788. *The Nature of the Low-temperature Transition in Hydrogen Peroxide prepared by Discharge-tube Methods.*

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When a mixture of atomic hydrogen and molecular oxygen, or water-vapour dissociated in an electric discharge, strikes a liquid-nitrogen-cooled surface, a glassy deposit is formed. This, on warming, froths violently at about $-110°$ c; oxygen is evolved and a white opaque solid formed which on further warming melts to give a concentrated aqueous solution of hydrogen peroxide. Observations made on the stoicheiometry of these reactions, on the heat evolved at $-110°$, and on glass formation with concentrated aqueous solutions of hydrogen peroxide, show that the glassy deposit is probably a mixed glass of water and hydrogen peroxide containing occluded oxygen. This devitrifies at $-110°$, releasing the oxygen.

DURING the last twenty-five years many workers [1] have observed the formation of hydrogen peroxide when water vapour is dissociated in an electric discharge and the products are allowed to impinge on a cold surface, and when a mixture of molecular oxygen with atomic hydrogen from a discharge similarly encounters a cold surface. There is general agreement on the following facts. No hydrogen peroxide is formed at surfaces hotter than about $-100°$ c, below which the yield of hydrogen peroxide increases as the temperature decreases. In the case of water, the gases from the discharge tube show the spectrum of hydroxyl radicals but not that of hydrogen peroxide. When the condensing surface is colder than $-150°$ the product is a colourless glass. On being warmed it froths violently at about $-110°$ evolving oxygen, and leaves a white opaque solid which later melts to a concentrated aqueous solution of hydrogen peroxide. Winkler and his co-workers [2] obtained a glassy deposit with the same properties when hydrogen peroxide vapour was similarly dissociated in an electric discharge and brought against a cold surface. Thus, it seems that the same glassy deposit can be obtained, under the correct conditions, from dissociated water-vapour, dissociated hydrogen peroxide vapour, or a mixture of atomic hydrogen and molecular oxygen.

Our object was the elucidation of the nature of the glassy deposit and of its change at $-110°$. Three types of measurement have been made: (i) determinations of the stoicheiometry of the reaction, (ii) measurement of the heat effect accompanying the process at $-110°$, and (iii) experiments on supercooling and glass formation with concentrated aqueous solutions of hydrogen peroxide.
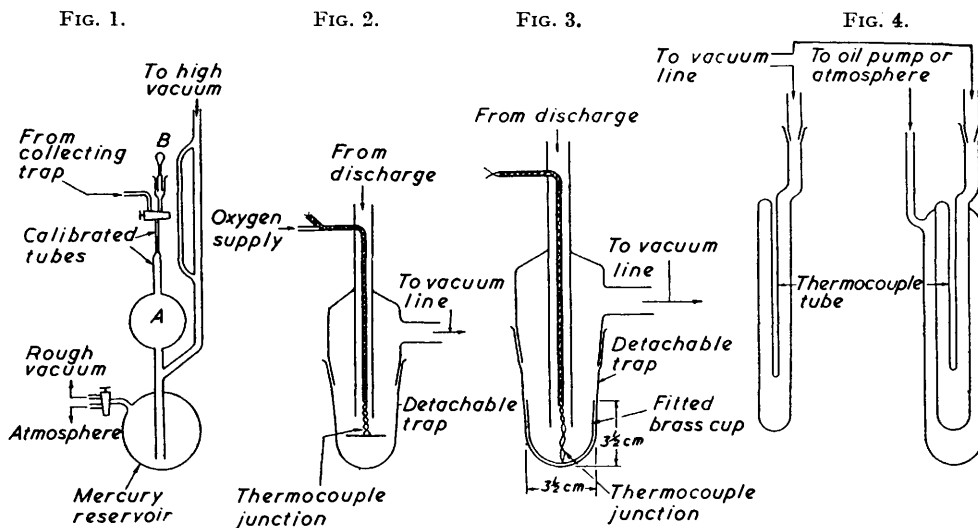
EXPERIMENTAL

