

CXXXIX.—*Periodic Electrochemical Phenomena.*

By ERNEST SYDNEY HEDGES and JAMES ECKERSLEY MYERS.

IN continuation of the work being developed in this laboratory on the principle of periodicity in chemistry, some of the periodic reactions previously described (J., 1924, **125**, 604, 1282; this vol., p. 445) have been examined from the electrochemical standpoint. This method not only furnishes a delicate means of following the course of reactions where the rate of evolution of gas is so slow as to render the manometric method inapplicable, but also provides data which are of importance in the elucidation of the mechanism involved in the periodic dissolution of metals. Further, it would seem that the method has a considerably wider scope, being adapted in particular to the case of reactions involving the deposition of metals, and it is intended to continue investigations in this direction.

There are scattered throughout the literature several reported cases of periodic electrochemical phenomena, and as consideration of these is important not only in their bearing on the work described here, but is also essential to the correct presentation of periodicity as a principle, a brief account is given of the results of previous investigators. The work may be considered in two sections: (a) where current is taken from the system, (b) where current is led into the system.

*Section (a).*—Early cases of such periodicity concerning an iron electrode are mentioned by Fechner (*Schweigg. Journ.*, 1828, **53**, 141) and by Schönbein (*Pogg. Ann.*, 1836, **38**, 444). Kistiakowsky ("Nernst-Festschrift, Knapps Verlag," Halle-a-S., 1912) obtained a periodic current from the cell—Fe(rusted)|5% K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, N-H<sub>2</sub>SO<sub>4</sub>|Fe (periodic)—in which the electrode responsible for the periodicity consisted of the purest iron, scrupulously cleaned and then immersed in 10% sulphuric acid before the experiment. By employing two electrodes of similarly treated iron in the same solution, he suc-

ceeded in making a cell which produced an alternating current—the two electrodes periodically reversing in polarity (*Z. Elektrochem.*, 1909, **15**, 268). It is interesting to observe that in this case the metal requires a quite definite form of treatment or activation. Kistiakovski also found (7th Intern. Congr. Appl. Chem., 1909, Sect. 10, 56) that iron becomes alternately active and passive in dilute nitric acid, chromic acid, or potassium permanganate solution.

Brauer (*Z. physikal. Chem.*, 1901, **38**, 441) obtained a fluctuating difference of potential between Ostwald's chromium and the solution in which it dissolved, and Antropoff (*ibid.*, 1908, **62**, 513) found the potential difference between mercury and hydrogen peroxide to vary periodically, synchronising with the periodic evolution of gas. Heyrovský (J., 1920, **117**, 28) describes sudden changes and fluctuations between the values 0.77 and 1.67 volts for the E.M.F. of the cell  $\text{Hg}|\text{Hg}_2\text{Cl}_2, N\text{-KCl}|\text{Al}$ . This is precisely similar to the periodic dissolution of aluminium amalgam in hydrochloric acid described by the present authors (*loc. cit.*, p. 622).

*Section (b).*—Periodic fluctuations in current were observed by Schönbein (*Archives de l'Electricité*, 1842, **2**, 269) in leading a current through the cell  $\text{Fe}|\text{dil. H}_2\text{SO}_4|\text{Pt}$ , and by Joule (*Phil. Mag.*, 1844, **24**, 106) when a potential difference of 3.3 volts was applied to the cell  $\text{Fe}|\text{H}_2\text{SO}_4|\text{Zn}$  amalgam. There were corresponding periods of dissolution of iron and evolution of oxygen at the anode. Heathcote (*Z. physikal. Chem.*, 1901, **37**, 368) states that when a current was passed through the cell  $\text{Pt}|\text{HNO}_3(d\ 1.4)|\text{Fe}$ , the needle of an ammeter placed in series exhibited regular oscillations. Different results were obtained with different pieces of iron and it may be observed that in many of these cases the influence of minute traces of impurities is not excluded, and the effect may be due—as in Ostwald's experiment with chromium—to an activating agent already present in the metal. Fredenhagen (*Z. physikal. Chem.*, 1903, **43**, 1) electrolysed sulphuric acid with an iron anode and obtained a periodic current after addition of chlorine ions. This result may be compared with the experiments of the present authors (experimental portion of this paper) on the deposition of iron on magnesium from solutions in sulphuric acid (non-periodic) and hydrochloric acid (periodic).

