STUDIES ON THE DECOMPOSITION AND
PHOTO-FORMATION OF HYDROGEN PEROXIDE.

Thesis Presented for the Degree of
Doctor of Philosophy

by

Roland Arthur Hamilton, B.Sc.

University of Edinburgh.

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## THE PHOTO-FORMATION OF $\text{H}_2\text{O}_2$

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THE THERMAL DECOMPOSITION OF HYDROGEN PEROXIDE VAPOUR.
INTRODUCTION.

The study of the properties and reactions of hydrogen peroxide has aroused the interest of chemists since its discovery by Thenard in 1818. Its inherent instability and the ease with which it gives off oxygen at ordinary temperatures renders it as interesting to the organic chemist as it is to the physical chemist, since it can be profitably used in oxidations with two advantages - (a) it is more reactive than oxygen, 23.1 k.cals. being liberated per mole, and (b) the residue is water, with normally no interference in the oxidation reaction.

Reactions involving hydrogen peroxide can be considered in two arbitrary classifications, those in which the peroxide is present in relatively large amounts, usually in the liquid phase, and those in which only small concentrations appear to be involved. In this latter category may be included the occurrence of hydrogen peroxide in the thermal combination of hydrogen and oxygen, in the photo-combination of hydrogen and chlorine in the presence of oxygen, and in the degradation of textile/
textile fabrics and dyestuffs on exposure to light in the presence of oxygen and water, this last reaction being generally accelerated by substances such as zinc oxide and titanium dioxide. Systematic examination of the decomposition of hydrogen peroxide has been largely confined to the liquid phase, with comparatively little corresponding investigation of gas phase systems; such reactions, particularly in the gas phase, are markedly heterogeneous in nature and so determined by the experimental conditions that little agreement appears to exist as to detailed mechanisms. A similar confusion exists as to the mode of formation and behaviour of hydrogen peroxide in the low concentration conditions referred to above, and further experimental investigation of all these aspects is certainly required.

The work to be described falls into two main divisions.

In the first, investigation has been made of the thermal decomposition of hydrogen peroxide vapour at pressures of the order of 1 mm. This may be considered as an extension of the work of Mackenzie and Ritchie \(^5^5\), who reported the decomposition to be second/
second order, in contrast to the results of all previous workers, in which unimolecular reaction rates were obtained. The actual silica reaction vessels used by Mackenzie and Ritchie were available: in one of these vessels remarkably reproducible results had been obtained. In a second vessel, the total observed increase in pressure due to complete decomposition was much greater than that expected from the peroxide pressure initially recorded, this indicating initial adsorption of peroxide by the vessel walls. It was hoped, therefore, to extend the investigation of hydrogen peroxide vapour decomposition, with particular reference to:

1. variation of pressure;
2. the possibility of the occurrence of a homogeneous gas decomposition;
3. the effect of various solid inhibitors and catalysts;
4. the influence of higher pressures of oxygen, water vapour, and inert gases such as nitrogen;
5. the kinetics of the decomposition in the possibly multimolecular layer in the second vessel.

In the second portion of the work, investigation has been made of the production of hydrogen peroxide by illumination in "white" light of various zinc oxide/
oxide, water and oxygen systems. Previous work on these lines has been mainly fragmentary, only very small amounts of peroxide being reported. It seems possible that such small amounts might represent an equilibrium concentration limited by the decomposition. Accordingly an attempt has been made to determine the conditions controlling such formation of peroxide, partly by means of the apparatus constructed for the thermal vapour decomposition, and partly by other specific arrangements.
Historical.

Hydrogen peroxide was first described by Thenard\(^1\), in a paper entitled "Observations sur la combinaisons nouvelle entre l'oxygen et divers acides". He first supposed that the liquids which he obtained by treating barium peroxide with nitric, sulphuric, arsenic, phosphoric and acetic acids to be "produits suroxygenes" of the different acids, but he later showed that the liquid, which he appropriately called "eau oxygenee", contained a super-oxide of hydrogen which had strong oxidising properties and decomposed into water and oxygen on heating.

The formula and structure of the peroxide molecule has aroused much interest since its discovery. Thenard stated the formula as being H\(_2\)O\(_2\) (water being HO), and this formula persisted until 1860; in 1865 it is quoted as HO or H\(_2\)O\(_2\)\(^7\) and by 1872 was established as H\(_2\)O\(_2\)\(^8\).

An interesting series of papers dealing with the chemistry and occurrence of hydrogen peroxide was published by Schöne, Berthelot and Leeds\(^10\). The subjects dealt with by these authors included (a) the occurrence of hydrogen peroxide in rain water/
water (b) the mutual decomposition of ozone and hydrogen peroxide\textsuperscript{10} (c) the mechanism of the decomposition of hydrogen peroxide in the presence of alkalis\textsuperscript{11} (d) the electrolysis of hydrogen peroxide\textsuperscript{12} (e) the decomposition of aqueous solutions of hydrogen peroxide\textsuperscript{13}.

Schöne also developed the well known permanganate titration for the estimation of hydrogen peroxide, this having been previously examined by Brodie\textsuperscript{14}.

The decomposition of aqueous solutions of hydrogen peroxide has been the subject of a great amount of research work, and, although a satisfactory explanation for one aspect has recently been suggested by Rice\textsuperscript{15}, many problems still remain to be solved.

The chemical properties of hydrogen peroxide suggested two possible structures for the molecule, viz: (a) the di-hydroxyl formula $\ce{H-O-O-H}$: 

(b) $\ce{H< O=> O}$. A third structure, a co-ordination formula $\left[\ce{H(O2)}\right]^+ \ce{H}$, has not received much recognition, (a) and (b) being the two generally regarded as probable/
probable structures. No definite choice could be made on the basis of chemical evidence alone, it being possible to explain some reactions by one formula and others by the second. It was later suggested that a resonance equilibrium existed between the two structures.

In 1934, Penney and Sutherland, on the basis of quantum mechanical calculations, suggested that the di-hydroxy formula in which the angles $\Theta$ (between the hydrogen atoms and the $O-O$ bond) and $\phi$ (the azimuthal angle) were both about $100^\circ$, was the most probable, this structure being about 10,000 calories more stable than the other possible di-hydroxy structures illustrated in figure I.

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{O} - \text{O} & \quad \text{H} \\
\text{H} & \quad \text{O} - \text{O}
\end{align*}
\]

Straight form. Cis-form. Trans-form.

**Figure I.**

The dipole moment calculated for this structure agreed with that observed by Linton and Maass, and this configuration also accounted for the Raman lines observed by Venkateswaram, and Simon and Feher, which could not be explained on the basis of the $H_2O:O$ formula.
An X-ray investigation into the structure of liquid hydrogen peroxide was carried out in 1937 by Randall$^{20}$ who showed that his results were in accordance with the structure assigned by Penney and Sutherland. Further work by Lu, Hughes and Giguere$^{21}$, Giguere and Schomaker$^{22}$, Zumwalt and Giguere$^{23}$, also served to confirm the structure suggested by Penney and Sutherland, as shown in Figure II.

![Figure II](image)

**Figure II.**

A further suggestion of tautomerism between the two structures (a) and (b) given above was put forward on the basis that it was difficult to explain the formation of hydrogen peroxide in the burning of hydrogen and oxygen by the 'di-hydroxyl' formula. Also Geib and Harteck$^{24}$ showed that the action of hydrogen/
hydrogen atoms on molecular oxygen at the temperature of liquid air produced an allotropic form of hydrogen peroxide. This was stable only below $-115^\circ\text{C}$, at which temperature it changed, with decomposition, into the form stable at ordinary temperatures. To the allotrope stable at low temperatures they assigned the formula $\frac{H}{H^\text{O}_2}$ (i.e. formula (b) above). They state that this seems likely in so far as an addition of two $H$ atoms to $O_2$ with preservation of the double bond constitutes only a mild chemical attack. This view is supported by Penney and Sutherland$^{16}$ who find by calculation that this configuration represents a very unstable form.

With regard to the question of resonance occurring between two or more of the possible structures, little can be said except that Feher$^{25}$ in an analysis of his Raman spectra postulates a resonance degradation. The infra-red spectrum, however, gives a type of band which is characteristic of a spindle shaped symmetrical top molecule which is fairly rigid and in which the complete rotation of the $OH$ groups about the $O-O$ bond must be strongly hindered. A very different band structure would appear if there were a free or weakly hindered rotation$^{23}$.
Preparation of Hydrogen Peroxide.

Various methods for the preparation of dilute solutions of hydrogen peroxide are summarised in the following list.

1. Deville\textsuperscript{26} found that hydrogen peroxide could be obtained by passing moist oxygen through a tube heated to 2,000\degree C and rapidly chilling the issuing gases.

2. Exposure of water to ultra-violet radiations leads to the formation of some hydrogen peroxide\textsuperscript{27}.

3. The formation of hydrogen peroxide is also observed when electric sparks are passed through liquid water\textsuperscript{29} or a mixture of steam and oxygen\textsuperscript{30}. It is also formed when a mixture of hydrogen and oxygen is exposed to a brush discharge\textsuperscript{31}.

4. If the flame of burning hydrogen is allowed to play on the surface of water cooled by ice, hydrogen peroxide can be detected in the water\textsuperscript{32}. It is also one of the products in the hydrogen-oxygen reaction and any mechanism for this reaction must take its formation into account\textsuperscript{33}.

5. Hydrogen peroxide is formed in small quantities when dyed cotton fabrics are exposed to sunlight and moisture. It was found that the presence of cobalt, iron/
iron and copper eliminated the formation of the peroxide. In the mechanism of the fading reaction it is suggested that H₂O₂ may be formed by the dismutation of HO₂ radicals.

6. Hydrogen peroxide is also formed by exposing moistened zinc oxide to light and air.

7. The most usual laboratory method of preparing hydrogen peroxide is by the action of dilute acids on sodium or barium peroxide.

8. Hydrogen peroxide is prepared on a commercial scale by one of four methods. The first is the chemical method, the treatment of peroxides with acids as described above. The other three are electrolytic processes. In the first of these processes a concentrated aqueous solution of sulphuric acid is electrolysed between platinum electrodes. High currents are used and the solution and electrodes are kept below 30°C to avoid decomposition of the product in the cell. The reactions at the anode and cathode are:

\[2H^+ + 2e^- \rightarrow H_2\]

\[2HSO_4^- - 2e^- \rightarrow H_2S_2O_8\]

The electrolyte in the anode compartment is continuously drawn off and the persulphuric acid it contains converted to hydrogen peroxide by warming in a still.
\[
\text{H}_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{O} = \text{H}_2\text{O}_2 + 2\text{H}_2\text{SO}_4
\]

The vapours of \(\text{H}_2\text{O}\) and \(\text{H}_2\text{O}_2\) are condensed to give a dilute solution of hydrogen peroxide while the sulphuric acid is returned to the electrolyte cell.

In the other two electrolytic processes, ammonium bisulphate is used as the electrolyte; in one case the ammonium persulphate formed is steam-distilled directly to regenerate ammonium bisulphate and produce hydrogen peroxide, while in the other it is first converted to potassium persulphate. The hydrogen peroxide vapour is recovered in the desired concentration by fractional condensation70.

In recent years the preparation of concentrated hydrogen peroxide has been greatly developed and there are now several laboratory and commercial methods of preparing highly concentrated solutions. Walton and Filson36 have described one method by which hydrogen peroxide of over 90% concentration can be prepared in one operation. If hydrazo-benzene dissolved in benzene is treated in a bomb with oxygen at 0°C and 370 pounds per square inch pressure, drops of peroxide separate from the liquid. Walton and Filson found that these drops contained 94% hydrogen peroxide and the/
the yield was 97% of the theoretical, calculated from the equation:

\[ C_6H_5\cdot NH\cdot NH\cdot C_6H_5 + O_2 = C_6H_5\cdot N\cdot N\cdot C_6H_5 + H_2O_2 \]

Hydrogen peroxide is soluble in several organic solvents in which water is insoluble. This fact may frequently be used for the rapid concentration of dilute solutions\textsuperscript{37}. If concentration is carried out in this way, however, it is possible that the resulting peroxide may contain impurities.

In 1920 Maass and Hatcher\textsuperscript{3} concentrated a 3% solution of hydrogen peroxide, prepared from barium peroxide and dilute sulphuric acid, by distillation in vacuo, using a specially designed sulphuric acid evacuating pump which, in addition to evacuating the system, also concentrated the solution of peroxide, the sulphuric acid acting as a desiccating agent. In this way a solution of 90% concentration could be obtained, further concentration to 100% being effected by fractional distillation.

Kilpatrick, Reiff and Rice\textsuperscript{3} evolved a rather less laborious method which gave higher yields but not quite such high concentrations. They distilled the crude solution, obtained from sodium peroxide, in vacuo, the distillate being collected in two receivers, the second of which was cooled to a lower temperature than the/
the first. The more concentrated peroxide solution collects in the first receiver, the solution in the second receiver being very weak. After distillation over silver sulphate to remove small traces of chlorides, the stronger solution was further concentrated by standing in a vacuum desiccator over concentrated sulphuric acid. In this way 88% hydrogen peroxide was obtained with little loss due to decomposition.

In 1939 Feher developed a cyclic process for the preparation of 100% deuterium peroxide, his method being an adaptation of the commercial process patented by Pietsch and Adolph. It consists of blowing D₂O vapour through a mixture of D₂SO₄ and K₂S₂O₈ maintained at 70°-90°C. The resulting mixture of D₂O - D₂O₂ is fractionally condensed, the weak solution being automatically returned to the starting point to pass through the cycle again. This cycle is repeated until the required amount of 100% deuterium peroxide is obtained. This method might be very useful for the preparation of 100% hydrogen peroxide, the apparatus being possible of simplification as the amount of water which can be used is unlimited while only small amounts of heavy water were available.
The apparent instability of hydrogen peroxide solutions has led to the use of many materials as stabilisers. These materials, except for acids, have probably no influence on the peroxide itself but serve to remove or inactivate catalysts: in this group are included the pyrophosphates, fluorides, cyanides and various organic compounds such as 8-hydroxy quinoline and acetaldehyde. Another group of stabilisers possibly owe their action to adsorptive powers: such substances as freshly precipitated alumina and silica, hydrous antimony oxide and hydrous stannic oxide are effective to varying degrees in increasing the stability of peroxide solutions. The best guarantee of high storage stability for concentrated solutions of hydrogen peroxide is extreme purity. Concentrated peroxide has obtained a reputation of being somewhat dangerous due to its instability, but with reasonable care in handling, very pure peroxide shows no explosive tendency. The presence of small traces of impurities or catalysts however may lead to rapid decomposition with a rise in temperature and resulting increase in pressure. The presence of combustible liquids such as methyl alcohol also increases the explosive/
explosive tendency of concentrated solutions.\textsuperscript{75} 

Hart\textsuperscript{76} investigated the rapid decomposition of the vapour over concentrated solutions and concluded that explosions originate in the vapour and not in the liquid phase.

Containers for very concentrated hydrogen peroxide are best made from high purity (99.6\%) aluminium\textsuperscript{40}, although containers of chemically resistant glass are also suitable. In some instances, polyvinyl chloride vessels have been used to hold hydrogen peroxide.

The decomposition of hydrogen peroxide is an exothermic reaction, 23 k.cals. per mole being liberated.\textsuperscript{41}

\[ H_2O_2(l) \rightarrow H_2O(l) + \frac{1}{2}O_2(g) + 23,450 \text{ cals.} \]

Under adiabatic conditions the calculated temperature and volume at atmospheric pressure is 750°C and 5,000 litres. The system has obvious possibilities as a power source, and is used as a rocket fuel.\textsuperscript{42} Furthermore the oxygen from the decomposition can be utilised for the combustion of fuel, thereby greatly increasing the total power yield per gram of fuel mixture.

Concentrated hydrogen peroxide has found wide application in organic chemistry\textsuperscript{39}, particularly as an oxidising agent.
Decomposition of Hydrogen Peroxide in Aqueous Solution.

While comparatively little work has been done on the decomposition of hydrogen peroxide vapour, the decomposition in aqueous solution under the influence of heat, light and catalysts has been widely investigated. A brief summary of the main work and important conclusions is given below for the purpose of comparison with the vapour phase experiments.

Photochemical Decomposition.

An excellent survey of the work done on the photo-decomposition of aqueous solutions of hydrogen peroxide is given by Kistiakowsky. Much doubt has been cast on the earlier results, however, by Rice's investigation into the effect of dust particles on the decomposition. Rice found that the rate of decomposition in a "dust-free" solution (prepared by distillation in vacuo without ebullition) in the light of a mercury vapour lamp was very much less than that in a solution prepared in the normal way. He suggested that the ratio of the rates in the two solutions should be 1:100, in which case the quantum yield in a "dust-free" solution would be unity. A chain mechanism would thus be unnecessary to explain the decomposition kinetics, the higher quantum yields observed by other workers (e.g. Kornfeld found a quantum/
quantum yield of 80 for a 2% solution while Almand and Style observed later that the quantum yield varied between 500 and 20 with increase in the intensity of the light) being due to the decomposition of hydrogen peroxide at the dust particles. Heidt verified the fact that with "dust-free" solutions and high light intensities the quantum yield approaches unity. Indeed, Rice and Kilpatrick claim to have found that the rate of photo-decomposition is proportional to the dust content of the solution. Kornfeld maintains that the influence of dust particles is only important in concentrated solutions and is negligible in dilute solutions. This view was refuted by an experiment carried out by Rice in which two quartz flasks containing 2% solutions, one of which was dust-free, were placed near a mercury vapour lamp. The ordinary solution appeared to boil while the effect of the light on the other solution was unnoticeable. There seems little doubt, therefore, that dust particles play an important part in the decomposition.

Urey, Dawsey and Rice investigated the absorption spectrum of hydrogen peroxide and its vapour. The energy of the longest wavelengths absorbed is sufficient to cause any of the following reactions:

\[
\begin{align*}
H_2O_2 + h\nu &= 20H \\
H_2O_2 + h\nu &= HO_2 + H \\
H_2O_2 + h\nu &= H_2O + O
\end{align*}
\]
They favoured the first of these three reactions and as the water bands (due to OH) appeared in fluorescence when the zinc spark lines from 2025 - 2138 Å were used for illumination, they concluded that the reaction occurring under these conditions was:

$$\text{H}_2\text{O}_2 + h\nu = \text{OH}^{(2P)} + \text{OH}^{(2S)}$$

For illumination with light of wavelengths between 2200 - 3000 Å they considered the most likely mechanism to be:

$$\text{H}_2\text{O}_2 + h\nu = \text{OH}^{(2P_1)} + \text{OH}^{(2P_{3/2})}$$

This is analogous to the primary processes occurring when halogens absorb light in the continuous region of their spectra.

The decomposition of the peroxide into two OH groups is the one which appears most probable from the structure of the molecule but although Blaedel, Ogg and Leighton tried to obtain direct spectroscopic evidence of the presence of OH as an intermediary in several photochemical reactions, including the photo-decomposition of hydrogen peroxide, no free hydroxyl was detected. They concluded that if it were present it must be at a concentration of less than $5 \times 10^{-5}$ mms.

On the other hand, the chemiluminescence of luminol (3-aminophthalic cyclic hydrazide) in the presence of hydrogen peroxide is supposed to be due to OH radicals arising from decomposition of the peroxide.
Catalytic Decomposition.

The catalytic decomposition of aqueous solutions of hydrogen peroxide has been widely investigated and it is impossible to give more than a brief account of the results obtained. Catalysis by the various substances falls into two groups - heterogeneous and homogeneous. In heterogeneous catalysis the hydrogen peroxide decomposes at the surface of the catalyst. This will be considered in the section on thermal decomposition.

Homogeneous catalysis of the decomposition is caused by a large number of substances dissolved in aqueous solutions of hydrogen peroxide. The cations of iron, copper and vanadium, and the hydroxyl ion are the most active in promoting decomposition, the activity of these catalysts being measurable at concentrations of a few parts per million. Certain cations such as those of the alkali metals appear to have little or no effect on the stability of peroxide solutions. It is also significant that cations of variable valency usually have some activity.

Pana\textsuperscript{50} showed that alkalis, such as NaOH, have an effect on the decomposition of hydrogen peroxide which cannot be accounted for on the assumption that the alkali contains small amounts of iron salts. The effect/
effect of alkalis and acids has also been studied by Wright and Rideal\textsuperscript{51}, who found that the greatest rate of decomposition occurred in solutions of pH corresponding to the iso-electric point for the surface, when, as hydrogen peroxide is practically a non-electrolyte, the adsorption will be greatest.

Jeu and Alyea\textsuperscript{52} carried out a series of experiments on the effect of dissolved negative catalysts on the photo-decomposition of solutions. In interpreting their results they employed the following equation derived from the unimolecular law:

$$\frac{dx}{dt} = \frac{K(1 - x)}{K_2 + kC}$$

where $dx$ is the fraction reacting in the time interval $dt$; $x$ is the fraction decomposed in the time $t$; $C$ is the concentration of the inhibitor; $K$, $K_2$, $k$ are constants.

**Thermal Decomposition.**

Two extensive papers on the thermal decomposition of peroxide solutions were published in 1914 by Lemoine\textsuperscript{53} and in 1915 by Clayton\textsuperscript{54}. Both these authors used peroxide solutions containing inhibitors. In the interpretation of their results they both employ the unimolecular rate equation, although the unimolecular constant obtained by Lemoine is rather variable. Lemoine also showed that unfiltered air passed/
passed through the solution accelerated the decomposition, while with filtered air the increase was very much less – demonstrating the importance of dust particles as suggested by Rice. He observed that strong solutions were more stable than weak and deduced from this fact that water acted as a catalyst for the decomposition. It has been shown, however, that water, at least in the vapour phase, can act as an inhibitor and the suggestion was made that this increase in stability with concentration is due to the destruction of active centres by the concentrated hydrogen peroxide.

The results of Clayton indicate that the purity of the water employed in the solution has a great effect on the rate of decomposition. This was further confirmed by Rice with his work on the effect of dust particles. He showed that the thermal decomposition is almost entirely suppressed if the reaction is carried out in dust free solution and in a vessel with a freshly fused surface. If the glass surface is roughened e.g. by hot cleaning solutions, it becomes very active catalytically. In 1927, Rice and Reif showed that with dust free solutions a zero order reaction is obtained, but with ordinary tap water the reaction becomes first order. Both these effects/
effects have been confirmed by Williams\textsuperscript{57} who suggests, in addition, that a silica vessel has a number of preformed "active points" at which decomposition occurs, while on a glass surface the hydrogen peroxide itself creates centres of activity.

A series of experiments on the heterogeneous decomposition of hydrogen peroxide in heavy water has been described by Giguere and Maass\textsuperscript{58} who found the reaction to be first order. From their results they also suggest that deuterium peroxide is more stable than hydrogen peroxide towards catalysts.

The results obtained from investigations on the decomposition of aqueous solutions of hydrogen peroxide may be briefly summarised as follows:

1. The rate of decomposition depends to a large extent on dust particles and colloidal matter present in the solution.
2. It also depends on the state of the surfaces in contact with the solution.
3. In the absence of dust particles and at a freshly fused surface decomposition practically ceases.
4. In dust free solutions the reaction is zero-order.
5. In normal "dusty" solutions the reaction tends to become first order.
6. A silica surface appears to have a number of preformed/
preformed active points for decomposition while the peroxide creates its own active points on a glass surface.

7. The greatest amount of decomposition occurs in solutions at a pH coincident with that required to bring the surface of the containing vessel to its isoelectric point.

Thermal Decomposition of Hydrogen Peroxide Vapour.

Although several papers have recently been published on the thermal decomposition of hydrogen peroxide vapour there is a lack of agreement as to the kinetics and mechanism of the reaction.

The first investigation was made by Hinshelwood and Pritchard in 1923. They used samples of 30% solution of hydrogen peroxide (Merck's perhydrol) which were sealed in glass bulbs of about 200 ml capacity, the quantity of peroxide being chosen to give a pressure in the bulbs of less than saturation pressure. The bulbs were heated in a carbon tetrachloride vapour bath to 76°C, the hydrogen peroxide vaporising almost instantaneously on immersion in the bath. After a suitable time interval, the bulb was removed from the bath, opened under water and the quantity of hydrogen peroxide/
peroxide remaining determined by titration with N/50 potassium permanganate. Using the same bulb in successive experiments they obtained results showing the decomposition to be approximately unimolecular. When the decomposition was carried out in a bulb containing glass wool, previously treated with nitric acid to remove free alkali, the rate was very much accelerated indicating that the reaction must be heterogeneous, the decomposition taking place at the glass surface.

