33. *Studies in Electrolytic Oxidation. Part XIII. The Electrolytic Oxidation of Formaldehyde.*

By A. Hickling and F. Rodwell.

The electrolytic oxidation of formaldehyde in acid, neutral, and alkaline solutions has been investigated at a variety of anodes over a wide range of current densities, and observations of the concomitant potential phenomena have been made. Three main sets of oxidation products are distinguished, *viz.*, formic acid and hydrogen, formic acid and water, and carbon dioxide and water, and the relative occurrence of the reactions leading to these products depends in a complex manner upon the experimental conditions. It is concluded that the oxidation is a chemical process in which the primary oxidising agent is hydrogen peroxide initially formed at the anode, nascent oxygen and oxides formed with the electrode materials playing supplementary parts.

The electrolytic oxidation of formaldehyde had not been very fully investigated, owing probably to the considerable difficulties involved in the complete analysis of the products, but the observations on record reveal a number of unusual features. Law (J., 1905, **87**, 198), from a limited examination of the process at a platinum anode, concluded that the main products were formic acid and carbon dioxide, with a certain amount of carbon monoxide particularly in acid solution. Müller and Hochstetter (*Z. Elektrochem.*, 1914, **20**, 367), however, showed that in alkaline solution at a copper anode, hydrogen was one of the products of the oxidation, and subsequent investigations (Müller, *Annalen*, 1920, **420**, 241; Fresno, *Anal. Fis. Quim.*, 1924, **22**, 121; Müller and Takegami, *Z. Elektrochem.*, 1928, **34**, 704) have been mainly directed to the study of this unusual phenomenon. It has been reported that the production of hydrogen is accompanied by the formation of formic acid, and that although the reaction occurs readily at copper, silver, and gold anodes, yet little or no hydrogen is obtained with metals of the platinum group. The reaction is favoured by the use of strongly alkaline electrolytes, and is apparently associated with the maintenance of a very low anode potential, although the exact circumstances leading to this are not clear, since low-potential stages are also observed with the anodes which do not give hydrogen.

No general theory of the electrolytic oxidation of formaldehyde has been advanced, but there has been considerable speculation concerning the mechanism of the anodic production of hydrogen. Müller and his co-workers (*loc. cit.*) suggested that the initial stage involved the discharge of the anion $CH_2(OH)\cdot O'$, derived from formaldehyde hydrate. In their latest view it was supposed that this formed an adsorbed radical which might break up to give formic acid, leaving an adsorbed hydrogen atom which could be further oxidised to a hydrogen ion, or two of the adsorbed radicals might decompose together to give a free hydrogen molecule and formic acid. The low-potential stage was considered in all cases to correspond to the discharge potential of the anion, but with electrodes which gave little hydrogen it was supposed that the first reaction was catalysed by the anode material, and the accumulation of discharged radicals was thus insufficient for the second process to occur.

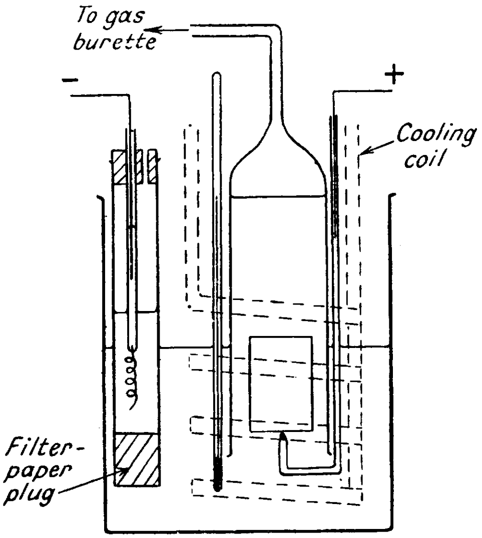
Although they provide a possible formulation of certain limited aspects of the electrolytic oxidation of formaldehyde, Müller's views on the mechanism of the process must be regarded as highly speculative and they afford little help in the prediction of experimental results. It appeared useful, therefore, to ascertain whether the hydrogen peroxide theory of electrolytic oxidation developed in the previous parts of this series (Glasstone and Hickling, J., 1932, 2345, 2800; 1933, 829; 1934, 10, 1772, 1878; 1936, 820; Hickling, J., 1936, 1453; Gross and Hickling, J., 1937, 325; Hickling and Westwood, J., 1938, 1039; 1939, 1109; Hickling and Richards, J., 1940, 256; see also Glasstone and Hickling, *Chem. Rev.*, 1939, **25**, 407) would throw any light upon the mechanism of the oxidation, and a comprehensive investigation of the process has therefore been carried out.

EXPERIMENTAL.

The Electrolytic Cell.—The cell generally employed is shown in Fig. 1. It consisted of a 800-c.c. beaker, which formed the anode compartment, provided with a thermometer and a glass cooling coil through which water could be circulated. The anode was in the form of a rectangular sheet (4 × 2·5 cm.) sealed into a bent glass tube, through which contact was made, and mounted vertically. Enveloping the anode was a glass hood connected by capillary tubing to a gas-measuring burette which was also connected to a small mercury trough. Initially the anolyte was drawn up so as completely to fill the hood, and the gaseous products of the anodic oxidation which collected above the liquid were then drawn off from time to time into the burette, their volume measured, and samples collected *via* the mercury trough for subsequent analysis. The cathode compartment of the cell consisted of a wide glass tube dipping into the anolyte and closed at its lower end by a tight filter-paper plug; the cathode was a spiral of platinum wire of 1 sq. cm. area.

The Electrolyte.—In general, the anolyte was 200 c.c. of M-formaldehyde in N-sulphuric acid, or in phosphate buffer of approximately pH 7 (0·1M-Na_2HPO_4 + 0·1M-KH_2PO_4), or in N-sodium hydroxide; these are subsequently referred to respectively as the acid, neutral, and alkaline stock solutions. Since commercial formalin solutions invariably contain methyl alcohol and are not very stable, B.D.H. paraformaldehyde was used as a convenient source of the formaldehyde. It was dissolved in water with warming, the solution standardised by Romijn's method, and diluted until it was exactly 2M with respect to formaldehyde; immediately before each electrolysis, 100 c.c. of this solution were mixed with 100 c.c. of supporting electrolyte to give anolytes of the quoted strengths. Several electrolyses were carried out with anolytes prepared from ordinary formalin solutions, and the results were identical, within the limits of probable error, with those obtained with solutions prepared from paraformaldehyde, showing the use of this substance to be justified. The catholyte was sulphuric acid or sodium hydroxide according to whether acid and neutral or alkaline stock solutions were being used as anolyte.

FIG. 1.



