THE HYDROGEN PEROXIDE THEORY OF ELECTROLYTIC OXIDATION

S. GLASSTONE[1]

Department of Chemistry, University of Sheffield, Sheffield, England

AND

A. HICKLING

Department of Chemistry, University College, Leicester, England

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I. INTRODUCTION

Electrolytic oxidation processes fall broadly into two classes involving reactions which are thermodynamically reversible and irreversible, respectively. In the first category,—as, for example, in the oxidation of ferrous to ferric ions, of ferrocyanide to ferricyanide, or of hydroquinone to quinone,—the process takes place at a definite potential almost identical with the reversible oxidation–reduction potential for the given system, and the electrode material, provided it is not attacked, has little influence, at least at low current densities. Apart from its effect on diffusion, which is only apparent at high currents, alteration of temperature does not produce any appreciable change either of the anode potential or of the efficiency of the oxidation reaction. When the electrolytic process is thermodynamically irreversible, however, as is the case in the oxidation of many organic compounds and of certain inorganic and organic anions, the phenomena are very complex and a satisfactory interpretation of the results appears difficult; it is this aspect of the subject of electrolytic oxidation with which the present review is concerned.

It had been assumed for many years that in electrolytic oxidation each definite electrode potential stage corresponded to a different process and that a high potential implied a more intense oxidation than a low one; an examination of the experimental data, however, shows that these views are incorrect. In the oxidation of thiosulfate to tetrathionate (18), of sulfite to dithionate (18), and of methyl alcohol (32, 42), formaldehyde (32, 42), formic acid (29, 31, 33), and ethyl alcohol (27) at platinum anodes, two distinct potential stages have been observed, but the nature

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[1] Present address: Frick Chemical Laboratory, Princeton University, Princeton, New Jersey.

of the products appears to be the same at each stage and to be quite independent of the potential. Further, acetic acid can be oxidized anodically either to ethane or to methyl alcohol; the latter presumably represents a higher state of oxidation, but it is obtained, nevertheless, at a lower potential than the former (20). It is remarkable, too, in connection with these reactions that the addition of small amounts of neutral salts to acetic acid solution can cause almost complete suppression of the formation of ethane and its replacement by methyl alcohol (20). Another aspect of the difficulties involved in an interpretation of irreversible anodic phenomena is apparent when the influence of electrode material is considered. In the oxidation of acetate (20) and acid-ester ions (26) the efficiency is high for a smooth platinum anode but is low for an electrode of platinized platinum or lead dioxide; in the conversion of iodate to periodate (30) and of chromic to chromate ions (23), however, there is a complete reversal of this behavior. The effect of changes of temperature and of acidity or alkalinity seems, at first sight, to be equally paradoxical. Increase of pH, for example, results in a decrease of efficiency for the conversion of thiosulfate to tetrathionate (18), but alkalinity favors the oxidation of iodate (30) and chromic ions (23).

During recent years the authors of this paper have studied a number of electrolytic oxidation reactions, and, as a result, a theory has been developed providing an adequate explanation of the facts recorded above and many others brought to light in the course of the investigation. It is proposed to give here an account of the development of this theory and its application to the phenomena of electrolytic oxidation.

II. ORIGIN OF THE HYDROGEN PEROXIDE THEORY

The anodic oxidation of sodium thiosulfate to tetrathionate can be formulated either as a purely electrical process,

$$2S_2O_3^{--} = S_4O_6^{--} + 2e$$

or as a chemical reaction brought about by active oxygen liberated at the anode by the discharge of hydroxyl or oxygen ions, thus:

$$2OH^- = H_2O + (O) + 2e \quad \text{or} \quad O^{--} = (O) + 2e$$

followed by

$$2S_2O_3^{--} + (O) + H_2O = S_4O_6^{--} + 2OH^-$$

or

$$2S_2O_3^{--} + (O) = S_4O_6^{--} + O^{--}$$

Thatcher (43) considered the oxidation reaction to be chemical in nature; this conclusion rested mainly on the inference, based on observations of electrode potential, that mercuric cyanide, which is a catalytic poison, inhibited the conversion of thiosulfate to tetrathionate. If the process were electrical in nature, it is improbable that a very small amount of mercuric cyanide would have any influence on the results, but if it involved a chemical reaction, with the electrode material acting as catalyst, traces of an active poison might be expected to inhibit the anodic oxidation.

In 1931 the present authors set out to test the value of, and if possible to utilize, Thatcher's observation as a criterion for distinguishing between chemical and electrical processes at an anode, and an examination was made of the electrolytic oxidation of sodium thiosulfate solutions. The experimental technique, involving the use of buffer solutions for the maintenance of constant pH, of electrodes with controlled oxygen content, and of an accurate analytical method for the estimation of tetrathionate, represented a marked advance on previous work; the results obtained were thus reliable and easily reproducible. It was found that traces of mercuric cyanide in solution resulted in a definite increase of anode potential, as observed by Thatcher, but the efficiency of oxidation of thiosulfate to tetrathionate was almost unchanged. It is evident, therefore, that although the poison changes the electrode potential, it has no influence on the actual anodic process. In extending this work, the effect of other catalytic poisons, such as carbon disulfide, arsenious oxide, and strychnine hydrochloride, was investigated, and the influence of cupric ions, which are known to accelerate catalytically a number of reactions involving thiosulfate, was also studied. The results obtained for 0.025 *M* thiosulfate, in a buffer solution at pH 7, with a smooth platinum anode at ordinary temperature are quoted in table 1 (18); the current density (*C.D.*) employed was about 0.0002 ampere per square centimeter.

TABLE 1

Influence of poisons and of copper ions on the electrolytic oxidation of sodium thiosulfate

ADDED SUBSTANCE	CURRENT EFFICIENCY FOR OXIDATION
	per cent
None	90
0.001 *M* mercuric cyanide	91
0.01 *M* carbon disulfide	91
0.01 *M* arsenious oxide	87
0.005 *M* strychnine hydrochloride	56
0.001 *M* copper sulfate	30

The data recorded in table 1 show that whereas some catalytic poisons, e.g., mercuric cyanide and carbon disulfide, have no influence on the anodic oxidation of thiosulfate, others, e.g., arsenious oxide and especially strychnine hydrochloride, diminish the efficiency. Further, the surprising effect is evident that the expected catalyst, copper sulfate, also inhibits the electrolytic oxidation and to a marked degree. In seeking for a property possessed in common by arsenious oxide, strychnine salts, and copper ions, it became apparent that they were all catalysts for the decomposition of hydrogen peroxide, copper salts being particularly active in this respect. To test whether this common property was merely fortuitous, or whether it was fundamentally connected with the results obtained in the electrolysis of thiosulfate solutions, experiments were made in which a number of substances known to be effective catalysts for hydrogen peroxide decomposition were added to the electrolyte. The catalysts chosen were as varied as possible in their chemical nature and were such as to be unlikely to react with either thiosulfate or tetrathionate ions. The data recorded in table 2 are for a 0.025 *M* solution of thiosulfate at pH 7, with a smooth platinum anode at ordinary temperature. These very remarkable results, and especially the fact that the presence of 0.001 *M* manganous sulfate is able to inhibit completely the electrolytic oxidation of thiosulfate ions, indicate clearly that hydrogen peroxide must play an important part in the reaction. The provisional assumption was made, therefore, that hydrogen peroxide is, at least in this instance, the effective anodic oxidizing agent, and further experiments were devised to test this view.

TABLE 2

Influence of catalysts for the decomposition of hydrogen peroxide on the electrolytic oxidation of sodium thiosulfate

Current density, in amperes per square centimeter	0.0002	0.001
CATALYST ADDED	CURRENT EFFICIENCY FOR OXIDATION	
	per cent	*per cent*
None	90	85
Animal charcoal, 0.5 g. per 100 ml.		83
Sheep's blood, 1 ml. per 100 ml.	85	
Powdered silver, 0.5 g. per 100 ml.		69
Solid cobaltic oxide, 0.5 g. per 100 ml.		59
Cobalt sulfate, 0.001 *M*		31
Ferrous sulfate, 0.001 *M*	32	
Copper sulfate, 0.001 *M*	30	
Solid manganese dioxide, 0.25 g. per 100 ml.	24	
Manganous sulfate, 0.0001 *M*		3
Manganous sulfate, 0.001 *M*		0

It has been known for many years (2) that the action of hydrogen peroxide on sodium thiosulfate leads to two alternative processes resulting in the formation of tetrathionate and sulfate, respectively, thus:

$$H_2O_2 + 2S_2O_3^{--} = S_4O_6^{--} + 2OH^-$$

and

$$4H_2O_2 + S_2O_3^{--} = 2SO_4^{--} + 2H^+ + 2H_2O$$

The first reaction predominates in acid solution and is catalyzed by hydrogen ions, whereas the second tends to occur in neutral and alkaline media.

TABLE 3

Influence of hydrogen-ion concentration on the electrolytic oxidation of sodium thiosulfate

pH	CURRENT EFFICIENCY	
	Tetrathionate	Sulfate*
	per cent	*per cent*
5	90	5
6	87	9
7	79	11
8	65	12
9	60	14

* The figures for sulfate formation, while only approximate, are probably not seriously in error.

TABLE 4

Influence of molybdate ions on the electrolytic oxidation of 0.025 M sodium thiosulfate in the presence of 0.001 M manganous sulfate at pH 5

	CURRENT EFFICIENCY	
	Tetrathionate	Sulfate
	per cent	*per cent*
Without molybdate	94	1
With 0.01 *M* ammonium molybdate	61	34

It has been found that, in addition to tetrathionate, a small proportion of sulfate is formed in the course of electrolytic oxidation of thiosulfate; if hydrogen peroxide is the active oxidant, then the amount should increase as the solution becomes more alkaline. The experimental results in table 3, for a 0.025 *M* thiosulfate solution and a current density of 0.0002 ampere per square centimeter, show that this is in fact the case.

