53. *Studies in Electrolytic Oxidation. Part XII. The Mechanism of the Electrolytic Formation of Periodates.*

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The electrolytic oxidation of iodates to periodates and the effect of variable factors such as the nature of the electrode material, acidity and alkalinity, temperature, anode potential, and the presence of foreign anions have been investigated. The process takes place with moderate efficiency at lead peroxide and nickel electrodes, to a less extent at platinised and smooth platinum, and with manganese dioxide and carbon anodes no appreciable oxidation occurs. The efficiency is least in acid and greatest in alkaline solutions. At platinum and lead peroxide electrodes factors favouring the formation of higher oxides on the electrode surface, *e.g.*, anodic prepolarisation, in general increase the efficiency markedly. Rise of temperature leads usually to an improvement in efficiency except in the case of a smooth platinum anode in alkaline solution. The anode potentials set up during the oxidation appear to be merely oxygen evolution values and no indication of a definite oxidation–reduction potential is found. Various mechanisms for the anodic process are considered, and it is concluded that the facts can best be explained by oxidation of the iodate by metallic peroxides formed on the electrode surface, a secondary rôle being attributed to hydrogen peroxide formed initially in the discharge of hydroxyl ions, and this explanation is supported by independent chemical experiments.

THE anodic oxidation of iodates to periodates was first recorded by Müller (*Z. Elektrochem.*, 1901, **7**, 509), and later more thoroughly investigated (Müller and Friedberger, *Ber.*, 1902, **35**, 2652; Müller, *Z. Elektrochem.*, 1904, **10**, 49, 753), mainly with a view to ascertain the optimum conditions for industrial utilisation of the process (see also Willard and Ralston, *Trans. Amer. Electrochem. Soc.*, 1932, **62**, 239). It was established that at a smooth platinum anode the oxidation only took place with reasonable efficiency in strongly alkaline solutions, and was favoured by the use of low current densities and temperatures, while with platinised platinum the process would take place to some extent even in neutral and in acid solutions. With a lead dioxide anode good efficiencies were obtained in neutral and in acid solutions. In the case of a platinum electrode, certain anions, in particular fluoride, were found to improve the oxidation efficiency. The mechanism of the oxidation was considered by Müller (*Z. Elektrochem.*, 1904, **10**, 49), who suggested that the anodic reaction was electrical and could be represented as $IO_3' + H_2O - 2e = IO_4' + 2H^{\cdot}$. The potential of this process was supposed to be high, and the oxidation could only occur where the overvoltage of the anode was such as to prevent oxygen evolution taking place preferentially. While accounting for some of the experimental observations, this theory meets with many difficulties, and in particular fails to account for the fact that the efficiency at lead dioxide and platinised platinum anodes is higher than at smooth platinum although the potentials are considerably lower. It appeared of interest, therefore, to reinvestigate the process and to see if any light could be thrown upon it by the 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).

EXPERIMENTAL.

The electrolytic apparatus consisted of a 400-c.c. beaker, forming the anode compartment, into which dipped a wide glass tube, stopped at its lower end with a tight filter-paper plug, which served to hold the catholyte. This arrangement had a low electrical resistance, which was necessary in view of the poor conductivity of certain of the iodate solutions, but completely prevented mixing of the anolyte and catholyte. The anode compartment also contained a cooling coil and thermometer. For most of the experiments a rectangular sheet-platinum anode of area 20 sq. cm. was used; this was mounted vertically, and rotated at 175 r.p.m. A platinum-wire cathode was employed. Current was supplied from a 100-volt generator through rheostats and a milliammeter. In general, 0·01 faraday of electricity was passed, and the anode solution was then analysed. Except where otherwise stated, the temperature of the anolyte was kept at about 18°, and the C.D. was 0·025 amp./sq. cm.

