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PARTS 2 AND 3.

THE ANODIC BEHAVIOUR OF ALKALINE BORATE AND PERBORATE SOLUTIONS.

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Perborates were first prepared in the pure state in 1898 by Melikoff and Pissarjewski,* and by Tanatar.† The one commonly prepared is the sodium salt $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$, this formula having been established by the above authors and confirmed later by Constam and Bennet,‡ who concluded from conductivity measurements that it is a salt of a monobasic acid, HBO_3 . It contains 10·38 per cent. of active oxygen, corresponding with one atom of oxygen in the formula, sodium metaborate being formed by its reduction. It is generally prepared by the action of H_2O_2 or Na_2O_2 on borax solutions, and on account of its oxidizing properties it finds increasing commercial application for bleaching and for laundry work. For such purposes an electrochemical method of preparation would be of value if it could be arranged as a continuous process, after the manner of the hypochlorite electrolyzers in use, fresh bleaching solution being drawn off as required and spent liquor returned to the cell, and such an apparatus has been described in a French patent, to which further reference will be made.

On this account an investigation of the electrolytic preparation of perborates appeared to offer an interesting field, especially as the only evidence hitherto available regarding the possibility of preparing perborates electrochemically is of a somewhat unsatisfactory nature.

Tanatar § states that he obtained sodium perborate by electrolysis of a concentrated solution of sodium orthoborate, but gives no details of the process. Later Tanatar || states that perborates are decomposed by the passage of the electric current. Constam and Bennet ¶ describe an experiment in which the anolyte, consisting of 20 grams borax and 4 grams NaOH in 60 c.c. of water, was contained in a Pukall cylinder which dipped into 10 per cent. NaOH as catholyte. They passed 0·5 ampere for 4 hours at a temperature

* *Ber.*, **31**, 678 (1898).

† *Z. Anorg. Chem.*, **25**, 265 (1900)

|| *Z. Phys. Chem.*, **29**, 162 (1899).

‡ *Z. Phys. Chem.*, **26**, 132 (1898).

§ Loc. cit.

¶ Loc. cit.

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of 4° to 6.5° C., but obtained no perborate, or at most a very small quantity (which they called H_2O_2), the oxygen evolved being practically equivalent to the total current. Like Tanatar, they omit all mention of such important factors as electrode material, current density, etc. Bruhat and Dubois* state that sodium perborate can be obtained by electrolysis of a solution of sodium orthoborate, but it is not clear whether they mean to imply that they themselves have prepared it by this method.

The only other evidence is that of a French patent by Pouzenc,† and two articles thereon by Beltzer‡ in French technical publications. The full details of these were not available when the present work was commenced, but it was known that the apparatus described consists of a vertical electrolyser divided into anode and cathode compartments by a vertical diaphragm, the electrodes being of polished platinum. The electrolyte used for making bleaching solutions is said to contain 24 grams borax + 6 grams NaOH per litre, and is cooled in a reservoir and allowed to flow through the cell, the current density being about 30 to 60 amperes per sq. dm. Later on an opportunity occurred of consulting the original patent and the papers referred to, and they will be discussed in the appropriate place below.

As regards the mechanism whereby sodium perborate might be produced electrolytically, Tanatar suggested oxidation of the borate by H_2O_2 formed at the anode by discharge of OH' ions thus :—

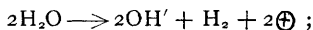


Riesenfeld and Reinhold,§ however, have shown that even under what they consider the most favourable conditions for this reaction (high alkali concentration, low temperature, and high current density) no H_2O_2 is obtained at the anode from NaOH, and with KOH at 0° C. the concentration only reached 1/1,000 molar after electrolysis for 2 hours with a current density at the anode of 33 amperes per sq. dm. Constam and Bennet make the remarkable statement that, since sodium perborate undoubtedly has the simple formula $NaBO_3$, one would not expect it to be formed electrolytically, because it could not be formed like persulphates or percarbonates by the union of discharging anions. Apparently they were unacquainted with the simple process of anodic oxidation, and there appears to be no good reason why, if sodium perborate can be produced electrolytically, it should not be by simple removal of negative charges, thus :—

Anode—



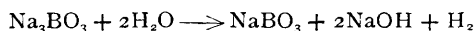
Cathode—



together—



or, writing in the sodium—



as the total result of the electrochemical process. The removal of negative charges might, of course, take place actually through the intermediate action of an "oxygen-charged" electrode, and not directly, || as shown. Besides

* *Compt. Rend.*, **140**, 506 (1905).

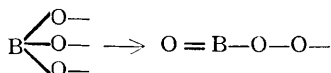
† French Patent, No. 411,258 (April, 1910).

‡ *Revue d'Electrochimie*, **5**, 1 (1911); *Le Moniteur Scientifique*, 1911, p. 10.

§ *Ber.*, **42**, 2977 (1909).

|| Cp. Grube on oxidation of ferro- to ferri-cyanides, *Z. f. Elektrochem.*, **18**, 189 (1912).

the loss of negative charges the BO_3''' ion would presumably undergo a structural change thus :—



Perborate ions might also conceivably result from anodic oxidation of various borate ions other than BO_3''' .

Whatever the mechanism, the conditions to be aimed at are those which lead to a high anodic potential, viz., polished platinum anode, at which the overvoltage is known to be higher than at any other, low temperature, and high current density. Low alkali concentration, by diminishing the tendency for discharge of hydroxyl ions, will also favour a high potential. Also, of course, a reasonably high borate concentration is desirable. In practice the simultaneous realisation of these conditions is somewhat difficult.

Detection and Estimation of Perborate.

Sodium perborate in solution can be titrated in presence of H_2SO_4 with permanganate, and behaves like H_2O_2 towards this reagent, two molecules of KMnO_4 corresponding to five of $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$. A sample obtained (as a white powder) from Kahlbaum was found on titration with KMnO_4 to contain only about 87 per cent. of $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$, which, however, on recrystallising, increased to 98 per cent. Numerous titrations with varying quantities of perborate and acid showed the permanganate method to be sufficiently reliable. In a 2 per cent. solution the perborate was found to decompose spontaneously at the rate of about 1 per cent. per hour at ordinary temperature.

Cooling Arrangements.

