

CXLV.—*The Periodic Electro-deposition of Metals through Secondary Reaction.*

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EXPERIMENTS described in a series of papers by the present author (J., 1926, 1533, 2580, 2878) have shown that periodic changes in current density and potential occur in the electrolytic dissolution of a number of metals in various electrolytes. The present communication contains an account of the inversion of this process—the periodic deposition of a metal at the cathode.

The method of investigation was essentially similar to that in the experiments on the anode (*loc. cit.*) but certain important improvements were made: Instead of measuring the total *P.D.* across the electrolytic cell, the *P.D.* between the cathode alone and a standard reference electrode was determined. Also, the measurements were made by a static instrument, so that absolutely no current was taken from the system. Since it was anticipated that rapid alterations of potential would have to be followed, a string electrometer was used as the measuring instrument. This has the advantage that it is entirely dead-beat, and can therefore be used for following very rapid vibrations, and its sensitivity is adjustable over a wide range.

The same electrolysis vessel was used as before, but it was now provided with a side-tube leading to a bridge of *N*-potassium chloride, making connexion with a *N*-potassium chloride calomel half-element. The cathode was connected to the string of the electrometer and the calomel cell was earthed. During electrolysis, the *C.D.* was progressively raised and the position of the fibre was noted on the scale in the eye-piece, the scale being adjusted so that 25 divisions corresponded to 1 volt. All the experiments were conducted at 30° and a platinum anode was used throughout.

Periods in Direct Deposition.

The conditions of the first experiments were designed to be as nearly as possible analogous to those known to be favourable to periodicity at the anode. Thus, attempts were directed towards depositing a metal in presence of an acid which would dissolve it, in the anticipation of reaching a boundary state where a deposit of metal would form and dissolve off alternately. Experiments of this type on the deposition of iron and of zinc from various solutions of their salts in presence of acids met with no result.

It was hoped to realise a periodic deposition of alkali metals in the electrolysis of solutions of their salts with a mercury cathode, for here there is a possibility of a balance between the rate of deposition of the metal and the rate of dissolution by the water. Experiments with $2N$ -, N -, and $N/10$ -solutions of alkali salts were unsuccessful. However, it seems that at these concentrations the sodium dissolves off the cathode too easily, for later experiments have shown that periods can be realised in the electrolysis of $4N$ -caustic soda with a mercury cathode.

Actually, periods were observed by Coehn (*Z. Elektrochem.*, 1901, 7, 633) in the electrolysis of caustic soda with a mercury cathode, although experimental details are not given. The experiment was repeated by Kremann and Lorbeer (*Sitzungsber. Akad. Wiss. Wien*, April, 1913) using $3N$ -caustic soda. The present author has confirmed these results and finds that the phenomenon is readily reproduced at 30° with $4N$ -caustic soda, at a *C.D.* of 300 milliamp./cm.². Alternate periods of amalgam formation and dissolution took place, the periods becoming longer with time. The electrical change was very slight, the cathode *P.D.* being — 2.08 volts during amalgam formation and — 2.00 volts during dissolution of the amalgam.

There seems little doubt that the periods mentioned by Förster (*Z. Elektrochem.*, 1902, 8, 500) in the deposition of copper from a nitric acid solution of the nitrate, and by Coehn (*ibid.*, p. 499) in electrolysing a solution of nitric acid in which bismuth had been dissolved, were due to a similar cause. The phenomenon mentioned by the present author (*J.*, 1926, 1543) concerning a copper anode in nitric acid was probably due to periodicity at the cathode, where deposition of copper took place.

During the experiments on film formation at an unattackable anode (*J.*, 1926, 2591), it was sought to deposit mercuric cyanide and cadmium cyanide, respectively, at the anode by electrolysing solutions of potassium mercuric cyanide or potassium cadmium cyanide; although this deposition did not occur, yet in both cases, between certain current densities, a periodically fluctuating potential

appeared, which had its source in the *cathode*, at which a periodic evolution of hydrogen bubbles was visible. The interpretation then placed on the phenomenon was that at the cathode, which had now become mercury (or cadmium) by deposition, potassium ions were discharged and periodically reacted with the solution giving hydrogen. In fact, this led to the experiments described above with alkali-metal salts.

