transducer was also used to measure the pressure and to indicate the occurrence of an explosion. The output of the transducer was recorded with a millivolt recorder. The stream was heated in a coil immersed in a bath of a eutectic mixture of 68% tin and 32% cadmium having a melting point of 347° F. The bath was heated electrically and could be controlled at any temperature in the range of interest. The pressure and temperature of the hot stream were measured immediately prior to a vapor-liquid separator of about 50 cc. total volume. Although not shown in the schematic diagram, the separator was also half immersed in the metal bath in order to maintain temperature control. A spark gap of a few thousandths of an inch in the vapor section of the separator was energized periodically by a Tesla coil. The liquid stream was passed through an after-cooled and discharged to a drain or withdrawn for analysis. After an explosion had occurred, the entire system was flushed with distilled water. The entire apparatus was contained in a concrete barricade and operated by remote control.

With this apparatus the ignition limit of hydrogen peroxide vapor, in a mixture of water vapor, oxygen, and nitrogen, was determined at pressures between 45 and 1000 p.s.i.a. At a constant total pressure, the temperature of the liquid 90% hydrogen peroxide stream was raised until an explosion was initiated in the vapor by a spark across the spark gap or by a hot wire. The criteria for a positive test was a rapid, momentary pressure rise which was indicated by the pressure transducer, a sudden unloading of excess pressure through the back pressure regulator, and, occasionally, by an audible report. In some cases, the explosions were initiated by the hot wall of the separator.

A dynamic system such as the one used has many advantages over a static system for dealing with hydrogen peroxide at elevated temperatures and pressures. The primary advantage is that decomposition losses can be minimized, and accurate analyses of the liquid phase under test conditions can be made. For all of the data reported, the inlet and outlet liquid compositions ranged

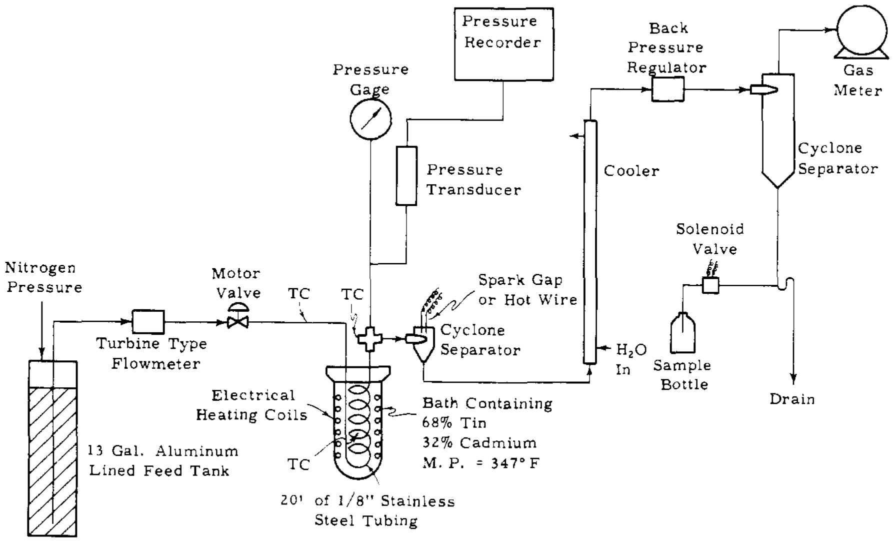

Figure 1. Apparatus for study of superatmospheric pressure vapor phase explosions

from 89.5 to 90.5% w. hydrogen peroxide as determined by the conventional ceric sulfate titration method. Direct determination of the vapor composition was not practical with this apparatus.

At the highest temperature reached, approximately 95% of the vapor phase was inert gas. A relatively small volume of vapor was present in the test chamber. Excess vapor passed out of the separator with the liquid phase. Withdrawal of vapor samples for analysis without significant loss from decomposition was not possible. Therefore, the vapor compositions were calculated from extrapolated vapor-liquid equilibrium data (*7*), which are known to have a high order of accuracy. The extrapolations depend primarily on calculations of the nonideality of the vapor phase as a function of pressure. Reliable procedures have been developed for this type of calculation (*1*).