The Anodes.—Experiments were carried out with smooth platinum, platinised platinum, lead, gas carbon, copper, silver, nickel, and gold anodes. Except where otherwise stated, the anodes were rectangular sheets of the element under consideration of 20 sq. cm. total superficial area. Systematic methods of preparing the electrodes were adopted before each electrolysis so as to obtain reproducible surface conditions; these methods were as follows:

Platinum. Cleaned with warm concentrated hydrochloric acid, water, warm concentrated nitric acid, water, and heated to redness. *Platinised platinum.* Replatinised before each electrolysis and cleaned as above, the heating to redness being omitted. *Lead.* Treated with warm concentrated hydrochloric acid to remove oxide, immersed in nitric acid until just attacked, then washed with water and polished with wire brush to give bright surface. *Carbon.* Initially cleaned by boiling with concentrated hydrochloric acid containing potassium chlorate, and then boiled with water until free from acid; kept under water and thoroughly washed with boiling water before each experiment. *Copper.* Freshly plated before each electrolysis to give pink surface. *Silver.* Freshly plated before each electrolysis and polished. *Nickel.* Freshly plated before each electrolysis to give matte coating. *Gold.* Formed by electrodeposition of gold on platinum sheet to give bright coating before each electrolysis.

General Conditions of Electrolysis.—Except where otherwise stated, 0·02 Faraday of electricity was passed in each electrolysis. Although sufficient to produce reasonable amounts of the oxidation products, this quantity of electricity did not change substantially the formaldehyde concentration in the anolyte. Current was supplied from a 100-volt generator through rheostats and a calibrated milliammeter. Three main C.D.'s, of 0·025, 0·010, and 0·004 amp./sq. cm., were used, corresponding to actual currents of 0·5, 0·2, and 0·08 amp. and times of electrolysis of 64, 160, and 402 mins. Electrolyses in neutral and acid solutions were carried out at 15°, but in alkaline solutions the temperature was maintained at 5° to minimise the Cannizzaro reaction which takes place spontaneously (see below).

Analysis of Products.—*Gas.* Samples of any gas evolved during electrolysis were transferred to a Bone–Newitt apparatus, and a complete analysis for carbon dioxide, oxygen, carbon monoxide, hydrogen, and hydrocarbons carried out. No hydrocarbons were found in any experiment.

Solution. Formic acid and carbon dioxide contained in the anolyte were estimated as below.

Formic acid. 20-C.c. portions of the anolyte after electrolysis were taken, and the formic acid estimated, after precipitation of the bulk of the formaldehyde as trithioformaldehyde, by the method of Hickling and Rodwell (J., 1941, 51). In alkaline solution, spontaneous decomposition of formaldehyde into formic acid and methyl alcohol takes place by the Cannizzaro reaction. To allow for this, every electrolysis was followed by a control experiment under identical conditions but with no current passing, and the amount of formic acid produced by chemical decomposition was estimated; this was then subtracted from the total formic acid found in the electrolysis.

Carbon dioxide. Measured portions of the anolyte (5 or 10 c.c.) were taken immediately after electrolysis and boiled with 25 c.c. of 2N-sulphuric acid. The carbon dioxide expelled was collected in 70 c.c. of approximately 0·1N-barium hydroxide solution, the barium carbonate filtered off in a fritted-glass funnel, washed thoroughly, and dissolved in 25 c.c. of approximately 0·1N-hydrochloric acid. The excess acid was then titrated with standard 0·1N-sodium hydroxide (methyl-orange as indicator). Control analyses were carried out to allow for incidental carbon dioxide entering during analysis, and for carbon dioxide absorbed from the air during electrolysis with alkaline electrolytes, and the appropriate corrections were made in all cases.

Results.—The chief possible anodic reactions may be formulated as follows, without making any assumptions as to the nature of the anodic oxidising agent or the mechanism of the processes.

(1) $2\mathrm{H{\cdot}CHO} + 2\mathrm{OH'} + 2\mathrm{F} = \mathrm{H_2} + 2\mathrm{H{\cdot}CO_2H}$

(2) $\mathrm{H{\cdot}CHO} + 2\mathrm{OH'} + 2\mathrm{F} = \mathrm{H_2O} + \mathrm{H{\cdot}CO_2H}$

(3) $\mathrm{H{\cdot}CHO} + 4\mathrm{OH'} + 4\mathrm{F} = 3\mathrm{H_2O} + \mathrm{CO_2}$

(4) $\mathrm{H{\cdot}CHO} + 2\mathrm{OH'} + 2\mathrm{F} = 2\mathrm{H_2O} + \mathrm{CO}$

(5) $4\mathrm{OH'} + 4\mathrm{F} = 2\mathrm{H_2O} + \mathrm{O_2}$

The results are expressed as percentage current efficiencies for these five reactions. The efficiency of (1) was calculated from the amount of hydrogen evolved, and that of (2) from the amount of formic acid after subtraction of that produced by (1). The efficiency of (3) was obtained from the total carbon dioxide produced both in the solution and in any gas evolved, and those of (4) and (5) were determined from gas measurement and analysis. The general order of reproducibility of these efficiency figures in duplicate analyses of any one anolyte and gas was as follows: (1), (4), and (5), ±0·2%; (2), ±2%; (3), ±5%.

Acid and neutral solutions. In Table I are summarised the results for electrolyses of the acid and the neutral stock solution at the three standard C.D.'s with certain anodes; the other electrodes dissolved when used as anodes in these solutions. The initially neutral anolytes tended to become acid on electrolysis and after use had a pH value of about 5.

TABLE I.

	Acid solutions.								*Neutral solutions.*							
	C.D., amp./ sq. cm.	Current efficiencies, %.							C.D., amp./ sq. cm.	Current efficiencies, %.						
Anode.		(1).	(2).	(3).	(4).	(5).	Total.	Anode.		(1).	(2).	(3).	(4).	(5).	Total.
Pt	0·025	0	74	4	2	18	98	Pt	0·025	0	54	7	1	35	97
	0·010	0	81	7	2	12	102		0·010	0	69	4	1	30	104
	0·004	0	77	14	1	4	96		0·004	0	64	5	1	15	85
Au [1]	0·025	0	43	12	0	43	98	Au [1]	0·025	0	38	8	0	52	98
	0·010	0	51	7	0	40	98		0·010	0	56	9	0	42	107
	0·004	0	56	8	0	30	94		0·004	0	62	6	0	26	94
Platinised	0·025	0	27	43	0	0	70	Platinised	0·025	0	19	75	0	0	94
Pt	0·010	0	30	45	0	0	75	Pt	0·010	0	17	75	0	0	92
	0·004	0	33	33	0	0	66		0·004	0	12	85	0	0	97
Pb [2]	0·025	0	19	37	0	0	56	Pb [2]	0·025	0	18	31	1	41	91
	0·010	0	19	32	0	0	51		0·010	0	14	30	1	47	92
	0·004	0	26	32	0	0	58		0·004	0	7	29	0	38	74
C [3]	0·025	0	4	41	3	3	51	C [3]	0·025	0	0	65	4	2	71
	0·010	0	0	54	3	2	59		0·010	0	0	60	4	1	65
	0·004	0	1	45	2	1	49		0·004	0	0	57	4	1	62

[1] This anode tended to become black during electrolysis and dissolved to some extent.