It is difficult to arrange an apparatus with the anode and cathode as close together as would be desirable, while still separating them by a suitable diaphragm and accommodating the necessary thermometer, etc., and the resistance due to the comparatively low conductivity of the solutions is further increased by the diaphragm and the gas evolution at the electrodes. It was therefore necessary in practically all the experiments, in order to keep the anolyte at the low temperature desired, to use a somewhat elaborate arrangement. A cooling liquid at -16°C . to -18°C . was prepared in a large cylindrical metal tank of 24 litres capacity by mixing crushed ice and salt with the necessary amount of water. The metal tank was contained in an outer vessel of earthenware standing on the floor. The liquid was sucked by means of a water-pump through a wire-gauze strainer, and then through the cooling coils in the electrolysis cell into a large glass bottle standing on the bench, with taps so arranged that from an outlet near the foot of the bottle the liquid could, when desired, be run straight back to the tank for further use, without interrupting the flow of cooling liquid through the apparatus.

First Form of Apparatus.

The first cell employed consisted of an outer glass vessel which contained the catholyte, and in this glass vessel stood a porous pot* which contained the anolyte. In order that the gas evolved might be collected, the pot was closed with a rubber stopper fitted with a delivery tube, and fixed through the stopper were also a thermometer, the ends of a glass spiral for cooling the anolyte, an inlet for running in NaOH from a burette, and the anode itself. The last consisted of strips of platinum wire or foil of suitable size to

* The porous pots and tubes used were made thinner and more uniform by grinding them on the lathe with emery.

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give the desired current density, and bent outwards so as to lie near the cooling spiral. The cathode consisted of a cylindrical sheet of nickel encircling the pot, leaving only sufficient space between for gas to escape freely. The top of the pot where it projected out of the liquid was waxed to make it airtight.

Composition of the Anolyte.

It appeared desirable in the first instance to try the solution of Pouzenc referred to above, viz., 24 grams borax + 6 grams NaOH per litre. Such a solution, however, was found to have too low a conductivity, the consequent heat evolution being excessive, and solutions were therefore used which contained more NaOH. As pointed out above, however, it is desirable, in order to get a high anodic potential, to keep the alkali concentration as low as possible, but suitable solutions cannot be obtained by merely dissolving larger amounts of borax in water, because 100 grams of water dissolve at 0° C. only 2.83 grams of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and at 10° C. 4.65 grams. Potassium borate was found to offer no great advantage in this respect, but by adding KOH a solution could be prepared which contained 27.4 grams K_2O and 50.7 grams B_2O_3 per litre (against 8.8 grams per litre of B_2O_3 in the Pouzenc solution), and such a solution, slightly diluted, was used in one case. Similarly with borax the concentration can be increased by adding NaOH (cp. Constam and Bennet, above). Thus a solution containing 80 grams borax + 20 grams NaOH per litre (29.3 grams per litre of B_2O_3) does not deposit any solid at 0° C., but in the earlier experiments with such solutions less ozone was produced than in other cases, and this was taken as an indication that the anodic potential was lower, and the conditions therefore less favourable, the alkali concentration being apparently too high. Later on it appeared that other factors are probably of greater importance, and that, moreover, the ozone production is a rather uncertain quantity and depends on various things. Of course in one respect an increase in the proportion of alkali might possibly be advantageous by increasing the concentration of BO_3''' ions. Apparently, however, the number of BO_3''' ions present in any alkaline borate solution is very small, the chief ion being probably $\text{H}_2\text{BO}_3'$. The composition which would nominally correspond to orthoborate would require, roughly, equal weights of borax and NaOH, but such solutions are very strongly alkaline owing to hydrolysis; in fact, according to Kahlenberg and Schreiner* practically all the excess of NaOH above that corresponding to metaborate is present in the free state, the solution being therefore no richer in BO_3''' ions than a less alkaline one.

The first few experiments showed that it was necessary to add a little NaOH to the anolyte from time to time to compensate for that removed by the electrolysis, otherwise the voltage across the cell rose rapidly. In some cases it was even necessary to add a little at the commencement in order to reduce the high resistance and consequent great heat evolution.

Experiments with First Form of Cell.

Some experiments with the first form of cell are briefly summarised in Table A. The first two columns give the composition of the anolyte in grams per litre of borax and caustic soda. The symbols used are as follows throughout the paper:—

T = Temperature of the anolyte.

C = Current through cell (in amperes).

D_A = Current density at anode in amperes per sq. dm.

V = Voltage across cell.

* *Z. Phys. Chem.*, **20**, 547 (1896).

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TABLE A.

	Borax.	NaOH.	T.	C.	D _A .	V.	Time.
1	29 gm.	18 gm.	4° to 5° C.	4'0	22	8'8 to 10'4	45 min.
2	24 "	17 "	-2° C.	4'0	73	10'4	35 min.
3	80 "	20 "	0° to -1° C.	3'3	60	11'2 to 8'0	2 hr.
4	80 "	20 "	-1° to -2° C.	3'5	106	11'6 to 9'6	1 hr.

The catholyte in each case was 4 per cent. NaOH. These and other similar experiments (in one case using potassium borate) gave negative results. The rate of evolution of oxygen was measured occasionally during each experiment and always corresponded as closely as could be ascertained to the total current. After each experiment the anolyte was tested with

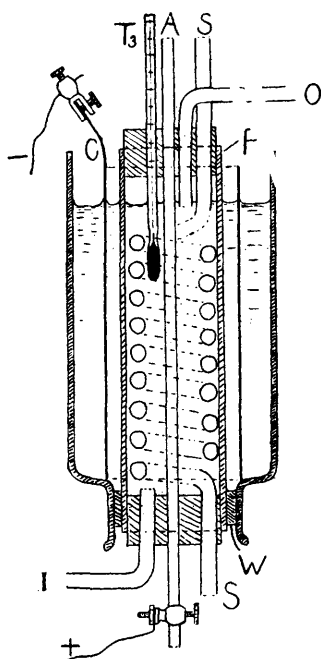


FIG. 1.

KMnO_4 . In no case was there any oxidising action except in No. 3, when 10 c.c. of anolyte decolourised one single drop of $\text{N}/4 \text{ KMnO}_4$.

The only hope of obtaining more favourable conditions appeared to lie in the employment of a cooled anode. Although the bulk of the liquid in some of the above experiments was at a temperature in the neighbourhood of zero, the portions surrounding the anode might be at a considerably higher temperature owing to the high anodic current density, and it seemed that by using a cooled anode this condition might be more or less reversed, the liquid in contact with the anode being kept at a sufficiently low temperature, while the bulk of the electrolyte need only be kept at a moderately low temperature. Thus Prausnitz* was able to obtain very satisfactory yields of

* *Z. f. Elektrochem.*, **19**, 676 (1913).

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hypochlorite by employing a cooled anode, even when at the same time the bulk of the liquid was actually warmed to reduce the potential drop. Moldenhauer,* who gives a theory of heat evolution at the electrode surface, obtained improved yields in various electrolyses. Cooled anodes have also been used in the preparation of persulphuric acid from sulphuric acid for the manufacture of hydrogen peroxide.

