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The formation of hydrogen peroxide in the combustion of hydrogen at low pressures

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[Plate 7]

Hydrogen peroxide has been obtained in appreciable concentrations when a flame of hydrogen and oxygen burning at pressures of 3 to 4 cm. mercury was directed against a surface cooled to -180°C (c. 5 to 10 %), and when an oxy-hydrogen mixture was exploded by the action of a spark, in glass or aluminium vessels c. 2×15 cm., cooled in liquid air, the products were shown to contain up to 30 % hydrogen peroxide (*w/v*), depending on the conditions.

The conditions controlling the formation of hydrogen peroxide in such explosions have been investigated more fully than was done by previous authors. It was found that as the overall gas pressure was decreased the yield of peroxide passed through a maximum value. The effects were also investigated of varying the dimensions of the vessels, the gas composition, the external temperature, and other factors.

A series of experiments was carried out in order to ascertain whether the hydrogen peroxide was formed in the gas phase or only on the walls. In these experiments, the ultra-violet absorption spectrum of the explosion region was studied. It was found that a considerable quantity of hydrogen peroxide was present in the gas phase, even when the walls of the reaction tube were not cooled.

The results are discussed in the light of modern views regarding the combination of hydrogen and oxygen. It would appear that the peroxide is formed by two mechanisms; one of these consists of recombination of hydroxyl radicals on the cold walls, the other involves the formation of an excited HO_2 radical, and its subsequent reaction with a hydrogen molecule to give a hydrogen atom and a molecule of excited hydrogen peroxide, which then decomposes unless it is stabilized and frozen on the walls. No other explanation has been found to account for all the observed facts, and at the same time not to contradict established mechanisms for the hydrogen oxygen reaction.

1. INTRODUCTION

At the British Association meeting in Johannesburg in 1929, one of the authors (A.C.E.) reported the results of some experiments on the ignition of hydrogen at low pressures. The apparatus which had been used for these experiments consisted of a 1 in. transparent silica tube, inserted in a furnace; into the silica tube projected

two concentric tubes to introduce the oxygen and hydrogen, the pressure being maintained at the required value by the regulation of a vacuum pump. The flash on ignition was observed through the end of the tube and the temperature determined by thermocouples in the gas stream. The ignition was thus effected by a method similar to that used by H. B. Dixon, but adapted for measurements at low pressures. Figure 1 gives a typical set of the results obtained. As the pressure decreased ignition occurred at lower temperatures. It was noted at the time that traces of hydrogen peroxide were detectable in the condensed water.

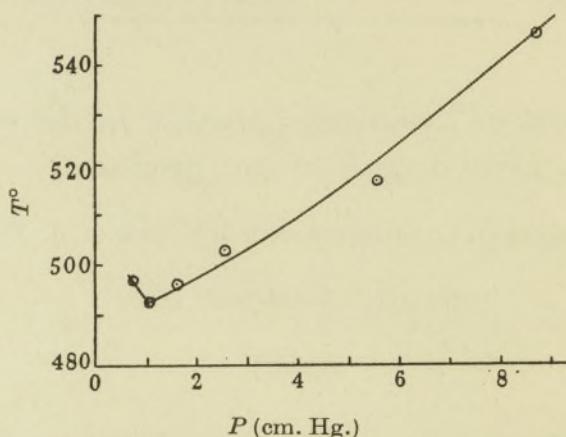


FIGURE 1. Ignition temperatures of hydrogen.

The experiments were only of a preliminary kind and were discontinued, because so much work was being done about that time (particularly by Hinshelwood and his collaborators) on the low-pressure ignition of hydrogen and oxygen which greatly advanced the knowledge of the mechanism of the hydrogen-oxygen reaction, and has culminated in a precise interpretation of the observed phenomena (Hinshelwood, 1946).

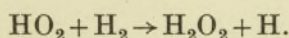
Pease (1930) has investigated the thermal reaction of hydrogen and oxygen at atmospheric pressure, and determined the amount of hydrogen peroxide formed. He found that when the reaction products were passed from the reaction tube (at 540° C) into a vessel cooled at -79° C, concentrations of up to 4 % hydrogen peroxide were obtained. In further experiments, spherical pyrex vessels, 4.3 cm. in diameter, were filled with a hydrogen-oxygen mixture containing 95 % hydrogen and heated for a short time, then rapidly cooled to -79° C. The products contained up to 25 % hydrogen peroxide. Pease, however, found under these conditions that no peroxide was formed at low pressures.

Poljakow and his co-workers (1934 and onwards) published a series of papers on the production of hydrogen peroxide during low-pressure explosions of hydrogen and oxygen. In general, the gas mixture was exploded by a spark, at pressures below 15 cm. mercury, in a small vessel immersed in liquid air; in some experiments, catalysis over platinum was used, leading to smaller yields of peroxide. A maximum

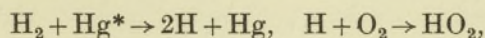
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yield of 13 % was obtained at 6 cm. pressure in an enamelled tube. Increase of tube diameter decreased the yield of peroxide; a maximum value of the yield was also found as the tube length was increased. Increase in the external temperature led to a smaller concentration of peroxide in the product. In one set of experiments, a platinum gauze surrounded the spark gap; the explosion products contained no peroxide. These experiments led the authors to conclude that the peroxide is formed on the cold surface from the recombination of hydroxyl radicals. The authors gave no information as to the method of estimating the reaction products. It was found during the present research that, though the determination of *c.* 10^{-5} g. peroxide was easily accomplished, the simultaneous determination of *c.* 10^{-4} g. water was not easy to obtain with accuracy. It is therefore possible that the percentage values of hydrogen peroxide quoted by Poljakow may have been on the low side.

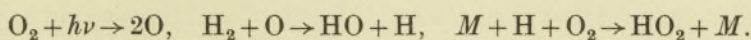
It is well known that hydrogen peroxide is the main product of the photochemical oxidation of hydrogen both in the sensitized and the unsensitized reactions (Kistiakowsky 1930; Cario & Franck 1922; Frankenberger & Klinkhardt 1931; Bates *et al.* 1933, 1935; Napravnik & Smith 1940). The reaction in general proceeds through the formation of the radical HO_2 , the reaction of this radical with hydrogen giving hydrogen peroxide and a hydrogen atom, i.e.



In the mercury-sensitized reaction, the chain initiation is due to hydrogen atoms,



while in the unsensitized reaction, oxygen atoms are formed:



Hydroxyl radicals may also react together, in three-body collisions (for instance, on the walls), to give hydrogen peroxide. Reactions of oxygen atoms and of hydroxyls, leading to the formation of water, are envisaged, together with the above mechanisms, by Napravnik & Smith (1940).

Another set of conditions in which hydrogen peroxide has been found is connected with experiments involving electric discharges through water vapour. It had been noticed that when the products of such discharges were cooled to -183°C hydrogen peroxide was formed. Campbell & Rodebush (1936) showed that hydrogen peroxide is only formed appreciably on surfaces cooled to liquid-air temperature. Geib (1934) found that atomic hydrogen only reacted with oxygen to give peroxide on a surface at temperatures well below -80°C . Campbell, Rodebush & Wende (1937) showed that the radicals H and OH react in traps at -80°C to give mainly gaseous products, and at -180°C to give *c.* 50 % peroxide. Frost & Oldenberg (1936) agree with these conclusions; they have also carried out ultra-violet absorption experiments which indicate that the hydrogen peroxide is not formed in the gas phase. All this evidence indicates that hydroxyl radicals recombine on surfaces cooled to -180°C , yielding hydrogen peroxide.