" AnalaR " Potassium iodate was used in preparing the anolyte, which was usually 0·1M-potassium iodate in either N-sulphuric acid or N-potassium hydroxide; occasionally a 0·1M-solution in water was used. These solutions are subsequently referred to as the acid, alkaline, and neutral stock solutions. 250 C.c. of anolyte were used in each experiment, and the catholyte was either dilute sulphuric acid or dilute potassium hydroxide solution according to whether an acid or an alkaline anolyte was being employed. The periodate formed in the electrolysis was estimated by Müller and Friedberger's method (*loc. cit.*). A measured quantity of the anolyte was taken, acid or alkali added until it was just alkaline to phenolphthalein, and solid sodium bicarbonate introduced, followed by excess potassium iodide; the iodine liberated was then titrated with standard arsenite solution, and the result expressed as a current efficiency.

Results.

Experiments with a Smooth Platinum Anode.—Before use, the platinum electrode was cleaned with warm concentrated hydrochloric acid, warm concentrated nitric acid, and water, and heated to redness.

Influence of acidity and alkalinity. To investigate the influence of acidity and alkalinity, acid, neutral, and alkaline stock solutions were electrolysed :

Electrolyte.	Acid.	Initially neutral.	Alkaline.
Efficiency, %	1	2	11

Obviously, periodate formation at a smooth platinum anode is markedly favoured by alkalinity. To ascertain at what p_H value in alkaline solution an optimum yield of periodate is obtained, electrolyses were carried out with 0·1M-potassium iodate in phosphate buffer, borate buffer, carbonate buffer, and potassium hydroxide solutions of various concentrations.

p_H	7	9	12	13	14	14·3
Efficiency, %	2	6	10	14	11	10

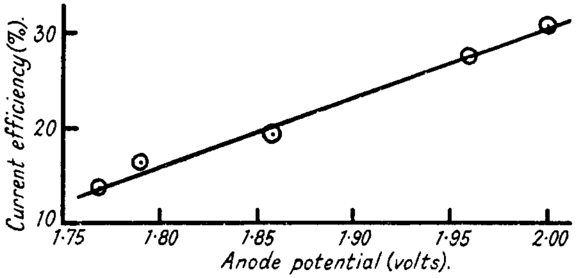
Hence, the maximum efficiency is obtained with an electrolyte of p_H 13.

Influence of anodic prepolarisation. To determine the effect of this procedure on the yield, the anode was prepolarised for 6 hours at the usual C.D., in either N-potassium hydroxide or N-sulphuric acid. The appropriate amount of iodate was then introduced without stopping the current, and the usual electrolytic experiment carried out. The results obtained, together with the efficiencies when the anode was used without prepolarisation, are given below in terms of the efficiency, % :

Electrolyte.	Acid.	Alkaline.
Prepolarised anode	1	31
Unpolarised anode	1	11

It is seen that prepolarisation markedly improves the yield in alkaline solution, but has no effect when an acid electrolyte is employed. The effect of the prepolarisation was found to be somewhat transient; *e.g.*, in one experiment, the anode after prepolarisation as above was kept in water for 5 minutes before the usual electrolysis with alkaline stock solution was carried out; the efficiency under these conditions was only 17%. The effectiveness of the platinum anode for periodate formation in alkaline solution seems closely connected with the potential it can attain. This is shown in Fig. 1, where the efficiencies obtained with anodes prepolarised for various times are plotted against the average potentials of the anodes observed during the electrolysis of alkaline stock solution at the usual C.D. The potentials are expressed on the hydrogen scale; they may involve a small resistance error which will, however, be the same in each case.

FIG. 1.



Influence of duration of electrolysis. Since anodic polarisation in alkaline solution favours the formation of periodate, it might be expected that in the ordinary electrolytic experiments the efficiency would increase with the duration of the electrolysis. To test this, alkaline stock solution was electrolysed with a clean platinum anode, various quantities of electricity being passed in separate experiments :

Quantity of electricity, faradays	0·0025	0·005	0·01	0·02	0·04	0·05
Efficiency, %	9·2	9·5	10·0	10·7	12·0	16·4

Influence of foreign anions. It was recorded by Müller (*Z. Elektrochem.*, 1904, **10**, 753) that certain foreign anions, in particular fluoride, markedly favoured the formation of periodate. A comprehensive survey has therefore been made of the effect of adding the salts of various acids to the electrolyte. The salts chosen were such as not appreciably to affect the p_H of the electrolyte, or to give rise to anodic products which could bring about secondary reactions, as would be the case, *e.g.*, with chloride. Observations were made in both acid and alkaline stock solutions. The electrolytes were in all cases made 0·1N with respect to the foreign anion. The efficiencies, %, are listed below.

