CXCVIII.—*Periodic Phenomena at Anodes of Copper and Silver.*

By Ernest Sydney Hedges.

The only case of the periodic dissolution of a metal under anodic polarisation which has received systematic examination is the periodic passivity of iron. A complete series of references to this and other periodic electrochemical phenomena is to be found in a paper by Hedges and Myers (J., 1925, **127**, 1013). In that paper, periodic electrochemical phenomena were classified in two groups: (*a*) systems which are capable of furnishing a periodic current, and (*b*) systems which behave periodically on electrolysis; and the experimental portion was devoted to section (*a*). The present work is an experimental investigation of section (*b*).

The reactions differ in several important respects from the experiments of Hedges and Myers (J., 1924, **125**, 604; 1925, **127**, 445) on the periodic dissolution of metals in various reagents in absence of applied current. For example, a metal which liberates hydrogen when dissolving in an acid may undergo electrolytic dissolution without production of any gas, or at suitable current densities oxygen may be evolved at its surface. The absence of gas evolution enables diffusion effects, supersaturation, and film formation to play important rôles, and the system may be further complicated by polarisation, overvoltage, etc.

It is not surprising, therefore, that the electrolytic periods described in the present paper should differ in some fundamental respects from the periodic phenomena in purely chemical reactions. Thus, the periods formerly described were (1) dependent on the presence of a third component, (2) dependent on a peculiar physical state of the metal, (3) increased in frequency linearly with the rate of dissolution, and (4) lengthened enormously or stopped altogether by catalytic poisons. On the other hand, the electrolytic periods now described are (1) independent of a third component, (2) independent of the state of the metal, (3) decreased in frequency with increasing rate of dissolution, and (4) unaffected by catalytic poisons.

There are reasons for supposing, however, that the fundamental causes of these manifestations of periodicity are not essentially different.

Experimental.

Apparatus.—The electrolysis was conducted in a wide-necked glass bottle of 200 c.c. capacity, the amount of solution used in each experiment being 100 c.c. The electrodes were of pure electrolytic metal sheet, 4 cm. × 2 cm., and were supported by nickel rods, to which they were fastened by means of a nickel screw, a small hole being drilled near the end of each electrode. A length of only 3 cm. of electrode was immersed in order to keep the nickel well clear of the solution. The metals were approximately 0·5 mm. thick, and the effective area of each may therefore be taken as 12 sq. cm. The distance between the electrodes was 2 cm. A rubber bung, closing the reaction vessel, served to carry the electrode supports and the glass tubes for stirring the solution. Except in experiments where it was undesirable, the solutions were vigorously stirred during electrolysis by a stream of air previously freed from carbon dioxide. The reaction vessel was immersed in a thermostat at 30°, except in those experiments where other temperatures are indicated.

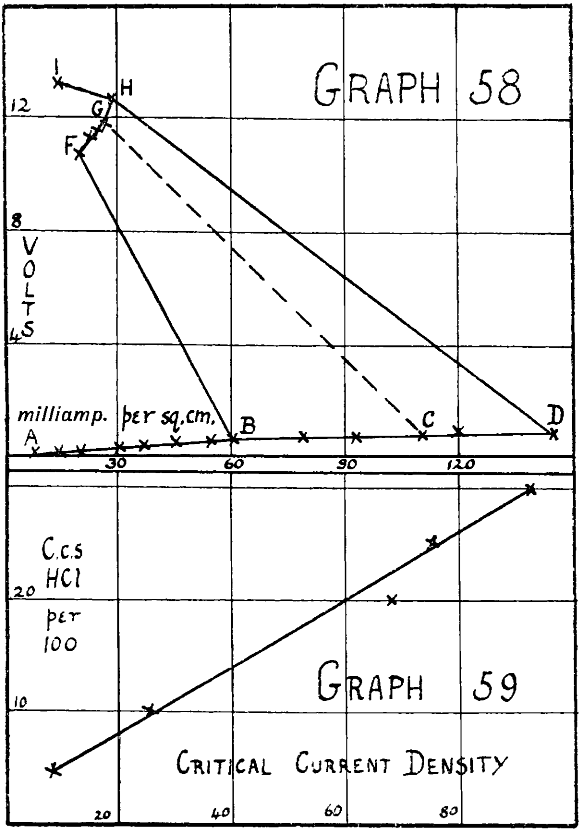
The source of current was a battery of twelve Edison storage cells of large capacity. The current passing through the circuit was read directly on an ammeter placed in series with the cell, and the *P.D.* between the electrodes was measured by a voltmeter of suitably high resistance placed across the electrode terminals. Both were quite dead-beat instruments. The course of the electrolysis was followed by taking readings of the voltmeter every 15 seconds, or, if necessary, every 5 seconds.

