686. *Glow-discharge Electrolysis. Part I. The Anodic Formation of Hydrogen Peroxide in Inert Electrolytes.*

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The electrolysis of dilute solutions of inert electrolytes has been investigated, with an anode withdrawn from the solution, by passing an electrical discharge at reduced pressure to the liquid surface. The main anodic product initially formed is hydrogen peroxide in amount proportional to the quantity of electricity passed; as this accumulates in the solution a decomposition reaction sets in and ultimately a stationary concentration of hydrogen peroxide is attained. The amount of hydrogen peroxide present in the solution after the passage of a given quantity of electricity is substantially independent of the current used and of factors affecting the nature of the discharge, and it can be accurately expressed by an equation of the form

$$(H_2O_2)\text{ equivs.} = V(1 - e^{-\frac{akq}{V}})/k$$

where q is the quantity of electricity in faradays, V is the volume of the solution, k is a velocity coefficient for the decomposition reaction, and a is a factor (value 1·1—1·9) expressing the number of equivalents of hydrogen peroxide initially formed for each faraday of electricity passed. The process is fundamentally the same for different solutions varying in pH from 1 to 9, with, however, some decrease in the amount of hydrogen peroxide formed at the extremes of this range; in strongly alkaline solutions no hydrogen peroxide can be detected, probably owing to its ready anodic decomposition by discharge of the perhydroxyl ion. The general features of the electrolysis are interpreted by the primary formation in solution of the hydroxyl radical, mainly by electrolytic action although the possibility of some direct dissociation of water molecules is not excluded; dimerisation then occurs to give hydrogen peroxide, which, when it attains a sufficient concentration, decomposes by interaction with hydroxyl radicals as fast as it is formed.

THE mechanism of electrode reactions in conventional electrolysis is complicated by the fact that the reactions occur at the surface of the electrodes used for passage of current through the solution, and in many cases the electrode material undoubtedly exercises a specific influence. This can be avoided by withdrawing the electrode under investigation into the gas space above, and on then working at reduced pressure and applying a moderately high voltage substantial currents can be passed to the liquid surface in the form of a glow-discharge. The technique was developed long ago (Gubkin, *Ann. Physik*, 1887, **32**, 114; Klüpfel, *ibid.*, 1905, **16**, 574; Makowetsky, *Z. Elektrochem.*, 1911, **17**, 217) but has since been used only to a limited extent, mainly by Klemenc and his co-workers (*Z. Elektrochem.*, 1914, **20**, 485; 1931, **37**, 742; *Z. physikal. Chem.*, 1927, **130**, 378; 1931, **154**, 385; 1933, **166**, 343; 1935, **27**, *B*, 369; 1937, **179**, 1; 1938, **182**, 91; 1938, **40**, *B*, 252; 1938, **183**, 217, 297; *Z. anorg. Chem.*, 1939, **240**, 167; *Monatsh.*, 1944, **75**, 42; 1946, **76**, 38; 1948, **78**, 243; 1950, **81**, 122; see also Cousins, *Z. physikal. Chem.*, 1929, **4**, *B*, 440; Thon, *Compt. rend.*, 1933, **197**, 1114; Braunbek, *Z. Physik*, 1934, **91**, 184; Hickling, *J.*, 1934, 1772; Fichter and Kestenholz, *Helv. Chim. Acta*, 1940, **23**, 209; Pavlov, *Compt. rend. Acad. Sci. U.R.S.S.*, 1944, **43**, 236, 383, 385). In much of this work, however, rather complex conditions have been employed, with concentrated electrolyte solutions susceptible to oxidation and reduction, and no very definite conclusions have emerged; frequently it is difficult to discriminate between reactions brought about electrolytically and those initiated by the electrical discharge.

The present investigation was undertaken to ascertain the nature of the anodic process in the glow-discharge electrolysis of very dilute solutions of inert electrolytes in which the only likely electrolytic reaction was the discharge of the hydroxyl ion; earlier work suggested that hydrogen peroxide was the product arising in these circumstances and an extensive study has therefore been made of its formation and decomposition.