Substance added.	(None.)	KF.	KNO_3.	$KClO_4$.	K_2SO_4.	KH_2PO_4.	H_3BO_3.
Acid stock	1	4	8	2	—	1	1
Alkaline stock	11	50	28	24	14	13	10

Of the anions tried, fluoride, nitrate, and to a less extent perchlorate, increase the efficiency in both acid and alkaline solutions; sulphate, phosphate, and borate ions do not have any marked influence. The acid stock solution normally contains sulphate ions, of course, but a separate experiment on the electrolysis of iodic acid alone gave the same efficiency as with the stock solution.

Influence of temperature. To ascertain the influence of temperature, acid and alkaline stock solutions were electrolysed with a clean platinum anode, water at various temperatures being circulated through the coil in the cell. The following efficiencies %, were obtained :

Temperature.	0°.	18°.	50°.	85°.
Acid stock	1	1	2	3
Alkaline stock	18	11	7	0

It is apparent that in alkaline solution the efficiency falls with rising temperature, and in acid solution the converse is the case.

Influence of C.D. To determine whether the use of a much lower C.D. would result in an enhanced yield of periodate, acid and alkaline stock solutions were electrolysed with the clean platinum anode at a C.D. of 0·00125 amp./sq. cm. The efficiencies, %, together with those for the ordinary C.D., are listed below.

C.D., amp./sq. cm.	0·00125.	0·025.
Acid stock	1	1
Alkaline stock	4	11

It may be noted that, whereas decrease in C.D. results in a lower efficiency in alkaline solution, it has no effect in acid.

Experiments with Lead Peroxide Anodes.—A lead sheet, 20 sq. cm. in area, was anodically polarised at the usual C.D. in N-sulphuric acid for 30 mins., washed with water, and used immediately. Between consecutive experiments the electrode was cleaned with concentrated hydrochloric acid, washed with water, polished with a wire brush, and repolarised. It was found impossible, however, to obtain reproducible results. In three apparently identical experiments for the electrolysis of acid stock solution, values for the efficiency of periodate formation were 18, 44, and 61% severally.

Glasstone (J., 1922, **121**, 2091) showed conclusively from potentiometric studies that oxygen evolution at a lead anode takes place through the formation of an oxide of lead higher than the dioxide, probably PbO_3, and that on allowing a polarised lead anode to stand, this oxide slowly decays. It appeared possible, therefore, that the anomalous behaviour of the lead anode in the present investigation might be due to the formation of this higher oxide in varying amounts. The formation of the oxide will obviously depend largely on the pretreatment of the anode, the time which elapses before use, the effective C.D. at various points on the surface during electrolysis, and possibly other, unknown factors. To test this point of view, an electrode of " AnalaR " lead was made up, and two sets of experiments were carried out. (i) The clean electrode was anodically polarised at a C.D. of 0·05 amp./sq. cm. in N-sulphuric acid for 30 mins., the C.D. then reduced to 0·0125 amp./sq. cm. and 0·1M-potassium iodate introduced, and the usual electrolysis carried out, the current not being interrupted at any point. (ii) The polarisation was carried out in the same way, but the electrode was allowed to stand for 30 mins. in distilled water before electrolysis of the iodate solution was performed. Between successive experiments the electrode was cleaned and polished. The efficiencies, %, for series (i) were 74 and 66, and for (ii), 20 and 25. Although the results are not precisely reproducible, it is apparent that in the first set of experiments, where conditions are such as to favour the formation of higher oxides of lead, the efficiency is vastly greater than in the second set, where opportunity is given for any such oxides to decay.