(1) *Copper Anode.*

Electrolysis of some Chloride Solutions.—When fairly strong solutions of hydrochloric acid are electrolysed between copper electrodes at low current densities, copper passes into solution at the anode as cuprous chloride. As a rule, this may be seen on the metal as a white coating which, however, does not appreciably impede the electrolysis. In the absence of atmospheric oxygen, no cupric salt is formed. At high current densities, a film which appears to be cuprous oxide forms over the metal; this film is highly resistant and the current passing falls to a low value; the electrode still dissolves, but a small portion of the current is employed in the liberation of oxygen, a few bubbles of which rise from the anode. At intermediate current densities the two effects alternate. The seat of this phenomenon is the anode, for the effect continues if platinum be substituted for the cathode, but not if the anode be changed for another metal. Further, the anode undergoes a visible periodic change.

The Current Density-Potential Curve.—Graph 58 (Fig. 1) shows the effect of gradual increase in current density in the electrolysis of hydrochloric acid, containing 25 c.c. of acid (*d* 1·16) in 100 c.c., using a copper anode and a platinum cathode at 20°. For values below 60 milliamp. per sq. cm. the potential rises slowly along the line AB: cuprous chloride is formed at the anode and dissolves in the hydrochloric acid, and at the cathode copper is deposited and hydrogen evolved. At the value corresponding to B the potential oscillates in regular periods between 0·55 and 10·6 volts, and simultaneously the current fluctuates between 60 and 20 milliamp. per sq. cm. The region of regular oscillations continues as the current density is increased along BD to the value 145 milliamp. per sq. cm., the amplitude here being from 1·0 to 12·7 volts. At an intermediate point C, the values of current density and potential oscillate between points C and G. At current densities greater than 145 milliamp. per sq. cm., the potential immediately rises (the current falling) to a voltage corresponding to H, at which it remains constant. Further attempts to increase the current are

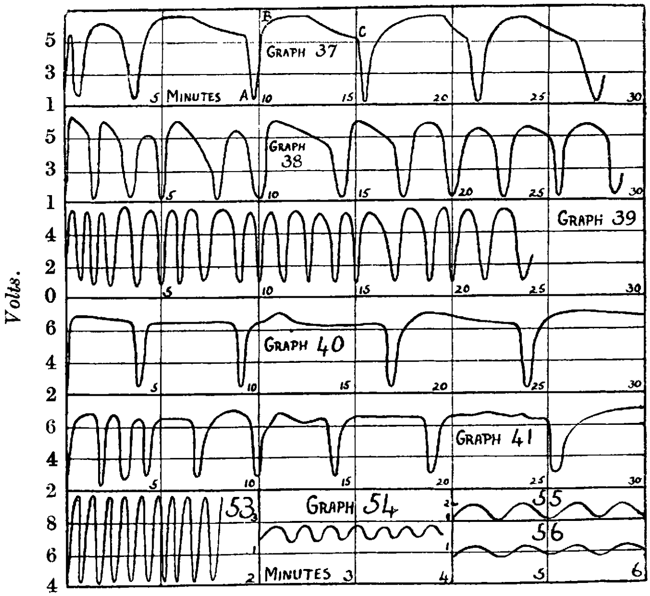
FIG. 1.



unsuccessful, for the film over the anode becomes more and more resistant and the effect is actually to decrease the current still further, along the line HI. The electrode, therefore, exists in one state along AB, in another state at H, and the area BFHD marks a region of instability where the electrode oscillates regularly between the two states.

The point B represents the critical current density required to produce periods. The value of this increases with the concentration of the hydrochloric acid and with rising temperature. The critical current densities for a series of solutions containing from 5 to 30 c.c. of hydrochloric acid per 100 c.c. of solution electrolysed between two copper electrodes have been determined, and Graph 59 indicates a direct proportionality between critical current density and concentration.

FIG. 2.