In feebly acid solutions molybdate ions markedly catalyze the formation of sulfate in the oxidation of thiosulfate ions by hydrogen peroxide; it was, therefore, of interest to see if a similar catalytic influence could be observed in the electrolytic process. An examination of the results of Abel and Baum (1) suggested that the experimental conditions should be such that the concentration of hydrogen peroxide was low, consequently the electrolyte, which consisted of 0.025 *M* thiosulfate in a buffer solution at pH 5, was made 0.001 *M* with respect to manganous sulfate. Observations were made on two solutions, with and without ammonium molybdate, respectively, and sufficient electricity was passed to ensure almost complete oxidation of the thiosulfate in each case. The current density was 0.001 ampere per square centimeter, and the current efficiencies for the formation of tetrathionate and sulfate are given in table 4. The fact that the electrolytic oxidation of thiosulfate, like the oxidation by hydrogen peroxide, may be diverted to a large extent into an alternative path by the presence of molybdate ions, provides strong support for the view that hydrogen peroxide is the effective anodic oxidizing agent.

III. STATEMENT AND APPLICATION OF THE THEORY

In view of the success of the hydrogen peroxide theory in accounting for the observations made in the electrolytic oxidation of thiosulfate, a comprehensive survey has been made of a number of other anodic reactions to see if a general theory of electrolytic oxidation could be developed. The behavior of sulfites (19), halides (21), chromic salts (23), acetates (20), and ester-acid salts, e.g., potassium ethyl malonate (26), has been investigated, and the theory of the anodic formation of hydrogen peroxide has assumed a form capable of interpreting experimental results of a very varied character.

A. The theory of the anodic formation of hydrogen peroxide

The primary postulate of the theory is that the OH radicals produced at the anode by the discharge of hydroxyl ions, which are always present in aqueous solutions, immediately combine *irreversibly* to form hydrogen peroxide, thus:

$$OH^- = OH + e$$

followed by the combination of the radicals in pairs,

$$2OH \rightarrow H_2O_2$$

If it is assumed that the *discharge* of hydroxyl ions occurs reversibly, then the requisite anodic potential will be given by an equation of the form

$$\pi = \pi_0 + \frac{RT}{F} \ln \frac{a_{OH}}{a_{OH^-}}$$

where a_{OH} and a_{OH^-} represent the activities of hydroxyl radicals and ions, respectively. If, as postulated, the radicals immediately combine *irre-*

versibly to give hydrogen peroxide, the term a_{OH} will be minute, and consequently the discharge potential of hydroxyl ions will be very low; hence this process will take precedence over, or will accompany to some extent, nearly all other anodic reactions. Under most conditions, therefore, it is to be expected that hydrogen peroxide will be formed, even at relatively low anode potentials, probably as a thin concentrated layer over the electrode surface. In the absence of a depolarizer capable of being oxidized, the hydrogen peroxide will decompose to give oxygen and water, but if a suitable depolarizer is present, it will bring about oxidation in its own characteristic manner; this may be accompanied by oxidation due to the nascent oxygen arising from the decomposition of the peroxide and possibly by evolution of oxygen gas. The extent to which oxidation by hydrogen peroxide takes place will depend on the stability of the latter under the conditions of electrolysis, and all factors capable of affecting the decomposition of the peroxide may be expected to have some influence on the electrolytic oxidation. The interpretation of anode potentials in relation to the theory of the anodic formation of hydrogen peroxide, and an explanation of the somewhat unexpected phenomena to which reference has been made in the introduction, will be discussed later (see section J).

B. Nature of anodic products

The hydrogen peroxide formed at the anode in the manner suggested above can react in at least five ways:

(*a*) It may bring about oxidation by accepting electrons from the depolarizer and being reconverted into hydroxyl ions. An example of this type of behavior is the oxidation of thiosulfate already considered, thus:[2]

$$H_2O_2 + 2S_2O_3^{--} = S_4O_6^{--} + 2OH^-$$

(*b*) The peroxide may bring about apparent reduction of highly oxidized compounds such as permanganate, chromate, and periodate ions, which react with hydrogen peroxide with the evolution of oxygen, e.g.,

$$2MnO_4^- + 5H_2O_2 + 6H^+ = 2Mn^{++} + 8H_2O + 5O_2$$

(*c*) The reaction of non-ionized organic compounds with hydrogen peroxide may result in the introduction of hydroxyl groups into the molecule. An example of this type of behavior is the chemical reaction between the peroxide and benzene to give phenolic derivatives (see, e.g., 9, 27).

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[2] It must not be assumed that writing the equation in this form implies any definite mechanism; it merely represents the net result of the process. It may be that $S_2O_3^-$ ions are first formed and that these combine to give $S_4O_6^{--}$, or that an S_2O_3 radical is produced which reacts with an $S_2O_3^{--}$ ion.

(*d*) The hydrogen peroxide or the active oxygen arising from its decomposition may bring about oxidation of a general nature.

(*e*) If no suitable depolarizer is present, oxygen gas will be evolved as a result of the decomposition of the peroxide.

The anodic oxidation of thiosulfate, sulfite, acetate, and similar ions provides examples of reactions which are mainly of type (*a*); these processes will be considered briefly.

(1) Electrolytic oxidation of thiosulfate gives mainly tetrathionate, but as is to be expected this is accompanied by some sulfate, the amount depending on the experimental conditions as already described. Since thiosulfate is stable towards oxygen and does not take part in reactions of type (*c*), the only other alternative is evolution of oxygen gas according to reaction (*e*), and this occurs, although only to a small extent.

(2) Sulfite is oxidized anodically to dithionate, thus:

$$H_2O_2 + 2SO_3^{--} = S_2O_6^{--} + 2OH^-$$

but it is always accompanied by a large proportion of sulfate. This may arise either from an alternative reaction with hydrogen peroxide, or as a result of oxidation produced by the decomposition of the peroxide (reaction (*d*)). Another possibility, at high current densities or with low concentrations of sulfite, is oxygen evolution (reaction (*e*)).

(3) The anodic oxidation of acetate ions results in the formation of ethane, together with carbon dioxide, according to the reaction

$$H_2O_2 + 2CH_3COO^- = C_2H_6 + 2CO_2 + 2OH^-$$

Under certain conditions methyl alcohol is the chief product, and this is probably the result of the decomposition of peracetic acid formed by a reaction of type (*d*), as follows:

$$CH_3COOH + (O) = CH_3COOOH$$

and

$$CH_3COOOH = CH_3OH + CO_2$$

A small amount of gaseous oxygen is generally found among the anodic products.

(4) Acid-ester salts, such as potassium ethyl malonate, undergo reactions similar to those described for acetate ions: with potassium ethyl malonate the chief product, in addition to carbon dioxide, is diethyl succinate. The oxidation may be written

$$H_2O_2 + 2C_2H_5OOCCH_2COO^- \\ = C_2H_5OOCCH_2CH_2COOC_2H_5 + 2CO_2 + 2OH^-$$

In addition to oxygen evolution (reaction (*e*)), some ethyl glyoxylate is formed, probably as a result of a primary reaction of type (*d*), thus:

$$C_2H_5OOCCH_2COOH + (O) = C_2H_5OOCCH_2COOOH$$

followed by decomposition of the per-acid

$$C_2H_5OOCCH_2COOOH = C_2H_5OOCCH_2OH + CO_2$$

and oxidation of the glycolate, probably by active oxygen, thus

$$C_2H_5OOCCH_2OH + (O) = C_2H_5OOCCHO + H_2O$$

The apparent reducing properties of hydrogen peroxide, referred to as reaction of type (*b*), account for the striking fact that in the electrolysis of acid solutions of permanganate and dichromate the proportion of oxygen evolved at the anode is appreciably greater than that required by Faraday's laws. The data recorded in table 5 give the ratio of oxygen to hydrogen obtained in the electrolysis of a 2 *N* sulfuric acid solution alone, and the same solution containing *N* potassium permanganate, at three different current densities; the time of electrolysis was 4 hr. in each case (24). The oxygen–hydrogen ratio in the sulfuric acid solution is seen to be slightly less than the theoretical value of 0.500; this is to be attributed to the formation of a small proportion of persulfuric acid. When perchloric acid was used as electrolyte, the ratio was 0.497 in the absence of permanganate, and 0.656 in its presence, at a current density of 0.05 ampere per square centimeter. With solutions containing dichromate the proportion of oxygen in the gases evolved on electrolysis is also higher than that obtained in an acid electrolyte alone, although the increase is not so great as in the permanganate solutions.

TABLE 5

Oxygen–hydrogen ratio in the electrolysis of acidified permanganate solutions

CURRENT DENSITY	OXYGEN-HYDROGEN RATIO	
	In 2 *N* sulfuric acid	In 2 *N* sulfuric acid plus *N* potassium permanganate
amperes per sq. cm.		
0.05	0.481	0.657
0.01	0.486	0.641
0.0036	0.492	0.543

An interesting aspect of reaction (*b*) has been observed in connection with the electrolytic oxidation of chromic salts to chromate in acid solution; the actual oxidizing agent in this reaction is probably active oxygen functioning through the formation of metallic peroxides with the electrode material. Since hydrogen peroxide formed anodically will tend by reaction (*b*) to convert the chromate back into chromic ions, however, the net efficiency of the oxidation is increased by the presence of catalysts able to bring about the decomposition of hydrogen peroxide (23).

