CXXXV.—*An Enquiry into the Cause of Periodic Phenomena in Electrolysis.*

By Ernest Sydney Hedges.

A considerable amount of data concerning periodic processes in electrolysis has been accumulated in recent years (Hedges, J., 1926, 1533, 2580, 2878; 1927, 1077; 1928, 969), and the systems studied have included periodic phenomena both at the anode and at the cathode. Whilst in every case the conditions of periodicity have been defined and it has been possible to deduce a number of generalities from the results, and even to forecast whether a given system is likely to exhibit periodicity, the experiments described so far have not been able to discriminate between the various explanations of the cause of the periodicity.

In an endeavour to elucidate the mechanism, some experiments with rotating anodes are now described and may be regarded as complementary to the series mentioned above.

Experimental.

The system chosen for investigation was the anodic dissolution of copper in hydrochloric acid, since this gives an effect of the greatest magnitude.

Apparatus.—The apparatus and conditions of experimentation were as described in the former papers (*locc. cit.*), except for the arrangement of the anode. The device adopted for rotating the anode was as follows. A nickel rod, provided with a nickel screw and washer for affixing the metal to be used as anode, is fitted tightly into a small wooden pulley by means of an indiarubber slip. The upper side of the pulley is bored, so as to hold a pool of mercury, which covers the end of the nickel rod. The mercury pool is partly covered by a thin card, leaving a small aperture for insertion of a lead connecting the electrode with the source of current and the string electrometer. The object of the card is to retain the mercury, which is otherwise centrifuged when high speeds are used. The electrodes were made of electrolytic sheet copper, measuring 6 × 1 × 0·1 cm., and a length of 3 cm. of the electrode was immersed in the hydrochloric acid.

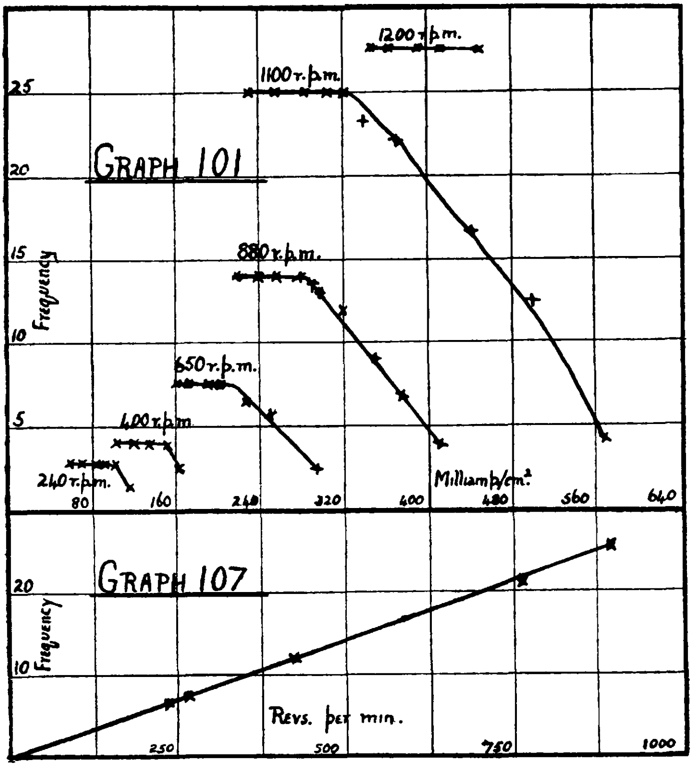
The Relation between Frequency and Current Density.—When a copper anode dissolves in not too dilute hydrochloric acid at low *C.D.*'s, cuprous chloride is formed and dissolves in the acid, but at high *C.D.*'s an oxidic film covers the anode and the current passing falls to a very low value. At intermediate *C.D.*'s, the two states alternate, the copper becoming covered with a dark film periodically, whilst periodic changes in *C.D.* and *P.D.* take place simultaneously (J., 1926, 1533). In the former experiments, the solution was kept in circulation by means of a stream of air or hydrogen bubbles, and it was found that the rate of stirring did not affect the results unless the stream was allowed to travel directly up the anode. Evidently, such a method of circulation is quite ineffective in regard to the solution in the immediate vicinity of the electrode surface, for the use of a rotating anode brings out quite different relations.