In 1927, Elder and Hideal\textsuperscript{60} published an account of their work on the decomposition of the vapour. They obtained their samples of hydrogen peroxide from two sources. One sample was distilled from a mixture of urea - hydrogen peroxide crystals ("Hyperol") and phosphoric acid, yielding a solution of 60% hydrogen peroxide. The second sample they prepared by the method developed by Kilpatrick, Reiff and Rice\textsuperscript{3}, this also being of 60% concentration. As a preliminary step they showed, by comparison of the vapour pressure of the original mixture before decomposition with that of the resulting water vapour, that the hydrogen peroxide vapour consisted of simple unhydrated peroxide molecules. Their method was an improvement on that of Hinshelwood and Pritchard as it enabled measurement/
measurement of the amount of the same sample decomposed at different times, and thus cut out errors due to variation in the samples and the surface of the vessel in successive runs. A small amount of the hydrogen peroxide solution was introduced into the reaction vessel and the apparatus then evacuated at room temperature with a Hyvac oil pump. A thermostat, maintained at 85°C, was then placed round the bulb and the reaction followed by measuring the increase in pressure in the vessel due to the decomposition of the hydrogen peroxide. The pressure was measured on an oil manometer. With a glass reaction vessel, Elder and Rideal found that their results were not reproducible, irrespective of the pre-treatment of the glass but some indication was obtained that the reaction in its early stages was zero-order passing into some form of first order or inhibited zero order reaction in the final stages. On a quartz surface, more or less reproducible results were obtained when the vessel was cleaned with chromic acid, heated almost to boiling, rinsed thoroughly with conductivity water and baked out with a bunsen flame. Elder and Rideal found that the reaction came to an abrupt end when only a small fraction of the hydrogen peroxide had decomposed, and to get an infinity reading (corresponding to complete decomposition)/
decomposition) the vessel had to be heated to 300 - 400°C in a Bunsen flame. From their results they conclude that the reaction on a quartz surface is of zero order, inhibited by one of the products which they suggest is oxygen adsorbed in the molecular state on the surface.

The decomposition at a platinum and a mercury surface was also examined. The platinum was introduced into the reaction vessel in the form of a wire, the decomposition then being first order, but with duplicate runs giving widely varying results for the rate constant. They also state that oxygen adsorbed at the surface does not enter into the kinetics of this reaction.

With mercury, they showed that reaction consisted of a preliminary direct oxidation of Hg to Hg₂O followed by a coupled oxidation of Hg₂O to HgO in which an amount of oxygen is liberated proportional to the amount of HgO formed. The HgO was not reduced by the hydrogen peroxide vapour.

In 1937, Kistiakowsky and Rosenberg published a note on an investigation of the decomposition of hydrogen peroxide vapour, without however giving any experimental details. They found the decomposition in a quartz vessel to be heterogeneous with a negligible/
negligible temperature coefficient. No stopping of the reaction after 15% decomposition as reported by Elder and Rideal, was observed. Flushing out the reaction vessel with oxygen prior to the reaction had no effect on the rate of decomposition. They conclude from this that oxygen has no effect on the reaction. A thin coating of paraffin wax applied to the interior of the quartz reaction bulb slowed down the decomposition somewhat.

Hydrogen peroxide is formed as an intermediary in the hydrogen-oxygen reaction, and an extensive study of this reaction by von Elbe and Lewis led to the following suggestion for the mechanism of the decomposition of hydrogen peroxide. The complete scheme consists of twelve steps, only the first four of which need be considered here.

\[ \text{H}_2\text{O}_2 + \text{M} \rightarrow 2\text{OH} + \text{M} \]
\[ \text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H} \]
\[ \text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O} \]
\[ \text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H} \]

In equation 1, M could be any molecule present in the gas phase or it could represent the wall of the vessel. The primary step is considered to be the decomposition into two hydroxyl groups, although the same net results would be obtained if it were assumed that/
that the first step was the decomposition of $\text{H}_2\text{O}_2$ to give $\text{H}_2\text{O}$ and $\text{O}$, although this appears improbable from the constitution of the $\text{H}_2\text{O}_2$ molecule.

Baker and Ouillet investigated the kinetics of the decomposition of the vapour from very pure 99.5% hydrogen peroxide at pressures of $10 - 20$ mms. of mercury and temperatures between $70 - 200^\circ\text{C}$. No explosive tendency was observed at a pressure of $180$ mms. of mercury up to a temperature of $335^\circ\text{C}$. The course of the decomposition was followed by measuring the increase in pressure in the reaction vessel with an oil manometer. Several pyrex reaction vessels of various sizes, some containing pyrex tubes, were employed. From the results obtained, Baker and Ouillet suggest that the reaction rate varies considerably with the size and shape of the vessel, the geometry of the vessel as well as the extent of the surface being important. The reaction in all cases went to completion and was found to be of first order up to a temperature of $140^\circ\text{C}$, above which it became more complex. They consider it unlikely that the decomposition proceeds by a chain reaction, because inert gases had no effect on the rate, the temperature coefficient between $120 - 150^\circ\text{C}$ was negligible, and considerable increase in temperature and pressure did not/
not lead to an explosion.

Mackenzie and Ritchie\textsuperscript{55} investigated the decomposition at pressures of less than 1 mm. of mercury, in a silica vessel, over the temperature range 15 - 140°C. The reaction was examined by measuring the increase in pressure in the reaction vessel using a sensitive all-glass Bourdon gauge system. They found that the equation governing the rate of the surface reaction was:

\[
-\frac{d[H_2O_2]}{dt} = \frac{k[H_2O_2]^2}{(1 + b[H_2O])^2}
\]

This equation was also derived from equilibrium considerations of adsorption at the surface of the vessel. Oxygen and nitrogen at low pressures (less than 10 mm) was found to have no inhibiting effect but at higher pressures these gases retard the decomposition to approximately the same extent, as would be expected from diffusion or adsorption theory. Water inhibited the reaction, as is shown in the equation above. In the presence of 10 mm. of mercury pressure of water vapour, periodic variations in the decomposition occurred. The apparent heat of activation over the range 60 - 140°C was approximately 7,500 calories per mole, but was much smaller - about 3,800 calories - over the range 15 - 60°C. The increase/
increase in the heat of activation at higher temperatures was attributed to the appearance of a homogeneous gas reaction.

It has been shown that, under favourable conditions, the slow oxidation of hydrocarbons can yield peroxides which have the properties of compounds of aldehydes with hydrogen peroxide. Harris found that these alkyl-hydrogen peroxides decompose heterogeneously. In order to compare the behaviour of these compounds with that of hydrogen peroxide under the same conditions, he carried out an investigation of the decomposition of hydrogen peroxide vapour, using a flow system similar to that used in hydrocarbon oxidation studies. The peroxide vapour was carried through the reaction vessel by a steady stream of nitrogen, the undecomposed peroxide being frozen out in a solid carbon dioxide trap at \(-60^\circ C\) and estimated by titration with potassium permanganate.

His results showed that hydrogen peroxide could exist at temperatures up to \(525^\circ C\), having a half-life of about 0.5 seconds at that temperature in the vessel used. The heterogeneity of the reaction was again illustrated by the increase in decomposition on packing the reaction vessel with tubing. Coating the vessel with potassium chloride led to a slight increase in/
in the rate of decomposition. On the other hand, a trace of mercury placed at the inlet of the reaction vessel led to the complete decomposition of all the hydrogen peroxide, some HgO being deposited in the vessel.

For his work on the vapour decomposition McLane used vessels coated with boric acid, which he found gave him very reproducible surfaces. A flow system was again employed, the concentration of hydrogen peroxide in the vessel being estimated photometrically by determining the optical density at the wavelength 2536Å. Decomposition of the vapour at temperatures from 470 - 540°C was found to be first order, with a heat of activation of 40 k.cals. per mole. The relation between the rate and surface area indicated that the reaction was not occurring exclusively at the surface. A higher heat of activation (50 k.cals. per mole) in a vessel of lower surface-volume ratio indicates that a greater proportion of a gas reaction must be occurring. A transition from the reaction of low activation energy occurring exclusively at the surface (as found by other investigators), to a gas reaction of high activation energy at higher temperatures must take place. McLane found that the energy of activation in the vessels of larger surface-volume ratio/
ratio was the same when either oxygen or nitrogen was used for the carrier gas, although the actual rates are somewhat faster with nitrogen. This energy of activation (40 k.cals. per mole) is too small by 13 k.cals. per mole for the reaction:

$$\text{H}_2\text{O}_2 + \text{M} = 2\text{OH} + \text{M} - 53 \text{ k.cals.}$$

If this is the important step in the decomposition, it must be assumed that there is a surface reaction of considerably lower activation energy occurring simultaneously to give an activation energy equal to the observed value. The experimental activation energy is larger than the heat of reaction of:

$$\text{H}_2\text{O}_2 + \text{M} = \text{H}_2\text{O} + \text{O} + \text{M} - 35 \text{ k.cals.}$$

This mechanism, however, would require considerable distortion of the peroxide molecule in order to reach an activated state which might decompose to the indicated products.

Giguere published results of work over the temperature range 50 - 420 °C, at pressures of 5 - 6 mms of mercury, using an all-glass Bourdon gauge to measure increases in pressure as the decomposition proceeds. The reaction in all but a few cases was found to obey the first order law on pyrex, soft glass, quartz and metallic surfaces, although the rate constants and energies of activation were very variable.
On the quartz surface, an induction period was observed during which the decomposition was very slow. The length of this induction period decreased with increasing temperature and practically disappeared at 175°C. An apparent activation energy of 12 k.cals. per mole was obtained on the quartz surface. Over the range 260 - 420°C, Giguere found the temperature coefficient in one particular pyrex vessel to be negligible, and concludes that the homogeneous decomposition of hydrogen peroxide vapour is still immeasurably slow at 420°C. Although the rates of decomposition on different surfaces do vary somewhat, there is no very specific action in the catalytic decomposition. Rates of the same order of magnitude were found on such widely different surfaces as glass, metals and paraffin oil, from which Giguere concludes that the adsorption is of a physical, rather than a chemical, nature. The polar character of the hydroxyl group leads to adsorption at the surface, thus orientating the peroxide molecule and straining the O-O bond so that only a low thermal activation is required for dissociation. All surfaces should, therefore, decompose hydrogen peroxide vapour at an appreciable rate.
Volman examined the photo-decomposition of hydrogen peroxide vapour in a quartz vessel, over the temperature range 25 - 50°C, the absorbed light having a wavelength of 2537 Å. An analysis of the products of the decomposition showed that no hydrogen was formed in the reaction, water and oxygen being the only products. Oxygen, nitrogen and water vapour had no effect on the rate of decomposition when added to the reaction system. The temperature coefficient over the range studied was negligible, this fact being used as additional evidence that the rate of decomposition depended only on the rate of radiation absorption.

A plot of log \( \frac{C_0}{C_t} \) against time gave a straight line for the greater part of the reaction, but Volman points out that this does not necessarily mean that the reaction is truly unimolecular, indicating rather a linear relationship between peroxide concentration and light absorption at the low pressures employed. The quantum yield of 1.7 was independent of peroxide concentrations and of \( I_{abs.} \), and is in reasonable agreement with the theoretical value of 2 obtained by stationary state consideration of the following suggested mechanism:

\[
\begin{align*}
H_2O_2 + h\nu &= 2OH \\
OH + H_2O_2 &= HO_2 + H_2O \\
HO_2 + HO_2 &= H_2O_2 + O_2
\end{align*}
\]
With initial pressures of hydrogen peroxide of 1.23 mmHg, the time for half-change was 4 - 5 minutes. It was found impossible to examine the decomposition at temperatures above 50°C as the thermal decomposition was too great as compared with the photo-reaction.

Although it is impossible to draw up any complete mechanism from the work done on the decomposition of hydrogen peroxide vapour, certain conclusions can be reached.

1. The decomposition is essentially heterogeneous, the state and pretreatment of the surface having a great effect on the rate of decomposition.

2. The primary step in the decomposition appears to be the splitting of the molecule into two OH radicals.

3. The reaction is not propagated by long chains.

4. The activation energy appears to be widely variable and very dependent on the state of the surface. Values from 0 - 30 kcal. per mole have been found up to temperatures of about 200°C.
I. PREPARATION OF HYDROGEN PEROXIDE.

EXPERIMENTAL.

Of the several methods available for the preparation of concentrated hydrogen peroxide solutions, an adaptation of the method developed by Kilpatrick, Heiff and Rice was employed, since conditions comparable with Mackenzie & Ritchie's experiments were desired and this method also seemed to be free from other objections.

(a) Estimation of $\text{H}_2\text{O}_2$ in solutions.

The concentration of the dilute solutions of the hydrogen peroxide was estimated by direct titration with decinormal potassium permanganate while for concentrated solutions a special procedure was adopted. A weighing bottle, half-filled with distilled water, was accurately weighed, 0.05 - 0.1 gms. of peroxide solution was added from a pipette, the lid replaced and the bottle again weighed. The contents of the bottle were then transferred to a 300 ml. conical flask containing about 100 mls. distilled water and 30 mls. dilute sulphuric acid, and the weighing bottle carefully washed with distilled water. The resulting solution was made up to approximately 200 mls. and titrated/
titrated with decinormal potassium permanganate solution. From the results the percentage of hydrogen peroxide by weight in the original solution could be calculated.

The potassium permanganate solution was standardised by the following method which, it is claimed, gives a very accurate result.

About 0.3 gms. of sodium oxalate, dried at 105°C for 15 minutes, was weighed accurately into a 600 ml. beaker. 250 mls. of a solution of sulphuric acid prepared by adding 15 mls. of concentrated H₂SO₄ to 285 mls. distilled water, boiling for 10 minutes and cooled to 27±3°C, were added. After the oxalate had dissolved, 40 mls. of the K₂MnO₄ solution were added with gentle stirring, at the rate of 30 mls. per minute. When the pink colour had disappeared the solution was heated to 55 - 60°C and the K₂MnO₄ solution added very slowly until a faint pink colour persisted for half a minute. A "blank" titration, omitting the sodium oxalate, was carried out under the same conditions and a suitable correction made.

(b) Preparation of dilute solution of H₂O₂.

The dilute hydrogen peroxide solution (5%) was prepared from A.R. sodium peroxide and a solution of 20% sulphuric/
20% sulphuric acid, made by diluting A.R. concentrated sulphuric acid with distilled water. Sodium peroxide, equivalent to 95% of the acid, was added in small quantities to 100 mls. of 20% acid, cooled in a freezing mixture, the acid being vigorously stirred. The temperature of the solution was kept as low as possible and was not allowed to exceed 10°C, so as to minimise decomposition. Crystals of sodium sulphate appeared when the addition of sodium peroxide was nearly complete. The mixture was allowed to stand for one hour at 0 - 5°C and was then filtered at the water pump. As the sulphate crystals contained a large amount of hydrogen peroxide, they were thoroughly washed with 200 mls. of ice-cold distilled water. In this way 280 mls. of a 4 - 5% solution of hydrogen peroxide were obtained.

(c) Concentration and purification of H₂O₂ solution.

Removal of the sodium sulphate and partial concentration of the solution was achieved by one distillation in vacuo. As hydrogen peroxide attacks rubber, the distillation apparatus was constructed entirely from soda-glass. This apparatus is shown in figure 3.

The dropping funnel F was sealed into the neck of the distilling flask A, which had a volume of 250 mls./
250 mls. The side arm of the flask was joined directly to the top of a vertical water condenser. In the first experiments the side arm was connected by means of a ground glass joint at K, but as it was found difficult to prevent the joint from becoming hot during a distillation (resulting in grease being sucked into the apparatus) the joint was removed and a direct glass seal made. The receivers B and C were connected to the apparatus by standard A19 interchangeable ground glass joints, and were duplicated to avoid any delay in changeover of receivers during the distillation. For the greater part of this distillation the apparatus was evacuated by means of a water pump to a vacuum of 10 - 12 mms., only in the final stages was the Hyvac oil-pump/
oil-pump used. H was a three-way tap, one arm of which was open to the atmosphere, so that, in changing the receivers, the vacuum in the distillation portion of the apparatus could be broken without disturbing that in the rest of the apparatus. E, a concentrated sulphuric acid trap, was cooled in ice water during evacuation with the oil-pump. This prevented $H_2O_2$ reaching the oil and mechanism of the pump and also acted as a desiccator for the peroxide. Taps and joints, when used, were lubricated with Apiezon L grease, Mackenzie’s work having shown this to be free from objection.

As the volume of solution to be distilled in the second distillation was small (about 60 mls.) the large flask was replaced by the specially constructed tube shown in figure 4. This was sealed directly to the condenser at point K.

![Figure 4](image-url)
The final concentration of the peroxide was carried out in the apparatus shown in figure 5.

![Figure 5](image.png)

Figure 5.

The distilling tube B was fitted at the top with a ground glass joint A of the same size as at the top of receiver B in figure 3. The final distillate was collected in receiver C. This piece of apparatus was connected to the oil-pump line of the decomposition apparatus (see figure 6). In this distillation the apparatus was evacuated by the Hyvac oil-pump through a sulphuric acid trap. The taps and joints were lubricated with Apiezon L grease, with the exception of the joint A. This was left clean, as the grease tended to suck into the apparatus during distillation. The non-greasing of A did not affect the vacuum appreciably or slow down the distillation. The distillation was carried out in presence of concentrated sulphuric acid contained in D. This acted as a/
a desiccator for the distilling vapour.

(d) Experimental procedure.

The distilling flask, condensers and receivers were first cleaned with chromic acid, thoroughly washed with distilled water and dried by evacuation. About 100 mls. of the "crude" peroxide solution was introduced into A, through F, and the apparatus evacuated with the water pump. The receiver B was cooled in a mixture of ice and water and cold water circulated through the condenser. Flask A was heated gradually in a water bath to about 25°C, the first signs of distillation appearing at this temperature. The temperature was increased very slowly to 35°C, the bulk of the solution being distilled at this point.

Whenever the volume of solution in A fell to about 50 mls., the vacuum in the flask was broken and a fresh sample of solution added to bring it back to 100 mls. The receiver B had, at first, a volume of 100 mls. but for the final two fractions of the distillation was replaced by a tube of 15 mls. capacity. The bulk of liquid distilling first, was water, and after a preliminary distillation during which analysis of the distillate was made at intervals to confirm this, the first 200 - 220 mls. were discarded. When all the "crude" solution had been added/
added, the temperature was again slowly increased until all but 20 - 30 mls. of solution had distilled over. At this point receiver B was replaced by a tube of smaller volume as mentioned above, receiver C was immersed in a freezing mixture of ice and salt in order to utilise the double distillation effect described by Kilpatrick, Reiff and Rice\(^3\) and the concentrated sulphuric acid trap was cooled in ice and water. The apparatus was now evacuated by the oil-pump. As the volume of solution remaining in A became small some crystals separated and the temperature of the water bath was gradually increased to maintain a reasonable rate of distillation. When the crystals in the flask appeared dry, the receiver at B was replaced by a duplicate tube, and the final fraction driven over by raising the temperature to 100\(^\circ\)C. The final fraction was the most concentrated in H\(_2\)O\(_2\) (about 70\%). The two final fractions of this first distillation were mixed for the next stage, yielding about 15 mls. of 30\% solution. The final fractions from two primary distillations, in all about 30 mls. 30\% H\(_2\)O\(_2\) solution, were used for the next stage. The volume of distillate collecting in receiver C, while much less than that in B, was still appreciable and contained very little H\(_2\)O\(_2\). The double distillation/
distillation effect has thus been useful in further concentrating the solution in receiver B.

It has been reported that hydrogen peroxide prepared in this way may contain slight traces of chloride\(^3\), and a very slight trace was found in the present preparation. This was removed by a second distillation of the peroxide over a few crystals of silver sulphate. As the volume of solution to be distilled was small, flask A was replaced by the tube shown in figure 4 and described above. A few crystals of silver sulphate were introduced into the dry flask, the 30\% peroxide solution added and the tube sealed in place of the flask. The distillation was carried out as before, evacuation in the preliminary stages being made with the water pump. Receiver B (15 mls. capacity) was cooled in an ice-salt freezing mixture to \(-15^\circ\text{C}\), and receiver C in a solid carbon dioxide - acetone mixture to \(-80^\circ\text{C}\). The amount of distillate collecting in C was always less than in B. When necessary, the receivers were replaced by duplicate tubes. The temperature of the water bath was raised gradually to maintain a steady rate of distillation without causing the solution to bump and froth. When the tube appeared dry it was immersed in boiling water for 5 minutes in order to drive/
drive over the last traces of very concentrated hydrogen peroxide. In the latter stages of the distillation the oil-pump was used for evacuation. Again the first fractions distilling over were very dilute and were consequently discarded, only the last two fractions collecting in receiver B having an appreciable concentration of peroxide. These two fractions on mixing yielded about 10 mls. of 75% H₂O₂.

In order to concentrate the peroxide still further a final distillation was carried out in the apparatus shown in figure 5. As described above, the joint at A (figure 5) was the same size as that on receiver B (figure 3). The two final fractions from the second distillation described above were mixed in the tube containing the more concentrated solution and the tube placed in position for the final distillation. Tap T₇ to the sulphuric acid trap was opened, a carbon dioxide-acetone freezing mixture placed round C and the apparatus evacuated by the oil-pump. B was now immersed in a water bath at 60°C, the temperature being gradually increased during distillation. Four fractions of 2-3 mls. were collected. The first two fractions so obtained were quite dilute but the concentration increased/
increased considerably in the third, while the fourth fraction had a concentration of 98 - 99% $H_2O_2$. As in the previous distillation, the distilling tube was immersed in boiling water for 5 minutes at the end of the distillation in order to drive over some of the peroxide which had condensed in the leading tubes. Finally the tube from which the peroxide had been distilled was replaced by a clean dry tube, and receiver C containing the final fraction was employed as a reservoir for the hydrogen peroxide used in the ensuing experiments on the decomposition.
DISCUSSION.

Although the details of several methods for the preparation of pure hydrogen peroxide are available (e.g. Maass and Hatcher$^3$, Feher$^4$) it was decided to use that described by Mackenzie and Ritchie as it had proved very successful for the rapid preparation of small quantities of pure, highly concentrated solutions of hydrogen peroxide. It was found necessary to make some small modifications to this method as described above.

As preliminary analyses showed that only the final fractions in the distillation contained appreciable quantities of hydrogen peroxide, it was decided that the bulk of the distillate could be collected in one large receiver and discarded, only the final fractions being preserved. This avoided repeated breaking of the vacuum during distillation in order to replace receivers with consequent decomposition of the hot peroxide solution in the distilling flask. For the same reason only in the final stages of the distillation was it considered necessary to utilise the double distillation effect. The cooling of the second receiver to a lower degree than the first had a definite effect on the concentration of the hydrogen peroxide in the first receiver.
receiver, about 9 - 10 mls. very dilute solution collecting in C while the final two fractions were collected in B in the first distillation.

Considerable difficulty was experienced at first due to the solution frothing and bumping in the distilling flask when the apparatus was evacuated with the oil-pump. This was overcome by using the water pump for evacuation during the initial part of the distillation, the pressure above the solution being 10 - 12 mms. The temperature was also raised very gradually. It was found under these conditions that the vacuum in the system could be broken to allow replacement of the receivers and the system re-evacuated without cooling the solution in flask A. Further, as the water pump was used for the greater part of the distillation, no difficulty was experienced with thickening of the pump oil as reported by Maass and Hatcher.\(^3\) In the final stages when the oil-pump was used the concentrated sulphuric acid trap adsorbed any vapours escaping condensation in the two receivers. As receiver C was always cooled to at least \(-15^\circ\)C when the oil-pump was in use the amount of vapour escaping condensation was very small.

Within limits, the time of distillation did not appear/
appear to affect the yield of peroxide appreciably. It is desirable, of course, that the distillation should be carried out as expeditiously as possible to avoid undue decomposition of the hot solution in the distilling flask. It was found, however, that a greater loss of peroxide was likely if the distillation was carried out at too high a temperature initially, the tendency for the solution to bump and froth being more marked in this case. As only a small quantity of hydrogen peroxide was required for the subsequent work no attempt was made to obtain high yields in the preparation, the yield being in the region of 40%. The main loss of peroxide is due to the discarding of all but the most concentrated fractions.

It was observed, towards the end of the distillation when the solution in the receiver was fairly concentrated that definite striae were formed when drops of more concentrated peroxide came in contact with solutions of lower concentration. The same effect was observed when samples of different concentrations were mixed. This would seem to indicate an increase in viscosity with concentration, but even the most concentrated solution was a clear, mobile liquid. Maass and Hatcher have shown, in fact, that the viscosity of hydrogen peroxide is almost the same as that of water.

The/
The very concentrated solutions of peroxide appeared to be quite stable. Solutions stronger than 92% showed little decomposition when kept in the receiver in which they were collected, even when the solution was shaken. If, however, a solution was poured into a fresh receiver decomposition immediately started at the surface, bubbles of oxygen appearing. This decomposition ceased after a short time. The same phenomenon was observed with the pipette used, for withdrawing samples for analysis, decomposition taking place at the surface of the pipette. For this reason, the first sample drawn into the pipette was allowed to flow out again and a second sample used for analysis. After using the pipette for some time no decomposition was observed, indicating that the hydrogen peroxide destroys the active centres on the surface, which then becomes "aged". This is probably the reason why solutions appear to increase in stability with concentration, the more concentrated solutions rapidly destroying the active centres. With more dilute solutions (less than 90%) the decomposition appeared to be somewhat greater, especially when the solutions were under vacuum. A further peculiarity observed was that these dilute solutions were readily supercooled, remaining liquid even when immersed in a carbon dioxide-acetone mixture at \(-80^\circ\text{C}\). This is in agreement/
agreement with the observation of Maass and Herzburg\textsuperscript{72}. With the more concentrated solutions no difficulty was experienced in freezing the liquid. These facts were used as a rough indication of the concentration of the peroxide in the reservoir.

The heterogeneity of the peroxide decomposition was indicated by the fact that, as the solid peroxide was melting in receiver C, decomposition took place at the surface of any solid peroxide in the solution. This is probably due entirely to a surface effect and not to any specific action of solid hydrogen peroxide on the solution.