The data obtained are given in Table I and Figure 2. Only data close to the ignition limit are reported. Of the two methods of initiation of explosion used, the spark gap gave more reproducible results and less frequent spontaneous ignitions. The spark gap was limited to a few thousandths of an inch since the high pressure prevented the formation of a spark across greater distances.

The force of the explosions at higher pressures was considerable as demonstrated by several spontaneous ignitions which occurred in the preheater and which caused rupture of the tubing.

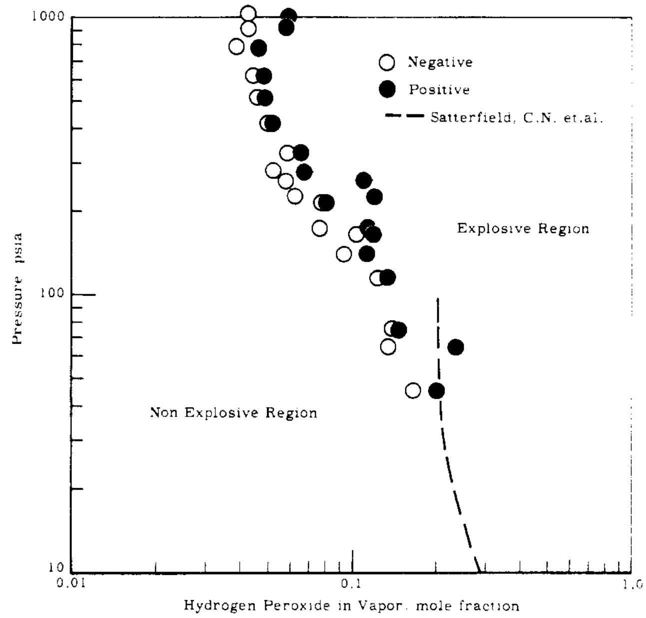

Figure 2. Superatmospheric ignition limit of hydrogen peroxide vapor

SUBATMOSPHERIC VAPOR PHASE EXPLOSIVE LIMIT

The subatmospheric pressure vapor phase ignition limit was investigated with the essentially all glass apparatus shown in Figures 3 and 4. All equipment was thoroughly cleaned and passivated. Vapor from a reboiler passed through an explosion chamber to a total condenser. The condensate was returned to the reboiler, sent to a takeoff receiver, or sent to a sample receiver. The pressure on the system was indicated by a mercury manometer and controlled by a rubber-diaphragm manostat. The vacuum source was a Duo-Seal or Megavac Vacuum Pump (Megavac used with the 7 × 26 inch chamber, Duo-Seal with the others). The ignition spark was produced between two 0.060 inch diameter tantalum electrodes by the discharge of two 28μ condensers in series, charged to 1500 volts.

In operation, the reboiler was charged (about 200 cc. for the small apparatus, 1800 cc. for the large apparatus) with liquid 90% peroxide, and the system was brought to the desired pressure. Heat was applied to the reboiler (supplied to the small reboiler by a glass-col mantle, to the large reboiler by steam coils), and the condensate returned to the reboiler until a steady state condition was reached. A predetermined amount of condensate was then

Table I. Superatmospheric Ignition tests with Hydrogen Peroxide Vapor

Press., P.S.I.A.	Temp. ° F.	Vapor Comp. Peroxide, Mole Fraction	Test Result
1015	363	0.043	N
	390	0.060	P
910	360	0.043	N
	383	0.059	P
775	320	0.039	N
	358	0.047	P
615	338	0.045	N
	342	0.049	P
515	334	0.046	N
	338	0.049	P
415	327	0.050	N
	331	0.053	P
325	324	0.059	N
	331	0.066	P
280	308	0.052	N
	324	0.068	P
260	311	0.058	N
	351	0.110	P
225	308	0.063	N
	348	0.121	P
215	315	0.079	N
	320	0.081	P
175	306	0.077	N
	338	0.114	P
165	320	0.104	N
	338	0.120	P
140	305	0.094	N
	316	0.113	P
115	310	0.124	N
	315	0.135	P
75	293	0.139	N
	297	0.149	P
65	284	0.135	N
	315	0.234	P
45	275	0.164	N
	286	0.201	P