The amplitude in Graphs 37—41 *is about half of that indicated in Graph* 58. *This is because half the number of cells was used in these experiments. When the highly resistant film forms, the voltmeter records almost the total* E.M.F. *of the battery, the resistance of the rest of the circuit being relatively small.*

The Nature of the Phenomenon.

The periodic changes in current and potential are accompanied by visible periodic changes at the anode. This is best described by reference to one of the waves on Graph 37 (Fig. 2). Simultaneously with the sudden rise in the potential (AB), there sweeps *up* the metal a very thin, dark grey film. The current slowly increases until the point C is reached. Then the potential rapidly resumes its initial low value and a white film sweeps *down* the metal. There is an interval of a fraction of a second between the drop in potential and the appearance of the white film. Careful observation shows that simultaneously with the drop in potential the smooth dark grey film breaks up into a rough red-brown film having the appearance of cuprous oxide. The transformation to the white film is almost immediate. The series of changes is repeated in each successive wave. The first film has the appearance of cupric oxide rather than cuprous, but there is doubt in assigning a composition to so thin a film. It is believed to be a form of cuprous oxide, for it changes directly into ordinary cuprous oxide and gives cuprous chloride by reaction with hydrochloric acid: further, no cupric salt is produced in the reaction. The white film is undoubtedly cuprous chloride.

It has been observed that wherever deposition of a film occurs in electrolysis, this starts at the sides and lower part of the electrode and travels up the electrode in the form of a **U** of diminishing concavity. This seems to be due to the concentration of current density at the corners and edges of the electrode and accounts for the manner in which the dark oxidic film travels up the anode. The downward sweep of the cuprous chloride film has been traced to the flow of hydrochloric acid down the electrode due to the downward fall of the reaction products, which is observed even when the solution is stirred. By allowing a stream of air bubbles to impinge on a point near the bottom of the anode, the reaction products can be washed upwards, and under these conditions the cuprous chloride film travels upwards also; but the oxide film could not be made to travel downwards.

The phenomenon is not affected by moderate rates of stirring, but when the solution in the vicinity of the anode is stirred very vigorously the frequency of the periods is increased or the potential may even remain constant at the low value. In the latter case, periodicity recurs on increasing the current density. Thus the phenomenon may be localised by directing a stream of air bubbles on a point about half-way up the electrode. In this case, the small area of metal affected by the rapid stirring exhibits rapid black and white flashes, while the main part of the electrode performs its slow periods unhindered. The voltmeter records curves showing short waves superimposed on the long waves.

These effects, which could be controlled by the air used for stirring, suggested that the phenomenon was due to oxidation and probably to an oscillation of the reaction product between the cuprous and cupric states. Experiments were therefore performed in which the solutions were stirred by a stream of hydrogen bubbles. The effects of localised stirring were the same as with air and in this case no cupric salt was formed. Further, the periods were produced when the hydrochloric acid contained 1% of sulphurous acid. Separate experiments showed that a copper anode did not give periods in 1% or 5% sodium hydrogen sulphite solution alone. It may be noted that in the presence of sulphurous acid a somewhat higher critical current density was required.

Observations taken on interrupting the periods have given a clue to their nature. If the circuit be broken or the electrodes be short-circuited while the high *P.D.* exists, the cuprous chloride film immediately forms over the anode. In this case, it does not travel down the metal, but appears simultaneously over the whole area. If the circuit be completed again directly, the oxide film is reinstated immediately and the *P.D.* again rises. When an interval of 1 or 2 seconds elapses before the circuit is remade, the film does not form again for a few seconds. By breaking and making the circuit several times in succession, preferably in an unstirred solution, the cuprous chloride film does not form when the *P.D.* drops, but, instead, the oxide film turns to the red colour and the white film appears when the circuit is again made; it is quickly followed by the oxide film, the *P.D.* rising once more.

These facts suggest the following interpretation. The critical current density is such that chlorine ions are discharged more rapidly than they can be replaced by diffusion; at a certain moment, therefore, hydroxyl ions are discharged and a highly resistant oxide film forms over the metal, causing the *P.D.* to rise to a high value. This film is unstable (as will be shown independently later) and changes to a stable state of relatively low resistance, the change being indicated by the change in colour and surface of the film. This is immediately followed by reaction with the chlorine ions, which have been accumulating through diffusion, to form cuprous chloride. When the current is broken for a fraction of a second, the oxide film (which is only stable at the high potential) immediately reacts with the available chlorine ions and then rapidly forms again as these become scarce. When, however, the circuit remains open for a few seconds, the chlorine ions have time to diffuse towards the anode and, on making the circuit once more, a few seconds elapse before the oxide film forms. By repeating this process several times in rapid succession, the solution in the immediate vicinity of the anode can be so deprived of chlorine ions that breaking the circuit causes the highly resistant film to change to the red stable state, in which form it persists for some little time; but closing the circuit causes it to react to form cuprous chloride.