In the electrolytic oxidation of aromatic hydrocarbons, e.g., benzene, toluene, and naphthalene, phenolic compounds are generally the primary products: in these cases reactions of type (*c*) are evidently of chief importance (10). Among the products of the oxidation of benzene, for example, there have been obtained phenol, catechol, quinol, and quinone; the processes may be represented thus:

$$\begin{tikzcd}
 & & o\text{-}C_6H_4(OH)_2 \arrow[r] & \text{oxidation products} & \\
C_6H_6 \arrow[r] & C_6H_5OH \arrow[ur] \arrow[dr] & & & \\
 & & p\text{-}C_6H_4(OH)_2 \arrow[r] & C_6H_4O_2 \arrow[r] & \text{oxidation products}
\end{tikzcd}$$

The introduction of first one and then a second hydroxyl group may be attributed to the direct action of the hydrogen peroxide, but other products, such as quinone and maleic acid, are probably formed by active oxygen resulting from the decomposition of the peroxide (reaction (*d*)). The benzaldehyde and benzoic acid detected in the oxidation of toluene are no doubt also the result of a reaction of the latter type.

C. Influence of anode material

If hydrogen peroxide is produced anodically, as postulated, then the catalytic effect of the electrode material on the decomposition of the peroxide should be related in some manner to the oxidation efficiency. For reactions such as those of types (*a*) and (*c*), described above, the efficiency should be low if the anode is an active catalyst, but it should be high where processes of types (*b*) and (*d*) are involved. The experimental results are in general agreement with these anticipations.

The materials commonly employed as anodes fall broadly into three groups according to their effectiveness in catalyzing the decomposition of hydrogen peroxide. Smooth platinum, and gold and nickel free from higher oxides, are relatively poor catalysts; carbon is a moderate catalyst, although its activity depends upon the state of division of the surface; finally, platinized platinum, manganese dioxide, lead dioxide, and gold and nickel covered with their effective oxides,[3] are good catalysts. In the

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[3] After electrolysis at high current densities, a nickel anode is usually found to be coated with a black deposit, probably nickel peroxide, and on being introduced into hydrogen peroxide solution causes vigorous momentary decomposition. The reaction is not truly catalytic, but is a mutual reduction and ceases when the nickel

presence of a good depolarizer, especially at low current densities, the surfaces of both gold and nickel remain free from higher oxides, and experiment has shown that the metals have then little catalytic activity, but at high current densities the metals, when used as anodes, become coated with dark colored oxides capable of bringing about vigorous decomposition of hydrogen peroxide.

It is now of interest to see how far the results obtained in various electrolytic oxidations may be correlated with the catalytic efficiencies of the materials used as anodes, and some relevant facts have been collected in table 6. Apart from the exceptional behavior of platinized platinum in the oxidation of thiosulfate, which is undoubtedly to be attributed to the poisoning action of the latter (7, 18), it is quite clear that in reactions I, II, III, or IV, which are all of type (*a*), involving direct action between hydrogen peroxide and the depolarizer, the highest efficiencies are obtained

TABLE 6

Current efficiencies for oxidations with different anodic materials

ANODE MATERIAL	REACTIONS†				
	I	II	III	IV	V
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
Smooth platinum	76	28	89	74	1
Gold	65	28			
Nickel	60	32			
Carbon*	51	3	21	22	1
Platinized platinum	(91)	7	3	0	53
Manganese dioxide	0	2	0		19
Lead dioxide			0	0	100
Gold covered with oxide			0	12	
Nickel covered with oxide			0		

* Various forms of carbon give different results; those quoted are for gas carbon.

† The reactions are:
I $S_2O_3^{--} \rightarrow S_4O_6^{--}$
II $SO_3^{--} \rightarrow S_2O_6^{--}$
III $CH_3COO^- \rightarrow C_2H_6 + 2CO_2$
IV $C_2H_5OOCCH_2COO^- \rightarrow C_2H_5OOCCH_2CH_2COOC_2H_5 + 2CO_2$
V $Cr^{+++} \rightarrow CrO_4^{--}$

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peroxide is reduced. Since, however, the oxide will be continually produced during electrolysis at high current densities, the net effect is the same as though an anode which is a good catalyst for hydrogen peroxide decomposition were employed (20). The lower oxides of nickel do not decompose hydrogen peroxide appreciably.

with those electrodes which are the poorest catalysts for the decomposition of hydrogen peroxide. The oxidation of chromic salts to chromates (reaction V) on the other hand, is not only brought about by active oxygen (reaction (*d*)), but the presence of hydrogen peroxide, as already explained, tends to reduce the chromate ions to chromic ions (reaction (*b*)) and so decreases the oxidation efficiency. The best yields of chromate are thus obtained, as seen in table 6, with anodes which are the most effective catalysts for hydrogen peroxide decomposition.

There is another aspect of the influence of anode material to which reference must be made: namely, the possibility that it may behave as a catalyst for the reaction between the depolarizer and active oxygen. The action of the latter on the electrode material may produce a peroxide which acts as a catalytic intermediate compound, suffering reduction by the depolarizer and subsequent re-oxidation by the oxygen produced when the hydrogen peroxide is decomposed. This type of catalytic action is probably operative in the oxidation of chromic salts to chromate, and of iodate to periodate, the anode material acting as an oxygen carrier. It will be seen from table 6 that the efficiency of a gas-carbon anode for the oxidation of chromic ions is somewhat less than would be expected from its ability to decompose hydrogen peroxide; carbon is, however, a poor oxygen carrier, and the oxidation efficiency must inevitably be small.

TABLE 7

Current efficiencies for ethane formation with platinized platinum anode

Poison	None	0.1 M $Hg(CN)_2$	0.1 M KCN	0.1 M NaF
Efficiency, in per cent	3	14	13	10

It has been recorded that the efficiency of a platinized platinum anode for the oxidation of thiosulfate is unexpectedly high because of the poisoning action of the depolarizer; it is possible, in an analogous manner, deliberately to poison an electrode and so increase its efficiency for reactions in which hydrogen peroxide is the effective oxidant. The current efficiencies in table 7 were obtained in the electrolysis of a solution of N potassium acetate and N acetic acid with a platinized platinum anode at an apparent current density of 0.25 ampere per square centimeter, in the presence of various poisons. Although the efficiencies are not very high, the catalytic poisons are seen to bring about a definite increase in the yield of ethane. A more striking effect was observed when the platinic chloride solution used for platinizing the anode was made 0.01 M with respect to mercuric chloride. With this electrode the efficiency for ethane formation was found to be 42 per cent, as compared with 3 per cent for an anode prepared in the same manner from a solution free from mercuric salt. As far as could be seen with the naked eye, the appearance of the poisoned and unpoisoned electrodes was the same.

One of the most striking achievements of the hydrogen peroxide theory is its ability to explain the effects of previous anodic and cathodic polarization on a platinum anode. It had been recorded by Friessner (16) that previous anodic polarization of a platinum anode increased, whereas cathodic polarization decreased, the amount of dithionate produced in the electrolytic oxidation of sulfite. Similarly Foerster and Piguet (15) noted that anodic pre-polarization favored the formation of ethane in the electrolysis of acetate solutions. These conclusions have been confirmed (19, 20), and the results in table 8 may be quoted to illustrate the nature of the effects in the oxidation of sulfite to dithionate (reaction II) at a smooth platinum anode and of acetate to ethane (reaction III) at a platinized platinum anode. The figures for the efficiency of the conversion of chromic ions to chromate (reaction V) at platinized platinum are also given (23). It is seen that the results in the third column indicate a behavior which is the reverse of that found in the oxidation of sulfite and acetate ions; previous anodic polarization of the electrode is detrimental to the formation of chromate, whereas cathodic pre-polarization is advantageous.

TABLE 8

Current efficiencies with pre-polarized platinum anodes

	CURRENT EFFICIENCIES		
	Reaction II	Reaction III	Reaction V
	per cent	*per cent*	*per cent*
Anodically polarized	33	36	43
Untreated	22		53
Cathodically polarized	12	3	97

The explanation of these results is provided by the observation of Spitalsky and Kagan (41) that anodic polarization of platinum decreases its catalytic power for the decomposition of hydrogen peroxide, whereas cathodic polarization greatly enhances it. Where anodic oxidation is brought about by the direct action of hydrogen peroxide, therefore, as is believed to be the case for reactions II and III, anodic pre-polarization should increase and cathodic polarization decrease the oxidation efficiency, as actually observed. On the other hand, where the presence of hydrogen peroxide tends to reduce the product, as in the oxidation of chromic salts to chromate in acid solution (reaction V), the effects of anodic and cathodic pre-polarization are reversed, as shown in table 8.

D. *Effect of catalysts for hydrogen peroxide decomposition*

Mention has been made in the section dealing with the origin of the theory of the anodic formation of hydrogen peroxide that catalysts for its decomposition diminish very markedly the efficiency of the electrolytic oxidation of thiosulfate to tetrathionate (table 2). In view of the results recorded above for reactions of different types, it is to be expected that the same effect should be observed for all reactions of type (*a*), in which hydrogen peroxide is the active oxidizing agent. When the oxidation product is decomposed by the peroxide, however, as in the formation of chromate in acid solution, the addition of catalysts should increase the net efficiency of the electrolytic process. The experimental results are again in harmony with expectation: the presence of lead, silver, manganous, cupric, cobalt, and ferrous or ferric ions diminishes the efficiency for the oxidation of sulfite to dithionate (19), of acetate to ethane (20), and of potassium ethyl malonate to diethyl succinate (26), as well as that for the oxidation of thiosulfate to tetrathionate (table 2). The conversion of chromic ions to chromate in acid solution, on the other hand, is favored by the presence of catalysts for hydrogen peroxide decomposition. The efficiencies observed in the oxidation of an approximately neutral solution of potassium ethyl malonate and of acidified chromic sulfate, at smooth platinum anodes, are quoted in table 9; the opposite influences of the catalysts in reactions of different types are here apparent. Complete parallelism between the two sets of results is not to be expected, since in the second reaction, the oxidation of chromic ions to chromate, the added catalysts have a second rôle to play in acting as carriers for the oxidation by oxygen, and in this respect, as found by direct experiment, they differ considerably (23).