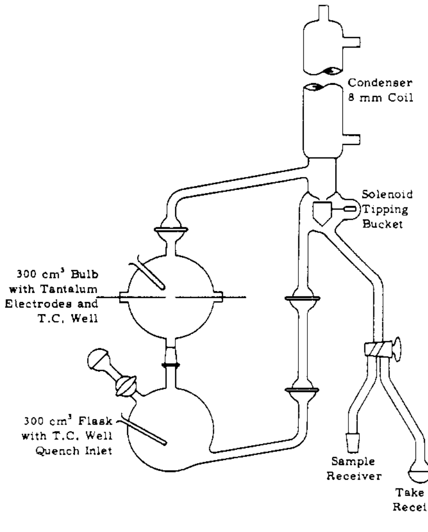

Figure 3. Explosion bulb apparatus for subatmospheric pressure

diverted to the takeoff receiver, thus raising the peroxide concentration in the reboiler and in the vapor produced. The condensate was again returned to the kettle until a new steady state was established. A small condensate sample, about 2 cc., was taken intermittently and the spark was energized. The system was shut down and the sample removed and analyzed by the ceric sulfate method. Successively higher peroxide concentrations were obtained from using the residual charge in the reboiler as the initial charge for the next experiment. The experiments were conducted in a barricade by remote control.

The experiments involving the most concentrated vapor at each pressure would be expected to give the most violent results at that pressure. At the lowest pressure, 0.135 p.s.i.a., sparking of the most concentrated mixture tested resulted in a brilliant flash in the explosion bulb, no audible noise, a pressure rise of only 0.193 p.s.i., and no apparent increase in the temperature of either the vapor or the liquid. At 0.290 p.s.i.a., sparking of the most concentrated vapor used gave a pressure increase of 0.580 p.s.i. accompanied by a temperature rise of about 100° F. in the vapor. At successively higher pressures, the pressure rise on sparking was increasingly larger while the vapor temperature increase remained about the same as that at 0.290 p.s.i.a. At 0.967 p.s.i.a. and higher pressure, the flame traveled to the kettle and was established there with temperatures then rising beyond the scale of the instruments used. In these cases, return to the reboiler of the condensed water from the decomposition products gradually lowered the reboiler concentration until a fire could no longer be maintained. The last three experiments at this pressure, 0.967 p.s.i.a., and all experiments at higher pressures were carried out in a modified apparatus containing a coil between the kettle and the explosion bulb. This coil, 6 feet of 1 inch ID glass tubing wound on a 4 inch diameter mandrel, was inserted to determine if the burning would develop into a detonation in the greater length then available. The pressure rise on sparking was greater with the coil than without, at the same or lower vapor concentration, with the 7 × 26 inch chamber intermediate in this respect. The lowest pressure at which any noise was heard was 1.451 p.s.i.a. This occurred with the 7 × 26 inch chamber. With the 300-cc. bulb, no noise was heard at pressures below 1.934 p.s.i.a. In both cases, the noise was a sharp click. The first instance of separation of the glass taper joints, of the small apparatus, was observed at 1.934 p.s.i.a., and indicated pressures above atmospheric. No spontaneous ignitions occurred in the small apparatus; however, one spontaneous ignition did take place in the large apparatus at a pressure of 1.934 p.s.i.a.