Although it has been reported that very concentrated hydrogen peroxide solutions are very liable to explode, no explosive tendency was observed at any stage of the present work.

The hydrogen peroxide solution in the reservoir was maintained at \(-80^\circ\text{C}\) by immersion in a carbon dioxide-acetone freezing mixture, to prevent decomposition. To perform an experiment, the reservoir was allowed to come to room temperature for the withdrawal of some vapour and was immediately refrozen thereafter. That this method does indeed preserve the concentration of the solution is shown by the fact that one sample showed no loss in concentration/
concentration over a period of ten weeks, in spite of being melted daily. The concentrated sulphuric acid trap and the removal of water vapour by pumping out the vapour in the reservoir when the solution had melted also served to maintain the concentration.
II. DECOMPOSITION OF HYDROGEN PEROXIDE VAPOUR.

EXPERIMENTAL.

Apparatus.

The apparatus used in the investigation is shown in figure 6.

![Figure 6](image)

The part of the apparatus below tap T6 is that already depicted in figure 5 and described above, and is used for the final distillation of the hydrogen peroxide. Receiver C acted as reservoir for the concentrated peroxide and, except when the peroxide had to be melted to permit the withdrawal of some vapour, was immersed in a solid carbon dioxide - acetone freezing mixture at -80°C. The reservoir was later moved to a position X just below tap T5 (see figure 5) and a tap T6, introduced between X and the main vacuum line. This was to minimise decomposition of the vapour/
vapour in the leading tubes, particularly when these were heated.

The whole apparatus, apart from the reaction vessel \( V \), was constructed in soda glass. The reaction vessels were silica and were cylindrical in shape with optically plane ends. Two vessels were used, one having a volume of 31.35 ml and apparent surface area of 54 sq. cm, while the second had a volume of 131.8 ml and surface area of 143.8 sq. cm. The vessels had capillary stems of 2 mm internal diameter and were joined to the apparatus by a ground glass joint \( J \).

Small changes of pressure were measured with an all-glass Bourdon gauge connected directly to the reaction vessel. The gauge was maintained at a constant temperature by water circulated from a gas heated thermostat. The maximum variation of temperature in the gauge jacket as recorded by the thermometer \( H \), was never more than \( 0.01^\circ C \) in any one run. Movement of the pointer of the gauge was observed on an eyepiece scale in a telescope \( N \).

Large changes in pressure were measured on the mercury manometers \( M_1 \) and \( M_2 \); the pressure in the apparatus being given by the difference in level of the mercury between \( M_1 \) and the standard \( M_2 \). The manometers were also used in the calibration of the Bourdon gauge as described below.

Oxygen,
Oxygen, nitrogen and carbon dioxide were stored in two litre bulbs and the gases introduced through tap T. Water vapour was obtained from the tube L which contained distilled water.

For temperatures below 90°C, the reaction vessel was immersed in a water thermostat maintained at the required temperature. The thermostat consisted of a three litre pyrex beaker, wound with resistance wire and well lagged with asbestos paper and insulating felt. The temperature control was of the usual mercury-toluene expansion type with a "Sunvic" control. For temperatures below 50°C, heat was supplied by a carbon filament bulb immersed in the bath. The bulb was coated with black paint to avoid any possible photochemical effect. Between 50 - 90°C, the water was maintained at a temperature a few degrees below that required by current passing through the resistance wire coil and controlled by a hand rheostat. The carbon filament bulb gave the fine temperature control. The water in the bath was kept in motion by an electrically driven stirrer. This thermostat was constant to ±0.03°C.

For temperatures above 90°C, the thermostat was replaced by an electric furnace, the temperature of which was controlled by a hand rheostat. The furnace was constructed in two parts to facilitate introduction of/
of the vessel, and consisted of heating coils wound on glass formers, the whole system being enclosed in a metal cover, well lagged with asbestos paper and string. This furnace gave a temperature steady to \( \pm 0.1^\circ C \) as measured by a thermometer placed centrally in the furnace. As the majority of experiments were carried out at low pressures (less than 10 mms.) no correction was required for variations in temperature.

For the experiments with added gases, the vessel was immersed in a bath maintained at a steady temperature by water circulating from the large gas heated thermostat. The vessel temperature in this case was constant to \( \pm 0.01^\circ C \). With very high pressures of added gas (200 - 400 mms.) the effect of temperature variations could be observed but did not seriously affect the pressure readings.

The entire system could be evacuated by means of a water pump and Cenco-Hyvac oil-pump to a residual pressure of 0.0004 mms. as measured by a Macleod gauge.

Joints and taps were lubricated with the minimum amount of Apiezon L grease.

**Calibration of Gauge.**

Before performing any experiments the gauge had to be calibrated so that differences in scale readings on the telescope scale could be converted into pressure/
pressure differences in mms. of mercury. The calibration was carried out by admitting dry air alternately to either side of the gauge and determining the movement of the pointer for an increase in pressure as measured by the mercury manometers. The sensitivity of the gauge did not vary with the total pressure in the system.

For work at low pressures (less than 1 mm.) gauges of a sensitivity approximately 0.03 mms. per scale division were employed. As the telescope scale could be read to 0.1 divisions, the smallest recordable change in pressure was of the order 0.003 mms. For work at higher partial pressures of hydrogen peroxide, gauges of sensitivity 0.112 and 0.060 mms. per scale division were used.

Purification of Gases.

All the gases employed were obtained from cylinders and were purified to remove any impurities - especially oxidising or reducing agents - which might have undesirable effects.

Nitrogen.

Nitrogen was obtained from a cylinder of special oxygen-free nitrogen. It was bubbled through distilled water and passed through two solid carbon dioxide-acetone freezing traps, to remove condensable vapours.
vapours.

Phosphorous pentoxide was not used to dry the gases for two reasons:— (a) It has been shown that P$_2$O$_5$ is a powerful catalyst for the decomposition and it was feared that some might be carried into the reaction system with the gas, and (b) intensive drying of the gases was not necessary as some water is always introduced into the vessel along with the peroxide, the vapour being drawn from an aqueous solution. Further, provided the gas is passed slowly through the freezing traps very little water will escape condensation.

**Oxygen.**

The purification train for oxygen is shown in figure 7.

![Figure 7](image)

**Figure 7.**

The gas passes successively through distilled water, alkaline potassium permanganate solution and dilute sulphuric acid, condensable vapours being removed in the
the two solid carbon dioxide-acetone freezing traps.
The only impurity likely to remain after this treat-
ment is nitrogen, and that only to a small extent.

**Carbon Dioxide.**

Carbon dioxide obtained from a cylinder may
contain as impurities O₂, N₂, CO, H₂S and SO₂. The
purification train therefore consisted of four gas
wash bottles containing alkaline potassium permanganate
solution, sodium bicarbonate solution, copper sulphate
solution and concentrated sulphuric acid, followed by
the two freezing traps. The carbon dioxide did not
freeze out in the freezing traps if the gas was kept
flowing at a reasonable speed. To remove the
permanent gases, oxygen and nitrogen, the carbon
dioxide was frozen out in the freezing traps by
immersing these in liquid air, the remaining gases
pumped off and the carbon dioxide allowed to vaporise
again.

**Water Vapour.**

As mentioned previously, water vapour was
obtained from the reservoir E (figure 6) which
contained distilled water. Under oil-pump vacuum
this gave a pressure of about 12 mms. at room
temperature.

**Experimental/
Experimental Procedure.

The saturated vapour pressure of hydrogen peroxide solution of 99.8% concentration is given by the expression:

\[ \log_{10} p = -0.5223 \frac{A}{T} + B \]

\[ A = 48530 \]
\[ B = 8.853 \]

Thus at a temperature of 10°C, the vapour pressure above a solution of this concentration will be 0.79 mms., increasing to 1.13 mms. at 15°C. A convenient pressure of peroxide vapour for the purposes of this investigation can thus be attained by allowing the hydrogen peroxide in reservoir C to come to room temperature.

Between 35 - 40°C, the vapour pressure rises to 4.2 - 5.7 mms. For the work done on higher pressures of hydrogen peroxide it was necessary therefore to heat the reservoir to about 40°C by immersing it in warm water. To prevent condensation of the vapour on the cold connecting tubes, these were heated to 40°C by means of resistance wire wound round the outside. The temperature of the water circulating round the gauge jacket was raised to 35°C.

The composition of the vapour over hydrogen peroxide solutions has been examined by Giguere and Maass58 who showed that the vapour over a solution at/
at 30 °C had the same composition as the vapour over the same solution at 60 °C. They also found that the percentage of hydrogen peroxide in the vapour over a solution was less than the percentage in the solution. From their results it appears that over a solution of 98% molar, the vapour has a composition of 91% H₂O₂ and 9% H₂O. Thus by taking the vapour from above a 98% solution of hydrogen peroxide at room temperature, one should obtain approximately 1 mm. pressure of a vapour having a composition 90 - 91% H₂O₂, 10 - 9% H₂O with a small amount of oxygen which is always present due to some decomposition of the vapour.

To perform an experiment with the apparatus illustrated in figure 6, the following procedure was adopted. The apparatus was first evacuated by means of the filter pump and Hyvac oil-pump. It was necessary to use the filter pump for the initial evacuation, for, if the evacuation were carried out entirely with the oil-pump, there was a danger that a difference in pressure between the gauge jacket and the vessel sufficient to fracture the gauge might result, due to the difference in lengths of the leading tubes. As the gauge had to be as sensitive as possible a difference in pressure of about 5 mms. between the two sides was sufficient to fracture it.
When the apparatus was completely evacuated, taps T₃ and T₄ were closed and the vessel and gauge alone evacuated for 45 minutes. During this time the freezing mixture was removed allowing the peroxide in C to melt and come to room temperature. When the peroxide had melted, tap T₇, connecting the reservoir to the concentrated sulphuric acid trap, was opened. This served to remove water vapour from above the solution and so helped to maintain the concentration of the peroxide in the reservoir. After 45 minutes, tap T₅ was closed and tap T₆ opened connecting the reservoir directly to the oil-pump. When the gases in the reservoir had been removed (some decomposition always occurred while the peroxide was at room temperature), tap T₇ was closed and 30 seconds later T₉ (or T₆₁ in later experiments), the zero reading of the pointer taken, and tap T₅ opened, allowing the peroxide vapour to enter the vessel. When the required pressure had been attained in the vessel, tap T₅ was closed and the time noted on a stop watch. Subsequent readings were taken at suitable intervals, depending on the rate of decomposition. The freezing mixture was replaced round the reservoir as soon as possible to minimise decomposition of the liquid peroxide. The "infinity reading", corresponding to complete/
complete decomposition was observed after several hours. On re-evacuation the zero reading of the pointer was again read to eliminate errors due to any accidental change in the telescope or gauge position between the first and final readings.

When gases were added to the reaction vessel, the method had to be modified due to the fragility of the gauge. The hydrogen peroxide was introduced into the vessel and the initial pressure reading taken as before. Tap T₅ was closed as quickly as possible after admission of the vapour to the vessel, T₉ opened, the tubes evacuated with the oil-pump for 1½ – 2 minutes to remove peroxide vapour from the connecting tubes, and T₉ closed again. Taps T₁, T₃ and T₄ were now opened and a pressure of gas in slight excess of the pressure in the vessel, admitted to the gauge jacket. This was necessary to prevent any peroxide vapour escaping from the vessel. Tap T₅ was then opened, the gas entering the vessel and equalising the pressure. At the same time more gas was gradually admitted through T₁ until the required pressure was attained. In the case of water vapour, the water was admitted only to the vessel, being balanced in the gauge jacket with dry air. The pressure of the added gases was determined from the manometers M₁ and M₂. The reading of the gauge pointer/
pointer was noted immediately after admission of the gas and pressure changes in the reaction vessel recorded as above.

The time taken to perform the operation varied with the pressure of gas introduced but was normally about 4 - 7 minutes. The "initial" value of the pressure was obtained by extrapolation of the pressure-time curve to zero time.

In view of the small pressures involved and also the small volume of the capillary tubing, no correction was considered necessary for the vapour swept back into the vessel on introduction of the gas.

**Determination of Concentration.**

As two molecules of reactant decompose to give three molecules of products according to the equation:

\[ 2H_2O_2 \rightarrow 2H_2O + O_2 \]

the net result of decomposition at constant volume and temperature is an increase in pressure equal to half the partial pressure of hydrogen peroxide decomposed or to the partial pressure of the oxygen formed. In the absence of interfering factors such as adsorption, after complete decomposition of the hydrogen peroxide, the increase in pressure should be equal to half the partial pressure of the peroxide introduced.

Thus/
Thus, if:

\[ p_i = \text{initial total pressure}. \]
\[ p_\infty = \text{total pressure after complete decomposition ("infinity" reading)}. \]

\[ \left[ H_2O_2 \right]_m = \text{percentage of } H_2O_2 \text{ in vapour introduced}. \]

Then:

\[ \left[ H_2O_2 \right]_m = \frac{2(p_\infty - p_i)}{p_i} \times 100 \]

It was found, however, that application of this expression gave values of \( \left[ H_2O_2 \right]_m \) which did not agree with that calculated, by the results of Giguere and Maass, from the concentration of hydrogen peroxide solution in the reservoir. Indeed in a large number of cases values of over 100\% were obtained for \( \left[ H_2O_2 \right]_m \). This is due to the adsorption of water and hydrogen peroxide vapour on the walls of the reaction vessel, giving a value of \( p_i \) which is too small. The extent of this adsorption increased with increasing water vapour pressure, but an appreciable amount of hydrogen peroxide vapour must also be adsorbed as some of the values obtained for the percentage of peroxide vapour cannot be explained solely on the basis of water adsorption. In practice, three different curves can be observed in the initial part of the pressure-time curves, depending on the relative effects of two factors: - (a) the rate of adsorption and (b) the rate of decomposition. Figure 8 illustrates these three possibilities.
In type 1, there is, initially, a slow increase in pressure for 4 - 5 minutes, followed by the normal pressure increase. In this case the rate of decomposition is faster than the rate of adsorption.

Type 2 illustrates the case when the pressure increase due to decomposition is exactly equal to the pressure decrease due to adsorption. The pressure then remains steady until adsorption is practically complete.

Curve 3 shows the effect when the rate of adsorption is greater than the rate of decomposition. A pressure decrease takes place initially, followed by the normal increase due to decomposition.

It is to be expected that an increase in temperature should decrease the duration of the "induction period" and favour the transition from type 3 to type 1. This was observed and indeed for temperatures above 100°C, no induction period appeared.
An increase in temperature will have a two-fold effect - (a) increase the rate of decomposition and (b) decrease the extent of the adsorption.

This observation of an "induction period" is in agreement with Giguère⁶ who also observed an induction period on a silica surface, the duration of the period decreasing with increase in temperature and disappearing completely at temperatures above 175°C.

- The true decomposition will only appear after adsorption is complete. Although the extent of the adsorption must vary during the reaction with change in the partial pressures of the vapours, it seems unlikely that such changes will be very large or that the pressure variation due to them will be measurable. In these circumstances the increase in pressure may be taken as being due entirely to the oxygen formed by decomposition of the hydrogen peroxide.

As the rapid adsorption which takes place on introduction of vapour to the vessel makes the accurate determination of the initial pressure \( p_i \) difficult, the percentage of hydrogen peroxide in the vapour introduced cannot be accurately calculated. However, as this reading does not affect the calculation of the partial pressure of hydrogen peroxide during the reaction (see below), it is not necessary/
necessary to obtain an accurate value, although it makes the estimation of water vapour introduced into the vessel difficult.

As the variation between successive runs in the first section of results is greater than any which could be caused by variation in water vapour pressure, $p_i$ is again not important. In the second section of experiments, when the large vessel was coated with octa-decyl alcohol, it is shown by the addition of relatively large quantities of water vapour, that the rate of decomposition is unaffected by it.

In view of these facts, it is clear that a determination of $p_i$ more accurate than that described below is unnecessary for the purpose of analysing the results.

The exact procedure followed in analysis of the results of an experiment is best illustrated by an example. The experimental values of the pressure obtained at suitable time intervals were plotted and a smooth curve drawn through the points. Figure 9 illustrates a typical pressure-time curve.

---

| Figure 9. |
The actual duration and character of the induction period varied as described above, but had an average length of 2 - 4 minutes. Thereafter the pressure increased with time quite regularly. To determine the initial concentration of hydrogen peroxide the following procedure was adopted. The pressure-time curve was extrapolated to zero time, intersecting the pressure axis at $P_1$. This extrapolation was quite simple as the curve was very shallow in the majority of cases and the time interval quite short. The pressure increase between zero and "infinite" time could thus be determined. Assuming that this pressure increase is due entirely to oxygen as discussed above, it is clear that the initial partial pressure of hydrogen peroxide will be twice the increase in pressure.

\[ [H_2O_2]_i = 2(P_\infty - P_1) \]

where:
- $P_\infty = \text{infinity pressure.}$
- $P_1 = \text{extrapolated value of initial total pressure.}$

Similarly the pressure of $H_2O_2$ vapour at any instant $t$ was determined:

\[ [H_2O_2]_t = 2(P_\infty - P_t) \]

where:
- $P_t = \text{total pressure at instant } t.$

It should be noted that this method of calculation gives the total amount of hydrogen peroxide present.
in the system, both in the adsorbed and vapour state.

Tables of hydrogen peroxide gas pressure at various times during the reaction can be calculated, on the assumption that the adsorbed hydrogen peroxide is relatively small in amount.
EXPERIMENTAL RESULTS.

The decomposition of hydrogen peroxide vapour was examined in two silica vessels of different sizes, both on the uncoated and coated surfaces. As the results in the first section show an apparent lack of reproducibility, they are most conveniently presented in several groups, which are described below in chronological order.

In all tables the following symbols are used:

\[[H_2O_2]\] for partial pressure of $H_2O_2$ at any time;
\[C_0\] for initial concentration of $H_2O_2$ in the vapour calculated from the "infinity" reading;
\[C_t\] for concentration of $H_2O_2$ in the vapour at the instant $t$;
\[a\] for the initial concentration of $H_2O_2$ in the vapour in the second order equations;
\[x\] for the concentration of $H_2O_2$ in the vapour at the instant $t$, in the second order equations;
\[k\] for the rate constant.
I. **Small Silica Vessel.**

The vessel was cylindrical in shape, with optically flat ends and a capillary stem of 2mms. diameter. The internal volume of the vessel was 31.35 mls. and the apparent surface area 54.0 sq. cms. The surface of the vessel was pretreated by soaking the inside of the vessel in A.R. nitric acid followed by thorough washing with distilled water. The vessel was then dried by evacuation.

**Group 1.**

After a few preliminary runs during which no increase in pressure was apparent in the reaction vessel, seven runs were carried out at temperatures 78 - 80°C. The results for one typical run are given in table 1 and figures 10 and 11. In these seven runs, the reaction followed a first order equation for 90% decomposition, a plot of $\log_{10} \frac{C_0}{C_t}$ against time giving a straight line. The apparent initial percentage of hydrogen peroxide as calculated from the infinity reading and the rate constants show considerable variation in successive runs (table 2).
Table 1.

Small reaction vessel. Temperature of vessel = 77.1°C.
Temperature of gauge = 25.1°C. P = 78.9%.

Experimental. Values from Smoothed Curve.

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Pressure (mm.)</th>
<th>Pressure (mm.)</th>
<th>$\left[\text{H}_2\text{O}_2\right]$ (mm.)</th>
<th>$\log_{10}\frac{C_0}{C_t}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.730</td>
<td>0.730</td>
<td>0.576</td>
<td>0.000</td>
</tr>
<tr>
<td>5</td>
<td>0.795</td>
<td>0.792</td>
<td>0.452</td>
<td>0.105</td>
</tr>
<tr>
<td>10</td>
<td>0.848</td>
<td>0.843</td>
<td>0.350</td>
<td>0.216</td>
</tr>
<tr>
<td>15</td>
<td>0.884</td>
<td>0.884</td>
<td>0.266</td>
<td>0.332</td>
</tr>
<tr>
<td>20</td>
<td>0.920</td>
<td>0.914</td>
<td>0.208</td>
<td>0.442</td>
</tr>
<tr>
<td>25</td>
<td>0.936</td>
<td>0.935</td>
<td>0.166</td>
<td>0.540</td>
</tr>
<tr>
<td>30</td>
<td>0.952</td>
<td>0.952</td>
<td>0.132</td>
<td>0.640</td>
</tr>
<tr>
<td>40</td>
<td>0.972</td>
<td>0.976</td>
<td>0.084</td>
<td>0.846</td>
</tr>
<tr>
<td>50</td>
<td>0.992</td>
<td>0.992</td>
<td>0.052</td>
<td>1.046</td>
</tr>
<tr>
<td>60</td>
<td>1.005</td>
<td>1.003</td>
<td>0.030</td>
<td>1.283</td>
</tr>
</tbody>
</table>

$\infty$ 1.018 1.018 0.000

$k = 0.0482$

Figure 10.
Table 2.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>k (1st order)</th>
<th>C₀</th>
<th>P</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0315</td>
<td>0.920</td>
<td>133.3%</td>
<td>77.8°C</td>
</tr>
<tr>
<td>2</td>
<td>0.0223</td>
<td>0.804</td>
<td>143.5%</td>
<td>80.0</td>
</tr>
<tr>
<td>3</td>
<td>0.0545</td>
<td>0.330</td>
<td>76.9%</td>
<td>77.1</td>
</tr>
<tr>
<td>4</td>
<td>0.0482</td>
<td>0.578</td>
<td>78.9%</td>
<td>77.1</td>
</tr>
<tr>
<td>5</td>
<td>0.0345</td>
<td>0.470</td>
<td>67.9%</td>
<td>77.1</td>
</tr>
<tr>
<td>6</td>
<td>0.0196</td>
<td>0.444</td>
<td>75.5%</td>
<td>78.0</td>
</tr>
<tr>
<td>7</td>
<td>0.0559</td>
<td>0.394</td>
<td>48.0%</td>
<td>82.0</td>
</tr>
</tbody>
</table>

Group 2.

Prior to the experiments in this group, a fresh sample of hydrogen peroxide was prepared and a new Bourdon gauge fitted. Seventeen runs were carried out and but for one exception, the decomposition was second order. The exception, which occurred in the middle of the group, was immediately after the replacing of a gauge, and the reaction was neither first/
first nor second order. This irregularity may be attributed to the introduction of a new surface in the gauge.

In second order equations the rate of disappearance of reactant is proportional to the square of its concentration.

\[ -\frac{d(a-x)}{dt} = k(a-x)^2 \]

\[ \therefore \quad kt = \frac{x}{a(a-x)} \]

Thus for a second order reaction the plot of \( x/a(a-x) \) against time should be a straight line. This is true for the experiments in this group as is shown by figure 12, the lines illustrated being typical of the results obtained. In two runs the apparent initial concentration of hydrogen peroxide exceeds 100%, although in both these runs the decomposition was second order. The rate constants and other details of several of the runs are given in table 3.
A good straight line is obtained for the first 30-40 minutes of the decomposition by which time more than 90% of the hydrogen peroxide vapour has decomposed. Thereafter the values of \( x/a(a-x) \) tend to be too small. The apparent divergence is due to the fact that when \( x \) is small compared with \( a \), a small error in \( x \) will lead to a comparatively large error in \( x/a(a-x) \). It may be taken, therefore, that the runs described above do obey a second order equation.

Table 3.

Small reaction vessel. Temperature of vessel=80.0°C.
Temperature of gauge=25.1°C.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>( k ) (2nd order)</th>
<th>( C_o )</th>
<th>( P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.217</td>
<td>0.533</td>
<td>56.1%</td>
</tr>
<tr>
<td>3</td>
<td>0.198</td>
<td>0.764</td>
<td>96.1%</td>
</tr>
<tr>
<td>8</td>
<td>0.351</td>
<td>0.587</td>
<td>67.3%</td>
</tr>
<tr>
<td>9</td>
<td>0.190</td>
<td>0.493</td>
<td>57.0%</td>
</tr>
<tr>
<td>10</td>
<td>0.283</td>
<td>0.751</td>
<td>90.1%</td>
</tr>
<tr>
<td>11</td>
<td>0.336</td>
<td>0.633</td>
<td>84.3%</td>
</tr>
<tr>
<td>16</td>
<td>0.243</td>
<td>0.656</td>
<td>115.2%</td>
</tr>
<tr>
<td>17</td>
<td>0.728</td>
<td>0.636</td>
<td>93.0%</td>
</tr>
<tr>
<td>18</td>
<td>0.728</td>
<td>0.708</td>
<td>112.5%</td>
</tr>
</tbody>
</table>

Group 3.

To examine the effect of temperature on the rate of decomposition, the temperature of the vessel was increased to 110°C. In these experiments the initial rate of decomposition was very rapid, making the accurate determination of the initial pressure readings difficult. The decomposition still followed/
followed a second order equation and although the rate constant was somewhat variable for successive runs, it was of the order 1.1 - 1.2. Table 4 and figures 13 and 14 give the results obtained in one typical experiment. The major part of the decomposition was complete in approximately 20 minutes.

