4. *Studies in Electrolytic Oxidation. Part IV. Anodic Polarisation in Halide Solutions.*

By S. Glasstone and A. Hickling.

It was first observed by E. Müller (*Z. Elektrochem.*, 1900, **6**, 573; 1902, **8**, 425; see also Wohlwill, *ibid.*, 1898, **5**, 52) that, on the electrolysis of chloride solutions with a smooth platinum anode, chlorine was first evolved at a potential in the vicinity of the reversible value, but as the *C.D.* was increased the anode potential rose suddenly by about 0·6 volt. This change was found to occur more readily in alkaline than in acid solution, although it was not observed when a platinised anode was used. Müller attributed the higher potential stage to the accumulation of hypochlorous acid, which he said was unstable in acid solution and in the presence of finely divided platinum. The abnormal polarisation phenomenon was subsequently investigated by Luther and Brislee (*Z. physikal. Chem.*, 1903, **45**, 216), who confirmed Müller's observations and also showed that the greater the concentration of chloride the higher was the *C.D.* at which the sudden polarisation occurred; these authors also noted that if the platinum electrode was polarised anodically before use in the chloride solutions, the lower potential stage, close to the reversible value, appeared to be entirely suppressed, the rise of potential occurring at a low *C.D.* Some of the observations were accounted for by supposing that chlorine evolution resulted from the discharge of Cl_2'' ions and that the rise of potential occurred when the rate of diffusion of these ions to the electrode was unable to keep pace with the rate of ionic discharge; it was also realised that the polarisation was related in some manner to the state of the electrode surface. A further study of the electrolysis of chloride solutions was made by Pfleiderer (*ibid.*, 1909, **68**, 49), who observed the variation of anode potential with time; he found, in general, that at any fixed *C.D.* the electrolysis proceeded at the lower potential stage for some time before the sudden rise of potential to the higher stage occurred. The time elapsing before the break was observed was smaller the larger the *C.D.* and the less acid the solution. Pfleiderer analysed the gases evolved at various *C.D.*'s from a number of hydrochloric acid solutions and found in every case traces, at least, of oxygen; he considered that the oxygen resulted from the action of chlorine on water, and that the polarisation was connected in some way with the formation on the surface of the anode of an oxide of platinum which catalysed this reaction.

. Boericke (*Z. Elektrochem.*, 1905, **11**, 71) found that the phenomenon of the sudden rise of potential could also be observed at a smooth platinum anode in neutral bromide solutions, and Foerster and Yamasaki (*ibid.*, 1910, **16**, 321) showed that the higher potential stage is favoured by the presence of oxygen in the anode and by the use of alkaline electrolytes. Similar results were obtained by Herrschel (Diss., Leipzig, 1912; see Grube, *Trans. Faraday Soc.*, 1913, **9**, 224; Foerster, *Z. Elektrochem.*, 1916, **22**, 85) with alkaline solutions of potassium iodide, but with neither bromide nor iodide solutions did the polarisation occur at a platinised platinum anode. Incidentally, Herrschel (*loc. cit.*) made the remarkable observation that in the electrolysis of potassium iodide solutions the polarisation occurred more readily at 40° than at 0°; this fact does not appear to have received the attention it merits.

In general reviews of electrode polarisation phenomena, Grube (*loc. cit.*) and Foerster (*loc. cit.*) discussed the observations made in halide solutions and concluded that the rise of potential is due to a retardation of one of the intermediate stages in the formation of molecular halogen from the discharged ions, brought about by an oxygen charge or oxide formed on the platinum anode. This theory is in harmony with the observations that the polarisation under discussion occurs most readily in alkaline solutions and with electrodes containing oxygen, and with the fact that the ease of polarisation diminishes in the order chloride, bromide, iodide, but it fails completely to account in a simple manner for Herrschel's discovery that the polarisation is *favoured* by an increase of temperature, since retardation effects are invariably decreased as the temperature is raised. Moreover, the theory cannot be used to explain many of the observations made in the course of the present work.

The electrode-potential phenomena observed in the electrolysis of halide solutions have a number of features in common with those found in the anodic oxidation of thiosulphate and sulphite solutions (J., 1932, 2345, 2800; 1933, 829) and it appeared that the theory of the formation of hydrogen peroxide at the anode, proposed in connection with the latter studies, could account in a simple manner for the results of previous workers. The present investigation was undertaken to provide confirmation of this point of view.