[2] This anode became somewhat brown during electrolysis, presumably by the formation of an oxide coating.

[3] This was attacked during electrolysis, giving rise to products which coloured the electrolyte brown.

The main conclusions from these results would appear to be as follows. No hydrogen (1) is produced by the electrolytic oxidation of formaldehyde in acid or neutral solution. The current efficiency for the formation of formic acid (2) depends upon the nature of the anode; it is high at platinum, fairly high at gold, much lower at platinised platinum and lead, whereas at a carbon anode scarcely any formic acid is formed. In general the efficiency is higher in acid than in neutral solutions, and in most cases it increases with decreasing C.D. Production of carbon dioxide (3) is small at platinum and gold anodes, but substantial with the other electrodes, and carbon monoxide (4) is formed in very small amounts in some cases, particularly at a carbon anode. Evolution of oxygen (5) is marked with platinum and gold electrodes, and with lead in neutral solution, and seems to be favoured by increase of C.D. If efficiencies (3), (4), and (5) are added together and the total taken to represent the current used in oxygen evolution or disintegrative oxidation brought about by oxygen, in contrast to limited oxidation to formic acid, which may be regarded as the primary oxidation reaction (see Discussion), then it is apparent that the former processes occur to a greater extent in neutral than in acid solutions and are favoured by rise of C.D.

The total current efficiencies for all the electrode processes studied are in general within reasonable distance of 100%, if the difficulties of the analytical methods and probable experimental errors are borne in mind, but certain discrepancies are apparent. For instance, with platinised platinum, lead, and carbon anodes in acid solution, and with the carbon anode in neutral solution, substantial fractions of the current passed are not accounted for by the five measured current efficiencies. With the lead and the carbon electrodes this may be due in part to oxidation of the anode material since, as pointed out in Table I, both these electrodes underwent some change. It seems doubtful, however, whether these factors will account wholly for the very considerable discrepancies, and, moreover, the case of platinised platinum in acid solution remains puzzling. It may be noted that the discrepancies chiefly arise where what has been termed disintegrative oxidation is very marked, and particularly in acid solution. Search was therefore made for other possible oxidation products of formaldehyde, such as oxalic acid, but none such could be detected. Check experiments were also carried out to ascertain whether formic acid might be lost by reaction with or adsorption by the anode material, and whether carbon dioxide, when present in large amounts, might be lost by diffusion through the anolyte to the atmosphere; the results of these experiments were negative. In the cases cited, therefore, it has not been possible to account for the whole of the current passed.

Alkaline solutions. In Table II are summarised the results for electrolyses of the alkaline stock solution at the three standard C.D.'s with the usual eight anodes.

Of the electrodes studied, silver gives a high efficiency for hydrogen formation by reaction (1), at gold the efficiency is appreciable, and at platinum and carbon very small but definite amounts of hydrogen are formed; at the other anodes no hydrogen is produced. Visual observation of the silver and gold anodes indicated that the formation of hydrogen was not uniform throughout the electrolysis; at silver the evolution was initially very vigorous but decreased with time, whereas at gold a pulsating evolution was noted. Formation of formic acid by reaction (2) accounts for the greater part of the remaining current in most cases and is accompanied by moderate oxidation to carbon dioxide, except where hydrogen formation is high when the efficiency of reaction (3) is very low. Small amounts of carbon monoxide (4) are formed with the carbon anode, and traces of oxygen (5) are obtained with several of the electrodes at the highest C.D. The total efficiencies for the five processes studied are in general within reasonable distance of 100% in view of the

TABLE II.

	C.D., amp./	Current efficiencies, %.							C.D., amp./	Current efficiencies, %.					
Anode.	sq. cm.	(1).	(2).	(3).	(4).	(5).	Total.	Anode.	sq. cm.	(1).	(2).	(3).	(4).	(5).	Total.
Pt	0·025	0·2 [1]	72	41	0	1	114	C [3]	0·025	0·5	43	65	1	1	111
	0·010	0·1 [1]	93	27	0	0	120		0·010	1·0	24	57	1	0	83
	0·004	0·2 [1]	65	29	0	0	94		0·004	2·4	61	27	1	0	91
Au	0·025	18	89	0	0	0	107	Ni [4]	0·025	0	70	29	0	1	100
	0·010	5	110	0	0	0	115		0·010	0	96	9	0	0	105
	0·004	11	74	0	0	0	85		0·004	0	75	30	0	0	105
Platinised Pt	0·025	0	61	39	0	0	100	Cu [5]	0·025	0	74	30	0	0	104
	0·010	0	101	3	0	0	104		0·010	0	97	3	0	0	100
	0·004	0	90	14	0	0	104		0·004	0	76	36	0	0	112
Pb [2]	0·025	0	61	33	0	1	95	Ag [6]	0·025	72	28	4	0	0	104
	0·010	0	65	11	0	0	76		0·010	58	25	1	0	0	84
	0·004	0	54	11	0	0	65		0·004	67	19	0	0	0	86

[1] Although these efficiencies are very small, they correspond to definite amounts of hydrogen which were isolated and burnt.

[2] The anode became brown and dissolved appreciably, particularly at the lower C.D.'s.

[3] This anode was attacked somewhat as in Table I.

[4] The surface of this anode darkened during electrolysis, and later became spotted with a bluish-green deposit.

[5] This anode blackened on electrolysis and ultimately became partly covered with a bluish-green deposit.

[6] This anode tarnished during electrolysis and there was a tendency for a brown deposit to form.

difficulties of the analytical methods, and in particular of the corrections which had to be made for the spontaneous occurrence of the Cannizzaro reaction; furthermore, as indicated in the table, the electrodes suffered attack in many cases, especially the lead anode.

Electrolysis at very low C.D.'s. Since hydrogen evolution was only observed in a few cases in the anodic oxidation of formaldehyde at the standard C.D.'s, and not at all at a copper anode where its formation had previously been reported, it was decided to investigate the electrolysis at a much lower C.D. A new cell was devised which would accommodate large cylindrical electrodes; it consisted of a large boiling-tube (approx. 15 cm. long and 5 cm. in diameter) provided with a rubber stopper carrying thermometer, cathode vessel, gas delivery tube, and anode support. The anodes were usually in the form of cylinders fitting fairly tightly in the cell and having an inner surface area of *ca.* 70 sq. cm. Such a volume of the stock alkaline electrolyte was used as nearly filled the cell (*ca.* 185 c.c.) and the remaining space was then evacuated. Electrolyses were carried out with a C.D. of 0·0004 amp./sq. cm. (actual current *ca.* 0·028 amp.) at 5°, the cell being externally cooled, and 0·002 F. of electricity was passed in each case. The gas evolved was collected as usual, that remaining in the cell at the end of the electrolysis being removed by pumping, and the hydrogen content determined by analysis. The formic acid formed was also determined, allowance being made for that produced by the Cannizzaro reaction. The results are given in Table III. In view of the smaller quantity of electricity passed, the experimental errors in the current efficiencies will be greater than those previously quoted, and very small amounts of hydrogen may have escaped detection.

