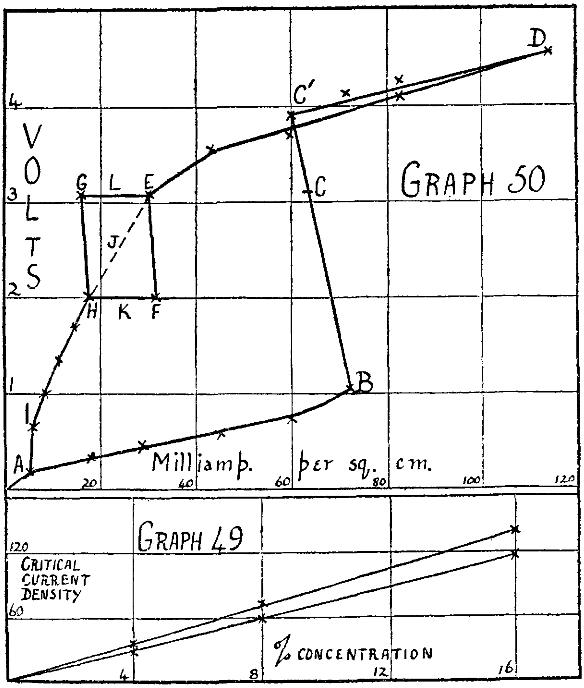
CCCXXXIX.—*Periodic Phenomena at Anodes of Magnesium, Zinc, Cadmium, Mercury, Tin, and Lead, and at an Unattackable Anode.*

By Ernest Sydney Hedges.

A recent paper (this vol., p. 1533) described the course of the electrolysis of a number of solutions with anodes of copper and of silver at varying current densities. It was shown that the electrode in many cases existed in one state at low current densities and in another state (covered with a poorly conducting film) at high current densities, whilst there existed a well-defined intermediate region in which the electrode alternated in regular periods between these two states. The present investigation is an extension of this work to other metallic electrodes.

One point of difference may be noticed between these experiments and those formerly described. Whereas in the experiments with copper and silver the region of periodicity could be reached by progressively increasing the current density, that is not always the case with the present series of metals. Instead, the electrode is first made to assume its pseudo-passive state by employing a high current density, and then the current is reduced until the region of periodicity is encountered.

Fig. 1.



EXPERIMENTAL.

The experimental method was described in the former paper (*loc. cit.*). The experiments were conducted at 30°, and the solutions were stirred by a stream of air bubbles. A platinum cathode was used throughout.

(1) *Zinc Anode.*

Sodium Hydroxide Solutions.—At low current densities a zinc anode dissolves in sodium hydroxide solution with formation of sodium zincate. At higher current densities a film forms over the metal, the *P.D.* rises, and oxygen is evolved, but at the same time the zinc continues to dissolve. By suitably reducing the current, a region of oscillating potential is encountered.

The Current Density-Potential Curve.—Graph 50 (Fig. 1) shows the *P.D.* between the zinc anode and the platinum cathode in electrolysing an 8% solution of sodium hydroxide with increasing current density. For low values of current density, the *P.D.* rises along the line AB until the critical value 72 milliamp./sq. cm. is reached. At this point a film forms over the electrode and the *P.D.* rises from 1·1 to 3·1 volts (C). After the lapse of a second or so, evolution of oxygen ensues and the *P.D.* rises to 3·9 volts (C′). Further increase in current density causes the *P.D.* to rise slowly along the line C′D. If the current is now gradually reduced, the *P.D.* retraces approximately the same path and continues to the point E. If an attempt is made further to reduce the *P.D.* along EJH, it falls of its own accord to a considerably lower value and then regains the value 3·0 volts by a series of *damped* oscillations, *i.e.*, the *P.D.* oscillates with damping between E and F, L and K, G and H, etc. The point H represents the lower limiting current density for periodicity, and on further reduction the *P.D.* falls along HI and at the point I decreases rapidly.