TABLE 9

Effect of catalysts for hydrogen peroxide decomposition

CATALYST	OXIDATION OF POTASSIUM ETHYL MALONATE	CATALYST	OXIDATION OF ACID CHROMIC SULFATE
	per cent		*per cent*
None	78	None	1
0.01 *M* Ag^+	50	0.01 *M* Ag^+	97
0.01 *M* Fe^{+++}	49	0.01 *M* Fe^{++}	2
0.01 *M* Co^{++}	45	0.01 *M* Co^{++}	8
0.01 *M* Cu^{++}	38	0.01 *M* Cu^{++}	2
0.01 *M* Mn^{++}	37	0.01 *M* Mn^{++}	7
0.01 *M* Pb^{++}	27	$PbSO_4$ (saturated)	70

In general the effectiveness of the metallic ions for hydrogen peroxide decomposition follows the order Pb, Ag, Mn, > Cu, Co, Fe, and their influence on electrolytic oxidation processes in which hydrogen peroxide is the effective oxidant usually follows a similar order. Since, in most cases, the catalytic activity of the metallic ion is bound up with the possibility of the formation of a metallic peroxide, it follows that their influence should be greater in neutral than in acid solution, and this is usually found to be the case. Furthermore, any factor which tends to hinder the accumulation of the active substance in the vicinity of the anode, such as high current density leading to vigorous gas evolution, lessens their effects.

E. Influence of acidity and alkalinity

Since hydrogen peroxide is more stable in acid than in alkaline solution, it follows that when electrolytic oxidation is to be attributed to the peroxide, the efficiency should be highest in acid solution and should decrease as the pH of the medium is made larger. The converse should hold where the presence of hydrogen peroxide tends to decrease the oxidation efficiency. Results of the first kind have already been quoted in table 3, for the electrolytic oxidation of thiosulfate ions, and a similar effect has been found in the conversion of sulfite to dithionate over the pH range of 7 to 13, when the efficiency decreases from 33 to 17 per cent. Another factor is operative in this case to which reference is made below. The anodic oxidation of chromic salts to chromate, in agreement with the arguments presented above, takes place more efficiently in alkaline than in acid solution, as is clear from table 10. Somewhat similar results have been recorded in the oxidation of iodate to periodate.

TABLE 10

Effect of acidity and alkalinity on chromate formation at a platinum anode

MEDIUM	EFFICIENCY
	per cent
0.5 *N* sulfuric acid	1
Water	63
0.5 *N* potassium hydroxide	77

Where the oxidation process involves direct interaction between hydrogen peroxide and the anion of a weak acid, then in addition to the stability of the peroxide it is necessary to take into consideration the fact that the concentration of the ions of depolarizer decreases as the solution becomes more acid. This factor will tend to diminish the oxidation efficiency as the pH decreases, and thus will oppose the increase which should result from the greater stability of the hydrogen peroxide. As a consequence of these two opposing influences, the efficiency of the anodic oxidation may be expected to increase to a maximum and then to dminish as the pH is increased: results of this kind have been obtained with solutions of sulfite (19), acetate (20), and ethyl malonate ions (26), as shown by the data in table 11. The values for the oxidation of sulfite were obtained with 0.025 *M* potassium sulfite in various buffer mixtures at a current density of 0.001 ampere per square centimeter. Except for the most alkaline, the acetate solutions were prepared from potassium acetate and acetic acid, the total concentration being 2 *N* in each case. The solution of pH 11 was prepared by adding a small quantity of ammonia to 2 *N* potassium acetate; the current density was 0.05 ampere per square centimeter. The malonate solutions consisted of mixtures of potassium ethyl malonate and hydrogen ethyl malonate of 2 *N* total concentration, the two alkaline solutions containing in addition 0.1 *M* potassium bicarbonate and carbonate, respectively; a current density of 0.5 ampere per square centimeter was employed. All the measurements were made with a smooth platinum anode at room temperature.

TABLE 11

Variation of current efficiency with pH of the electrolyte

SULFITE IONS		ACETATE IONS		ETHYL MALONATE IONS	
pH	Efficiency	pH	Efficiency	pH	Efficiency
	per cent		*per cent*		*per cent*
1	4	2.3	67	1.4	70
3	11	4.3	70	2.9	75
5	24	4.7	77	3.5	74
7	33	5.2	74	4.8	74
9	33	9.5	71	7.0	70
11	26	11	*ca.* 50	8.3	64
13	17			10	59

F. Influence of temperature

The rate of decomposition of hydrogen peroxide increases with rise of temperature, and hence it is to be expected that anodic oxidations brought about by the peroxide should decrease in efficiency as the temperature is raised. Conversely, anodic oxidations due to active oxygen and hindered by hydrogen peroxide should show increasing efficiency with rise of temperature. These points are illustrated by the figures in table 12 for the efficiency of the formation of diethyl succinate from ethyl malonate ions (26), and of chromate from an acidified solution of chromic sulfate (23);

a smooth platinum anode was used in each case, and the current densities were 0.5 ampere per square centimeter and 0.01 ampere per square centimeter, respectively. The efficiency for the oxidation of a 20 per cent solution of potassium acetate to ethane also decreases from 83 per cent at 0°C. to 12 per cent at 90°C. (38), as is to be anticipated, but the formation of periodate is also said to be favored by low temperatures (30); this result is unexpected in view of the probable nature of the anodic process, but the subject requires further investigation. It must be mentioned that other temperature-variable factors, in addition to those mentioned above, may have an important influence on the anodic oxidation efficiency. Rise of temperature may increase the rate of the chemical reactions, for example, between the depolarizer and active oxygen, but it may also facilitate the liberation of oxygen gas in the molecular form and thereby diminish the tendency for oxidation to occur. The operation of these factors may lead to results which are difficult to analyze: for example, the oxidation of alkaline solutions of formate ions is favored by increase of temperature at iron and nickel anodes, but at a smooth platinum anode there is a marked decrease of efficiency, especially in the early stages of electrolysis (14). It appears, however, in agreement with the hydrogen peroxide theory, that, in general, increase of temperature facilitates those reactions involving oxidation by active oxygen, but sometimes so many influences are at work that it is not possible to interpret the results in a simple manner.

TABLE 12

Influence of temperature on the formation of diethyl succinate and of chromate

TEMPERATURE	SUCCINATE FORMATION	CHROMATE FORMATION
°C.	*per cent*	*per cent*
10	74	
20		1
30	63	21
50	56	47
60		60
70	37	77
90	22	77

G. Effect of current density

When the hydrogen peroxide formed at the anode takes part almost wholly in one oxidation reaction, the current efficiency for oxidation should be greatest at low current densities, for at large current densities the concentration of hydrogen peroxide at the anode is high and its rate of spontaneous decomposition is considerable. These conditions appear to apply to the oxidation of thiosulfate, where the efficiency, as shown in table 13, for a 0.025 *M* solution at pH 7, decreases with increasing current density at a smooth platinum anode.

The position is, however, not always so simple as implied above and as apparently exists in the anodic oxidation of thiosulfate. If the reaction between hydrogen peroxide and the depolarizer does not occur very rapidly, it may be necessary for there to be an appreciable concentration of the former for the process to take place with reasonable efficiency; this is probably the case in the oxidation of acetate ions to ethane, for which the data are given in table 14. They were obtained with a solution containing *N* acetic acid and *N* potassium acetate using a smooth platinum anode.

TABLE 13

Efficiency of oxidation of thiosulfate at different current densities

CURRENT DENSITY × 10^3	EFFICIENCY
amperes per sq. cm.	*per cent*
0.2	90
0.4	88
1.0	85

TABLE 14

Efficiency for oxidation of acetate ions to ethane at different current densities

CURRENT DENSITY	EFFICIENCY
amperes per sq. cm.	*per cent*
0.005	52
0.025	71
0.05	77
0.25	89
0.5	89

In some cases, both the factors mentioned above seem to be operative, and the efficiency increases to a maximum and then decreases as the current density is raised; this is the case, for example, with the formation of diethyl succinate from potassium ethyl malonate, for which there is an optimum current density of about 0.12 ampere per square centimeter when an electrolyte consisting of *M* potassium ethyl malonate and *M* hydrogen ethyl malonate is used. Where an anodic oxidation is brought about by active oxygen, a low current density is usually favorable, the dominating factor being probably the rate at which the electrode material can catalyze the reaction.

H. Influence of depolarizer concentration

No matter what is the effective oxidant, an increase of depolarizer concentration should result in an increase of efficiency, and this is generally found to be the case. A number of illustrations are recorded in table 15, the concentrations being in terms of molarity: *C* represents the total concentration, and *E* the efficiency per cent for the formation of the main product. A small concentration of depolarizer will result in the decomposition of a larger proportion of the hydrogen peroxide, and therefore a general oxidation process with active oxygen, of type (*d*), may be favored. As will be seen shortly, this phenomenon occurs in the electrolysis of organic acids and their salts, e.g., acetic acid and acetates, when the formation of ethane is replaced by that of methyl alcohol. If the concentration of depolarizer is made too low, the oxidation reactions, whether brought about by hydrogen peroxide or active oxygen, will be so slow that oxygen evolution may take place.