EXPERIMENTAL

The type of cell most frequently employed is shown in Fig. 1. It consisted of a boiling-tube, of approx. 5 cm. diameter, fitted with a rubber stopper carrying the cell components. The anode was usually a straight platinum wire which was carried in an adjustable holder so that it could be fixed at any distance from the electrolyte surface; the cathode was a spiral of platinum wire of 1 sq. cm. area contained in a glass tube of 1 cm. diameter closed at its lower end by a tight filter-paper plug which effectively prevented mixing of anolyte and catholyte. The anode and cathode compartments were each connected to a vacuum line of a conventional type which included a float manostat so that the pressure in the apparatus could be maintained constant over long periods.

The power supply was a Leland power unit providing voltages of 0—1500 v adjustable by means of a Variac transformer, and capable of a maximum output of 0·4 amp. at 1000 v. It was connected to the cell through a calibrated Sangamo Weston multirange ammeter and a ballast resistance of 2000 ohms. The discharge was started by momentarily including in the circuit the secondary of a spark coil. Once initiated the discharge was remarkably steady and took the form of a sharply defined cone between the tip of the anode (which became red hot) and the electrolyte surface; the glow-spot in the surface was pink, and of area usually somewhat less than 1 sq. cm. The current passing would remain constant without adjustment over long periods, and the cell voltage (which is nearly all developed across the discharge) was in the range 500—700 v, varying according to experimental conditions. With increase of current the area of the glow-spot increased, and it appeared likely that the effective current density at the surface was approximately constant. The heat dissipated in the discharge is very considerable and this makes the control of temperature of the electrolyte difficult. In the present work the cell was cooled in ice-water, and the bulk temperature was found to rise very rapidly on electrolysis to about 15° and then more slowly to about 25°, the average bulk temperature over the greater part of electrolysis being between 20° and 25°; the local temperature in the glow-spot is probably appreciably higher than this.

FIG. 1. *Electrolytic cell.*

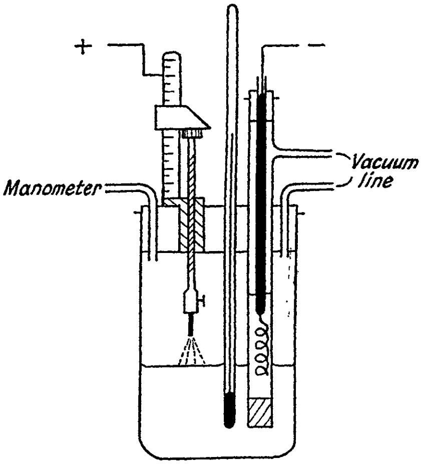
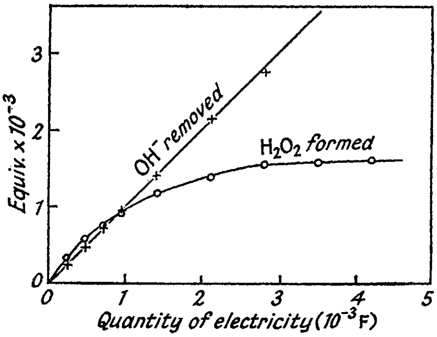


FIG. 2. *Glow-discharge electrolysis of* 0·05M-Na_2HPO_4.



The anolyte most frequently used was 50 ml. of a boiled-out solution of 0·05M-disodium hydrogen phosphate; the catholyte was 5 ml. of 0·5M-disodium hydrogen phosphate. The pH of the anolyte was initially 9·5, dropping rapidly on electrolysis to 6·4 and remaining constant at this value. The volume of the anolyte was measured after electrolysis and the solution then analysed. The amount of acid developed or hydroxyl ion discharge was found by titration with 0·01N-sodium hydroxide to the thymolphthalein end-point; check experiments had shown that hydrogen- and hydroxyl-ion migration in the anolyte was negligible under the conditions employed. The hydrogen peroxide was determined by titration with 0·01N-potassium permanganate in acid solution; this analysis was checked iodometrically in a number of cases and satisfactory agreement found. Blank determinations were carried out on the anolyte in all analyses.