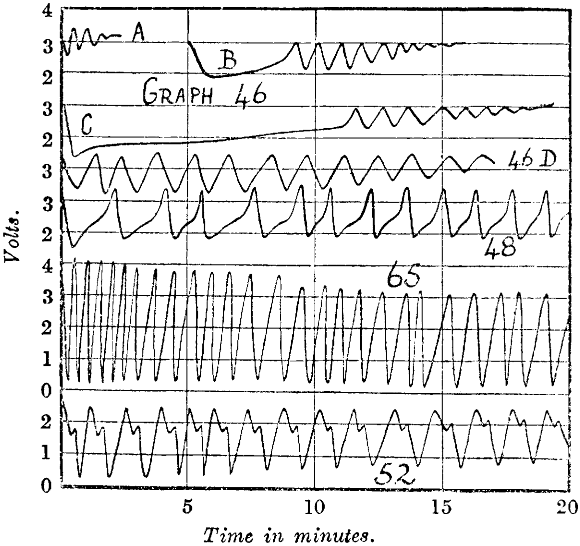
The Nature of the Damped and Continuous Periods.—In order to realise the conditions for periodicity in this system, a current density somewhat greater than 72 milliamp./sq. cm. should be used, and after the film has formed and the *P.D.* has assumed the high value, it should be reduced slowly to 3·0 volts and then quickly to any value between 2 and 3 volts. Examples of the damped curves are given in Graph 46 (Fig. 2), where A shows the rapid damping when the *P.D.* is reduced to 2·9 volts, B represents a reduction to 2·8 volts, C shows the effect of reducing the *P.D.* to 2·7 volts, and D records well-developed oscillations obtained by reducing it to 2·3 volts. In general, the further the *P.D.* is reduced in the direction of H (Graph 50) the slower is the damping of the oscillations, whilst systems represented between E and J are rapidly damped. The longer series are preceded by an induction period (not plotted in Graph 46D).

In 16% sodium hydroxide solution the same series of events occurs, but the oscillations taking place within the corresponding region of periodicity are continuous instead of damped. They may continue for many hours. The difference is doubtless due to the superior solubility of zinc oxide in the stronger alkaline solution. The limits between which the periods are to be observed are also much wider. An example of these continuous waves is given by Graph 48 (Fig. 2). These periods were investigated at 20—80°; with rising temperature the critical current density required to produce the film and the frequency of the periods both increased. In 4% sodium hydroxide solution, damped periods were obtained, but their region of existence was very narrow.

Graph 49 (Fig. 1) shows that the critical current density required to produce the film, the final current density after formation of the film, and the potential of oxygen evolution are all linear functions of the concentration of the solution between the values 4% and 16%

At the critical current density, a white film, probably of zinc hydroxide, travels up the metal and the *P.D.* rises. Almost immediately the film turns brown, oxygen is evolved, and the *P.D.* rises still further. Eventually the film becomes black. This film was observed by Newbery (J., 1916, **109**, 1073), who promised an investigation of its nature. It may be simply zinc oxide, for it is readily soluble in acids and alkalis, and zinc oxide is known to pass into a brown form under the influence of compression, light, etc. (Tafel, *Ann. Physik*, 1903, **11**, 613).

Fig. 2.



The production of periods depends on reducing the *P.D.* to just below the point of incipient oxygen evolution. The line GLE is almost equipotential with C (Graph 50). In 8% solutions, the film remains on the anode throughout the periods and oxygen is evolved just at the peaks of the waves. In 16% solutions, at the peaks of the waves where evolution of oxygen occurs, the film is thrown off into the solution and a fresh film forms at the lower value of potential. The electrode only preserves its metallic surface below the point represented by I, where a sudden drop in the *P.D.* occurs. The oscillation, then, is not between the states represented by AB and C′D, as in the experiments with copper, but is, in this case, between the states BC and CC′. This explains why the periods are obtained by reduction from a high voltage rather than by progressive increase in current density. The periods are formed by carefully setting the system in the state represented by point C, where it has equal opportunities of existing in the state CC′ or CB; but the point C cannot be reached from below, for the film sets in at B and the *P.D.* rises rapidly.