TABLE 15

Influence of concentration of depolarizer on oxidation efficiencies at a platinum anode

THIOSULFATE IONS		SULFITE IONS		ACETATE IONS		ETHYL MALONATE IONS		CHROMIC IONS	
C	*E*	*C*	*E*	*C*	*E*	*C*	*E*	*C*	*E*
0.02	75	0.025	36	0.2	44	0.2	30	0.02	20
0.05	85	0.10	37	1.0	64	0.5	68	0.05	36
		0.20	37	2.0	77	1.0	70	0.1	53
				4.0	77	2.0	74	0.2	66
						4.0	78		

I. Influence of foreign anions

It has been found that in the electrolysis of salts of some organic acids the presence of inert inorganic salts tends to inhibit the main anodic reaction and leads to the formation of an alternative product; the effect is particularly marked in acid solutions. For example, in the electrolysis of an aqueous solution of acetic acid a high efficiency for ethane formation is observed, but if an inorganic acid or the potassium salt of an inorganic acid is added, the efficiency is greatly decreased[4] and methyl alcohol is

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[4] Some textbooks of organic chemistry state that ethane can be obtained by electrolysis of aqueous acetic acid solutions, whereas others say that it is not formed in this manner; the negative results obtained by many workers are to be explained by the addition of some free mineral acid, e.g., sulfuric acid, in order to increase the conductivity of the feebly conducting acetic acid solution. In doing so the conditions have been unwittingly changed from those requisite for ethane formation to those resulting in the production of methyl alcohol.

formed (Hofer–Moest reaction) instead of ethane. As a consequence of experiments (20), the results of which are reproduced in table 16, it is clear that the effect is related to the mobility of the added anion; it is more marked the greater the speed of the ion.

This interesting phenomenon, which is also shown in the electrolysis of acid-ester salts (26), is readily explicable on the basis of the hydrogen peroxide theory. For the formation of ethane to occur at a reasonable rate, a fairly high concentration of acetate ions is necessary in the vicinity of the anode to react with the hydrogen peroxide produced there. Some of these ions may arrive at the anode by diffusion from the main body of the solution, but in the acid electrolyte this process will be very slow, since the acid is only weakly dissociated and the bulk concentration of ions is low. The majority of the acetate ions will be brought up to the anode in transporting the current, and at not too high current densities will give a concentration sufficient for good synthesis to occur. If, now, an inorganic electrolyte is added, the foreign anion will take over to a considerable extent the transport of current to the anode and therefore interrupt the supply of acetate ions; the concentration of these ions near the electrode

TABLE 16

Influence of 0.01 N potassium salts on the formation of ethane from 2 N acetic acid at a platinum anode

ADDED SALT	EFFICIENCY	MOBILITY OF ANION
	per cent	
None	71	
KF	30	47
$KClO_4$	20	64
KNO_3	19	62
KH_2PO_4	17	
KCl	5	65
K_2SO_4	3	69
$K_3Fe(CN)_6$	0	97

TABLE 17

Effect of added salt at various current densities

CURRENT DENSITY	EFFICIENCY		DECREASE OF EFFICIENCY
	No added salt	0.02 N K_2SO_4	
amperes per sq. cm.	*per cent*	*per cent*	
0.05	43	34	9
0.2	76	42	34
0.5	70	11	59

will therefore fall, and hence the efficiency should decrease. The effect should be related to the mobility of the added anion, as is found to be the case. If the view put forward is correct, it would be expected that the influence of added salts should be greatest at high current densities, since here ordinary diffusion to the electrode will supply only a negligible fraction of the depolarizer ions required. This is borne out by the figures in table 17 for the synthesis of diethyl succinate by the electrolysis of 2 *M* ethyl hydrogen malonate with and without potassium sulfate added (26).

In solutions of salts of the organic acids it is to be expected that the effect of added anions will be less, since the concentration of depolarizer ions is much greater, and hence ordinary diffusion to the electrode is more marked, and the ions can also compete effectively with foreign anions in carrying the current. This is found to be true in practice: thus with *N* potassium acetate and *N* acetic acid and the same current density as was employed in the experiments recorded in table 16, the efficiency of ethane formation was only reduced from 77 to 42 per cent by the presence of 0.2 *N* potassium sulfate.

J. Electrode potential phenomena

No mention has hitherto been made of the interpretation of electrode potentials by means of the theory of the anodic formation of hydrogen peroxide; this important aspect of electrolytic oxidation must now be considered. The essential postulate is that the measured potentials are set up *indirectly* by electromotively active substances formed at the anode, and these potentials may have no direct connection with the nature of the products. The electromotively active material may be either oxygen, arising from the decomposition of the hydrogen peroxide, or discharged radicals produced by the action of the latter on the depolarizer; these two possibilities will be considered separately.

(I) The only electromotively active substance is oxygen arising from the decomposition of the hydrogen peroxide

It is well known that although the equilibrium between oxygen gas and hydroxyl ions represented by the equation

$$\tfrac{1}{2}O_2 + H_2O + 2e \leftrightarrows 2OH^-$$

is generally not strictly reversible, a given concentration of oxygen nevertheless gives rise to a more or less definite potential. It may be assumed, therefore, that the potential of an anode, in the present circumstances, will be determined by the amount of oxygen accumulated on the electrode. When oxygen is added to a virgin platinum anode, two stages of potential are observed (6): a lower one, less than 1 volt, corresponding to the formation of a layer of oxygen atoms on the platinum surface, and a higher corresponding to oxygen evolution. The actual values of the potentials are dependent, of course, on the hydroxyl-ion concentration of the solution. It is to be expected, therefore, that for an electrolytic oxidation in which hydrogen peroxide is the effective agent and the potential is due to the accumulation of oxygen at the anode, two stages of potential should be observed, a lower one indicating the covering of the platinum surface with oxygen atoms and a higher one corresponding to very slow oxygen gas evolution. If the oxidation process is efficient at low current densities, or if the oxygen itself can react with the depolarizer, the lower potential stage will be prolonged; this is particularly the case in the oxidation of sulfite ions. Any factor which tends to lengthen the period required for the saturation of the surface with oxygen, such as low current density or a platinized surface, should increase the quantity of electricity which must be passed before the potential rise from the first to the second stage is observed. On the other hand, factors tending to increase the rate of oxygen formation, e.g., the addition of catalysts for hydrogen peroxide decomposition, should shorten the lower potential stage; in these cases the oxidation efficiency is also low, as explained previously. A catalytic poison, such as mercuric cyanide, which is strongly adsorbed by platinum, may eliminate almost entirely the adsorption of oxygen corresponding to the lower stage of potential; the potential should then rise rapidly to the higher stage, but in these circumstances there is no reason why the oxidation efficiency should be appreciably affected. The phenomena considered are very elegantly shown in the electrolysis of thiosulfate solution (18). In figure 1 are reproduced the curves of anode potential plotted against quantity of electricity passed, for 0.025 *M* thiosulfate solution in pH 7 buffer at various currents with a smooth platinum anode of area approximately 55 sq. cm.; the oxygen evolution potential for the buffer alone at the lowest current is also given. The two potential stages are clearly seen, and it is observed that as the current is increased, leading to more rapid decomposition of the anodic hydrogen peroxide, the lower stage is shortened; the higher potential is seen to be rather less than the oxygen evolution potential given and corresponds undoubtedly to very slow oxygen evolution.

The effect of catalysts for hydrogen peroxide decomposition is shown in figure 2. The broken curve is for 0.025 *M* thiosulfate at pH 7 with a current of 0.01 ampere, while the other curves are for the same solution containing copper sulfate, ferrous sulfate, and solid manganese dioxide, respectively; the quantities added are as given in table 2. As expected, the lower potential stage is shortened and the higher potential raised corresponding to a greatly increased rate of oxygen formation.

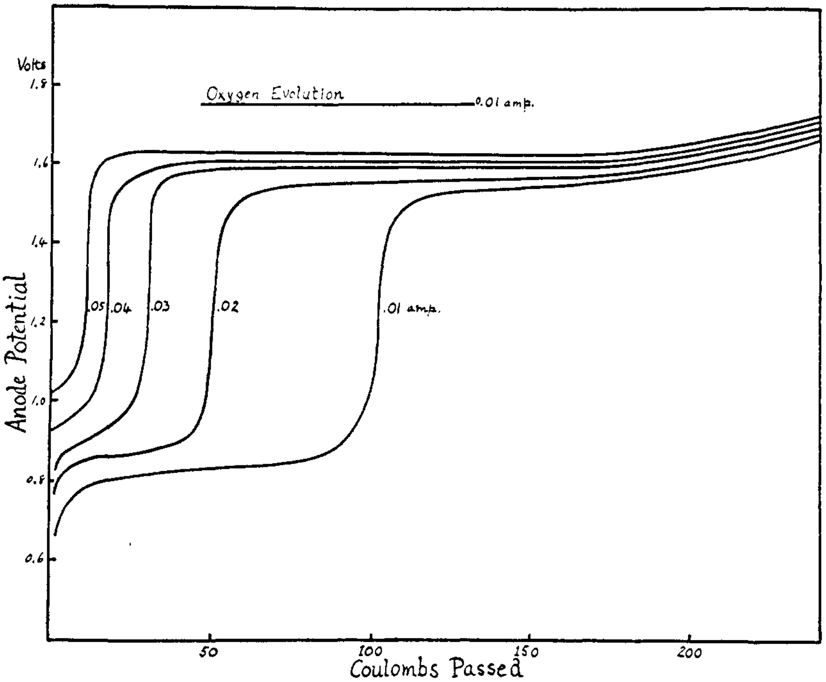

FIG. 1. Anode potential plotted against quantity of electricity passed for 0.025 *M* thiosulfate solution in pH 7 buffer at various currents with a smooth platinum anode of area approximately 55 sq. cm.

