

# SOME ASPECTS OF THE CATALYTIC DECOMPOSITION OF CONCENTRATED HYDROGEN PEROXIDE BY SILVER

## PART 2.—ELECTRICAL CONDUCTIVITY AND pH OF SOLUTIONS OF HYDROGEN PEROXIDE CONTAINING SILVER

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Measurements of the pH and electrical conductivity of concentrated hydrogen peroxide solutions (20-80 % w/w) containing silver dissolved from the metal are reported. The results are consistent with the view that silver dissolves in hydrogen peroxide with the formation of the ions  $\text{Ag}^+$  and  $\text{HO}_2^-$ . The accelerating rate of decomposition which occurs when such a solution becomes saturated with these ions results from the continuous precipitation of particles of silver as decomposition proceeds. The changes in pH and electrical conductivity of saturated solutions have been measured during the course of decomposition. The results show that the ions  $\text{Ag}^+$  and  $\text{HO}_2^-$  are removed from solution as the peroxide concentration falls, the amounts remaining in solution being just sufficient to satisfy the limiting ionic product  $[\text{Ag}^+][\text{HO}_2^-]$ , which decreases progressively with the fall in peroxide concentration.

The behaviour of mixtures of hydrogen peroxide and water has been studied by Wynne-Jones who has reported<sup>1</sup> a method for measuring the pH of such mixtures using the glass electrode. Wynne-Jones has also shown<sup>2</sup> that ionization takes place essentially according to the reaction



and has reported values for the ionic product,  $[\text{H}^+][\text{HO}_2^-]$ .

In part 1, values were reported<sup>3</sup> for the rate of solution and solubility of silver in concentrated solutions of hydrogen peroxide. It was postulated that the criterion for the onset of rapid catalysis in these solutions is the attainment of the solubility product of argentous hydroperoxide ( $\text{AgO}_2\text{H}$ ). Part 2 is concerned with the measurement of electrical conductivity and pH for such solutions, further evidence being provided as to the nature of the ions produced when silver dissolves in hydrogen peroxide.

It was also shown in part 1 that the rate of solution of silver in concentrated hydrogen peroxide (> 50 % w/w) is diffusion-controlled and that the rate of decomposition of the hydrogen peroxide falls as saturation is approached. Once saturation is attained, however, the decomposition rate rises quickly and small particles of silver are observed in the solution. A study of such solutions is rendered difficult by the accelerating rate of decomposition and consequent rise in temperature. It was thought likely that the increased rate of decomposition was due to the increase in catalytic surface provided by the particles of precipitated silver and in the experiments described here it was found possible to maintain temperature control by filtering off the particulate silver at suitable intervals. Thus, using this technique, it was possible to measure the conductivity and pH of solutions of hydrogen peroxide saturated with silver during decomposition from concentrated hydrogen peroxide to water.

## EXPERIMENTAL

## UNSATURATED SOLUTIONS

The apparatus<sup>3</sup> which was designed to study the solution of silver under controlled conditions was used in the present investigation. A cylinder of fine silver (99.97%) 1 cm long and 1 cm in diameter was attached to an electric stirring motor and rotated at 5000 rev/min whilst immersed in 400 ml of freshly distilled hydrogen peroxide maintained at about 2°C. At suitable time intervals the silver cylinder was withdrawn from the solution and weighed. The hydrogen peroxide concentration, pH and conductivity of the test solution were then determined as desired. Hydrogen peroxide concentrations of about 20, 30, 50, 60, 70 and 80 % w/w containing various amounts of dissolved silver were examined in this way. Owing to the decomposition which occurs whilst silver is dissolving in hydrogen peroxide (up to 5 % w/w in some of these experiments) it was not possible to carry out a series of pH and conductivity measurements at exactly the same hydrogen peroxide concentration.