Adler (*Z. physikal. Chem.*, 1912, **80**, 385) extended Joule's experiments on the periodic electrolytic dissolution of iron and studied the effect of varying current density and other conditions of experiment. Smits (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 807; *Versl. Kon. Akad. Wetensch. Amsterdam*, 1915, **24**, 745;

1918, 27, 159) found that with certain current densities an iron electrode immersed in a solution containing a mixture of ferrous sulphate and ferrous chloride gave a potential rapidly alternating from a positive to a negative value with an amplitude of 1.74 volts. He explains this as due to the periodic acceleration of establishment of inner equilibrium in the metal by the chlorine ions, but admits that this cannot explain Adler's results.

Another instance of periodic electrolytic phenomena occurring at the anode is given by Müller (*Z. Elektrochem.*, 1904, **10**, 519), who observed pulsations in the E.M.F. of a manganese electrode dissolving in faintly acid sodium phosphate solution. Byers observed a similar effect (*J. Amer. Chem. Soc.*, 1908, **30**, 1729), using a cobalt anode in sodium sulphate solution. Liebreich (*Z. Elektrochem.*, 1921, **27**, 94; compare also Kleffner, *ibid.*, 1923, **29**, 448) describes periodic phenomena in the electrolysis of chromic acid. Kohlrausch reports (*Physikal. Z.*, 1900, **1**, 88) that, when electrolysing platinum tetrachloride for the purpose of preparing pure platinum, he had once obtained a periodic evolution of gas, but subsequent attempts to repeat this had proved unsuccessful.

Periodic changes in anodic potential and in current density were observed by Küster (*Z. anorg. Chem.*, 1905, **46**, 113) and by Köhlichen (*Z. Elektrochem.*, 1901, **7**, 629) during the electrolysis of sodium sulphide solution with platinum electrodes. There was a corresponding periodic formation and dissolution of a film of sulphur over the anode surface. The chief factors in the production of waves were found to be the *size, position, and nature of surface* of the platinum electrodes. In general, the phenomenon did not occur at all when bright platinum foil was used, and a rough surface was found to answer best. These facts find a ready explanation in the light of the experiments of the present authors concerning the activation of metals. In all probability, the periods were only obtained when the platinum was in the active state. Kremann and Schoulz (*Monatsh.*, 1912, **33**, 1291) observed a similar periodicity in the electrolysis of alkali iodides between platinum electrodes. Examples are given of irregular waves resembling those often obtained by the present writers when the activating agent has been a metal. Windelschmidt (*Diss.*, Münster, 1907) and Dietrich (*Diss.*, Münster, 1910) obtained a periodic current in the electrolysis of ammoniacal solutions of nickel salts.

Several cases are also on record of periodic electrochemical phenomena occurring at the cathode. Förster (*Z. Elektrochem.*, 1902, **8**, 500) found the deposition of copper from a strongly acid solution of the nitrate to be periodic at high current densities, and a similar case is quoted by Cohen (*ibid.*, p. 499) in electro-

lysing an acid solution of bismuth nitrate. Kremann and Suchy (*Wiener Sitz.*, April, 1913) found a periodically changing cathode potential in the deposition of a 50% iron-nickel alloy from a mixture of the sulphates. Coehn (*Z. Elektrochem.*, 1901, 7, 633) electrolysed a solution of an alkali salt with a mercury cathode and noticed that the surface of the mercury alternately became grey and then bright, whilst hydrogen was evolved during the bright periods. The course of the phenomenon was registered photographically by Kremann and Lorbeer (*Wiener Sitz.*, April, 1913). Mercury is the one metal which the present authors believe to be normally periodically active. Haber (*Z. Elektrochem.*, 1901, 7, 634) observed periods in the electrolytic reduction of nitrobenzene in alcoholic solution at a platinum cathode.