The apparatus was of conventional design. The discharge tube was of 3 cm. tubing, with a total distance of 1 m. between the water-cooled aluminium electrodes. In order to minimise recombination of radicals, which is known to be greatest near the electrodes, these were each 25 cm. distant from the gas-stream; for the atomic hydrogen experiments, it was also necessary to coat the walls of the discharge tube with phosphoric acid. A transformer giving 1500 v at 200 mA was fed from the mains through a " Variac " transformer, and conditions in the discharge were controlled by adjustment both of the flow-rate of gas and of the voltage. The collecting trap, cooled with liquid nitrogen, was placed as close as possible to the discharge tube. For the water-vapour experiments, water vapour at a pressure of about 1 mm. was passed through the discharge at rates of up to 1 g./hr., and for the atomic hydrogen experiments hydrogen from a cylinder was passed through at about 0·2 mm. pressure at about 1 l./hr. Oxygen from a cylinder was admitted, so as to mix with the atomic hydrogen just as the gas stream impinged on the cold surface, at a rate such that the proportions $H_2 : O_2$ were 4 : 1. Maximum yields of 60% (about 0·5 g. of H_2O_2/hr.) were obtained in the water experiments, and of 75% (about

[1] For full references see Schumb, Satterfield, and Wentworth, " Hydrogen Peroxide," Reinhold, New York, 1955.
[2] Batzold, Luner, and Winkler, *Canad. J. Chem.*, 1953, **31**, 262.

0·2 g. of H_2O_2/hr.) in the atomic hydrogen experiments. These yields relate respectively to the water and oxygen used.

For both reactions the products and reactants were analysed. The water used and total liquid product formed were weighed by weighing the relevant traps, and the amounts of hydrogen and oxygen used were gauged by observations of the pressure in the globes containing them. Gases uncondensed in the collecting trap could be collected for analysis by backing the diffusion pump with an initially evacuated 20 l. globe, of accurately determined volume. Uncondensed gas could only be thus collected for short periods, however, since the pressure soon became too high for the satisfactory operation of the discharge. Gas evolved during the warming of the condensed product was collected in the graduated volume A (Fig. 1). The percentage of oxygen was then found by bringing the gas into contact with white phosphorus in the vessel B. The oxygen content of the gas from the 20 l. globe was determined by transferring a sample to A. Hydrogen peroxide was estimated by titration with permanganate.

FIG. 1.   FIG. 2.   FIG. 3.   FIG. 4.

In the first experiments on the heat evolution from the glassy product, a U-tube trap was used, each arm of which contained a cylinder of copper foil to which was soldered one junction of a copper–constantan thermocouple. The product condensed on the first cylinder, and when the U-tube was allowed to warm slowly the plot of the thermocouple potential against time furnished a differential warming curve in which a peak corresponded to evolution of heat by the glassy deposit. In later experiments the deposit was obtained on a light copper disc suspended within a cylindrical trap (Fig. 2). In most of the work, however, a cylindrical trap was used (Fig. 3) which had been shrunk on a brass cup $\frac{1}{2}$ mm. thick and weighing about 50 g. This was coated with Bakelite varnish (as were the copper supports for the thermocouples in the other traps) and a five-junction thermocouple, similarly coated, was sealed with the same material into small holes in the base of the cup. For the warming process the traps were surrounded with a mechanically stirred bath of light petroleum fitted with a small heating coil and initially cooled with liquid nitrogen. For direct warming curves the reference thermocouple junctions were kept in liquid nitrogen or ice–water, while for differential warming curves they were in the bath of light petroleum. The thermocouple e.m.f. was measured with a Cambridge vernier potentiometer. For the differential experiments the bath temperature was measured by means of a second thermocouple whose cold junction was in liquid nitrogen. In Fig. 3 the trap with the brass cup is connected to the discharge tube with water vapour passing through; in Fig. 2, the trap with the suspended disc is arranged for the atomic hydrogen–molecular oxygen type of experiment. In fact both types of trap were used for both types of experiment.

The traps used in the supercooling experiments with concentrated hydrogen peroxide solutions were as shown in Fig. 4. A single-junction thermocouple was placed in the re-entrant

tube. Slow warming was carried out as in the discharge-tube experiments with a bath of well-stirred light petroleum fitted with a heating coil. With the jacketed trap the rate of cooling or heating could be varied by adjusting the pressure of air in the jacket. Before any experiment, the traps were left full of fuming nitric acid at 80° c for several hours, and then with concentrated hydrogen peroxide solution for a similar period. The final washing was with distilled water, re-distilled from alkaline permanganate, which was also used for diluting the samples. Rigorous precautions were taken to exclude dust. " High test peroxide " was used, which contained 86·5% (w/w) of hydrogen peroxide.