The experimental conditions usually employed were: Anolyte: 50 ml. of unstirred 0·05Mdisodium hydrogen phosphate exposing a surface of approx. 19 sq. cm. Anode: platinum wire, the tip of which was 0·5 cm. from the electrolyte surface. Pressure: 50 mm. of mercury. Current: 0·075 amp. These are referred to as the "standard conditions" and are to be taken to apply when the experimental variables are not otherwise specified. In a number of instances the anolyte was stirred during electrolysis. This was achieved by introducing into the cell a small bar-magnet in a glass envelope and rotating it at uniform speed by means of an external field; check experiments showed that the presence of the magnetic field did not influence the results appreciably.

RESULTS

Influence of General Factors.—Quantity of electricity. In Fig. 2 are shown the results of a series of experiments in which 0·05M-disodium hydrogen phosphate was electrolysed under standard conditions for different times; the number of equivalents of acid produced or hydroxyl ions removed, and of hydrogen peroxide formed, are plotted against the quantity of electricity passed expressed in faradays.

It is seen that the hydroxyl-ion discharge is accurately in accordance with that expected from Faraday's laws, while the hydrogen peroxide formed is initially proportional to the quantity of electricity passed, although the yield is slightly greater than 1 equivalent per faraday, but it decreases with increasing quantity of electricity and the amount of hydrogen peroxide in solution eventually approaches a limiting value. The general inference to be drawn is that two processes are occurring—an initial formation of hydrogen peroxide in amount proportional to the quantity of electricity passed, and a decomposition reaction as the peroxide accumulates in the electrolyte, a stationary state being ultimately attained. It is apparent that in investigating the influence of experimental variables it is necessary to distinguish their effects on the initial formation reaction from those on the system when the stationary state has been achieved.

Current. In Table 1 are shown the yields of hydrogen peroxide obtained for increasing quantities of electricity at each of three currents (0·10, 0·075, and 0·05 amp.) severally.

TABLE 1. *Influence of current on hydrogen peroxide formation.*

Quantity of electricity (10^{-3}F)	H_2O_2 formed (10^{-3} equiv.) 0·10	0·075	0·05 amp.
0·223	0·314	0·316	0·312
0·466	0·558	0·555	0·552
0·933	0·929	0·915	0·931
1·40	1·21	1·19	1·16
2·10	1·36	1·38	1·34
2·80	1·60	1·54	1·51
3·50	1·60	1·58	1·55
4·20	1·64	1·60	1·57

With increasing current the voltage of the discharge rose somewhat (from 560 to 600 volts) and the power dissipated in it increased very markedly (from 28 to 60 watts), but in spite of this the yields of hydrogen peroxide were substantially independent of the current used. Since the times of electrolysis were very different at the different currents, this result suggests that both the formation and the decomposition of the peroxide are due to some primary species which is produced electrolytically.

Volume of electrolyte. Table 2 shows the results obtained on varying the volume of the anolyte from 25 to 100 ml. under otherwise standard conditions, different quantities of electricity being used; the small quantity of $0·373 \times 10^{-3}$ faraday corresponds to the state in which the formation reaction predominates and the decomposition reaction has not become appreciable, while the larger quantities of electricity are those corresponding to the attainment of the stationary state.

TABLE 2. *Influence of volume of anolyte.*

Volume of anolyte (ml.)	Quantity of electricity (10^{-3}F)	H_2O_2 formed (10^{-3} equiv.)	Volume of anolyte (ml.)	Quantity of electricity (10^{-3}F)	H_2O_2 formed (10^{-3} equiv.)	H_2O_2 concn. (N)
100	0·373	0·442	100	5·60	3·16	0·0316
75	0·373	0·438	75	4·20	2·43	0·0323
50	0·373	0·447	50	4·20	1·60	0·0320
25	0·373	0·424	25	2·80	0·815	0·0326

The interesting result which clearly emerges is that in the formation reaction the yield of hydrogen peroxide is independent of the volume of the anolyte, but the rate of the decomposition reaction is apparently proportional to the *concentration* of peroxide, so that in the stationary state it is the concentration of peroxide, not its absolute amount, which becomes constant.