The thermal reaction of hydrogen and oxygen has been very closely studied (Hinshelwood 1946; Lewis & von Elbe 1942). The theory accounting for the observed facts may now be said to be in a high state of development. The theory allows for the production of hydrogen peroxide in the gas phase, in the slow thermal reaction, via $\text{HO}_2 + \text{H}_2 + M \rightarrow \text{H}_2\text{O}_2 + \text{H} + M$, under the conditions which held in the experiments of Pease (Lewis & von Elbe 1942, p. 376). In the low-pressure explosion region, the behaviour at the limits is fully accounted for without the formation of any H_2O_2 ; in fact, unlike in the photochemical oxidation, it would not be expected to be sufficiently stable at the temperature of explosion to exist as such.

With this estimate of the knowledge about the production of hydrogen peroxide in the combustion of hydrogen, the ignition experiments, to which reference was made at the commencement of the Introduction, and the experiments of Poljakow seemed well worth further study. The significant result of the investigation to be described is that under certain conditions in the low-pressure thermal explosion of hydrogen and oxygen, more than 30 % of the condensate can consist of hydrogen peroxide.

2. EXPERIMENTAL

The various sections of the experimental work will be described separately.

(a) *Flame experiments*

The apparatus which had been used for the experiments made in 1928-9 still existed and was adapted to produce hydrogen peroxide continuously by heating a stream of hydrogen, by means of a tungsten heating coil, to such a temperature that on mixing with oxygen ignition would occur, the products being rapidly cooled by impinging on the bottom of the silica tube, which was immersed in liquid air (see figure 2). The results obtained for the quantity of H_2O_2 in the water condensed are summarized in table 1. The H_2O_2 was estimated iodometrically by back titration with thiosulphate.

TABLE 1

total pressure (cm. Hg)	$\text{H}_2:\text{O}_2$	total rate of flow (c.c./min.)	% H_2O_2 in the water condensed
4	1:1	1500	0.8
4	1:1	1500	0.8
4	1:1	1500	0.6
4	1:1	1500	1.5
4	1:1	1500	1.0
3	1:1	800	10.0
3	1:2	800	6.0
3	2:1	800	6.0
3	1:1	800	6.0

In the following experiments at 3 cm. pressure, hydrogen and oxygen were supplied at the rate of 200 to 300 c.c./min. (measured at atmospheric pressure). The rate of formation of product was c. 0.8 g. in 10 min. The lower part of the outer

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tube was now made of aluminium instead of silica. The aluminium tube was no improvement over the silica tube; the last two results showed that the flame must be chilled within 1.5 cm. of the jet if the efficiency is not to be reduced. When air was used instead of oxygen, the mixture refused to burn.

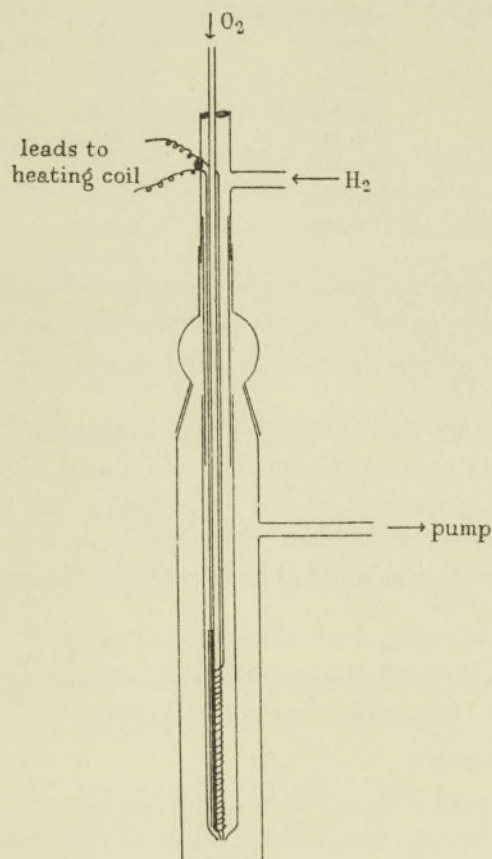


FIGURE 2. Silica combustion vessel.

TABLE 2. EFFECT OF DISTANCE OF JET FROM COOLED SURFACE

distance of jet from cooled surface (cm.)	cooling agent	lining	yield % $\text{H}_2\text{O}_2/\text{H}_2\text{O}$
1.3	liq. O_2	Al	4.0
1.3	liq. O_2	Al	4.5
1.3	liq. O_2	Al	5.0
4.0	liq. O_2	Al	2.0
0.3	liq. O_2	Al	5.0

The effect of lining the internal surface on the yield was next investigated (table 3). A surface treated with potassium chloride decreased the yield of peroxide. The effect

of boric acid, or of boron oxide, was equivalent to that of silica. This agrees with observations of Lewis & von Elbe (1942, p. 370) regarding the kinetic course of the reaction in lined vessels.

TABLE 3

distance of jet from cooled surface (cm.)	cooling agent	lining	yield % $\text{H}_2\text{O}_2/\text{H}_2\text{O}$
1.3	liq. O_2	KCl	2.5
1.3	liq. O_2	KCl	1.0
1.3	liq. O_2	H_3BO_3	3.0
1.3	liq. O_2	H_3BO_3	5.5
1.3	liq. O_2	H_3BO_3	4.5
1.3	liq. O_2	B_2O_3	7.0

All attempts to condense the products by cooling at the temperature of ice or of cold water failed. Anhydrous calcium chloride was used as a lining, and water as a cooling agent; after reaction, the calcium chloride was washed out and tested for peroxide, with negative results.

There were considerable difficulties in these experiments in maintaining the tungsten heating coil in good condition. It was therefore decided to maintain a spark to ignite the gases as they entered and mixed in the tube. The first experiments in the new apparatus designed on such lines did not give a yield of peroxide more than about 1 %, so it was decided to investigate the conditions necessary to obtain a higher yield.

(b) *Production of hydrogen peroxide in thermal explosions
induced by spark at low pressures*

(i) *Preliminary experiments*

Preliminary experiments were made in a steel pressure vessel of 10 cm. length, 1.3 cm. diameter, but, although considerable attack of the steel occurred, no appreciable hydrogen peroxide was formed, even when a glass or aluminium liner was used; on repeating the experiments and cooling the vessel in liquid air, a good yield of hydrogen peroxide was obtained (for results see table 4). The weight of water is that theoretically expected assuming all the hydrogen is oxidized.

TABLE 4

total pressure (cm. Hg)	H_2/O_2	% H_2O_2^*	total pressure (cm. Hg)	H_2/O_2	% H_2O_2^*
4	1.5	30	4	2.5	20
5	1.5	11	6	2.5	12
6	1.5	5	8	2.5	5
11	1.5	0.4	10	2.5	2
			12	2.5	0.6

* Calculated as $\frac{\text{wt. H}_2\text{O}_2}{\text{wt. H}_2\text{O theoretically expected}} \times 100.$

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The hydrogen peroxide was estimated colorimetrically with the titanous chloride reagent. The optimum pressure was about 4 cm.; below this pressure no ignition occurred. Ignition also depended on the potential across the spark gap and the size of the gap.

These results indicated that it was possible to obtain a considerably greater yield of peroxide in the explosion of hydrogen and oxygen at low pressures than Poljakow had obtained.

(ii) Experiments in pyrex vessels; single explosions

The mixture was let into a pyrex tube 13 to 14 cm. long, 1.4 cm. diameter, completely immersed in liquid air. The apparatus was similar to that shown in figure 5, but without the mixing tube and the exit tube. The pressure was adjusted to the required value. The mixture consisted of 1.5 parts hydrogen and 1 part oxygen. After explosion, the tube was allowed to warm up to room temperature, and the contents rinsed with distilled water into a 10 c.c. graduated flask, and then determined colorimetrically in a Klett colorimeter by comparison with standard solutions of H_2O_2 using the titanous chloride reagent.