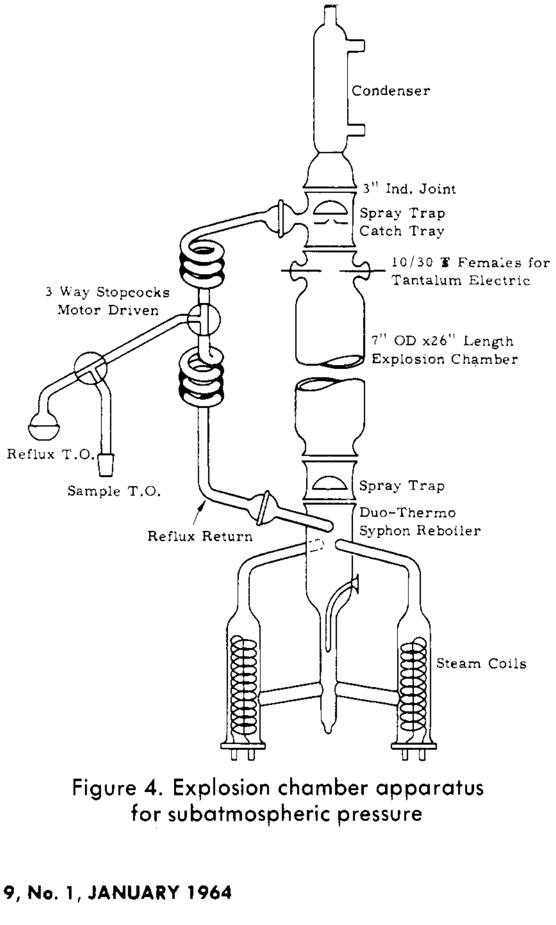

Figure 4. Explosion chamber apparatus for subatmospheric pressure

The only damage to the equipment occurred in an experiment with the 300-cc. bulb and coil at 2.90 p.s.i.a. with a vapor concentration of 77.8% mole H_2O_2. Upon sparking, there was a sharp report, and the entire coil and reboiler were shattered.

The criterion for a positive ignition test was that the computed volume occupied by decomposed vapor and diluents be greater than the volume of the explosion chamber. Any computed volume less than that of the chamber implied that the decomposition ceased before all of the peroxide was consumed. The calculated decomposition volume is that volume occupied by the diluents and the products of the decomposition and necessary to give the observed pressure rise. In this calculation, the vacuum pumping rate was neglected (it is negligibly small), and the pressure and temperature were assumed to be uniform at any given time. Appropriate corrections were made for heat loss. The data are given in Table II and Figure 5.

The ignition limit of hydrogen peroxide vapor was also determined at pressures of 1.93, 6.75, and 14.7 p.s.i.a. with an explosion tube apparatus described in detail (*2*). Briefly, this apparatus consisted of a continuous feed system, reboiler, explosion tube, quench chamber, and vacuum system. The explosion tube itself was a 2 inch diameter, schedule 80-type 6063-T6 aluminum pipe 8 feet long. It was provided with a spark gap, sampling ports, manometer connections, thermocouples, and pressure pickups. Explosions were detected with oscilloscopes and associated electronic equipment connected with the pressure pickups and thermocouples. Immediately prior to a test, vapor samples for analysis were obtained at three points along the tube so that the level and the uniformity of the vapor composition under test could be established. The source of initiation was 3500-volt capacitive spark obtained by the discharge of two 28 mfd. condensers across a gap of about 1/32 inch between two tantalum electrodes (one 3/8 inch in diameter, the other 1/8 inch. An ignition occurring in the tube was detected with chromel-alumel thermocouples and with SLM piezoelectric pressure transducers connected to oscilloscopes. The criterion for a positive test was any temperature and pressure rise recorded by all of the thermocouples and transducers in the tube. The data are given in Table III and Figure 5. In Figure 5, the data are shown in comparison with other ignition limit data determined in this investigation and with data from the literature.

DISCUSSION

It appears reasonable to postulate that, in order for an explosion to occur, there must be at least a certain minimum number of molecular collisions per unit volume per unit time involving hydrogen peroxide molecules possessing at least a certain minimum energy. The ignition limit would then be defined by this number of collisions being a constant.