Sulphuric Acid Solutions.—Solutions of the following concentrations * were examined : 100, 90, 60, 50, 45, 42, 40, 35, 30, 5, 2, 1, 0·5, 0·1%. The 100% and 90% solutions were almost non-conducting, owing to the formation of an insoluble film of zinc sulphate. In the 60% and 50% solutions, the sulphate film readily formed over the electrode, the *P.D.* rising to a high value and oxygen being evolved. With solutions below 35%, the preliminary reaction of the zinc with the acid was very energetic and no film formed on the electrode over the range of current densities employed. In the case of the very dilute solutions (below 2%), an oxide film formed on the electrode at high current densities, but this was loosely adherent and did not appreciably affect the strength of the current.

The range of concentrations favourable to periodic phenomena is 40—45% of sulphuric acid, which is intermediate between the regions of permanent existence and of non-existence of the sulphate film : the best concentration is 42%—in this solution, at a current density of 142 milliamp./sq. cm., a white film sweeps up the metal and the *P.D.* rises to 3·3 volts. The *P.D.* should then be reduced to below 2·5 volts. As in the sodium hydroxide solutions, in this case also the *P.D.* drops of its own accord some way farther still and then periodically regains the value 2·5 volts, which is the potential of oxygen evolution in this solution. An example of the continuous periods produced, showing an amplitude of 2 volts, is given in Graph 52 (Fig. 2). A visible sign of the periodicity is the evolution of oxygen every time the *P.D.* reaches its highest value. Reduction of the *P.D.* to different values showed that the frequency increases at lower current densities.

Since the phenomenon is produced under conditions such that the zinc sulphate film is given opportunities both of being formed and of dissolving, it was hoped to obtain similar effects in strong aqueous

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* Throughout this paper " % concentration of acid " means the number of c.c. of sulphuric acid (*d* 1·84), nitric acid (*d* 1·42), or hydrochloric acid (*d* 1·16) per 100 c.c. of solution.

solutions of zinc sulphate. These were not realised, however, for all changes were exceedingly sluggish, perhaps as a result of the high viscosity of the liquid. A solution saturated at 30° with $ZnSO_4,7H_2O$ took a current of 20 milliamp./sq. cm. before the formation of a film. This indicated that such a solution can dissolve considerably more anhydrous zinc sulphate. When the film formed, the *P.D.* rose from 0·8 volt to 4·6 volts in the course of several minutes, and then oxygen was evolved. Periods could not be obtained on reducing the *P.D.*, every movement of the voltmeter needle taking several minutes for its completion. Similar unsuccessful attempts were made with solutions 90% and 80% saturated.

Experiments in Other Solutions.—The following is a list of solutions in which periodic phenomena were not encountered, together with brief notes on their behaviour : Hydrochloric acid, 10, 5, 2, 1, 0·5% : at very high current densities a dark grey film formed on the metal, but did not affect the current strength; nitric acid, 20, 12·5, 10, 5, 2·5, 1, 0·5% : at high current densities, a non-adherent, white, flaky substance fell continuously from the anode; potassium cyanide, 20, 10, 5, 2·5% : these solutions behaved as if they were dilute potassium hydroxide solutions; ammonium chloride, 5, 2%; ammonium sulphate, 10, 5, 2, 1%; sodium nitrate, 5% : loose gelatinous zinc hydroxide fell continuously from the anode even at fairly low current densities; potassium iodide, 3%; potassium chromate, 10%; sodium phosphate, 5% : insoluble films readily formed over the anode; sodium hydrogen sulphite, 4, 2%; sodium acetate, 7·2%; acetic acid, 6%.

(1A) *Zinc Amalgam Electrode.*

Periods similar to those described for zinc were obtained with an amalgamated zinc electrode in 42% and 30% solutions of sulphuric acid. In the former case, a white film formed over the anode at a current density of 50 milliamp./sq. cm. and the *P.D.* rose to 11·5 volts. On reducing it to 2·6 volts, continuous oscillations between 2·6 and 0·8 volts ensued. These had a period of 30 seconds.