It was found that an electrode formed by the deposition of lead dioxide on smooth platinum would give reproducible results when used as an anode in the electrolysis of iodate solutions, although the efficiencies were considerably lower than those observed with polarised lead anodes, and this type of electrode was therefore employed in the subsequent investigation in order to obtain reliable results for the effects of variable factors. The most satisfactory method of preparing the electrode was found to be the deposition of lead dioxide from N-lead acetate solution at the usual C.D. for 5 mins.; the anode was then rotated in distilled water for 10 mins. and used immediately.

Influence of acidity and alkalinity. Acid, neutral, and alkaline stock solutions were electrolysed, and the following results obtained :

Electrolyte.	Acid.	Initially neutral.	Alkaline.
Efficiency, %	6	13	38

As with smooth platinum, periodate formation is favoured by alkalinity.

Influence of foreign anions. To determine whether certain foreign anions would improve the yield of periodate at a lead peroxide anode, as was observed with smooth platinum, electrolyses were carried out of acid stock solution containing 0·1N-potassium fluoride, -potassium nitrate, and -potassium perchlorate, these substances having proved particularly effective with the smooth platinum anode. No increase in efficiency was found, as shown by the results below :

Substance added.	(None.)	KF.	KNO_3.	$KClO_4$.
Efficiency, %	6	6	6	6

Influence of temperature. The acid stock solution was electrolysed at various temperatures :

Temperature.	0°.	18°.	55°.	85°.
Efficiency, %	6	6	39	56

The efficiency is markedly improved by rise of temperature.

Other Electrode Materials.—In order to determine the influence of other anode materials, simple experiments under normal conditions were carried out with acid, neutral, and alkaline stock solutions, the size, shape, and apparent area of each electrode being the same as that of the smooth-platinum anode. Platinised platinum, manganese dioxide, nickel, and gas-carbon electrodes were used. Before use, the platinised platinum anode was cleaned with warm concentrated hydrochloric acid, warm concentrated nitric acid, and washed in water. The manganese dioxide was deposited on grey platinum by electrolysis of a slightly acidified solution of N-manganese sulphate at the usual C.D. for 10 mins.; it was then washed and used immediately. The nickel electrode was washed with water and polished prior to use. The gas carbon was thoroughly washed with boiling water The results are summarised below, those for smooth platinum and lead dioxide being included for comparison.

	Efficiency, %.		
Anode material.	Acid.	Neutral.	Alkaline.
Smooth Pt	1	2	11
Platinised Pt	2	6	14
PbO_2	6	13	38
Ni	3	14	30
MnO_2	0	0	0
Gas C	0	0	1 *

* This result is doubtful, as the anode was badly attacked.

Potential Measurements.—In order to make measurements of the potentials at which the oxidation occurs, a small stationary platinum anode of area 0·1 sq. cm. was used, and its potential at a series of currents measured against that of a saturated calomel electrode by the potentiometer–voltmeter method. Experiments were carried out at room temperature using stirred solutions with (*a*) the smooth platinum anode in N-sulphuric acid, acid stock solution, acid stock + 0·1N-potassium fluoride, N-potassium hydroxide, alkaline stock solution, alkaline stock + 0·1N-potassium fluoride, and with alkaline stock solution after the anode had been prepolarised for 6 hours under the usual conditions; (*b*) the smooth platinum anode coated with lead dioxide in N-sulphuric acid, and acid stock solution; and (*c*) the anode after platinising in N-sulphuric acid, acid stock solution, N-potassium hydroxide, and alkaline stock solution. Except where otherwise stated, the anodes were polarised for a few minutes at the highest C.D. to be used, and the potentials were then read as the current was decreased, and immediately afterwards a repeat experiment was carried out. The potentials, which were very definite, were in general reproducible within 2 centivolts. The values are given in Figs. 2 and 3 in the form of C.D.–potential curves, the potentials being expressed on the hydrogen scale.

It may be noted that the anode potentials in the electrolysis of iodate solutions are not in general markedly different from the values for solutions of the same hydrogen-ion concentration not containing iodate; *i.e.*, they appear to be merely oxygen evolution potentials. Prepolarisation of the smooth platinum anode leads to a marked increase in potential, as does also the presence of fluoride; addition of potassium nitrate also led to an increase in anode potential.