Table 4.
Small reaction vessel. Temperature of vessel = 109.3°C. Temperature of gauge = 25.1°C. P = 64.6%.

| Experimental |
| Values from Smoothed Curve |

<table>
<thead>
<tr>
<th>Time</th>
<th>Pressure</th>
<th>Time</th>
<th>Pressure</th>
<th>([E_2O_2])</th>
<th>(x/a(a-x))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.790</td>
<td>0</td>
<td>0.790</td>
<td>0.510</td>
<td>0.00</td>
</tr>
<tr>
<td>(\frac{1}{2})</td>
<td>0.852</td>
<td>1</td>
<td>0.887</td>
<td>0.316</td>
<td>1.20</td>
</tr>
<tr>
<td>1</td>
<td>0.887</td>
<td>2</td>
<td>0.926</td>
<td>0.238</td>
<td>2.24</td>
</tr>
<tr>
<td>2</td>
<td>0.926</td>
<td>3</td>
<td>0.950</td>
<td>0.190</td>
<td>3.30</td>
</tr>
<tr>
<td>3</td>
<td>0.950</td>
<td>5</td>
<td>0.975</td>
<td>0.140</td>
<td>5.18</td>
</tr>
<tr>
<td>4</td>
<td>0.966</td>
<td>7(\frac{1}{2})</td>
<td>0.995</td>
<td>0.100</td>
<td>8.04</td>
</tr>
<tr>
<td>5(\frac{1}{2})</td>
<td>0.972</td>
<td>10</td>
<td>1.008</td>
<td>0.074</td>
<td>11.55</td>
</tr>
<tr>
<td>7(\frac{1}{2})</td>
<td>0.999</td>
<td>15</td>
<td>1.024</td>
<td>0.042</td>
<td>17.60</td>
</tr>
<tr>
<td>10</td>
<td>1.003</td>
<td>20</td>
<td>1.035</td>
<td>0.020</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1.030</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1.034</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\infty)</td>
<td>1.045</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(k = 1.118\)

Figure 13.
Group 3A.

As the experiments in group 3 apparently showed an increase in rate with temperature, two sets of experiments were carried out in this group at temperatures of 60°C and 80°C. In the runs at 60°C, an apparent "induction" period was observed as discussed above. In this case the pressure initially remained constant for a short time. The runs at 80°C did not show any "induction" period. The runs in this group were second order. The rate constants for the various runs are listed in table 5, with the temperatures, initial concentrations and apparent percentages. Although the rates show some variation in successive runs at the same temperature, the/
the rate does appear to have increased with temperature.

Table 5.

Small reaction vessel. Temperature of gauge = 25.1°C.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>C₀</th>
<th>P</th>
<th>k(2nd order)</th>
</tr>
</thead>
<tbody>
<tr>
<td>79.6</td>
<td>0.485</td>
<td>89.8%</td>
<td>0.323</td>
</tr>
<tr>
<td>79.2</td>
<td>0.563</td>
<td>86.8%</td>
<td>0.386</td>
</tr>
<tr>
<td>78.9</td>
<td>0.626</td>
<td>93.0%</td>
<td>0.323</td>
</tr>
<tr>
<td>80.1</td>
<td>0.696</td>
<td>94.6%</td>
<td>0.449</td>
</tr>
<tr>
<td>61.8</td>
<td>0.570</td>
<td>73.1%</td>
<td>0.173</td>
</tr>
<tr>
<td>61.6</td>
<td>0.508</td>
<td>90.9%</td>
<td>0.192</td>
</tr>
</tbody>
</table>

Group 3B.

The experiments in this group were carried out to cover a wider range of the temperature-rate relationship. As the values obtained for the rate constant in successive runs at the same temperature were varying, the temperature was altered for each run in this group. A fresh sample of hydrogen peroxide was also used for these experiments. The decomposition was still second order, as can be seen from figure 15 which shows the plot of \( x/a(a-x) \) against time for two typical runs. The rate constants in this series vary very little with temperature - table 6.
Table 6.
Small reaction vessel. Temperature of gauge = 25.1°C.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$k$(2nd order)</th>
<th>$C_0$</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>62.5°C</td>
<td>0.241</td>
<td>0.916</td>
<td>63.0%</td>
</tr>
<tr>
<td>83.3</td>
<td>0.203</td>
<td>1.046</td>
<td>114.3%</td>
</tr>
<tr>
<td>93.6</td>
<td>0.266</td>
<td>0.968</td>
<td>109.6%</td>
</tr>
<tr>
<td>99.2</td>
<td>0.263</td>
<td>0.942</td>
<td>94.1%</td>
</tr>
<tr>
<td>113.8</td>
<td>0.247</td>
<td>0.936</td>
<td>100.0%</td>
</tr>
<tr>
<td>111.4</td>
<td>0.235</td>
<td>0.889</td>
<td>99.3%</td>
</tr>
<tr>
<td>107.3</td>
<td>0.272</td>
<td>0.720</td>
<td>84.6%</td>
</tr>
<tr>
<td>107.0</td>
<td>0.261</td>
<td>0.732</td>
<td>93.3%</td>
</tr>
<tr>
<td>107.0</td>
<td>0.250</td>
<td>0.920</td>
<td>107.7%</td>
</tr>
</tbody>
</table>

Figure 15.

Group 4.

The initial pressure of hydrogen peroxide introduced into the vessel was now increased to 4 - 5 mms. A new gauge of reduced sensitivity (0.112/
(0.112 mms. per division) was fitted. In order to obtain a suitable pressure of peroxide vapour, the reservoir C was immersed in hot water at 45°C. The connecting tubes between the vessel and reservoir were also heated with current passing through a coil of resistance wire wrapped round the tubes, to prevent condensation of hydrogen peroxide on the cold surface.

The temperature of the water circulating in the gauge was increased to 35°C. In the first experiments, the percentage of hydrogen peroxide in the vapour reaching the vessel tended to be rather low, due to decomposition in the hot connecting tubes. To overcome this difficulty, the reservoir was moved to position X, nearer the vessel - see figure 6. Values of over 100% for the apparent percentage of H₂O₂ in the vapour were then obtained. In both cases, the decomposition was first order for more than 90% of the reaction, although again the rate constants show some variation - table 7.
Table 7.

Small reaction vessel. Temperature of vessel = 62°C.

Temperature of gauge = 35°C.

I. First position of reservoir.

<table>
<thead>
<tr>
<th>$k$ (1st order)</th>
<th>$C_0$</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.145</td>
<td>3.553</td>
<td>85.4%</td>
</tr>
<tr>
<td>0.145</td>
<td>2.665</td>
<td>67.5%</td>
</tr>
<tr>
<td>0.122</td>
<td>2.235</td>
<td>52.5%</td>
</tr>
<tr>
<td>0.081</td>
<td>2.032</td>
<td>53.1%</td>
</tr>
<tr>
<td>0.156</td>
<td>1.803</td>
<td>37.7%</td>
</tr>
<tr>
<td>0.098</td>
<td>1.600</td>
<td>28.5%</td>
</tr>
</tbody>
</table>

II. Second position of reservoir.

<table>
<thead>
<tr>
<th>$k$ (1st order)</th>
<th>$C_0$</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.087</td>
<td>5.510</td>
<td>109.3%</td>
</tr>
<tr>
<td>0.057</td>
<td>8.966</td>
<td>177.4%</td>
</tr>
<tr>
<td>0.094</td>
<td>3.556</td>
<td>103.7%</td>
</tr>
<tr>
<td>0.057</td>
<td>7.366</td>
<td>166.6%</td>
</tr>
<tr>
<td>0.105</td>
<td>3.378</td>
<td>102.3%</td>
</tr>
<tr>
<td>0.094</td>
<td>3.302</td>
<td>106.5%</td>
</tr>
<tr>
<td>0.090</td>
<td>4.496</td>
<td>110.0%</td>
</tr>
<tr>
<td>0.159</td>
<td>3.073</td>
<td>92.4%</td>
</tr>
<tr>
<td>0.110</td>
<td>3.556</td>
<td>87.0%</td>
</tr>
</tbody>
</table>
Curves calculated from:

1. $C_e = C_0 / (1 + 0.123 C_0)$  \[ C_0 = 0.706 \]
2. $C_e = C_0 / (1 + 0.140 C_0)$  \[ C_0 = 0.558 \]
Points represent expt. values.

Figure 16.

Figure 17.
II. Large Vessel.

To examine the effect of a change in surface-volume ratio of the vessel and in the hope that a different silica surface would yield results more reproducible than those obtained in the small reaction vessel, the small vessel was replaced by a larger one of the same geometric shape but with a volume of 131.8 mls. and surface area of 143.8 sq. cms. The vessel was treated as before by leaving overnight filled with A.R. concentrated nitric acid and washing out thoroughly with distilled water.

Group 5.

Of the sixteen runs carried out in this group, all but two are exactly first order, although again there is variation in the rate constant. The two exceptions, which occurred in the middle of the series and under apparently identical conditions, were second order. Figure 16 shows the agreement between the experimental values of the hydrogen peroxide pressure and the values calculated from the second order equation: \[ C_t = \frac{C_0}{1 + kC_0 t} \] for these two runs. The agreement over the greater part of the decomposition is good. Figure 17 shows the plot of \[ \log_{10} C_0 / C_t \] against time for several of the first order runs, illustrating/
illustrating the agreement with the first order equation. The rate constants of these runs are listed in table 8.

Table 8.
Large reaction vessel. Temperature of gauge = 25.1°C.

<table>
<thead>
<tr>
<th>k (1st order)</th>
<th>C₀</th>
<th>P</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0663</td>
<td>0.273</td>
<td>123.7%</td>
<td>61.5°C</td>
</tr>
<tr>
<td>0.0796</td>
<td>0.371</td>
<td>98.5%</td>
<td>61.5</td>
</tr>
<tr>
<td>0.0714</td>
<td>0.464</td>
<td>100.0%</td>
<td>61.5</td>
</tr>
<tr>
<td>0.0744</td>
<td>0.423</td>
<td>97.3%</td>
<td>61.6</td>
</tr>
<tr>
<td>0.0557</td>
<td>0.551</td>
<td>91.2%</td>
<td>60.0</td>
</tr>
<tr>
<td>0.0295</td>
<td>0.522</td>
<td>109.3%</td>
<td>45.9</td>
</tr>
<tr>
<td>0.0363</td>
<td>0.634</td>
<td>108.2%</td>
<td>45.9</td>
</tr>
<tr>
<td>0.0210</td>
<td>0.388</td>
<td>118.9%</td>
<td>45.9</td>
</tr>
<tr>
<td>0.0220</td>
<td>0.679</td>
<td>129.3%</td>
<td>45.9</td>
</tr>
<tr>
<td>0.0359</td>
<td>0.470</td>
<td>115.1%</td>
<td>46.0</td>
</tr>
</tbody>
</table>

Group 6.
Metals of variable valency act as catalysts for the decomposition of dilute solutions of hydrogen peroxide, cobalt ions having a comparatively slight activity in solution as compared with iron and copper ions. To examine the effect of solid catalysts on the decomposition of the vapour, the surface of the vessel was coated with a thin film of cobalt naphthenate. This was introduced in a dilute solution in ether and the vessel pumped dry. About 0.005 gms. of naphthenate were introduced in this way. The results obtained at two temperatures, 20°C and 40°C, were/
Figure 18.

Figure 19.
were at first quite reproducible but after a few experiments became erratic, due probably to the chemical action of the peroxide on the naphthenate.

The order of decomposition in this case was found to be 2.5. Figures 18 and 19 show the experimentally determined rates compared with the values calculated from the equation:

\[ \text{Rate} = k \left[ H_2O_2 \right]^{2.5} \]

The rate constant is almost trebled (0.552 cfd. with 1.550) on raising the temperature from 20 to 40°C. The experimental values of the rates were obtained by taking tangents on the \( H_2O_2 \) pressure-time curves.

On recoating the vessel with 0.005 gms. cobalt naphthenate, the rate of decomposition was too rapid for any pressure measurements to be made.

The same effect was observed with a cobalt nitrate film, no measurements being possible due to the very rapid decomposition of the vapour on introduction into the vessel.

It is probable that other metal salts (e.g. of iron) which are stronger catalysts than cobalt in aqueous solution will also give rates which are too fast for measurement in the present system.

Group 7.

In/
Figure 20.

Figure 21.
In aqueous solution, acetanilide inhibits the decomposition of hydrogen peroxide. To examine any possible inhibition on the decomposition of the vapour, the vessel was coated with 0.005 gms. acetanilide, introduced in a solution of A.R. acetone. The reaction was found to be second order for 65-70% decomposition, apparently changing in the latter stages to a first order reaction. Figure 20 shows the plot of \( \frac{x}{a(a-x)} \) against time for two of the runs, and figure 21, the plot of \( \log_{10} \frac{C_0}{C_t} \) against time for the latter stages. The rate constants are listed in table 10.

**Table 10.**

Large reaction vessel. 0.005 gms. acetanilide.

Temperature of vessel = 40°C. Temperature of gauge = 25.1°C.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>( k ) (2nd order)</th>
<th>( k ) (1st order)</th>
<th>( C_0 )</th>
<th>( P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.117</td>
<td>0.0161</td>
<td>0.754</td>
<td>105.0%</td>
</tr>
<tr>
<td>2</td>
<td>0.088</td>
<td>0.0194</td>
<td>1.038</td>
<td>152.5%</td>
</tr>
<tr>
<td>3</td>
<td>0.081</td>
<td>0.0207</td>
<td>0.742</td>
<td>110.0%</td>
</tr>
<tr>
<td>4</td>
<td>0.051</td>
<td>0.0196</td>
<td>1.170</td>
<td>108.3%</td>
</tr>
<tr>
<td>5</td>
<td>0.036</td>
<td>0.0213</td>
<td>1.032</td>
<td>149.6%</td>
</tr>
</tbody>
</table>

The second order rate constants show a regular decrease in successive runs, while the first order constants tend to increase. It appears, therefore, that the surface is altering in some way with exposure to hydrogen peroxide vapour.

On/
On recoating the vessel with 0.06 gms. acetanilide, the decomposition in the first few runs was somewhat erratic but tended to be first order. The rate constant observed in one run which was exactly first order; was 0.0336. Comparing this constant with the average value obtained on the uncoated surface at 45.9°C (viz. 0.0290), it appears that the acetanilide has little or no effect on the measured rate of decomposition. (See Discussion - page 110).

Group 8.

As all the experiments described above showed that extensive adsorption was taking place on the walls of the vessel, an attempt was made to decrease the adsorption by coating the vessel with a hydrophobic compound. It was necessary that this compound should not react chemically with the hydrogen peroxide. To this end, a film of pure octa-decyl alcohol was deposited on the walls of the vessel from acetone solution. Although the adsorption of the vapour was apparently not affected by this treatment (e.g. values of over 100% were still obtained for the apparent percentage of peroxide in the vapour) the resulting surface yielded remarkably reproducible results. In the first instance 0.006 gms. octa-decyl alcohol was introduced but/
Figure 22.

Figure 23.
but subsequent addition of 0.006 gms. and 0.04 gms. had no effect on the rate or order of the reaction. This surface suffered from one disadvantage in that the temperature could not be raised very high as the alcohol melts at 59°C.

However, the effect of added gases and water vapour and temperature over the range 18 - 50°C were successfully examined.

The decomposition, in all cases, was first order for the greater part of the decomposition.

(a) Table 11 gives the results for one typical run in this series, the pressure-time curve and $\log_{10}(C_0/C_t)$-time plot being depicted in figures 22 and 23. As can be seen from figure 23, the agreement with the first order equation is very good.

An apparent "induction" period was observed in these runs (see figure 22). The value of the pressure at $t_0$ was obtained by extrapolation as discussed above (see page 69).

Table 12 shows the reproducibility of the rate constant obtained in successive runs. Run 18 was carried out after the effect of added gases and temperature had been examined, and after the hydrogen peroxide in the reservoir had been redistilled. The results for run 20 were obtained after the vessel walls/
walls had been recoated with octa-decyl alcohol.

Table 11.

Large reaction vessel. 0.006 gms. octa-decyl alcohol.
Temperature of vessel = 27.16°C. Temperature of gauge = 26.6°C.

Apparent percentage of $H_2O_2$ = 87.4.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Pressure (mm)</th>
<th>Time (min)</th>
<th>Pressure (mm)</th>
<th>$H_2O_2$ (mm)</th>
<th>$\log_{10} \frac{C_o}{C_t}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.570</td>
<td>0</td>
<td>0.530</td>
<td>0.578</td>
<td>0.000</td>
</tr>
<tr>
<td>2</td>
<td>0.546</td>
<td>5</td>
<td>0.549</td>
<td>0.540</td>
<td>0.030</td>
</tr>
<tr>
<td>5</td>
<td>0.552</td>
<td>10</td>
<td>0.566</td>
<td>0.506</td>
<td>0.058</td>
</tr>
<tr>
<td>9</td>
<td>0.567</td>
<td>15</td>
<td>0.582</td>
<td>0.474</td>
<td>0.086</td>
</tr>
<tr>
<td>14</td>
<td>0.576</td>
<td>20</td>
<td>0.596</td>
<td>0.446</td>
<td>0.113</td>
</tr>
<tr>
<td>20</td>
<td>0.600</td>
<td>25</td>
<td>0.610</td>
<td>0.418</td>
<td>0.141</td>
</tr>
<tr>
<td>23</td>
<td>0.603</td>
<td>30</td>
<td>0.623</td>
<td>0.392</td>
<td>0.169</td>
</tr>
<tr>
<td>29</td>
<td>0.624</td>
<td>40</td>
<td>0.647</td>
<td>0.344</td>
<td>0.225</td>
</tr>
<tr>
<td>36</td>
<td>0.636</td>
<td>50</td>
<td>0.669</td>
<td>0.300</td>
<td>0.285</td>
</tr>
<tr>
<td>41</td>
<td>0.651</td>
<td>60</td>
<td>0.688</td>
<td>0.262</td>
<td>0.344</td>
</tr>
<tr>
<td>49</td>
<td>0.663</td>
<td>70</td>
<td>0.704</td>
<td>0.230</td>
<td>0.400</td>
</tr>
<tr>
<td>57</td>
<td>0.684</td>
<td>80</td>
<td>0.717</td>
<td>0.204</td>
<td>0.452</td>
</tr>
<tr>
<td>71</td>
<td>0.699</td>
<td>90</td>
<td>0.728</td>
<td>0.182</td>
<td>0.502</td>
</tr>
<tr>
<td>81</td>
<td>0.720</td>
<td>$\infty$</td>
<td>0.810</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$k(1st\ order) = 0.0138$

Table 12.

Large reaction vessel. Temperature of vessel = 27.16°C.

Temperature of gauge = 26.6°C.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$k$ (1st order)</th>
<th>$C_o$</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0143</td>
<td>0.612</td>
<td>97.9%</td>
</tr>
<tr>
<td>2</td>
<td>0.0138</td>
<td>0.578</td>
<td>87.4%</td>
</tr>
<tr>
<td>3</td>
<td>0.0140</td>
<td>0.454</td>
<td>39.2%</td>
</tr>
<tr>
<td>4</td>
<td>0.0137</td>
<td>0.530</td>
<td>53.5%</td>
</tr>
<tr>
<td>18</td>
<td>0.0141</td>
<td>0.422</td>
<td>62.8%</td>
</tr>
<tr>
<td>20</td>
<td>0.0141</td>
<td>1.526</td>
<td>198.6%</td>
</tr>
</tbody>
</table>
(b) **Effect of Added Gases.**

Water vapour, oxygen, nitrogen and carbon dioxide had no effect on the rate of decomposition. The constants obtained for the runs with higher pressures of added gases show a slight variation due to the difficulty in determining the exact initial pressure of vapour and in maintaining very accurate temperature control.

Table 13 shows the results obtained.

**Table 13.**

<table>
<thead>
<tr>
<th>[N₂] [mm.]</th>
<th>[O₂] [mm.]</th>
<th>[CO₂] [mm.]</th>
<th>[H₂O] [mm.]</th>
<th>k (1st order) [mm./min.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0132</td>
</tr>
<tr>
<td>104.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.0135</td>
</tr>
<tr>
<td>-</td>
<td>4.3</td>
<td>-</td>
<td>-</td>
<td>0.0140</td>
</tr>
<tr>
<td>-</td>
<td>99.6</td>
<td>-</td>
<td>-</td>
<td>0.0136</td>
</tr>
<tr>
<td>-</td>
<td>448.0</td>
<td>11.1</td>
<td>-</td>
<td>0.0137</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.98</td>
<td>0.0135</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.81</td>
<td>0.0148</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.50</td>
<td>0.0148</td>
</tr>
</tbody>
</table>

No added gases 0.0142

(c) **Effect of Higher Pressure of Water Vapour.**

The addition of 9.1 mms. of water vapour to the reaction vessel led to a periodic variation in pressure as the H₂O₂ decomposed, similar to that observed by Mackenzie and Ritchie⁵⁵. The results for this run are given in table 14 and figure 24.
Figure 24.
During this experiment the temperature of the thermostat round the vessel was carefully observed and never varied more than ±0.01°C. This variation would have no effect on the pressure at 10 mms.

**Table 14.**

Large reaction vessel. Temperature of vessel = 27.00°C. Temperature of gauge = 26.50°C. 9.1 mms. H₂O vapour.

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Pressure (mm.)</th>
<th>Time (min.)</th>
<th>Pressure (mm.)</th>
<th>Time (min.)</th>
<th>Pressure (mm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.830</td>
<td>33</td>
<td>9.597</td>
<td>73</td>
<td>9.669</td>
</tr>
<tr>
<td>1</td>
<td>0.809</td>
<td>35</td>
<td>9.597</td>
<td>75</td>
<td>9.693</td>
</tr>
<tr>
<td>5</td>
<td>9.779</td>
<td>39</td>
<td>9.606</td>
<td>79</td>
<td>9.708</td>
</tr>
<tr>
<td>7</td>
<td>9.741</td>
<td>41</td>
<td>9.612</td>
<td>81</td>
<td>9.723</td>
</tr>
<tr>
<td>9</td>
<td>9.714</td>
<td>43</td>
<td>9.609</td>
<td>83</td>
<td>9.732</td>
</tr>
<tr>
<td>10</td>
<td>9.702</td>
<td>44</td>
<td>9.606</td>
<td>85</td>
<td>9.738</td>
</tr>
<tr>
<td>11</td>
<td>9.687</td>
<td>47</td>
<td>9.621</td>
<td>87</td>
<td>9.753</td>
</tr>
<tr>
<td>12</td>
<td>9.663</td>
<td>49</td>
<td>9.621</td>
<td>89</td>
<td>9.756</td>
</tr>
<tr>
<td>13</td>
<td>9.663</td>
<td>51</td>
<td>9.633</td>
<td>91</td>
<td>9.768</td>
</tr>
<tr>
<td>16</td>
<td>9.648</td>
<td>55</td>
<td>9.633</td>
<td>95</td>
<td>9.783</td>
</tr>
<tr>
<td>17</td>
<td>9.636</td>
<td>57</td>
<td>9.633</td>
<td>97</td>
<td>9.786</td>
</tr>
<tr>
<td>23</td>
<td>9.603</td>
<td>63</td>
<td>9.612</td>
<td>103</td>
<td>9.816</td>
</tr>
<tr>
<td>27</td>
<td>9.603</td>
<td>67</td>
<td>9.642</td>
<td>107</td>
<td>9.822</td>
</tr>
<tr>
<td>31</td>
<td>9.603</td>
<td>71</td>
<td>9.663</td>
<td>113</td>
<td>9.846</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>123</td>
<td>9.753</td>
</tr>
</tbody>
</table>

(d) **Effect of Temperature.**

Two or three runs were carried out at each temperature, the results for any one temperature being quite reproducible. Exactly first order rates were obtained in every case and the rate constant showed a steady increase with temperature. Table 15 gives the/
the average rate of decomposition in molecules per second at each temperature. In this series, the duration of the "induction" period decreased with increase in temperature.

**Table 15.**

Large reaction vessel. Temperature of gauge = 26.60°C.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Rate x 10^{-9}</th>
<th>Log_{10}(Rate)</th>
<th>1/T °K</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.9</td>
<td>0.826</td>
<td>-9.083</td>
<td>0.003438</td>
</tr>
<tr>
<td>27.2</td>
<td>1.643</td>
<td>-8.785</td>
<td>0.003351</td>
</tr>
<tr>
<td>31.2</td>
<td>2.037</td>
<td>-8.691</td>
<td>0.003287</td>
</tr>
<tr>
<td>32.0</td>
<td>2.531</td>
<td>-8.597</td>
<td>0.003279</td>
</tr>
<tr>
<td>36.8</td>
<td>3.128</td>
<td>-8.505</td>
<td>0.003227</td>
</tr>
<tr>
<td>45.9</td>
<td>5.902</td>
<td>-8.229</td>
<td>0.003137</td>
</tr>
</tbody>
</table>

The heat of activation at any temperature is given by the equation:

\[
\text{Rate} = ke^\frac{E}{RT}
\]

where \(k\) is a constant depending on the concentration; \(e\) is the natural base of logarithms; \(E\) is the apparent energy of activation; \(R\) is the gas constant; and \(T\) is the absolute temperature. Thus:

\[
\log_e(\text{Rate}) = \log_e k - \frac{E}{RT}
\]

Therefore, if \(\log_{10}(\text{Rate})\) is plotted against the reciprocal of the absolute temperature a straight line should be obtained, the slope of which is equal to \(E/2.303\). Figure 25 shows the straight line so obtained by plotting the values given in table 15, the value/
value of the heat of activation calculated from the slope of this line being 12,460 calories per mole.

Figure 25.