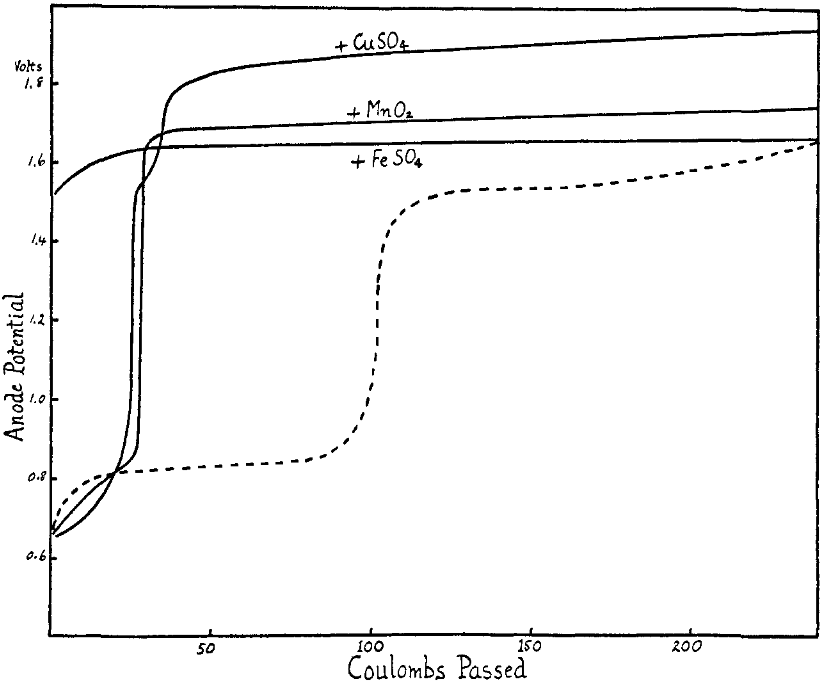

FIG. 2. The effect of catalysts for hydrogen peroxide decomposition

Figure 3 shows the inhibition of the first potential stage by mercuric cyanide. The broken curve is for thiosulfate alone under the same conditions as before, while curves I, II, and III are those observed with solutions containing 0.001 *M*, 0.0001 *M*, and 0.00001 *M* mercuric cyanide, respectively. It is seen that the lower potential stage is shortened, but the higher potential is unaffected; this is to be expected, since the poison does not influence the oxidation efficiency and therefore the rate of oxygen formation.

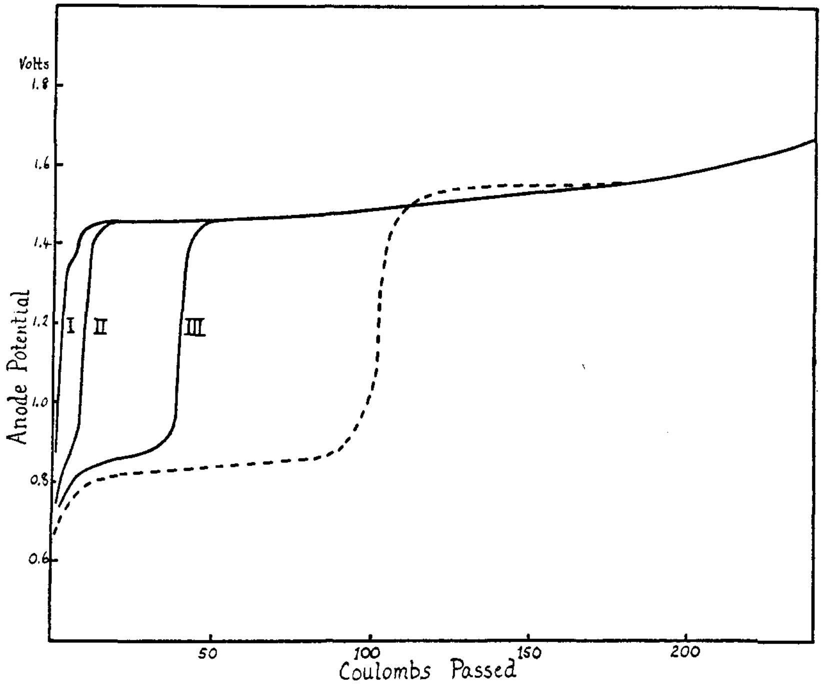

FIG. 3. The inhibition of the first potential stage by mercuric cyanide. Broken curve, thiosulfate alone. Curves I, II, and III were obtained with solutions containing 0.001 *M*, 0.0001 *M*, and 0.00001 *M* mercuric cyanide, respectively.

Similar observations have been made in the electrolytic oxidation of sulfites (19), methyl alcohol (32, 42), formaldehyde (32, 42), and ethyl alcohol (28). Where an electrolytic oxidation is carried out at high current densities, or the oxidation process is not very efficient, the rate of formation of free oxygen is naturally high; the lower potential stage may then be so short as not to be observable, and the anode potential will be in the vicinity of that for oxygen evolution from the commencement of electrolysis.

With anodes other than platinum,[5] there does not appear to be a lower

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[5] It is possible that some of the other metals of the platinum group, e.g., rhodium or iridium, may behave similarly to platinum.

potential stage corresponding to oxygen adsorption, and thus the anode potential in electrolytic oxidation is usually in the neighborhood of that requisite for oxygen evolution.

(II) Hydrogen peroxide reacts with the depolarizer giving discharged radicals capable of setting up a potential with respect to the corresponding ions in solution

Two possibilities may be distinguished:

(*a*) *The liberated radicals may set up a potential below that of oxygen evolution.* This is the case, for example, in the electrolysis of halides (21). The hydrogen peroxide will react with the halide to liberate free halogen, which sets up its own potential against the ions in solution. (At this potential, of course, direct discharge of some halide ions may take place.) The oxygen arising from the simultaneous decomposition of the peroxide accumulates on the anode. At first it goes to form the adsorbed oxygen layer, and since the potential of this is below the halogen potential, it is not apparent. Eventually, however, the electrode surface becomes saturated with oxygen and the potential rises to that for slow oxygen evolution. Any factor tending to increase the rate of decomposition of the hydrogen peroxide causes the jump of potential to occur sooner. These points are well brought out by the curves in figure 4, giving the potentials against quantity of electricity passed for the electrolysis of chloride solutions under various conditions (21). The results were obtained with a rotating, smooth platinum anode, of approximately 55 sq. cm. area. Owing to the presence of an electrical resistance between the anode and the tip of the siphon connecting it to the calomel reference electrode, all the potentials recorded are higher than the true values, but the time elapsing before the sudden rise of potential occurs, which is the phenomenon of immediate interest, remains unaffected. The curves in figure 4A show the variation with time of the anode potential in a 0.1 N hydrochloric acid solution electrolyzed with currents of 0.1, 0.25, and 0.5 ampere, respectively. It is seen that the higher the value of the current used, the smaller is the quantity of electricity that has to be passed before the sudden rise of potential occurs. The effect of varying the hydrochloric acid concentration is seen in figure 4B; the anode potential–time curves are for 0.05, 0.1, and 0.2 N solutions electrolyzed with a constant current of 0.25 ampere; it is evident that decrease of concentration favors the polarization. Figure 4C shows the effect of varying the hydrogen-ion concentration at constant chloride-ion concentration; the curves are for (*a*) N sodium chloride in 0.1 N sodium hydroxide, (*b*) N sodium chloride, and (*c*) 0.9 N sodium chloride in 0.1 N hydrochloric acid, a current of 0.25 ampere being used in each case. As would be expected, the onset of polarization is markedly favored by alkalinity of the electrolyte. The effect of catalysts for hydrogen peroxide decomposition is shown in figure 4D; the solutions were prepared from 0.1 *N* hydrochloric acid and in addition were either 0.001 *M* with respect to manganous or ferrous chlorides or contained 0.5 g. of powdered manganese dioxide, precipitated silver, or animal charcoal suspended in 100 ml. of electrolyte. The influence of the added substances in facilitating the onset of polarization is very marked. Solutions of bromides and iodides were found to behave similarly to chlorides but, as would be expected since hydrogen peroxide reacts more readily with the former substances, polarization did not take place so readily as in chloride solutions.

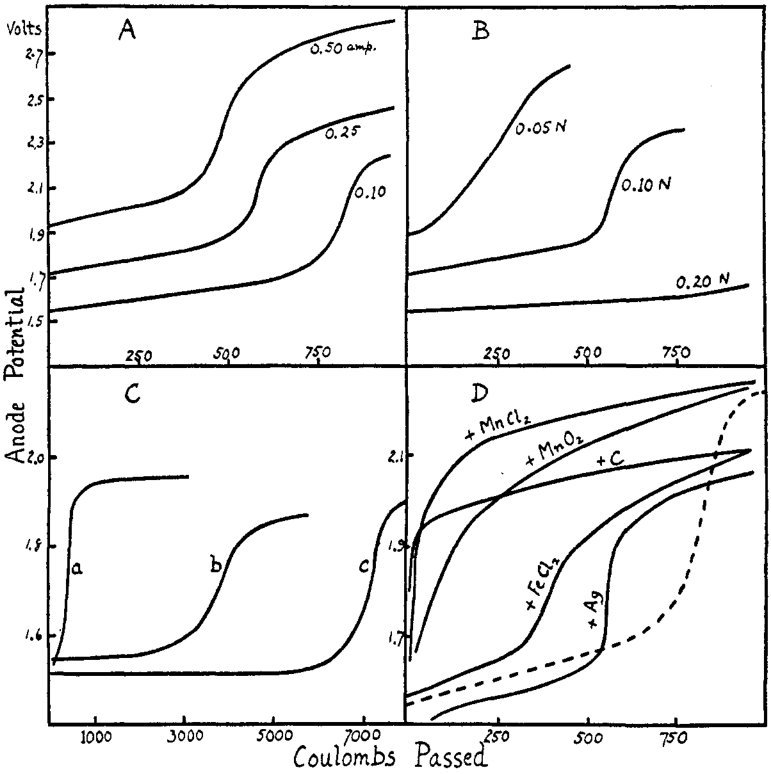

FIG. 4. (A) The variation with time of the anode potential in a 0.1 *N* hydrochloric acid solution electrolyzed with currents of 0.1, 0.25, and 0.5 ampere. (B) The effect of varying the hydrochloric acid concentration. (C) The effect of varying the hydrogen-ion concentration at constant chloride-ion concentration. (D) The effect of catalysts for hydrogen peroxide decomposition.