RESULTS

Stoicheiometry of the Reaction.—In both the water and the hydrogen–oxygen reactions the appearance of the solid deposit was the same. There was always a ring of ice on the vertical tube from the discharge, inside the trap, while on the walls of the trap itself was a colourless, glassy deposit. When enough of the deposit had been collected, the flow of gas through the discharge was stopped, and the trap allowed to warm with the apparatus still evacuated; the solid underwent the changes described earlier.

FIG. 5. *Warming curve for discharge product with water, observed with the five-junction thermocouple between the trap and liquid nitrogen.*

FIG. 6. *Differential warming curve for discharge product with hydrogen–oxygen, observed with the five-junction thermocouple between the trap and the warming bath.*
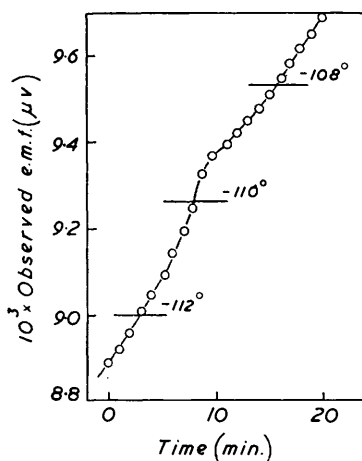
Product contains 0·61 g. of H_2O_2.
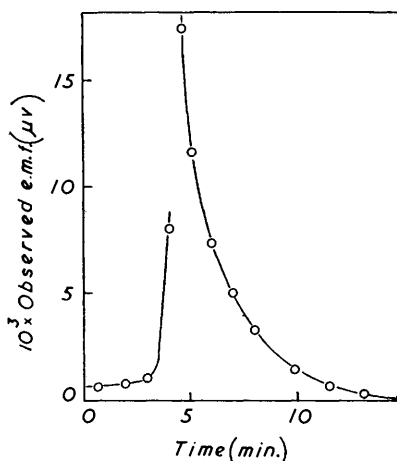
Product contains *ca.* 1·7 g. of H_2O_2.

If the trap itself was removed before the ice on the vertical tube had melted, the concentration of the peroxide solution was usually about 75% (occasionally 80%). In the analytical work now discussed this ice was never allowed to melt, so that the following relates to the actual deposit. The gross composition was determined by collecting and analysing the gas (oxygen) evolved during and after the frothing; by finding the total weight of hydrogen peroxide solution left in the trap; and finally analysing for hydrogen peroxide. In a typical experiment with the water discharge, $1·0 \times 10^{-3}$ mole of oxygen was produced during the warming of the trap (no hydrogen was formed) and this was then found to contain $3·0 \times 10^{-3}$ moles of hydrogen peroxide and $1·9 \times 10^{-3}$ moles of water, thus giving a H : O ratio for the deposit of 0·99. In six experiments, the values of the H : O ratio were 0·99, 1·06, 1·00, 1·09, 1·22, and 1·10. Thus it appears that its approximate gross composition is $(OH)_n$. The molar percentage yields of hydrogen peroxide from the glassy deposit in the same six experiments were 61, 55, 65, 60, 42, and 58. In two similar experiments with the atomic hydrogen–oxygen system, the H : O ratio for the glassy deposit was 1·00 and 1·03.

Heat Effect accompanying the Change at $-110°$.—Many measurements were made of the heat evolution accompanying the change at $-110°$. In some cases the temperature–time curve was determined when the glassy deposit was allowed to warm from liquid-nitrogen

temperature to room temperature. An evolution of heat was then shown by an increase in the slope of this curve or by a small peak. In other experiments differential heating curves were obtained in which heat evolution was shown by a peak. Typical curves are shown in Figs. 5 and 6. Rough estimates of the heat evolved were obtained from these curves, the warming rate of the cup or disc around $-110°$ in excess of that at temperatures just below this region being assumed to be due to the heat evolved by the process at $-110°$. These determinations were made on the glass from both the water discharge and the atomic hydrogen–oxygen experiments, and there was no discernible difference between the types of heating curves, the temperatures of heat evolution (always about $-110°$) or the actual heat evolutions, in either case. In six determinations the heat evolution was within the limits 1—2 kcal./mole of hydrogen peroxide finally present.