With this system, although the method of procedure outlined above is the readiest means of producing the effect, the periods enter without any adjustment of the potential if a slightly lower current density than that advised is employed and the electrolysis is allowed to proceed for an hour or so. Joule (*Phil. Mag.*, 1844, **24**, 106) noticed periodic film formation in this system.

(2) *Cadmium Anode.*

Sodium Hydroxide Solutions.—Cadmium oxide, unlike zinc oxide, is not soluble in sodium hydroxide solution, and periodic film formation is therefore not to be expected. A brown film formed over the anode and oxygen was evolved at quite low current densities. Since the oxide is soluble in ammoniacal solutions, however, an attempt was made, but unsuccessfully, to produce periodic phenomena by electrolysing various mixtures of sodium hydroxide and ammonia.

Sulphuric Acid Solutions.—The following concentrations were examined over the range of current densities available : 100, 80, 60, 40, 35, 30, 25, 20, 10, 5, 2, 1%. In solutions of 60% and above, an insoluble sulphate film readily formed over the electrode, and no film formed at the current densities used in solutions weaker than 20%. The concentration range of existence of periodic phenomena is 25—35% of sulphuric acid. Since the best effect is obtained in 30% acid, the conditions will be described for that concentration. The concentration range is below that of zinc.*

In 30% sulphuric acid solution, a white film formed over the cadmium when the current density was raised to 108 milliamp./sq. cm. and the *P.D.* rose from 0·3 volt to 12·0 volts, oxygen being evolved. The *P.D.* was then reduced to 4·0 volts and continuous periods of large amplitude followed. An example in which the *P.D.* oscillated between 0 and 3—4 volts is given in Graph 65 (Fig. 2). At the peaks of the waves evolution of oxygen occurred.

Potassium Cyanide Solutions.—Oscillations between 2·6 and 3·0 volts were obtained in 5% potassium cyanide solutions by using a current density of 42 milliamp./sq. cm. and, after formation of the film, reducing the *P.D.* to 3·0 volts. The cadmium then dissolved as the double cyanide. In a 2·5% solution, periods from 2·2—2·4 volts were obtained similarly. Periods were not produced in 10% and 20% solutions.

Experiments in Other Solutions.—The following did not furnish periodic phenomena : Hydrochloric acid, 10, 5, 2, 1% ; nitric acid, 10, 5, 2, 1% : in the more dilute solutions a white, flaky substance fell continuously from the anode at somewhat elevated current densities; ammonium sulphate, 10, 5, 1%.

(3) *Mercury Anode.*

The mercury used in these experiments was redistilled immediately before use. It was contained in a small glass cup 1 cm. in diameter, of the type used in the ordinary mercury voltameter. A

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* The following incident testifies to the reproducibility of these results. The author was given a sheet of metal reputed to be cadmium; its behaviour in various solutions was investigated and the limits of periodic action were determined. The results obtained were identical with those for zinc, and it was then found that the metal was in reality zinc.

special feature of the mercury periods is that a concomitant periodic change in the surface tension occurs, causing the mercury surface alternately to be flattened and elevated.

Potassium Cyanide Solutions.—These experiments were conducted at 20° and the solutions were not stirred. The mercury surface remained bright until the current density reached 70 milliamp./sq. cm. At this point a black film spread over the surface, causing the meniscus to flatten, and the *P.D.* rose from 2·3 to 4·0 volts, oxygen being evolved. The periods were best produced by then lowering the *P.D.* to 3·0 volts. This gave a continuous oscillation in 10-second periods between 2·6 and 2·9 volts. On slightly increasing the current density the oscillation was between 2·8 and 3·3 volts and, in accordance with the general rule, the frequency was lower at the higher current density. The film remained throughout, but a few bubbles of oxygen were evolved at the crests of the waves. The mercury meniscus flattened perceptibly while the potential was at the lower value and became more convex at the higher value.