With a stationary anode, the frequency of the periods decreased rapidly with increasing *C.D.* On the other hand, with a rotating anode, the frequency is independent of *C.D.* over a certain range and later decreases almost linearly with increasing *C.D.* This is shown by Graph 101 (Fig. 1), in which the frequency (number of waves per sec. × 100) has been plotted against the *C.D.* The system represented is a copper anode in 25% hydrochloric acid (% by vol. of acid of *d* 1·16) and each curve refers to a different speed of rotation, varying between 240 and 1200 r.p.m. The graph shows (1) that the critical *C.D.* for periodicity increases with speed of rotation, (2) that there is a "characteristic frequency," independent of *C.D.* and increasing with speed of rotation, and (3) that a second critical *C.D.* exists, at which the frequency ceases to be independent of *C.D.* and which also rises with speed of rotation. The measurements of frequency were taken by altering the *C.D.* and observing the time for 10 successive waves by means of a stop-watch. The measurements in Graph 101 are not regarded as having the same degree of accuracy as those in the following graphs, since improvements were subsequently made in the control of the speed of rotation.

The existence of a characteristic frequency, independent of *C.D.* and increasing with the speed of rotation, indicates at once that the frequency is not dependent on the rate at which metal ions leave the electrode. That the phenomenon is quite independent of the velocity of dissolution of a metal is confirmed by previous work on the periodic formation of films at an unattackable anode (J., 1926, 2591).

The most probable interpretation of the second part of each curve, where frequency decreases with increasing *C.D.*, is that at a sufficiently high *C.D.* some product begins to accumulate on the anode.

FIG. 1.



Until this second critical *C.D.* is reached, the rotation is rapid enough to wash away the product as fast as it is formed. The rise of the second critical *C.D.* with increasing speed of rotation is consistent with this view. It will be shown later that the product concerned is cuprous chloride.

The Relation between Frequency and Speed of Rotation at Constant Concentration.—Graph 107 (Fig. 1) shows the relation between frequency and speed of rotation for a copper anode in 40% hydrochloric acid. The readings on this graph were made by determining the frequency–*C.D.* curve for each speed and then plotting the "characteristic frequency" (see above) against the speed. The points lie on a straight line passing through the origin. It appears, therefore, that the frequency is independent of the rate of dissolution of the anode, but is in direct proportion to the speed of rotation. The graph indicates that one complete period is produced for every 58 revolutions (approx.) of the electrode, independently of the rate of revolution. (*Note.* In this graph frequencies are in seconds and revolutions in minutes.)

Variation of the speed of rotation can produce two effects: (1) the anodic product is washed away more rapidly, (2) chlorine ions are supplied to the anode at a greater rate. If the frequency were determined by the first of these effects, it would not be independent of *C.D.*; consequently, it may be inferred that the frequency is controlled by the rate of supply of chlorine ions to the anode.

The Relation between Frequency and Current Density at Constant Speed for Different Concentrations.—Apart from variation in the speed of rotation, the rate of supply of chlorine ions to the anode can be varied by altering the concentration of the hydrochloric acid. Experiments have been carried out with solutions of hydrochloric acid varying in concentration between 10 and 40%, a constant speed of 880 r.p.m. being used, and the results are shown in Graph 106 (Fig. 2). Instead of plotting the frequency, its reciprocal—the "periodic time" or duration of a period in seconds—has been plotted against the *C.D.* As expected from the considerations given above, both the critical *C.D.* required to produce the periods and the characteristic frequency increase with the concentration of acid. The graph also shows that the independence between frequency (or periodic time) and *C.D.* is not realised in solutions of hydrochloric acid whose concentrations are below 20% and that the region of independence is more marked the higher the concentration. This suggests that the product responsible for the change of frequency with *C.D.* at low speeds and low concentrations is cuprous chloride, which is far more readily soluble in the concentrated acid. Some experiments have therefore been conducted in which 1%, 2%, or an excess of cuprous chloride was added directly to a system consisting of a copper anode rotating at 880 r.p.m. in 30% hydrochloric acid, and the results are represented by Graph 118 (Fig. 3). With increasing amounts of cuprous chloride, both the critical *C.D.* required to produce periods and the frequency of the periods are lowered, and the horizontal part of the curve, indicating independence between frequency and *C.D.*, is destroyed. In fact, Graph 118 is precisely similar to Graph 106, and it may therefore be inferred that cuprous chloride is the responsible product.