It is realised that little quantitative significance attaches to these figures. The great difficulty in the experiments was that the conditions of good thermal contact between the liquid-nitrogen bath and condensing surface which are required for the production of a good yield of glassy deposit are incompatible with the condition of good insulation from the surroundings which is needed for an accurate determination of the subsequent heat effect. In the brass-cup experiments it was not difficult to obtain a good yield, and the heat could be quite accurately measured with the five-junction thermocouple—but much heat must then have been lost to the surroundings. On the other hand, conditions in the suspended-disc
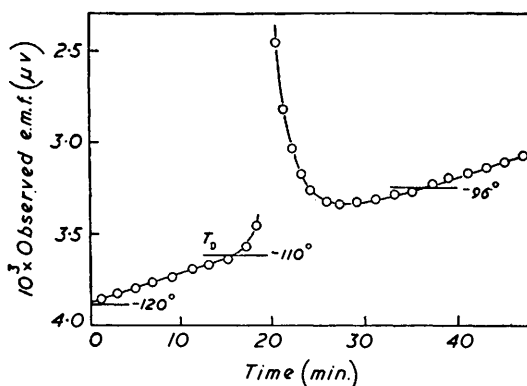

FIG. 7. *Warming curve for the glass produced from* 16·9 g. *of solution containing* 54·2% *of* H_2O_2 *observed with the single-junction thermocouple between the trap and ice–water.*

experiments were much more nearly adiabatic, but for this reason only a small amount of deposit could be obtained on the disc. Again, the temperature rise was less accurately determinable, because of the impracticability of using a thermocouple with more than one junction. The figure of 1—2 kcal./mole of hydrogen peroxide thus certainly represents a lower limit for the heat effect, but taking all factors into account we consider that the true figure cannot be more than twice as great.

In a few cases the trap was cooled again to liquid-nitrogen temperatures after the process at $-110°$ had occurred, but before the product had melted. When warming again took place there was never any heat evolution at $-110°$.

It seems that the process at $-110°$ is an irreversible phase transition rather than a chemical reaction. The obvious further conclusion that it is the devitrification of a glass was tested in the following experiments.

Glass Formation with Concentrated Hydrogen Peroxide Solutions.—Preliminary experiments showed that a stable glass could be formed by rapid cooling with liquid nitrogen of aqueous solutions containing 45—80% of hydrogen peroxide by weight. Near these limits the glass crystallised fairly rapidly, and outside them no glass could be formed under the conditions used.

Warming curves were observed for solutions falling within the above range after rapid cooling with liquid nitrogen. There was always a well-marked evolution of heat at about $-110°$ (Fig. 7). More detailed work showed that heat evolution might start anywhere within the range $-108°$ to $-112°$, and that the precise temperature was not regularly related either to the composition of the solution (solutions with 54·2, 56·4, and 67·8% of hydrogen peroxide were used) or to the rate of warming before the change, which varied from 0·3 to 2·0 deg./min. Moreover, the heat evolution at or near $-110°$, which will be termed T_D (the devitrification

temperature) occurred regardless of the time (from 0 to 26 hr.) for which the system had been kept at liquid-nitrogen temperature. The warming curve of Fig. 7 corresponded with a heat evolution of about 1 kcal., about 20% less than the heat of fusion estimated for the actual weight of hydrogen peroxide solution used.

Glass formation could also be brought about by slow cooling initially, followed by rapid chilling. Such experiments were usually done with the 60% solution, for which the glass seems to have maximum stability. Cooling curves for this solution showed an arrest and slight rise of temperature at a mean temperature, T_a, some 6° below the solidification temperature, T_s, for that solution. (By T_s we mean the temperature at which, according to the phase diagram, solid should first appear for the solution in question.) Below T_a the supercooled liquid was extremely viscous. Further slow cooling caused visible crystallisation at a temperature T_c; this was followed by a rise in temperature to the solidification temperature T_s. T_c varied somewhat for a given solution, from one experiment to another, but was usually about 20° below T_a. If slow cooling in the jacketed trap to T_a was followed by rapid cooling brought about by admission of air to the jacket, it was possible to pass through T_c without crystallisation's occurring, as was shown both by visual observation and by the lack of heat evolution at T_c.