TABLE III.

Anode	Au.	Ag.	Cu.	Ni.	Pt.	Pb.	C.
Current efficiency (1), %	86	84	77	47	0	0	0
,, ,, (2), %	10	4	8	51	93	61	76
,, ,, total, %	96	88	85	98	93	61	76

The electrodes were oxidised to a much less extent than in the electrolyses at the higher C.D.'s; no appreciable attack could be detected with the platinum, gold, nickel, and silver anodes, although the copper anode tended to blacken slightly. The lead anode became white and appreciable amounts of metal dissolved, whereas the surface of the carbon anode became rather soft, probably indicating oxidation of the electrode, although the electrolyte was not coloured as in former cases; oxidation of the anodic material probably accounts for the total current efficiencies with the last two being appreciably lower than 100%.

From Table III it is apparent that, in general, the current passed is almost wholly utilised in reactions (1) and (2), and although platinum, lead, and carbon electrodes give no hydrogen, the low C.D. has an extremely favourable influence on hydrogen production at gold, silver, copper, and nickel anodes. This is particularly striking in the case of the last two, which gave no hydrogen at all in the ordinary C.D. range, whereas with gold and silver the previous efficiencies are appreciably increased. With the nickel anode it was observed that the hydrogen evolution decreased suddenly about half-way through the electrolysis, so the initial efficiency must have been considerably greater than the average value recorded.

Influence of alkalinity. To ascertain to what extent the formation of hydrogen depends upon the electrolytes being strongly alkaline, electrolyses were carried out with the silver anode at 0·0004 amp./sq. cm., M-formaldehyde being used in buffer solutions of various pH values. Sodium hydroxide solutions were used for pH 14 and 13, and mixtures with sodium carbonate and borax for pH 12 and 11. The results are given below.

pH value	14	13	12	11
Current efficiency (1), %	84	66	5	14

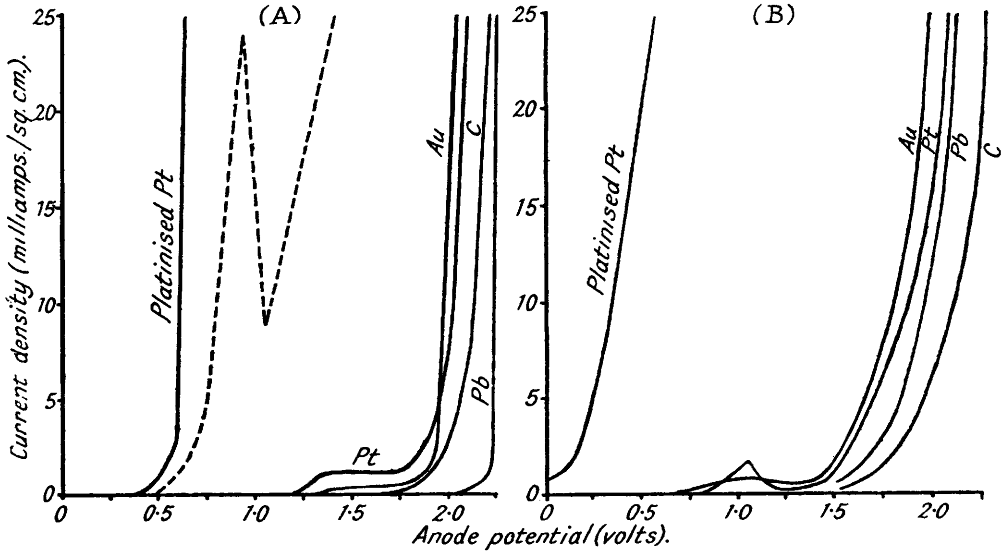
The formation of hydrogen is markedly favoured by the use of strongly alkaline solutions. It was noted that darkening of the anode (probably indicating oxide formation) developed more rapidly in the less alkaline solutions.

Potential Measurements.—The variation of anode potential with quantity of electricity passed was studied in all the experiments at the standard C.D.'s by making frequent measurements of the potential relative to a saturated calomel electrode by the potentiometer–voltmeter method. The siphon of the calomel electrode was approached as nearly as possible to the anode, but in view of the high currents used the potential measurements include marked resistance errors, and no precise significance should therefore be attached to the quoted values.

In acid and neutral solutions the anode potential at platinum, gold, lead, and carbon electrodes rose almost at once to a value in the region of that for oxygen evolution, *ca.* +2 volts on the hydrogen scale, but with platinised platinum the value was much lower, about +0·4 to +0·8 volt, although it tended to drift upwards, particularly at the highest C.D. in neutral solution. In alkaline solution with lead and carbon anodes the potential again rose rapidly to the oxygen evolution region, *ca.* +1·4 volts, but with platinum there was initially a tendency for a lower potential stage (−0·2 to +0·4 volt) to exist, and this was clearly marked at 0·004 amp./sq. cm., the potential rising suddenly after about 500 coulombs of electricity had been passed. At nickel and copper anodes the potential was in the region of +0·8 volt, tending to drift upwards with time, particularly at the highest C.D., while with silver the value was very low and remained in the region of 0 volt throughout the electrolyses. With the gold anode in alkaline solution an interesting periodic fluctuation of potential was noted which was particularly marked at the highest C.D. At first brisk evolution of hydrogen took place, the anode potential being about +0·1 volt; the potential then rose with increasing rapidity, the evolution of gas at the same time diminishing, to a value of about +1·4 volts, whereat sudden rapid development of gas again took place and the potential dropped to its original value. These fluctuations occurred throughout the electrolysis, the cycle occupying 1—2 mins. At the lower C.D.'s, the periodic phenomenon was not so clearly marked, but the same tendency was apparent, the periods being much longer.

To obtain more precise information as to the anode potentials set up in the electrolysis of formaldehyde solutions, C.D.–potential curves were studied. To minimise resistance errors, small anodes were used, 1 sq. cm. in acid and neutral solutions and 0·1 sq. cm. in alkaline solution, so that the total currents passed were low. The electrolyte, which was not stirred, was the appropriate stock solution; it was contained in an open beaker into which the anode, thermometer, and cathode vessel dipped. As before, electrolyses were carried out at 5° in alkaline and 15° in neutral and acid solutions. A saturated calomel electrode was employed as reference electrode, the siphon being connected to the anode by a Luggin capillary, and potentials were measured to the nearest centivolt by the potentiometer–voltmeter method. Since the anode potential depends upon the time of electrolysis, it was necessary to control the duration of the observations at each C.D. to obtain reasonably reproducible results. The method used was to fix a certain e.m.f. on the potentiometer and then to adjust the polarising current until the anode–calomel system had the same value. In general, 1 min. was allotted to each of the observations, which were made at intervals of 0·1 volt commencing from the static value. The potential was fixed at the beginning of the minute, and the current adjusted at the half minute and read; the next potential was fixed at the conclusion of the minute, and so on. The observations were made first with steadily increasing potentials and then with decreasing values. All potentials are given on the hydrogen scale.