Surface area and stirring. A large number of early observations suggested that the hydrogen peroxide was initially formed immediately under the glow-spot and diffused both laterally across the surface and inwards into the bulk of the electrolyte. The local concentration of peroxide in the region of the glow-spot is therefore higher than in the bulk of the solution, and, since the decomposition reaction depends on the concentration of peroxide, any factor tending to favour diffusion from the glow-spot would be expected to raise the yield of peroxide obtained in the stationary state. In conformity with this it was found that, while increase of surface area of anolyte and stirring had no appreciable effect on the yield of hydrogen peroxide for the passage of a small quantity of electricity, *i.e.*, while the formation reaction is predominating, these factors increased the stationary concentration of peroxide attained when a large quantity of electricity was passed. A selection of results is given in Table 3. In unstirred electrolytes, the introduction of any large obstruction in the surface was found, as would be expected, to decrease the stationary concentration of peroxide attained. The effect appears to be a purely mechanical one of hindering diffusion; no specific wall reactions seem to occur since on packing the anolyte loosely with glass wool the results were not appreciably affected.

TABLE 3. *Influence of surface area and stirring.*

Surface area (sq. cm.)	Quantity of electricity (10^{-3}F)	H_2O_2 formed (10^{-3} equiv.)	Surface area (sq. cm.)	Quantity of electricity (10^{-3}F)	H_2O_2 formed (10^{-3} equiv.)	H_2O_2 concn. (N)
10	0·373	0·414	10	2·80	1·04	0·2008
19	0·373	0·447	19	2·80	1·54	0·0308
38	0·373	0·445	38	2·80	1·59	0·0318
10 stirred	0·373	0·433	10 stirred	2·80	1·60	0·0320
19 stirred	0·373	0·440	19 stirred	2·80	1·65	0·0330

Influence of Factors affecting the Discharge.—Electrode distance. In Table 4 are shown the results of a series of experiments in which the distance of the anode from the electrolyte surface was varied from 0·1 to 2·0 cm., standard conditions being otherwise employed.

It is seen that variation of electrode distance does not apparently affect the yield of hydrogen peroxide appreciably for the passage of either small or large quantities of electricity, until the electrode is brought within 0·25 cm. of the surface : a slight increase in the amount of hydrogen peroxide is then found.

TABLE 4. *Influence of electrode distance.*

Distance (cm.)	Voltage (v)	H_2O_2 formed (10^{-3} equiv.) 0·373 × 10^{-3}F	2·80 × 10^{-3}F	Distance (cm.)	Voltage (v)	H_2O_2 formed (10^{-3} equiv.) 0·373 × 10^{-3}F	2·80 × 10^{-3}F
2·0	700	0·451	1·52	0·5	580	0·447	1·54
1·5	680	0·432	1·49	0·25	540	0·488	1·67
1·0	620	0·446	1·51	0·1	520	0·489	1·74
0·75	600	0·434	1·49				

Shape and nature of electrode. To see if the results were dependent in any way on the shape, size, or nature of the electrode a series of experiments was carried out under standard conditions, with platinum electrodes in the form of a vertical wire, an L-shaped wire with the lower arm parallel to the liquid surface, and with ring and disc electrodes also parallel to the surface; vertical rod electrodes of tungsten, nickel, copper, nichrome, and graphite were also tried. The results are summarised in Table 5 and it is seen that none of these factors appreciably affected the results obtained. The graphite electrode tended to disintegrate and fragments of carbon fell into the electrolyte, probably bringing about some catalytic decomposition of the peroxide.