The amplitude of the periods obtained with a rotating anode is, in general, less than that of the periods with a stationary anode. The amplitude is about 1 volt during the stage where frequency is independent of *C.D.*, but increases considerably after the second critical *C.D.* has been passed. With a stationary anode, amplitudes of about 12 volts were recorded. This suggests that when cuprous chloride begins to collect at the anode, a much thicker oxide film is produced—probably by hydrolysis of the cuprous chloride.

FIG. 2.

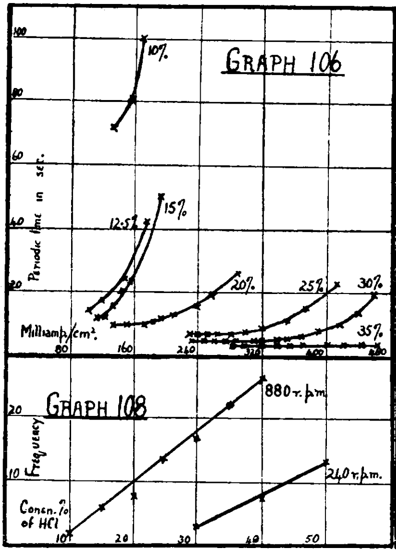
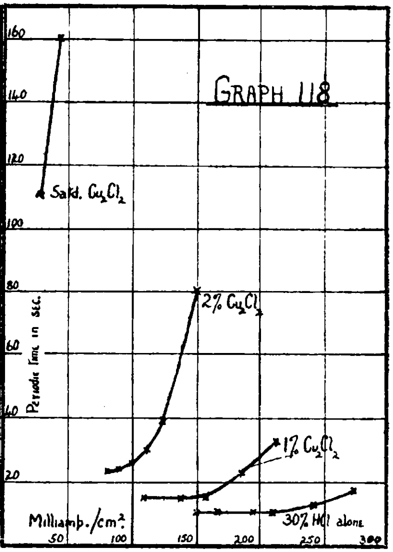


FIG. 3.



The Relation between Frequency and Concentration at Constant Speed.—If the frequency is determined by the rate of supply of chlorine ions to the anode, a linear relation between frequency and concentration of hydrochloric acid is to be expected. That this is realised is shown by Graph 108 (Fig. 2), where the characteristic frequency is plotted against concentration for two different speeds, *viz.*, 880 and 240 r.p.m. The points were obtained by determining the frequency–*C.D.* curve for each concentration, and plotting the value of the frequency corresponding to the horizontal portion of the curve.

Discussion.

The experiments indicate that the frequency of the periods is independent of the *C.D.*, but proportional to the rate of stirring and to the concentration of the acid. Three factors can be concerned in determining the frequency: (1) rate of removal of ions from the metal, (2) rate of removal of anodic product, (3) rate of supply of chlorine ions to the anode. Since (1) and (2) are dependent on the *C.D.*, it may be inferred that the rate of diffusion of chlorine ions is the controlling factor. The distinction between (1) and (3) holds only at these high *C.D.*'s considered—*i.e.*, above the critical *C.D.* At low *C.D.*'s it is not possible to distinguish between (1) and (3), but at high *C.D.*'s negative ions other than chloride (*e.g.*, hydroxyl) compete; the rate of supply of chlorine ions is determined by the stirring, and the rate of ionisation of the metal is determined by the *C.D.*