The anode used in the apparatus to be described consisted of a platinum tube† 20 cm. long, 3 mm. external diameter and 0.17 mm. in thickness, the area of the portion actually immersed in the electrolyte being approximately 8 sq. cm.

Cooled Anode Apparatus.

The electrolysis cell is shown in Fig. 1 in section. P is a porous tube of 3×12 cm., held in place by the rubber washer W. S is the cooling spiral,

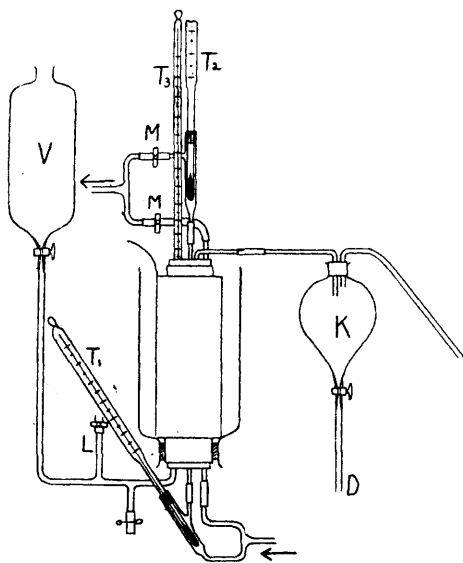


FIG. 2.

A the anode, T_3 a thermometer, and C the cathode, a cylindrical sheet of nickel as before. The outer glass vessel served to contain the catholyte. The anolyte flowed in at I and gas and liquid came out at O.

The general arrangement of the apparatus is shown in Fig. 2. The vessel V contained the anolyte (generally about 100 to 125 c.c.), the tap regulating its flow to the anode compartment. Gas and liquid collected in K, the former passing on through the delivery tube, while the latter could be drawn off at D and returned to V, a continuous circulation of the anolyte being maintained. A burette containing NaOH was connected at L, a few c.c. being run in as required. The cooling liquid, which entered at the foot

* *Z. f. Electrochem.*, **11**, 307 (1905).

† An attempt was made to use an anode of platinised brass tube. The platinising was carried out with the citrate solution of Langbein (*vide* Schlötter's *Galvanostegie*, p. 187), the tube being rotated in the liquid. It was found possible by this means to obtain an excellent platinum surface, which could be well polished and was highly resistant mechanically; but unfortunately when used as anode in alkaline solution at high current density it rapidly disintegrated, cupric hydroxide being ultimately found in the liquid.

as shown by the arrows, was divided between the anode and the glass spiral, the proportion being regulated by the screw clips M.

No electrical leakage took place through the salt solution flowing through the anode; in some cases two ammeters were connected in the circuit, one on each side of the cell, and these agreed perfectly.

The thermometers T_1 and T_2 give the temperature of the liquid entering and leaving the anode.* The mean of these is the nearest indication that can be obtained of the actual temperature of the anode and is given as T_A below.

T is the temperature of the anolyte, as given by thermometer T_3 . The other letters below have the same significance as before. The catholyte was 4 per cent. NaOH in each case. The composition of the anolyte is stated at the commencement in each case.

Experiments with Cooled Anode Apparatus.

1. 80 grams borax + 20 grams NaOH per litre.—

$C = 4.8.$	$D_A = 60.$	$V = 18 \text{ to } 20.$
$T_A = -11^\circ \text{ C. to } -7^\circ.$		$T = 4^\circ \text{ to } 6^\circ \text{ (finally } 15^\circ).$
	Time, $1\frac{1}{2}$ hr.	

Ozone production very slight.

2. 38 grams borax + 40 grams H_3BO_3 per litre.†—

$C = 4.8.$	$D_A = 60.$	$V = 25.$
$T_A = -10.5^\circ \text{ to } -5^\circ.$		$T = 13^\circ \text{ to } 20^\circ.$
	Time, $1\frac{1}{2}$ hr.	

Evolved oxygen smelt very strongly of ozone. This anolyte contained more B_2O_3 than No. 1 (37 grams per litre against 29.3), but was much less alkaline; at the commencement it was almost neutral, but was kept faintly alkaline throughout. Although such a solution contains complex anions, it would presumably be capable of furnishing some BO_3''' or other ion necessary for perborate formation.

3. 28 grams borax + 5 grams NaOH per litre.—

$C = 2.4.$	$D_A = 30.$	$V = 18 \text{ to } 15.$
$T_A = -13^\circ \text{ to } -10^\circ.$		$T = 4^\circ \text{ to } 0^\circ.$
	Time, $1\frac{1}{2}$ hr.	

Ozone production slight.

Attempts were also made to employ much higher current densities, but as the current through the cell could not be increased without undue rise of temperature, it was necessary to cover up portions of the anode by means of closely fitting glass tubing, and the uneven current distribution and cooling gave rise to difficulties. In one case, however, it was found possible to carry on the electrolysis for 1 hour at a current density of 200, T_A being -7.5° and T about 20° .

The above and all similar experiments also gave negative results, except that in No. 3 the resulting anolyte showed faint oxidizing action, 50 c.c. decolourising 1 drop of $N/4$ $KMnO_4$.

It appeared therefore desirable to ascertain whether, if sodium perborate were present in the anolyte at the commencement of such an experiment, its concentration would actually diminish.

* The difference between these varied with the rate of flow, but never exceeded 5.5° C.

† McLaughlan, *Z. Anorg. Chem.*, **37** (1903), 371.

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The following experiment was therefore carried out.

4. 28 grams borax + 5 grams NaOH per litre + some perborate.—

$$\begin{array}{lll} C = 4.8. & D_A = 60. & V = 30. \\ T_A = -11.5^\circ \text{ to } -4.5^\circ. & & T = 15^\circ \text{ to } 11^\circ. \\ & \text{Time, 1 hr.} & \end{array}$$

Samples of the anolyte were titrated with KMnO_4 solution before and after the electrolysis.

10 c.c. of anolyte required :—

Before, 2.7 c.c. of $\text{N}/4 \text{ KMnO}_4$.

After, only 2 drops of $\text{N}/4 \text{ KMnO}_4$.

Throughout the experiment no ozone could be detected, except a faint trace at the very end.

This experiment was repeated in another form, the perborate being added during the electrolysis instead of before the commencement.