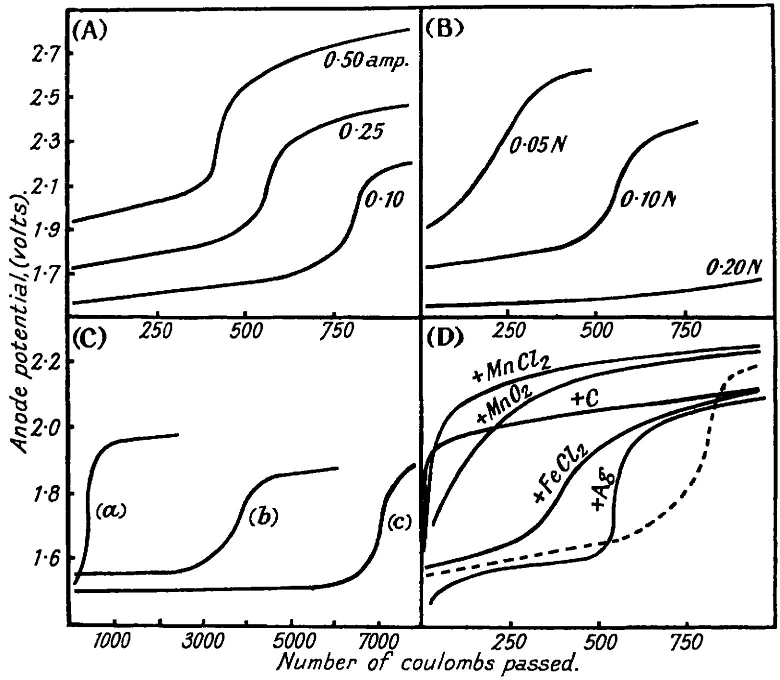
EXPERIMENTAL.

Observations have been made of the variation of anode potential with time at constant *C.D.*, as in previous work, and also of the influence of *C.D.* on potential in the electrolysis of halide solutions under various conditions. For the potential–time studies, the apparatus used was that already described (J., 1932, 2345), a smooth cylinder of platinum gauze of area 55 sq. cm., mounted vertically and rotated at a speed of 550 r.p.m., being employed as anode. For the potential–current curves the electrical circuit was fitted with rheostats permitting of a smooth variation of current from a fraction of a milliamp. to 1 amp.; the potential was measured by the usual potentiometer–voltmeter method to 0·01 volt. In the chloride solutions, the anode was a spiral of platinum wire of area 1 sq. cm.; it was mounted and rotated in the same manner as the large anode used in the potential–time experiments. For the bromide and iodide solutions, higher *C.D.*'s were required, and so a platinum wire of 0·1 sq. cm. area was used as anode; it was mounted as a stationary electrode, and the solutions were agitated by means of an independent stirrer. Before use, the platinum electrodes were cleaned and their oxygen contents controlled in the manner described in previous work; unless otherwise stated, they were used in the smooth unplatinised condition. A number of observations have also been made with a gas-carbon anode. All experiments, except those mentioned under the heading of the influence of temperature, were carried out at room temperature (about 18°) and potential measurements are recorded on the hydrogen scale.

Results.

Chloride Solutions.—Anode potential–time curves. The results obtained under various conditions with chloride solutions are shown in Fig. 1; the numbers of coulombs passed are used as abscissæ, instead of times, so that curves for different currents are directly comparable. Owing to the presence of an electrical resistance, amounting, *e.g.*, to about 1 ohm in 0·1*N*-hydrochloric acid, between the rotating anode and the tip of the siphon connecting it to the calomel electrode (cf. Glasstone, J., **1923**, **123**, **2926**), all the potentials measured are higher than the true values; the differences are probably constant throughout for any one current and are roughly proportional to the current strengths. These resistance errors will consequently have no influence on the general form of the curves although their position will be affected; for example, the three curves in Fig. 1A should be moved downward so that their initial portions almost coincide at about 1·4 volts, but the time elapsing before the sudden rise of potential occurs, which is the phenomenon under investigation, remains unaffected.