The results are expressed as

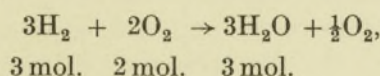
$$\frac{\text{g. H}_2\text{O}_2 \text{ formed}}{\text{g. H}_2\text{O formed assuming 100 \% formation of H}_2\text{O}} \times 100.$$

The weight of water was calculated as follows:

$$\text{Vol. of gas} = 18 \text{ c.c. at 4 cm. pressure.}$$

$$\text{Vol. at 76 cm. pressure} = 18 \times \frac{4}{76} \text{ c.c.}$$

Assuming complete formation of water,



5 parts of gas lead to 3 of water; since the reaction is probably not 100 % complete, the factor used was $\frac{1}{2}$; the weight of water expected is then

$$18 \times \frac{4}{76} \times \frac{18}{22400} \times \frac{1}{2} = 3.80 \times 10^{-4} \text{ g.}$$

The gases did not reach the temperature of liquid air before being exploded, as they were only in the vessel a short time before sparking. The pressures in the vessel were measured in liquid air and in air, and the maximum ratio was 1.66 to 1. Thus, the weight of water expected should not be more than $1.66 \times 3.80 = 6.3 \times 10^{-4} \text{ g.}$ Using this value, the true yield of peroxide estimated is not less than the figure given. Table 5 shows the variation in yield with pressure and composition of the gas mixture.

In later experiments, the pressure changes during reaction were observed using a butyl phthalate differential manometer. Results were rather erratic and seemed to indicate that reaction was complete only to the extent of 60 to 90 %. Results

were calculated, however, on the assumption that the reaction was 100 % complete. The estimate of H_2O_2 formed may therefore be considerably lower than the true value. The weight of peroxide formed, however, seemed reasonably consistent.

TABLE 5

pressure (cm. Hg)	H_2/O_2	% yield	
		Pt electrodes	Ni electrodes
2	1.0	2?	1? (difficult to detect)
3	1.0	11	—
4	1.0	4	3
6	1.0	0.8	0.8
2	2.0	0?	0?
3	2.0	16	9
4	2.0	16	17
5	2.0	5	5
8	2.0	—	0
3	2.5	19	—
4	2.5	20	—
4	2.5	20	—
5	2.5	12	—
6.5	2.5	6.2	—
8	2.5	3.5	—

The above experiments, and those carried out to investigate the effect of argon and of nitrogen, are summarized in figures 3 and 4.

The 'dead-space' in the reaction vessel consisted of 1.0 c.c. in the side-arm through which the gas mixture was introduced; this gas was exploded.

Blank experiments with a spark in oxygen showed that any ozone formed was insufficient to affect the TiCl_3 reagent. At first experiments were carried out using platinum electrodes, 1 to 2 mm. long. After the tube had been once cleaned with nitric acid, the yield rose in successive experiments to a steady value, 8, 12 and 15 %; on further cleaning 7, 8.5 %; the electrodes were then cut off short and filed flush with the glass, and yields of 22, 27 and 27 % were then obtained.

(iii) *Experiments in pyrex vessels; successive explosions*

The mixed gases were next introduced and exploded in succession without removal of the tube from the surrounding liquid air. After a given number of explosions had taken place the tube was removed and the yield of peroxide in the contents determined as before. Interposed between such sets of multiple explosions, the effect of a single explosion would be determined. The tubes were cleaned out with water and acetone between such experiments.

number of explosions	yield	number of explosions	yield
1	27	10	12
50	12	1	25
1	28	3	18
1	28	2	16
24	10		

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These results indicated that the film of deposited water reduced the yield of subsequent explosions. In order to eliminate the deposit of platinum which formed on the walls, nickel electrodes were used, and the tube was cleaned with hydrofluoric

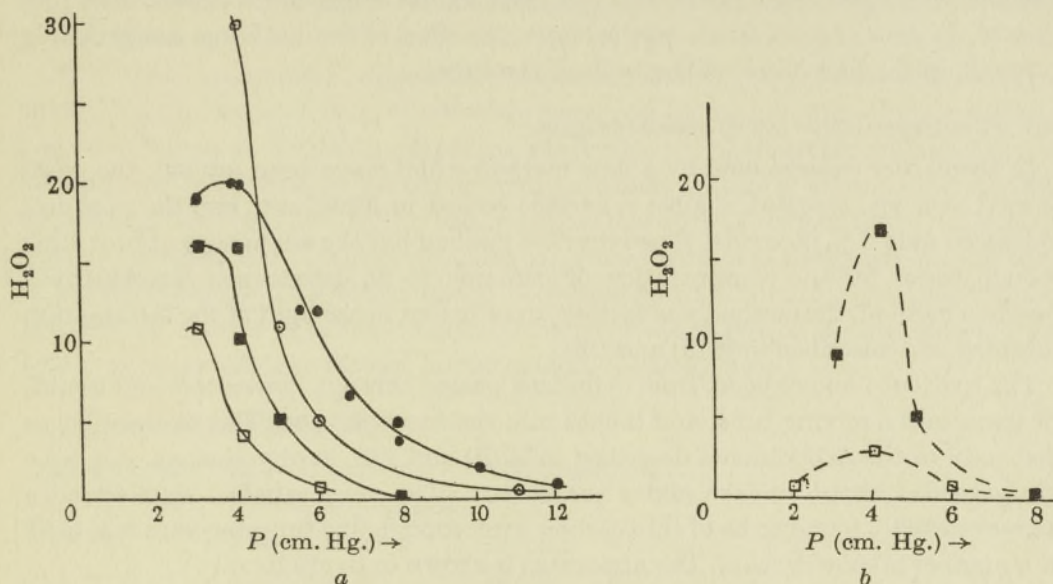


FIGURE 3. Single explosions. *a*, Pt electrodes; *b*, Ni electrodes; $H_2/O_2 =$ —□— 1.0, —○— 1.5; —■— 2.0 and —●— 2.5.

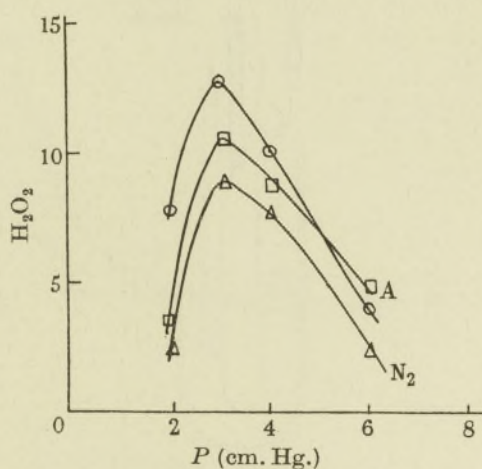


FIGURE 4. Effect of inert gases on single explosions. —○— 1.7 $H_2/1 O_2$, —□— 1.7 $H_2/1 O_2 + 5\%$ A., —△— 1.7 $H_2/1 O_2 + 5\%$ N_2 .

acid. Nickel electrodes led to a steady yield of 18 %, while with platinum the yield rose from 18 to 25 % and then gradually decreased, in single explosions.

Successive explosions were once more investigated. The experimental technique was modified as follows: after the first explosion, the discharge from a Tesla coil

was applied to the exterior of the reaction tube while the latter was being evacuated. This process being repeated after each explosion, it was found that, using nickel electrodes, the yield remained steady at 20 % for as many as ten successive explosions. With platinum electrodes, the yield fell off much more slowly than previously. In view of conclusions reached later, the effect of the discharge was probably to break up the film of ice on the walls of the tube.

(iv) *Flow experiments using spark ignition*

In the earlier experiments by a flow method which have been quoted, the gases burned at a jet, directed against a surface cooled in liquid air, but the products contained only 5 % peroxide. Since the flow method has the advantage of providing enough water for the concentration of peroxide to be determined directly by a titration method, the method was further investigated in the light of the information obtained and described in §§ (ii) and (iii).