Direct evidence of the instability of the highly resistant oxide film is gained by observing the effect of partially lifting the anode out of the solution when in the state represented by H in Graph 58. When this is raised 1 cm., the change to the stable state is observed to take place in the upper part of the electrode and a well-defined ridge forms about 0·5 cm. above the surface of the solution, marking the boundary between the stable and unstable forms. Each time the electrode is progressively raised, a further area remote from the solution undergoes the change and a new boundary forms, below which the grey film persists. This boundary marks the extent of the electrode which is under the influence of the high current density. The highly resistant film is stable, then, above a current density of 145 milliamp. per sq. cm., and its metastability between the values 60 and 145 milliamp. per sq. cm. is the cause of the periodicity.

Having deduced the mechanism of the process from direct experimental observation, it is necessary to show how this is supported by a study of the effect of varying the conditions of reaction.

Effect of Conditions.

(a) *Current Density.*—For any given concentration, the frequency of the periods decreases greatly with increasing current density. This is illustrated by the following values in a solution containing 25 c.c. of hydrochloric acid per 100 c.c.

Milliamp.	58	72	86	117
Min.	1·25	2·0	4·25	9

Such a result is to be expected, for the high current density (1) more rapidly exhausts the anolyte of chlorine ions, and (2) stabilises the resistant film.

(b) *Temperature.*—At a given current density, the frequency of the periods increases with rising temperature. This effect takes place in a particular way, however. The lower part of the curve (Graph 37) is unaffected and only the portion BC is shortened. On raising the temperature still higher, the amplitude AB is gradually reduced until finally the effect dies out and the potential remains constant at the low value. Periodicity can then be recovered by increasing the current density. Thus, a system at 20° under a current density of 80 milliamp. per sq. cm. gave an amplitude of 5·7 volts, the high *P.D.* lasting for 120 seconds; at 35°, the amplitude was 4·8 volts, lasting for 30 seconds; at 45°, 2·8 volts for 10 seconds; at 55°, 0·3 volt for 5 seconds. In each case, the low *P.D.* had a duration of 30 seconds.

Above 60°, no oscillation was perceptible, but by increasing the current density to 108 milliamp. per sq. cm. variations between 0·4 and 0·8 volt were recorded; at 126 milliamp. per sq. cm. the *P.D.* oscillated between 0·5 and 4·1 volts.

Thus, the effect of raising the temperature is to decrease the stability of the resistant film, and in every way it acts in an opposite sense to increasing current density : the two are mutually antagonistic.

(c) *Concentration.*—Graphs 37, 38, and 39 (Fig. 2) show that for a fixed temperature and current density (in this case 30° and 71 milliamp. per sq. cm.) the frequency of the periods increases with increasing concentration of hydrochloric acid. The rate of dissolution of the metal remains the same in the three cases. This result would be anticipated from the explanation advanced, for the anolyte is with greater difficulty depleted of its store of chlorine ions. The linear relation between the critical current density and the concentration of solution is likewise compatible. The wave-length gradually increases during the course of the electrolysis. This is due partly to decrease in concentration of the chlorine ions and partly to formation of cupric chloride through oxidation by the air-stream. Direct addition of 1% of cupric chloride was found to double the length of the waves.

(d) *Rate of Stirring.*—This factor is inconsiderable when the solution is kept in circulation without violently disturbing the solution at the anode. When the stream of bubbles is allowed to travel up the anode the frequency of the periods is increased and the critical current density raised. This is due to the rapid replenishing of the depleted chlorine ions, causing the effective concentration to be higher.