In a mixed gas composed of rigid, elastic, spherical molecules of kinds one and two, the number of collisions per unit volume per unit time between like molecules is given by:

$$N_{11} = 2n_1^2\sigma_1^2(\pi kT/m_1)^{1/2} \tag{1}$$

and the number of collisions per unit volume per unit time between unlike molecules is given by:

$$N_{12} = 2n_1n_2\left(\frac{\sigma_1 + \sigma_2}{2}\right)^2\left[\frac{2\pi kT\ (m_1 + m_2)}{m_1m_2}\right]^{1/2} \tag{2}$$

Of the hydrogen peroxide molecules present, the fraction having energy at least equal to E may be approximated by $\exp(-E/RT)$. This represents the fraction of the collisions between peroxide and other molecules which involve a peroxide molecule possessing an energy at least equal to E. In collisions between two peroxide molecules, the fraction of such collisions involving at least one peroxide molecule with energy E or greater is $2\exp(-E/RT)$. Thus the total number, N, of molecular collisions per unit volume per unit time involving at least one peroxide molecule having an energy at least equal to E is given by:

$$N = 2N_{11}\exp(-E/RT) + N_{12}\exp(-E/RT) \tag{3}$$

Substituting Equations 1 and 2 and assuming that the molecule diameters and molecular masses of the molecules present are not far different from the corresponding values for hydrogen peroxide—*i.e.*, that $\sigma_2 \rightarrow \sigma_1$ and that $m_1 \rightarrow m_2$—this may be written as:

$$N = \left[4n_1^2\sigma_1^2\left(\frac{\pi kT}{m_1}\right)^{1/2} + 4n_1n_2\sigma_1^2\left(\frac{\pi kT}{m_1}\right)^{1/2}\right]\exp(-E/RT) \tag{4}$$

Regrouping and substituting n for $(n_1 + n_2)$ reduces this to:

$$N = 4n_1n\sigma_1^2(\pi kT/m_1)^{1/2}\exp(-E/RT) \tag{5}$$

Assuming that the gas is ideal and that liquid and vapor are in equilibrium, one may substitute y_1P/kT for n_1 and P/kT for n to obtain:

$$N = \frac{4\sigma^2\pi^{1/2}y_1P^2}{m^{1/2}k^{3/2}T^{3/2}}\exp(-E/RT) \tag{6}$$

Grouping constants gives:

$$N = Ay_1P^2T^{-3/2}\exp(-E/RT) \tag{7}$$

Substituting $\exp 2B$ for the constant N/A and $2C$ for E/R one obtains:

$$\exp 2B = y_1P^2T^{-3/2}\exp(-2C/T) \tag{8}$$

which can be expressed as:

$$\ln(y_1^{1/2}PT^{-3/4}) = B + C/T \tag{9}$$

The mole fraction y_1 can be calculated from the observed temperature and pressure and from the vapor pressure of

Table II. Subatmospheric Ignition Limit of Hydrogen Peroxide Vapor

Press., P.S.I.A. (Mm.)	Temp., °F.	Vapor Comp. Peroxide, Mole Fraction	Test Result
0.252	...	0.475	N
(13)	131	0.643	N
	139	0.722	P
0.271	...	0.315	N
(14)	...	0.354	N
0.290	...	0.445	N
(15)	141	0.562	N
	150	0.674	P
	...	0.717	P
	...	0.740	P
0.387	...	0.575	P
(20)			
0.496	...	0.572	P
(25)	...	0.699	P
	...	0.775	P
0.580	...	0.323	N
(30)	...	0.447	N
	...	0.495	N
	148	0.512	N
	152	0.584	P
	...	0.663	P
	...	0.713	P
0.677	152	0.535	N
(35)	165	0.697	P
	...	0.757	P
0.967	...	0.391	N
(50)	...	0.441	N
	158	0.487	N
	159	0.500	P-N
	160	0.517	P
	...	0.589	P
	...	0.603	P
	...	0.711	P
1.45	156	0.320	N
(75)	170	0.466	P
	...	0.602	P
1.93	...	0.416	P
(100)	...	0.531	P
	...	0.567	P
	...	0.598	P
	...	0.797	P
2.42	...	0.361	P
(125)	...	0.688	P
	...	0.781	P
2.90	...	0.675	P
(150)	...	0.778	P[a]