## SATURATED SOLUTIONS

For the experiments with saturated solutions the procedure was modified as follows. 100 ml samples of distilled hydrogen peroxide were used, the samples being contained in a 250 ml flat-bottomed flask as described previously.<sup>3</sup> The silver catalysts consisted of short lengths (0.100 ± 0.002 in.) of 14 s.w.g. wire (0.080 in. diam.). The solution was magnetically stirred and maintained at about 2°C with an ice + water bath. The rate of decomposition of the hydrogen peroxide was measured when required by use of a nitrometer burette.

The piece of silver wire was immersed in the hydrogen peroxide until it was saturated with silver, the wire then being removed. Saturation was marked by an increasing rate of decomposition and the gradual appearance of small particles of silver floating on the liquid surface. The temperature of the solution was then carefully noted and when it began to rise steadily, due to the accelerating rate of decomposition of the hydrogen peroxide, the solution was quickly filtered through a glass wool plug. This had the effect of greatly reducing the rate of decomposition of the solution. The concentration, pH and electrical conductivity of the solution were then measured as required and the test continued. Since silver is precipitated continuously as decomposition of the peroxide occurs it was necessary to repeat the filtration procedure several times during the course of a run as the peroxide concentration fell to zero.

## MEASUREMENT OF pH

The measurement of pH was made according to the method described by Wynne-Jones.<sup>1</sup> Two Muirhead glass electrodes were used in conjunction with a Pye pH meter. The samples of hydrogen peroxide were contained in a Morton half-cell fitted with a saturated calomel reference electrode and this assembly was mounted on a block of paraffin wax to provide good electrical insulation. The apparatus was placed in an incubator maintained at 25° ± 0.5°C. The glass electrodes were standardized in the following way. The e.m.f. was measured in various concentrations of hydrogen peroxide (0, 20, 50, 63, 69, 78 and 82 % w/w) containing various amounts of A.R. perchloric acid ( $\log [H^+] = -3.0, -2.3, -2.0$  and  $-1.3$ ). The total ionic strength of the solutions was kept constant at 0.1 by additions of recrystallized potassium perchlorate. Graphs of e.m.f. against  $\log [H^+]$  were obtained for the different peroxide concentrations. The straight lines were extrapolated to  $\log [H^+] = 0$ , to give the  $E_0$  values. Graphs of  $E_0$  against peroxide concentration were then drawn for the two electrodes and used for calculating the pH values of the test solutions from experimentally determined e.m.f.s and concentrations.

## MEASUREMENT OF CONDUCTIVITY

The electrical conductivity of concentrated hydrogen peroxide solutions can be measured successfully provided that care is taken in the choice of a suitably compatible electrode material. Tin is probably the most suitable material and was used in the present investigation. Two dip-cells were used with equal success, one being specially made and the other adapted from a commercial conductivity cell. The first cell consisted of two block-tin electrodes held rigidly in a polythene base with the faces 0.5 in. apart and protected by a glass sheath. Each electrode was machined from one piece of tin to

dimensions  $0.75 \times 0.75 \times 0.25$  in. The stems were 0.25 in. in diameter and 2.5 in. long and were provided with sockets at the ends to take wander-plug leads to the conductivity bridge. The second cell was made from a commercial (Mullard) conductivity cell in the following way. The platinum black on the electrodes was removed with aqua regia and tin deposited from a solution containing 80 g/l. of sodium stannate and 12.5 g/l. of caustic soda. A current density of about  $10 \text{ A ft}^{-2}$  was employed for 1 h, the electrolyte being maintained at a temperature of  $70\text{--}75^\circ\text{C}$ .

The cells were used in conjunction with a Cambridge conductivity bridge (visual indicator) operating at a frequency of 1000 c/sec and the cell constants were determined using six A.R. potassium chloride solutions varying in strength from 0.0001 N to 0.01 N.

## RESULTS

Fig. 1 shows a graph of measured pH values against concentration of dissolved silver for hydrogen peroxide solutions of nominal strength 21, 59, 69 and 79 % w/w. Curves representing calculated values of pH for change in silver concentration in the same hydrogen peroxide concentrations are also shown.