The following view of the mechanism is taken. At low *C.D.*'s cuprous chloride is formed at the anode: this, being soluble in the acid solution, is washed away from the anode continuously, and fresh chlorine ions diffuse in continuously. The *P.D.* therefore remains constant at a low value. It is to be noted that in the formation of the cuprous chloride–hydrochloric acid complex the chlorine ions are removed, as such, from the sphere of action. At a certain critical *C.D.*, the rate of disposal of chlorine ions begins to overtake the rate of diffusion of fresh chlorine ions to the electrode. This produces two effects: (*a*) the scarcity of chlorine ions in the layer of liquid immediately contiguous to the anode allows hydroxyl ions to be discharged, and (*b*) hydrogen ions migrate away from the positively charged anode. The effect (*b*) tends to make the layer of liquid alkaline. The discharge of hydroxyl ions (*a*) makes the anolyte as a whole more acid, but the hydrogen ions so produced migrate from the vicinity of the electrode according to (*b*). It is necessary to distinguish between this thin alkaline liquid sheath and the anolyte as a whole, which, of course, tends to become more acid. The thin alkaline sheath is of greater importance in the behaviour of the anode. Both effects (*a*) and (*b*) have the same result—the formation of an oxidic film (basic salt or oxide) on the metal, (*a*) by direct discharge of hydroxyl ions, or (*b*) by hydrolysis of the primary anodic product. This film, which is visible, explains the rise in potential, or passivity in its widest sense.

In the case of the easily passivated metals, such as iron, the visible film reduces the active area of the electrode, raising enormously the effective *C.D.* at the uncovered spots, so that an invisible, highly protective oxide film forms at these points and rapidly spreads to cover the entire electrode according to the mechanism suggested in a previous paper (J., 1928, 977).

The subsequent fall of potential is due to the action of the hydrochloric acid on the oxidic film, changing it to cuprous chloride, which subsequently dissolves in the acid. This change is easily visible and its direction of propagation over the electrode always follows the direction of flow of the hydrochloric acid, which can be varied at will. It is easy to see that after the fall of potential, the original *C.D.* being reinstated, the oxidic film will form again. The fundamental problem is why the dissolution of the film takes place in definite periods instead of there being set up a state of dynamic equilibrium. The experiments showing that the frequency depends entirely on the rate of accumulation of chlorine ions appear to leave no escape from the conclusion that dissolution of the film does not occur until a certain critical concentration is reached, but that when reaction occurs in each " pulse " it is complete. This is analogous to the " all-or-nothing " law so familiar in physiology, according to which a system does not respond to a stimulus until this reaches a threshold value, but the response is complete when that value is reached. Evidence of the existence of such critical concentrations will be given later.

A view frequently expressed with regard to the older cases of periodic electrolysis is that the resistance of the film decreases the current, so allowing the ions to collect by diffusion until they attack the film, and the consequent increase in current brings about once more the condition for the formation of a new film. As Ostwald pointed out long ago (*Z. physikal. Chem.*, 1900, **35**, 210), two such continuous processes would not produce a periodic course, but would set up a dynamic equilibrium condition, where the rates of formation and dissolution of the film substance were equal. In order to account for periodicity, a *discontinuity* must occur somewhere in the process. It is interesting to note that the necessary discontinuity has been provided for in ways other than critical concentration. For example, Joule (*Phil. Mag.*, 1844, **24**, 106) explains the periodic anodic dissolution of zinc amalgam in sulphuric acid as follows: the zinc dissolves smoothly until, at a certain critical *C.D.*, more sulphate ions are being discharged than can be replaced by diffusion. An oxide film then forms and oxygen is evolved. The stirring effect produced by the oxygen brings a layer of fresh solution, rich in sulphate ions, into contact with the electrode. Here, the discontinuity is provided by the stirring. This view is not capable of a very wide application, since in many cases (of which that described in the experimental portion of the present paper is the best example) no appreciable amount of gas is evolved.