[a] Equipment shattered

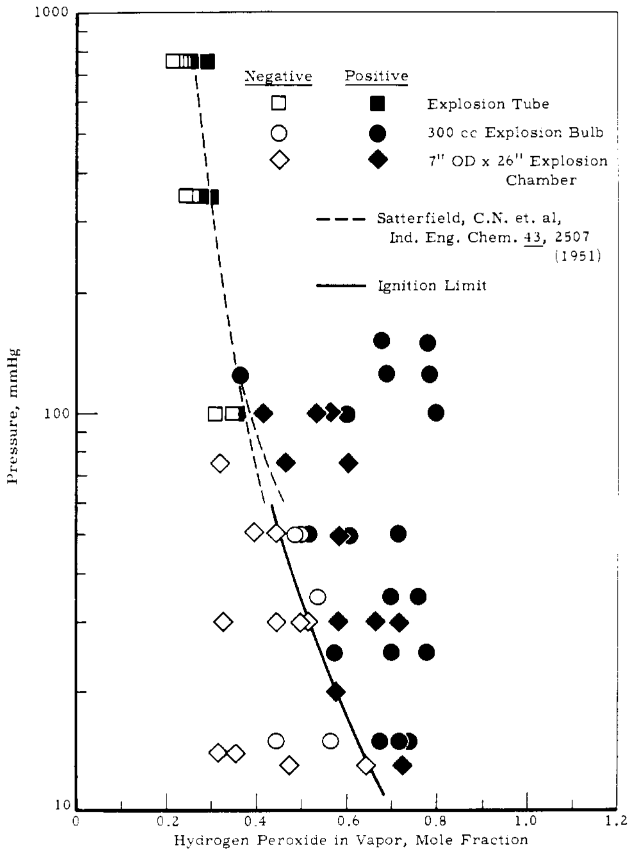

Figure 5. Subatmospheric ignition limit of hydrogen peroxide vapor

Table III. Subatmospheric Ignition Limit of Hydrogen Peroxide Vapor

Press., P.S.I.A. (Mm.)	Temp., °F.	Vapor Comp. Peroxide, Mole Fraction	Test Result
	...	0.242	N
	...	0.245	N
	...	0.253	N
	238	0.255	N
	239	0.259	P
	...	0.285	P
	...	0.288	P
6.75	...	0.243	N
(350)	...	0.244	N
	...	0.266	N
	209	0.269	N
	211	0.280	P
	...	0.282	P
	...	0.285	P
	...	0.295	P
1.93	...	0.303	N
(100)	171	0.350	N
14.7	...	0.214	N
(760)	...	0.231	N
	173	0.357	P
	...	0.360	P

the liquid phase according to the relationship $y_1P = \gamma_1x_1p_1^0$ after making the proper corrections for imperfection of the vapor phase at the elevated pressures (*1*).

The final equation suggests that if $\ln(y_1^{1/2}PT^{-3/4})$ is plotted *vs.* $1/T$ for the vapor phase ignition limit for vapor in equilibrium with liquid of a constant composition a straight line should result. Such a plot is shown in Figure 6 for a constant liquid composition of 90% w. hydrogen peroxide. Data derived from vapor in equilibrium with liquid of other concentrations (*3, 4*) were recalculated to correspond to a 90% w. liquid composition. This was done by accepting the given peroxide vapor composition and calculating the temperature required to yield that peroxide vapor composition at the given total pressure from 90% w. liquid hydrogen peroxide while taking into account the presence of any inert gas. This is consistent with previous reports (*4*) that, at lower pressures, substitution of nitrogen or oxygen for water vapor has no effect on the position of the explosion limit.