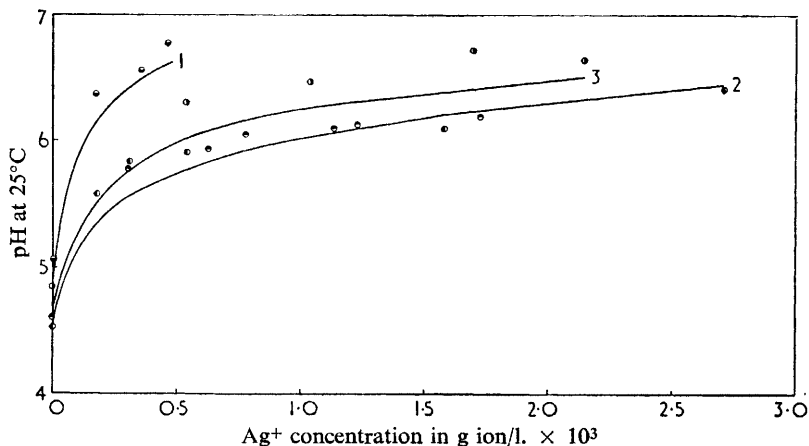


FIG. 1.—The pH of hydrogen peroxide solutions containing silver dissolved from the metal.

measured values	concentration of $\text{H}_2\text{O}_2$ , % w/w	calculated curves
●	$21 \pm 0.5$	1
●	$59 \pm 2.0$	2
●	$69 \pm 1.0$	same as for 59 %
●	$79 \pm 2.0$	3

The variation of specific conductivity with silver concentration was measured at  $2^\circ\text{C}$  for five nominal concentrations of hydrogen peroxide, 30, 47, 59, 68 and 78 % w/w. The results are shown in fig. 2. The variation of equivalent conductivity with hydrogen peroxide concentration is shown in fig. 3. The results of measurements of pH and conductivity carried out on saturated solutions after filtration are shown in fig. 4 and 5. Fig. 4 shows the results obtained for the variation in pH of a solution of hydrogen peroxide saturated with silver, determined at various times as the peroxide concentration fell from 76 to 0 % w/w. A calculated curve is also shown on fig. 4.

Fig. 5 shows the variation in specific conductivity of solutions of hydrogen peroxide saturated with silver as the hydrogen peroxide concentration falls. The results of four tests are shown, the initial  $\text{H}_2\text{O}_2$  concentration being 76, 56, 50 and 36 % w/w.

## DISCUSSION

### pH VALUES

Fig. 1 shows that the pH increases with the amount of silver dissolved, the values being higher for the 21 and 79 % w/w solutions than for the 59 and 69 %

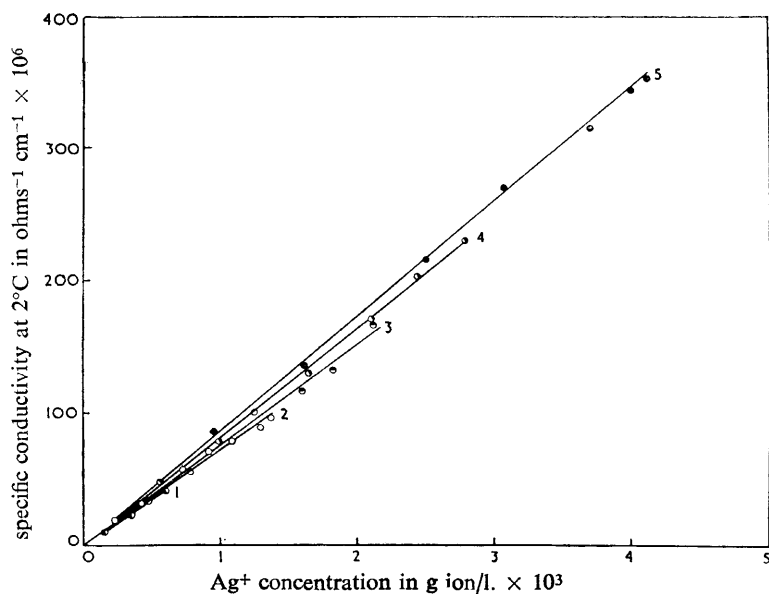


FIG. 2.—The specific conductivity of hydrogen peroxide solutions containing silver dissolved from the metal.