TABLE 5. *Influence of shape, size, and nature of electrode.*

		H_2O_2 formed (10^{-3} equiv.)			H_2O_2 formed (10^{-3} equiv.)	
	Electrode	0·373 × 10^{-3}F	2·80 × 10^{-3}F	Electrode	0·373 × 10^{-3}F	2·80 × 10^{-3}F
Pt :	Wire	0·447	1·54	Pt	0·447	1·54
	L-shaped wire	0·450	1·53	W	0·456	1·51
	Ring	0·442	1·50	Ni	0·447	1·58
	Disc	0·475	1·47	Cu	0·441	1·48
				Nichrome	0·458	1·52
				C	0·430	1·29

Nature of gas. To ascertain whether the nature of the gas present in the apparatus would influence the process occurring, experiments were carried out under the usual conditions with different gases present. In the first of two series all air in the apparatus was displaced by the gas to be studied and then electrolysis was carried out in the usual way; in a second set a current of the gas was also blown continuously across the discharge during the electrolysis. The results are given in Table 6. The nature of the gas present has surprisingly little influence on the amount of hydrogen peroxide formed; with oxygen the amount is somewhat higher, and with hydrogen rather lower, than the average, but the differences are not substantial. With the gas flowing across the discharge there is a general tendency for the yield of hydrogen peroxide to be somewhat greater, but this may well be an incidental effect due to the higher pressure in the region of the discharge and to some stirring of the electrolyte surface. The fact that the nature of the gas has so little effect supports the idea that the discharge is essentially one in water vapour; this is not unlikely since the local temperature of the liquid under the glow spot must be relatively high.

TABLE 6. *Influence of nature of gas.*

		H_2O_2 formed (10^{-3} equiv.)				H_2O_2 formed (10^{-3} equiv.)	
	Gas	0·373 × 10^{-3}F	2·80 × 10^{-3}F		Gas	0·373 × 10^{-3}F	2·80 × 10^{-3}F
Static:	Air	0·447	1·54	Flowing:	Air ...	0·499	1·65
	N_2	0·448	1·52		N_2	0·476	1·64
	O_2	0·465	1·58		O_2	0·514	1·66
	H_2	0·411	1·50		H_2 ...	0·424	1·62
	N_2O	0·427	1·53		N_2O ...	0·479	1·66

Pressure. Experiments were carried out under the usual standard conditions at different pressures of air, and the results are summarised in Table 7. Some loss of hydrogen peroxide may occur at the lowest pressures by boiling of the solution; apart from this the effect of pressure seems to be relatively slight, there being some tendency for the amount of hydrogen peroxide formed to increase with rise of pressure.

TABLE 7. *Influence of pressure.*

Pressure	Voltage	H_2O_2 formed (10^{-3} equiv.)		Pressure	Voltage	H_2O_2 formed (10^{-3} equiv.)	
(mm.)	(v)	0·373 × 10^{-3}F	2·80 × 10^{-3}F	(mm.)	(v)	0·373 × 10^{-3}F	2·80 × 10^{-3}F
150	660	0·477	1·56	50	580	0·447	1·54
100	620	0·459	1·57	35	560	0·429	1·46
75	600	0·448	1·58	25	550	0·415	1·16

Influence of Factors affecting the Solution.—Nature and pH *of electrolyte.* The formation of hydrogen peroxide and its dependence on quantity of electricity passed were comprehensively investigated, a wide variety of inert electrolytes being used, both stirred and unstirred, under standard conditions. The essential features of the results are summarised in Table 8. The initial yield of hydrogen peroxide in equiv./faraday has been found from the slope of the tangent to the initial section of each formation curve.

TABLE 8. *Influence of nature of electrolyte.*

Electrolyte	Approx.	Initial yield of H_2O_2 (equiv./F)		Stationary concn. of H_2O_2 (N)	
(0·05M)	pH	Unstirred	Stirred	Unstirred	Stirred
NaOH	13—12	0	—	0	—
Na_2CO_3	11	0	—	0	—
$Na_2B_4O_7$	9	—	—	0·013	—
$NaHCO_3$	8	1·9	1·8	0·033	0·040
Na_2HPO_4	7	1·5	1·3	0·032	0·040
K_2SO_4	7—2	1·3	1·3	0·032	0·040
H_2SO_4	1	1·1	1·1	0·022	0·028