FIG. 1.

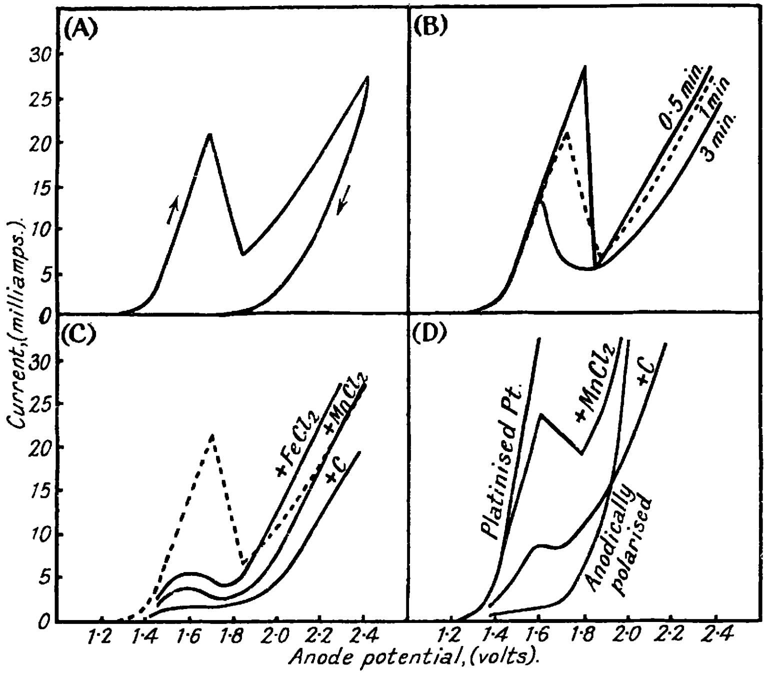


The curves in Fig. 1A show the variation with time of the anode potential in a 0·1*N*-hydrochloric acid solution electrolysed with currents of 0·1, 0·25, and 0·5 amp. respectively; the theoretical quantity of electricity (965 coulombs) required for the liberation of all the halogen present in the anode compartment (100 c.c. of solution) was passed in each case. 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 Fig. 1B; the anode potential–time curves are for 0·05, 0·1, and 0·2*N*-solutions electrolysed with a constant current of 0·25 amp.; it is evident that decrease of concentration favours the polarisation. Fig. 1C shows the effect of varying the hydrogen-ion concentration at constant chlorine-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 amp. being used in each case. The onset of polarisation is evidently markedly favoured by alkalinity of the electrolyte.

In view of the remarkable influence of catalysts for the decomposition of hydrogen peroxide in the electrolytic oxidation of thiosulphate and sulphite ions observed in previous work (J., 1932, 2345; 1933, 829), the effect of such substances on the potential-time curves for the electrolysis of hydrochloric acid was studied; some of the results obtained are presented in Fig. 1D. 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 c.c. of electrolyte. At the temperature and dilution of the acid used, the manganese dioxide did not dissolve to any detectable extent in the course of electrolysis. The influence of the added substances in facilitating the onset of polarisation is very marked. Similar results were obtained with a specimen of charcoal which had been specially purified by extraction with acid and washing.

Anode potential–current curves. Since the electrode potential depends on the time of electrolysis, it is necessary to control the duration of the observations at each *C.D.* in order to obtain reasonably reproducible results. The method used was to fix a certain *E.M.F.* on the potentiometer and then rapidly to adjust the polarising current until the anode–calomel electrode system had the same value. In general, 1 minute was allotted to each of the observations which were made at intervals of 0·1 volt commencing from the reversible *E.M.F.* The potential was fixed at the beginning of the minute, the adjustment of current was then made in a few seconds, and the value of the current read at the half minute; the next potential was fixed at the conclusion of the minute, and so on. Observations were made first with steadily increasing potentials and then with decreasing values; the results obtained in this way for 0·1*N*-hydrochloric acid are plotted in Fig. 2A. Since the currents used in this portion of the work did not exceed 0·03 amp., with an electrode of 1 sq. cm., the resistance error is small and the potentials may be regarded as substantially correct. The curves show that at low *C.D.*'s the potential set up is approximately that for reversible chlorine-ion discharge, but at a certain point the current suddenly drops to a low value and only increases again after the potential is raised appreciably. On decrease of the potential applied to the polarised anode, the current falls rapidly at first and then more slowly to zero; the lower potential stage is apparently completely suppressed. This is in agreement with the well-established observation that the rise of potential occurs at very low *C.D.*'s if the electrode is previously polarised anodically.