symbol	no.	initial [H <sub>2</sub> O <sub>2</sub> ], % w/w	final [H <sub>2</sub> O <sub>2</sub> ], % w/w
●	1	32.6	27.5
○	2	49.8	44.7
◐	3	60.9	56.8
◑	4	70.3	64.9
●	5	80.5	75.0

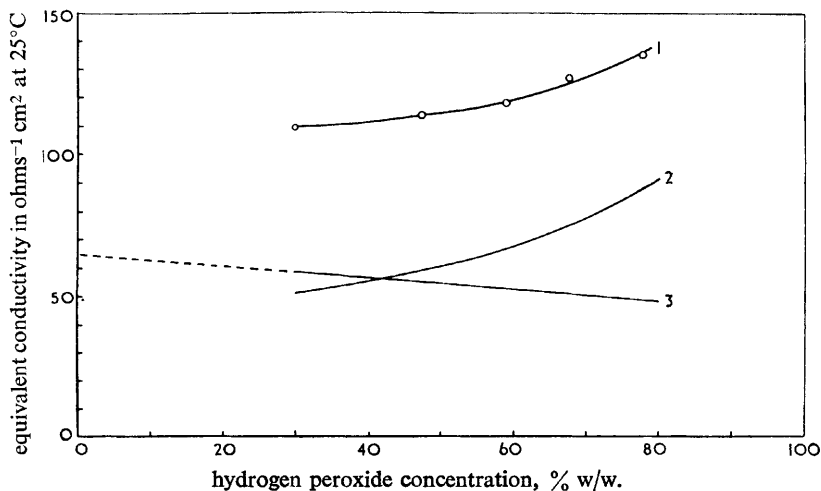


FIG. 3.—The equivalent conductivity of hydrogen peroxide solutions containing silver dissolved from the metal.

1. experimental values.
2. limiting ionic mobility of the HO<sub>2</sub> ion (ref. (4)).
3. ionic mobility of the Ag<sup>+</sup> ion by difference.

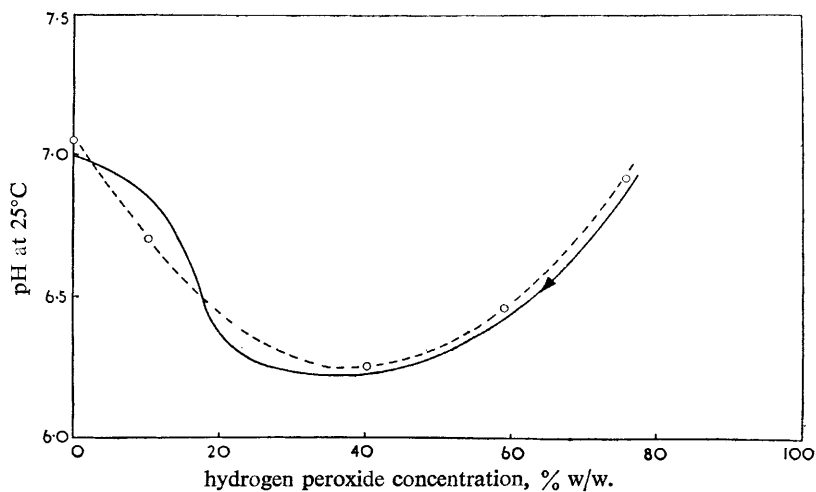


FIG. 4.—The change in pH of a hydrogen peroxide solution saturated with silver as it decomposes.

○ measured value ; full line, calculated curve.