In strongly alkaline solutions no hydrogen peroxide can be detected after electrolysis, but in all other solutions the formation of hydrogen peroxide and its decomposition seem to follow essentially the same path, independently of the nature of the electrolyte. Over the pH range 8—2 the stationary concentration of hydrogen peroxide attained is substantially the same although the initial yield of hydrogen peroxide seems to increase somewhat with rising pH; similar results were also found when the electrolyte was a heterogeneous buffer (approx. pH 6 or 4) made by partly precipitating the metallic hydroxides from zinc and aluminium sulphates. At pH's 1 and 9 the stationary concentrations of hydrogen peroxide drop appreciably. The addition of catalysts for hydrogen peroxide decomposition such as $MnSO_4$, $CuSO_4$, $FeSO_4$, and $CoSO_4$ at 0·01M-concentration to a 0·05M-K_2SO_4 electrolyte was found to decrease somewhat the amount of hydrogen peroxide formed, but the effect was relatively slight.

Concentration. Increase of concentration of the electrolyte was found in general to raise both the initial yield of hydrogen peroxide and the stationary concentration attained. This is illustrated by the results in Table 9 obtained with a sodium dihydrogen phosphate electrolyte under standard conditions. The effect appeared to be independent of the chemical nature of the electrolyte, and it is noteworthy that increase of concentration beyond a certain point had no further influence.

TABLE 9. *Influence of concentration.*

Concn. of NaH_2PO_4 (M)	0·1	0·2	0·5	1·0
Initial yield of H_2O_2 (equiv./F)	1·5	1·6	1·9	1·9
Stationary concn. of H_2O_2 (N)	0·033	0·040	0·048	0·048

TABLE 10. *Influence of temperature.*

Average temp. of electrolyte (approx. only)	40°	30°	20°
H_2O_2 formed (10^{-3} equiv.) $0·373 \times 10^{-3}$F	0·481	0·431	0·417
$2·80 \times 10^{-3}$F	2·05	2·12	2·43

Temperature. As has been mentioned, control of temperature in the electrolysis is very difficult, but some experiments were carried out with a stirred solution of 0·05M-disodium hydrogen phosphate and a pressure of 150 mm., the average bulk temperature being maintained at different values by altering the cooling-bath; the results are given in Table 10. While too much significance should not be attached to these results, it does appear that rise of temperature increases somewhat the initial yield of hydrogen peroxide but decreases the stationary concentration attained.

FIG. 3. *Glow-discharge electrolysis of hydrogen peroxide.*

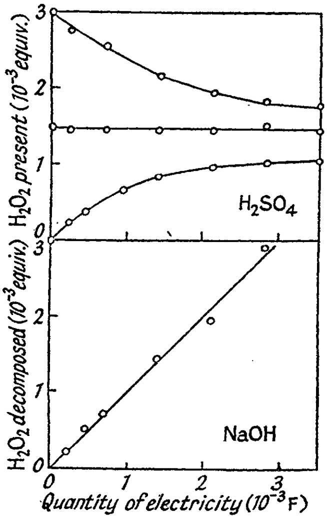
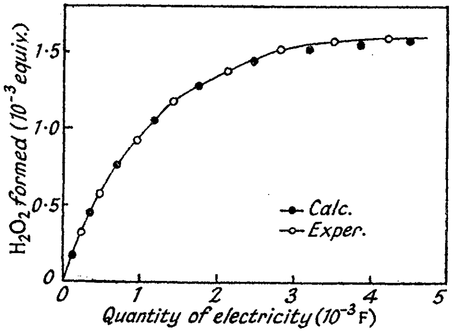


FIG. 4. *Formation of hydrogen peroxide: calculated and experimental values.*



Decomposition of Hydrogen Peroxide by Glow-discharge Electrolysis.—The decomposition of hydrogen peroxide by glow-discharge electrolysis was studied in 0·05M-H_2SO_4, -Na_2HPO_4, and -NaOH electrolytes by starting with solutions containing different initial amounts of hydrogen peroxide, and finding that present after the passage of various quantities of electricity, standard conditions being employed. Typical results are illustrated in Fig. 3.