FIG. 8. *Cooling curve of 12·1 g. of a 61·1% H₂O₂ solution observed with the single-junction thermocouple between the trap and ice–water.*
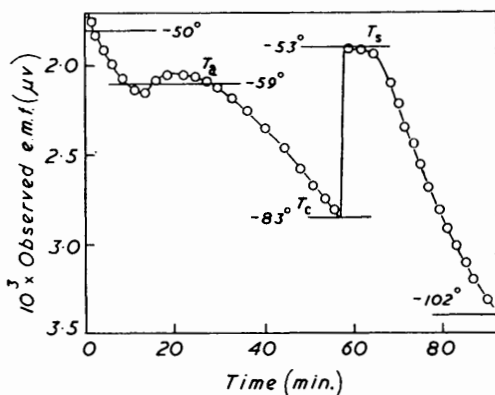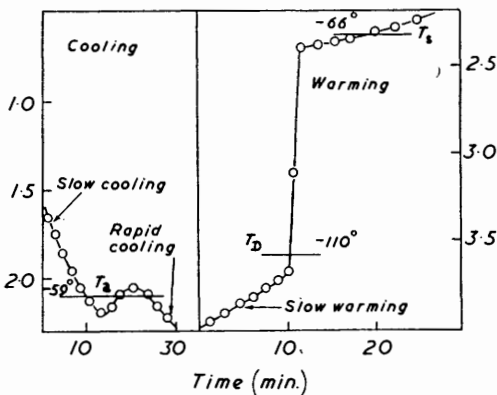
FIG. 9. *Cooling and warming curves for 9·6 g. of 63·2% H₂O₂ solution, observed as in Fig. 8.*

Subsequent warming from liquid-nitrogen temperatures then gave the usual heat evolution at T_D, and ultimately normal melting at T_s. In these cases, however, the product looked less glassy than that obtained by rapid chilling from room temperature, and the devitrification at T_D took place more gradually. Thus the solid may have been less completely vitreous in these cases. Solutions cooled slowly to T_c, which then crystallised and were further cooled to liquid-nitrogen temperature, showed no heat evolution at T_D on heating, but normal melting at T_s. Solutions cooled slowly below T_a, but not further, passed directly into the liquid state on warming, with arrests at neither T_a nor T_s. This behaviour is summarised in Figs. 8 and 9, and also in the Table where + indicates an arrest or peak in the temperature–time curve.

	T_a	T_c	T_s		T_D	T_s
Slow cooling	+		Heating from just below T_a			
Slow cooling	+	+	Heating from −180°			+
Slow cooling	+		Rapid cooling to −180° followed by heating		+	+
Rapid cooling to −180° followed by heating					+	+

Besides this main series of experiments on the 60% solution, observations were made on solutions with 50% and 70% of hydrogen peroxide. For 70% hydrogen peroxide the cooling curves showed a slight inflection at T_a, but crystallisation then took place almost immediately. For 50% hydrogen peroxide it was possible to obtain a glass by slow cooling through T_a followed by rapid cooling, but the process at T_D on subsequent warming was much more gradual than for the 60% solution, indicating that the 50% " glass " may have been largely crystalline. The lower stability was also shown by the fact that crystallisation often occurred when the glass was slowly warmed from a temperature just below T_a.

DISCUSSION

The governing factor in both the water discharge and the atomic hydrogen–oxygen reactions is clearly the ease with which OH radicals [or $(OH)_2*$ collision complexes] can be condensed or adsorbed on a cold surface. (The OH radicals would be formed in the atomic hydrogen experiments by the reactions $H + O_2 \longrightarrow HO_2$; $H + HO_2 \longrightarrow 2OH$.) Solid OH would presumably have a hydrogen-bonded structure and hence physical properties not very different from those of ice and solid HF. It might therefore be expected to condense at $-80°$, even at the small pressure of the discharge tube. At this temperature, however, no H_2O_2 is formed. It may be that any OH which condenses at $-80°$ has an average thermal energy large enough for the rapid occurrence of the reaction $2OH(c) \longrightarrow O_2(g) + H_2(g)$, whereas at lower temperatures this is less likely.

Granted that the reaction involves the condensation of OH, three possible mechanisms can be distinguished: (*a*) OH radicals condense, and at $-110°$ react with each other; (*b*) OH radicals condense, and subsequently react with OH or H from the gas-phase to give H_2O_2 and H_2O; (*c*) OH radicals or $(OH)_2*$ collision complexes condense, and almost at once react with each other to give H_2O_2, H_2O, and O_2.

In each case the possibility of hydrogen peroxide's decomposing in the solid state at and above $-110°$ should be considered, in order to explain the observed evolution of oxygen from the solid.

Mechanism (*a*) can be excluded at once, because of the small heat evolution at $-110°$; the process $2OH \longrightarrow H_2O_2$ would evolve more than 50 kcal./mole.