(e) Small Vessel.

Finally two runs were carried out in the small reaction vessel coated with 0.024 gms. octa-decyl alcohol. Concordant first order runs were again obtained at 27.20°C, the rate constant being 0.0187.
DISCUSSION.

Experimental Discussion.

The apparatus described above is essentially similar to that employed by Ritchie and co-workers\textsuperscript{50} for the investigation of, inter alia, the hydrogen-chlorine reaction, the hydrogen-bromine reaction and the decomposition of hydrogen peroxide. The main advantage of this system is that pressure changes are measured by an all-glass system, hence eliminating any effects which the use of oil or mercury manometers might have on the reaction.

It had been shown by Mackenzie and Ritchie\textsuperscript{55} that apiezon L grease had no effect on the decomposition of hydrogen peroxide and, as is apparent from the description of the apparatus, this grease was used to lubricate such taps and joints as were unavoidable in the present work.

At first, it was intended to work mainly at a temperature of $80^\circ$C, to obtain results comparable with those of other workers, particularly Mackenzie and Ritchie. It was found, however, that the rate of decomposition at that temperature, and under the conditions prevailing in the greater part of the investigation, were too fast for accurate measurement. In view of this, the temperature of the reaction vessel was/
was altered as necessary to suit the conditions.

As the decomposition was studied almost entirely at total pressures of less than 5 mms. of mercury, no correction was necessary for the slight variation in thermostat temperature which was steady to ±0.02°C as described above. For the few experiments at high pressures (more than 100 mms.) of added gas, slight pressure fluctuations due to variation in temperature were apparent but were not serious enough to require correction.

In spite of rigid precautions to ensure that conditions in the reaction vessel and experimental procedure remained unaltered in a series of runs, great difficulty was experienced in obtaining reproducible results. Although more than one hundred runs were carried out on the uncoated silica surface and the vessel was pre-treated in several ways (see below) in an attempt to stabilise the surface, the rates of decomposition, the extent of adsorption of H₂O₂ vapour and even the order of reaction in some cases varied in successive runs. On the other hand, when the vessel was coated with octa-decyl alcohol, the results obtained were reproducible even when the surface was recoated with fresh alcohol.

It seems desirable to prevent any direct contact between/
between the reaction vessel and mercury manometers and also to protect the vessel from any possible traces of oil vapour from the pump by using a liquid air trap. These rigid precautions were not observed in the first part of the work but latterly were strictly followed. It is impossible, without further investigation, to state definitely whether these precautions have any effect on the decomposition, but in view of the fact that small traces of certain substances have a marked influence on the decomposition (e.g. small traces of mercury - page 32) such precautions appear advisable.

Extensive adsorption of vapour on the walls of the vessel always occurred as described above (page 66). This made the exact determination of the partial pressure of water vapour in the system difficult, but this is unavoidable in the system used here. Similarly no allowance could be made for peroxide in the adsorbed and gaseous state, the calculation of hydrogen peroxide from the infinity reading giving a measure of the total peroxide, adsorbed and gaseous, in the reaction vessel. As the course of the reaction is followed by measuring the rate of increase in pressure, attributed to the formation of oxygen, there exists/
exists the possibility that adsorption and desorption of vapour may affect these pressure readings. After the first rapid adsorption of vapour, it seems unlikely that pressure changes due to this cause will be very great in comparison with the increase in pressure due to decomposition. Similarly, change in the amount of water vapour adsorbed as the partial pressure changes must also be small at such low pressures. These facts seem to be confirmed by the reproducibility of the results in the latter section (vessel coated with octa-decyl alcohol) when, although initial pressures and apparent percentages of hydrogen peroxide were widely variable, very reproducible rate constants were obtained.

In order that the main decomposition of the vapour might occur in the silica reaction vessel, the volume of the capillary tubing between the vessel and gauge was kept as small as possible. That the main decomposition did occur in the vessel was shown by a preliminary experiment where the vessel was replaced with a sealed off joint. The rate of decomposition in the capillary tubing was much faster than in a normal run with the vessel in position, but as the volume of the vessel is greater than the capillary tubing, calculation shows that in practice/
practice the observed rate is almost entirely due to decomposition in the vessel.

In the first few experiments with the small silica vessel, no increase in pressure was observed even after several hours. After several attempts, however, measurable pressure increases were obtained. In the experiments with coated surfaces a similar effect was observed, the first few runs being rather erratic. That this is not due to grease on the taps is shown by the fact that regreasing tap T_3 or joint J during a series of runs had no effect. This irregularity is apparently due to the necessity of ageing the surfaces in contact with the vapour, a requirement which has been observed by previous workers. In view of this, when a new surface was introduced into the system it was customary to flush the system out several times with hydrogen peroxide vapour before making any measurements.

**Discussion of Results.**

In spite of the fact that the silica vessel and general procedure used in the present work were the same as used by Mackenzie and Ritchie\textsuperscript{55}, it is immediately obvious from a comparison of the results that conditions are no longer the same. Apart from the/
the lack of reproducibility in the results, the absolute rates of decomposition are some 7 - 8 times faster than those obtained by Mackenzie and Ritchie, the reaction shows both first and second order characteristics under the same conditions and the energy of activation in the second order reactions is apparently negligible (see Group 3B, page 80).

Giguere$^{68}$ found that pretreating a quartz vessel with hydrochloric acid retarded the rate of decomposition of hydrogen peroxide vapour. In view of this fact, it is of interest to review the previous history of the small silica vessel. This vessel was used by Mackenzie and Ritchie for the work on hydrogen peroxide during the two years 1942 - 1944 and had not been in use since that date until used for the present investigation, a period of four years. For two years prior to 1942, it was used in an investigation of the photo-combination of hydrogen and chlorine$^{80c}$. During this work it was observed that a white film formed on the surface of the vessel after it had been in use for some time. This film could only be removed with difficulty by mechanical means. Bodenstein$^{78}$, in attempting to explain erratic results obtained in a similar photo-combination of hydrogen and chlorine, postulated an attack/
attack on the silica surface by chlorine atoms, to form a chloride which is subsequently hydrolysed to a form of silica of different surface activity. It is possible, therefore, that the surface of the vessel was in a condition of different activity when used by MacKenzie and Ritchie, but over a period of four years has reverted to a different state. Although pre-treatment of the vessel with both concentrated hydrochloric acid and aqua regia, illumination of hydrochloric acid in the vessel with a mercury vapour lamp and filling the vessel with 30% solution of hydrogen peroxide, had no effect on the decomposition, the continued exposure of the surface to both chlorine atoms and hydrochloric acid produced by illumination and possibly hydrogen atoms, may have rendered the surface of such a nature as to show predominantly a relatively slow bimolecular decomposition. The present series of experiments in the small vessel does confirm the fact that under certain conditions the decomposition of hydrogen peroxide vapour may be exactly second order (see Group 2 - page 75), a result previously obtained only by MacKenzie and Ritchie, other workers in the field finding the reaction to be first order.
In a larger silica vessel of the same geometric shape, second order reactions were obtained both on the uncoated silica surface (Group 5 - page 84) and on an acetanilide film (Group 7 - page 87). This indicates that the second order reactions in the small vessel are not induced by an additional mechanism involving chlorine, hydrochloric acid or compounds of these with silica but is inherent in the nature of the surface itself. It should be mentioned that both vessels were obtained from the same source, viz. the Thermal Syndicate, the large vessel not having been used previously. It appears, therefore, that under suitable conditions, the decomposition can follow either a first or a second order equation. The reaction at the low temperatures employed here must be almost entirely heterogeneous (see e.g. Giguere⁶⁸).

Mackenzie and Ritchie found that the decomposition of the vapour was inhibited slightly by water vapour (see page 30) and unaffected by small quantities of oxygen and inert gases. On the other hand, Elder and Rideal found the reaction ceased after 15% decomposition and attributed this to inhibition by oxygen. This has not been observed by any other worker and it seems probable that the cause of the cessation/
Figure 26.

Figure 27.
cessation lies in the apparatus used, rather than in the reaction.

Due to the irregularity of the results obtained on the uncoated silica surface, in the small vessel, it is impossible to say definitely whether water vapour does act as an inhibitor in the present experiments, but any effect it may have must be much smaller than in Mackenzie and Ritchie's experiments. This is shown by the agreement between the experimental points and the calculated curves in figures 26 and 27. The first curve is for a first order decomposition, the curve being calculated from:

\[ P_t = P_i + \frac{1}{2} C_0 (1 - e^{-kt}) \]

where:
- \( P_t \) is the total pressure at time \( t \).
- \( P_i \) is the extrapolated value of initial total pressure.
- \( C_0 \) is the initial concentration of \( \text{H}_2\text{O}_2 \) vapour.
- \( k \) is the first order rate constant.
- \( t \) is the time in minutes.
- \( e \) is the base of natural logarithms.

Figure 27 shows the agreement in the second order decomposition, the curve being calculated from:

\[ P_t = P_i + \frac{1}{2} C_0 \left( \frac{k C_0 t}{1 + k C_0 t} \right) \]

where the symbols have the same meaning as above, \( k \) in this case being the second order rate constant.
It is possible that the slight differences from the exact second order equation is due to a very small inhibition by water vapour. A further source of discrepancies may be the adsorption and desorption of vapours during the reaction. However, as can be seen from figures 26 and 27, agreement between experimental and calculated values is good, indicating that any effect these two factors may have must be small.

The usual theoretical approach applied to such heterogeneous reactions is based on the assumption of a unimolecular layer of adsorbed molecules tending to a definite saturation limit, the order of the reaction being very dependent on the extent of this adsorption. If the reactant is sparingly adsorbed and the reaction is fundamentally bimolecular, the rate of reaction will be determined by the chance that two molecules will occupy positions on the surface sufficiently close to make interaction possible, i.e. on the square of the surface concentration which in turn will depend on the square of the partial pressure. The direct proportionality between adsorbed and gaseous concentration when the reactant is sparingly adsorbed can be derived as follows:-

Let \( \sigma \) = fraction of surface covered with adsorbed gas.
Then \((1 - \sigma) = \text{fraction of surface left uncovered.}\)

"Surface" in this case refers to that part of the surface having active centres capable of adsorption. Equilibrium is established when the rate of evaporation from the surface is equal to the rate of condensation on the surface. At constant temperature:

\[
\text{Rate of condensation} = k_1 p (1 - \sigma)
\]

where \(k_1\) is a constant, since the absolute rate of condensation is proportional to the number of impacts per second on the uncovered part of the available surface and this number is proportional to the pressure of the gas and to \((1 - \sigma)\).

Also:- \(\text{Rate of evaporation} = k_2 \sigma\)

where \(k_2\) is a constant, since the rate of evaporation depends only on the amount of gas adsorbed on the surface. For equilibrium conditions:

\[
k_1 p (1 - \sigma) = k_2 \sigma
\]

When the adsorption is slight, i.e. 1, the equation reduces to:- \(k_1 p = k_2 \sigma\)

or:- \(\sigma = k_1 p / k_2\)

The amount of gas adsorbed is thus directly proportional to the pressure.

If, on the other hand, the surface is completely covered with adsorbed molecules, the apparent order of reaction will be zero, since the number of groups of/
of two molecules adsorbed cannot alter with pressure so long as the surface remains covered.

In intermediate cases, the apparent order will lie between zero and two, depending on the pressure and extent of adsorption.

The results obtained are in agreement with such a generalisation in that the order showed a tendency to decrease with increase in pressure. The experiments in Group 4 (page 81) show that, with higher initial pressures of hydrogen peroxide, the decomposition is first order for 80 - 90% of the reaction. Due to the limit imposed by the sensitivity of the gauge employed for the higher pressure work, it was impossible to follow the reaction nearer to completion to observe any appearance of a second order reaction in the latter stages.

Comparing the present results with those obtained by Mackenzie and Ritchie, it is clear that the extent of the adsorption of vapour is much greater in this work. Thus, while Mackenzie and Ritchie obtained experimental values for the initial concentration of hydrogen peroxide in the vapour introduced into the reaction vessel, which agreed to within 2% of the values calculated from the concentration of the reservoir peroxide according to the data of Giguere/
Giguere and Maass, in the present experiments the percentage compositions obtained experimentally as described above, varied considerably and in some cases were over 100%. Also, no induction period was observed by Mackenzie and Ritchie, again indicating that the extent of the adsorption of hydrogen peroxide is much less in their experiments.

It has been shown that the adsorption of water vapour on powdered silica corresponds to a layer 0.1 molecules thick at a pressure of 1 mm. at 30°C. To account for the experimental values of over 100% obtained for the concentration of peroxide, adsorption of peroxide vapour on the walls of the vessel must occur to an appreciable extent, as it does not seem likely that the adsorption of water on the silica surface will exceed that observed on powdered silica.

The surface of the vessel must have altered in nature since used by Mackenzie and Ritchie, the adsorption of hydrogen peroxide vapour now being considerably enhanced. A possible explanation of this change is suggested above. In the experiments carried out by Mackenzie and Ritchie, conditions will favour the appearance of a second order reaction, (the reactant being weakly adsorbed), water vapour inhibiting the reaction by occupying active centres and/
and so reducing the number available to the hydrogen peroxide (see e.g. reference 81a). In the present case, since adsorption is considerably greater, the number of active centres must also be greater, and the relatively strong adsorption may have the effect of reducing the order by one, as described above. Similarly, the effect of water vapour will not be so great, as many more active centres are available for adsorption.

If this argument is valid, the reaction at higher pressures should tend to zero order. Due to the limitation imposed by the system employed it was impossible to follow the reaction at pressures above 5 mms. hydrogen peroxide, up to which pressure no zero order reaction was observed. Of previous investigators, Elder and Hideal are the only authors who have obtained results indicating a zero order reaction in the vapour phase.

It is of interest to note that the "induction period" observed in the second order reactions was very short compared to those in the first order experiments, and was of the type 1, described above (page 67). This seems to confirm the fact that adsorption is less in these cases.

With the large vessel on the uncoated silica surface, the rate of decomposition follows a first order/
order equation in nearly all the experiments.

If water acts as an inhibitor and is strongly adsorbed, the free surface available to the hydrogen peroxide will be inversely proportional to the water vapour pressure. If the reaction is still second order with respect to hydrogen peroxide, the rate equation reduces to:

\[ \frac{dx}{dt} = k(a - x)^2/x \]

from which, by integration, the time of half change is given by:

\[ t_{1/2} = \frac{1}{k(1 - \log 2)} \]

The time for half change is thus independent of the initial concentration and the apparent order of the reaction will be the first.

At first sight, therefore, it would appear that strong adsorption by water would have the effect of reducing the order by one i.e. from second to first. As mentioned above, however, water can apparently have only a small effect on both the first and second order decompositions (see figures 26 and 27), and so the change of order cannot be due to this effect. In order to confirm this, the vessel was coated with a hydrophobic compound, octa decyl alcohol, to reduce, if possible, the strong adsorption of water vapour which would be required for the above mechanism. If the effect of water is that described above,
above, on a non-adsorbing surface the reaction should become second order. The results of this series of experiments are discussed below, but it should be mentioned here that all the results obtained indicate a first order reaction. Further, it does not seem possible to devise any kinetic scheme, assuming a second order decomposition of hydrogen peroxide retarded by water, which will give a first order reaction throughout.

The change of order from second to first may thus be regarded as due to a change in the surface action of the silica and not to a retardation by water vapour.

Giguere observed that a variety of surfaces had very little effect on the absolute rates of decomposition of the vapour, such widely differing substances as glass, paraffin oil and metals giving rates of the same order of magnitude. This fact was again observed in the present work, acetanilide and octa-decyl alcohol having little effect on the rate, although cobalt salts accelerated the decomposition somewhat. Giguere concludes from the non-specific action of the surface that the adsorption of the vapour must be of a physical rather than a chemical nature.

The fact that acetanilide, which is a well-known/
known inhibitor in aqueous solution, has no effect on the rate of decomposition of the vapour may be due to one of two causes:— (a) the roughening of the surface by coating with acetanilide may lead to an acceleration to an extent equal to the inhibiting action of the acetanilide, the two effects thus cancelling out, or (b) the acetanilide may not affect the mechanism of the decomposition, acting merely as a surface for reaction. The inhibiting action in aqueous solution would then involve a different mechanism.

From the results obtained here, it is impossible to say which of the two alternatives is the correct explanation.

Salts of metals of variable valency act as catalysts for the decomposition of aqueous solutions of hydrogen peroxide. It has been observed that Co$^{3+}$ and Ni$^{2+}$ adsorbed on silica gel are active catalysts, but lose this activity quite rapidly. $[\text{Co(H}_2\text{O)}_n]^{++}$ ions are active only in the presence of alkali bromides, while $[\text{Co(NH}_3)_n]^{++}$ and cobalticitic ions have greater activity. A mechanism for the decomposition in aqueous solution catalysed by Co(OH)$_3$ has been suggested as follows. The decomposition occurs in a monomolecular film at the catalyst surface, the adsorption of the peroxide redistributing/
redistributing the intramolecular force fields resulting in an increased tendency for one hydrogen atom to ionise. This "loosened" ion is removed as water by the impact of OH' ions, leaving the unstable O₂H' ions adsorbed on the surface, these subsequently decomposing to OH' ions and oxygen.

\[
\text{S}::\text{O} = \text{H} + \text{OH}' \rightarrow \text{S}::\text{O} = \text{O}^\cdot + \text{H}_2\text{O} \rightarrow \text{S} + \frac{1}{2}\text{O}_2 + \text{OH}'
\]

It was found that the addition of alkali to these solutions increased the catalytic activity of the Co(OH)₃, this being satisfactorily explained by the postulated mechanism. The activity of the catalyst decreased with hydrogen peroxide concentration.

Since cobalt ions are less active in aqueous solution than iron and copper ions, the decomposition of the vapour on cobalt salt surfaces was first examined. As can be seen from the results (Group 6 - page 85), cobalt naphthenate and cobalt nitrate accelerated the rates considerably. This might be due to roughening of the surface, but it seems more probable that an additional mechanism, perhaps similar to that occurring in solution, is involved. The fractional order (2.5) and the fact that the results became erratic after some time, indicate some interaction between the surface and the hydrogen peroxide.
peroxide. Since cobalt salts have such a great effect on the rate of decomposition, it seems that the present system is not suited for an examination of catalysis by iron and copper salts, which will have, presumably, greater activity.

As mentioned above, a series of experiments was carried out in the large vessel coated with pure octa-decyl alcohol. It was hoped that the alcohol molecules would orientate themselves on the silica surface with the hydrocarbon outwards as shown in figure 28, thus presenting a hydrophobic surface to the vapour. Since the silica surface appeared to adsorb the hydrogen peroxide molecule comparatively strongly, the hydroxyl group in the alcohol molecule should be adsorbed in preference to the hydrocarbon chain.

\[
\begin{array}{c}
| \quad \text{H-C-H} \quad \text{H-C-H} \\
| \\
\text{H-C-H} \quad \text{H-C-H} \\
| \\
\text{OH} \quad \text{OH} \\
\end{array}
\]

Surface.

Figure 28.

This was done with a view to cutting down the adsorption of water vapour which, as discussed above, may have the effect of reducing the order of the reaction. It was found,
found, however, that the adsorption was not appreciably reduced, due probably to some of the hydrocarbon chains being wrongly orientated, and presenting hydroxyl groups on the surface. Hydrogen peroxide and water, having polar molecules, will be readily adsorbed at these groups. The coating of alcohol presented a very stable surface, however, and very reproducible results were obtained even when the vessel was recoated with increasing amounts of alcohol (see Group 3 - page 88). As can be seen from the results, the decomposition was exactly first order for the greater part of the reaction and the absolute rate of reaction was of the same order of magnitude as that observed on the uncoated surface of the large vessel.

The reproducibility of the results, previously lacking, made it possible to examine the effect of temperature and added gases.

Oxygen and nitrogen, even at high pressures, and carbon dioxide and low pressures of water vapour had no effect on the rate of decomposition. This is in agreement with Baker and Quillet\textsuperscript{63}, who also found the reaction to be first order up to a temperature of 140\textdegree{}C and unaffected by added gases. The lack of effect of water vapour is contrary to the inhibition observed by Mackenzie and Ritchie. If, however, the surface/
surface of the alcohol is such that hydrogen peroxide is preferentially adsorbed and the argument discussed above is correct, water should have no effect. On the other hand, if the water vapour inhibits the second order reaction other than by occupying active centres, the mechanism in the two cases must be entirely different.

The fact that added gases have no effect on the rate of decomposition, even at high pressures, may be due to either of the following causes:— (a) the slowing down of the diffusion of hydrogen peroxide vapour to the walls may be exactly compensated by collision with gas molecules (b) the rate of diffusion to the walls may not affect the actual rate of decomposition.

Since wide variation in the pressure of added gases had no effect on the rate, it seems that the first alternative is not valid. The rate of decomposition cannot, therefore, depend on the rate of diffusion of peroxide molecules to the walls.

The decomposition in the presence of 10 mms. of water vapour showed periodic variations in pressure (see Table 14 – page 92) similar to those observed by Mackenzie and Ritchie on an uncoated silica surface. Periodic variations in the rate of decomposition of hydrogen/
hydrogen peroxide solutions decomposing at various surfaces, e.g. mercury\textsuperscript{85}, have also been reported although no such periodicity has been observed for the vapour decomposing at a mercury surface.

At the relatively high pressure of water vapour, the amount of water adsorbed on the walls will be much greater than at the low pressures previously discussed, the hydrogen peroxide pressure remaining as before. It seems probable that a different mechanism is involved in the presence of high pressures of water vapour, and as there is no evidence for complex formation between hydrogen peroxide and water in the vapour phase\textsuperscript{60}, the periodic variation in pressure is not due to a gas phase reaction but is dependent on conditions at the surface. The decomposition curve obtained experimentally can be explained as follows. The initial decrease in pressure is due to the rapid adsorption of water and peroxide vapour, forming a layer of predominantly water molecules on the surface. Subsequent to this adsorption, some hydrogen peroxide will dissolve in the water film. The decomposition will then be one occurring in the liquid rather than the vapour phase. The decomposition of the dissolved hydrogen peroxide will produce sufficient heat, locally, to "clear" a small/
small area of surface round the centre of reaction, the resulting increase in pressure being followed by a decrease due to readsoption of the water vapour.

**Energy of Activation.**

In the small vessel it was difficult to obtain an accurate indication of the temperature coefficient due to the variation in the rate constants at any one temperature. Thus, while the results of the experiments in groups 3 and 3A (page 77) seem to indicate an increase in rate with temperature, group 3B (page 80) shows the temperature coefficient to be negligible. This is in agreement with both Kistiakowsky and Rosenberg,\(^6^1\) and Baker and Quillet.\(^6^3\)

In the large vessel, however, the first order rate on the uncoated surface was approximately trebled by an increase in temperature of 20\(^\circ\)C (see Group 5 – page 84). The energy of activation calculated from the results given in this group is of the order 11 - 12 k.cals. per mole, which is in agreement with a value of 12 k.cals. obtained by Giguere\(^6^8\) on a quartz surface at temperatures up to 175\(^\circ\)C, and also with the value of 12,460 calories per mole (see page 94) obtained on an octa-decyl alcohol surface in the large vessel over the temperature range 18 - 50\(^\circ\)C.

This is greater than the value obtained by Mackenzie/
Mackenzie and Ritchie, who found the heat of activation to be 3,800 calories per mole for the second order reaction over the range 15 - 60°C, increasing to an average value of 7,500 calories from 60 - 140°C. They attribute this increase in heat of activation to the appearance of a gas phase reaction at the higher temperatures. If the retarding action by water vapour is due to covering of active centres by preferential adsorption, increasing the temperature will tend to decrease the extent of the water adsorption hence leaving more centres available for the decomposition of hydrogen peroxide, with a consequent increase in rate by a factor greater than the true temperature coefficient.

It is generally accepted that the primary step in the decomposition of hydrogen peroxide is:

\[ \text{H}_2\text{O}_2 \xrightarrow{M} 2\text{OH} \quad 53 \text{ k.calories} \]

It seems improbable in view of the high endothermic heat required, that any appreciable gas reaction will take place until comparatively high temperatures are reached. The value of 12 k.cals. per mole obtained for the heat of activation of the first order reaction also indicates the essentially heterogeneous nature of the decomposition.

Finally, an attempt is given here at calculating the/
the rate of the reaction from the theory of absolute reaction rates using the value of the heat of activation given above.

The equation for the rate of reaction of a first order heterogeneous reaction is:

\[ v = \frac{c_g c_s \left( \frac{\sigma}{\sigma_t} \right)}{6 \pi^2 (8 \pi^3 ABC)^{\frac{1}{3}} (2\pi m)^{\frac{1}{2}} kT} \left( \frac{1}{2} \right) e^{-\frac{\mu}{kT}} \]

where
- \( v \) = rate of reaction;
- \( c_g \) = concentration of reactant in gas phase;
- \( c_s \) = number of reaction sites per sq. cm.;
- \( \sigma, \sigma_t \) = symmetry numbers of the molecule of reactant and activated complex;
- \( s \) = total number of sites adjacent to any centre;
- \( h \) = Planck's constant = 6.55 x 10^{-27}
- \( k \) = Boltzman's constant = 1.37 x 10^{-16} ergs/degree;
- \( A, B, C \) = moments of inertia of the molecule;
- \( \epsilon_0 \) = heat of activation at 0°C;
- \( T \) = absolute temperature;
- \( m \) = mass of molecule of reactant;
- \( e \) = natural base of logarithms.