In H_2SO_4 and Na_2HPO_4 electrolytes, the hydrogen peroxide present changed in amount on electrolysis until the concentration approached the previously found stationary values, whereafter it remained constant. In the NaOH electrolyte, continuous decomposition of the hydrogen peroxide occurred, the amount decomposed being proportional to the quantity of electricity passed and corresponding approximately to 1 equiv./faraday.

DISCUSSION

The experimental results have shown that, contrary to what might have been expected, electrolysis of inert aqueous solutions with a glow-discharge anode leads to relatively simple and reproducible results. There appears to be an initial formation of hydrogen peroxide followed by a subsequent decomposition, the rate of both reactions depending on the current passing, and a simple interpretation which will cover many features of the process can be reached on a purely electrolytic basis. Since it seems improbable that electrons could be emitted directly from the surface of the liquid electrolyte, the current must be conveyed by positive gaseous ions which are driven into the liquid from the gas phase and subsequently discharged, and, as has been mentioned previously, it seems likely that the discharge is primarily one through water vapour. We have no certain knowledge of the nature of the ions present in ionised water vapour at pressures corresponding to those used in the present work, but observations at much lower pressures made by use of mass spectrometer have shown that under these conditions the main positive ion present is H_2O^+, with substantial amounts of OH^+, smaller quantities of H^+ and H_3O^+, and trifling amounts of other ions (see Barton and Bartlett, *Phys. Review*, 1928, **31**, 823; Smyth and Mueller, *ibid.*, 1933, **43**, 116; Mann, Hustrulid, and Tate, *ibid.*, 1940, **58**, 340). If it is assumed that the main ions carrying the current in the present work are the H_2O^+ and OH^+ ions, then on entry of these into the solution the following simple reactions might occur :

$$H_2O^+{}_{\text{gas}} + H_2O_{\text{liq.}} \longrightarrow OH + H_3O^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

$$H_2O^+{}_{\text{gas}} + OH^-{}_{\text{liq.}} \longrightarrow OH + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

$$OH^+{}_{\text{gas}} + OH^-{}_{\text{liq.}} \longrightarrow 2OH \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

$$OH^+{}_{\text{gas}} + H_2O_{\text{liq.}} \longrightarrow 2OH + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (d)$$

Each of these reactions leads to the formation of the OH radical as the primary species produced in solution, the yield being 1 equiv. of OH per faraday for reactions (*a*) and (*b*), and 2 equiv. of OH per faraday for reactions (*c*) and (*d*); in addition each reaction leads to the development of 1 equiv. of acid for each faraday passed. If then the OH radicals initially formed dimerise to give hydrogen peroxide

$$2OH \longrightarrow H_2O_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (e)$$

an initial yield of 1—2 equivs. of hydrogen peroxide per faraday would be expected. As the hydrogen peroxide accumulates in the electrolyte, however, interaction with OH radicals must occur as postulated in the well-known Haber–Weiss mechanism

$$H_2O_2 + OH \longrightarrow H_2O + HO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (f)$$

and decomposition of the peroxide to water and oxygen will follow. At any time, therefore, the rate of increase in the amount of hydrogen peroxide will be given by an equation of the form

$$\frac{d(H_2O_2)}{dt} = a \cdot \frac{I}{F} - a \cdot \frac{I}{F} k[H_2O_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where (H_2O_2) is the amount (in equiv.) of hydrogen peroxide and $[H_2O_2]$ is its concentration, a is the yield of the primary species OH per faraday, I is the current, and k is a coefficient for the decomposition reaction. On integration and application of the condition that there is no hydrogen peroxide present at the start of electrolysis, the equation becomes

$$(H_2O_2) = V(1 - e^{-\frac{akq}{V}})/k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where q is the quantity of electricity in faradays and V is the volume of the solution.* Two special cases of the application of this equation are apparent : when q is small $(H_2O_2) \simeq aq$, *i.e.*, the amount of hydrogen peroxide is proportional to the quantity of electricity; when q is large, $(H_2O_2) = V/k$, *i.e.*, $[H_2O_2] = 1/k$ and a stationary concentration of the peroxide is attained. Equation (2) has been tested in numerous cases by inserting experimental values of a and V/k and it fits the experimental observations remarkably well. In Fig. 4, for example, are shown the experimental and calculated