Since the experiments on the deposition of sodium and potassium at similar concentrations at a mercury cathode gave negative results, attention was directed to the simultaneous deposition of mercury and potassium at a platinum cathode.

Experiments on the Simultaneous Deposition of Metals.

Preliminary experiments showed that a *N*/10-solution of mercuric chloride was almost non-conducting, and the small amount of product formed at the cathode appeared to be calomel. This is not surprising since, according to Luther (*Z. physikal. Chem.*, 1901, **36**, 402), a solution of mercuric chloride saturated at 25° contains 1.5×10^{-4} mol. per litre of the HgCl^+ ion and only 10^{-8} of the Hg^{++} ion. It was found, however, that deposits of mercury were readily formed when the solution also contained *N*/10-potassium chloride or *N*/10-hydrochloric acid. It may be noted that, since the solution contains practically no mercuric ions, the mercury is deposited through a secondary reaction, *i.e.*, either potassium or hydrogen is discharged first and reacts with the complex HgCl_4^{--} ion, and perhaps with undissociated HgCl_2 .

The Deposition of Potassium with Mercury.—Periods were first observed in the electrolysis of a solution containing *N*/10-mercuric chloride and *N*/10-potassium chloride, using a *C.D.* of 16 milli-amp./cm.². The cathode potential then oscillated between - 1.6 and - 2.0 volts in periods of 1 minute. (Normal calomel electrode taken as zero.) In these experiments, two platinum electrodes, each of 12 sq. cm. available area, were used, although the cathode necessarily soon became a mercury electrode. Periods were obtained under similar conditions when an electrode of pure mercury was used, but it seemed better for practical reasons to use a cathode of platinum and allow the deposited metal to form a coating thereon.

It was evident that these periods required the simultaneous deposition of two metals, for when such a system was oscillating the electrodes were removed and placed in *N*/10-potassium chloride and *N*/10-mercuric chloride separately. No periods could be obtained in either solution, but when the electrodes were put back into the original solution of the mixed substances the periods continued.

At first, certain difficulties were encountered in the reproduction of these results, and these were traced to the fact that during electrolysis the ratio of mercury to potassium in the solution continuously diminishes; for ultimately the mercury is entirely deposited, whilst the potassium content of the solution remains unaltered. One source of difficulty was that at the commencement of the electrolysis, when the solution was rich in mercuric chloride, a film of mercurous chloride tended to form on the cathode. This could be loosened and thrown off the cathode by breaking and making the circuit several times in succession, or by increasing the cathode potential to the point of incipient hydrogen evolution.

A second inconsistency was that the conditions of formation of the periods appeared to differ in each experiment and did not correspond with any definite values of *C.D.* and potential. The general relations were these: below a certain critical *C.D.* mercury was deposited; above a higher critical *C.D.* hydrogen was evolved (potassium ions discharged); between these limits the electrode oscillated from one state to the other in regular periods. But the limits of the region of periodicity varied continuously throughout the course of the electrolysis. This was traced to the change in the concentration of the mercuric chloride, and it appeared that the critical limits of *C.D.* were lower the greater the ratio of potassium to mercury in the solution. Thus, a mixture consisting of *N*/40-mercuric chloride and *N*/10-potassium chloride gave a continuous evolution of hydrogen at the lowest *C.D.*'s, whilst a mixture consisting of *N*/5-mercuric chloride and *N*/10-potassium chloride required initially a high *C.D.* in order to reach the lower limit of the region of periodicity, although this critical *C.D.* fell continuously as the solution became weaker in mercuric chloride.