FIG. 2.

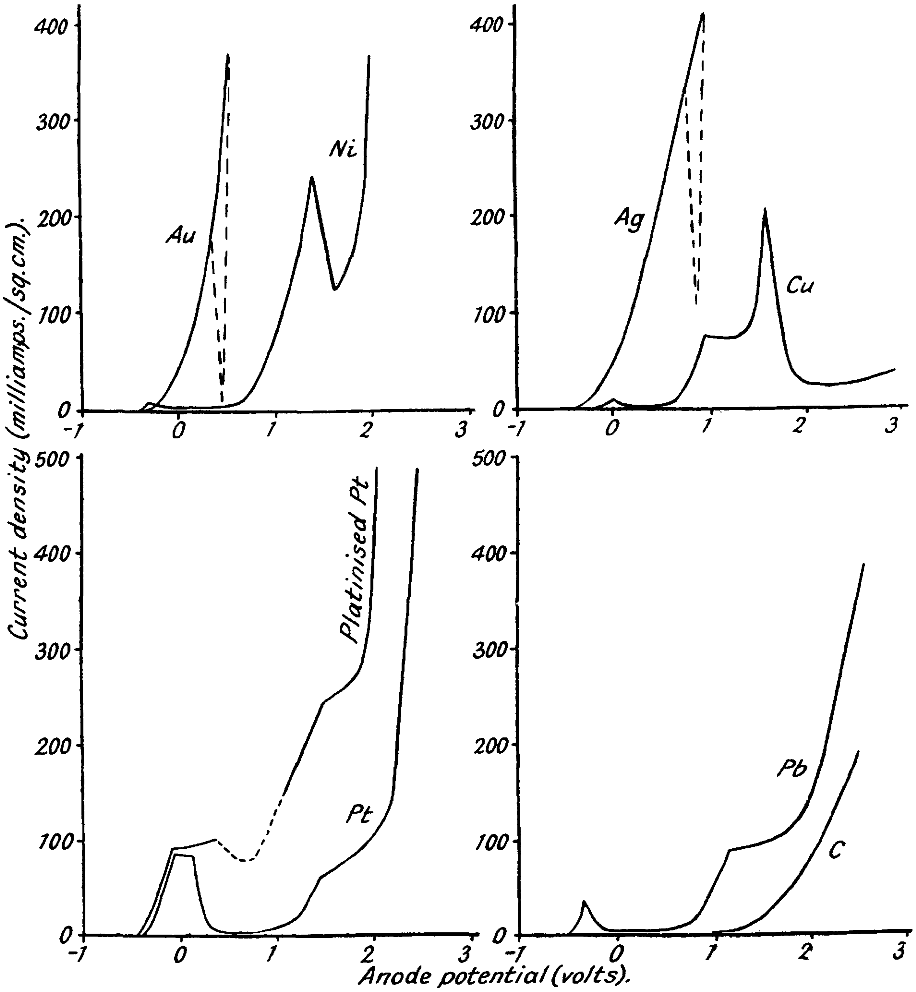


The results for the acid and neutral stock solutions are shown in Figs. 2*A* and 2*B*, respectively. With lead and carbon anodes the potentials rise very rapidly with increasing C.D. to high values in the region of those for oxygen evolution. With platinum and gold there appear to be lower-potential stages at small C.D.'s, the potentials jumping rapidly to higher values when critical C.D.'s are reached. With the platinised platinum electrode a low-potential stage is very marked, so much so that over the normal C.D. range considered no jump of potential takes place. If, however, higher C.D.'s are used, an abrupt transition to a higher potential can be observed, as is shown by the broken graph which was obtained with a 0·1 sq. cm. electrode and for which the C.D. scale is increased 20 times. The graphs for acid and neutral solutions are fundamentally similar, but in neutral solution the potentials are displaced downwards, as would be expected if they are dependent upon hydroxyl-ion concentration (*e.g.*, as would be the case for oxide and oxygen potentials). The graphs for decrease of C.D., which are omitted from the figures in order to avoid confusion, were essentially similar to those for increasing C.D., but any low-potential stages tended here to be suppressed, suggesting that these are due to irreversible anodic polarisation.

The graphs obtained with alkaline stock solution were very complex and are shown in Fig. 3; over certain ranges the currents were sometimes unstable and the broken lines indicate probable values. It is seen that very much higher C.D.'s are required to bring about anodic polarisation, which implies that formaldehyde is a much more effective depolariser in alkaline than in acid or neutral solution. With all anodes except carbon, at which the potential immediately attained a high positive value, there are indications of several potential stages. Current first begins to pass at a very low potential (0 to −0·5 volt), this being accompanied by hydrogen evolution at gold, silver, copper, and nickel anodes but not at lead or either type of platinum electrode. At a critical C.D., which is very low with copper and nickel, rather higher at lead, considerable at platinised and smooth platinum, and relatively enormous at gold and silver, an abrupt transition to a higher-potential stage sets in, and where gas evolution had previously been noted this either ceased or greatly decreased. With gold and silver no permanent shift of potential was observed, but fluctuations in which the current suddenly dropped momentarily to a very low value were recorded and are indicated by the broken lines; these fluctuations seemed to indicate the commencement of shifts to higher potentials which were, however, never attained, the electrodes resuming almost at once their low potential states. Following the initial transition, the potential at nickel, copper, platinum (smooth or platinised), and lead anodes then rises discontinuously with increase of C.D. through at least one and sometimes more stages to a final high positive value at which oxygen was freely evolved. These later transitions appeared with nickel, copper, and lead to be associated with the formation of visible oxide deposits on the electrodes, and with copper a blue film of high resistance was ultimately formed which is probably responsible for the final decrease of current at this electrode. The graphs obtained on decrease of C.D. were essentially similar to those shown, although the potentials were sometimes displaced downwards, and where complete polarisation had taken place the lower-potential stages tended to be suppressed.

Each anode appears very largely to give its own specific potential behaviour; there is no sharply defined common potential which might correspond to a definite oxidation–reduction potential of the depolariser, and there are no common critical C.D.'s at which the transitions occur from low to high potential stages. Of the electrodes which are known to give hydrogen at low C.D.'s, ease of polarisation decreases in the order Cu, Ni > Au > Ag.

FIG. 3.



Chemical Oxidation of Formaldehyde.—An enquiry was made into the chemical oxidising action of substances likely to be formed at an anode.