5. 35 grams borax + 5 grams NaOH per litre.—

$$C = 4.8. \quad D_A = 60. \quad V = 35 \text{ to } 40.$$

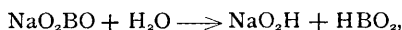
At commencement—

$$T_A = -6^\circ. \quad T = 25^\circ.$$

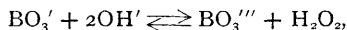
After current had been passing for 10 minutes the perborate (0.5 gram dissolved in 35 c.c. of water) was added, T_A being -6.5° , $T = 16^\circ$. The evolved oxygen smelt strongly of ozone when the perborate was added, but this gradually disappeared, and 10 minutes later no ozone could be detected, although there was no appreciable change in the temperatures, T_A being -7.5° , $T = 16^\circ$. Samples of the anolyte were titrated from time to time with KMnO_4 .

Time. (From addition of perborate.)	Titre (10 c.c.). (In c.c. of $\text{N}/4 \text{ KMnO}_4$.)
0 minutes	2.0 (calculated)
25 "	1.4
45 "	0.7

These experiments suggested that the perborate acts in some way as a depolariser, lowering the anodic potential (which would account for the effect on ozone production) and being itself decomposed. It appeared, however, that probably this is due not to the perborate itself, but to H_2O_2 formed by its hydrolysis. Pissarjewski,* from extraction experiments with ether, concluded that in aqueous solution at 25°C . sodium perborate is almost completely hydrolysed, and he supposes the hydrolysis to take place thus :—



the sodium hydroperoxide thus formed being further hydrolysed to NaOH and H_2O_2 . The hydrolysis might take place in various ways, depending on the conditions, and on what borate ions were produced. Thus in alkaline solution, if BO_3''' were formed, the reaction could be simply represented thus,† omitting the sodium—



and apparently the hydrolysis would be less the lower the alkali concentration, e.g., in acid solution (although the perboric acid might then decompose otherwise). Whatever may be the exact mechanism, it is certain that perborates in solution are very largely hydrolysed to H_2O_2 . The reaction with

* *Z. Phys. Chem.*, **43** (1903), 170.

† This equation is purely formal, and is not intended to imply any particular "mechanism" of H_2O_2 formation.

permanganate shows this, and a dilute solution of sodium perborate has the characteristic taste of H_2O_2 .

If, therefore, in an experiment such as No. 5 above, H_2O_2 be added instead of perborate, one would expect the result to be similar, and this was found to be the case, the ozone production ceasing and the permanganate titre diminishing rapidly. One experiment was continued till the H_2O_2 concentration was vanishingly small, when ozone commenced to be produced again, increasing gradually in strength.

It might be argued that the disappearance of H_2O_2 , and therefore of perborate, is due to chemical decomposition, and not to an electrochemical effect as suggested above; but experiment showed that the rate of decomposition of H_2O_2 in a 1 per cent. solution of NaOH is comparatively small at ordinary temperatures, although above 40°C . it increases rapidly. Moreover, an electrolysis experiment with acid (phosphoric) anolyte, which will be described below, gave precisely similar results, and under these conditions the chemical decomposition would be very much slower than in alkaline

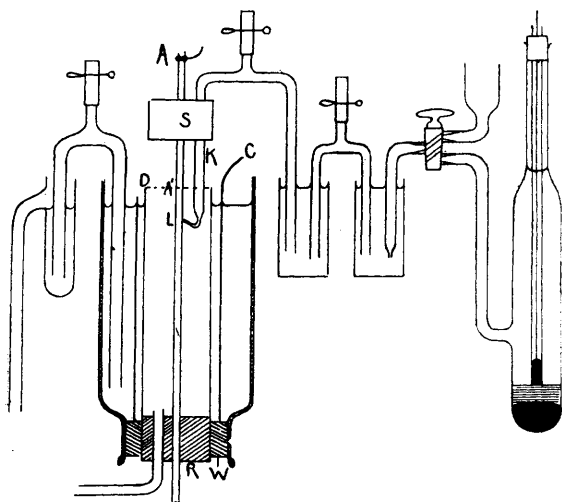
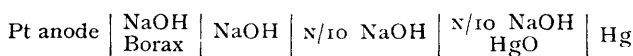


FIG. 3.

solution. The non-production of ozone might also be due to chemical interaction with the H_2O_2 ,* but it appeared probable that it was chiefly due to lowering of the anode potential. In any case it was thought that actual measurements of the anodic potentials in a few cases would be of interest, especially as no such measurements in alkaline solutions appear to have been carried out hitherto.

Anode Potential Measurements.

The method adopted was to measure a combination of the type



the standard electrode employed being the $\text{Hg} \left| \begin{array}{c} \text{HgO} \\ \text{N/10 NaOH} \end{array} \right|$ electrode devised by Donnan and Allmand.† The one actually used was made up

* Schöne, *Liebigs Annalen*, **196** (1879), 239.

† *Trans. Chem. Soc.*, **99**, 845 (1911).

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precisely according to the directions given by these authors, and was checked by comparison against a similar electrode, its e.m.f. being taken as $E_s = +0.168$ volts at the temperature of the laboratory. The e.m.f. of the combination was measured by the potentiometer method, using a standard cadmium cell, an accurate platinum-iridium bridge wire, and a sensitive galvanometer.

The apparatus is shown diagrammatically in Fig. 3, the cell being shown in section. As the chief thing is to maintain a solution of constant composition round the anode, a large volume of electrolyte was contained in a reservoir (not shown in the diagram) of 800 c.c. capacity, and was allowed to flow fairly rapidly into the anode compartment. The anode was the platinum tube used in the previous experiments. The diaphragm D consisted of a sheet of asbestos paper* wrapped round the close spiral used for cooling the anolyte, and fixed at the foot between the rubber stopper R and the rubber washer W. The liquid entered the anode compartment at the foot and flowed partly through and partly over the asbestos (the anode compartment being open at the top) into the cathode compartment, from which it overflowed by means of the syphon, the side tube being introduced to keep the level constant. The cathode C consisted, as before, of a cylindrical nickel sheet encircling the anode compartment. The advantage of allowing the electrolyte to flow through both anode and cathode compartments is that its composition (as regards borate and alkali) remains unaltered, and it can be returned again to the reservoir. The standard electrode was connected in the usual way through the various intermediate solutions to the glass tube K, which terminated in a small capillary. This tube was held in place by the rubber stopper S, the end of the capillary being pressed firmly against a small flattened portion of the anode. The cooling spiral and the thermometers are omitted from the diagram for convenience.

The potential actually measured is that between the liquid in contact with the anode at L and the top of the anode A. The latter is practically the same as the potential of the anode at L, because no current flows through the portion AA' (the current entering the foot of the anode) and very little through the portion A'L. The capillary was placed fairly near the surface to minimise the potential drop † between A' and L.