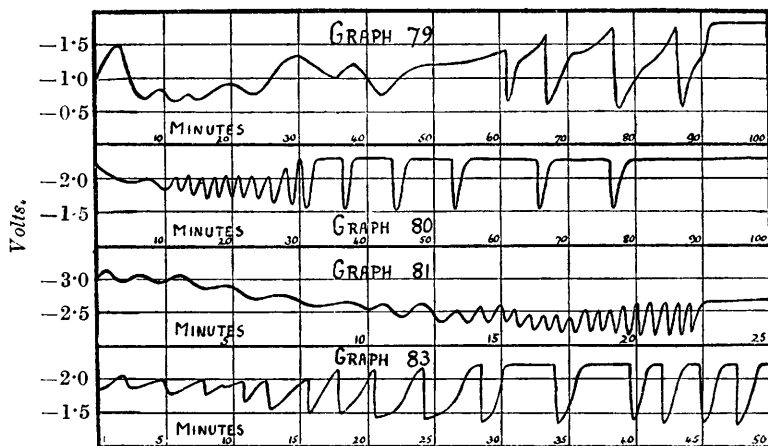
The use of a mercury anode would *increase* the concentration of mercury continuously, even if it were permissible in a chloride solution. The composition of the solution could be kept constant by employing a saturated solution of mercuric chloride in potassium chloride in presence of excess of solid mercuric chloride. Although this has not been done in the system under discussion, it has been done in other systems, and the resulting waves have been regular and continuous.

The most favourable mixtures were solutions containing *N*/10- or *N*/20-mercuric chloride and *N*/10-potassium chloride, and the method devised for securing comparable conditions was to electrolyse with a constant *C.D.* of 42 milliamp./cm.². This was below the critical *C.D.* required at the commencement of the electrolysis, but, owing to the gradual deposition of the mercury, after a time the solution reached a composition such that this *C.D.* produced

periods, and finally the *C.D.* employed corresponded to the upper limiting value for the solution, causing steady evolution of hydrogen.

Thus, for a given composition of solution there exists a current density-region of periodicity, and for a given *C.D.* there is a composition-region of periodicity. The latter is illustrated by Graphs 79 and 80, showing the transition of the electrode from the state of mercury deposition, through the region of periodicity, and into the state of continuous hydrogen evolution. Graph 79 represents the change with time of the cathode potential in the electrolysis of a mixture containing *N*/20-mercuric chloride and *N*/10-potassium chloride, using a *C.D.* of 9 milliamp./cm.². Graph 80 similarly represents the electrolysis of *N*/10-mercuric chloride and

FIG. 1.



N/10-potassium chloride with a *C.D.* of 42 milliamp./cm.². The periods have an amplitude of about 0.8 volt. At the more negative values of potential very strong evolution of hydrogen occurred in the form of small bubbles and the surface was dull through the formation of potassium amalgam, whilst at the less negative values the mercury was bright and only a few large bubbles of hydrogen adhered to it.

Deposition of other Metals with Mercury.—Similar periods were obtained in the simultaneous deposition of sodium and mercury. Graph 81 records the variation of the cathodic potential with time in the electrolysis of a solution containing *N*/10-mercuric chloride and *N*/10-sodium sulphate with a *C.D.* of 42 milliamp./cm.². During the first stage of the reaction, mercury was deposited and the electrode became covered with a few large bubbles of hydrogen. In the second, oscillatory stage, violent evolution of hydrogen in

the form of small bubbles occurred at regular intervals, whilst after 22 minutes steady hydrogen evolution set in. The initial fall of *P.D.* is due to the gradual increase in conductivity of the solution due to the liberated chlorine ions from the complex anions. The periods were fairly rapid, having an interval of 30 seconds.

Equally good periods were obtained in the electrolysis of a solution of *N/10*-mercurous nitrate and *N/10*-sodium nitrate.

A solution of *N/10*-mercuric chloride and *N/10*-barium chloride electrolysed with a *C.D.* of 4 milliamp./cm.² gave excellent periods, the cathode *P.D.* changing from -0.8 to -1.8 volts every 30 seconds. Similarly, with a solution containing *N/10*-mercuric chloride and *N/10*-strontium chloride the *P.D.* oscillated between -1.7 and -2.4 volts in 2-minute periods, using a *C.D.* of 42 milliamp./cm.². Graph 83, which was obtained with *N/10*-mercuric chloride and *N/10*-calcium chloride under the same *C.D.*, is typical of the results obtained with these mixtures.