The solid curve in Figure 6 was drawn to represent the limit between negative and positive points. This curve is consistent with the solid curve given in Figure 5.

The rather naive model which was assumed correlates all of the available data, which include a pressure range of four orders of magnitude, a concentration range from 0.04 to 0.7 mole fraction, and a temperature range from 140° to 390° F., quite well. The only data which do not fit are the superatmospheric points of Satterfield (*6*) and co-authors, and which do not agree with the present experimental data as shown in Figure 2. The experimental procedure used by the above authors appears to have generated vapor essentially unmixed with nitrogen and of higher water content than the present procedure, although, as stated above, this is not known to alter the explosion limit for the vapor. The divergence may be caused merely by differences in the criteria for a positive test.

The correlation in Figure 6 is valid only for vapor in equilibrium with 90% w. hydrogen peroxide. Curves for vapor in equilibrium with liquids of other concentrations would be approximately parallel to the curve given. The absence of a liquid phase or the addition of any superimposed relationship among the variables T,P, and composition invalidates the curve in Figure 6. This is shown by examination of Equation 9.

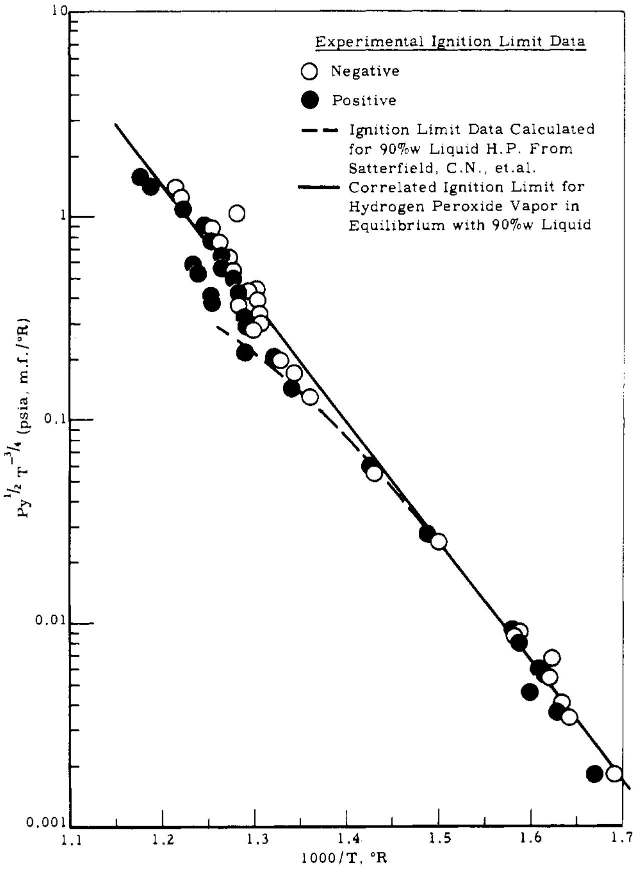

Figure 6. Correlation of ignition limit data

The total pressure in Equation 9 can be expressed as the sum of the partial pressures of the vapor components:

$$\ln[y_1^{1/2}(P_1 + P_2 + P_3)T^{-3/4}] = B + C/T \qquad (1)$$

In the vapor phase in the absence of a liquid phase, increasing P_3 and decreasing P_2 by equal amounts, all else remaining constant, should not change the explosive limit. In the experiments to date, however, the vapor phase has been in equilibrium with a liquid phase. In this situation, the partial pressures of peroxide and water depend on the activities and vapor pressures of the pure components:

$$\ln[y_1^{1/2}(\gamma_1x_1p_1^0 + \gamma_2x_2p_2^0 + P_3)T^{-3/4}] = B + C/T \qquad (11)$$

Equation 11 shows that under vapor-liquid equilibrium conditions the only method of changing the value of P_2 (other conditions constant, *e.g.*, T) is by a change in x_2 which simultaneously affects x_1 and y_1. Therefore, in the presence of a liquid phase the values of B and C depend on the liquid composition.