From published data, the following values for hydrogen peroxide may be inserted in the above equation:

\[ c_g = 3.24 \times 10^{16} \text{ molecules (1 mm. at 300.1°C)} \]

\[ c_s / \]
\( c_s = 10^{15} \) (reference 79 - page 180);

\( \sigma = \sigma_0 \) (reference 79 - page 180);

\( s = 4 \) (reference 79 - page 374);

\( A = 33.2 \times 10^{-40} \text{ gms. cm.}^2 \) (reference 21);

\( B = 33.5 \times 10^{-40} \text{ gms. cm.}^2 \) (reference 21);

\( C = 2.7 \times 10^{-40} \text{ gms. cm.}^2 \) (reference 21);

\( m = \frac{34}{6.06 \times 10^{23}} \text{ gm.} \);

\( T = 300.1^\circ \text{A}; \)

\[ \frac{E_0}{k} = \frac{E_0}{R} \]

where \( E_0 \) = heat of activation per mole at \( 0^\circ \text{A}; \)

\( R = \text{gas constant} = 1.98 \text{ cals.}/\text{degree}. \)

If the experimental heat of activation is constant over the complete range of temperature, the value for any temperature can be substituted for \( E_0 \).

Substituting the value, 12,460 calories, obtained above we find:-

\[ v = 4.4 \times 10^{12} \text{ molecules H}_2\text{O}_2 \text{ cm.}^2 \text{ sec}^{-1} \]

The experimental value of the rate at \( 300.1^\circ \text{A} \) is given by:-

\[ \text{Rate} = 0.0140 [\text{H}_2\text{O}_2] \text{ mms./min.} \]

This is readily converted into molecules per second per sq. cm., taking the volume of the vessel as 131.8 mls. and the surface area as 143.8 sq. cm. The value so obtained/
obtained is $6.9 \times 10^{12}$ molecules H$_2$O$_2$ cm$^{-2}$ sec$^{-1}$ which is in good agreement with the calculated value.

**Experimental** $v = 6.9 \times 10^{12}$ molecules H$_2$O$_2$ cm$^{-2}$ sec$^{-1}$

**Calculated** $v = 4.4 \times 10^{12}$ molecules H$_2$O$_2$ cm$^{-2}$ sec$^{-1}$
SUMMARY.

1. A convenient method for the preparation of small quantities of chemically pure, very concentrated hydrogen peroxide has been further developed.

2. The decomposition of hydrogen peroxide vapour has been examined on various surfaces at pressures up to 5 mms. at various temperatures in the range 18 - 110°C. The appearance of both second and first order characteristics on a silica surface is attributed to a change in the surface action rather than to a strong retardation of the decomposition by water vapour.

3. Octa-decyl alcohol was found to give a very stable surface and very reproducible results were obtained in a silica vessel coated with this compound. Oxygen, nitrogen, water vapour and carbon dioxide were found to have no effect on the rate of decomposition.

4. Films of cobalt salts were found to accelerate the rate of decomposition but acetonilide and octa-decyl alcohol gave rates which were of the same order of magnitude as on the uncoated silica surface.

5. The second order decomposition was found to have a negligible temperature coefficient but the first order decomposition had a heat of activation of approximately/
approximately 12 k.cals. per mole, both on a silica surface and octa-decyl alcohol.

6. - With high pressures of water vapour, periodic variations in pressure were observed. A possible explanation of this behaviour is discussed.

7. Since high pressures of oxygen and nitrogen (400 mms.) have no effect on the rate, it is suggested that the rate of diffusion in the bulk of the vapour has no effect on the rate of decomposition.

8. An attempt has been made to evaluate the absolute velocity of reaction from an equation derived from the theory of absolute reaction rates. The velocity so determined was found to be $4.4 \times 10^{12}$ molecules $H_2O_2$ cm.$^{-2}$ sec.$^{-1}$ at a temperature of 27.2°C on an octa-decyl alcohol surface, in good agreement with the experimental value of $6.9 \times 10^{12}$ molecules $H_2O_2$ cm.$^{-2}$ sec.$^{-1}$
THE PHOTOFORMATION OF

HYDROGEN PEROXIDE.
When a system is not sensitive to light of a certain wavelength, it is sometimes possible, by the addition of a small quantity of another substance, to make the system sensitive to light absorbed by that substance. If the substance is unaltered at the end of the reaction it is known as a photo-sensitiser and the reacting system is said to be photo-sensitised.

Various substances, e.g. zinc oxide and other white pigments, dyes, etc., are capable of sensitising photochemical reactions. One very important aspect of this is the photo-sensitised bleaching of dyes and degradation of textiles.

In the simple photochemical system:

Sensitiser - substrate - oxygen

the initial process, responsible for all subsequent phenomena, is the absorption of light energy by the sensitiser, the energy so absorbed raising an electron of the absorbing molecule to a higher energy level. This increase in energy may be dissipated in one of four ways.

1. The energy acquired may be rapidly degraded to heat with the return of the excited molecule to the ground state. As a result of the short life of the activated state, the absorbing molecule will be unable/
unable to pass the energy on to colliding molecules and, therefore, will be an inefficient sensitiser.

2. The excited electron may return to normal energy level with the emission of energy as fluorescence. In this case the molecule can remain in the activated state without converting the absorbed energy into heat. For this reason fluorescent compounds are generally good sensitisers.

3. The activated molecule can return to the ground state as a result of a collision, the energy being transferred to the colliding molecule.

\[ S^* + M \rightarrow S + M^* \]

The asterisk designates the activated state.

4. The excited molecule may enter into chemical reaction with another molecule. Two cases are then possible.

(a) The excited electron may leave the activated molecule and may or may not enter the other molecule.

\[ S^* + M \rightarrow S^* + M + e \]

(b) The lower energy level vacated by the excited electron may be filled by an electron from the colliding molecule.

\[ S^* + M \rightarrow S^- + M^+ \]

Baur has suggested that the mechanism of sensitised/
sensitised photolysis is exactly the same as electrolysis. In addition to the four methods of energy dissipation discussed above, Baur suggested that the excited sensitiser molecule may transfer the absorbed energy to the surrounding medium and discharge ions, e.g. the zinc oxide sensitised photo-decomposition of silver nitrate is explained by the following scheme.

\[
\text{ZnO}^* + \text{Ag}^+ \rightarrow \text{Ag}^0 \\
\text{ZnO}^* + \text{OH}^- \rightarrow \frac{1}{4}\text{O}_2 + \frac{1}{2}\text{H}_2\text{O}
\]

\(\text{ZnO}^*\) represents the excited molecule of sensitiser.

Historical.

The first systematic investigation of the photochemical activity of zinc oxide was made by Eibner\textsuperscript{106}, who was examining the fading and decolourising of oil and water colour paintings under the influence of light. Reputedly stable mineral colours (e.g. Prussian blue) were also found to be decolourised. The addition of glycerine to the paint accelerated the bleaching. Eibner established that the zinc oxide in the paint was responsible for this bleaching and observed that other compounds of zinc, notably zinc sulphide and zinc silicate also had this effect. \(\text{CaCO}_3\), \(\text{BaSO}_4\) and \(\text{PbCO}_3\) were not active.

Winther\textsuperscript{107} observed that an oxidising agent, which he thought was ozone, was formed when oxygen and/
and zinc oxide were illuminated in light of wavelength longer than 3500Å. As oxygen undergoes change to ozone only when illuminated with light of wavelength shorter than 2000Å, Winther suggested that the zinc oxide absorbed the longer wavelengths and emitted light of shorter wavelength which led to the formation of ozone. He was unable to detect any secondary ray, however, by normal physical methods, and this conception is not in agreement with either Stokes' law or Einstein's photochemical equivalence law. The same author, from a detailed spectographic study of mixtures containing zinc oxide, deduced the following facts:

1. During the sensitising, the zinc oxide remains chemically unchanged.
2. The reactions studied were independent of the basic character of the zinc oxide.
3. Light absorption by zinc oxide begins in the violet and shows a maximum at 3660Å.

During the course of this work, he observed the great sensitivity of aqueous solutions of silver nitrate containing zinc oxide to light of a mercury vapour lamp, the solution rapidly darkening. This was explained by Kolschutter and d'Almondra as being due to a reduction of the silver nitrate in the presence of zinc oxide. Crystals of silver could be observed/
observed under the microscope and zinc ions were detected in the solution. These workers, however, did not determine the fate of the oxygen from the zinc oxide.

Perret\textsuperscript{95} made a thorough examination of this reaction, his results being briefly summarised below.

1. Oxygen was liberated in the course of the reaction but no hydrogen was detected.
2. No hydrogen peroxide or nitrogen dioxide was detected in the solution after illumination by sunlight.
3. Zinc ions were present in solution and silver, silver oxide and silver peroxide present in the solid phase.

From his results Perret concluded that the primary process is the formation of silver peroxide which decomposes with heat into silver oxide and oxygen, zinc oxide being dissolved by the nitric acid formed in course of the reaction. He suggested a mechanism based on Baur's electrolytic theory\textsuperscript{105} to explain the results, two mechanisms being proposed:-

(a) $$\text{ZnO} + \text{OH}^- \rightarrow \frac{1}{2}\text{O}_2 + \frac{1}{2}\text{H}_2\text{O}$$

(b) $$\text{ZnO} + \text{OH}^- \rightarrow \text{peroxide} + \frac{1}{2}\text{H}_2\text{O}$$

A similar mechanism was suggested for the photolysis/
photolysis of HgCl₂.

Organic reducers such as glucose and sucrose were found to greatly accelerate the reaction. Perret suggests (after Baur) that this is due to a "depolarising" action similar to that which is necessary to allow direct current electrolysis to proceed.

It was shown by several control experiments that zinc oxide was essential for the reaction and that silver carbonate and calcium carbonate had little or no activity;

Battachary and Dhar⁴⁴ made an extensive investigation of reactions which are sensitised by zinc oxide, including the oxidation of fluorescent and non-fluorescent dyes. These authors consider Baur's theory to be unsatisfactory and suggest an alternative mechanism for the silver nitrate photolysis. The zinc oxide molecules absorb energy and become activated. These activated molecules come in contact with the molecules of silver nitrate and activate them by transference of energy. Salts of heavy metals have a tendency to decompose and this increase in energy, by collision with an activated molecule of zinc oxide, makes the decomposition more probable. The decomposition of silver nitrate then takes/
takes place according to the following equation.

\[ 2\text{AgNO}_3 + \text{H}_2\text{O} = 2\text{Ag} + 2\text{HNO}_3 + 0 \]

The nitric acid is neutralised by the zinc oxide. Dhar mentions that calcium carbonate and strontium carbonate, which can also neutralise the free acid, bring about the decomposition of solutions of silver nitrate in sunlight although the effect is not as great as with zinc oxide.

With reference to the supposed activity of calcium carbonate, Perret carried out several experiments showing that the decomposition of silver nitrate in presence of calcium carbonate (first observed by Schultze in 1727) was due to a double decomposition:

\[ 2\text{AgNO}_3 + \text{CaCO}_3 = \text{Ca(NO}_3)_2 + \text{Ag}_2\text{CO}_3 \]

The darkening of the solution was due to the decomposition of traces of silver chloride.

The first observation that hydrogen peroxide is produced when an aqueous suspension of zinc oxide is illuminated in the presence of air, was made by Baur. Suspensions of zinc oxide were exposed to sunlight for several hours in the presence of air and the hydrogen peroxide produced estimated both iodometrically and with titanium sulphate. Baur states that in the absence of oxygen no hydrogen peroxide formed, nor was any detected when the suspensions were kept in
the dark. Glycerine and glucose added to the solution led to increased production of hydrogen peroxide, Baur suggesting that these substances act as "depolarisers" allowing the reaction to proceed, e.g., for glycerine the scheme suggested was:

\[
\begin{align*}
\text{ZnO} & \quad \text{CH}_2\text{OH} - \text{CHOH} - \text{CH}_2\text{OH} + 2\text{OH}^- = \text{CH}_2\text{OH} - \text{CO} - \text{CH}_2\text{OH} + \text{H}_2\text{O} \\
\text{e} + 2\text{H}^+ + \text{O}_2 & = \text{H}_2\text{O}_2
\end{align*}
\]

Rao and Dhar\textsuperscript{116} found that the yield of hydrogen peroxide was increased by adding very small quantities (0.01M) of ethylamine, methylamine, aniline, phenol, acetone, alcohol, organic acids such as acetic and benzoic acids and inorganic substances such as caustic soda. It is of interest to note that these substances also inhibit the photochemical decomposition of hydrogen peroxide\textsuperscript{115}.

The photo-synthesis of hydrogen peroxide in the presence of zinc oxide has also been studied by McMorris and Dickinson\textsuperscript{96}, Yamazaki, Hisatoeda and Imagawa\textsuperscript{88} and Chari and Qureshi\textsuperscript{90, 91}.

McMorris and Dickinson illuminated suspensions of zinc oxide obtained by roasting zinc nitrate. They suggested that the oxidising agent formed was nitrogen peroxide, since a pink colour was obtained with sulphanilic acid - naphthylamine reagent\textsuperscript{120}, which is said to be specific for nitrogen dioxide. They showed that the active light lay in the ultra-violet or/
or near ultra-violet region by filtering the light through 0.065N solution of potassium ferrocyanide. No oxidising agent was formed on illumination with visible light.

Yamahuzi, Nisioeda and Imagawa claim that hydrogen peroxide can be detected in the absence of oxygen, although in reduced quantity, when biological photo-sensitisers are present. The addition of glucose, glycerol or glycine increased the hydrogen peroxide formation when suspensions of zinc oxide were illuminated in presence of oxygen, but none was detected when the suspensions were kept in the dark. Water was also found to be essential for the reactions. These workers state that zinc oxide does not take up oxygen on illumination.

Chari and Qureshi studied the photolysis in both sunlight and artificial ultra-violet light. They, also, found that certain organic compounds e.g. phenol increased the yield of hydrogen peroxide, and suggest that these substances act as stabilisers. An increase in the pH of the solution was found to favour the formation of hydrogen peroxide. Several samples of zinc oxide prepared in different ways were examined, that prepared by the ignition of the carbonate having the greatest activity. CdO, SnO₂ and ThO₂ were also found to act as sensitisers.
The variation in behaviour of zinc oxide depending on its mode of preparation was first observed by Winther\textsuperscript{107} who found that an oxidising agent was formed only when certain samples of zinc oxide were illuminated.

Jung and Kunau\textsuperscript{111} prepared samples of zinc oxide in several ways - pure zinc burned in oxygen, roasting of zinc carbonate, zinc sulphate and zinc nitrate. They found that only that prepared from the nitrate had any activity and even this disappeared on prolonged heating of the oxide. They suggested that the sensitiser might be zinc oxynitrate, and considered the oxidising agent produced to be neither hydrogen peroxide (since no water was present) nor nitrogen peroxide (since no oxidising agent was formed when nitrogen was used instead of oxygen).

Goodeve\textsuperscript{93} observed that freshly precipitated dried zinc oxide showed only a very weak brown fluorescence which changed to bright yellow when the oxide was heated above 800°C. By a reflection method, he showed that the absorption of light by zinc oxide occurred in the near ultra-violet and states the threshold wavelength to be 3850Å.

Winter\textsuperscript{92} examined zinc oxide prepared in two ways:
A. By the burning of zinc vapour in air (French process).

B. By burning zinc vapour in air containing reducing gases (American process).

Sample A showed no visible fluorescence in ultraviolet light at room temperature and had photochemical activity leading to the formation of hydrogen peroxide on illumination of an aqueous suspension. Sample B showed a strong yellow fluorescence and had no photochemical activity. Winter suggests that sample A utilises the light as photochemical energy while B dissipates it as lower energy radiation.

The photochemical behaviour of certain photosensitive dyes is very similar to that of zinc oxide, and a consideration of some of the results obtained with these dyes is of interest.

In the presence of oxygen and water, certain dyes lead to the photosynthesis of hydrogen peroxide. Blum and Spealman investigated the nature and origin of the peroxide formed when solutions of fluorescein dyes are illuminated. 0.001M solutions of carefully purified fluorescein dye were illuminated with a 200W Mazda lamp for 20 hours. The yield of hydrogen peroxide, determined iodometrically, was 0.001N solution.

A priori, this peroxide may arise from one of four sources.
sources:— (1) Impurities in the dye (2) the dye itself (3) decomposition products of the dye and (4) water.

Since the concentration of the peroxide formed was of the same order as the dye, it was highly improbable that it was due to any impurity in the dye.

The rate of bleaching of eosin in aqueous solution was also examined and it was found that, after 20 hours irradiation, the molar concentration of peroxide was at least five times that of the dye. The rate of increase in peroxide concentration did not seem to show any direct relation to the destruction of the dye, indicating that the peroxide was not a compound of decomposition products of the dye. The peroxide could be readily separated from the dye by precipitation of the latter as its acid or as a lake. No trace of peroxide could be detected in the precipitated dye. These results indicated that the peroxide arose from the water and was in fact hydrogen peroxide. This was confirmed by examining the rate of reduction of HI in the peroxide and also the decomposition with catalase, the results obtained agreeing with those expected for dilute hydrogen peroxide solutions. Catalase has no effect on organic peroxides. In the absence of oxygen, neither/
neither bleaching of the dye nor peroxide formation occurred.

Scholefield and Goodyear\textsuperscript{98} obtained hydrogen peroxide by irradiating neutral and acid suspensions of active yellow and orange vat dyes but Landolt\textsuperscript{99} obtained it only in alkaline solution, caustic soda apparently increasing the amount of hydrogen peroxide produced. NaOH inhibits the photodecomposition of aqueous solutions of hydrogen peroxide although it accelerates the thermal decomposition.

The investigations carried out by Kautsky et al.\textsuperscript{100} indicate that the light energy absorbed by the dye is transferred to the oxygen of the atmosphere. From his results Kautsky suggests that the sensitised dye molecule can exist in a long lived metastable state capable of imparting its energy to an oxygen molecule with the formation of an activated oxygen molecule. This activated molecule diffuses towards the "acceptor", considerable deactivation of the active molecules occurring during diffusion over relatively large distances, especially at high pressures.

Examples of such photo-sensitive dyes are chlorophyll, porphyrins, eosin, etc., most of which have been shown to produce hydrogen peroxide when illuminated in the presence of air and water.

As is discussed above, the system, dye - oxygen - water, when illuminated, leads to the formation of hydrogen/
hydrogen peroxide. Since Kautsky’s results indicate that, in the absence of water, an activated form of oxygen appears, there are two possible schemes\textsuperscript{97} for the production of hydrogen peroxide in the presence of water.

(a) \textit{Activated dye} + oxygen $\rightarrow$ \textit{Dye} + activated oxygen

\textit{activated oxygen} + water $\rightarrow$ hydrogen peroxide

(b) \textit{Activated dye} + oxygen + water $\rightarrow$ \textit{dye} + H\textsubscript{2}O\textsubscript{2}

\textit{i.e. without the appearance of activated oxygen as an intermediate.}

Egerton\textsuperscript{97} has put forward additional evidence to distinguish between the two schemes. Nylon dyed with a vat dye suffers as much degradation in dry air as in moist, when illuminated, even though a volatile peroxide can only be detected in moist air. Experiments show that the effect of volatile peroxide is slight, this being the reason for the negligible effect of humidity on the degradation. If the second scheme suggested above for the production of hydrogen peroxide is correct, the degradation in moist air should be less than in dry, since no activated oxygen is formed. In view of this, Egerton\textsuperscript{97} suggests that the first scheme is the correct one.

\textit{i.e. Dye} + hv $\rightarrow$ \textit{activated dye}

\textit{activated dye} + oxygen $\rightarrow$ \textit{dye} + activated oxygen

\textit{activated oxygen} + water $\rightarrow$ hydrogen peroxide
Vartanian\textsuperscript{101,102} examined the photo-conductivity of thin layers of dyes in the solid state. The conductivity of the majority of the dyes in the dark was very small. When the dyes were illuminated in vacuo, there was a more or less marked conductivity depending on the dye. The conductivity decreased slowly when the light was switched off. Certain important sensitising dyes such as the basic dye rhodamine "S", and the acid dye eosin, did not show photo-conductivity. The photochemical behaviour of these dyes is essentially similar to that of photo-conducting basic dyes such as Malachite Green and Auramine O. In view of this, Egerton suggests that there is no direct connection between the phenomenon of photoconductivity and photo-sensitisation by dyes.

The question of conductivity must be further considered in the case of zinc oxide which is known to be a reduction semi-conductor\textsuperscript{112}. As discussed above, when energy is supplied to an atom e.g. in the form of light, one or more electrons can be raised from the normal ground state to a higher energy level and the atom becomes "excited". In the case of a gas where the atoms are relatively far apart, there is little interaction of the electrical fields of the atoms. In solids, however, the atoms are close and regularly spaced, resulting in interaction of the electrical/
electrical fields and superposition of the higher energy levels. Thus, while the electrons in low energy levels belong to individual atoms or ions, the electrons in the higher levels belong to the solid as a whole. Electrons which have been excited to higher energy levels are free to move through the crystal lattice. Usually the "permitted" energy levels are so numerous that bands of permitted levels are formed, separated by forbidden bands where the electron cannot exist in equilibrium. Normally an electron can only cross the forbidden bands with difficulty but can readily be excited to a higher energy level in the band in which it already is.

When an external field is applied to an electron gas, those electrons moving in the direction of the applied field will be accelerated while those moving in the opposite direction will be retarded. In this case, the accelerated electrons must gain energy and so rise to a higher energy level in the band, the retarded electrons similarly losing energy. Pauli's Exclusion Principle prevents more than two electrons occupying any discrete energy level. Thus the only electrons which can be accelerated or retarded are those in an energy band which is not completely occupied. Of course, an electron which is in the top/
top energy level of a completely filled band may cross the forbidden band to a higher band, provided that the latter is at least partially empty. In general, however, the forbidden gap is so wide that the probability of any such transition is small.

It is clear from these considerations that different types of solids are possible depending on the state of the energy levels. In electrical insulators, the lower energy bands are normally completely full and the higher bands completely emptied, the two regions being separated by a wide band of forbidden energy levels. The electrons cannot be accelerated by an applied field and no conduction takes place.

In metals, on the other hand, the lower energy levels are likewise completely full but there are a large number of permitted higher levels which are normally partially empty. Electrons in these levels can be accelerated by an applied field and the solid can thus conduct. The electrons by which the current is carried are known as conduction electrons and the band of energy levels as the conduction band.

It is possible to envisage a solid whose properties will lie somewhere between the two extremes of insulator and metallic conductor. In this case, the forbidden band is comparatively narrow and/
and the probability of an electron reaching the conduction band from the full levels is appreciable. In such a case, a positive hole or "deficit" electron is left in the lattice. This has a mobility similar to that of an electron and can move through the lattice. A neighbouring electron falls into the "positive" hole and neutralises it, this being continued through the lattice. In such a solid both the electron in the conduction band and the positive hole contribute towards the conductivity. This type of solid is known as an "intrinsic" semi-conductor. It is considered unlikely that any semi-conductors of this type really exist, at any rate at room temperature. At higher temperatures, the forbidden band may be more readily crossed and the probability of intrinsic semi-conductivity will be increased.

Normal semi-conductors owe their electrical conductivity to "impurity" centres or lattice defects, which result in a distortion of the regular periodicity of the electrical fields.

Zinc oxide is known to be a semi-conductor of this type, the conductivity being attributed to an excess of zinc ions in the lattice. It falls into the n-type or reduction semi-conductors. Bevan and Anderson\textsuperscript{113} have suggested that the conductivity of zinc oxide may be due to the exciting of electrons from the d-levels of the zinc ion to the conduction band/
These authors investigated the conductivity at 500-900°C of zinc oxide prepared from three sources, that prepared by ignition of zinc carbonate having greater conductivity than that prepared by direct burning of zinc in oxygen or by ignition of zinc oxalate. The chemisorption of oxygen at the surface decreased the conductivity. Bevan and Anderson suggested that the oxygen traps the electrons in the conduction band by converting oxygen atoms to $O^-$ ions at surface lattice points.

Of the photo-sensitisers similar to zinc oxide which are capable of bringing about the photosynthesis of hydrogen peroxide, it is interesting to note that those which have been examined for semi-conductivity, viz. CdO, TiO$_2$ and ZnS, all are $n$-type or reduction semi-conductors similar to zinc oxide.

From the brief survey given above, it is clear that the work done on the photo-sensitising activity of zinc oxide has led to a number of conflicting results. In view of this it is not proposed to draw any conclusions as regards mechanism at this point, this being considered more fully in the Discussion.
EXPERIMENTAL.

The experimental work was carried out in two sections, viz. aqueous phase and gas phase experiments. These two sections are described below.

I. A. Liquid Phase Apparatus.

The apparatus used for examining the conditions under which hydrogen peroxide is formed by illumination of aqueous suspensions of white pigments, was very simple, consisting of a tube with a side arm, and a leading tube for bubbling oxygen through the suspension. The side arm was closed with a ground glass stopper to exclude any foreign matter, as shown in figure 29. The tube was placed 15 cms. from a 400W Osira mercury vapour lamp and was cooled by circulating water round it, the temperature being maintained at $7 \pm 0.5^\circ C$. Gas was obtained directly from cylinders, the nitrogen being from a cylinder of special oxygen-free nitrogen. The rate of flow was measured approximately on a simple flowmeter to ensure a steady and reproducible flow of gas. For a few experiments, the tube was replaced by two identical test tubes placed at the same distance from the lamp. These were used in order to/
to eliminate the effect of light intensity variations due to power cuts.