The periods may also be formed directly by electrolysing the solution with a *P.D.* of 2·0 volts; the black film will then form in 15 minutes or so and will be followed by the oscillations. The formation of the film is generally preceded by much trembling on the part of the mercury surface and the voltmeter needle. The upper limit of the region of periodicity is 3·5 volts. Similar periods of lower frequency were obtained in 10% potassium cyanide solution. The reaction is probably similar to the experiments with copper—hydroxyl ions are discharged first and the mercurous oxide dissolves in the potassium cyanide.

Sodium Hydrosulphide Solutions.—In a 10% solution a black film readily formed over the anode. Periods similar to those obtained in potassium cyanide solution were produced by applying a current density of 7 milliamp./sq. cm. These were between 1·0 and 1·2 volts.

Nitric Acid Solutions.—The concentrations examined were 40, 25, 10, 5%. In the last two solutions, a yellow, basic mercurous nitrate formed at a certain critical current density. In the 40% solution, a grey, crystalline film, probably of mercurous nitrate, formed at high current densities. In the 25% acid at a current density of 20 milliamp./sq. cm., a grey film formed and the mercury surface pulsated rapidly and continuously, although the voltmeter needle remained constant at 1·1 volts. After a time, the *P.D.* rose suddenly to 3·2 volts, the film became thick and white, and the pulsations ceased. On reducing the current very slightly, the *P.D.* dropped again to 1·1 volts and the rapid pulsations (3 or 4 per second) continued. Occasionally the pulsations did not affect the mercury meniscus as a whole, but took the form of gyrations starting from some point on the periphery.

Experiments in Other Solutions.—Periodicity was not encountered in the following solutions : Hydrochloric acid, 25% : insoluble mercurous chloride formed on the anode at the lowest current densities; sulphuric acid, 100, 20, 10, 5, 2, 1% : insoluble mercurous sulphate formed; sodium hydroxide, 8% : at the lowest current densities an insoluble, yellow film formed on the electrode and oxygen was evolved. Potassium iodide solutions (40, 30, 20%) were expected to yield periodic phenomena, since the film formed dissolved in the solution when the circuit was broken. All attempts to render the system periodic by increasing the solvent power of the potassium iodide (employing strong solutions and extending the examination up to 60°) were fruitless. When mercurous iodide dissolves in potassium iodide, however, it goes into the mercuric state, with separation of mercury. It seems possible that this complication stops the periodicity.

(4) *Magnesium Anode.*

Only one example, and that a poor one, of periodicity at a magnesium anode has been found.

Sulphuric Acid Solutions.—The following concentrations were examined : 100, 95, 90, 80, 75, 70, 65, 60, 55, 50, 45, 40%. The behaviour was not quite the same as in the corresponding experiments with zinc and cadmium. In solutions of concentration 70% and above, a resistant film very readily formed on the anode and the *P.D.* rose to a high value; the metal, however, then assumed a peculiarly bright lustre. On breaking the current, the high potential state persisted. This is not unlike the passivity phenomenon observed with anodes of iron and nickel. The metal continues to dissolve when in this state. In solutions weaker than 50%, magnesium dissolved with great vigour and the surface remained dull. Only at the concentration 65% was any periodic effect observed. With a current density of 50 milliamp./sq. cm., the *P.D.* rose suddenly to 5·0 volts. On reducing it slowly to 1·8 volts, slow oscillations between 1·2 and 1·5 volts followed.

In this group of elements, therefore, the limits of periodicity in sulphuric acid solution are defined by the following concentrations : Magnesium, 65% ; zinc, 45—40% ; cadmium, 35—25% ; mercury, nil.

Experiments in Other Solutions.—All these failed to give periodic effects : Hydrochloric acid, 3% ; sodium hydroxide, 8% ; ammonium chloride, 1% ; ammonium sulphate, 5, 0·5% ; potassium iodide, 2% ; potassium cyanide, 10, 5, 2, 1% ; sodium nitrate, 2% ; sodium phosphate, 5%.