The hydrogen and oxygen, from cylinders, passed through flowmeters and liquid-air traps into a mixing-tube, and thence into the reaction tube. This was similar to that used in the experiments described in §§ (ii) and (iii), except that an exit tube was provided about an inch above the bottom. The most satisfactory electrodes were eventually found to be of thin carbon wire, though fine tungsten wire was used in a number of experiments. The apparatus is shown in figure 5.

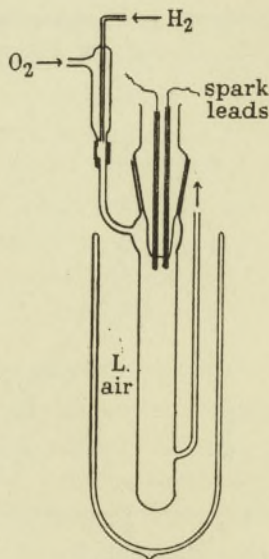


FIGURE 5. Continuous-flow apparatus.

The procedure was as follows. The apparatus was evacuated by a Hyvac pump. With the pump still running, the flow first of one gas, then of the other, was adjusted to pass through the apparatus, and out through the pump, at the partial pressures required. A spark was then passed continuously across the electrodes; the energy for the spark was derived from a medium-size induction coil; the potential was

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sufficient to cross a gap of about 3 in. in air. The gases exploded as frequently as the required pressure was built up, and in fact appeared to burn almost continuously. After a given time, the reaction tube was removed and the frozen product melted; the concentration of peroxide was then determined by titration with acid potassium permanganate.

After some preliminary, apparently erratic, results, it was realized that for given conditions the concentration of peroxide depended on the amount of product which had been frozen on the walls. That this effect was due to thermal insulation by the ice film was confirmed by an experiment in which a known volume of water was spread over the walls and frozen before explosions were carried out; the decrease in yield of peroxide was then in very close agreement with that calculated on the basis of this hypothesis. This fact made it necessary to obtain curves relating yield of peroxide to volume of product formed whenever the effects of various factors were being investigated. The factors investigated were as follows:

(1) Nature of the electrodes:

Conditions:	Overall pressure	5 cm. mercury
	Hydrogen/oxygen	1.6/1.
	Tube diameter	1.4 cm.
	Tube length	14 cm.

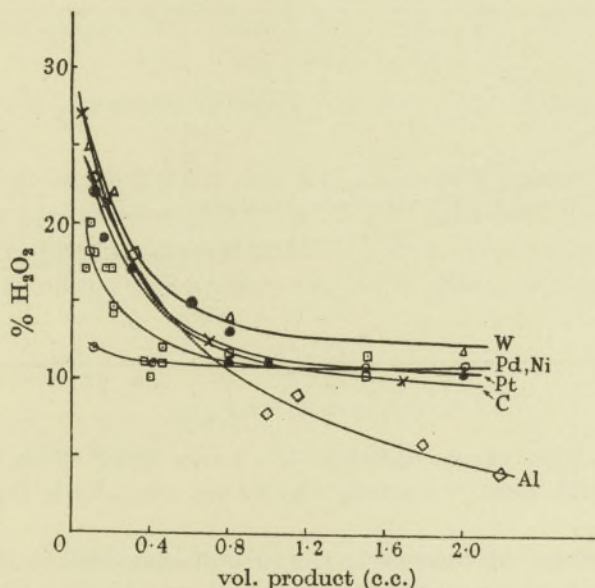


FIGURE 6. Effect of electrodes. —●— Pt, —○— Ni, —△— W, —□— Pd, —◇— Al, —×— C.

The experimental results show that with platinum, tungsten and carbon electrodes the rate of decrease of peroxide yield with increasing volume of product was similar. In spite of this, with aluminium electrodes (which are believed not to sputter) the

yield decreased somewhat more rapidly. Palladium produced a rapid decrease in the yield of peroxide, after which the product was of almost constant composition. Nickel electrodes were associated with a decrease in yield so rapid as to be almost unobservable, followed again by a product containing 11 % peroxide. In all cases except that of aluminium, the product obtained when over 2 c.c. had been produced contained approximately 11 % peroxide. The initial yield appeared to have been between 30 and 35 %.

A comparison of these results with the relative tendencies of the metals to sputter (Waran 1931)

Al, 0, Mg, 1, Ni, 11, Pt, 44, Pd, 100,

shows that indiscriminate gas-phase destruction of peroxide by hot metal particles is not the chief controlling factor.

(2) *Effect of tube diameter:*

Conditions: Overall pressure 5 cm. mercury

Hydrogen/oxygen 1.6/1.

Electrodes Tungsten

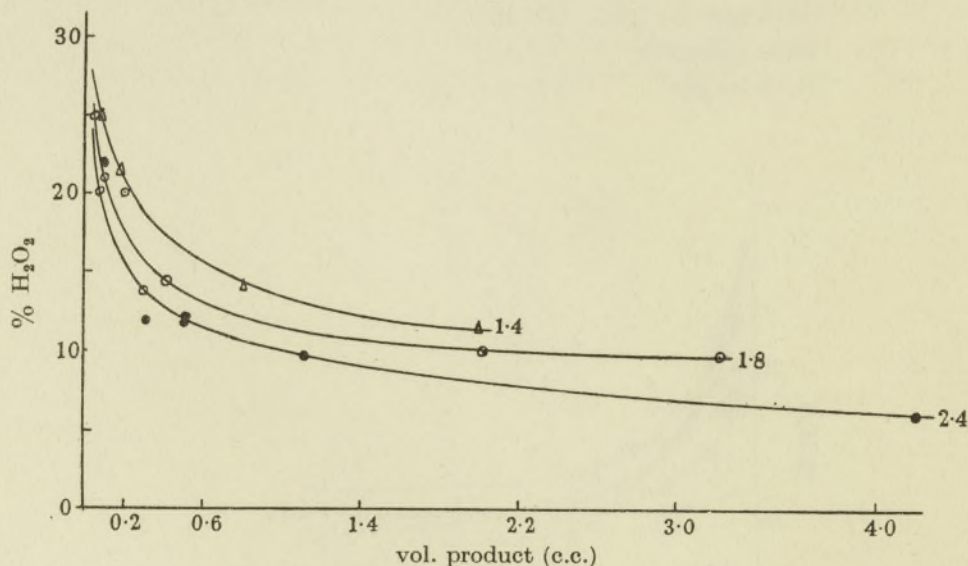


FIGURE 7. Effect of tube diameter. \triangle —1.4 cm. diam., 14 cm. long;
 \circ —1.8 cm. diam., 9 cm. long; \bullet —2.4 cm. diam., 5 cm. long.

(a) Tube length 14 cm. An increase in the tube diameter led to a product which reached a steady concentration of 15 % peroxide.

(b) In order to have strictly comparable conditions (*viz.* equal rates of flow of gas), tubes of different diameters were constructed with equal volumes. The results showed that increasing diameter reduces the concentration of peroxide in the product. This observation is in accordance with that of Poljakow, in his experiments under static conditions.

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(3) Effect of tube length:

Conditions: Overall pressure 5 cm. mercury
 Hydrogen/oxygen 1.6/1.
 Electrodes Tungsten
 Diameter 2.4 cm.