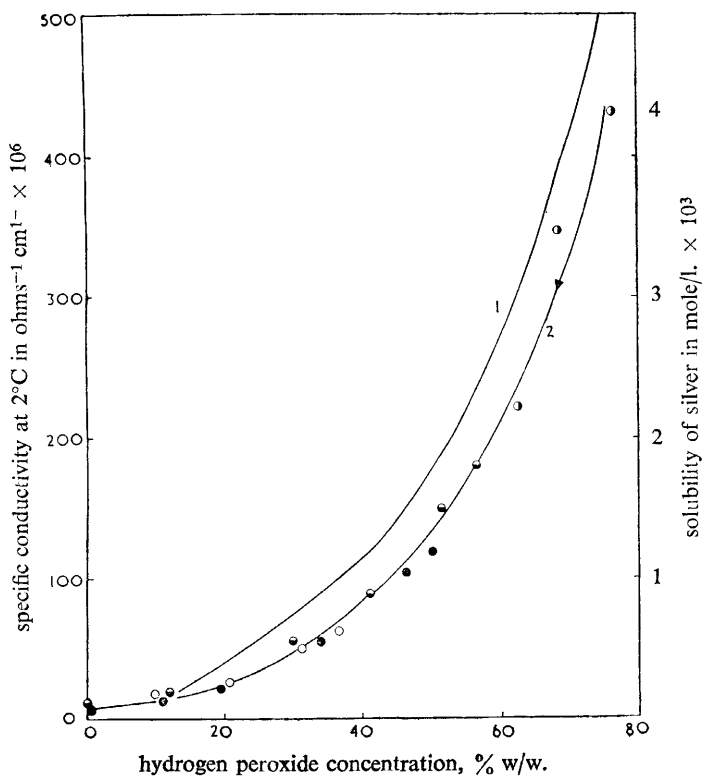
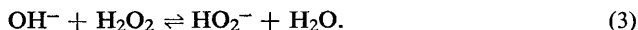
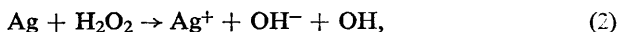


FIG. 5.—The conductivity of hydrogen peroxide solutions saturated with silver decomposing at 2°C.

1. solubility of silver (ref. (3)).
2. specific conductivity.

w/w solutions. Fig. 1 also shows the corresponding calculated curves which were obtained in the following way. It was assumed that reactions (2) and (3) are operative in the hydrogen peroxide solutions under consideration :



The replacement of hydroxyl ions by hydroperoxide ions in hydrogen peroxide + water mixtures results from the much greater acidity of hydrogen peroxide than water in such solutions.<sup>2</sup> Reaction (2) is not necessarily regarded as the reaction step which leads to solution of silver (this may occur by reaction with the radicals OH or HO<sub>2</sub>) but in all cases the final ionic species produced would be Ag<sup>+</sup> and HO<sub>2</sub><sup>-</sup>. Theoretical pH values can be calculated on the basis of reactions (2) and (3) and from a knowledge of the ionic product  $K_m = [\text{H}^+][\text{HO}_2^-]$  for hydrogen peroxide + water mixtures.<sup>2</sup> The agreement between the measured values and the calculated curves is reasonably close.

Fig. 4 shows the variation in pH of a peroxide solution saturated with silver as it decomposes from 76 to 0 % w/w. A calculated curve is also shown on the same graph and the agreement is seen to be good. In this case the theoretical pH values were calculated by assuming that the fall in concentration of the peroxide is accompanied by a fall in the concentration of the ions Ag<sup>+</sup> and HO<sub>2</sub><sup>-</sup> in accordance with the values of the solubility product  $[\text{Ag}^+][\text{HO}_2^-]$  reported previously.<sup>3</sup> For any particular concentration of peroxide,  $[\text{HO}_2^-]$  was therefore taken as equal to  $([\text{Ag}^+][\text{HO}_2^-])^{\frac{1}{2}}$ . Theoretical pH values could then be calculated from a knowledge of the ionic product  $[\text{H}^+][\text{HO}_2^-] = K_m$  for hydrogen peroxide + water mixtures.<sup>2</sup>