Oxygen. Gaseous oxygen does not react with formaldehyde solutions at room temperature, except in the presence of catalysts such as platinum black, but it is readily absorbed at 100—200° (Delépine, *Bull. Soc. chim.*, 1897, **17**, 938; Euler, *Ber.*, 1904, **37**, 3417). The nature of the products under these conditions has not been established, but it seems likely that formic acid is first formed and that this is further oxidised; in the presence of platinum black, complete oxidation to carbon dioxide and water occurs. It seems probable that nascent oxygen at an anode would bring about some oxidation at room temperature.

Hydrogen peroxide. In acid and neutral solutions hydrogen peroxide reacts slowly with formaldehyde, but in alkaline solutions the reaction is enormously accelerated (Kastle and Loevenhart, *J. Amer. Chem. Soc.*, 1899, **21**, 262). The initial product is probably bishydroxymethyl peroxide $CH_2(OH)\cdot O\cdot O\cdot CH_2\cdot OH$ which then undergoes decomposition (Wieland and Wingler, *Annalen*, 1923, **431**, 301; see also Hatcher and Holden, *Trans. Roy. Soc. Canada*, 1926, **20**, 395; Rieche and Meister, *Ber.*, 1933, **66**, 718; 1935, **68**, 1465).

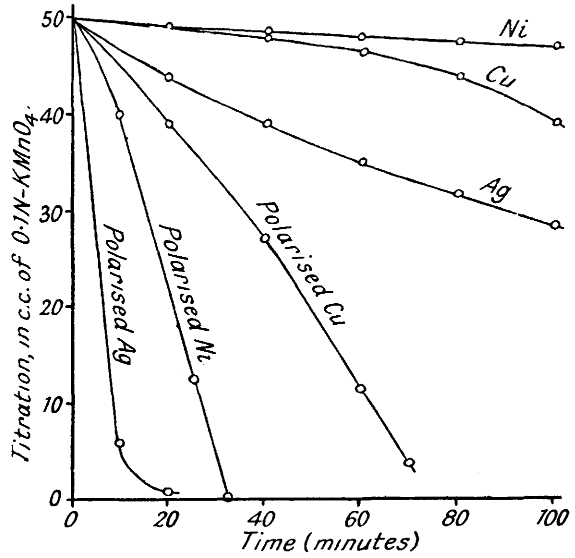
The nature of the final products in acid solution has been established by Fry and Payne (*J. Amer. Chem. Soc.*, 1931, **53**, 1975), who investigated the reaction at 60°. With very low concentrations of hydrogen peroxide, oxidation to formic acid and hydrogen (1) occurred, accompanied by simple oxidation to formic acid and water (2). As the concentration of hydrogen peroxide was increased, the occurrence of reaction (1) diminished rapidly while that of (2) increased. Oxidation to carbon dioxide and water (3) took place to an increasing extent as the concentration of hydrogen peroxide was further raised, and as it was invariably accompanied by evolution of oxygen, the process may perhaps be mainly ascribed to the action of nascent oxygen.

In strongly alkaline solution hydrogen peroxide is reported to react very vigorously with formaldehyde at room temperature to give quantitative liberation of hydrogen (1) (Beilstein, " Handbuch," Vol. I, p. 572, 1918). To obtain more precise information, the reaction was investigated under conditions roughly comparable with those used in the electrolytic experiments. 0·01 Mol. of hydrogen peroxide in the form of a dilute solution was added gradually to 185 c.c. of M-formaldehyde at 5° so that the final volume of the solution was 200 c.c. Solutions of pH 14, 13, and 12 were used. The gas evolved in the reaction was measured and analysed, and the formic acid produced in the solution estimated. Gas evolution was extremely vigorous at pH 14, much more moderate at pH 13, and very slow at pH 12. The reaction was allowed to go to completion in the first two cases, but in the third the formic acid analysis was made after 5 hours when the solution still gave a moderate test for hydrogen peroxide; in this last case, therefore, the formic acid result may not be wholly reliable, since some oxidation may have occurred during the analysis. The results are calculated as efficiencies for reactions (1) and (2) and are summarised below. It is apparent that in reaction with hydrogen peroxide, as in the electrolysis, hydrogen production is markedly favoured by strongly alkaline solutions.

pH	14	13	12
Efficiency, (1), %	98	80	20
,, (2), %	0	8	74

Metallic oxides. The action on formaldehyde of the metallic oxides and peroxides likely to be formed at the anodes was qualitatively investigated. Oxides used were: Ag_2O, Ag_2O_2, Cu_2O, CuO, Au_2O_3, PtO, PtO_2, PtO_3, NiO, NiO_2, PbO, PbO_2. In alkaline solution the oxides of silver, gold, and copper were reduced to the metals with marked evolution of hydrogen gas; the reaction was very vigorous with the silver oxides, somewhat slower with gold oxide, and with the copper oxides there was a period of induction before reaction occurred and the cuprous oxide reacted less readily than the cupric oxide. The oxides of platinum were reduced to the metal, the lowest oxide reacting most rapidly, but there was scarcely any gas evolution. Nickel peroxide and lead peroxide were slowly reduced to the lower oxides, but again with very little gas evolution, whereas nickel and lead monoxides were not apparently reduced. In neutral and acid solutions the action of the oxides was very slight at room temperature. In both cases platinum monoxide (and to a less extent the dioxide) were reduced slowly to metal, and nickel and lead peroxides appeared to react slowly in the acid solution.

FIG. 4.



The hydrogen evolution with silver, gold, and copper oxides in alkaline solution was quantitatively investigated by taking a weighed quantity of each oxide corresponding to 0·02 equiv. of available oxygen, allowing the reaction with 200 c.c. of alkaline stock solution to proceed to completion, and measuring and analysing the gas evolved. The results expressed as efficiencies for reaction (1) were: Ag_2O 38, Ag_2O_2 50, Au_2O_3 40, Cu_2O 107, and CuO 93%.