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* An equation somewhat similar in form has been deduced by Klemenc.

points for the electrolysis of 0·05M-disodium hydrogen phosphate under standard conditions.

The failure to obtain hydrogen peroxide in strongly alkaline electrolytes is readily understood from the electrolytic standpoint. A recent investigation (Hickling and Wilson, *J. Electrochem. Soc.*, 1951, **98**, 425) has shown that in alkaline solution hydrogen peroxide is very readily decomposed at an anode by discharge of the perhydroxyl ion

$$HO_2^- - 2e \longrightarrow H^+ + O_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (g)$$

and the present work has also shown that hydrogen peroxide is quantitatively and continuously decomposed in alkaline solution by a glow-discharge anode, probably by the same reaction; in the light of these observations no appreciable amount of hydrogen peroxide would be expected to accumulate in the glow-discharge electrolysis of alkaline electrolytes.

The main features of the glow-discharge electrolysis and the initial formation of hydrogen peroxide in amounts rather greater than those expected from Faraday's laws can be fairly well explained therefore on a simple electrolytic view. The fact that the initial yield of hydrogen peroxide is greater than 1 equiv./faraday implies that some reduction product must be formed also, and analysis of the gas present in the cell showed this reduction product to be hydrogen. Determination of all the products, gaseous and in solution, showed that throughout electrolysis the yield in equivalents of $H_2O_2 + O_2 - H_2$ was equal to the quantity of electricity passed in faradays; in the later stages of electrolysis no hydrogen remains in the cell gas since it is removed by combination with oxygen to give water in the gas phase.

On points of detail the above explanation is less satisfactory. It is not clear, for example, why the initial yield of hydrogen peroxide should increase with concentration of electrolyte and with rise of pH over the range 2—8, and a yield of 1·9 equiv./faraday would imply that nearly all the current was being carried to the electrolyte surface by gaseous OH^+ ions, which seems very unlikely. It is of course entirely possible that entry of positive gaseous ions into the solution may bring about dissociation of water molecules by either ionisation or excitation in the general way now attributed to ionising radiations of many types (cf. Dainton, *Ann. Reports*, 1948, **45**, 5). The primary species leading to the formation of hydrogen peroxide would again be the OH radical and subsequent reactions would be the same, but the yield of hydrogen peroxide might be considerably greater than that expected from simple electrolysis. In the present work, however, the importance of quantity of electricity as the main variable, and the substantial independence of the results of factors affecting the electrical discharge, favour the view that the hydrogen peroxide arises mainly, if not solely, by simple electrolysis.

The present results carry some important implications for the mechanism of the discharge of hydroxyl ions at solid anodes in ordinary electrolysis. Much work on electrolytic oxidation has suggested that hydrogen peroxide may well be an intermediate between the discharge of the hydroxyl ion and the formation of oxygen and water (see Glasstone and Hickling, *Chem. Reviews*, 1939, **25**, 407), but hydrogen peroxide can rarely be detected in these circumstances. In view, however, of its further decomposition by interaction with OH radicals, and the high local concentrations at a solid surface, this is not surprising. It has been suggested (Hickling, *Quart. Reviews*, 1949, **3**, 95) that a possible mechanism for the electrode reaction is

$$\begin{aligned} OH^- - e &\longrightarrow OH \\ 2OH &\longrightarrow H_2O_2 \\ OH + H_2O_2 &\longrightarrow H_2O + HO_2 \\ OH + HO_2 &\longrightarrow H_2O + O_2 \end{aligned}$$

and the present work seems to lend some support to this general idea.

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