Mechanism (*b*) has been suggested [3] in order to account for the reported fact that the concentration of the hydrogen peroxide solutions obtainable by these reactions never exceeds about 65% by weight. If the reactions $OH(c) + OH(g) \longrightarrow H_2O_2$ and $OH(c) + H(g) \longrightarrow H_2O$ had an equal probability of occurrence, an equimolar mixture of water, and hydrogen peroxide should result, containing about 65% of H_2O_2 by weight. In our experiments, however, the initial composition of the glassy deposit was approximately $(OH)_n$, which appears to exclude this mechanism. We always observed a ring of ice on the warmer inlet-tube of the liquid-nitrogen-cooled trap, which may have come from undissociated water-vapour, or from gas-phase reactions. We took care never to allow this ice, on melting, to mix with the product in the trap which then gave concentrations of hydrogen peroxide as great as 80%. Such a separation seems not to have been made by previous workers.

There remains mechanism (*c*). Jones and Winkler [4] explained the identity of the products from the water and atomic hydrogen reactions on the basis of collision complexes $(OH)_2*$, formed by gas-phase reaction in both cases, and existing as an equilibrium mixture of two isomers. This equilibrium mixture could be stabilised at a sufficiently cold surface, when form *A* would give solid hydrogen peroxide and form *B* would decompose to water and oxygen.
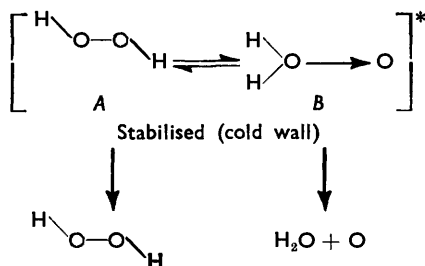
In either case there is the further possibility that some of the hydrogen peroxide may decompose while still solid, to yield more water and gaseous oxygen. On mechanism (*b*)

[3] Rodebush, Keizer, McKee, and Quagliano, *J. Amer. Chem. Soc.*, 1947, **69**, 538.
[4] Jones and Winkler, *Canad. J. Chem.*, 1951, **29**, 1010.

the observed evolution of oxygen could only be explained by such decomposition. Jones and Winkler also suggested that form B of the collision complex might give, on stabilisation, an isomer of hydrogen peroxide which would decompose to water and oxygen at about $-110°$. On the other hand, if mechanism (c) operates any oxygen formed at the same time as the hydrogen peroxide and water might be occluded in the solid, and then released at a higher temperature. We believe this to be the case. It is hard to see why solid hydrogen peroxide should decompose, when it is a quite stable liquid at a much higher temperature. The source of the necessary activation energy is not obvious, although enough OH radicals might still be present to act as chain initiators. In addition, the thermal decomposition of hydrogen peroxide is exothermic to the extent of about 23 kcal./mole, and much less heat than this was evolved during the frothing. Jones and Winkler's isomer would presumably evolve even more heat on decomposition.

Thus we believe that Jones and Winkler's mechanism is essentially correct, but we further suggest that the glassy deposit is a mixed glass of water and hydrogen peroxide containing occluded oxygen molecules. At a more or less definite temperature the glass will devitrify, and the oxygen be released. The first process will evolve a few kcal./mole (approximately the heat of fusion) and the second process none, in agreement with our observations. Moreover, the same mixed glass could result from a condensation or adsorption of hydroxyl radicals rather than $(OH)_2$* collision complexes; we shall now examine this alternative and simpler hypothesis.

Any reaction in a deposit of OH must take place almost immediately, since we observed no heat evolution between liquid-nitrogen temperature and $-110°$. As each layer of OH was deposited, the heat of condensation would be available to initiate reaction in the previous layer, and the heat of reaction could then initiate further reaction, the excess
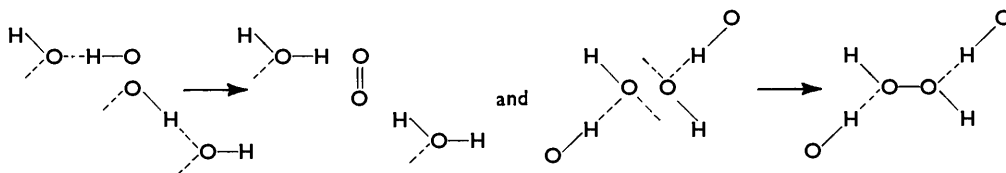
being conducted away by the cooling bath. The reaction products would be randomly distributed, and might include some unchanged OH radicals. Glasses are well known to be formed when vapours impinge on a well-cooled surface, but the present case is possibly unique in that the glass finally obtained may arise from chemical reactions subsequent to the initial deposition of such a disordered layer.