B. Experimental Procedure.

A weighed quantity of finely ground analar zinc oxide (British Drug Houses' preparation) was placed in the tube with a measured volume of distilled water, the gas bubbling through serving to agitate the suspension as well as supplying oxygen for the reaction. The suspension was illuminated and samples withdrawn for analysis at suitable intervals, by means of a pipette inserted through the side arm. The samples were filtered rapidly to remove suspended zinc oxide and analysed for hydrogen peroxide.

Four methods of analysis were employed initially, in order to show that the oxidising agent formed was indeed hydrogen peroxide.

(a) This method is simply a modification of that described by Cumming and Kay\textsuperscript{117} for the analysis of solutions of normal concentration of hydrogen peroxide. To a measured volume of solution to be analysed, was added a few crystals of potassium iodide and sodium bicarbonate, the liberated iodine being titrated with N/500 sodium thiosulphate added from a micro-burette, starch being used as indicator.

(b) This test, depending on the reducing power of hydrogen/
hydrogen peroxide in alkaline solution, is due to Deniges. The test solution was prepared as follows. To 5 or 6 drops of 3% silver nitrate was added, with shaking, 2 ccs. of 7N ammonia and two drops of a 6% solution of potassium ferricyanide. A yellow liquid, which could be kept for several hours, was obtained. To carry out a test using this reagent, 3 drops of the reagent were added to 5 ccs. of the solution to be analysed, a distinct turbidity developing after about 5 minutes when hydrogen peroxide was present. This turbidity was estimated on a Spekker photometer, using neutral grey filters, a calibration curve being first prepared. The method of preparation of reagent and rate of addition to the solution for analysis must be standardised to ensure good results. As the "blank" for the photometer, 3 drops of reagent were added to 5 mis. of distilled water. The reaction occurring can be summarised by the equation:

\[ 2K_2Fe(CN)_6 + 2NH_4OH + 8AgNO_3 + H_2O_2 = 2Ag_4Fe(CN)_6 + O_2 + 6KNO_3 + 2H_2O \]

(c) The reagent used for the third test was prepared by dissolving 5 gms. A.R. ammonium thiocyanate in 1 litre of A.R. methyl alcohol, a few drops of A.R. concentrated sulphuric acid being added. The sulphuric/
sulphuric acid apparently acts as a preservative for the solution. Immediately before use, a suitable volume of this reagent was shaken up with a small quantity of A.R. ferrous ammonium sulphate, the excess solid allowed to settle and the resulting solution decanted into a second bottle. A pale pink solution which could be kept for about one hour was thus obtained. A known amount of solution to be analysed was placed in a 50 ml. graduated flask and made up to 50 mls. with the reagent. In the presence of hydrogen peroxide, the characteristic colour of ferric thiocyanate rapidly developed. The concentration of peroxide was estimated in the usual manner using a Spekker photometer (spectrum green H603 filters) some of the reagent being used as a blank. The Spekker was previously calibrated and estimation of hydrogen peroxide to a limit of 0.2 mgms. per litre was possible.

After several preliminary analyses had shown that the first three methods gave the same concentration of a "standard" sample of hydrogen peroxide, method C was used for all subsequent analyses.

(d) As it has been reported that the oxidising agent formed on illumination of zinc oxide is nitrogen peroxide96, a specific reagent for nitrogen peroxide was also prepared and the solutions tested with this. This/
This reagent was sulphanilic acid - \( \alpha \)-naphthylamine (Griess-Ilosvay reagent\textsuperscript{120}), prepared as follows:-

0.5 gms. of sulphanilic acid were dissolved by heat in 150 ccs. 2N acetic acid. 0.1 gms. \( \alpha \)-naphthylamine were dissolved by heating in 20 ccs. concentrated acetic acid, filtered from charcoal to remove colour, and made up to 150 ccs. with 2N acetic acid. These solutions were kept separate and immediately before use, equal volumes were mixed. In the presence of nitrogen peroxide, a pink colour develops. This reagent is unaffected by hydrogen peroxide or ozone.

\section*{II. A. Gas Phase Apparatus}

The apparatus used for the gas phase was that already described for the decomposition of hydrogen peroxide vapour (page 54). A 400W Osira mercury vapour lamp was used as a source of light, the light beam being focussed on the reaction vessel by means of a condensing system. The reaction vessels employed had a volume of about 20 mls. (see below) and were constructed in pyrex glass, being joined directly to the gauge sickle by a ground glass joint. The vessels were cylindrical in shape, the front face being flat and the back slightly concave to facilitate deposition of the solid films. The films were deposited on face A - figure 30. The vessel was maintained/
maintained at the same temperature as the gauge jacket (27.1^\circ C) by water circulating from the large thermostat. In all other respects the apparatus was identical with that previously described.

**B. Experimental Procedure.**

In preparing a film for illumination, the zinc oxide (or ZnS, TiO_2) was finely ground in an agate mortar and about 0.1 gms. introduced into the reaction vessel. The dry powder was then moistened with a few drops of distilled water, the paste swirled round the concave face of the vessel to make a smooth film and dried by evacuation with a water pump, the vessel being warmed slightly over a heating mat. When the film was dry, the vessel was joined to the apparatus and the whole system evacuated for several hours by the oil-pump, with a liquid air trap between the pump and the vessel. Oxygen and water were obtained from reservoirs as described above (page 58).

When oxygen was used in the reaction, the vessel, after evacuation, was washed out with a little oxygen and re-evacuated. The required pressure of oxygen was then admitted. The taps to the vessel and gauge were then closed and after conditions became steady (about one hour), the film was illuminated. Subsequent changes in pressure were recorded at suitable time intervals. When the gauge pointer moved/
moved too far down the telescope scale and out of focus, a little oxygen was removed from the gauge jacket, the pointer thus being brought back to a suitable position.

With water vapour, the pressure of vapour introduced into the vessel was balanced by the admission of dry air to the gauge jacket. A much longer time (several hours) was required for conditions to become steady due to slow adsorption of water vapour on the film.

To convert pressure changes in scale divisions to actual molecules of oxygen, a knowledge of both the sensitivity of the gauge and the volume of the reaction system was required. The gauge was already calibrated (see page 57) and the volume of the system was determined by the method described below.

**Volume of Reaction System.**

The reservoir E (figure 6 - page 54) containing distilled water was replaced by a bulb of about 100 mls. volume. The volume of this bulb and the tubes up to tap $T_1$ (figure 31) was measured by weighing, first empty and then filled with distilled water up to and including the bore of the stop-cock $T_1$, giving volume $V_3$. The apparatus was completely evacuated and $T_1$ closed, cutting off the measured volume. About 500 mms./
500 mms. of dry air were now admitted, tap T2 closed (cutting off the manometer and gauge jacket) as well as tap T3 to the reaction system, and the leading tubes shown in figure 31 evacuated. The pressure in the system was measured by means of the mercury manometers, and the air in the reaction system then expanded into the evacuated leading tubes, the change in pressure in the vessel and gauge sickle balanced by the removal of air from the gauge jacket. The pressure at equilibrium was noted and the air expanded again, into the known volume V3, a third pressure reading being obtained. Assuming the dry air obeys Boyle's Law, the volume of the reaction system can then be determined.

Let $V_1 =$ volume of reaction system.

$V_2 =$ volume of leading tubes.

$V_3 =$ measured volume of bulb.

$P_1$, $P_2$, $P_3$, are the pressures corresponding to the three stages described above.

Then: $P_1 V_1 = P_2 (V_1 + V_2) = P_3 (V_1 + V_2 + V_3)$

Hence the values of $V_1$ and $V_2$ can be calculated.

The actual results for the determination of the volume of one system are given.

Volume of measured bulb, $V_3 = 143.2$ mls.

$P_1 = 462.5$ mms.

$P_2 = 254.0$ mms.

$P_3 = 58.9$ mms.
\[ 58.9(V_1 + V_2 + 143.2) = 254.0(V_1 + V_2) \]
\[ \therefore V_1 + V_2 = 43.23 \text{ mls.} \]
\[ 462.5V_1 = 43.23 	imes 254.0 \]
\[ V_1 = 23.74 \text{ mls.} \]

Two reaction vessels of similar shape were used, one slightly larger than the other, the volume of the reaction system in the two cases being 23.74 and 22.41 mls.
EXPERIMENTAL RESULTS.

I. Aqueous Phase.

(a) Preliminary experiments were carried out to determine the nature of the oxidising agent formed on illumination of zinc oxide - water suspensions. It has been suggested that this may be hydrogen peroxide \(^{97}\), ozone \(^{107}\) or nitrogen peroxide \(^{96}\). A sample of zinc oxide was illuminated for 2 hours in 30 mls. water, the zinc oxide removed by filtration and the resulting solution tested with the four reagents described above. The results are shown in Table 16, with the corresponding reactions of hydrogen peroxide, ozone and nitrogen peroxide. "+" indicates a positive reaction and "-" a negative reaction.

<table>
<thead>
<tr>
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<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
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<tbody>
<tr>
<td>(\text{H}_2\text{O}_2)</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
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<tr>
<td>(\text{O}_3)</td>
<td>+</td>
<td>-</td>
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<td>(\text{NO}_2)</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Test soln.</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
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</table>

The reagents are: - A. Starch-iodide reagent; B. Deniges ferricyanide reagent; C. Thiocyanate reagent; D. Sulphanilic acid - \(\alpha\)-naphthylamine reagent.

The test solution gave a negative result with the/
the sulphanilic acid reagent, indicating the absence of nitrogen peroxide. The test with reagent B was positive, the concentration of "active" agent determined from this test being the same as the concentration determined by A and C. Since reagent B depends on the reducing effect of hydrogen peroxide in alkaline solution and is unaffected by ozone and nitrogen peroxide it is clear that the "active" agent must be hydrogen peroxide.

(b) To determine the conditions necessary for the production of hydrogen peroxide, a series of experiments were carried out.

(i) A quantity of distilled water was boiled for ten minutes to expel oxygen and allowed to cool while nitrogen (oxygen-free) was bubbled through it. A suspension of 0.1 gm. finely ground zinc oxide in 40 mls. of this water was illuminated for two hours in the apparatus described above, nitrogen being bubbled through the suspension both to exclude adsorption of oxygen from the atmosphere and to agitate the suspension. A sample of the suspension was tested, after two hours illumination, with thiocyanate reagent with negative results. The concentration of peroxide formed in a similar suspension illuminated for two hours in the presence of oxygen, was 17 mgms. per litre. Oxygen is therefore/
therefore necessary for the formation of peroxide.

(ii) 40 mls. of oxygenated distilled water was illuminated for two hours in the absence of zinc oxide. No peroxide was detected.

(iii) A sample of dry zinc oxide was illuminated for two hours in the presence of oxygen and subsequently treated with both distilled water and dilute sulphuric acid. No peroxide was detected in either solution.

(iv) A suspension of zinc oxide in distilled water, agitated by oxygen, kept in the dark for six hours contained no peroxide at the end of this period.

(v) 0.1 gms. zinc oxide in 40 mls. distilled water was illuminated for two hours in the presence of oxygen. The concentration of peroxide in the solution at the end of this period was 17 mgms. per litre (M/2,000).

(vi) A series of experiments was now carried out under identical conditions viz. 40 mls. distilled water, 0.1 gms. finely ground zinc oxide, steady rate of flow of oxygen and at a temperature of 7°C. The concentration of peroxide was determined at suitable intervals as described above (test C) samples of 3 mls. being withdrawn through the side tube. Four or five estimations were made in each experiment. The values for the concentration at various/
Figure 32.
various time intervals show quite good reproducibility. The results obtained are shown in table 17 and figure 32.

Table 17.

0.1 gms. ZnO. 40 mls. distilled water.

Temperature 7°C. Oxygen bubbled through suspension.

<table>
<thead>
<tr>
<th>Time mins.</th>
<th>Conc. of H₂O₂ mgms./litre</th>
<th>Time mins.</th>
<th>Conc. of H₂O₂ mgms./litre</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. 0</td>
<td>0.00</td>
<td>105</td>
<td>14.90</td>
</tr>
<tr>
<td>5</td>
<td>2.60</td>
<td>120</td>
<td>16.90</td>
</tr>
<tr>
<td>10</td>
<td>2.80</td>
<td>IV. 55</td>
<td>10.55</td>
</tr>
<tr>
<td>15</td>
<td>4.25</td>
<td>82</td>
<td>13.45</td>
</tr>
<tr>
<td>20</td>
<td>5.60</td>
<td>130</td>
<td>17.10</td>
</tr>
<tr>
<td>25</td>
<td>7.40</td>
<td>V. 37</td>
<td>6.40</td>
</tr>
<tr>
<td>II. 15</td>
<td>4.65</td>
<td>43</td>
<td>7.40</td>
</tr>
<tr>
<td>45</td>
<td>9.15</td>
<td>242</td>
<td>24.10</td>
</tr>
<tr>
<td>60</td>
<td>10.70</td>
<td>320</td>
<td>28.70</td>
</tr>
<tr>
<td>75</td>
<td>12.70</td>
<td>VI. 30</td>
<td>7.20</td>
</tr>
<tr>
<td>III. 5</td>
<td>1.90</td>
<td>35</td>
<td>7.80</td>
</tr>
<tr>
<td>30</td>
<td>7.20</td>
<td>270</td>
<td>26.80</td>
</tr>
<tr>
<td>50</td>
<td>10.00</td>
<td>285</td>
<td>27.20</td>
</tr>
<tr>
<td>90</td>
<td>14.15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Roman numerals indicate the different runs.

The rate of formation of hydrogen peroxide under the above conditions, can be determined by taking the tangents at suitable intervals on the concentration – time curve. If the reciprocal of the rate is plotted against concentration, a straight line is obtained as shown in table 18 and figure 33.

Extrapolation of the straight line so obtained gives an intercept of -3.88 on the concentration axis, while the slope of the line is 1.73.
Figure 33.
The equation for the graph is then:

\[ \text{Rate} = \frac{k_1}{k_2 + \text{concn.}} \]

where:
\[ k_1 = 1.73 \]
\[ k_2 = 3.88 \]

On integration this gives:

\[ \text{Concentration} = k_2 \left[ \left(kt + 1 \right)^{\frac{1}{2}} - 1 \right] \]

where:
\[ K = \frac{2k_1}{(k_2)^2} \]
\[ = 0.230 \]
\[ t = \text{time in mins} \]

Table 19 gives the comparison of calculated and experimental values for the rate and concentration.

**Table 18.**

<table>
<thead>
<tr>
<th>Time (mins.)</th>
<th>Conc. of H(_2)O(_2) (mgms./litre)</th>
<th>Rate (mgms./min.)</th>
<th>(1/\text{Rate})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0</td>
<td>0.245</td>
<td>4.08</td>
</tr>
<tr>
<td>10</td>
<td>3.3</td>
<td>0.153</td>
<td>6.54</td>
</tr>
<tr>
<td>30</td>
<td>7.2</td>
<td>0.124</td>
<td>8.07</td>
</tr>
<tr>
<td>50</td>
<td>9.7</td>
<td>0.107</td>
<td>9.35</td>
</tr>
<tr>
<td>70</td>
<td>12.0</td>
<td>0.092</td>
<td>10.87</td>
</tr>
<tr>
<td>100</td>
<td>15.0</td>
<td>0.080</td>
<td>12.50</td>
</tr>
<tr>
<td>130</td>
<td>17.5</td>
<td>0.072</td>
<td>13.89</td>
</tr>
<tr>
<td>160</td>
<td>19.7</td>
<td>0.066</td>
<td>15.15</td>
</tr>
<tr>
<td>200</td>
<td>22.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 19.**

<table>
<thead>
<tr>
<th>Time (mins.)</th>
<th>Rate (Expt.) (mgms./min.)</th>
<th>Rate (Calc.) (mgms./min.)</th>
<th>Conc. (Expt.) (mgms./litre)</th>
<th>Conc. (Calc.) (mgms./litre)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.245</td>
<td>0.245</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>10</td>
<td>0.154</td>
<td>0.158</td>
<td>3.3</td>
<td>3.2</td>
</tr>
<tr>
<td>30</td>
<td>0.124</td>
<td>0.126</td>
<td>7.2</td>
<td>7.1</td>
</tr>
<tr>
<td>50</td>
<td>0.092</td>
<td>0.091</td>
<td>9.7</td>
<td>9.8</td>
</tr>
<tr>
<td>100</td>
<td>0.066</td>
<td>0.065</td>
<td>15.0</td>
<td>15.1</td>
</tr>
<tr>
<td>200</td>
<td>0.056</td>
<td>0.058</td>
<td>22.4</td>
<td>22.7</td>
</tr>
<tr>
<td>250</td>
<td>0.055</td>
<td></td>
<td>25.6</td>
<td>25.8</td>
</tr>
</tbody>
</table>
(c) Two samples of zinc oxide, one from a Hopkins & Williams A.R. preparation and the other from B.D.H., yielded the same concentration of hydrogen peroxide on illumination for the same length of time under the same conditions.

The addition of a small amount of acetanilide (0.001 gm.) led to an increase in the concentration of peroxide formed - 15 mgms./litre as compared with 11 mgms./litre in the absence of acetanilide.

(d) A sample of zinc oxide heated to red heat in the flame of a Mekker burner and cooled in vacuum, yielded no hydrogen peroxide on illumination in aqueous suspension. The zinc oxide, after heating, had a yellowish colour and was of a harder "texture" than the unheated zinc oxide.

(e) The illumination of zinc sulphide suspensions yielded only a trace of hydrogen peroxide. With titanium dioxide suspensions, the analysis of the illuminated solution was carried out in the usual manner. The filtering of the suspension did not remove completely the solid particles, a "colloidal" suspension coming through the paper. Testing this with thiocyanate reagent gave a slow development of colour indicating the presence of an oxidising agent. (See discussion - page 169).

(f) The production of hydrogen peroxide was also examined/
examined briefly using a simple flow system. Oxygen was passed over zinc oxide contained in a small boat and illuminated by the mercury vapour lamp. The tube containing the boat was cooled by tap water circulating through a jacket. Only in cases where starch iodide paper was in actual contact with moist zinc oxide was any indication of an oxidising agent observed, dry zinc oxide having apparently no effect on the starch iodide paper. Similarly, when moist starch iodide paper was placed a few mms. from dry zinc oxide, no oxidising agent was detected.

II. Gas Phase.

(a) The illumination of zinc oxide films under a pressure of oxygen led to a decrease in pressure. The exact conditions for this uptake were not determined, for it was found that some films, prepared in exactly the same way, and under the same conditions, showed no uptake of oxygen or a very slow uptake. The reason for this anomaly was not discovered, although various attempts, such as the introduction of small quantities of mercury to the reaction vessel, were made. This is further discussed below.

In the case of the films which did adsorb oxygen on illumination, readings of the gauge pointer were taken at suitable intervals and the decrease in pressure plotted against time. The results for one typical run are given in table 20 and figure 34.
The pressure decrease ceased immediately the light was cut off and no further change of pressure occurred in the dark.

The rate of oxygen uptake at various instants can be determined from figure 34. Table 21 shows the values of $R_{10}$ (rate of uptake per ten minutes) compared with the total oxygen uptake ($\Sigma O_2$) at the same instant. Figure 35 shows the plot of these values.

**Table 20.**

<table>
<thead>
<tr>
<th>Time (mins.)</th>
<th>$\Sigma O_2$ scale divs.</th>
<th>Time (mins.)</th>
<th>$\Sigma O_2$ scale divs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0</td>
<td>154</td>
<td>3.6</td>
</tr>
<tr>
<td>5</td>
<td>0.2</td>
<td>240</td>
<td>5.0</td>
</tr>
<tr>
<td>13</td>
<td>0.6</td>
<td>270</td>
<td>5.6</td>
</tr>
<tr>
<td>20</td>
<td>0.8</td>
<td>295</td>
<td>5.8</td>
</tr>
<tr>
<td>35</td>
<td>1.2</td>
<td>338</td>
<td>6.3</td>
</tr>
<tr>
<td>45</td>
<td>1.4</td>
<td>355</td>
<td>6.6</td>
</tr>
<tr>
<td>60</td>
<td>1.9</td>
<td>420</td>
<td>7.2</td>
</tr>
<tr>
<td>83</td>
<td>2.7</td>
<td>455</td>
<td>7.7</td>
</tr>
<tr>
<td>112</td>
<td>3.0</td>
<td>478</td>
<td>8.0</td>
</tr>
<tr>
<td>140</td>
<td>3.6</td>
<td>507</td>
<td>8.2</td>
</tr>
</tbody>
</table>

**Table 21.**

<table>
<thead>
<tr>
<th>$R_{10}$ divs./10 mins.</th>
<th>$\Sigma O_2$ scale divs.</th>
<th>$R_{10}$ divs./10 mins.</th>
<th>$\Sigma O_2$ scale divs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.350</td>
<td>0.50</td>
<td>0.130</td>
<td>5.41</td>
</tr>
<tr>
<td>0.295</td>
<td>1.28</td>
<td>0.115</td>
<td>6.41</td>
</tr>
<tr>
<td>0.260</td>
<td>1.99</td>
<td>0.100</td>
<td>7.31</td>
</tr>
<tr>
<td>0.220</td>
<td>2.63</td>
<td>0.090</td>
<td>7.83</td>
</tr>
<tr>
<td>0.195</td>
<td>3.02</td>
<td>0.077</td>
<td>8.62</td>
</tr>
<tr>
<td>0.175</td>
<td>3.49</td>
<td>0.060</td>
<td>9.27</td>
</tr>
<tr>
<td>0.165</td>
<td>3.92</td>
<td>0.056</td>
<td>9.60</td>
</tr>
<tr>
<td>0.155</td>
<td>4.30</td>
<td>0.050</td>
<td>10.17</td>
</tr>
</tbody>
</table>
The rate falls off quite rapidly at first as \( \Sigma \text{O}_2 \) increases and the plot of \( R_{10} \) against \( \Sigma \text{O}_2 \) becomes linear in the latter stages (figure 35). Extrapolation of this linear portion to zero rate gives a value of 13.1 scale divisions for the total oxygen uptake by the zinc oxide film. This can be readily converted into an actual weight of oxygen, knowing the sensitivity of the gauge (0.030 mms./div.) and the volume of the reaction system (22.41 mls.).

Weight of oxygen = \( \frac{32.00}{22.400} \times \frac{22.41}{760} \times (0.030 \times 13.1) \times \frac{273}{500.1} \)

= 1.5 \times 10^{-5} \text{gms.}

This is 0.012\% by weight of the zinc oxide film.

The analar limit for oxidisable matter in the zinc oxide is quoted as 0.002\%.

(b) Effect of Pressure.

To examine the effect of the pressure of oxygen on the rate of uptake, the pressure above the film was reduced, during illumination, in stages. A film of 0.0774 gms. zinc oxide was illuminated in the large vessel at an initial pressure of 100 mms. oxygen. After a suitable length of time, the pressure was quickly reduced to 50 mms. and illumination continued for a period, and finally to 25 mms. As can be seen from figure 36, no change in rate occurred with reduction in pressure. The pressure was reduced to 50 mms. /
Figure 36.
50 mms. at point A and 25 mms. at point B (figure 36). Extrapolation of the linear portion of the curve gives a value of 10.6 scale divisions for the total oxygen uptake. The volume of the large reaction system was 23.74 ml, which gives a value of $1.3 \times 10^{-5}$ gms.

The volume of the large reaction system was 23.74 ml, which gives a value of $1.3 \times 10^{-5}$ gms.

(c) Reversibility of Oxygen Uptake.

Evacuation of the system to a residual pressure of 0.0006 mms. and leaving overnight led to a partial reversal of the oxygen uptake. This is shown by the curve to the right of figure 36 (part c) which shows the rate of oxygen uptake after re-admission of 25 mms. of oxygen. Clearly evacuation has led to an acceleration of the uptake. No increase in pressure was observed on leaving the film overnight after evacuation. A slight reversal, but to a very much smaller extent, was observed on leaving the film in the presence of 25 mms. oxygen in the dark overnight.

(d) Effect of Water Vapour.

Preliminary work (unpublished results - MacFarlane and Ritchie) had shown that illumination of zinc oxide in presence of water vapour led to a small (0.03 mms.) but definite increase in pressure. Some indication was also obtained that this pressure change increased with/
with increase in the water vapour pressure. Since no such pressure change was observed with thallous bromide, it seems unlikely that this pressure change is due to a heat effect consequent to the absorption of light energy. No pressure change was observed under similar circumstances in the present work. On admission of water vapour to the vessel and zinc oxide film, there was a slow pressure decrease for some time due to adsorption of vapour on the surface. When conditions were steady, i.e. no pressure change over a long period, the film was illuminated, without any apparent change in pressure.

This increased pressure effect, if real, will be very dependent on the previous treatment of the zinc oxide. If, as is suggested later, there is an activated adsorption of oxygen on illumination of the film in oxygen, followed by a slow diffusion into the interior of the solid, subsequent illumination with water may lead to the formation of hydrogen peroxide, which, on decomposing, will give off oxygen and lead to a small increase in pressure. An equilibrium point should then be reached, depending on the extent of the previous activated adsorption of oxygen. Further work is required, on this point, however, before any definite conclusions can be reached.