(e) *Addition of Agents.*—Addition of a reducing agent, such as sulphurous acid, served to shorten the periods and to raise the critical current density. On the other hand, oxidising agents such as hydrogen peroxide lengthened the periods. A system with a normal period of 4·25 mins. produced periods of 4·5 mins. after addition of 1 c.c. of 20-volume hydrogen peroxide, 6·5 mins. in the presence of 2 c.c. of hydrogen peroxide, and 10·5 mins. with 4 c.c. Addition of 0·5% of potassium cyanide or 0·5% of formaldehyde failed to " poison " the oscillations. The presence of 0·02% of gelatin did not affect the phenomenon. No difference could be observed between the behaviours of cold-rolled and well-annealed copper.

The periodic phenomenon takes place in solutions of other chlorides in similar circumstances and the same general effects are observed. Thus, equally well-marked periods are produced when

10% or 5% ammonium chloride is used for the solution to be electrolysed. Graph 40 (Fig. 2) illustrates the periodic dissolution of a copper anode in 5% ammonium chloride solution. Graph 41 records a similar experiment using 5% sodium chloride solution. In the latter case, the reaction product is mainly cuprous oxide, which is insoluble but does not adhere to the electrode; it soon causes the solution to become opaque, thus preventing observation. Long periods are obtained when 5% cupric chloride solution is used as the electrolyte.

Electrolysis of Potassium Cyanide Solutions.

Anodes of copper in 2·5% and 5% solutions of potassium cyanide rapidly become enveloped by a golden-green film which readily dissolves in the electrolyte on breaking the circuit. This is generally described as a basic cyanide. At certain current densities, the voltmeter needle trembles violently and occasionally executes rapid fluctuations of about 1 volt. The phenomena are much more definite in a 10% solution. At low current densities, no film forms over the anode and the copper dissolves as potassium cuprocyanide. When the current density is raised to 59 milliamp. per sq. cm. a dark grey oxide film sweeps up the metal and the *P.D.* between the electrodes rises from 1·6 to 2·7 volts. After a few seconds, the dark film gives place to a white film, presumably of cuprous cyanide, which travels down the metal, and the *P.D.* resumes its former value. The two states oscillate thereafter in regular periods.

In every respect this phenomenon is similar to the periodic electrolysis of chloride solutions, and the oxide film reacts towards interruption of the current just as in the former cases. It is therefore a logical deduction that the mechanism is precisely similar. The limits of the conditions favouring periodicity in the cyanide solutions are, however, very much narrower than in the chloride solutions. If a current density–potential curve similar to Graph 58 be constructed for a cyanide solution, the region of instability BFHD is very short and is indeed easily overshot, the electrode often going straight from the state represented by B to that represented by H. It is only by increasing the current density cautiously that the intermediate oscillating condition can be realised in this system.

Another point differentiates the systems. On further increasing the current density to 86 milliamp. per sq. cm., a pale green film permanently covers the anode. At this stage, cuprous cyanide is being formed more quickly than it can dissolve in the potassium cyanide solution. The onset of this film is marked by a rise in potential from 3·6 to 6·2 volts, after which a second series of oscillations ensues. These are most diverse in character, varying in amplitude from 0·1 to 6·0 volts and in wave-length from 0·1 to 5·0 seconds. Occasionally they become regular for some few minutes, after which the voltmeter needle behaves in an erratic manner, violent trembling being interspersed with sudden momentary darts up to a high value. Current densities exceeding 140 milliamp. per sq. cm. are beyond the region of periodicity in the cyanide film, but the erratic behaviour may be repeated by again lowering the current density. Since no change can be observed in the film in this second series of oscillations, there are as yet no data to afford an explanation. Analogy would suggest that the cyanide is first deposited in an unstable form at the high current density employed.

The phenomena are even better marked in 20% potassium cyanide solution. Illustrations of periodicity in the oxide film and of regular periods in the cyanide film are shown in Graphs 54 and 53 (Fig. 2), respectively. All these experiments on cyanide solutions were conducted at 20° because of the high frequency, and the solutions as a rule were not stirred in order to avoid loss of hydrogen cyanide. Control experiments in stirred solutions gave similar results, except that somewhat higher current densities were required in every case.

Electrolysis of Other Solutions.