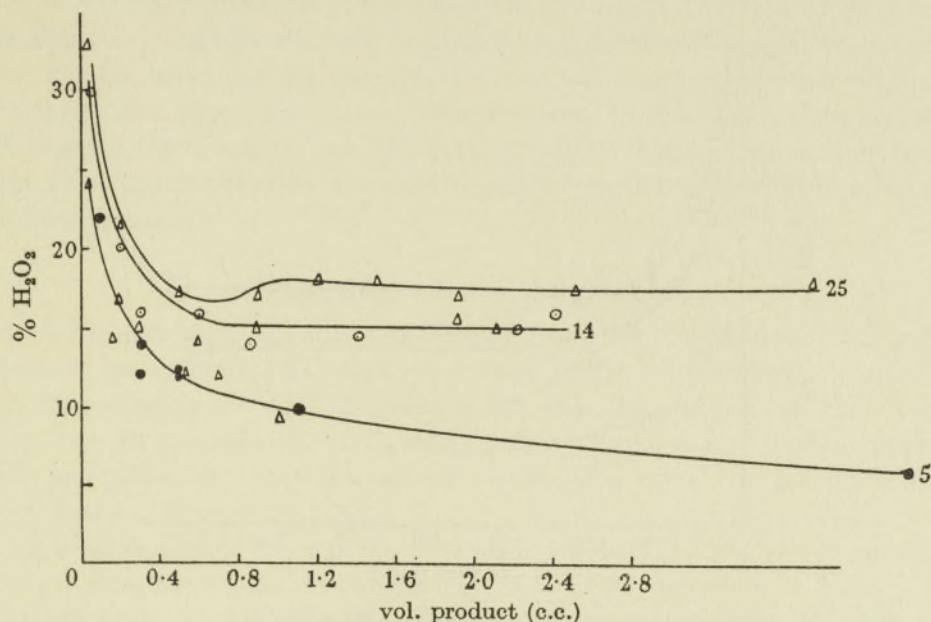


FIGURE 8. Effect of tube length. —●— 5 cm., —○— 14 cm., —△— 25 cm.

It was found that increasing the length of the tube increased the concentration of peroxide in the final product. With the longest tube used (25 cm.), erratic results were obtained for small volumes of product. This may be due to irregular deposition of product on the large wall surface available, until a fairly thick film has been built up.

(4) Effect of pressure:

Conditions: Hydrogen/oxygen 1.6/1.
 Electrodes Tungsten
 Tube 2.4 × 14 cm.

Variation of pressure showed that the maximum yields of peroxide were obtained with pressures of 4, 5 and 6 cm. mercury. The influence of pressure was less marked than in the static experiments, probably because here the pressure was less even, owing to the intermittent explosions.

(5) Effect of hydrogen/oxygen ratio. A brief investigation showed that results were unaffected when the ratio of hydrogen to oxygen was greater than 1.6; below this value, the yield decreased rapidly.

(6) *Effect of surface.* A reaction tube 1.4×14 cm. lined with cellophane gave results identical with those obtained with a glass surface. An aluminium tube was also found to give similar results.

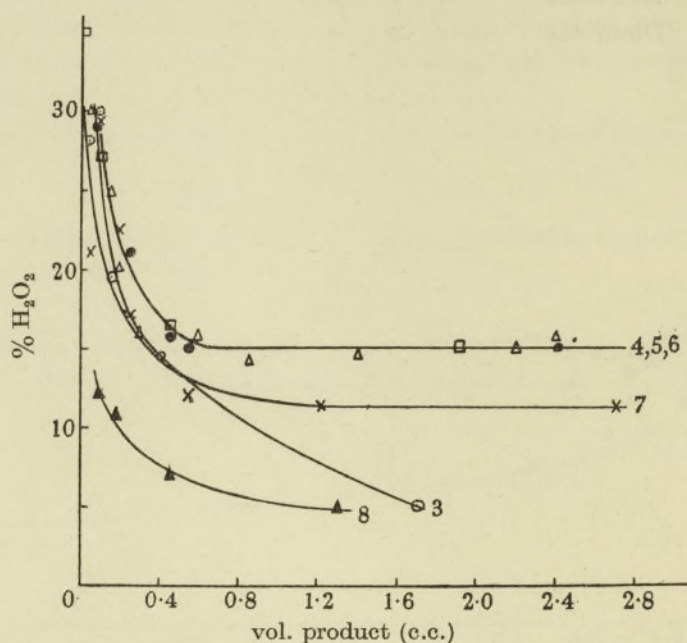


FIGURE 9. Effect of pressure. —○— 3 cm. Hg, —●— 4 cm. Hg, —△— 5 cm. Hg, —□— 6 cm. Hg, —×— 7 cm. Hg, —▲— 8 cm. Hg.

(7) *Effect of external temperature.* An experiment was carried out with a reaction tube 2.4×14 cm. under conditions which led to a yield of 15 % when the walls were cooled to *c.* -180°C ; in this experiment, however, the walls were cooled to -79°C , and a yield of 6 % was obtained. In another experiment the tube surrounding the electrodes was enclosed in a water-jacket; the products then passed downwards into the bottom of the tube, which was cooled in liquid air. The yield obtained was only 2 %.

(v) *Summary of evidence that hydrogen peroxide is formed in the combustion of hydrogen at low pressures*

The experiments described in the preceding sections have shown that hydrogen peroxide is formed in the low-pressure explosion of hydrogen with oxygen, when the reaction vessel is cooled to -183°C . The yield of peroxide is maximum for a critical value of the gas pressure, and is decreased by the presence of excess oxygen, or of nitrogen, or, to a lesser extent, of argon. The yield of peroxide is also decreased by increasing vessel diameter, and by increased external temperature; the film of product formed on the wall of the reaction vessel also reduces the amount of peroxide isolated.

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Frost, Linnett & Raynor (1945) have published work which supports the view that the low-pressure hydrogen-oxygen explosion initiated by sparking does not differ appreciably from the low-pressure explosion to which the considerations of Lewis & von Elbe, and of Hinshelwood (1946) apply. Experiments have been carried out in the course of the work being described which show that the formation of peroxide was due to the explosion and not to the spark (see also p. 160): the continuous-flow apparatus was modified so that the explosive mixture entered by what was previously the exit tube; after passing through the reaction chamber, the gas encountered a spark situated away from the reaction chamber; explosion was then propagated back through the incoming gas, before the latter could come into contact with the spark. The yield of peroxide was unaffected. The product appeared to be frozen in a uniform deposit.

(c) Seat of formation of hydrogen peroxide

The hydrogen peroxide might be formed from the recombination of hydroxyl radicals at the surface, their extra energy being removed by rapid cooling and the H_2O_2 remaining stable. It is also conceivable that the action is not exclusively at the surface, for example, that HO_2 reacts with hydrogen to give hydrogen peroxide in the gas phase, and that the peroxide exists long enough to reach the surface before decomposition takes place.

This third section of the experimental work was designed to find out whether the hydrogen peroxide existed in the gas phase during the explosion. A beam of ultra-violet light was passed through the tube during the explosion, and the absorption by the hydrogen peroxide formed was measured in a narrow region of wave-lengths.

Hydrogen peroxide absorbs continuously below 2800 Å. Its presence could therefore be detected by the decrease in intensity of a beam of ultra-violet light passing through the reaction region. The mercury line at 2537 Å was selected, as it could be easily isolated, and since its intensity would not be affected by anything else present in the reaction (except possibly ozone: see below).

A low pressure mercury lamp was used as a source. The radiation was very strong at 2537 Å. The remaining light was filtered off by means of a Christiansen filter (Gaydon & Minkoff 1946). Using an iron arc, it was shown that a band of only 20 to 30 Å was transmitted.

Measurement of the light intensity with a photocell was attempted, but was found, for various reasons, to be impracticable. The photocell was consequently replaced by a plateholder, on which a number of photographs of the beam could be taken. Ilford 'Zenith' plates were used; the intensities of the photographs were compared using a Hilger microphotometer. The experimental arrangement is shown in figure 10.