Evans (" Metals and Metallic Compounds," Vol. 1, p. 382) suggests that periodic passivity in iron is due to the accumulation of hydrogen ions in the neighbourhood of the anode, due to the discharge of hydroxyl ions, and that the acid so produced activates the passive electrode. It may be noted that inherent in this theory is the assumption that the acid does not activate the metal until a certain critical concentration is reached, or otherwise a state of equilibrium would be realised. But, in view of the fact that such hydrogen ions are produced only as a result of the formation of a protective film on the metal and also that they tend to migrate from the positively charged anode, it is difficult to imagine that the hydrogen ions would get to the electrode by diffusion against a potential gradient. The phenomena described in the experimental portion of the present paper take place equally well whether the electrolyte is hydrochloric acid, sodium chloride, or ammonium chloride, again suggesting the chlorine ion rather than the hydrogen ion as the active agent. In any case, there are numerous instances of the phenomenon occurring in alkaline solutions, and this view cannot explain periodicity at the cathode.

The former experiments on the anodic dissolution of copper in hydrochloric acid (J., 1926, 1538) seemed to indicate that the oxidic film was first deposited in an unstable state which in time reverted to a stable, poorly resistant film. The change in state of the film affords the necessary discontinuity. If this explanation were correct, the frequency would depend on the stability of the film and not on the rate of stirring, and it therefore seems probable that the changes observed in the film are due to the action of the hydrochloric acid. In a recent paper, Lillie (*Science*, 1928, **47**, 593) discusses the analogies between the periodic passivity of iron immersed in nitric acid of certain concentrations and physiological periodicity, and maintains that the interval between the active periods "represents a temporary non-transmissive or 'refractory' period, during which the reactive molecules are to be regarded as assembling at the surface, and presumably there undergoing orientation or other change favorable to reaction." This view is identical with the unstable-film theory mentioned above, but the present experiments do not support any view based on a change occurring in the metal or in the film with which it is coated. It is evident that the cause of the activation lies in the solution and not in the electrode.

Periodic phenomena in electrolysis are encountered only between certain well-defined border-line conditions, and the idea of a critical concentration of some ion required to effect the change of the electrode from one state to the other is capable of extension to all the systems examined, both at the anode and at the cathode. Indeed, experiments on the periodic electrodeposition of metals through secondary reaction (J., 1927, 1077) afford strong independent support for the view, and are difficult to explain in any other way.

Physiologists use a similar view to explain the periodicity of breathing: respiration occurs every time the carbon dioxide content (hydrogen-ion concentration) of the blood reaches a threshold value. Although the older idea, that the heart-beat is caused by alternate reaction with or absorption of calcium and potassium ions, does not appear to be greatly favoured by physiologists, it may be pointed out that analogous mechanisms do exist. For example, in the electrolysis of mercury potassium cyanide solutions, under certain conditions the potassium liberated at the mercury cathode reacts alternately with water molecules and with the complex $Hg(CN)''_4$ ions or undissociated salt, the effect being a periodic evolution of hydrogen alternating with deposition of mercury. The supposition is here that reaction of potassium with the complex ions does not take place until the ions reach a certain critical concentration by diffusion. In colloid systems, critical concentrations of ions are required for coagulation, and such systems appear to be particularly favourable for periodic phenomena.

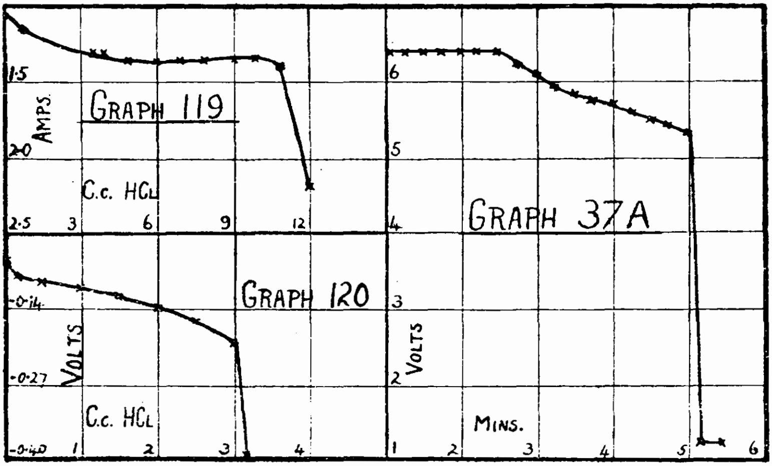
One experimental result appears to contradict the theory that has been developed. The temperature coefficient of the periods given by a rotating copper anode in 40% hydrochloric acid, determined by measuring the frequency at 30° and at 40°, was found to be 1·8 per 10°—a high value if the frequency is controlled entirely by a diffusion process. However, the difficulty of interpreting the temperature coefficient of a complicated series of chemical and physical processes is well known. The temperature coefficient of the heart-beat is anomalous (Bayliss, "General Principles of Physiology," p. 43).