(5) *Tin Anode.*

Sulphuric Acid Solutions.—100, 90, 60, 40, 30, 20, 10, 5, 3, 1, and 0·5% Solutions were examined. The phenomena observed were in every respect similar to those with zinc and cadmium electrodes. Periods were produced only in the 5% solution. With a current density of 175 milliamp./sq. cm. a white film formed over the anode, the potential rising from 1·7 to 4·4 volts. After the lapse of a second or so, evolution of oxygen set in and the potential rose further to 5·7 volts. Reduction to 4·0 volts gave a damping oscillation. Reduction to 3·0 volts proved to be too low, for the film came off entirely. By reducing the potential to 3·5 volts, continuous oscillations between 2·2 and 3·2 volts followed, having a period of one minute.

Nitric Acid Solutions.—100, 80, 60, 40, 30, 20, 10, 5, 2, 1, and 0·5% Solutions were examined. In those stronger than 40% the preliminary reaction was extremely vigorous, giving a voluminous product of hydrated stannic oxide. In 100% nitric acid, once the reaction had started, it required a current density of roughly 10,000 milliamp./sq. cm. to form a coherent film of oxide, which stopped further action even when the circuit was broken. In solutions below 20%, a grey substance (probably a mixture of stannic and stannous oxides) fell continuously from the anode. Periodic phenomena occurred in 1% and 0·5% solutions. In the former case, a black film formed over the anode at a current density of 30 milliamp./sq. cm. and the *P.D.* rose from 1·1 to 1·6 volts. By reducing it to 1·3 volts, continuous oscillations between 1·1 and 1·5 volts followed.

Experiments in Other Solutions.—No periodic phenomena observed: Hydrochloric acid, 30, 15, 10, 5, 2, 1%: in the last two solutions a dark film of stannous oxide formed slowly at high current densities, but did not appreciably impede the current; potassium cyanide, 20, 10%: the solution behaved as though it were dilute potassium hydroxide; ammonium chloride, 10, 2%; sodium nitrate, 10, 5%: these solutions soon became cloudy with a white, gelatinous precipitate, part of which loosely adhered to the anode. With sodium hydroxide (32%), there should be a possibility of periodicity. A film formed on the anode at a certain critical current density, but on breaking the circuit the film was very slow to dissolve. Experiments were then carried out at various temperatures up to 80° in an attempt to quicken the dissolution of the film, but the movements of the voltmeter needle were still very sluggish.

(6) *Lead Anode.*

The experiments with lead have furnished only one case of a periodic effect. In fact, the behaviour of lead as an anode is truly saturnine, all changes in potential being exceedingly sluggish and sometimes taking 10 minutes for completion. In general, periodic phenomena seem to be best developed in a film which forms rapidly over the electrode, whilst experience goes to show that a slowly-forming film does not exhibit periodic phenomena. If the periodicity is in all these cases connected with a certain instability of the film as first deposited (this point having been demonstrated at least in the case of copper), it may be that a slowly forming film assumes a stable state before its completion.

Sodium Hydroxide Solutions.—At low current densities, the lead anode dissolved smoothly and at a certain value a film of lead peroxide formed over the metal, the *P.D.* rose, and oxygen was evolved. Solutions of composition 32, 16, 8, 4, 1% were examined at 20—60°. The formation of the film was very slow and only at the higher temperatures and concentrations did the film redissolve when the circuit was broken. Continuous periods were never realised, but in a 32% solution at temperatures above 50° the rise in *P.D.* denoting film formation was always preceded by several preliminary oscillations. It appears that the film may exhibit periodicity when incompletely formed, but not after it has entirely covered the electrode.

Negative Results with Lead.—In the following solutions, changes in potential were exceedingly sluggish and periodicity was not observed: Hydrochloric acid, 100, 60, 40, 25, 10, 5, 2, 0·5% at 30—90°; sulphuric acid, 100, 50, 20, 5%; nitric acid, 30, 20, 10, 5, 2, 1%; potassium cyanide, 10, 2·5%; ammonium acetate, 10, 1%; potassium iodide, 3%.

Discussion.