The light from the lamp was itself directly photographed both before and after nearly each experiment in which the light had been photographed while it passed through the explosion. Emission from the flame was investigated to ensure that no light at 2537 Å came from it; this was every time confirmed. There was a certain

irregularity in the results obtained owing to the precise number of separate explosions in a given time being indeterminate. These results are shown in table 6. The first four results in the table show clearly that absorption does take place. Results 2A' (1) and (2), in which light passed through the gases which were being sparked, although they were not exploding, indicate that the absorption was connected with the explosion. In the next four experiments explosions were taking place in the presence of excess hydrogen, to destroy any ozone formed (by the spark or otherwise); they, and 3B (1), indicate that absorption was not due to ozone. In other experiments the spark was passed across water vapour at a pressure of *c.* 1 mm., but no absorption occurred. These observations support the conclusion that some peroxide is formed in the gas phase during the explosion.

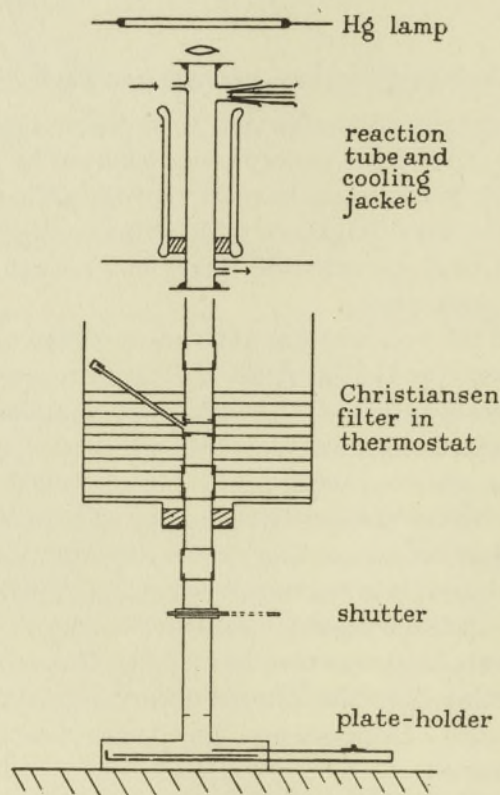


FIGURE 10

As the absorption was fairly uniform throughout the patch of light falling on the plate, particularly when the alinement was good, there is indication that the hydrogen peroxide was certainly not formed exclusively on the walls. If the peroxide were only formed on the sudden cooling, for instance, of OH radicals at the walls cooled by liquid air, a higher concentration might be expected round the periphery, if there were any absorption at all. The results are contrary to this expectation. Therefore another mechanism involving gas-phase formation must enter.

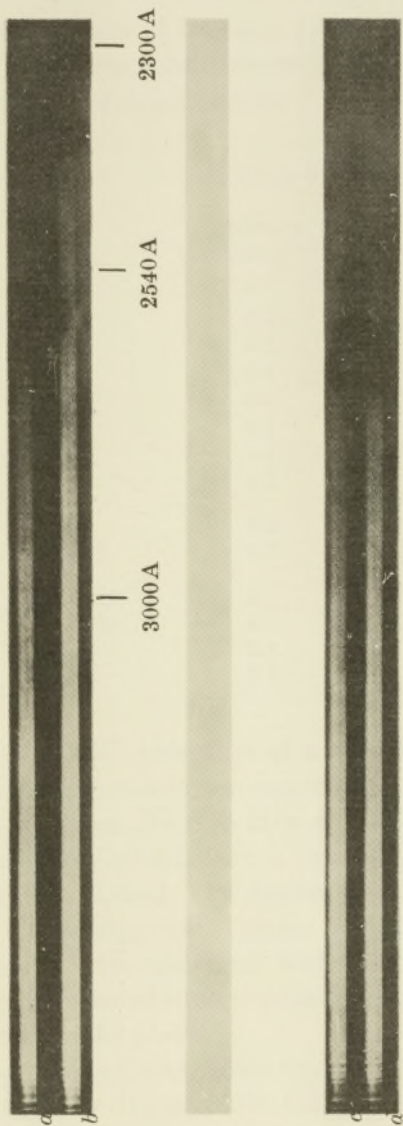


FIGURE 11. *a, c*, hydrogen discharge spectra viewed through explosion region, showing absorption beyond *c*. 2800 A. *b, d*, hydrogen discharge spectra viewed direct.

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In order to obtain some idea of the concentration of peroxide present in the gas phase, parallel experiments were carried out in which the light absorption was measured with hydrogen peroxide vapour passing through the reaction tube under controlled conditions. Such experiments indicated that the average partial pressure of hydrogen peroxide during reaction was of the order of 3 to 4 mm. mercury. Calculations based on the data of Dawsey, Rice & Urey (1929) also indicated that the amount of 'peroxide' was commensurable with that actually isolated. These estimates are, of course, very approximate.

TABLE 6

exp.	H ₂ /O ₂	pressure (cm.)	% extinction	
1A	1.0	5.1	83	
1B	1.0	5.1	76	
2A	1.0	5.1	89	
2B	1.0	5.1	61	
2A' (1)	3.3	5.1	7	very few explosions
2A' (2)	3.3	5.1	14	very few explosions
2B' (1)	2.1	5.1	62	
2B' (2)	2.1	5.1	27	few explosions
3A (1)	2.6	6.3	52	yield of peroxide generally smaller
3A (2)	2.6	6.3	53	
3B (1)	O ₂ only	2	c. 10	i.e. negligible
3B (2)	H ₂ only	4	c. 0	
3A' (1)	1.6	5.1	66	reaction tube not cooled
3A' (2)	1.6	5.1	30	

Instead of measuring the absorption of a monochromatic beam of ultra-violet light, the next series of experiments were made by measuring the absorption throughout the ultra-violet spectrum (3000 to 2100 Å). Since the background provided by an iron arc was not entirely satisfactory, a 'special' hydrogen discharge tube giving a continuous spectrum was used. The spectroscope was a Hilger (medium) quartz spectroscope, and the photographic plates were again Ilford 'Zenith'. The intensities of blackening were measured with the same microphotometer, and a calibration curve was drawn relating the blackening of the plate to the amount of light which had fallen on the plate.

In one set of experiments it was shown that no light was absorbed when it passed through either hydrogen or oxygen in the tube, even though the spark was switched on. In all other experiments the explosions studied were of mixtures in which the partial pressures were 1.8 cm. oxygen and 3.3 cm. hydrogen respectively. Photographs of the light from the discharge tube passing through the explosion region were bracketed with photographs of the light passing through the tube with no explosion taking place; this was intended to provide evidence that the windows of the tube had not become at all opaque. Both time of exposure and slit width were varied in different experiments. The percentage light transmitted at particular

wave-lengths was calculated for a large number of experiments, and mean values derived. This was necessary in order to compensate to some extent the irregularities due to spasmodic explosions. Two specimen pairs are shown in figure 11, plate 7. In table 7 the mean values of $\log_e I_0/I$ are compared with values derived from the data of Dawsey, Rice & Urey. It is seen that absorption increases steadily towards the ultra-violet without significant interruptions. Nevertheless, the rate of increase of absorption with decreasing wave-length observed was not as great as that indicated by the figures of the above authors. This is consistent with the following reasoning: in the periods between explosions, when no light is absorbed in the tube, more light falls on the plate at all wave-lengths than would be the case if hydrogen peroxide were absorbing; therefore, the decrease in intensity of blackening due to peroxide will be most masked where the overall intensity is least, i.e. towards shorter wave length.