It is interesting to speculate on the reaction mechanism in terms of the probable structure of the initial deposit. Both ice and solid hydrogen peroxide have hydrogen-bonded structures [5] with a tetrahedral environment for the oxygen atoms, the structure of hydrogen peroxide being considerably more compact than that of ice. We may therefore suppose an OH glass to have its oxygen atoms on a tetrahedral lattice, joined to each other by hydrogen bonds. There will only be enough hydrogen atoms for half the maximum number of hydrogen bonds possible in such a structure, and it is the distribution of these hydrogen atoms which affords the randomness in the structure. In addition there will be local distortions and defects. Some oxygen atoms will thus be near one another, others further apart, and others will have hydrogen atoms between them. Only small displacements will therefore be needed to give either of the three molecules O_2, H_2O, and H_2O_2, and in the light of the previous remarks these are probably formed almost as soon as the hydroxyl radicals find their places in the glass. In terms of hydrogen-bonded groups, such reactions might be written as in the annexed scheme. Free oxygen atoms

[5] Bernal and Fowler, *J. Chem. Phys.*, 1933, **1**, 515; Abrahams, Collin, and Lipscomb, *Acta Cryst.*, 1951, **4**, 15.

or OH radicals might also migrate through the glass. All these processes should require a minimum of movement and activation energy. It is possible on this basis to account roughly for the observed yields of hydrogen peroxide from the glassy deposit, if we assume that this all comes from reactions between groupings H–O O–H. The chance that a given pair of oxygen atoms have no hydrogen between them is $3/4 \times 3/4 = 9/16$ if there is uniformly tetrahedral co-ordination. Thus the limiting yield of hydrogen peroxide might be about 9/16 or 55%, as compared with the observed yields of 42—65%. The picture is grossly over-simplified—it would require molecular oxygen to be formed only from migrant oxygen atoms and never by reaction between adjacent hydroxyl groups—but it may still be suggestive.

Jones and Winkler found that no hydrogen peroxide was formed when the trap temperature was above $-120°$, while below this temperature the yield increased rapidly. This variation with temperature is no doubt due to the different temperature coefficients of the reactions involved. They also observed that oxygen was evolved from the products only when the trap temperature was below $-150°$, and that the amount evolved then increased as the temperature decreased. Moreover, in their experiments the total weight of oxygen evolved from a product collected at a given temperature was proportional to the time for which the product was collected, and was independent of the way in which it was warmed to room temperature. The latter observation is strong evidence for the view that the oxygen is formed at the same time as the hydrogen peroxide and water; if it arose from the subsequent decomposition of the hydrogen peroxide, or from any other reaction within the glassy deposit at any stage of the warming, the quantity formed should be determined by the warming procedure. Jones and Winkler explained the variation in oxygen yield with temperature in terms of a shift in the equilibrium between the forms A and B of the collision complex. Alternatively, if the oxygen is formed by reaction within a glassy layer of OH as the latter is deposited, it will be retained within the glass the more readily the lower the temperature. The fact that the ratio H : O for the glassy deposit was equal to or slightly greater than unity in our experiments may then mean that most of the oxygen was thus retained at liquid-nitrogen temperatures, but that at the progressively higher temperatures of Jones and Winkler's experiments increasing amounts were lost as the reaction took place.

After reaction has occurred, the glass will consist of water, hydrogen peroxide, and oxygen molecules and perhaps also a few trapped hydroxyl radicals and oxygen atoms, randomly disposed, but with the oxygen still essentially on a tetrahedral lattice and still bonded to the neighbouring atoms either by covalent bonds or by hydrogen bonds. Ice and solid hydrogen peroxide are reported not to give solid solutions [6] but an unstable compound $H_2O_2,2H_2O$. Also, whenever solid hydrogen peroxide separates from its aqueous solutions much of the liquid is included in the crystals, often very tenaciously. It is therefore reasonable that water and hydrogen peroxide should form a mixed glass, especially when the component molecules are formed by chemical reaction *in situ*. Devitrification of a glass may in principle occur at any temperature; in the present case this will no doubt be aided by the presence of included oxygen molecules. When this happens, the crystalline product will presumably be the compound $H_2O_2,2H_2O$, intimately mixed with excess of solid H_2O_2. The entrapped oxygen will be released, mostly during devitrification, but perhaps partly at higher temperatures. The heat of devitrification will be a fraction of the heat of fusion, its actual magnitude depending on the proportion of the glassy deposit which was actually vitreous and the proportion already crystalline. The release of the occluded oxygen, on the other hand, should involve little or no heat effect. Thus the total heat evolved would be of the same order of magnitude as that observed in our experiments.