The present work and the previous experiments on copper and silver embody the results of the examination of more than 500 different systems, and from this exhaustive study it is possible to lay down some of the conditions necessary to secure periodic effects. (1) A film must form over the anode. (2) This film must be soluble in the electrolyte when the circuit is broken. It follows that the electrode may exist in one of two possible states—with or without the film. This leads to the third condition. (3) The current density must be between two well-defined limits which depend on the temperature, concentration, and nature of the solution. Periodic phenomena can be realised by so arranging the current density that the electrode has almost equal chances of remaining in one state or passing into the other. The result is that the electrode oscillates continuously between these two states. The region over which this periodic effect can be observed is often very narrow, but sometimes (as in the case of copper in hydrochloric acid) is quite extensive.

The results which have been described illustrate very forcibly the conditions which have just been laid down. Some other factor is required, however, in order to explain the fundamental *cause* of the periodicity. Although in one case it has been shown that the film first appears in a metastable form, there is not yet sufficient evidence to regard this as a general explanation. It is hoped that further evidence on this point will result from the experiments at present in progress.

(7) *Platinum Anode.*

In order to test the conclusions set forth in the Discussion from a different point of view, experiments were carried out on film formation at an unattackable anode of platinum.

If a film is deposited electrolytically on the anode under such conditions that it will redissolve in the electrolyte when the circuit is broken, periodic film formation should occur when the current density is such that the rates of formation and dissolution of the film are approximately equal.

To devise favourable cases for such a study at the anode was a matter of some difficulty. The most suitable case would be the electrodeposition of sulphur from solutions of alkali sulphides and of iodine from alkali iodides. The former case was examined by Köhlichen (*Z. Elektrochem.*, 1901, **7**, 629) and by Küster (*Z. anorg. Chem.*, 1905, **46**, 113), and well-defined regular periods were observed under certain conditions. Similar periods were observed by Kremann and Schoulz (*Monatsh.*, 1912, **33**, 1291) in the electrolysis of solutions of iodides. Although the cause of this effect was not apparent at the time, it seems that the periodicity was observed between certain limits such that the film had approximately equal chances of forming and of dissolving. The fact that ease of periodic film formation was parallel with facility of polyiodide formation is additional evidence on this point.

Windelschmidt (*Diss.*, Münster, 1907) and Dietrich (*Diss.*, Münster, 1910) examined the anodic deposition of nickel hydroxide from ammoniacal solutions of nickel sulphate and found that under certain conditions a film of nickel hydroxide alternately formed and dissolved in the ammonia.

The author has studied the electrolysis of a number of solutions of this type and has observed periodicity in several cases. In many instances, however, the films are poorly adherent and the resulting waves are very irregular, whilst in others the films are so loose that the current strength is not affected thereby. No attempt has been made to fix the best conditions for the appearance of periodic phenomena in these systems, the sole object of the examination being to test the views expressed above on periodic anodic phenomena.

Ammoniacal Silver Nitrate Solutions.—Solutions of silver nitrate containing a considerable excess of ammonia deposited all the silver on the cathode. Solutions which were precipitated by ammonia, the precipitate being incompletely redissolved, after filtration deposited silver on the cathode and black silver peroxide on the anode. By using a little more ammonia the silver peroxide was given an opportunity to redissolve, and then periodic phenomena were realised between certain limiting current densities. A typical solution consisted of 50 c.c. of $N/10$-silver nitrate, and 10 c.c. of $2N$-ammonia made up to 100 c.c., and was electrolysed at 30° with a current density of 40 milliamp./sq. cm. The *P.D.* oscillated between 2·4 and 2·7 volts in periods of 1·5 minutes. The frequency decreased with increasing current density. Several other solutions of varying composition were tried with equal success, but no systematic examination of the effect of varying the conditions was attempted.

Incidentally, although silver peroxide is produced at the anode when strong solutions of silver nitrate are electrolysed, it is curious that it should be obtained in the ammoniacal solutions described above, where all the silver is supposed to exist as the $Ag(NH_3)_2^{\bullet}$ ion. This point might repay investigation, for the effect is not produced if ammonia is added in excess.