Periods were also obtained in the electrolysis of a solution of *N/10*-mercuric chloride and *N/10*-aluminium sulphate. These were somewhat irregular, but had an average interval of 2 minutes and an amplitude of about 0.4 volt.

Periods were not observed under any conditions in the electrolysis of solutions containing *N/10*-mercuric chloride with an *N/10*-solution of magnesium, zinc, copper, or nickel sulphate.

It was of interest to determine whether positive amalgam formation was necessary for the production of periods, or whether the direct discharge of hydrogen could produce a similar effect, and therefore the electrolysis of a solution containing *N/10*-mercuric chloride and *N/10*-hydrochloric acid was investigated. When hydrogen evolution started, however, the gas left the cathode in the form of very large bubbles, so that a constant *P.D.* could not be obtained and it was not possible to decide the point. Similar experiments at a cadmium cathode (*vide infra*), however, show that in this case hydrogen cannot act in such a way.

Deposition of Metals with Cadmium.—The salts of cadmium resemble those of mercury in their tendency to complex formation, and it is not surprising, therefore, to find a similar behaviour in the simultaneous deposition of cadmium and sodium. A solution containing *N/5*-cadmium nitrate and *N/10*-sodium sulphate gave at low *C.D.*'s a deposit of cadmium on the cathode, whilst at high *C.D.*'s a gelatinous film of cadmium hydroxide formed round the cathode and hydrogen was evolved. Intermediate *C.D.*'s covered a wide region in which the film of cadmium hydroxide formed periodically, whilst the cathode *P.D.* oscillated regularly between -2.25

and -2.4 volts; in these periods it was at the higher negative value while the film was on the electrode and hydrogen was being evolved, and at the lower potential the film as a whole slipped off the cathode, and metallic cadmium was deposited.

The following table shows that the frequency of these periods increases rapidly with increase of *C.D.* (The reverse was found to hold for the anodic periods, *q.v.*)

Milliamp./cm. ²	13	15	17	25	33	42	58
Period (secs.)	26	19	14	7	5	3	2

The only difference between these periods and those with mercury is that cadmium hydroxide is formed at the cathode in place of metallic mercury. This is due to the relative ease with which the oxide of mercury is reduced.

As it is not necessary further to multiply instances, experiments have not been conducted with other alkali metals and cadmium, although there is every reason to suppose that they would behave similarly. It was of interest, however, to examine the effect of hydrogen itself, and solutions containing *N/5*-cadmium nitrate and *N/2*-, *N/5*-, and *N/10*-sulphuric acid, respectively, were electrolysed. No periods were observed.

Deposition of other Metals with Alkali Metals.—Electrolysis of solutions of zinc sulphate with sodium sulphate gave no periods, and negative results were likewise obtained in electrolysing mixtures of copper sulphate with sodium sulphate, and silver nitrate with sodium nitrate. In these cases the metals are deposited directly and not by secondary reaction.

Electrolysis of Cyanide Solutions.—Double cyanides on electrolysis furnish excellent examples of the deposition of a metal through a secondary reaction, and therefore promised to be a fruitful ground for the study of periodicity of the type under discussion. The extreme regularity of the periods is a feature of these experiments, enabling these systems to be used for a quantitative examination.

Mercury potassium cyanide. Mercuric chloride solution was added to 50 c.c. of *N/2*-potassium cyanide until a permanent precipitate was formed, and the solution was then made up to 100 c.c. Electrolysing with a *C.D.* of 9 milliamp./cm.², excellent periods were obtained from this system, though the amplitude was on the whole considerably less than in the foregoing cases.

The following table shows how, in such an experiment, the amplitude increases to a maximum and then declines, whilst the frequency simultaneously increases (period decreases) and then falls off. It will also be observed that the product of amplitude and period is as constant as could be expected.