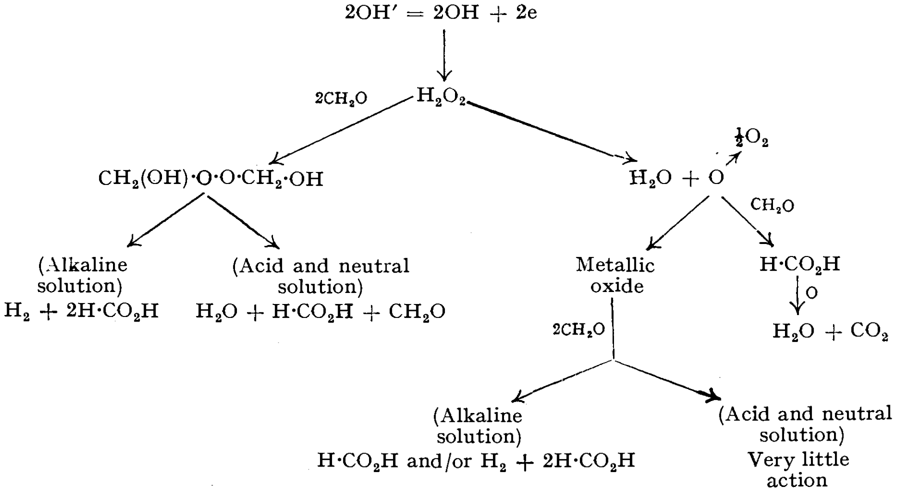
Catalytic Decomposition of Hydrogen Peroxide.—It has been found that anodic polarisation decreases the activity of platinum as a catalyst for hydrogen peroxide decomposition (Spitalsky and Kagan, *Ber.*, 1926, **59**, 2905), but with lead it is known that the metal itself is a poor catalyst but it becomes very effective when oxidised. It appeared of interest, therefore, to ascertain whether the activity of the other metals used as anodes was markedly affected when they became coated with oxides, as happens in certain circumstances in the electrolysis of formaldehyde solutions. The metals were used in the form of the 20 sq. cm. electrodes, mounted vertically, and rotated at 430 r.p.m. in a solution of hydrogen peroxide in N-sodium hydroxide at 15°. The rate of decomposition of the hydrogen peroxide was followed by withdrawing 5 c.c. portions from time to time and titrating these, after acidification, with 0·1N-potassium permanganate. Two sets of experiments were carried out: in the first, the metals were prepared in the usual way and used, and in the second set they were subjected to anodic polarisation at 0·1 amp. in 0·01N-sodium hydroxide until covered with a visible oxide film before being used as catalysts. The results for silver, copper, and nickel are shown graphically in Fig. 4, in which titrations in c.c. of permanganate are plotted against the time in minutes, so that the steepness of each graph affords a measure of the efficiency of the material as a catalyst for hydrogen peroxide decomposition.

It is apparent that in each case the coating of the metal with oxide enormously increases its activity as a catalyst for hydrogen peroxide decomposition. No graph for gold is shown, since it was found impossible to obtain any substantial oxide coating on anodic polarisation in sodium hydroxide alone, but it seems likely that the same conclusion will hold, since qualitative tests with a gold anode which had been used in the electrolysis of formaldehyde solutions and had become covered with a dark coating showed that in this state it was a much more vigorous catalyst for hydrogen peroxide decomposition than was the clean metal.

DISCUSSION.

As the experimental investigation has shown, the phenomena associated with the electrolytic oxidation of formaldehyde are extremely complex, particularly as regards the number of possible anodic reactions and their complicated dependence upon the experimental conditions. The results lend no support to the view of Müller *et al.* (*loc. cit.*) that any stage in the oxidation corresponds to the discharge of an anion derived from formaldehyde. Such a process could only conceivably occur in strongly alkaline solutions, since formaldehyde behaves as an extremely weak acid, and should be associated with a definite oxidation–reduction potential at the anode. Inspection of the C.D.–potential curves reveals no such potential. Although it is true that many of the electrodes show low potential stages, yet these appear to be specific to the electrodes rather than due to any definite oxidation reaction of the depolariser. The influence of C.D. is also directly contrary to that to be expected from the electrical mechanism since, if hydrogen formation is due to the interaction of pairs of discharged radicals, it might be supposed that this would be greatly favoured by rise of C.D. increasing their concentration at the electrode surface, whereas in practice the converse is found. Furthermore, the view fails to account for the progressive polarisation in electrolyses at constant C.D., the diminution of hydrogen production with rise of potential, the nature of the oxidation at the high-potential stages, and the whole of the results in neutral and acid solution. To summarise, therefore, any purely electrical mechanism is both inadequate and at variance with the experimental results, and it appears that the electrolytic oxidation of formaldehyde must be essentially a chemical process; but no simple view postulating either oxygen or an oxide with the anode material as the effective oxidising agent, seems adequate to explain all the phenomena.

Nearly all the results, however, can be accounted for if the view put forward in the previous parts of this series is adopted, *viz.*, that the primary action at any anode in aqueous solution is the formation of hydrogen peroxide by the irreversible combination of discharged hydroxyl radicals. There will then be a number of possibilities. Part of the hydrogen peroxide first formed may oxidise the formaldehyde in its own characteristic way, but a portion will decompose to give oxygen and water, the amount depending upon the concentration and stability of hydrogen peroxide under the experimental conditions. The nascent oxygen formed by the decomposition of the hydrogen peroxide will itself act in several ways: part may form an oxide with the electrode material which may react with the formaldehyde, a further portion may itself directly oxidise the formaldehyde, and the remainder will be evolved as gaseous oxygen. The accompanying scheme summarises the various possible reactions, and the extent to which each is likely to occur can be predicted from the experimental data.



In acid solution hydrogen peroxide is relatively stable and does not react very rapidly with formaldehyde. Hence there will be a very high local concentration of hydrogen peroxide at the anode surface, and the primary oxidation reaction should be that of hydrogen peroxide at high concentrations in acid solution; this, as has been pointed out, leads mainly to formic acid and water. Hence, at anodes which are poor catalysts for hydrogen peroxide decomposition the main product should be formic acid. At the same time a portion of the hydrogen peroxide will decompose, and the nascent oxygen formed may itself bring about a certain amount of oxidation to carbon dioxide and water, and the remainder should be evolved as gaseous oxygen. At anodes which are good catalysts for hydrogen peroxide decomposition, the fraction of the hydrogen peroxide decomposing should be greatly increased, and hence the efficiency of formic acid production should be much lower and that of disintegrative oxidation and oxygen evolution should be much higher. This is closely in agreement with the experimental results. Smooth platinum and gold (when free from oxide) are relatively poor catalysts for hydrogen peroxide decomposition and give fairly high efficiencies for formic acid production, whereas platinised platinum and lead when covered with dioxide, as tends to happen in the electrolysis, are excellent catalysts and give very small efficiencies. Since, as previously pointed out, platinised platinum greatly accelerates the oxidation of formaldehyde by oxygen, and lead dioxide can itself oxidise formaldehyde in acid solution, there is little oxygen evolution in these two cases. The position of the carbon anode is somewhat anomalous; in general, carbon in the massive form can only be regarded as a moderate catalyst for hydrogen peroxide decomposition and hence should give a fairly high formic acid efficiency, whereas that observed is extremely low; it seems likely that this anomalous result is connected in some way with the very low total efficiency of electrolysis and the fact that the carbon anode is itself seriously attacked.

In the neutral solution (which becomes slightly acid on electrolysis) essentially the same considerations will apply as in the acid electrolyte, but since hydrogen peroxide is less stable in neutral than in acid solution it would be expected that the formic acid efficiency should be rather lower at all electrodes and that of disintegrative oxidation or oxygen evolution should be higher. This is in excellent agreement with the experimental results shown in Table I. It is noteworthy that lead dioxide does not react with formaldehyde in neutral solution, and hence considerable oxygen is here evolved instead of being used in oxidation.