Potassium Silver Cyanide Solutions.—When an excess of potassium cyanide was used, the only product was silver at the cathode. Filtered solutions containing insufficient potassium cyanide to redissolve all the precipitated silver cyanide gave, in addition to silver at the cathode, a deposit of silver cyanide on the anode. By adding a very slight excess of potassium cyanide irregular periods were produced. The lack of regularity is probably to be traced to the " patchy " nature of the film.

Copper Solutions.—Solutions of cupric chloride or cupric sulphate containing just sufficient ammonia to redissolve the precipitated hydroxide gave different products at the anode, according to the current density used. To 50 c.c. of 5% cupric chloride was added the required amount of ammonia and the solution was then made up to 100 c.c. In addition to a deposit of metallic copper on the cathode, at a current density of 4 milliamp./sq. cm., a black deposit of cupric oxide formed on the anode : at a current density of 8 milliamp./sq. cm., the anodic product was blue cupric hydroxide, whilst at current densities above 40 milliamp./sq. cm. no film formed and oxygen was evolved.

In the presence of a slight excess of ammonia feeble periods were observed in the onset of the first cupric oxide film. On addition of more ammonia the only anodic product was oxygen. At low current densities the cupric oxide was deposited on the platinum anode initially in a film so thin as to give a series of bright interference colours resembling those to be seen on the surface of copper (compare Evans, J., 1925, **127**, 2487).

Solutions of copper salts were precipitated by potassium cyanide and the precipitate was just redissolved. The results of electrolysis were similar to those in the case of ammoniacal solutions in that at low current densities a golden-brown cyanide film formed on the anode, whilst on slightly increasing the current density the product was a green basic cyanide and at higher current densities only oxygen was produced. In these solutions, however, periodicity was never observed.

Electrolysis of Other Solutions.—Feeble periods were encountered in the electrolysis of solutions of cobalt sulphate to which had been added a slight excess of ammonia, and in solutions of chromium sulphate containing a slight excess of sodium hydroxide. These gave deposits of hydroxide on the anode. Zinc cyanide, redissolved in a slight excess of potassium cyanide, gave a deposit of zinc cyanide on the anode, and between certain values the current was always unsteady.

Anodic films were obtained in the electrolysis of solutions of aluminium sulphate, stannic chloride, and stannous chloride in sodium hydroxide, but these were very loose and did not impede the current. Lead acetate in sodium hydroxide solution gave a deposit of lead peroxide which was not sufficiently readily soluble in the solution to produce periodicity. Cuprous chloride in hydrochloric acid gave cupric chloride as a soluble anodic product. Mercuric potassium iodide gave mercuric iodide and iodine at the anode and would probably have served admirably for the purpose of obtaining a periodic electrolysis, but further experiments were not carried out since the iodine alone could account for the effect. Silver chloride in ammonia gave a loose deposit of silver chloride at the anode, which was unsuitable for the present purpose.

Anodic deposits were not produced when ammoniacal solutions of cadmium nitrate or of zinc sulphate were electrolysed, or in the electrolysis of sodium zincate solutions.

Experiments on the electrolysis of mercury potassium cyanide solutions and of cadmium cyanide gave well-marked periods where the seat of the periodicity was the *cathode*, at which a periodic evolution of hydrogen was visible. These are the first examples of periodicity at the cathode that the author has observed, and attention is being directed to them.

Summary.

Periodic changes in potential and in current strength were observed between certain current densities in the electrolysis of the following solutions, a platinum cathode being used throughout: Zinc anode with sodium hydroxide, sulphuric acid; amalgamated zinc anode with sulphuric acid; cadmium anode with sulphuric acid, potassium cyanide; mercury anode with potassium cyanide, sodium hydrosulphide, nitric acid; magnesium anode with sulphuric acid; tin anode with sulphuric acid, nitric acid; lead anode with sodium hydroxide.

In each case the conditions of concentration of the solution and current density were worked out and their effects on the nature of the periods determined.

Some of the conditions for periodic phenomena at the anode have been deduced. The conclusions have been verified by experiments on the electrolysis of solutions producing a film at an unattackable anode. Periodic phenomena were observed when the film had equal chances of dissolving and of forming.

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