TABLE 7. $\log_e I_0/I$

wave-length	3130	3000	2800	2700	2537	2400	2300	2200	2100
experimental values	0.32	0.36	0.52	0.69	0.64	0.69	0.87	0.82	1.24
D., R. & U.	0.04	0.05	0.12	0.20	0.45	0.75	1.1	1.45	1.65

The absorption of light by ozone has been shown by Fowler & Strutt (1917) to have a maximum value in the region of 2500 Å, and to be small before *c.* 2200 Å. These features are clearly not observed in the results here recorded, proving that if ozone is present under these conditions, its concentration is much smaller than that of hydrogen peroxide.

The possibility that the absorption was due to small particles of vapour (i.e. a fog) has been considered. Such particles, if present, would absorb all wave-lengths; in fact, absorption in the whole spectrum was observed in one or two experiments (which have not been made use of in the calculation of transmission coefficients), but not in any others. This shows that when fine particles were present in the gas phase, they could be detected by the decrease in intensity of the visible region of the spectrum, and that they were not responsible for the normal absorption in the ultra-violet.

It may thus be taken as proved that hydrogen peroxide is, indeed, formed in the gas phase during the low-pressure explosion of hydrogen with oxygen, and that this is so even when the walls of the reaction vessel are not cooled. The order of magnitude of the concentration of this peroxide in the gas phase may be very roughly estimated to be 10 %.

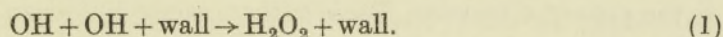
3. DISCUSSION

In the experimental work which has been described, three features are of special importance. In the first place, it is found that as the total pressure is increased, so the concentration of hydrogen peroxide in the product passes through a maximum value, and eventually becomes negligible. Secondly, there is the observation that as an increasing thickness of ice is built up on the walls, so the concentration of

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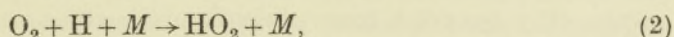
hydrogen peroxide in the product decreases from 30 to 35 % to a steady value of 10 to 15 %, which is approximately independent of the thickness of the ice film. Finally, there is the observation that the explosion region absorbs continuously in the ultra-violet in a manner which indicates the presence of a considerable quantity of peroxide in the gas phase; this happens whether the walls are cooled to -180°C or are not cooled at all, although in the latter instance, the peroxide cannot be detected appreciably in the products.

The effect of the ice film is clearly due to its insulating properties. The thermal conductivity of the wall decreases as the film thickens, hence decreasing the rate of heat transfer through the walls. This means that the freezing-out of hydroxyl radicals (with subsequent formation of H_2O_2) becomes less efficient, since at temperatures much above -180°C it is well known that hydroxyls do not react on the cold surface to give H_2O_2 (Rodebush 1937). It can thus be deduced that the part of the products which is formed in smaller amount as more overall products are formed (i.e. while the concentration of hydrogen peroxide falls from 30 to 15 %) is probably due to the mechanism

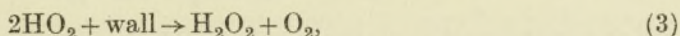


The remaining hydrogen peroxide formed (i.e. 10 to 15 % of the product) is presumably that whose presence has been detected in the gas phase, and has been formed in a gas-phase reaction.

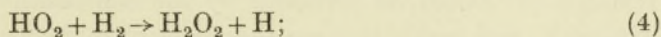
Hydrogen peroxide is indeed postulated as an intermediary in the reaction schemes proposed by Lewis & von Elbe (1942), and by Hinshelwood (1946), but its role is then to continue chains in the so-called slow, thermal reaction, at pressures above the second limit. H atoms, which are chain-carriers in the low-pressure explosion, are removed by three-body collisions with oxygen



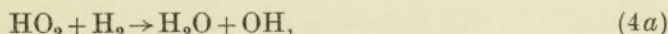
whence the product HO_2 is either destroyed (later) at the surface as



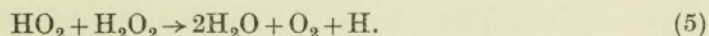
or else it reacts with hydrogen to give hydrogen peroxide as



or to give water, as

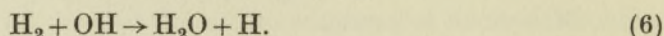


it can also destroy H_2O_2 by the reaction



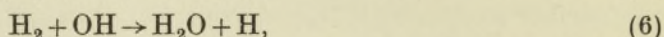
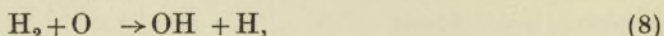
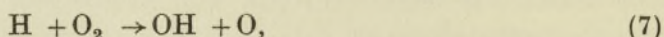
(The isolation of H_2O_2 from the slow thermal reaction has been confirmed by Pease 1930). It is specified, nevertheless, that the gas-phase reactions 4, 4a and 5 only become important beyond the upper limit of the low-pressure explosion. Even if these reactions were more important than the above authors assume, they would not explain the phenomena described in this communication (even apart from their

effect on the explosion limits), because they follow on three-body collisions forming HO_2 (2), which would be expected to be favoured by increasing pressure, unlike the bimolecular reactions leading to the formation of water, e.g.



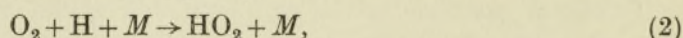
This, however, does not agree with the experimentally observed decrease in yield of H_2O_2 with increasing pressure.

No other mechanisms are mentioned in the papers referred to above, which lead to the formation of H_2O_2 in the gas phase. The mechanism for the formation of water in the low pressure explosion, as shown below, is of no direct help. The scheme is

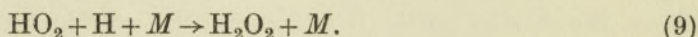


together with suitable chain-breaking reactions.

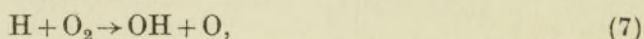
The work of Geib & Harteck (1932) seems at first sight to have a direct bearing on the present discussion. These authors mixed hydrogen atoms (from a discharge) with a stream of oxygen, at a pressure of 0.5 mm., in a vessel cooled to low temperatures. The product contained a high percentage of H_2O_2 , which reached 100 % when the external temperature was -252°C (liquid hydrogen). The formation of the peroxide is due to the formation of HO_2 , first,



and its subsequent reaction with an H atom,

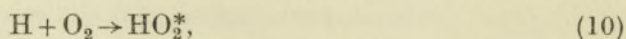


The authors point out that as these reactions involve very little, if any, activation energy, they are much more probable under these conditions than the alternative bimolecular exchange reactions of the type

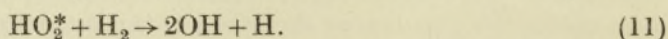


which require much more energy of activation. Nevertheless, this mechanism cannot be applied directly to the conditions of the low-pressure explosion, partly because reaction (7) would be favoured by the comparatively high temperature of the explosion, and partly because the mechanism does not account for the decreasing yield of H_2O_2 with increasing pressure.

The only way which seems to remain of explaining the formation of H_2O_2 under the conditions of the low-pressure explosion is based on a modification of a mechanism which was proposed by Kassel & Storch (1935) to account for the low-pressure explosion. It was assumed that HO_2 was formed in an activated form by direct association of H and O_2



and that it then reacted with hydrogen to give an H atom and two hydroxyls

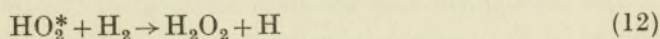


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It had to be assumed that reaction (11) was much more rapid than was deactivation of the excited HO_2 by further collisions. Lewis & von Elbe (1942) point out that this mechanism could function concurrently with that described above, and that it would satisfy their derived rate expressions. Kassel (1937), however, repudiated these steps in the reaction-chain mechanism, becoming convinced that the formation of HO_2 only occurred in three-body collisions. Kassel quotes the work of Cook & Bates (1935), Bodenstein & Schenk (1933), and Farkas & Sachsse (1934) as proof of this. The argument is invalid, however, for the purpose of the present discussion, because all these authors worked at comparatively high pressures.