(*b*) *The liberated radicals may set up a potential above that of oxygen evolution.* This is the case, for example, in the electrolysis of acetates and acid-ester salts. The potential at which the Kolbe reaction takes place is about 2.4 volts[6] and that for the Brown–Walker synthesis is about 2.8 volts, while the oxygen evolution potentials for the same solutions are about 2.0 volts or less. These figures provide a very awkward problem for the old theories of electrolytic oxidation: since the processes of electrosynthesis require a higher potential than that for oxygen evolution, how is it, if the anode potential is the determining factor, that these processes ever take place? One would expect that, in aqueous solution, the requisite potential could never be attained, oxygen evolution taking place preferentially. The hydrogen peroxide theory, however, encounters no such anomaly; there is no reason why hydrogen peroxide formed *irreversibly* at the anode should not give rise by chemical reaction to electromotively active radicals capable of setting up potentials considerably higher than those for oxygen evolution. As long as the reaction is maintained, therefore, a high potential will be observed. If, however, the decomposition of the hydrogen peroxide to give oxygen is favored, e.g., by introducing catalysts, the synthetic reaction will be largely inhibited and the concentration of the radicals at the anode due to it will fall considerably; the potential corresponding to the electrosynthesis will therefore decrease and may fall below that for oxygen evolution. The latter process will then determine the observed potential. These points are well illustrated by the curves in figure 5 for the electrolysis of ethyl malonate ion solutions under various conditions. The electrolyte used consisted of M potassium ethyl malonate and M hydrogen ethyl malonate, and all observations were at room temperature (26). Curve A is the current density–potential curve for smooth platinum, curve B that for platinized platinum, curve C that for gold, and curve D that for lead dioxide; the broken curve (E) is for smooth platinum in a phthalate buffer of the same pH as the electrolyte, and indicates approximately what should be the ordinary oxygen evolution potential for the malonate solution if no electrolytic oxidation processes

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[6] Shukla and Walker (40) recorded the potential of the Kolbe synthesis as 2.14 volts; this referred, however, to the first break in the current density-potential curve, and not to the potential actually observed when the synthesis was proceeding with good efficiency at high current density. Glasstone and Hickling (20), using the commutator-extrapolation method, obtained appreciably higher values, but the results were admittedly only approximate owing to the very rapid fall of potential on switching off the polarizing current. Unpublished observations by Hickling and Westwood, using a new method (25) for the measurement of polarization potentials, give a value of 2.42 volts for N acetic acid + N potassium acetate independent of current density over the range 0.05 to 1.5 amperes per square centimeter.

took place. It is seen that when the formation of diethyl succinate takes place with high efficiency, as at a smooth platinum anode (curve A), the potential is about 2.8 volts, but when the synthesis is inhibited by using

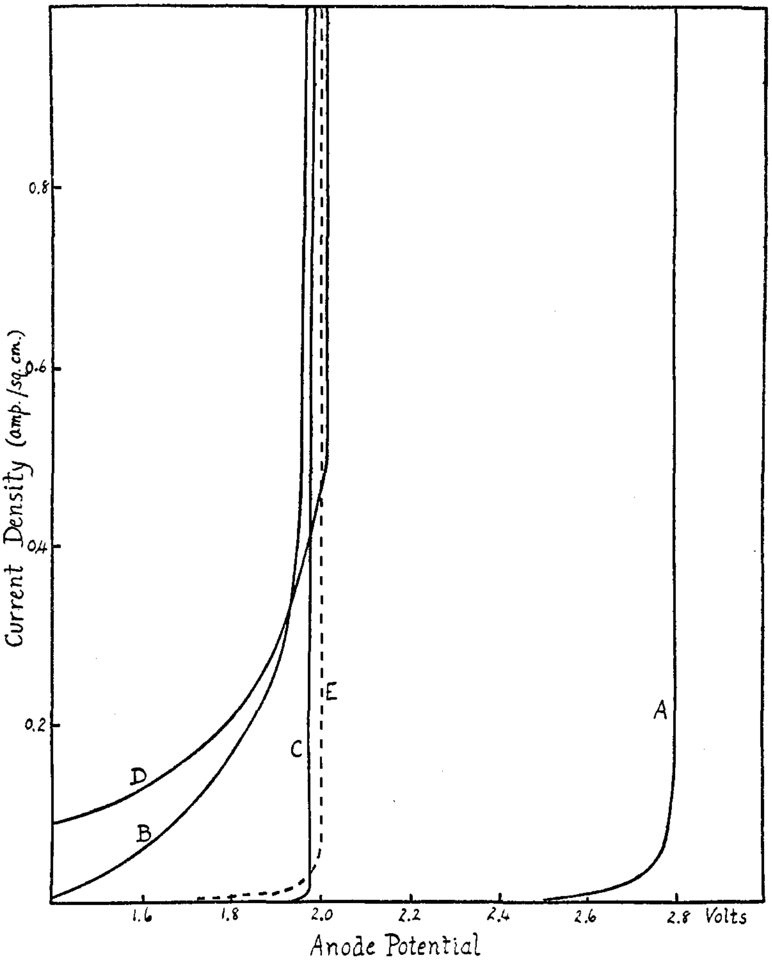

FIG. 5. The electrolysis of ethyl malonate ion solutions under various conditions. Current density-potential curves for smooth platinum (curve A), for platinized platinum (curve B), for gold (curve C), for lead dioxide (curve D), and for smooth platinum in a phthalate buffer of the same pH as the electrolyte (curve E).

anodes which are good catalysts for hydrogen peroxide decomposition (curves B, C, and D), the potential drops to the region of oxygen evolution, at about 2 volts. It may even drop somewhat lower, at small current densities, when oxygen depolarization can occur at some anodes, leading to alternative anodic oxidation products.[7]

K. Detection of hydrogen peroxide at the anode

If hydrogen peroxide is the primary product at the anode in the electrolysis of aqueous solutions, as maintained by the authors, it might be expected that the hydrogen peroxide could be detected analytically. This has been done in certain cases in the electrolysis of sulfuric acid and salts of organic acids, but there is the possibility that it may arise here by secondary reactions. Riesenfeld and Reinhold (36), however, were able to detect small quantities of hydrogen peroxide at the anode in the electrolysis of potassium hydroxide solution at low temperatures; here there appears to be no possibility of a secondary reaction. More recently Rius (37) has shown that very appreciable quantities of hydrogen peroxide may be obtained at the anode in the electrolysis of potassium hydroxide solution at low temperatures, if fluoride is present. The difficulty of detecting hydrogen peroxide at an anode is attributed by the writers to the fact that it is formed in a layer of high local concentration, on a metal surface, probably locally heated, which is a good catalyst for its decomposition. Under these conditions the rate of decomposition of the peroxide will be extremely high. If an electrolysis could be carried out without any anode material in contact with the electrolyte, then it should be possible to obtain hydrogen peroxide in quantity. In support of this view it has been shown (22) that if various solutions are electrolyzed by passing a discharge from an anode placed in an evacuated space above the surface of the electrolyte, then hydrogen peroxide is formed in quantities approximating those required by Faraday's laws. It should be emphasized that the peroxide is not merely the result of the high tension electrical discharge, for it is not obtained when the electrode in the gas space is made the cathode.

IV. DIFFICULTIES AND CRITICISMS OF THE HYDROGEN PEROXIDE THEORY

It will be clear from the preceding pages that, provided the reactions of hydrogen peroxide and of active oxygen on the depolarizer are known and the possibilities of interaction with the oxidation product are taken into account, the more important features of many electrolytic processes can be explained. There is, however, one important difficulty: it is not always possible to imitate anodic oxidations quantitatively using hydrogen peroxide as chemical oxidizing agent. By the action of hydrogen peroxide

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[7] The application of reaction rate theory to electrode potential phenomena (H. Eyring, S. Glasstone, and K. J. Laidler: J. Chem. Phys. **7**, 1053 (1939)) may necessitate some modification of the interpretation given above.

on a 0.025 *M* solution of sodium thiosulfate in a phosphate buffer at pH 7, it was found that 82 per cent of the thiosulfate was oxidized, 74 per cent being converted into tetrathionate and 8 per cent into sulfate (18), in close agreement with the results of anodic oxidation, but treatment of sulfite solution with hydrogen peroxide under various conditions gave not more than 2 per cent of dithionate, compared with yields of about 30 per cent obtained electrolytically. It appears that the difficulty of duplicating chemically the anodic process is connected with the possibility that the hydrogen peroxide may take part in two different reactions. For example, in the oxidation of sulfite reactions of types (*a*) and (*d*) can occur simultaneously, the first leading to dithionate and the second to sulfate; it is probable that the latter process is generally much more rapid than the former, and hence it is only under the special conditions existing in electrolysis that appreciable amounts of dithionate are formed. It must be remembered that the relatively dilute solution of hydrogen peroxide involved in chemical oxidation may behave quite differently, especially when two alternative reactions are possible, from the thin layer of hydrogen peroxide, of high concentration, which would be formed continuously at an anode.