Chemical Oxidation of Potassium Iodate.—The chemical oxidising action of the substances likely to be formed at an anode was investigated.

Oxygen. Gaseous oxygen was passed through a sintered-glass bubbler at room temperature for 24 hours into acid, neutral, and alkaline stock solutions. No oxidation could be detected in any case. The experiment was then repeated for 3 hours using boiling solutions, but again there was no action.

FIG. 2.

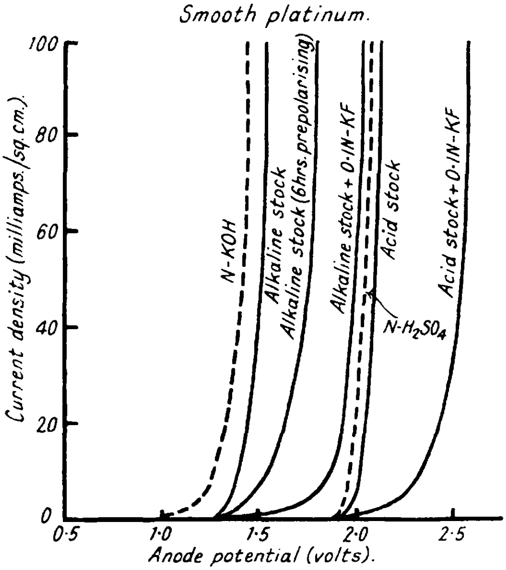
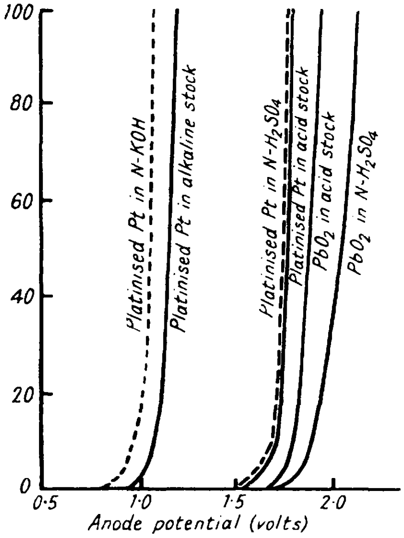


FIG. 3.



Hydrogen peroxide. Tanatar (*Ber.*, 1899, **32**, 1015) recorded that hydrogen peroxide reacts with periodate solutions with evolution of oxygen, but the process does not appear to have been investigated thoroughly. A more detailed study of the reaction has therefore now been made. A known amount of hydrogen peroxide was allowed to react with a known excess of potassium periodate and the process allowed to go to completion. The oxygen evolved was measured, and the amounts of periodate and iodate were separately determined; no hydrogen peroxide could be detected. From the figures obtained, a satisfactory weight balance for the formation of iodate and oxygen against the decomposition of hydrogen peroxide and periodate according to the equation $KIO_4 + H_2O_2 = KIO_3 + O_2 + H_2O$ was obtained. The velocity of the reaction in acid and alkaline solutions was investigated at 18° by measuring the rate of evolution of oxygen. From the values obtained, it appears that the reaction velocity can be fairly accurately represented by a second-order equation. The velocity constants calculated on this basis were 5 for the reaction in N-sulphuric acid and 26 for N-potassium hydroxide (units: moles/l., mins.). The presence of anions such as nitrate and fluoride did not affect the velocity constants.