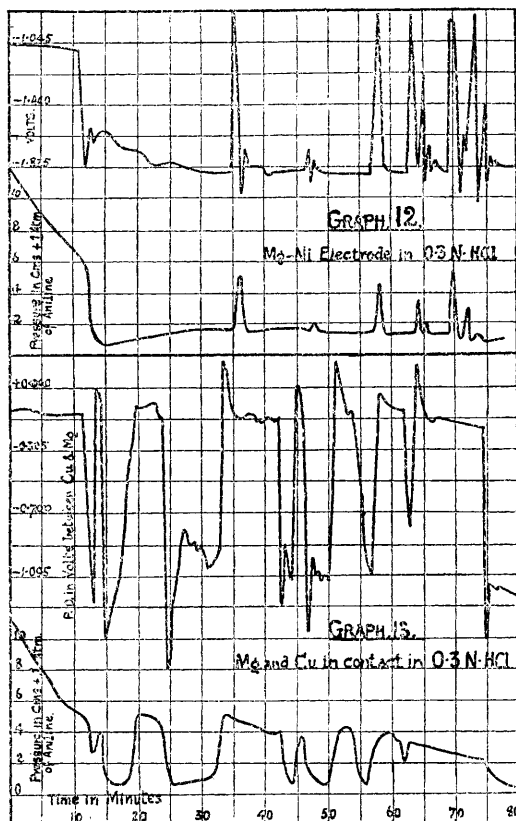
It is relevant to mention the pulsations of the mercury surface observed by Roshdestwensky and Lewis (*Trans. Faraday Soc.*, 1912, 8, 220) when mercuric cyanide was used in a capillary electrometer.

#### EXPERIMENTAL.

*The Apparatus.*—The measurements of potential were made with a Dolezalek quadrant electrometer, the needle of which was charged to 90 volts by means of a battery of dry cells. The system consisted of one or more metal electrodes immersed in the appropriate solution contained in a glass bottle of 100 c.c. capacity, which was fitted with a wide rubber stopper carrying glass tubes through which the electrodes were sealed. The reading scale was so placed that one volt gave a deflection of 273 divisions (mm.). By means of a bridge of saturated potassium chloride solution leading to an auxiliary saturated calomel electrode, it was possible to determine the potential difference between the two metal electrodes immersed in the solution or between each metal and the standard reference electrode. In either case, one electrode was earthed and the other connected to one pair of quadrants of the electrometer, the other pair also being earthed. The method of suspension of the metal electrodes was found to be of importance and in the first experiments, where the metals were suspended from platinum hooks sealed into glass tubes, constant results were not always obtained. The difficulty was overcome by fastening the metals to a stout platinum rod with the aid of a platinum screw. The rod was soldered to copper wire and sealed into glass by means of wax.

In later experiments, in order to compare the chemical and electrical effects, the apparatus was combined with that described by the authors in a previous paper (*loc. cit.*), the course of the reactions being recorded simultaneously on the electrometer scale and on the manometer. The two sets of curves agree very closely

when the frequency and amplitude of the oscillations are not great, but in order to register the short waves electrically it would be necessary to use a more dead-beat instrument. The natural period of the electrometer needle suspended as in these experiments was 16 seconds. Simultaneous readings of potential and of gas pressure were taken every 30 seconds and the potentials recorded



are expressed with reference to the saturated calomel electrode. All the experiments were carried out at room temperature.

#### *Examination of some Metal Systems.*

The authors have already shown (*loc. cit.*) that certain metallic couples dissolve in acids in a periodic manner after the second metallic component (*i.e.*, the cathodic metal which does not dissolve) has been treated or "activated" by certain processes. Graph 12 represents the potential against the saturated calomel

electrode acquired by such a couple of magnesium and nickel sheet dissolving in 0.3*N*-hydrochloric acid, and below is plotted the synchronous variation in gas pressure. The periods are not very regular, but this is often a feature of systems where the activating agent is a second metallic component, and in a former communication (this vol., p. 445) a study was made of the conditions necessary to ensure regularity of wave form.

Simultaneous periodic curves of this type have been obtained with couples of magnesium with platinum, gold, cobalt, and copper in ammonium chloride solution, and with aluminium amalgam in hydrochloric acid. In the example illustrated in the graph, and in many of the other instances mentioned, the periodic nature of the evolution of gas was easily visible to the eye. It appeared that during the periods of high gas pressure the excess of hydrogen came from the nickel or other cathodic metal, the dissolving magnesium preserving at all times a slow and apparently steady rate of evolution of gas. This is quite in accordance with other experiments which indicate that the seat of the periodicity is the second metallic component.