In alkaline solution hydrogen peroxide is much less stable than in acid or neutral solution, but this will be offset to a great extent by the fact that it reacts extremely rapidly with formaldehyde and the concentration of hydrogen peroxide at the anode will thus be kept relatively low. Hence, under conditions such that the decomposition of the peroxide is not markedly catalysed by the anode material, a moderate efficiency for the formation of the products of the action of hydrogen peroxide on formaldehyde in alkaline solution would be expected, and these are hydrogen and formic acid according to reaction (1). The nascent oxygen arising from the decomposition of the hydrogen peroxide will probably initially form oxides with the anode material, and these in general have been observed to react rapidly with the formaldehyde. Some of them, notably Ag_2O, Ag_2O_2, Au_2O_3, Cu_2O, and CuO, have been found to give large amounts of hydrogen in their action on formaldehyde, and in these cases therefore, under appropriate conditions, the efficiency of reaction (1) may be supplemented. The other oxides studied which react with formaldehyde but do not produce appreciable hydrogen probably give formic acid and water (2). Oxygen not utilised in oxide formation is likely to bring about oxidation first to formic acid and ultimately to carbon dioxide and water (3), and since formaldehyde is very readily oxidised in alkaline solution, very little gaseous oxygen should be evolved (5). This gives in outline the various reactions which may take place, but their relative extents will depend very largely on the experimental conditions. For instance, it has been shown that the metals, silver, gold, copper, and nickel are comparatively poor catalysts for the decomposition of hydrogen peroxide when free from oxides, but become extremely effective when covered with oxide layers. It is apparent, therefore, that C.D. will have a predominant effect on the electrolytic oxidation at these anodes. If it is sufficiently low, so that oxides are removed as fast as they are formed, by reaction with formaldehyde, then the results will be those to be expected for anodes which are poor catalysts for hydrogen peroxide decomposition, while if the C.D. is such that oxide removal cannot keep pace with its formation, then the results will be those for anodes which are good catalysts for hydrogen peroxide decompositions; in some cases a transition from one state to the other may take place during electrolysis as the oxide accumulates. The critical C.D. ranges will obviously differ widely for the different metals. Silver oxides react very rapidly with formaldehyde in alkaline solution, gold oxide rather more slowly, and with copper and nickel oxides the initial reaction is very slow; with silver and gold anodes, therefore, the critical C.D.'s should be high, while with copper and nickel a very low C.D. should be necessary to prevent oxide accumulation. It is furthermore apparent that, where a metallic oxide reacts only slowly with formaldehyde, this mode of oxidation may account for a substantial fraction of the current at low C.D.'s, while at high C.D.'s it may be negligible. The experimental results agree closely with these predictions. Of the anodes used, silver, gold, and copper give the greatest efficiencies for hydrogen production at low C.D.'s, since the actions of both the hydrogen peroxide and the metallic oxides lead to this product; the efficiencies decrease with increasing C.D., very sharply in the case of copper and least with silver as expected. Nickel in the unpolarised state gives a moderate efficiency for hydrogen formation which falls off abruptly with increasing C.D. Smooth platinum and carbon anodes, which are poor catalysts for hydrogen peroxide decomposition independently of C.D., give hydrogen in the ordinary C.D. range although the yields are smaller than might be expected; the anomaly with platinum, however, is readily explicable since it has been found (Wöhler, *Z. anorg. Chem.*, 1904, **40**, 423) that the lower oxides of platinum readily oxidise gaseous hydrogen to water at room temperature, and hence, even if the initial efficiency for hydrogen formation is substantial, only traces of the gas are likely to be evolved. At platinised platinum and lead (which readily oxidises to the dioxide and goes into solution) no hydrogen would be expected, since the decomposition of hydrogen peroxide is markedly catalysed, and none is found.

The present view provides a plausible explanation of the peculiar potential phenomena which have been observed. The hydrogen peroxide theory postulates that immediately hydroxyl ions are discharged at the anode the radicals combine irreversibly to give hydrogen peroxide, and hence the discharge potential of the hydroxyl ions will be very low. The actual observed potentials will be set up indirectly by electromotively active substances formed at the anode, and in the present case the most likely substance is oxygen. Since, however, oxygen itself reacts with formaldehyde, its rate of accumulation at the anode will be slow. At first it will tend to form an oxide with the electrode material, and this, if electromotively active, will set up its own potential. When the surface is saturated for this mode of oxygen attachment, any further oxygen accumulating at the anode may form a higher oxide, with consequent abrupt jump of potential to a new characteristic value, and ultimately there may be a rise to a potential corresponding to a very slow rate of oxygen evolution. Thus the general form of the potential phenomena will be as follows. The ultimate potential attained at high C.D.'s or on prolonged electrolysis will be a value corresponding to slow oxygen evolution for the anode material under consideration; preceding this there may occur one or more low-potential stages corresponding to formation of oxides at the electrode. The duration of these low-potential stages will depend upon the rate of oxygen accumulation, the rate of reduction of the oxides by formaldehyde, and the surface area of the anode. In alkaline solution where the oxides are readily reduced it would be expected that the low-potential stages should be more marked than in acid or neutral solution, as is the case. Where the oxides are reduced very readily or where the real surface of the anode is very large, the attainment of the oxygen evolution value may necessitate extremely high C.D.'s; the first factor is apparently operative in the case of silver and gold anodes in alkaline solution, and the second factor with platinised platinum. The actual values of the low-potential stages will depend upon the dissociation pressures of the oxides, their concentrations in the metal (where solid solutions are formed), and the hydroxyl-ion concentration of the electrolyte. The potential phenomena will thus be characteristic of the anode material, not of the oxidation processes in which the formaldehyde is involved. Essentially similar phenomena have been observed in a number of other cases of electrolytic oxidation, *e.g.*, thiosulphate, sulphite, methyl alcohol, and ethyl alcohol (see Glasstone and Hickling, *Chem. Rev.*, 1939, **25**, 427, for fuller discussion).

From the foregoing discussion it is apparent that the hydrogen peroxide theory affords an explanation of the main features of the electrolytic oxidation of formaldehyde. The actual mechanism of the oxidation of formaldehyde by hydrogen peroxide has not been specially considered, but only the end products to which it is known to give rise. It seems clear, however, from the work of Wieland and Wingler (*loc. cit.*) that bishydroxymethyl peroxide is an essential intermediate. The decomposition of this substance is very strongly accelerated by alkali to give hydrogen and formic acid, thus accounting for the rapidity of the reaction of formaldehyde and hydrogen peroxide in alkaline solution, while in acid and neutral solutions the decomposition is much slower and tends here also to give formic acid and water, this reaction being particularly marked in the presence of excess hydrogen peroxide.

UNIVERSITY COLLEGE, LEICESTER.

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