It is significant that a mixed glass of water and hydrogen peroxide, devitrifying at about the temperature of the frothing in the glassy deposit, can also be formed by rapid

[6] Foley and Giguère, *Canad. J. Chem.*, 1951, **29**, 123.

cooling of concentrated aqueous solutions of hydrogen peroxide. De Nordwall and Staveley [7] have recently reported experiments in which a number of pure compounds were obtained as glasses both by condensation of the vapour on a liquid-oxygen- or liquid-nitrogen-cooled surface, and by rapid cooling of the liquid. They deduced the heat and temperature (T_D) of the subsequent devitrification from warming curves. For a given compound, T_D was the same whether the glass was produced from the vapour or from the liquid, and it was markedly insensitive both to the previous history of the sample and to the percentage of it in the vitreous condition. This is in striking agreement with our observations. de Nordwall and Staveley discuss their results in terms of a theory of homogeneous nucleation. In more qualitative language we may say that glass formation is possible if the liquid can be cooled rapidly enough through the region in which the rate of nucleation is appreciable into the region in which molecular movements have become difficult. This is the region of the so-called glass-transformation temperature, T_g. When the resulting glass is warmed, devitrification may occur at a temperature T_D somewhat above T_g. For such systems, therefore, there is both an upper and a lower crystallisation temperature. The upper temperature T_c (almost always lower than the true melting-point) is determined by the rate of nucleation, while the lower temperature T_D is determined by the ease of the translational and orientational movements of the molecules. In the latter case existing nuclei can grow sufficiently for crystallisation to occur.

These considerations apply to hydrogen peroxide solutions, whose tendency to supercool has often been noticed. Such pronounced supercooling has been attributed to the adsorption on impurities of the growing (homogeneous) nuclei, whose decomposition is thereby catalysed.[8] The fact that glasses are formed only from hydrogen peroxide solutions with 45—85% of peroxide can then be explained as follows. The phase diagram for the H_2O_2—H_2O system [6] shows two eutectics, at about 45% and 55% of H_2O_2, with a shallow maximum between at the composition $H_2O_2,2H_2O$. Below 45% of peroxide, ice separates as the solid phase, there is no " self-scavenging " tendency, and sufficient supercooling for glass formation is impossible. Above 45% of H_2O_2, the solid phase is either H_2O_2 or the compound $H_2O_2,2H_2O$, and the self-scavenging effect will operate. Above about 85% of H_2O_2, however, the solidification temperature is so high that the supercooling necessary to reach the temperatures around T_g will be excessive, and so for this different reason a glass may not form.

The facts that the devitrification temperature is virtually the same for the glassy deposit as for glasses formed by rapid cooling of hydrogen peroxide solutions, and that this temperature is insensitive to both concentration and the rate of heating, must mean that the ease of atomic and molecular movements in the glass increases very rapidly as temperature increases in the critical region, so that devitrification always occurs at about the same temperature regardless of other factors. In both cases, crystallisation nuclei will be present—nuclei which have been " frozen-in " in the case of the glasses formed by rapid cooling, and nuclei formed by the randon positioning of the hydroxyl radicals in the case of the glassy deposit. From our rough assessment of the heat released on devitrification of the glass, both in the quenching and in the discharge-tube experiments, it seems that a much greater proportion of the glass was actually vitreous than was the case with the glasses of pure compounds obtained by de Nordwall and Staveley. This is hardly surprising in view of the more exacting geometrical requirements for the formation of separate crystalline phases in the hydrogen peroxide–water case.

The small hump at T_a, observed when hydrogen peroxide solutions are cooled slowly, is probably due to the formation of a few crystals which, owing to the operation of the self-scavenging effect, cannot grow further. This does not prevent the subsequent formation of a glass when the system is cooled rapidly after the hump T_a has been passed. It must, however, be remembered that transformations in this system are exceptionally

⁷ de Nordwall and Staveley, *Trans. Faraday Soc.*, 1956, **52**, 1207.
⁸ Cooper and Watkinson, *ibid.*, 1957, **53**, 635.

sluggish; it is stated [8] that a supercooled solution of hydrogen peroxide can be seeded with small crystals of hydrogen peroxide without crystallisation being induced.

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