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NOMENCLATURE

N_{11} = number of collisions per unit volume, unit time between like molecules, cc.$^{-1}$ sec.$^{-1}$
N_{12} = number of collisions per unit volume, unit time between unlike molecules, cc.$^{-1}$ sec.$^{-1}$
n = number of molecules per unit volume, cc.$^{-1}$
σ = molecular diameter, cm.

k = Boltzmann constant, g. cm.^{2}/sec.^{2}, ° R.
m = molecular mass, g.
y = mole fraction in vapor
x = mole fraction in liquid
γ = activity coefficient in liquid
P = total pressure, p.s.i.a.
P_1 = partial pressure of component (1) in the vapor, p.s.i.a.
p^0 = vapor pressure of pure component, p.s.i.a.
T = absolute temperature, ° R.
R = gas constant, cal. ° R.$^{-1}$
A = $4\sigma^2\pi^{1/2}m^{-1/2}k^{-3/2}$
B = correlation constant, ln $(N/A)^{1/2}$
C = correlation constant, $E/2R$
E = activation energy, cal.

Subscripts

1 = hydrogen peroxide
2 = water
3 = oxygen and nitrogen

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Detonations in Hydrogen Peroxide Vapor

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Experiments have been conducted at 2.90, 6.77, and 14.7 p.s.i.a. in order to obtain information concerning the detonation characteristics of hydrogen peroxide vapor. Within the experimental conditions employed, no detonations were observed at 2.90 and 6.77 p.s.i.a. At atmospheric pressure, detonation with a velocity of 6700 feet per second was observed in vapor with a composition of 35 mole per cent hydrogen peroxide.

A FUNDAMENTAL factor in the safe handling of hydrogen peroxide, especially under some of the more severe conditions encountered in military and space applications, is the vapor phase explosion hazard. Previous investigations have been concerned primarily with ignition phenomena. It was of prime interest to know whether or not the vapor would detonate and to gain information concerning some characteristics of the system inside the ignition limits.

The problem is fraught with experimental hazards and the realization of any meaningful data is a laborious procedure. Most of the trouble is caused by the homogeneous and catalytic heterogeneous decomposition of the vapor which greatly complicates obtaining a shock tube filled with vapor of known uniform composition, temperature, and pressure. Generation of vapor with a dynamic system operated by remote control is essential.

EXPERIMENTAL

The system used for study of the hydrogen peroxide vapor explosion velocities is shown schematically in Figure 1. All of the equipment was cleaned and passivated with caustic, nitric acid, and 90%w. hydrogen peroxide. The feed vessel rested on a scale which was used to determine the feed rate. Liquid hydrogen peroxide flowed from the feed vessel to a constant level feed reservoir. The flow was controlled by a level controller and motor valve. From the feed reservoir, the peroxide entered a reboiler where part of it was vaporized and part drawn off as a bottoms stream. The stainless steel reboiler was of the thermosyphon type, heated by high pressure (up to 150 p.s.i.) steam. The liquid drawn off as bottoms passed through a cooler and into a receiver. The bottoms receiver was vented to the atmosphere during experiments made at atmospheric pressure. During experiments made at lower pressures this receiver was connected to another separate vacuum pump. A sample of bottoms was taken by diverting the stream to a separate receiver. The bottoms rate was determined by measuring the time over which a sample was collected.

Vapor was separated from the liquid in a cyclone which was an integral part of the reboiler. The vapor then entered a 3-inch diameter, 6-inch long vertical section packed with 3/16-inch glass helices supported by stainless steel screens (in later experiments these screens were replaced with aluminum screens). From the packed section, the vapor went directly to the explosion tube. It entered the tube at a right angle to the axis of the tube, which was mounted horizontally. After passing through the length of the tube (7-feet 8-inches from center of inlet to center of outlet),