In Graph 13 is recorded the periodic potential difference existing between electrodes of magnesium and activated copper in contact immersed in 0.03*N*-hydrochloric acid. Comparison of this with the foregoing graph shows that the periodic evolution of hydrogen is attended by simultaneous variations in (*a*) the potential of the couple as a whole with respect to the solution and (*b*) the potential difference between the two components. In the latter case, the copper appeared to be quite inert so long as the high potential difference lasted, and when the potentials of the two metals approached each other hydrogen was evolved from the surface of the copper. In the case of magnesium couples, another easily visible indication of the periodicity is to be observed in the behaviour of a dark grey oxide film which appears on the magnesium. This film forms even in acid solution at the point of contact of the two metals and extends for the distance of a millimetre or two. During the periods of strong gas evolution, the film begins to spread and may grow to a length of 1 or 2 cm. When the next slow rate of evolution commences, the film dissolves gradually, but not completely. The formation or dissolution of this oxide film has been observed always to follow and never to precede the change in potential of the couple. The authors therefore regard its appearance as a concomitant effect of the inherent periodicity rather than as a cause of the phenomenon, as in the case of the periodic mercury-hydrogen peroxide catalysis (*loc. cit.*, p. 1283).

Periods have not been obtained, in experiments with platinum,

gold, silver, and nickel as activating agents, when the cathodic and dissolving metals were not in contact. Some contradictory results obtained, with copper, were probably due to the slow dissolution of this metal, which is known to take place in hydrochloric acid, followed by reduction at the surface of the magnesium.

*Effect of Activation on the Potential of Metals.*

It is well known that the condition of the surface of a metal has a considerable influence on the potential it acquires, and experiments by Vieweg (*Ann. Physik*, 1924, **74**, 146) show that the contact potentials, measured against a standard metal, of aluminium, copper, nickel, gold, and platinum are affected by heating in a vacuum in a similar way to the change produced by mechanical cleaning of the surface. It has now been found that the value for the metal after treatment differs considerably from that of the inactive metal. The change is in the negative direction in the cases of copper and silver, and positive in the case of platinum and of gold. The potential of ordinary copper foil in 0.3*N*-hydrochloric acid against the saturated calomel electrode was determined as  $-0.11$  volt and the values  $-0.26$ ,  $-0.19$ ,  $-0.22$  volt were obtained with different specimens of the active metal after scraping. A sample of copper after vacuum-heat treatment registered a potential of  $-0.18$  volt. A silver electrode after vacuum-heat treatment changed its potential in *N*-hydrochloric acid by 0.03 volt in the negative direction. Gold in 0.1*N*-hydrochloric acid gave an initial value of  $+0.17$  volt, changing, after vacuum-heat treatment, to  $+0.25$  volt. Platinum (platinised) in *N*-hydrochloric acid registered a potential of  $+0.19$  volt, which became  $+0.38$  volt after treatment. The difference is not so great as that brought about by depositing platinum black on a platinum surface. The potential of a piece of bright platinum foil in 0.1*N*-hydrochloric acid was  $+0.19$  volt, and this became  $+0.48$  volt after platinising from a solution of chloroplatinic acid. After keeping for 3 days, this high value sank to  $+0.41$  volt. The potentials of activated metals gradually return to the normal value on keeping, corresponding with the previously described dying of the activity.

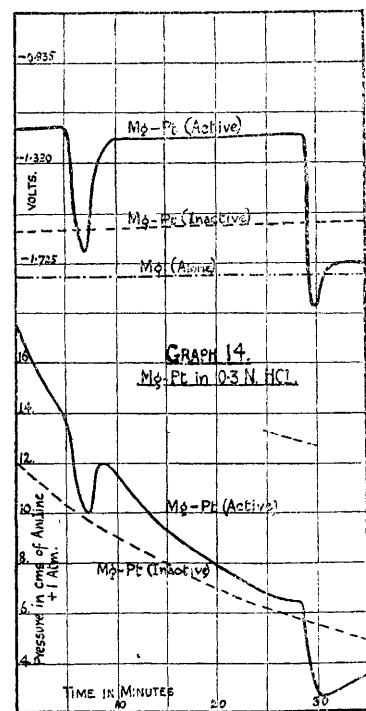
Another factor entering into the consideration of the potentials assumed by activated metals during the reactions is the influence of the hydrogen with which the solution soon becomes saturated and which is absorbed by the metal. The effect of this is to make the metal more negative, but on standing for an hour there is a partial return to the former value. In the case of activated copper, the effect due to the hydrogen is complicated by the partial return



of the metal to the inactive state—a factor operating in the reverse direction. Graph 14 conveys a clear impression of how the dissolution of magnesium in 0.3N-hydrochloric acid is affected by contact with activated and with inactive platinum, both from the electrical and from the chemical point of view.