The first attempts to measure the potential with dilute alkaline borate solutions (such as Pouzenc's) were not successful. The high resistance made the readings difficult, and violent fluctuations occurred. If the specific conductivity of the solution be taken as 0.02 (that of N/10 NaOH) the potential gradient round the anode with $D_A = 38$ would be $0.38/0.02 = 19$ volts per cm. It is therefore evident that a very minute movement of the capillary might greatly affect the readings.

* This had to be renewed from time to time, as it becomes weakened by the action of the alkaline liquid.

† This can be calculated thus: Assuming the current density to be uniform, the current flowing in the anode at a point x cm. below the surface will be $\frac{x}{l} \cdot C$, C being the total current, and l the length of the anode immersed in the liquid. The potential difference between this point and the surface will therefore be $\int_0^x C \cdot R \cdot dx$ (where R is the resistance of unit length of the anode), which becomes $\frac{CR}{2l} \cdot x$.

With the capillary 15 mm. below the surface, and $C = 5$ amperes, this becomes 0.5 millivolts, which is negligible. If, however, the capillary were half-way down, the value would be 3.5 millivolts.

Later on it was found possible, by fixing the capillary more rigidly, and shaping it in such a manner as to prevent gas bubbles collecting in it, and by using a more sensitive galvanometer, to obtain satisfactory measurements with such a solution. In the first instance, however, more alkaline solutions were used, and the readings with these were very satisfactory, the relative error of any one measurement being not more than a few millivolts.

The exact values, however, in a given case are not reproducible, as they depend on the precise condition of the anode surface at the given moment.

The method adopted to find the effect on the potential of adding H_2O_2 to the electrolyte was to wait until the potential was constant, or at least not rising rapidly, then to add the requisite number of c.c. of concentrated H_2O_2^* to the liquid in the reservoir. When it was desired to continue the measurements for a considerable time, the solution issuing from the cell was rapidly titrated, H_2O_2 added to restore the original concentration, and the liquid poured back into the reservoir.

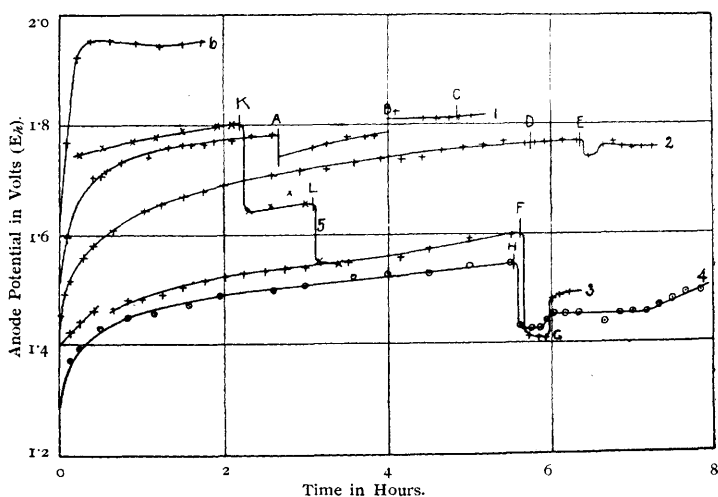


FIG. 4.

The chief measurements carried out are shown graphically in Fig. 4, the numbers on the curves corresponding with the numbers below.

The liquid potentials—

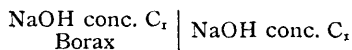


were calculated from the formula

$$e = (2x - 1) 0.058 \log C_1/C_2,$$

neglecting the difference in ionisation at the two concentrations.

The liquid potential in such cases as—



was neglected. For the present purpose the absolute values within 10 or 20

* Merck's *Perhydrol* (diluted).

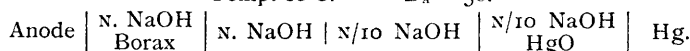
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millivolts are of no importance. Slight fluctuations of the potential are probably largely due to variations in the rate of flow of the electrolyte, which may cause variations in the local concentration round the anode.

In Nos. 1 to 4 the anode was not cooled, the anolyte being cooled by means of iced water. In Nos. 5 and 6, both anode and anolyte were cooled with freezing mixture, as in the former experiments.

1. *N. NaOH + 35 grams borax per litre.*—

Temp. 10°C. $D_A = 38$.



This curve shows the rapid rise at the commencement, and the effect of altering D_A .

At—

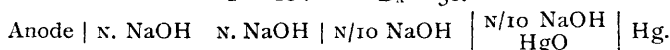
A (2 hr. 40 min.) D_A was reduced to 19.

B (4 hr. 0 min.) D_A was raised again to 38.

C (4 hr. 50 min.) H_2O_2 was added to the electrolyte to make 0.01 Molar (34 gram per litre), but there was no effect on the potential.

2. *N. NaOH.*—

$T = 10^\circ$. $D_A = 38$.



Omission of the borax would presumably have no great effect on the potential and would simplify the conditions, as there will only be H_2O_2 and no perborate present.

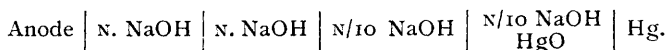
At D (5 hr. 45 min.), H_2O_2 added to make 0.01 M., but there was no effect on the potential. At E (6 hr. 22 min.), H_2O_2 made 0.10 M. Potential fell slightly, viz. from 1.770 to 1.740, then rose again to 1.766, although the concentration was maintained. After this experiment, the anode, which was used without cleaning or polishing in any way after No. 1 (i.e. some 12 hours at 38 amperes per sq. dm.) had acquired a brownish colour. This appearance had been noticed before, but never to the same extent. It was carefully rinsed with water (to remove all H_2O_2) and gently rubbed on a piece of filter paper, moistened with KI and starch, a deep blue stain being produced. This indicated the presence on the anode surface of one of the higher oxides of platinum.

The next experiment was carried out at a much lower current density, as it appeared probable that under these conditions the effect of H_2O_2 on the potential might be more marked.

3. *N. NaOH.*—

$T = 10^\circ$. $D_A = 3.8$.

Freshly polished anode.



The irregularities at the commencement were caused by a defective connection, with consequent fluctuations and momentary stoppage of the current. At F (5 hr. 37 min.), H_2O_2 added to make 0.077 M. Potential fell from 1.595 to 1.407, then remained steady till the reservoir was refilled (no further H_2O_2 being added, its concentration being now 0.059 M. The potential then rose (G 6 hr. 0 min.) to a higher value.

4. Same as No. 3, only adding sodium perborate instead of H_2O_2 . The method adopted was to select a moment when the reservoir was just becoming empty, and fill it up with a solution of the same composition, but containing in addition the necessary quantity of perborate, the concentration of the latter being such that if completely hydrolysed it would give approximately the same H_2O_2 concentration as in No. 3; i.e. the KMnO_4 titre was approximately the same.