Experimental Evidence of Critical Concentrations.

If the fall of potential is due to the hydrochloric acid slowly reaching a critical concentration by diffusion in the neighbourhood of the anode, it should be possible to produce the same effect by adding hydrochloric acid directly to a permanently "passive" anode. This has been done. A copper anode was rotated at 120 r.p.m. in 15% hydrochloric acid, a *C.D.* of 300 milliamp./cm.^{2} being used. The film soon appeared and the *C.D.* fell to 147 milliamp./cm.^{2}, at which it remained constant, for the high *C.D.* is above the region of periodicity, the film remaining permanently. Hydrochloric acid (*d* 1·16) was added in small quantities at a time to the stirred liquid, and the amount of current passing was read after each addition. In Graph 119 (Fig. 4) the total current is plotted inversely against the number of c.c. of hydrochloric acid. Gradual addition of hydrochloric acid causes a slow fall in potential until a certain concentration is reached, whereupon the fall becomes sudden. That this artificial process is identical with that occurring naturally in the periodic dissolution is evident by a comparison of Graph 119 with Graph 37A (Fig. 4) (reproduced from part of Graph 37; J., 1926, 1536), which shows the manner of fall of potential during one period.

Further evidence has been sought in the change from passive to active iron, the passivity being produced by purely chemical means. Previous work has shown that a change from the passive to the active state can generally be made to proceed periodically, whether the passivity is produced by chemical means or by anodic polarisation. A strip of electrolytic iron was rotated at 180 r.p.m. in nitric acid (d 1·46), and successive small quantities of hydrochloric acid (d 1·16) were added at intervals. After each addition, the potential against a N-calomel electrode was measured by means of a string electrometer. The results are plotted in Graph 120 (Fig. 4) and show that here also activation occurs suddenly when a certain critical concentration of chlorine ions is reached.

FIG. 4.



From the form of the curves and from general considerations, it does not seem likely that *no* reaction occurs until the critical concentration is reached, but that the rate of reaction with a given ion increases very rapidly with the concentration of the ion until it becomes practically instantaneous. This is the significance of the critical concentration, just as in crystallisation the older view of the existence of a definite metastable limit has been replaced by the idea of a rapid increase in the number of nuclei with the degree of supercooling (Tammann, " Kristallisieren und Schmelzen," Leipzig, 1903).

Summary.

Experiments designed to elucidate the mechanism of periodic phenomena in electrolysis have been conducted by using a rotating anode, the system chosen for examination being the anodic dissolution of copper in hydrochloric acid. The frequency of the periods is independent of *C.D.* over a certain range and later decreases with increase of *C.D.* It is shown that this second stage is due to the accumulation of cuprous chloride at the electrode. The characteristic frequency (*i.e.*, that during the stage which is independent of *C.D.*) increases linearly with the rate of rotation of the anode and with the concentration of the hydrochloric acid. The periods are independent of the rate of formation of ions from the metal, but depend on the rate of supply of chlorine ions to the anode, and it appears that the chlorine ions have to accumulate to a certain critical concentration before the film covering the anode during each period can be dissolved : reaction in each pulse is complete and this gives rise to the periodicity. Direct evidence of the existence of such critical concentrations has been obtained by the progressive addition of hydrochloric acid to (*a*) copper rendered passive by anodic polarisation in hydrochloric acid, (*b*) iron rendered passive by concentrated nitric acid. A theory of anodic polarisation and its relation to passivity previously advanced is amplified.

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