TABLE 18

Comparison of gases obtained in electrolysis of acetate and by action of persulfate

GASES	OBTAINED BY ACTION OF PERSULFATE	OBTAINED IN ELECTROLYSIS OF ACETATE
	per cent	*per cent*
CO_2	80.2	82.6
O_2	0.1	0.3
C_2H_4	0.4	0.2
CO	0.6	0.5
H_2	0.2	0.1
C_2H_6	9.8	10.2
CH_4	8.6	5.2

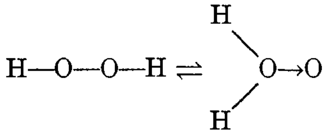
It may be recorded in support of this view that persulfates, which hydrolyze gradually in solution to yield a continuous supply of hydrogen peroxide, can often imitate anodic processes even when hydrogen peroxide itself does not do so. As an illustration may be quoted the oxidation of acetates: the action of hydrogen peroxide, under various experimental conditions, was found to give mainly oxygen together with some carbon dioxide, but only very small amounts of ethane and methane. When persulfate is used as the oxidizing agent, however, appreciable quantities of ethane and methane can be obtained. In table 18 is given the analysis of the gas resulting from the action of 30 g. of 93 per cent sodium persulfate on a solution of 75 cc. of 0.1 *N* acetic acid and 0.1 *N* potassium acetate at 85°C.; the figures may be compared with those obtained by the electrolysis of a solution of 4 *N* acetic acid and 4 *N* potassium acetate with a platinum anode at a current density of 0.0025 ampere per square centimeter (20).

The oxidizing action of persulfate is thus similar to that of an anode at low current density. The presence of manganese and cobalt salts, which catalyze the decomposition of hydrogen peroxide, in the mixture of persulfate and acetate was found to inhibit the formation of hydrocarbons, as observed in the electrolytic oxidation of acetate. It is important to note, further, that when the catalysts were added the rate of gas evolution was decreased, although the gas often contained relatively large amounts of oxygen: this result implies that the behavior of the catalysts is not due to their action on persulfate, but on a substance formed from it, presumably hydrogen peroxide, which is the effective agent for the production of hydrocarbons by oxidation of the acetate.

It has been shown in recent years by Fichter and his coworkers that many of the oxidations brought about electrolytically can be closely imitated using fluorine as oxidizing agent (11). The exact significance of this, however, seems to have been overlooked. Fichter formally represents the oxidations as involving change of electrical charge only, by the conversion of a fluorine atom to an ion; since the oxidations only take place in aqueous solution, however, and since fluorine reacts instantly with water, it does not seem probable that this is the mechanism. Nor does the formation of nascent oxygen, in view of the work of the authors, seem to afford any likelihood of explaining the oxidations. On the other hand, it has been shown (4, 12) that under appropriate conditions of stabilization, the action of fluorine on a solution of potassium hydroxide gives primarily hydrogen peroxide, and it appears probable that the peroxide is always formed, although it may decompose rapidly to give oxygen. In this case, the hydrogen peroxide will be formed continuously in a thin layer of high local concentration on the surface of each bubble of fluorine, in exact imitation of what probably occurs at an anode. Hence the close similarity between the action of fluorine and electrolytic oxidation might be expected. It is interesting to note that, as the result of a study of a large number of anodic oxidations, Fichter and J. Müller (13) were led to state that "Von allen chemischen Oxydationsmitteln kommt das Wasserstoffperoxyd in seiner Wirkung dem anodischen Sauerstoff am nächsten."

The difference in behavior between hydrogen peroxide formed at an anode and the ordinary chemical reagent may be accounted for in at least two ways, which must be regarded as largely speculative. In the first place, it was suggested by

Raikov (35) that hydrogen peroxide is a tautomeric system comprising a dihydroxyl and peroxide form:



$$H{-}O{-}O{-}H \rightleftharpoons \begin{matrix}H\\ \\H\end{matrix}\!\!>\! O \rightarrow O$$

and Geib and Harteck (17) claim to have isolated II by the action of hydrogen atoms on oxygen at low temperatures. If Raikov's view is correct, it is possible that the unique reactions of hydrogen peroxide are due to I, and general oxidation, indistinguishable from that of active oxygen, to II; thus in the formation of dithionate we should have

$$2SO_3^{--} + (OH)_2 \rightarrow S_2O_6^{--} + 2OH^-$$

while in sulfate production

$$SO_3^{--} + O{\cdot}OH_2 \rightarrow SO_4^{--} + H_2O$$

At the moment of the formation of hydrogen peroxide by the combination of discharged hydroxyl radicals, the dihydroxyl form is likely to predominate, and hence it is probable that the unique reactions of hydrogen peroxide will be more marked electrolytically than when the ordinary chemical reagent is employed. At high current densities the concentration of the dihydroxyl form relative to the peroxide form is likely to be raised, and hence we should expect that where two anodic oxidations are possible, the characteristic oxidation should be favored by high current density; this has already been shown to be the case.

Another possibility is that the active anodic oxidant is the hydroxyl radical; this would certainly account for the speed and vigor of the oxidation, but it would be necessary to make several subsidiary assumptions to account for the experimental facts. To explain the influence of anode material and catalysts for hydrogen peroxide decomposition in various electrolytic processes, it must be postulated that the catalytic decomposition of hydrogen peroxide occurs through the intermediate formation of hydroxyl radicals. The specific reactions of the peroxide, such as the conversion of sulfite to dithionate, would then be ascribed to these radicals. This point of view is fundamentally the same as that which attributes the oxidizing action to a form of hydrogen peroxide, except that it ascribes the characteristic behavior of the compound to an intermediate species whose chemical properties cannot be studied. Since hydrogen peroxide is known to be produced anodically, it seems preferable, for the present, to assume that this is the active oxidizing agent, especially as when it is formed at high concentration at the anode, perhaps in an active form as suggested above, its properties might be somewhat different from those of the ordinary reagent. A serious objection to the suggestion that hydroxyl radicals are responsible for anodic oxidation is the fact that in the Kolbe reaction the potential set up, presumably due to the discharge of acetate radicals, is much higher than that required for the discharge of hydroxyl ions and the evolution of oxygen; to account for this, it would be necessary to suppose that the process

$$OH + CH_3COO^- = OH^- + CH_3COO$$

is irreversible. Although this is possible, it does not appear to be very probable.

The theory of the anodic formation of hydrogen peroxide has been criticized adversely by Walker and Weiss (44) and by Butler and Leslie (8), chiefly on the grounds that (*a*) it is unlikely that hydroxyl radicals will combine together in solution to give hydrogen peroxide, and (*b*) the effect of catalysts can be explained in an alternative manner. With regard to the first criticism, there appears to be no reason to suppose that the process is impossible. It seems to be proved conclusively by the work of Rodebush and Wahl (39) and of Oldenberg (34) that hydroxyl radicals do actually combine in the gas phase to yield hydrogen peroxide, and there seems to be no fundamental objection to the postulate that the same process occurs in solution. If hydroxyl radicals do not unite to give hydrogen peroxide in solution, the observed formation of the peroxide with a glow-discharge anode must be accounted for, and certainly no satisfactory alternative explanation has yet been proposed. The second criticism is based to a large extent on the fact that the addition of certain metallic salts, e.g., lead, silver, and manganese, leads to the deposition of oxides on the anode with consequent lowering of the anode potential and inhibition of the electrolytic oxidation process. The authors have frequently noted that metallic oxides are formed on the anode, but this is not usually the case: for example, the presence of ferrous or ferric salts diminishes oxidation of those depolarizers in which direct reaction with hydrogen peroxide has been suggested, but no anodic deposit is formed. Such a deposit is, in fact, not expected, since the catalytic effect of ferrous and ferric ions is generally attributed to purely homogeneous reactions; on the other hand the activity of manganese, lead, and silver ions is probably due to the higher oxides, and anodic deposits of these oxides might be anticipated. That such deposits are not essential, however, is also proved by the fact that insoluble catalysts, particularly powdered charcoal, have been found to reduce the anodic efficiency in several instances. It is true, of course, that the effect of a catalyst is most marked when the active agent, e.g., higher oxide or ion, is produced at the anode where the hydrogen peroxide is formed. An extremely important aspect of this question is that the addition of catalysts for hydrogen peroxide decomposition frequently raises, not lowers, the potential to a marked extent, e.g., in the electrolysis of thiosulfate or sulfite solutions, yet the oxidation is inhibited; facts of this kind are not easily explained without the assumption that the factors responsible for the anodic process and the potential are to a great extent independent.

The theoretical views of the present authors have been criticized by Bancroft[8] (3), who puts forward the objection that hydrogen peroxide is only a moderately weak oxidizing agent with a potential of about 1.16

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[8] This paper contains a number of misstatements and misrepresentations, to which it is hoped to refer in greater detail elsewhere.

volts in acid solution (5); if hydrogen peroxide gave rise to a reversible oxidation–reduction system this objection would be valid, but it is very doubtful whether it does so, and whether the potential quoted has any fundamental significance. The fact that hydrogen peroxide is able to liberate chlorine from hydrochloric acid solution, the reversible potential for which is about 1.35 volts, shows that the situation is by no means as simple as has been supposed. Bancroft's statement, "If Glasstone and Hickling were right, the electrode of the lead storage cell would be an impossibility," is based on a failure to understand the hydrogen peroxide theory.

V. CONCLUSION

In concluding this review it can be stated definitely that no serious objection to the theory of the anodic formation of hydrogen peroxide has been put forward, and no alternative view has been proposed which is able to account in such a simple and complete manner for the observed phenomena of electrolytic oxidation. The authors would welcome any other view capable of explaining adequately the large variety of facts mentioned in this paper, but for the time being there is no doubt that the hydrogen peroxide theory provides a valuable guide for the interpretation of many anodic processes. When further investigations are made, it is hoped to develop the theory even further and widen its scope so as to include observations which are still difficult to understand.

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