As mentioned above, no change in pressure was recorded/
Figure 37.
recorded with water vapour in the present work, and thus no correlation could be observed between results with different samples subjected to different periods of illumination.

(e) Detection of Oxidising Agent.

After illumination, the gases in the reaction vessel were pumped out, through a small freezing trap immersed in liquid air. About 1 ml. distilled water was placed in the tube to absorb any hydrogen peroxide or other oxidising agent which may be formed in the vessel. No such agent could be detected in this way from any of the films illuminated.

(f) Zinc Sulphide.

A film of zinc sulphide (pure) was prepared in the same way as zinc oxide. The illumination of this film in presence of oxygen also led to a decrease in pressure, but to a smaller extent than zinc oxide. Figure 37 illustrates the usual rate curve for a 0.1734 gm. zinc sulphide film in the large vessel at 25 mms. oxygen pressure. At point A, the film was left in the dark overnight in the presence of oxygen while at B the vessel was evacuated. As can be seen a reversal occurs in both cases. No pressure change was observed with water vapour.

(g) Titanium Dioxide.

For the purpose of comparison, a film of titanium dioxide/
Figure 38.

Figure 39.
dioxide (prepared by J. Mackenzie, from TiCl₄ by hydrolysis¹²¹) was also illuminated in the presence of oxygen (0.1 gms. titanium dioxide - 52 mms. oxygen). A very rapid decrease in pressure occurred on illumination (figure 38), the rate of oxygen uptake becoming constant after a time (figure 39). After evacuation (point B - figures 38 and 39) a slight reversal occurs but the rate quickly returns to a steady value. No change in the rate of uptake was observed after the film was allowed to stand in the dark overnight (point A). Before evacuation the oxygen uptake was 60 scale divisions corresponding to 9.9 x 10⁻⁵ gms. oxygen or 0.1% of the titanium dioxide by weight.

Table 22 gives the values of R₁₀ and ΣO₂ for this film.

Table 22.
0.1 gms. TiO₂. 52 mms. O₂. Temperature 27.10°C.

<table>
<thead>
<tr>
<th>R₁₀ (divs/10 mins.)</th>
<th>ΣO₂ (scale divs.)</th>
<th>R₁₀ (divs./10 mins.)</th>
<th>ΣO₂ (scale divs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.30</td>
<td>2.8</td>
<td>0.55</td>
<td>48.5</td>
</tr>
<tr>
<td>2.70</td>
<td>6.4</td>
<td>0.50</td>
<td>50.5</td>
</tr>
<tr>
<td>2.10</td>
<td>10.0</td>
<td>0.50</td>
<td>53.9</td>
</tr>
<tr>
<td>1.60</td>
<td>15.4</td>
<td>0.50</td>
<td>57.2</td>
</tr>
<tr>
<td>1.30</td>
<td>19.8</td>
<td>0.50</td>
<td>59.2</td>
</tr>
<tr>
<td>1.10</td>
<td>23.4</td>
<td>0.50</td>
<td>evacuated</td>
</tr>
<tr>
<td>1.00</td>
<td>25.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.90</td>
<td>29.3</td>
<td>0.85</td>
<td>60.3</td>
</tr>
<tr>
<td>0.85</td>
<td>32.7</td>
<td>0.55</td>
<td>61.5</td>
</tr>
<tr>
<td>0.80</td>
<td>34.4</td>
<td>0.50</td>
<td>63.3</td>
</tr>
<tr>
<td>0.75</td>
<td>38.8</td>
<td>0.50</td>
<td>66.0</td>
</tr>
<tr>
<td>0.65</td>
<td>45.0</td>
<td>0.50</td>
<td>68.7</td>
</tr>
<tr>
<td>0.60</td>
<td>46.3</td>
<td>0.50</td>
<td>70.5</td>
</tr>
</tbody>
</table>

¹²¹ Eosin
(h) **Eosin on Zinc Oxide.**

A film of eosin on zinc oxide (1.05 mgms. on 0.1 gms. zinc oxide) was illuminated in 50 mms. oxygen. No pressure change was detectable.
DISCUSSION.

Experimental Discussion.

The technique involved in the gas phase experiments is that used in studies on the photo-oxidation of chlorophyll in solid films\textsuperscript{122}. Since the light from the 400W Osira mercury vapour lamp was filtered through several layers of soft glass, all wavelengths less than 3600 Å were removed. The active wavelengths involved are, then, presumably in the near ultra violet. Goodeve\textsuperscript{93} has shown that zinc oxide and titanium dioxide have threshold frequencies of 385 and 400 μm respectively.

Since the pressures of oxygen employed in the gas phase experiments were quite high (50 - 100 mms.) it was necessary that the temperature of the vessel and gauge should be kept as steady as possible. This was achieved by use of the thermostat system previously described, the temperature being constant to ±0.01°C. Since the bath round the reaction vessel was fairly large, a small electrically driven stirrer was employed to ensure good circulation of water from the constant head.

Care was taken to prevent the diffusion of any foreign vapour, oil or mercury, to the reaction vessel. A liquid air trap was always placed in position between/
between the vessel and oil-pump before evacuation was commenced, and the mercury manometers were cut off by a tap from the vessel while the pressure in the apparatus was still a few mms. In actual fact, mercury was shown to have no effect on the oxygen uptake, by incorporating a small trace in one film.

Before commencing a run, the film and reaction vessel were always "washed out" by admitting a few mms. of the appropriate gas or vapour and re-evacuating. Considerable adsorption of water vapour always occurred on admission of the vapour to the vessel, but no such adsorption was observed with oxygen.

Apiezon L grease was again used for all taps and joints in the apparatus.

In the case of the liquid phase experiments no rigid control of the temperature of the cooling water round the reaction tube was observed, since no pressure changes were being measured and the experiments were, on the whole, qualitative. It is very probable that variation in the temperature will affect the rate of decomposition of the hydrogen peroxide with resulting effect on the measured concentration, but since the variation was only of the order 0.5°C, this effect will be very small. The bubbling of oxygen through the suspension served to maintain the zinc oxide in reasonable agitation, although/
although a certain amount of solid settled to the bottom of the tube. For accurate quantitative work, more vigorous agitation of the suspension would be necessary, mechanical shaking of the tube being probably the most convenient method.

Discussion of Results.

Since the nature of the oxidising agent formed by the illumination of aqueous suspensions of photosensitisers of the zinc oxide type has been the subject of some discussion, the first experiments carried out were designed to identify this oxidising agent by the use of certain specific tests as described above.

Winther\textsuperscript{107} claimed to have detected ozone when dry zinc oxide is illuminated in oxygen, McMorriss and Dickinson\textsuperscript{96} state the agent to be nitrogen peroxide, while Baur\textsuperscript{87} and Egerton\textsuperscript{97} (inter al) favour hydrogen peroxide. The tests described above form a convenient method for distinguishing between these three possibilities. The starch-iodide and ferrous thiocyanate reagents are sensitive to all three compounds. Deniges\textsuperscript{3} test utilises the reducing power of hydrogen peroxide in alkaline solution and peroxide, is therefore specific for hydrogen\textsuperscript{A} while the sulphanilic acid - \(\alpha\)-naphthylamine reagent depends on \(a/\)
a diazotisation reaction with nitrogen peroxide and is therefore unaffected by ozone and hydrogen peroxide. This latter test is very sensitive to small traces of nitrogen peroxide, even at concentrations present in the atmosphere and care must be taken to prevent contamination. As can be seen from the results, the use of these reagents indicates hydrogen peroxide as the oxidising agent. Although ozone is stated to act as a reducing agent\textsuperscript{123} under certain conditions, the ferricyanide test is unaffected by it. Further, since no free oxidising agent was observed, at least in concentrations great enough to affect any of the reagents, when dry zinc oxide was illuminated, it seems very improbable that ozone is formed.

The identification of the agent as hydrogen peroxide is in agreement with the work of Blum and Spealman on fluorescein dyes, the illumination of aqueous solutions of these dyes leading to the formation of hydrogen peroxide.

Hydrogen peroxide was also formed, but in smaller quantities, when aqueous suspensions of zinc sulphide were illuminated (compare Egerton\textsuperscript{97}).

When suspensions of titanium dioxide were illuminated no free hydrogen peroxide was detected. On filtering the sample for analysis, some titanium dioxide/
dioxide in colloidal form passed through the filter. On adding this sample to thiocyanate reagent, a pink colour developed after some time (approximately 1 hour) indicating slow oxidation. Since the reagent itself, on standing, slowly develops a pink colour, two standards were prepared for comparison. The first standard was simply a portion of the reagent used in the test. To a further volume of the reagent was added a small quantity of un-illuminated titanium dioxide. The test solution developed a deeper shade of pink than the two standards indicating that an oxidising agent is formed by illumination of titanium dioxide suspension, but this agent cannot be "free" hydrogen peroxide since the development of the colour is very slow. In connection with this, an observation made by O. and A. Deny-Henault\(^\text{124}\) is of interest. These authors, examining the effect of solutions of hydrogen peroxide containing titanium dioxide on photographic plates, found that the plates were unaffected by the hydrogen peroxide until the titanium dioxide was saturated with hydrogen peroxide. They state that a compound TiO\(_2\)·H\(_2\)O\(_2\), stable in sulphuric acid, is formed. The hydrogen peroxide formed by the illumination of titanium dioxide suspensions will combine with the titanium dioxide to/
to form this stable compound and while it will still function, presumably, as an oxidising agent it will not be so strong or rapid as free hydrogen peroxide. Under certain conditions a volatile oxidising agent has been reported as detectable when titanium dioxide is illuminated in moist oxygen.

The increase in concentration of hydrogen peroxide, when small quantities of acetanilide are added to the suspension must be attributed to the inhibition of decomposition. The illumination of acetanilide solution in the absence of zinc oxide or of suspensions of zinc oxide in the acetanilide solution in the absence of oxygen did not yield any oxidising agent. In the case of caustic soda, it is not clear whether the increase in concentration is due entirely to inhibition of decomposition or to an additional mechanism involving OH′ ions. (see below).

The experiments with the flow system indicate that, for the production of hydrogen peroxide, zinc oxide, water and oxygen must be in close contact. The results obtained do not, however, exclude the possible formation of activated oxygen of a very short life. Indeed, it appears that the oxygen is a necessary factor and any mechanism which is based on the primary decomposition of water to form OH radicals and/
and subsequent formation of hydrogen peroxide without involving oxygen does not appear feasible.

Rabinowitch\textsuperscript{103} suggests that the primary step is the formation of hydrogen and OH radicals on the surface of the zinc oxide made possible by the assumption of large heats of adsorption of these radicals. The presence of oxygen is considered to remove the H atoms thus preventing the recombination of H and OH to water. This mechanism, however, does not give any explanation of the action of sensitisers in dry oxygen leading to the degradation of fibres.

The illumination of zinc oxide films in an atmosphere of dry oxygen leads to an uptake of oxygen. This "activated" adsorption of oxygen occurs only when the film is illuminated, ceasing immediately the light is cut off. The total amount of oxygen adsorbed is in considerable excess (see results) of any oxidisable matter which might be present in the zinc oxide and it appears quite conclusive that activated adsorption of oxygen is occurring.

The graphs obtained for the rate of oxygen uptake by zinc oxide against total oxygen uptake (figures 35 and 36) are rather similar to those obtained in the photo-oxidation of chlorophyll\textsuperscript{122}, an initial rapid decrease in rate being followed by a linear portion which/
which may be extrapolated to zero to give a measure of the total oxygen uptake. Only about 15% of the oxygen adsorbed can be removed by evacuation (see figure 36). This would appear to indicate that there are two stages in the adsorption of oxygen. The primary adsorption on illumination must be followed by a slow diffusion of oxygen (or oxygen ions) into the lattice where they are bound to the solid.

As the amount of dry oxygen adsorbed by a 0.1 gm. zinc oxide film (approximately 1.5 x 10^{-5} gms.) is insufficient to explain the amount of hydrogen peroxide detected in aqueous suspensions of 0.1 gm. zinc oxide (80 x 10^{-5} gms. after four hours), the liquid water must clear the surface of the "activated" oxygen, leaving the surface clear for the activation of more oxygen. In the presence of water, therefore, the slow diffusion of adsorbed oxygen into the solid must be completely prevented. Thus, the curve, showing the increase in concentration of hydrogen peroxide with time of illumination, should rapidly approach a maximum if saturation of the zinc oxide by oxygen was occurring. As far as the production has been followed in this work, no such maximum has been observed (see results). It is probable, however, that an equilibrium value will be approached due to the increased decomposition of the hydrogen peroxide in the/
the solution as it becomes stronger.

A further indication in support of the diffusion of the adsorbed oxygen into the solid is afforded by the rate curves for the adsorption of oxygen by a titanium dioxide film (figure 39). After the initial rapid decrease in rate, the rate becomes constant for a long period, and the oxygen uptake is only slightly reversed by evacuation. The constant rate of oxygen uptake is ascribed to the slow diffusion of adsorbed oxygen from the surface to the interior of the solid, leaving the surface clear for further adsorption. The amount of oxygen adsorbed by the present titanium dioxide sample is very much more (at least 20 times) that adsorbed by the zinc oxide sample.

In the case of zinc sulphide, while the rate curves and reversibility (figure 37) are somewhat more erratic, the same general remarks are applicable.

Finally, although the illumination of zinc oxide films in water vapour did not lead to the production of detectable quantities of hydrogen peroxide, this is probably due to the instability of the hydrogen peroxide under the present experimental conditions.

Theoretical Discussion.

Since the photochemical behaviour of photosensitive white pigments is very similar to that of photosensitive/
photosensitive dyes, a brief consideration of the main theories advanced to explain the tendering of textiles by the latter substances is of interest.

Although Kaustky's experiments with acriflavine and leuco-malachite green indicate that an active form of oxygen, capable of energy transferrence over short distances, is formed on illumination of acriflavine, some doubt exists as to whether this active agent might not be hydrogen peroxide from the residual moisture contained in the silica gel used as supporting solid. On the other hand, Egerton has shown that vat dyed nylon suffers as much degradation on illumination in dry as in moist air. Egerton deduces from this, and also from the fact that no degradation occurs in the absence of oxygen, that the mechanism of degradation involves the transfer of energy from the excited sensitiser molecule to oxygen, which can then act as a strong oxidising agent. This transferrence of energy leading to the activation of oxygen was also suggested by Kaustky as an explanation for the quenching of fluorescence by oxygen.

Bamford and Dewar, however, state that there is no relation between the quenching of fluorescence by oxygen and the sensitised tendering of textiles. In the mechanism suggested by these authors, the primary step involves the transfer of an electron from/
from an $\text{OH}^-$ ion to the excited sensitiser molecule.

$$D^+ + \text{OH}^- \rightarrow D^- + \text{OH}.$$  

The formation of hydrogen peroxide is explained by reaction of various intermediates, e.g.

$$D^- + \text{H}^+ \rightarrow \text{DH} \rightarrow \frac{1}{2} \text{D} + \text{HO}_2$$

$$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$$

In the absence of moisture, they consider the initial reaction to be:

$$D^+ + \text{Cell-H} \rightarrow \text{DH} + \text{Cell}.$$  

where $\text{Cell-H}$ represents cellulose.

The white pigments, when present in the fibre, can cause tendering in dry oxygen in a very similar manner. It seems probable that the mechanism in both cases will be, if not identical, rather similar in nature. It is difficult to envisage any reaction by which the excited pigment molecule could remove an H atom directly from the cellulose molecule.

With these pigments, tendering only occurs in dry air, if the pigment is in intimate contact with the textile fibre. Thus, if titanium dioxide or zinc sulphide are actually incorporated, by spinning or precipitation, in the fibre, degradation occurs in dry air. Separation of the pigment and fibre prevents this degradation. This is taken as a further indication of the formation of a short lived activated oxygen, as neither Bamford and Dewar's nor Rabinowitch's/
Rabinowitch's mechanism can give a satisfactory account of this effect.

Since degradation occurs in dry air only when the sensitiser and fibre are in close contact, it is clear that the activated oxygen can have no separate existence apart from the surface of the sensitiser. In the work carried out here, no volatile oxidising agent could be detected when dry zinc oxide was illuminated in the vicinity of starch iodide paper.

It seems reasonable to assume, therefore, that the action of the white pigments, and by analogy, the photosensitive dyes, involves the formation of an activated form of oxygen on the surface of the sensitiser.

Franck and Livingstone\textsuperscript{128} suggest, in the case of dyes, that the excited dye molecule $\text{RH}^*$ undergoes a tautomeric change into an active form $\text{HR}$, which, in the presence of oxygen, gives $\text{HO}_2\$, this radical being the active oxidising agent. It should be possible, however, if this mechanism were correct, to detect hydrogen peroxide in the absence of water. Further, this mechanism cannot be applied satisfactorily to the photo-sensitive pigments, $\text{ZnO}$, $\text{TiO}_2$ and $\text{ZnS}$, to explain their activity.

According to Weiss\textsuperscript{129}, the initial step in the majority of dye sensitised oxidations is reaction between/
between the excited dye molecule and the acceptor yielding the semi-quinone and the oxidised acceptor. The semi-quinone (or its leuco-base, DH$_2$ or DH$^-$) is then re-oxidised by molecular oxygen in a thermal process. This mechanism is described by the following reaction scheme.

\[
\begin{align*}
    \text{DH}^- + O_2 & = \text{DH} + O_2^- \\
    O_2^- + H^+ & = H_2O_2 \\
    \text{DH}^- + HO_2^- & = \text{DH} + HO_2^- \\
    HO_2^- + H^+ & = H_2O_2 \\
    2\text{DH} & = \text{DH}_2 + D
\end{align*}
\]

As can be seen this mechanism also explains the formation of hydrogen peroxide in aqueous solution. In some cases, reaction between the excited dye molecule and molecular oxygen may lead to the direct formation of O$_2^-$. This mechanism:

\[
\text{D}^* + O_2 = \text{D}^+ + O_2^-
\]

might have a possible application to the white pigments. The primary step, following the absorption of light, is the exciting of the electron to a higher energy level where it may be transferred to an oxygen molecule. It has been shown$^{126}$ that oxygen molecules in the gaseous phase can pick up electrons, produced electrically, to give O$_2^-$ ions. The possibility exists that they can also pick up electrons produced photochemically./
photochemically.

Bevan and Anderson\textsuperscript{113}, explain the decrease in semi-conductivity of zinc oxide films (at 500°C) in presence of oxygen, by the following mechanism:

\[
\begin{align*}
O_2 \text{ gas} & \rightarrow O_2 \text{ adsorbed} \\
O_2 \text{ adsorbed} + 4e & \rightarrow 2O^- 
\end{align*}
\]

They also point out that the assumption that zinc oxide is an impurity semi-conductor, may be at fault. As an alternative, they suggest that the conductivity could be explained by the exciting of electrons from the d-level in the Zn\textsuperscript{2+} ions, to the conduction band. The adsorption of oxygen could then trap the electrons from the conduction band by converting O atoms to O\textsuperscript{2-} ions at surface lattice points.

In the normal temperature range of oxide catalysis (c.200°C and upwards), the mobility of oxygen atoms in the lattice is believed to be quite small, although somewhat higher in the case of semi-conductors than in insulators. The slightly higher mobility in semi-conductors leads to the formation of lattice defects, which, at normal temperatures, are confined to surface layers. The importance of these defects lies in the fact that a large number of surface energy levels may be produced round the defects. Some of these energy levels may lie in the range required/
required (a) for electron exchange reactions and (b) for the facilitation of chemical bonding of molecules and atoms on the surface\textsuperscript{130}.

For example, work on the semi-conductivity of Cu\textsubscript{2}O\textsuperscript{131} has shown that oxygen adsorbed on Cu\textsubscript{2}O surfaces (c.200\degree C) undergoes a series of reactions:

\[ \text{O}_2 \rightarrow \cdot \text{O} \rightarrow \cdot \text{O} = \cdot \text{O} = \cdot \text{O} \]

The energy required for the initial excitation of electrons in the normal catalysis is derived thermally, but it is possible in the case of those oxides which absorb light of a suitable wavelength, that the necessary energy is obtained by the absorption of a light quantum at room temperature.

Although there is a great deal of evidence in favour of the intermediate formation of oxygen ions, as described above, in the case of the photo-formation of hydrogen peroxide in zinc oxide systems there is the difficulty that the production of hydrogen peroxide is increased in alkaline solution. It is difficult to envisage any mechanism between O\textsuperscript{-} and OH\textsuperscript{-} ions leading to the formation of hydrogen peroxide. If it is assumed, however, that the Na\textsubscript{2}O\textsubscript{2} acts as a stabiliser for the hydrogen peroxide, without occurring in the mechanism of the formation, this difficulty may be overcome.

It/
It is possible, therefore, to formulate two mechanisms based on (a) Weiss' theory of oxygen ions and (b) Kaustky's activated oxygen molecule.

(a) \[ \text{ZnO} + \text{hv} \rightarrow \text{ZnO}^* \]
\[ \text{ZnO}^* + \text{O}_2 \rightarrow \text{ZnO} \cdots \text{O}_2^- \]
\[ \text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2 \]
\[ \text{HO}_2 + e \rightarrow \text{HO}_2^- \]

(b) \[ \text{ZnO} + \text{hv} \rightarrow \text{ZnO}^* \]
\[ \text{ZnO}^* + \text{O}_2 \rightarrow \text{ZnO} \cdots \text{O}_2^* \]
\[ \text{ZnO} \cdots \text{O}_2^* + \text{H}_2\text{O} \rightarrow \text{ZnO} \cdots \text{O} \cdot \text{OH}_2 \]
\[ \text{ZnO} \cdots \text{O} \cdot \text{OH}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O}_2 \]

In mechanism (b) \( \text{O} \cdot \text{OH}_2 \) is the structure of the metastable form of hydrogen peroxide observed below \(-115^\circ \text{C}\), but it is possible that the conditions of adsorption serve to stabilise it, particularly in presence of NaOH, giving by rearrangement the normal H-O-O-H structure. This mechanism might be considered to be the reverse of that suggested for the decomposition of hydrogen peroxide at \( \text{Co(OH)}_3 \) particles. (see page 111).

The stability of the \( \text{HO}_2^- \) would also be increased in alkaline solution.

As mentioned above, the total amount of dry oxygen adsorbed by zinc oxide films is insufficient to account for the concentration of hydrogen peroxide formed/
formed in aqueous suspensions. It would appear that
the adsorption of oxygen leads to a saturation of the
surface with adsorbed molecules. In the presence of
water, these adsorbed molecules are removed in the
form of hydrogen peroxide, leaving the surface clear for
further adsorption of oxygen. Since the adsorption
of dry oxygen is incompletely reversible, some
"diffusion" of the oxygen must occur so that molecules
of oxygen become firmly bound in the lattice. The
removal of oxygen by water must therefore take place
before this irreversible "diffusion" can occur.

It is interesting to note that in the case of
titanium dioxide, were the reversibility of the oxygen
uptake is small, the quantity of oxidising agent
detectable is very much less than in the case of
ZnO and ZnS where the reversibility is somewhat greater.
This may indicate more rapid diffusion of oxygen into
the titanium dioxide grain or alternatively, as
suggested above, the formation of a stable compound,
$\text{TiO}_2\cdot\text{H}_2\text{O}_2$.

Finally, as mentioned above, in general the
behaviour of the white pigments, ZnO etc., is
undoubtedly similar to that of the photosensitive dyes.
Both lead to the formation of hydrogen peroxide under
suitable conditions, in presence of water and oxygen;
and to the degradation of textiles. In both cases,
the absorption of light may be considered to lead to the non-localisation of electrons. It is true that certain dyes e.g. acriflavine, do not show photo-conductivity as might be expected if the mechanism involving $O_2^-$ ions is correct, but in large molecules of this type, the upper electronic state, on the absorption of light, corresponds to a partial non-localisation of the $\pi$ electrons. A third point of similarity is the adsorption of oxygen by the pigments on suitable illumination. Many organic compounds of suitable unsaturation readily form hydroperoxides or other peroxide compounds with oxygen adsorption. Such compounds may be stable and of a fixed composition with the oxygen in a position which can be definitely located; in some cases the oxidation may be partially reversible e.g. haemoglobin, chlorophyll, rubrene, carotene, etc. Finally, in other compounds there is some evidence that the oxygen linkage is extremely mobile, the linkage being possibly through the $\pi$ electrons.

Although the experiments carried out with eosin did not show, within the limits of accuracy of the pressure change measurements, any definite oxygen adsorption which might be related to the mechanism suggested above for $H_2O_2$ formation, further experiments on this subject are clearly desirable.
SUMMARY.

1. Zinc oxide, titanium dioxide and zinc sulphide have been shown to adsorb dry oxygen on illumination with visible light. This adsorption is partially reversible.

2. Aqueous suspensions of zinc oxide, titanium dioxide and zinc sulphide produce an oxidising agent when illuminated in presence of oxygen.

3. The oxidising agent produced, in the case of zinc oxide suspensions, has been shown to be hydrogen peroxide.

4. Several mechanisms suggested to explain the degrading action of photosensitive dyes on textiles are discussed and their application to the activity of the white pigments considered.

5. An activated form of oxygen, either an excited molecule or an oxygen ion, is suggested as being formed on the illumination of the white pigments in dry oxygen. This activated oxygen is considered to be an intermediate in the formation of hydrogen peroxide in aqueous suspensions.
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