At H (5 hr. 32 min.) the perborate was added (to make 0.070 M.).

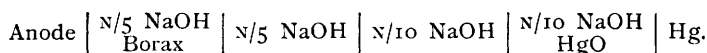
The potential fell from 1.544 to 1.432. After 6 hr. 10 min. the titre was maintained constant by adding H_2O_2 , but the readings fluctuated somewhat.

5. 8 grams NaOH + 35 grams borax per litre.—

Cooled anode.

$$D_A = 50$$

i.e. a solution similar to those used in the electrolysis experiments and under similar conditions.



Temperature of anolyte varied between 13.5° and 17°.

Temperature of anode varied between -4° and -6°.

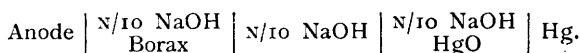
No readings were obtained at the commencement.

At K (2 hr. 12 min.), H_2O_2 added to make 0.095 M. Potential fell from 1.797 to 1.644, then rose slowly until at L (3 hr. 5 min.) the H_2O_2 concentration was doubled (0.19 M.). Potential then fell from 1.655 to 1.550, the drop being nearly the same as at K.

6. 4 grams NaOH + 35 grams borax per litre.—

Cooled anode (freshly polished).

$$D_A = 50.$$



Temperature of anolyte, 15° to 19°.

Temperature of anode, -4° to -8°.

The potential rose very rapidly at first, owing presumably to the high current density and freshly polished anode. The high value reached ($E_A = 1.953$) is probably also due to the low alkali concentration. The subsequent slight fall may be due to temperature variation.

No H_2O_2 or perborate was added.

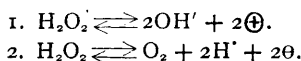
No conclusions were drawn from these experiments as regards ozone evolution. The form of the apparatus made it more difficult than in the case of the electrolysis experiments to determine whether ozone were present or not, and it was detected with certainty only in the case of No. 1, and in this case it vanished on the addition of H_2O_2 , although the potential remained the same.

The above measurements, together with the previous experiments on the diminution of the H_2O_2 concentration, show that H_2O_2 placed round a polished platinum anode which is strongly polarised tends to lower the potential, the actual drop depending on the various conditions, while the H_2O_2 itself is destroyed.

These facts are in accordance with the theory, which is now generally accepted, that the overvoltage at such a platinum anode is essentially determined by the platinum oxides* contained in the surface layers.

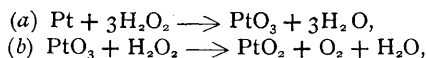
This theory is chiefly due to Grube,† who from measurements of the potentials in H_2SO_4 of electrodes made of various oxides of platinum, concluded that when a platinum electrode is anodically polarised the surface layers contain varying amounts of PtO , PtO_2 , and PtO_3 in solid solution. The PtO_3 has a much higher potential than the other two, and the greater its concentration, the higher will be the potential of the electrode.‡ It is formed by oxidation of the PtO_2 by the anodically produced oxygen, but is unstable, and breaks up again into oxygen and a lower, more stable oxide, its final concentration therefore depending on a balance between its rate of production from PtO_2 and its rate of spontaneous decomposition; the greater the former, the higher will be the final PtO_3 concentration, and the greater the anodic potential. The actually observed formation of one of these higher oxides, referred to above under Experiment 2, is of interest in this connection.

Hydrogen peroxide can act electrochemically in two ways, corresponding to its chemical action as an oxidising and a reducing agent respectively.



This was first clearly shown by Haber,§ and was applied by Foerster || to the action of H_2O_2 on a platinum anode, on the theory that an oxide PtO_x was formed, which in the light of the subsequent work by Grube we may call PtO_3 .

Foerster's equations then become



corresponding to 1 and 2 above.

Most of the experiments which have been carried out by other workers on H_2O_2 potentials are concerned with equilibrium conditions. In the present case, however, H_2O_2 was placed round an anode which was strongly polarised, and in which the PtO_3 content was therefore very high. We should therefore expect action (b) to take place, resulting in a lowering of the potential and disappearance of the H_2O_2 . Grube found that the rate of self-discharge of his PtO_3 electrodes was greatly accelerated by addition of H_2O_2 , the potential falling rapidly; in the present case, however, fresh PtO_3 is continuously being produced, and the actual fall of potential may be comparatively small, as the experiments showed. The final value reached, if the H_2O_2 concentration be maintained, will again represent a state of balance between formation and decomposition of PtO_3 and will depend on the H_2O_2 concentration, the current density, the temperature, etc.

Applying these considerations to the electrolytic preparation of perborates, it appears that, supposing that perborate ions can actually be formed at potentials attainable in practice, the H_2O_2 produced by hydrolysis will have a

* At very low current densities capillary phenomena also play a part.

† *Z. f. Elektrochem.*, **16**, 621 (1910).

‡ When the anodic polarisation is very high, Grube considers that a still higher oxide, probably PtO_4 , is also present.

§ *Z. f. Elektrochem.*, **7**, 441 (1901).

|| *Z. Phys. Chem.*, **69**, 254 (1909).

twofold action. Firstly, it may affect the further formation of perborate by lowering the potential. Secondly, it will be itself destroyed, causing further decomposition of the perborate already formed. As both these effects will increase with increase of the H_2O_2 concentration, an equilibrium concentration of perborate will finally be obtained.

It is probable that the same effect plays a part in the electrolytic preparation of persulphates and percarbonates. Persulphates, however, are only very slightly hydrolysed at ordinary temperatures; percarbonates are certainly considerably hydrolysed, but the conditions under which they are produced (generally from a very concentrated solution of K_2CO_3) are more favourable than in the case of perborates. In the case of persulphuric acid, it is known that the mono-persulphuric acid formed by hydrolysis acts as a depolariser and affects the yield. It is also possible, of course, that persulphates and percarbonates can be produced at lower potentials than perborates.

It was suggested above that the hydrolysis might be less in acid solution. It also seemed probable that higher potentials would be reached in acid solution. An experiment was therefore carried out (No. 1 below) using the cooled anode apparatus, with an anolyte consisting of boric acid in presence of phosphoric acid. Of course it was not expected that free perboric acid would be formed in quantity, but it appeared that the solution might show some oxidising properties.

Further Experiments with Cooled Anode.

1. $N. H_3PO_4$ (33 grams/litre) + 20 grams H_3BO_3 per litre.—

$C = 2.4.$ $D_A = 30.$ $V = 21$ to $22.$

Time, 70 min.