*Some Reactions involving the Deposition of Metals.*

When magnesium dissolves in dilute hydrochloric acid containing ferrous sulphate in solution, reduction takes place and iron is deposited as a black film on the surface of the magnesium. By suitably choosing the concentration of the reagents, periodic phenomena may be observed in this reaction. This particular case was first found by the visible periodic changes which occur in the system; in fact, the system itself serves admirably as an optical demonstration of chemical periodicity. After an initial lapse of time dependent on the relative concentrations of the reagents, a film of reduced metal spreads from one or two centres on the magnesium surface until it covers about half the metal electrode. Then it proceeds to dissolve, leaving the electrode with a bright surface. The black film grows a second time, covering a greater surface of electrode, and then redissolves, leaving a few black patches on the magnesium.



These two processes continue in alternation a number of times and in each successive period both the area covered by the growing film and the area of the film remaining after the partial dissolution increase. This continues until finally the film, even in its partially dissolved state, entirely covers the electrode. There is no reason to suppose that the periodic phenomenon is then at an end. It is probable that the film continues to grow periodically in thickness as it can no longer do so in extent, and when the surface is once complete no further change in the potential is to be expected. Hydrogen is evolved throughout.



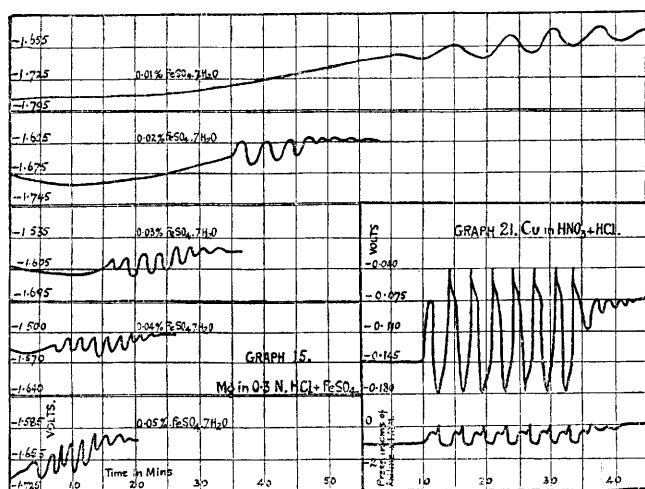
The change has been followed in the apparatus described, simultaneous observations being made of the potential of the dissolving metal, the pressure of the evolved hydrogen, and the appearance of the film. The electrical change synchronised exactly with the chemical change indicated by the appearance of the film. The potential of the magnesium became more positive as its surface was covered by the growing film of iron and returned in the negative direction as the surface brightened through dissolution of the film.

The mean amplitude was in most experiments about 0.03 volt. The amplitude of the oscillations decreased throughout the experiment consistently with the relative areas covered by the film at the maxima and minima of successive waves. The rate of evolution of hydrogen remained steady throughout. The frequency of the oscillations increased with the concentration of ferrous sulphate and was independent (between the limits 0.6*N* and 0.2*N*) of the concentration of acid. The authors have found (*loc. cit.*, 1924, p. 611; this vol., p. 447) that the frequency of other periodic reactions is proportional to the concentration of reagent and *decreases* with increasing amount of activating agent. The hydrochloric acid and the ferrous sulphate are not to be regarded, therefore, as reagent and activating agent respectively, but rather the ferrous sulphate is the reagent and the reduced iron is an active second metallic component. This is also consistent with the absence of periodicity in the rate of evolution of hydrogen. Experiments in which the solution was vigorously stirred by means of an air blast showed that the phenomena were not affected thereby in any way. This removes any possibility of a periodic diffusion of the reactants or reaction products.

Graph 15 represents some of the experiments which have been carried out on this system, and shows the effect of varying the concentration of ferrous sulphate between the limits 0.01% and 0.05% of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , the hydrochloric acid being kept at 0.3*N* strength. In these curves, the first reading was taken 3 minutes after the commencement of the experiment, in order to eliminate the initial vigorous swinging of the electrometer needle. In an experiment in 0.3*N*-hydrochloric acid with addition of 0.1% of crystallised ferrous sulphate, the periodic film formation was observed during the first 3 minutes, after which the permanent deposit set in, so that electrical measurements could not be taken. It is probable that in stronger solutions, where the deposition takes place immediately on immersing the metal, very rapid oscillations incapable at present of detection are actually existent.