FIG. 2.

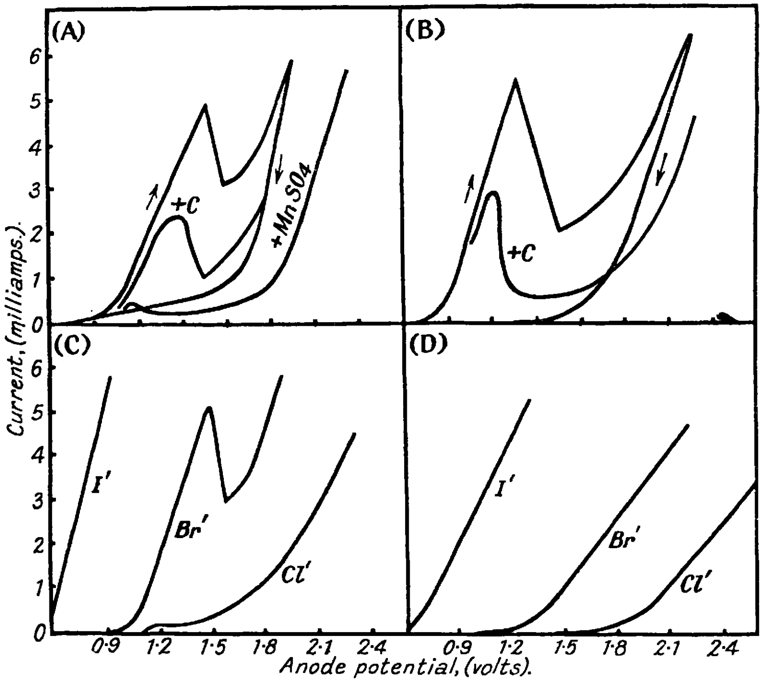


The effect of varying the time permitted for each observation is shown in Fig. 2B; the electrolyte used was 0·1*N*-hydrochloric acid in each case. As is to be expected from the effect of time on the potential (Fig. 1), the onset of polarisation occurs at lower *C.D.*'s the longer the time taken for measurements; this fact will, of course, militate against the reproducibility of the observations, but this does not appear to have been appreciated by previous workers.

The effect of the addition of some of the catalysts already mentioned for hydrogen peroxide decomposition is seen in Fig. 2c; the electrolyte was 0·1*N*-hydrochloric acid in each case. The anode potential–current curve for the acid alone is included (dotted line) for comparison; it is clear that in accordance with the results represented in Fig. 1D the catalysts have a marked effect in shortening the first potential stage.

Previous workers have found that the polarisation to the second potential stage does not occur in hydrochloric acid solutions when using a platinised platinum electrode; this is certainly the case in the absence of catalysts for hydrogen peroxide decomposition, as is shown by the curve in Fig. 2D for 0·1*N*-hydrochloric acid. The addition of 0·001*M*-manganous chloride or of 0·5 g. of animal charcoal to 100 c.c. of solution, or previous anodic polarisation of the electrode, permits the onset of the higher potential condition.

FIG. 3.



Bromide and Iodide Solutions.—On account of the large currents necessary to bring about polarisation of anodes in these solutions in reasonable time, the potential–time curves were not studied in detail. The results obtained with chlorides, however, show that very little more can be learnt from these curves than from those showing the variation of potential with *C.D.* obtained under standard conditions, *viz.*, allowing one minute per reading; the latter method of studying the polarisation in bromide and iodide solutions was, therefore, adopted. In Fig. 3A are seen the anode potential–current curves for 0·1*N*-potassium bromide alone and for the same solution to which had been added either manganous sulphate (0·001*M*) or carbon (0·5 g./100 c.c.) as catalyst. Fig. 3B shows the curves for 0·1*N*-potassium iodide in 0·1*N*-potassium hydroxide solution and for the same solution containing animal charcoal (0·5 g./100 c.c.) in suspension. In both cases the addition of catalysts for the decomposition of hydrogen peroxide favours polarisation of the anode.