$T = 3^\circ$ to $4^\circ.$ $T_A = -9^\circ.$

Samples of the anolyte were tested with $KMnO_4$ 55 and 70 min. from the commencement, but there was no trace of decolourisation.

Hydrogen peroxide was then added to the anolyte to make 0.1 N, (1.7 grams per l.), the temperatures being maintained about $T = 2^\circ$ $T_A = -5^\circ$. In 50 minutes the $KMnO_4$ titre fell from 3.8 to 2.0. This is of interest because in presence of phosphoric acid the chemical decomposition of H_2O_2 is very slight. In this experiment ozone continued to be produced even in presence of the H_2O_2 .

It was pointed out above that in the earlier experiments in which the anolyte consisted of excess of borax dissolved in NaOH, the ozone production was very slight. In the light of the information subsequently gained, however, even if the potential in such cases is lower, other advantages might possibly outweigh this. In the first place it appeared that probably the temperature of the anolyte could be kept lower, which would probably tend to diminish the hydrolysis.* The increase in the total borate concentration would also be an advantage. An experiment was therefore carried out (with cooled anode) using the solution of Constam and Bennet (see above) containing 282 grams borax + 56 grams NaOH per litre. Such a solution deposited solid only slowly at $0^\circ C$.

As this was the only experiment in which perborate was produced in appreciable, although still very small quantity, it will be given somewhat more fully.

* Pissarjewski, loc. cit.

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2. 282 grams borax + 56 grams NaOH per litre.—

Freshly polished anode.

Catholyte — 8 per cent. NaOH. Vol. of anolyte — 142 c.c.

$C = 4.8$, $D_A = 60$ during first 20 min.

$C = 2.4$, $D_A = 30$ thereafter, to enable anolyte to be kept at low temperature.

The course of the experiment is shown in tabular form below.

A few c.c. of 16 per cent. NaOH had to be added soon after the commencement to prevent deposition of solid. The titre given is of 10 c.c. of anolyte against $N/4$ $KMnO_4$. V was 20 to 23 at first. At the lower current density V was 13 to 16.

Time.		Temperatures.		Titre.	Remarks.
Hr.	Min.	T	T_A		
0	0	7° C.	— 14°	0	
0	10	4°	— 12.5°	—	NaOH added. Ozone distinct
0	20	—	—	1 drop	C reduced to 2.4
0	40	2.5°	— 9.5°	2 drops	Still ozone
1	0	0°	— 9.0°	2 drops	Ozone less strong
1	45	— 1°	— 7.5°	0.26 c.c.	No ozone
2	20	0°	— 9.5°	0.30 c.c.	"
2	40	0°	— 8.5°	0.35 c.c.	"
3	0	0°	— 5.0°	0.38 c.c.	"

The final concentration of perborate represents a chemical yield of about 0.15 per cent. and a current efficiency of about 0.48 per cent. It must be remembered, however, that only about one-third of the anolyte is actually in the cell at a given moment, the whole being kept in constant circulation through the cell. The exact significance of these figures is therefore doubtful.

Constam and Bennet, as stated above, also obtained some decolourising effect on $KMnO_4$ as the result of their experiment, but said that it was due to production of H_2O_2 . As there will presumably be an equilibrium between H_2O_2 and perborate, their reason for making this statement is not clear.

One further experiment was performed with the cooled anode apparatus to determine whether under the conditions of the above experiment, if the perborate concentration in the anolyte were comparatively high, it would tend to diminish.

3. At the commencement the anolyte was identical with that in the last experiment, but only half the quantity was placed in the reservoir, the remaining half, containing perborate, being added only after some perborate had been formed in the cell. By this method it was ensured that the conditions were as favourable for perborate formation as in the previous case. The temperatures, etc., were as nearly as possible the same as in No. 2; D_A was 30 from the commencement, the anode being again freshly polished. As before, a little NaOH had to be added to prevent crystallization, but the amount added after the addition of perborate, to compensate for that removed by electrolysis, did not exceed 5 c.c., so no appreciable error is caused in the titrations on this

BORATE AND PERBORATE SOLUTIONS

account. Time was allowed for the perborate to become uniformly distributed throughout the anolyte before any titrations were made.

Time.		Temperatures.		Titre.	Remarks.
Hr.	Min.	T	T _A		
0	0	7°C.	— 13.5°	0	—
0	15	—	—	0.13 c.c.	Ozone distinct. NaOH added.
0	20	3°	— 11°	—	Ozone strong.
0	20	—	—	—	Remainder of anolyte + perborate added.
0	30	4°	— 10°	—	Ozone very faint.
0	40	—	—	4.20 c.c.	—
1	0	3°	— 9.5°	3.64 c.c.	No ozone.
1	15	0°	— 8°	3.18 c.c.	"
1	25	0°	— 7.5°	2.89 c.c.	"
1	43	1°	— 8°	2.52 c.c.	"

The titre given in this case is of 2 c.c. against N/10 KMnO₄.

From these figures, and those in the previous experiment, it appears that the equilibrium concentration which would finally be obtained would be very low, probably not very much greater than that actually reached in No. 2 (after electrolysing for nearly 3 hours) which represents a very small yield indeed.

It is possible that better results might be obtained by the use of still more concentrated solutions (if such can be obtained) and still lower temperatures; or by the use of solutions containing a larger proportion of alkali, which may possibly contain more BO₃^{'''} ions, but the experiments have not so far been extended in these directions, nor does it seem probable that satisfactory yields would be obtained under any conditions.

THE POUZENC PATENT.

Under these circumstances it is difficult to account for the existence of the French patent by Pouzenc referred to above. Reference to the patent specification revealed the fact that it contains only a brief description of the apparatus, consisting of the vertical electrolyser referred to above. The two papers by Beltzer, however, were found to contain various details, some of which have already been given. According to these, solid perborate* can be obtained by filtering the liquid flowing out of the anode compartment of the Pouzenc cell, the filtrate being mixed with the catholyte and used again. Beltzer says that for preparation of solid perborate it is best to use a "concentrated solution of sodium orthoborate," while for making bleaching solutions he recommends the solution containing 24 grams borax + 6 grams NaOH per litre, which he ascribes to Pouzenc. He also states that the electrolyte must flow rapidly through the cell, and that the solid perborate must be removed immediately from the action of the current and the alkaline liquid, otherwise it "redissolves in the liquid and decomposes."

As a matter of fact, from the diagrams of the apparatus it seems that the

* According to Melikoff and Pissarjewski 100 grams H₂O dissolve 2.55 grams NaBO₃·4H₂O at 15°C., so if good yields were obtained solid would separate.

amount of liquid actually in the cell at a given moment is comparatively small ; in other words the "current-concentration" is high. Such a condition is necessary in cases where the product is chemically unstable, e.g. in the case of hyposulphites ; but it has been shown that the important factor in the case of perborates is the electrochemical decomposition.