When the hydrochloric acid was replaced by 0.3*N*-sulphuric

acid, no periodicity was observed, the reduced iron gradually forming a permanent deposit. Experiments have also been conducted in hydrochloric acid in which the ferrous sulphate has been replaced by an equivalent quantity of nickel chloride or cobalt chloride. In the case of nickel chloride, reduction did not take place in acid solution, and in neutral solution the hydroxide was formed. Reduction of cobalt chloride in both hydrochloric and sulphuric acids readily took place, but a permanent deposit occurred without the advent of periodicity. In ammonium chloride solution, the phenomenon was more marked than in hydrochloric acid, but this system does not serve well from a quantitative point



of view, since the solution quickly becomes alkaline with ammonia and reacts with the metal salt. Periodic phenomena similar to those described above have been observed with magnesium dissolving in 2% ammonium chloride solution with addition of 0.001% of crystallised cobalt chloride, 0.05% of crystallised ferrous sulphate, 0.001% of crystallised nickel chloride, or 0.002% of crystallised copper sulphate. The smallness of the quantities involved is characteristic of the conditions underlying periodic chemical action. In all these instances, the rate of evolution of hydrogen was also periodic. This may be a secondary effect, for it has been shown by the authors (this vol., p. 495) that couples of magnesium with these metals reduced in ammonium chloride solution are very active, decomposing water at the ordinary temperature. It is to be expected, therefore, that the rate of evolution of hydrogen would,

under these conditions, be dependent on the area of magnesium covered by the reduced metal.

### *Autoperiodic Systems.*

With a view to obtain periodic phenomena from the simplest reacting systems, continuous measurements of the electro-potential of single activated metals reacting with a suitable solution have been made. The object has been to dispense with a separate second metallic component and incorporate it with the dissolving metal, causing the reacting electrode to function as its own activating agent.

Some experiments were carried out with aluminium, magnesium, and zinc after treatment by the usual methods. Aluminium, after vacuum-heat treatment or after scraping, in dissolving in hydrochloric acid registered a fluctuating potential, and a similar behaviour was noticed in the case of magnesium after vacuum-heat treatment. Magnesium gave a perfectly steady reading after scraping and attempts to activate zinc by either method were unsuccessful. The fluctuations were of the order of 0.02 volt and were rather rapid and very irregular, but the potential-time curve was very different from that obtained in the case of ordinary untreated aluminium or magnesium in hydrochloric acid. The changes were too small to affect the gas pressure.

The positive results served to demonstrate the possibility of constructing autoperiodic systems, though these particular cases did not lend themselves to quantitative development. The feeble activation which could be induced in these metals was very probably on account of the difficulty in hardening them and for this reason subsequent attention was devoted to copper, which has been found easily susceptible to activation. In all the experiments cited below, the copper was activated by cold rolling to the specified thickness from an original thickness of 0.022 in.

Activated copper, dissolving in nitric acid, showed no sign of periodicity, but continuous observation over the course of several hours of the potential of activated copper in hydrochloric acid revealed a slow oscillation—about one wave per hour. Copper slowly dissolves in hydrochloric acid containing atmospheric oxygen. By substituting nitric acid for the oxygen, attempts were made to increase the frequency.

Graph 21 was obtained from copper (rolled out to 0.0105 in.) dissolving in an acid mixture containing 25 c.c. of nitric acid ( $d$  1.42), 10 c.c. of hydrochloric acid ( $d$  1.16), and 65 c.c. of water. The graph illustrates the synchronous periodic variation in the potential of the copper electrode and in the pressure of the evolved

gas. The negative pressures recorded require some explanation : the gas evolved consists mainly of nitric oxide, which reacts with atmospheric oxygen with decrease in volume of the gaseous system as a whole. The fine capillary delays the entry of air and the pressure of gas in the apparatus is therefore slightly below atmospheric.

The series of changes to be observed at the surface of the dissolving metal under these conditions is most striking. Initially, the surface preserves its natural colour : then there is a sudden appearance of a black film deposited in the form of vertical streaks : the black film next turns dull grey : this is followed by a sudden flash due to the film turning white : the film then dissolves, leaving the metal with its original colour. Then the black film forms again, the whole cycle being repeated in each oscillation. After the point where the amplitude of the waves suddenly decreases (see Graph 21), the oscillation is between the black and the grey film, and the white film no longer appears ; finally, the black film becomes permanent and the pulsations cease. This cessation is due not to any change in the metal but to a change in the composition of the solution during the progress of the reaction, for when the metal, in this final state, is removed from the solution and placed in a new acid mixture the oscillations recommence. The onset of the black film is marked by a movement of the electropotential in the positive direction and by an increase in the rate of evolution of gas, whilst, corresponding with the gradual turning grey of the film, the electropotential and the gas pressure slowly move towards their former values. The sudden appearance of the white film is accompanied by a rapid change of the electropotential in the negative direction and an equally rapid increase in the rate of gas production. The latter effect is easily visible, resembling a miniature eruption. As the white film dissolves, both the electropotential and the gas pressure regain their initial values.