The relative polarisability of a smooth platinum anode in chloride, bromide. and iodide solutions is demonstrated by the curves in Fig. 3c; each electrolyte was initially neutral and was 0·1*N* with respect to the halide ion. The smallest platinum anode (0·1 sq. cm. area) was used in each case in the smooth state.

Influence of Temperature.—The observation of Herrschel (*loc. cit.*) that increase of temperature causes the platinum anode to polarise more rapidly in iodide solutions has been confirmed by using the potential–time method. With an electrolyte consisting of *N*-potassium iodide in 0·9*N*-potassium hydroxide and a current of 1 amp., the rise of potential to the higher stage occurred after 225 minutes at room temperature, whereas at 60° the polarisation was attained 5 minutes after switching on the current. Indications of a similar effect were observed with chloride solutions; for instance, with *N*-sodium chloride, using a current of 0·25 amp., the break in the potential–time curve occurred after about 220 minutes at ordinary temperature but only 5 minutes were required at 60°. With bromides, however, temperature appeared to have little effect on the polarisation between 18° and 60°.

Carbon Anode.—The potential–current curves for a gas-carbon anode, having a superficial area of 1 sq. cm., in 0·1*N*-sodium chloride, -potassium bromide, and -potassium iodide in 0·1*N*-potassium hydroxide, are plotted in Fig. 3D. Although there is very marked polarisation, particularly in the chloride and bromide solutions, there is no break in the curves; in view of the results obtained in the oxidation of thiosulphate at a carbon anode (J., 1932, 2805), this is not unexpected.

DISCUSSION.

None of the theories proposed hitherto is able to account in a simple manner for the observations on anodic polarisation in halide solutions now reported. The pronounced effect on the potential–time and potential–current curves of the addition of such diverse substances as a manganous salt and powdered carbon, both of which are, however, good catalysts for the decomposition of hydrogen peroxide, suggests that, as in the anodic oxidation of thiosulphate and sulphite ions, hydrogen peroxide plays an important part in the electrolysis of halide solutions. If, as previously suggested (J., 1932, 2353), hydroxyl ions can be discharged to form hydrogen peroxide *irreversibly*, then right from the commencement of the electrolysis, even when the anode potential is well below that for reversible hydroxyl-ion discharge, the current will be utilised partly in the liberation of free halogen by the discharge of halogen ions and partly in the formation of hydrogen peroxide.* The latter will react immediately with halide ions—in neutral solution with bromide and iodide and in slightly acid solution with chloride (Maass and Hatcher, *J. Amer. Chem. Soc.*, 1922, **44**, 2476; Hiebert and Maass, *ibid.*, 1924, **46**, 290)—yielding eventually free halogen, thus: $H_2O_2 + 2X' = X_2 + 2OH'$. The net result, at low *C.D.*'s, is almost quantitative liberation of halogen at potentials in the vicinity of the reversible value for the discharge of the respective ions, *viz.*, *ca.* 1·4 volt for chlorine, 1·1 volt for bromine, and 0·6 volt for iodine. There is, however, another effect of considerable importance: a small fraction of the hydrogen peroxide will decompose spontaneously, giving oxygen which will be adsorbed by the electrode. At first, the potential of the platinum–oxygen system may be below the reversible value for the halogen (cf. J., 1932, 2345; 1933, 829) and so will not be observed, but eventually saturation will be attained and, as in the oxidation of thiosulphate and sulphite, the potential must then rise rapidly towards that for oxygen evolution. This mechanism, which is in harmony with that proposed in connexion with other anodic processes, accounts in a simple manner for the general form of the potential–time curves.