Sulphuric Acid.—Investigations were carried out at intervals of 10% over the concentration range 100—10%, and also at 5, 2, and 0·5% (expressed as % by volume of acid, *d* 1·84). With concentrations above 50%, very little current would pass, the *P.D.* rapidly rising to a high value. After a time, cupric sulphate could be seen as crystals on the anode. Electrolysis followed a normal course below 10%, and at intermediate concentrations the potential rose to a high value at a certain critical current density. This was followed by a partial fall in the 40, 30, and 20% systems, but in no case was a periodic effect produced. It is probable that the highly resistant film was in this case copper sulphate. In the more dilute solutions (below 10%), some loosely adherent cupric oxide was always formed at high current densities. The 40% system was examined over a temperature range of 20° to 75°. Between these limits the critical current density increased from 58 to 138 milliamp. per sq. cm., but periodic effects were not produced.

Nitric Acid.—The concentrations examined were 10, 5, 2, and 0·5% (by volume of acid of *d* 1·42). In all these cases, the electrolysis pursued a steady course over the whole range of current densities. At the end of each experiment, the anode was covered with a slimy, black deposit, probably of cupric oxide, which did not increase the resistance of the system. In one experiment with 5% nitric acid, continuous oscillations with a 30-second period between 0·8 and 1·0 volt were observed, using a current density of 36 milliamp. per sq. cm. Subsequent attempts to repeat this have failed. It is possible that the periods were due to some accidental circumstance, or that their range of existence was very narrow.

Sodium Hydroxide.—Solutions of concentrations graded from 8% to 0·4% were used. With the 8% solution at current densities below 5 milliamp. per sq. cm. a resistant film of cupric oxide slowly formed on the anode, the *P.D.* rising from 1·2 to 2·3 volts, at which oxygen was evolved. The film disappeared on increasing the current further and a greenish-yellow substance could be observed going into solution. Periods were not observed in any of these systems or in concentrated solutions of ammonia. A large number of mixtures of solutions of caustic soda and ammonia were also tried without success.

Miscellaneous.—Solutions of the following compositions were electrolysed with a copper anode over the range of current densities possible with the apparatus described and no trace of periodicity was observed. Ammonium acetate, 5 and 2·5%; sodium acetate, 8·4%; acetic acid, 12·4%; ammonium sulphate, 5, 2·5, and 1·25%; sodium nitrate, 5%; sodium hydrogen sulphite, 5 and 1%; potassium iodide, 5 and 1%; potassium chromate, 5 and 1%. With the last two substances, insoluble films immediately formed over the anode.

(2) *Silver Anode.*

Although general considerations would lead one to anticipate that periodic phenomena might be observed at a silver anode in similar circumstances, the practical application is beset with difficulty in consequence of the insolubility of so many silver salts. Only the cyanide experiments can be repeated under precisely analogous conditions, but the insolubility of silver chloride has been overcome by the employment of ammoniacal solutions of chlorides. With these modifications, the phenomena observed are similar to the experiments with a copper anode, but, in general, the effects are much less striking; the amplitude of the oscillations is relatively small and the frequency is in all cases very high. The latter fact precludes direct experiment on the properties of the films, and it is therefore necessary at present to rely on the analogy with copper for an explanation of the phenomena. This seems a safe course in view of the similarity in every respect between the two cases.

Electrolysis of Potassium Cyanide.—Since, except in the strongest solutions employed, the highest amount of current passing is small, the limits will be defined by the *P.D.* between the electrodes. With a 5% solution, the anode dissolves normally as potassium argentocyanide when the *P.D.* is less than 2·3 volts; at this value, a brownish-black film of silver oxide sweeps up the metal and the potential rises to 3·2 volts and then oscillates rapidly (about twice per second) between 3·2 and 3·0. Simultaneously, the upper part of the anode displays alternate black and white flashes—a rapid periodic dissolution of the silver oxide film by the potassium cyanide. The phenomenon is precisely similar to the case of copper, the black oxide film sweeping up and the white cyanide film rolling down, the frequency increasing with current density, concentration, and temperature. On slightly increasing the current, the alternation is so quick as to resemble a twinkling.

Similar effects were observed in solutions of concentrations 2·5, 1, 0·5, and 0·25%. The 2·5% solution gave an amplitude of 0·4 volt between the critical limits 1·7 and 2·9 volts. Below the value 1·7, no oxide film appeared and above 2·9 it existed permanently. The 1% solution gave an amplitude of 0·4 volt between the limits 1·8 and 2·7 volts. The limiting voltages for the 0·5% solution were 1·8 and 2·4, and in the case of the 0·25% solution they were 1·6 and 1·7. In the last case, the periods were as long as 30 seconds. It is seen from these figures that the extent of the unstable region decreases with progressive dilution.