The limits between which the concentration of the various components of the solution can be varied are narrow. Thus, the mixture 25 c.c. of nitric acid, 10 c.c. of hydrochloric acid, 65 c.c. of water always produced the periodic phenomena when acted on by rolled copper, but, if the total volume of solution was kept constant at 100 c.c. and the amount of hydrochloric acid at 10 c.c., mixtures containing 30 c.c., 20 c.c., or 27.5 c.c. of nitric acid did not favour the production of periodicity. Similarly, if the amount of nitric acid was kept constant at 25 c.c. and the total volume again at 100 c.c., mixtures made up with 15 c.c., 5 c.c., or 12.5 c.c. of hydrochloric acid did not give a periodic reaction. For this reason, in order to secure uniform conditions throughout the experi-

ments, a large stock of the standard acid mixture was made up and 100 c.c. were withdrawn for each experiment. Other more widely divergent mixtures were tried, but in these cases the reaction pursued a quite steady course. The concentration of the two acids being kept in the optimum ratio, 25 c.c. of nitric acid : 10 c.c. of hydrochloric acid, the best effect is produced by using 70 c.c. of water, thus making the total volume 105 c.c. No periodicity was observed when the amount of water used was 45 c.c. or 55 c.c. Using 75 c.c. of water, the electropotential and the gas evolution both became periodic, but the film forming over the copper surface alternated between the grey and white forms, the black film never appearing, and the frequency was higher than in the preceding experiments. Thus, under different conditions, the oscillation may be between the grey and white, grey and black, or black and white films : in the former two cases, the amplitude of the electrical effect is correspondingly smaller.

Some experiments have been performed with copper rolled to different thicknesses from the original 0.022 in. sheet. The unrolled copper was incapable of furnishing a periodic reaction under these conditions. Similarly, a piece which had suffered slight deformation by rolling to 0.020 in. was non-periodic. The other specimens, which were rolled to 0.010 in., 0.009 in., 0.0085 in., 0.007 in., and 0.004 in., respectively, all produced the periodic phenomenon and at approximately the same frequency. A sample of the 0.0085 in. copper, after keeping for 3 days, retained its inherent periodicity unabated.

#### *Summary.*

Some typical examples of periodic reactions which have been described previously by the authors have now been investigated from the electrochemical standpoint, using an apparatus in which the electrical and chemical effects of the reactions could be registered simultaneously. In the case of activated metallic couples dissolving in hydrochloric acid or ammonium chloride, the difference of potential between the couple as a whole and the solution, and between the two components of the couple undergo periodic fluctuations which synchronise with the periodic evolution of gas. A difference of potential exists between the activated and inactive forms of a metal. Some new reactions, involving the periodic deposition of metals, are described. The change consists in an alternate formation and dissolution of a metallic film which is accompanied by a corresponding oscillation of the electropotential. In some cases, the rate of evolution of hydrogen is also periodic. Examples are given of "autoperiodic" reactions, where one electrode serves both as the reacting metal and as the activating

agent. The best case is furnished by copper, activated by cold rolling, dissolving in a mixture of nitric and hydrochloric acids: this example furnishes very regular waves representing both the electropotential and the pressure of the evolved gas. This is accompanied by a striking series of visible changes in a film formed over the metal surface. The effect of varying the concentration of acids has been studied and the optimum mixture consists of 25 c.c. of nitric acid ( $d$  1.42), 10 c.c. of hydrochloric acid ( $d$  1.16), and 70 c.c. of water.

The results of several previous experimenters are correlated with the authors' investigations on periodicity as a general principle.

The authors desire to acknowledge the help derived from a grant from the Research Fund of the Chemical Society and from a grant made to the Department by Messrs. Brunner Mond and Co., Ltd.

THE UNIVERSITY, MANCHESTER.

[*Received, February 12th, 1925.*]

---