With large currents the stationary or equilibrium concentration of hydrogen peroxide is high and its rate of decomposition is consequently greater than when small currents are employed; the break in the anode potential–time curve thus occurs sooner the larger the current used (Fig. 1A). Similarly, a decrease in the concentration of the halide permits the accumulation of hydrogen peroxide owing to the reduced rate of reaction; the anode thus becomes more quickly saturated with oxygen and the rise of potential occurs sooner (Fig. 1B). Any factor which favours the decomposition of hydrogen peroxide should facilitate the polarisation of the anode to the higher potential stage; the remarkable effect of the addition of manganous ions, ferrous ions, manganese dioxide, powdered charcoal, or precipitated silver is thus explained (Fig. 1D). The influence of the p_H of the electrolyte (Fig. 1C) is also probably related to the varying stability of the peroxide, although such

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* It is necessary to emphasise that the *rapid and irreversible* removal of discharged hydroxyl radicals is an essential postulate of the theory proposed by the present authors; if this were not so, it would be impossible for the potential set up by the oxygen which accumulates at the electrode surface to be independent of the discharge potential of the hydroxyl ions.

factors as discharge of hydroxyl ions and suppression of the reaction between peroxide and the halide ion, both of which are favoured in alkaline solution, will also be effective.

It may be noted that cobaltous chloride and cobaltic oxide were found to have only a very small influence on the potential–time curves with hydrochloric acid, although the oxide is normally a good catalyst for the decomposition of hydrogen peroxide; experiments showed, however, that its efficiency in the presence of hydrochloric acid was very slight compared with that of manganese dioxide.

It is well known that halogen ions themselves are able to catalyse the decomposition of hydrogen peroxide, their effectiveness increasing in the order chloride, bromide, iodide; it might be anticipated, therefore, that the onset of anodic polarisation in halide solutions under comparable conditions should occur in the reverse order. The actual observations (Fig. 3C) are directly opposed to this expectation. It must be remembered, however, that the reaction between hydrogen peroxide and the halide occurs far more readily with iodide than with chloride, so that the stationary concentration of peroxide at the anode increases rapidly in the order iodide, bromide, chloride. In any case, the catalytic influence of the halogen ions on the decomposition of hydrogen peroxide is relatively so small that it would hardly affect appreciably the rate of accumulation of oxygen at the anode, and the onset of polarisation is determined mainly by the reaction between peroxide and the halide.

The potential–current curves require little comment in the light of the previous discussion; the influence of the time allowed for each observation of potential (Fig. 2B) and the effect of catalysts (Figs. 2C and D, and 3A and B) can be readily understood. With platinised platinum the surface is greatly enhanced and the time taken to saturate it with oxygen is consequently prolonged. It is noteworthy that the catalytic decomposition of hydrogen peroxide by the platinised platinum, which might be expected to be appreciable, is probably poisoned by the free halogen (cf. Bredig and Ikeda, *Z. physikal. Chem.*, 1901, **37**, 63). Previous work (J., 1932, 2350) has indicated a marked stability of the platinum–oxygen system responsible for the polarisation, and the oxygen in this form appears also to react only slowly with halide solutions; it is not surprising, therefore, to find that on decreasing the current after the second potential stage is attained (Fig. 2A), or by using an electrode previously polarised anodically (Fig. 2D), the lower potential condition is not observed.

Although it was not possible to predict that increase of temperature would favour the higher potential condition, the hydrogen peroxide theory gives a reasonable explanation of this unusual polarisation phenomenon. The rate of oxygen accumulation depends on the rate of decomposition of the peroxide, and this is dependent on its stationary or equilibrium concentration at the electrode; the latter depends to a great extent on the rate of reaction between the peroxide and halide, and the net effect of temperature will be determined by its relative influence on two velocity coefficients. If the rate of spontaneous or catalytic decomposition of the hydrogen peroxide increases with temperature more rapidly than the rate of reaction with halide, then increase of temperature will favour the accumulation of oxygen at the anode and the consequent rise of potential. This evidently occurs in the chloride and iodide solutions studied in the present work and in the iodide solutions used by Herrschel (*loc. cit.*).