These results were for unstirred solutions at 20°. In stirred solutions, the frequency was even higher. Since the low amplitude and high frequency of these periods were reminiscent of the anodic dissolution of copper in hydrochloric acid at higher temperatures, some experiments were conducted on silver in potassium cyanide solutions at 0°, and a maximum amplitude of 2·1 volts was then obtained with a 10% solution of potassium cyanide.

Experiments were also conducted in 10 and 5% ammonium thiocyanate solutions. Although above a certain current density the oxide film formed slowly, it seemed to be permanent. The 10% solution was investigated over the temperature range 20—80° in an attempt to quicken the dissolution of the film, but the experiments were not successful in producing periods.

Electrolysis of Ammoniacal Solutions.—When solutions of ammonium chloride were electrolysed with a silver anode, a highly resistant chloride film immediately formed. Attempts were therefore made to add just sufficient ammonia to dissolve the film as fast as it formed. Periodic effects were observed in these experiments, the anode becoming intermittently coated by a dark brown oxide film. The best result was with a solution of 50 c.c. of 10% ammonium chloride and 50 c.c. of ammonia solution (*d* 0·880). With a current density of 44 milliamp. per sq. cm., the *P.D.* oscillated between 3·0 and 4·1 in periods of 20 seconds. Rapid oscillations were also observed with a silver anode dissolving in a mixture of 50 c.c. of 10% ammonium sulphate solution and 50 c.c. of ammonia (*d* 0·880).

Electrolysis of strong ammonia solutions alone might be anticipated to yield periodic phenomena on the basis of the explanation advanced here. Such solutions were tried without success, but the failure is most likely due to the fact that very little current can be made to pass. Endeavours to obviate this difficulty by adding progressively increasing amounts of caustic soda to the solution met with no success.

Electrolysis of Sulphuric Acid.—Solutions varying in composition from 100 to 2% were electrolysed. The anode dissolved continuously only in the most concentrated solutions, a sulphate film forming above a certain critical current density and the potential rising very sluggishly. Periods were obtained in these systems at higher temperatures. With 90% sulphuric acid at 50°, the waves shown in Graph 55 (Fig. 2) were obtained at a current density of 36 milliamp. per sq. cm., whilst Graph 56 represents 50% sulphuric acid at 75° under a current density of 17 milliamp. per sq. cm. The solutions always became cloudy, preventing observation of the state of the anode.

Electrolysis of Other Solutions.—In addition to those mentioned above, the following solutions gave no periodic effects: caustic soda, 8, 4, and 0·4%; nitric acid, 2, 1, and 0·5%; silver nitrate, 1·7%; acetic acid, 12·4%; potassium chromate, 9·7, 4·8, 2·4, and 0·6%; sodium thiosulphate, 3·4%; sodium hydrogen sulphite, 5%. In the last two cases, where periodicity might have been expected, the reaction followed a complex course, the main product being silver sulphide, whilst the solution developed the smell of hydrogen sulphide.

The investigation is being extended to anodes of other metals and will include the cathodic deposition of metals.

Summary.

Periodic changes in current strength and in the *P.D.* between the electrodes were observed in the anodic dissolution of copper in solutions of hydrochloric acid, ammonium chloride, sodium chloride, cupric chloride, and potassium cyanide, and of silver in solutions of potassium cyanide, sulphuric acid, and ammoniacal ammonium sulphate and ammonium chloride. In every case, periodic film formation over the anode occurred. The case of copper in hydrochloric acid was the subject of a detailed examination. The pheno-

menon took place between certain limiting values of current density and the critical current density required to produce the periods was a linear function of the concentration of the electrolyte. The frequency of the periods increased with rising temperature and concentration, and decreased with rising current density. The periods were not affected by catalytic poisons. At the critical current density, an oxidic film formed over the metal and it was shown that this film was stable above a certain value of the current density; its metastability between this value and the critical current density is believed to be the cause of the phenomenon. This case appears to be typical of all the others investigated.

The author is much indebted to Dr. J. F. Spencer for his interest in these experiments and to the Chemical Society for a grant in aid of the research.

BEDFORD COLLEGE (UNIVERSITY OF LONDON),
REGENT'S PARK, N.W. 1.

[*Received, April* 13*th*, 1926.]