Time (mins.).	Amplitude (volts).	Period (secs.).	Product.	Time (mins.).	Amplitude (volts).	Period (secs.).	Product.
0	0.2	0.4	0.08	30	0.3	irreg.	?
3	0.3	0.29	0.087	34	0.3	0.31	0.093
6	0.35	0.24	0.082	36	0.25	0.42	0.105
9	0.4	0.20	0.080	38	0.2	0.5	0.100
12	0.4	0.24	0.096	40	0.1	1.1	0.110
17	0.4	0.19	0.076	42	0.0	∞	—
24	0.35	0.20	0.070				

In this system, the frequency decreases greatly with increasing *C.D.*, as shown by the following table :

Milliamp./cm. ²	6.2	8.3	9.2	10.0	12.5	17.7
Period (sec.)	ca. 0.1	0.2	1.1	5.0	13.0	∞

The frequency was measured by taking the time for 10 successive periods with the aid of a stop-watch. Experience showed that it was possible faithfully to count periods at the rate of 6 per second, although values for higher frequencies were not trustworthy. At the *C.D.* of 6 milliamp./cm.², the period was judged to be about 0.1 sec. because the movement of the electrometer fibre, as judged by the eye, bordered on to continuity. At a slightly lower *C.D.*, the period was almost certainly rather less than this value.

Taking 0.1 sec. as the smallest duration of a period that has been observed, however, it becomes of interest to calculate the thickness of the film of mercury deposited during that period. Thus, a current of 6.2 milliamp. deposits during 0.05 sec. (mercury is deposited only during each half-period) 3.24×10^{-7} g. of mercury on an area of 1 cm.². Assuming that the mercury has its normal density of 13.6, the thickness of the mercury film deposited in each period is 2.4×10^{-8} cm., *i.e.*, of the order of molecular thickness.

No significance is to be attached to this result in the theory of the subject, for it can be shown that in other cases the thickness of the film formed in each period corresponds to several thousands of molecules; but the important point is that *we have here a case of periodicity in the smallest amount of chemical change.*

At these low *C.D.*'s the amount of chemical change was not sufficient to produce visible periodic evolution of hydrogen, but, nevertheless, the periodicity was easily visible, for the hydrogen bubbles, with which the surface of the cathode became covered, pulsated synchronously with the periodic change of potential. This effect, due to the periodically changing surface tension at the mercury-hydrogen interface as a result of the periodic formation of amalgam, showed itself in a pulsating flattening of the bubbles. The effect was perceptible when the amount of metal deposited in each pulsation could not have exceeded a few molecules in thickness.

Cadmium potassium cyanide. Even better periods were obtained

with a solution made by adding cadmium nitrate to 50 c.c. of $N/2$ -potassium cyanide until a permanent precipitate formed, and then making up to 100 c.c. These differed from the periods last mentioned in that considerably higher $C.D.$'s could be used, the amplitude was larger (generally about 0.5 volt), and the frequency *increased* with rise of $C.D.$ It is noteworthy that in cyanide solutions the frequency is always high.

The next table shows the change in frequency with increase of $C.D.$ In the third column appear values of K , the product of the square of the current into the period, and it will be seen that over a wide range these are remarkably constant, considering the error in measuring such small periods.

Total current (milliamp.).	Period (secs.).	K .	Total current (milliamp.).	Period (secs.).	K .
0.25	2.0	0.125	0.55	0.32	0.097
0.30	0.9	0.082	0.60	0.22	0.080
0.35	0.8	0.098	0.65	0.18	0.076
0.40	0.6	0.096	0.75—1.75	very rapid	—
0.45	0.5	0.101	1.9	0.00	—
0.50	0.4	0.100			

In this case then, the period is inversely proportional to the square of the $C.D.$ In this experiment, excess of cadmium cyanide was added so that the composition of the solution should not change during electrolysis. Similar results were obtained whether a cadmium or a platinum cathode was used. Pulsating evolution of hydrogen was visible.