Metallic oxides. The reaction of metallic oxides, which might possibly be formed at the various electrodes, with potassium iodate was investigated. 250 C.c. portions of acid, neutral, and alkaline stock solutions were treated in separate experiments with a weight of oxide containing 0·01 g.-equiv. of available oxygen (corresponding to the normal electrolysis). Arbitrary conditions for investigating the reaction in the hot and the cold were adopted, *viz.*, boiling the mixture for 1 hour, or keeping it at room temperature with periodic agitation for 60 hours; the solutions were then filtered and analysed for periodate in the usual way. The yield was expressed as a percentage of that which would have been obtained if all the available oxygen had been used in converting iodate into periodate. The oxides used are given below. The first two were prepared in a pure state by routine methods; the third was prepared by Chirnoaga's method (J., 1926, 1698). The oxides of platinum were made according to the methods described by Wöhler *et al.* (*Z. anorg. Chem.*, 1904, **40**, 423; *Ber.*, 1909, **42**, 3326). Owing to the limited amount of platinum available, amounts of the oxides smaller than above specified were used (0·005—0·002 g.-equiv. of available oxygen). The results obtained are summarised in the following table.

		PbO_2.	MnO_2.	NiO_2.	PtO_2.	PtO_3.
Cold	Alkaline	0	0	0	0	0
	Neutral	5	0	2	0	0
	Acid	30	0	0	0	0
Hot	Alkaline	0	0	trace	0	12
	Neutral	0	0	1	0	0
	Acid	42	0	0	0	0

DISCUSSION.

The experimental results seem to indicate conclusively that the electrolytic oxidation of iodate to periodate is not a purely electrical reversible process represented by the equation $IO_3' + H_2O - 2e = IO_4' + 2H^{\cdot}$. Such a process should be characterised by a definite oxidation–reduction potential, and provided that potential can be attained, the oxidation should be largely independent of variable factors such as anode material, temperature, etc. In the present case the C.D.–potential curves show no sign of any definite potential associated with the reaction; on the contrary, the oxidation takes place more efficiently at lead dioxide and platinised platinum anodes at a low potential than it does at smooth platinum at a higher potential. For instance, in acid stock solution at the usual C.D., anode potentials at lead dioxide, platinised platinum, and smooth platinum were 1·85, 1·80, and 2·05 volts respectively, whereas the efficiencies were 6, 2, and 1%. Many other such anomalies can be quoted. It is true that in the case of any one electrode, in which anodic polarisation is attended by a rise of potential, such polarisation is in general accompanied by an increase in efficiency, and it was on this basis that the original mechanism for the oxidation was advanced (Müller, *Z. Elektrochem.*, 1904, **10**, 49). Nevertheless, consideration of the potentials at the different electrodes (see above) renders this explanation definitely untenable.* Further grounds for the rejection of the electrical mechanism lie in the influence of temperature; although in the case of smooth platinum in alkaline solution increase of temperature leads to a decrease in efficiency, which is in accordance with Müller's view since the oxygen over-voltage of the electrode will be lowered by rise of temperature, yet this is not borne out by the influence of temperature in other circumstances in which the effect is reversed. It may be noted that attempts to measure the static potential of the periodate–iodate system have not given significant results (Müller, *ibid.*, 1903, **9**, 584; see also Abel and Smetana, *Monatsh.*, 1932, **60**, 181). The simple view that oxygen is first formed at the anode and then brings about chemical oxidation of the iodate to periodate, seems equally unsatisfactory. The chemical experiments show that gaseous oxygen does not oxidise iodate, and the C.D.–potential curves show no depolarisation for oxygen except to a small extent in the case of a lead dioxide anode.

The main features associated with electrolytic periodate formation which emerge from the present investigation, and for which any theory must satisfactorily account, are as follows: (*a*) the effect of anode material, (*b*) the increasing yield with anodic polarisation, (*c*) the effect of acidity and alkalinity, and (*d*) the influence of temperature.

All the observations can be accounted for if the actual oxidation is regarded as brought about by metallic oxides formed on the anode surface, a secondary effect being attributed to hydrogen peroxide which, according to the general theory previously developed, is formed initially in the discharge of hydroxyl ions. The chemical experiments show that certain metallic oxides will oxidise iodate to periodate, and in addition it has been shown that

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* The anomaly in the case of lead dioxide was recognised by Müller, who attempted to explain it by an additional *ad hoc* hypothesis involving a specific catalytic action.