It is quite possible that the formation of HO_2 by two-body collisions is not always highly improbable. It is now generally accepted that in most simple reactions, the reactants come together for a short period of time, to form what is usually termed the transition state complex (Glasstone, Laidler & Eyring 1941). This complex represents a state of high potential energy; it possesses all degrees of freedom except that of translational energy in the co-ordinate of decomposition. For any reaction of H with O_2 the transition state can be formally represented by the formula HO_2^* . When some of its energy of formation has been removed it has an appreciable existence as an entity. This has been shown by approximate calculations (e.g. Rosen 1933), and by the number of reaction mechanisms in which it is an integral link. It has always been assumed that if some energy is not removed, decomposition to $\text{OH} + \text{O}$ will occur before other reactions can take place. This is not necessarily true. If the number of collisions with other molecules is suitable it should be possible for the energy in the newly formed bond to be shared, for a short period of time, with the vibrational and rotational degrees of freedom. The HO_2 radical should thus have a short but definite lifetime in the excited state; this will be referred to as HO_2^* .

That part of the mechanism which involves interaction of a hydrogen atom with an oxygen molecule can now be regarded as follows. The first entity formed, as explained above, is the activated complex HO_2^* ; below a certain pressure the number of collisions will be so small that most HO_2^* will disintegrate into OH and O before any third body encounters it. At a higher pressure, so long as there is a high enough concentration of hydrogen molecules, collisions may occur with the HO_2^* . The excess energy associated with the latter will generally be sufficient for the reaction



to be frequent. The excess energy will be removed partly by the H atom as translational energy, and partly by the peroxide. It is known from the experiments described previously that the peroxide exists long enough for its absorption spectrum to be recorded, even if the walls are not cooled. It follows, therefore, that the energy of formation of the peroxide does not immediately pass into the $\text{HO}-\text{OH}$ bond, causing rupture of the molecule; it must therefore be distributed amongst the vibrational and rotational degrees of freedom for a short period of time. After this, if the energy is not removed on the cold walls, the hydrogen peroxide decomposes, most probably into two hydroxyls. Collisions with oxygen molecules, or other

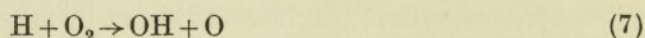
molecules which can take up energy, will result in stabilization of HO_2^* , and hence in a decrease in the amount of peroxide formed by this mechanism; this effect is especially noticed when excess oxygen is present.

As the pressure is further increased, so the number of actual three-body collisions will become greater, resulting in the formation of a higher proportion of stabilized HO_2 radicals, and hence of a smaller concentration of peroxide.

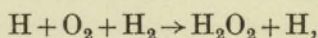
The effect of introducing nitrogen, which can take up rotational and vibrational energy, is similar to that of oxygen, namely, to lead to a decrease in yield. Small quantities of argon, which can take up translational energy only, decrease the yield of peroxide less than does nitrogen, as is to be expected.

It should be emphasized that the mechanism postulated above for the formation of peroxide is only of importance within the low-pressure explosion range, but operates very infrequently at the pressures in the neighbourhood of the actual lower and upper explosion limits. This means that the rate—and limit—expressions calculated by the above authors (Lewis & von Elbe 1942; Hinshelwood 1946), remain unaffected.

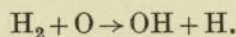
The fact that the branched-chain reaction



has been replaced to some extent by the reaction summarized as



in which the reaction chain is continued without branching, is not of great importance, for the following reasons. First, O atoms resulting from the decomposition of H_2O_2 , or from some other source, will still give rise to the branched-chain reaction (8)



Then, under normal conditions, when the walls are not cooled, the peroxide decomposes into two hydroxyls, giving rise to a branched chain, as shown by Kassel & Storch (1935). Finally, there is the argument of Semenov (1929), discussed by Hinshelwood & Williamson (1934), that in such a reaction the excess translational energy removed by the hydrogen atoms would be sufficient to break up some hydrogen molecules into atoms, i.e. to increase the number of chain-carriers.

The mechanism also accounts for most of the other observations made in the course of the present investigation. The effect of increased tube diameter is to increase the time for the peroxide to reach the walls, and thus reduces the probability of the peroxide being stabilized; similarly, the wall reactions involving hydroxyls are made less probable. The effect of tube length may perhaps be explained if it is supposed that the longer the tube the smaller is the effect of reflexion of the hot zone from the ends of the tube, leading to less destruction of the peroxide in the gas phase before the peroxide reaches the walls. The only factor which has not been elucidated is that relating the yield to the metal used in the electrodes; no relation appears to exist between the yields with different metals and any properties of these metals. It is possible that the spark produces small quantities of silica, silicates and

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oxides of metals, which tend to catalyse the decomposition of the peroxide. In fact, some of the peroxide produced has on occasion been noticeably turbid and prone to decomposition. As impurities have a very specific action on the decomposition of hydrogen peroxide, the effects obtained using different metals as electrodes are not surprising.

It should be pointed out that the hydrogen peroxide is formed in an excited state, whence the excess energy has to be rapidly removed, unlike that formed in the ordinary thermal or photochemical oxidations of hydrogen, but that the peroxide appears to be perfectly normal once it has been frozen out and melted. This observation differs from that of Geib & Harteck (1932); these authors stated that the peroxide which they obtained from the reaction of hydrogen atoms with oxygen at low temperatures possessed unusual properties.

This work leads to the conclusion that even in exceedingly rapid explosion processes, the mechanism is one which is essentially related to the process of peroxidation. Peroxides are not necessarily formed, but removal of excess energy immediately allows the peroxide to be formed. The experiments are being continued, and it is interesting that at low pressures methane explosions have been found also to provide peroxides, but in this case not hydrogen peroxide.

The authors wish to record their thanks to Radiation Ltd. for the provision of the Radiation Fellowship tenable at the Department of Chemical Technology at the Imperial College, which one of them held (G.J.M.), during this work; also to the Admiralty (Department of Scientific Research) for support of the work and to the General Electric Co. for the gift of the low-frequency mercury lamp. They wish particularly to thank Dr A. G. Gaydon for his helpful advice in the spectroscopic work and in its interpretation.

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A general kinetic theory of liquids

IV. Quantum mechanics of fluids

BY M. BORN, F.R.S.,* AND H. S. GREEN

(Received 7 March 1947—Read 26 June 1947)

In this paper the classical theory of liquids developed in the first three parts of this series is translated into the quantum formalism. After the fundamental equations have been reformulated, it is shown that in the classical limit $\hbar = 0$, they go over into the corresponding classical equations. A quantized proof of the Boltzmann distribution law is given which is simpler and more direct than that of the Darwin-Fowler method. Then the equation of state is derived in a form which exhibits clearly the deviations from the classical law at very low temperatures.

An approximate method of solution of the fundamental equations is developed in a form suitable for practical application. Finally, the quantum equations of motion and energy transport are obtained, and it is shown that they are formally identical with the classical 'hydrodynamical equations'. This enables a discussion of the viscosity and thermal conductivity of quantum liquids to be given which exposes clearly the alternative explanations of the abnormal properties of liquid He II.

1. INTRODUCTION

In the first three parts of this series the theory of liquids was treated with the help of classical mechanics. In the present paper we propose to apply instead quantum mechanics. This is necessary because there are physical phenomena which indicate quantum effects, namely, the superfluidity of He II, and the superconductivity of certain metals; further, it seems very likely that atomic nuclei must be treated as

* I have signed this paper, as it is part of the programme with which we started this series. My contribution consists of some general suggestions, such as the use of the density matrix as the proper tool, and many critical remarks. The work itself is due to Mr Green.—M. BORN.