Electrolysis of other Systems.—Periods could not be obtained at the cathode in the electrolysis of solutions of the double cyanides of potassium with copper, silver, iron, nickel, cobalt, and zinc. With the exception of zinc, the hydrogen overvoltage is low, and therefore hydrogen was liberated simultaneously with the metal at all $C.D.$'s, and the zinc potassium cyanide solutions were hydrolysed too readily. Unsuccessful experiments were also carried out with solutions of zinc hydroxide and of lead hydroxide in caustic soda. Poor periods were obtained, however, in the deposition of tin from a solution prepared by adding excess of caustic soda to 25 c.c. of $N/2$ -stannous chloride and then making up the volume to 100 c.c. The cathode potential varied between -1.36 and -1.48 volts in slow periods of 15 minutes, using a $C.D.$ of 7 milliamp./cm.².

Discussion.

The mechanism of the periodicity will be considered for the typical case of the electrolysis of cadmium potassium cyanide solutions. At low $C.D.$'s potassium ions are discharged, and react with the complex $Cd(CN)_4''$ ions: cadmium is deposited and no

hydrogen appears. But at a certain critical *C.D.* more potassium ions are discharged than can react with the complex ions, so the excess react with the water molecules and hydrogen is evolved. It is evident that the liberated potassium ions dispose of the complex $\text{Cd}(\text{CN})_4''$ ions preferentially, and only react with water when these become scarce.

The surprising feature is that after a short interval of time the discharged potassium ions cease to react with water, and again are entirely concerned with the complex ions of cadmium.

This point touches the fundamental question of the cause of periodicity, to which an answer cannot at present be given, research so far having been directed towards discovering the conditions under which periodicity is manifested. A discontinuity must occur at some stage in the mechanism of the reaction. In the experiments on the anode there was some evidence to show that the film as first deposited was unstable and changed suddenly to a stable state. This may also be the case here, although it may be pointed out that the phenomenon is equally explicable on the assumption that a certain critical concentration of the complex ions in the immediate vicinity of the cathode is necessary before reaction takes place.

Whether this be the case or not, it is tolerably certain that the discharged potassium ions react alternately with the complex cadmium anions and with the water molecules. The variation of the period with the inverse square of the *C.D.* finds a ready explanation when one considers the relations in the layer of solution immediately contiguous to the cathode; for, suppose the *C.D.* to be increased n times: then the rate of discharge of potassium ions is increased n times, and the rate of migration of the complex anions from the immediate vicinity of the cathode is increased n times. Since there are n times as many potassium ions discharged, and $1/n$ of the number of $\text{Cd}(\text{CN})_4''$ ions to react with, the latter become used up n^2 times as quickly.

It is to be remembered, however, that in the electrolysis of mercury potassium cyanide solutions the period *increased* with rise of *C.D.*; but another factor enters here, for whereas with cadmium potassium cyanide the discharged potassium ion is confronted with the alternatives of reacting with the complex anions or with water molecules, yet another possibility is open in the case of mercury potassium cyanide in that the potassium atom may stay as such in the mercury. Moreover, increase of *C.D.* will stabilise the potassium amalgam, diminishing its tendency to react.

The present work shows that a satisfactory explanation of periodic phenomena in electrolysis must be founded upon as wide a basis as

possible in order to include both anodic and cathodic reactions and the discharge of one or more ions. Elsewhere (Hedges and Myers, "The Problem of Physico-chemical Periodicity," Arnold and Co., 1926) the author has gathered together some reports of earlier experiments of this type. Since these are mostly isolated cases, the earlier investigators proposed a specific mechanism for each. It is now evident that an explanation should be of general applicability. It is hoped by further experiment to eliminate some of the factors which at present lead to ambiguity in interpretation.

Summary.

Periodic changes in the cathode potential and current strength occur between certain limiting current densities during the electrolysis of solutions composed of a mixture of mercuric chloride or mercurous nitrate with solutions of the salts of alkali metals, alkaline earths, or aluminium, and in solutions of mercuric cyanide or cadmium cyanide in potassium cyanide. The phenomenon consists of the alternate deposition of two metals, and has been observed only when one of the metals is deposited through a secondary reaction. The values of the limiting current densities, between which the region of periodicity exists, depend on the relative amounts of the components of the mixed solution. Periodicity has been realised where the amount of metal deposited in each period does not exceed a few molecules in thickness.

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