The suggestion has already been made that part of the halogen liberated at the anode will arise from direct reversible discharge of the corresponding ions and part by the oxidation of the halide by hydrogen peroxide. If this is so, then the presence of a catalyst for the decomposition of the peroxide should bring about a decrease in the total efficiency of halogen liberation; this point was tested in the following manner. The porous pot used as anode compartment was fitted with a stopper, and a rapid stream of air was aspirated across the surface of the liquid and passed into potassium iodide solution. After electrolysis the iodine liberated from this and from the addition of potassium iodide to the anolyte in the porous pot was titrated with standard thiosulphate solution; the titre was assumed to correspond to the total amount of free halogen liberated at the anode. The results, which are given below, can only be regarded as approximate although reproducible to 1—2%; they were obtained after the passage of 483 coulombs with the large rotating smooth platinum anode, a current of 0·25 amp. and 100 c.c. of anolyte being used. The latter was halide solution only or the same solution containing 0·001*M*-manganous chloride (for the chloride solutions) or 0·001*M*-manganous sulphate (for the bromide solution).

Efficiency of halogen liberation, %.

	0·1*N*-HCl.	0·1*N*-NaCl.	0·1*N*-KBr.
Without catalyst	94	50	83
With catalyst	25	29	70

The definite decrease of efficiency in the presence of the catalyst for hydrogen peroxide decomposition is most probably due to the elimination of the indirect process of halogen liberation, since it is very unlikely that the presence of the manganese compound could suppress the reversible discharge of halogen ions. In the presence of the catalyst, the higher potential stage sets in very rapidly, so that most of the electrolysis occurs in this condition (Fig. 1D); it is possible, therefore, that, in addition to the catalytic effect of the manganous salt, the state of the electrode surface or its potential may have some influence on one or more of the stages involved in the reaction between halide and hydrogen peroxide. This point of view is suggested by the observation that, when a previously polarised anode was used, the current efficiency for halogen liberation was in some cases appreciably lower than the normal value; the subject is, however, too complex for further discussion at present.

It may appear surprising that the presence of manganous chloride brings about a reduction in efficiency for halogen liberation in sodium chloride solution, since hydrogen peroxide appears to be without action in neutral solution and so the whole of the halogen should result from direct discharge. The unbuffered solution, used in order to avoid possible complications of other anions, becomes appreciably acid, however, during electrolysis, and the work of Hiebert and Maass (*loc. cit.*) has shown that very dilute hydrochloric acid can be oxidised by concentrated hydrogen peroxide. Support for this explanation of the observations was obtained by an experiment with 0·1*N*-sodium chloride in phosphate buffer of p_H 7; the current efficiency for halogen evolution in the absence of a catalyst was found to be only about 15%. Under these conditions no oxidation of the chlorine ions by hydrogen peroxide occurs, and the efficiency is much less than the 50% obtained with the unbuffered solution under the same conditions.

SUMMARY.

1. The variation with time of the potential of a platinum anode in the electrolysis of chloride solutions at constant current density has been studied under a variety of conditions; two potential stages are observed: one corresponds approximately to that for reversible chlorine-ion discharge, and the other is about 0·6 volt higher. The change from the lower to the upper potential condition is favoured by increased current density, lower concentration of halide, increase of p_H, and the presence of catalysts for the decomposition of hydrogen peroxide.

2. Two similar stages are found when the anode potentials at a series of current densities are measured at short intervals of time in chloride, bromide, and iodide solutions; the ease of onset of the polarisation corresponding to the higher electrode potential decreases in the order given. The addition of hydrogen peroxide catalysts tends to suppress the lower potential condition.

3. The potential of a platinised platinum anode does not normally rise appreciably above the reversible value for chlorine-ion discharge, but in the presence of hydrogen peroxide catalysts, or if the electrode is previously polarised anodically, the two stages of anode potential can be readily observed.

4. Increase of temperature has been found to favour the polarisation to the upper potential condition in certain chloride and iodide solutions.

5. The current efficiency for halogen liberation at the anode can in some cases be markedly decreased by the addition of manganous salts to the electrolyte.

6. The results are discussed in the light of the theory that there is, in addition to the reversible discharge of halogen ions at the anode, the irreversible formation of hydrogen peroxide resulting from the combination of discharged hydroxyl ions. The peroxide is

able, under certain conditions, to oxidise the halide ions to form free halogen, or else it may decompose yielding oxygen. The relative extent to which these two processes occur determines the influence of the nature of the halide, the effect of concentration of the halide, current strength, p_H of the electrolyte, temperature, and the presence of catalysts for peroxide decomposition, on the onset of the higher potential condition.

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