As regards temperature, -5°C. is mentioned by Beltzer, but it is not clear whether this is meant to refer to the electrolyte itself, or the brine used to cool it.

In one of the papers a commercial form of the apparatus is described, but it is clearly stated at the commencement that the electrochemical method was not so far (1911) used for the manufacture of perborates, and a careful study of the papers gives the impression that the author has not actually carried out any experiments on the subject.

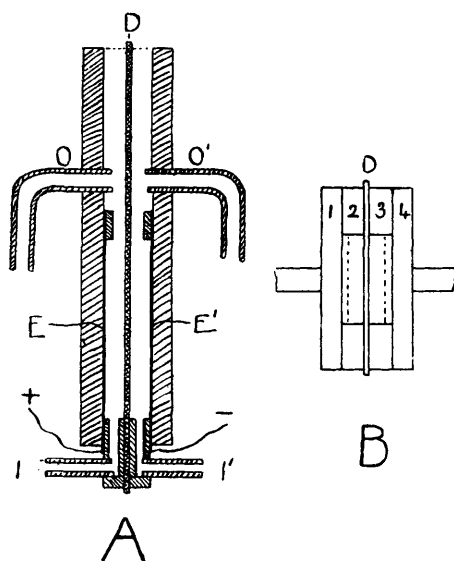


FIG. 5.

Experiments with the Pouzenc Apparatus.

A small cell constructed to imitate as nearly as possible the Pouzenc electrolyser on a small scale is shown in Fig. 5.

A is a vertical section through the middle of the cell. B is a plan of the top of the cell. It was constructed of four portions of ebonite sheet (numbered in the diagram) which were clamped together by large clamping screws (not shown in the diagram), thin rubber washers being interposed to make the cell watertight. The electrodes of fairly stout and well-polished platinum foil, shown in the diagram by the dark lines E and E', were fixed between 1 and 2 and 3 and 4, the diaphragm D of asbestos paper being between 2 and 3. The electrolyte entered the anode and cathode compartments, which were identical, at I and I', and overflowed a little above the tops of the electrodes at O and O', the part of the cell above that serving as a settling chamber for

spray. The inlet and outlet tubes were of glass, fixed in by a suitable cement.

The dimensions of the cell were as follows :—

Area of electrodes	8 sq. cm. each.
Distance apart	12 mm.
Volume of anolyte	5 c.c.
„ catholyte	„

The electrolyte was contained in a glass reservoir in which it was cooled by glass spirals through which flowed the usual cooling liquid. Separate glass tubes conveyed it to the anode and cathode chambers, the rate of flow through each being separately regulated by screw clips. The glass tubes were as short as possible, and well lagged, to prevent access of heat.

Experiments were first carried out with the Pouzenc solution, containing 24 grams borax + 6 grams NaOH per litre. With 2 amperes passing through the cell ($D_A = 25$) the voltage across the cell was 25, and although the solution was cooled almost to its freezing-point (-0.89°C .) the anolyte leaving the cell had a temperature of 17°C . It was tested with KMnO_4 , but showed no trace of oxidising action. It is difficult to imagine that such a solution could be used commercially, as the heat produced in the cell, and the power absorbed, would be excessive. Determination of its conductivity showed the latter to be, at—

$$\begin{aligned} 0^\circ\text{C. } k &= 9.02 \times 10^{-3}, \\ 18^\circ\text{C. } k &= 14.87 \times 10^{-3}. \end{aligned}$$

This is less than the conductivity of an $N/10$ solution of NaOH, which has a conductivity of about 20×10^{-3} at 18° .

Experiments were then carried out with a solution whose composition corresponded to sodium orthoborate. The electrolyte consisted of a large volume (1 litre) of a solution containing 95.5 grams borax + 100 grams NaOH per litre,* cooled to about -5°C . It was very strongly alkaline. Experiments were carried out at current densities of 30 and 60 (the values given by Beltzer) and various rates of flow.

With $D_A = 30$ (2.4 amperes) V was 6.5, and with a sufficiently rapid flow the temperature of the anolyte leaving the cell was as low as 2° to 3° . In order that it might not exceed 10° the rate of flow had to be not less than 10 c.c. per minute through the anode compartment, and at $D_A = 60$ correspondingly greater. When all the electrolyte had run through it was passed through a second time without interrupting the current, to obtain the benefit of any rise of the anode potential, the total time being 30 to 50 minutes. Samples of the anolyte leaving the cell were tested immediately, but in no case did 10 c.c. decolourise a single drop of $N/20$ KMnO_4 . This is not surprising when one considers the very slow rate of perborate formation, and very small yields obtained, even with the cooled anode apparatus.

In view of these results it is difficult to believe that solid perborate has ever been prepared by means of the Pouzenc cell. It is, however, possible that impurities in the borax used (stated to be "commercial") might give rise to slight oxidizing properties in the solution, e.g. chloride giving rise to hypochlorite. Throughout the present investigation the purest materials were used.

* A solution of double this concentration deposited the solid at this temperature.

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SUMMARY.

The previous work on the electrolytic production of perborates has been briefly reviewed and criticised.

Experiments have been carried out in which solutions of alkaline borates of various composition were used as anolyte in suitable electrolytic cells, under various conditions of temperature and current density, a hollow cooled anode being employed in some cases. With dilute and slightly alkaline solutions, such as would be suitable industrially for bleaching purposes, no perborate (or at most a minute trace) was formed in any of the experiments, even with the cooled anode apparatus. Even with much more concentrated solutions only a very small quantity was formed.

It has been shown that an equilibrium is obtained between the rate of formation of the perborate and its decomposition owing to the H_2O_2 formed by its hydrolysis acting as a depolariser, tending to lower the anode potential and being itself destroyed.

Measurements have been carried out of the actual potentials obtained at the anode in certain cases, and of the effect of hydrogen peroxide on the potential. The results accorded well with Grube's theory of overvoltage at a platinum anode and the known electrochemical behaviour of H_2O_2 .

Finally, a French patent for the electrochemical manufacture of perborates has been discussed and investigated, a similar apparatus having been constructed on a small scale. It was found to give negative results in practice, no trace of perborate being formed in any of the experiments.

In conclusion the author wishes to express his sincere thanks to Dr. A. J. Allmand, at whose suggestion the above investigation was carried out, for his invaluable assistance and advice.

MUSPRATT LABORATORY,
THE UNIVERSITY, LIVERPOOL,
May, 1914.