#### CONDUCTIVITY VALUES

Fig. 2 shows that the specific conductivity increases linearly with silver ion concentration, i.e. for a given peroxide concentration the equivalent conductivity does not change significantly with silver ion concentration. Since this indicates complete dissociation the slopes of the plots were taken to give approximate values for the equivalent conductivities of the electrolyte at infinite dilution in the different concentrations of hydrogen peroxide. These values are shown in fig. 3 calculated for 25°C using an experimentally determined temperature coefficient of 2.4 % per degree for the temperature range 2-25°C. It is clear from fig. 3 that the equivalent conductivity increases with hydrogen peroxide concentration. Also shown on fig. 3 are values for the limiting ionic mobility of the HO<sub>2</sub><sup>-</sup> ion in hydrogen peroxide + water mixtures determined by Wynne-Jones.<sup>4</sup> Assuming that the ionic species involved are Ag<sup>+</sup> and HO<sub>2</sub><sup>-</sup> the ionic mobility of the Ag<sup>+</sup> ion in these mixtures can be obtained by difference. As shown in fig. 3, the mobility of the Ag<sup>+</sup> ion decreases slowly with increase in hydrogen peroxide concentration. Extrapolation of the values for Ag<sup>+</sup> to  $[\text{H}_2\text{O}_2] = 0$  gives a value of about 65, which is in reasonable agreement with a reported value<sup>5</sup> of 61.9.

Fig. 5 shows the variation in specific conductivity of solutions of hydrogen peroxide saturated with silver as they decompose (curve 2). Also shown on the graph is the variation in solubility of silver with peroxide concentration<sup>3</sup> (curve 1). The values of the equivalent conductivity calculated from (1) and (2) are in good agreement with those shown on fig. 3 for solutions of hydrogen peroxide containing amounts of silver less than those needed for saturation.

#### CONCLUSIONS

The measurements of pH and conductivity, when used in conjunction with the values of the ionic product  $[\text{H}^+][\text{HO}_2^-]$  and the mobility of the HO<sub>2</sub><sup>-</sup> ion reported by Wynne-Jones,<sup>2, 4</sup> provide strong evidence for the formation of the

ions  $\text{Ag}^+$  and  $\text{HO}_2^-$  when silver dissolves in concentrated hydrogen peroxide. The measurements of pH and conductivity in saturated solutions are consistent with the view that  $\text{Ag}^+$  and  $\text{HO}_2^-$  ions are removed from solution as the peroxide concentration falls, the amounts remaining in solutions being determined by the values of the limiting ionic product  $[\text{Ag}^+][\text{HO}_2^-]$  already reported.<sup>3</sup>

The effect of filtration on the decomposition rate in saturated solutions shows that the enhanced decomposition in such solutions is largely or entirely heterogeneous and results from the precipitated silver particles. Although the decomposition rate at a given silver surface in a solution saturated with silver ions is much lower than that for the same silver surface in a solution containing little or no silver ion,<sup>3</sup> the very large surface area presented by the precipitated silver particles results in an overall high decomposition rate. The fact that discreet silver particles become visible in such solutions and are easily removed by filtration suggests that the primary silver particles produced by decomposition of the silver hydroperoxide intermediate postulated in part 1<sup>3</sup> act as nuclei for further decomposition and crystal growth.

<sup>1</sup> Mitchell and Wynne-Jones, *Trans. Faraday Soc.*, 1955, **51**, 1690.

<sup>2</sup> Mitchell and Wynne-Jones, *Trans. Faraday Soc.*, 1956, **52**, 824.

<sup>3</sup> Maggs and Sutton, part 1.

<sup>4</sup> Wynne-Jones, private communication.

<sup>5</sup> Shedlovsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1411.