hydrogen peroxide reduces periodate to iodate. The total process at the anode might therefore be represented as follows :

$$\begin{tikzcd}
2OH' + 2\oplus \arrow[r] & 2OH \arrow[r] & H_2O_2 \arrow[r] \arrow[d] & H_2O + O \arrow[r] \arrow[d] & \tfrac{1}{2}O_2 \\
 & & \text{Reduces } IO_4' \text{ to } IO_3' & \text{May oxidise } IO_3' \text{ to } IO_4' \text{ through formation of a metallic peroxide} &
\end{tikzcd}$$

The criteria, therefore, for a high yield of periodate in electrolysis will be primarily that a suitable metallic peroxide can be formed, and secondarily, that conditions shall be such as to favour the decomposition of hydrogen peroxide.

The influence of anode material can then readily be explained. It has been shown that lead dioxide will oxidise iodate to periodate, and moreover, it is an excellent catalyst for hydrogen peroxide decomposition. It would be expected therefore that a lead dioxide anode would give good yields in the electrolysis, as is found to be the case. The anomalous behaviour of the uncontrolled lead peroxide anode and the increased current efficiency attendant on prepolarisation, may then be explained as previously indicated by the formation of an unstable oxide, higher than PbO_2, which is a better oxidising agent. In the case of platinum it has been shown that of the oxides which have been examined only the higher will convert iodate into periodate, and smooth platinum is only a moderate catalyst for the decomposition of hydrogen peroxide. Hence, platinum anodes should in general give a low efficiency for periodate formation, but one which should be markedly improved by conditions favouring the formation of higher oxides on the anode and the decomposition of hydrogen peroxide. As an example of the first factor we have the influence of anodic polarisation, and as an example of the second there is the increase in efficiency which results on platinising the electrode. The effect of anions such as fluoride and nitrate in increasing the efficiency at a platinum anode is not entirely clear, but the measurements show that these anions bring about an increase of potential, and hence it may be supposed favour the production of higher oxides at the platinum surface. That the effect is one on the electrode material was shown by an experiment in which the smooth platinum anode was prepolarised for 10 minutes in a solution of 0·1N-potassium fluoride in N-potassium hydroxide, after which it was removed from this solution, quickly washed, and used for a normal electrolysis of alkaline stock solution; a current efficiency of 21% was obtained which is considerably higher than the usual value.

In the case of nickel a fairly high current efficiency was observed, and although the yield by chemical oxidation does not stand very well in relation to this value, when compared with lead dioxide for example, it is noteworthy that actual chemical oxidation has been brought about by NiO_2. With a manganese dioxide anode, however, the zero value of current efficiency is reflected in the absence of chemical oxidation. That a gas-carbon anode should yield poor efficiencies is not unexpected on the present theory, since the oxides of carbon are not good oxidising agents.

The general effect of alkalinity in improving the oxidation efficiency must be attributed to the secondary action of the hydrogen peroxide at the anode. In alkaline solution the rate of decomposition of hydrogen peroxide is vastly greater than in acid solution and hence the hydrogen peroxide formed will have less chance of destroying the periodate. In order to demonstrate that actual reduction of periodates at an anode can take place, an experiment was carried out in which a 15% solution of periodic acid was electrolysed at a current density of 0·00125 amp./sq. cm., and the ratio of the oxygen evolved to the hydrogen from a standard coulometer was determined by gas analysis. A mean value of 0·524 for the molar ratio was obtained. Attempts to improve the current efficiency of periodate formation in the normal electrolysis by the introduction of metallic salts capable of bringing about hydrogen peroxide decomposition were unsuccessful owing to precipitation of the metallic ion by either iodate or periodate.

According to the view put forward for the mechanism, it would be anticipated that increase in temperature would result in increase in oxidation efficiency, since it should facilitate oxidation by the metallic oxide, and at the same time assist in the decomposition of hydrogen peroxide. This is in agreement with the results obtained with one exception, *viz.*, that of smooth platinum in alkaline solution. This anomaly might conceivably be attributed to an effect of temperature in decreasing the polarisation and hence hindering the formation of the higher oxide of platinum which is considered necessary to bring about the oxidation.

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