CCCLXXXIV.—*The Periodic Electrochemical Passivity of Iron, Cobalt, Nickel, and Aluminium.*

By Ernest Sydney Hedges.

Shortly after it had been recognised that iron could assume the passive state, the remarkable observation was made that under certain conditions pulsations are set up, the iron behaving as though it were alternately active and passive; the literature contains many references to this periodic phenomenon which obtains both for the passivity induced by chemical reagents (*e.g.* nitric acid) and for that caused by anodic polarisation.

The results of a study of other periodic electrolytic systems (this vol., pp. 1533, 2580) have now been applied to those metals which readily assume the passive state.

EXPERIMENTAL.

Details of the experimental methods are given in preceding papers (*locc. cit.*). In brief, solutions at 20° were electrolysed with a platinum cathode and an anode of the metal under investigation, readings of the *P.D.* between the electrodes being taken while the current density was being progressively increased. The metals used were all of electrolytic origin and had been rolled into sheets, roughly 0·5 mm. thick. The portion of metal immersed measured 2 × 3 cm. The metals were cleaned in hydrochloric acid and then in water immediately before use.

Iron Anode.

Experiments in Sulphuric Acid Solutions.—In 100, 80, and 60% * solutions a low *C.D.* was sufficient to cause the *P.D.* to rise to a high value, oxygen being evolved. The whitish appearance of the anode suggested the formation of a film of anhydrous ferrous sulphate. In a 40% solution at a *C.D.* of 160 milliamp./cm.², the *P.D.* rose from 1·2 to 3·2 volts and oxygen was evolved. Thereafter, the *P.D.* oscillated continuously between 1·1 and 3·3 volts, in periods of 50 seconds. At the lower value of *P.D.* hydrogen was evolved; this ceased as the *P.D.* rose and then gave place to oxygen evolution; during the next fall of *P.D.* the oxygen evolution ceased and slow hydrogen evolution was reinstated. Immediately before the evolution of oxygen a white film could be observed to sweep up the anode. The iron was permanently in the passive state at current densities greater than 250 milliamp./cm.², and permanently active when the *C.D.* was below 160 milliamp./cm.².

If the iron was removed from the solution when in its high-potential state, the high *P.D.* persisted on plunging it back again; but if in the meantime the iron was dipped into water it was found to be active on plunging it back into the solution. It is concluded that in these solutions the iron becomes enveloped in a resistant film of anhydrous ferrous sulphate, which is much less soluble in strong solutions of sulphuric acid than in water. It was found also that the passivity obtained in the 100, 80, and 60% solutions was removable by immersing the electrode in water.

In weaker solutions of sulphuric acid, the passivity seems to be quite different. In 10% solution, great difficulty was experienced in inducing passivity, and it was found best to complete the circuit before immersing the anode, so that the initial *C.D.* was very high. By breaking the circuit momentarily, the iron became active,

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* See footnote (this vol., p. 2584) for convention as to expression of concentrations throughout this paper.

but, with an increase of current, it again became passive. Thus, with a *C.D.* of 420 milliamp./cm.^{2} the *P.D.* oscillated continuously between 1·5 and 3·3 volts, in periods of 40 seconds. No gas was evolved during the active state of the metal, but oxygen evolution occurred while the metal was in the passive state. In this case, however, the anode was lustrous during the passive periods but acquired a dull, dark grey film during the active periods. Each time passivity set in, the film peeled off and subsequently dissolved in the solution. Evolution of oxygen then ensued, beginning at the lowest part of the electrode, up which the passive state rapidly travelled until the whole of the metal was evolving oxygen. At the end of the period, the oxygen evolution ceased and the metal slowly acquired its grey film, which again peeled off at the next period of oxygen evolution.

In 5% sulphuric acid solution, the precaution mentioned above was still more necessary to secure passivity of the iron; continuous oscillations between 2·4 and 4·0 volts, having a period of 30 seconds, were obtained with a *C.D.* of 850 milliamp./cm.^{2}. The film in this case did not peel off, however, but apparently dissolved, uncovering the lustrous surface.

Closer observation showed that the film is completed just before the *P.D.* rises, then oxygen is evolved, and the film disappears : it does not seem to be an attribute of the active metal, but rather a transitional state between the active and passive states.

Experiments in Nitric Acid Solutions.—In 100% nitric acid, the iron became passive before the current was started. In a 90% solution, the reaction was very vigorous, but the metal could be rendered passive by adopting the device described for the more dilute sulphuric acid solution: passivity then spread from the first point of contact over the whole electrode. Although this solution did not cause passivity, yet it did not activate the passive metal, and on disconnecting the circuit the metal remained permanently passive. In 60% nitric acid, the behaviour was similar, except that on breaking the circuit the iron dissolved with great vigour.

Periodic passivity occurred in 40 and 20% solutions, the *P.D.* oscillating between 1·6 and 3·4 volts. The metal had a brown-coloured surface at the low potential and was bright during the passive periods, when oxygen was evolved. The *C.D.* used for the 20% solution was 1800 milliamp./cm.^{2}, and the periods succeeded each other at intervals of 10 seconds. In 10, 2, and 1% solutions passivation took place more readily, but did not become periodic.

Experiments in Phosphoric Acid Solutions.—In 5% orthophosphoric acid, iron became passive at a *C.D.* of 50 milliamp./

cm.^{2}, the *P.D.* rising from 2·2 to 3·8 volts. Oscillations of the potential between 3·65 and 3·85 volts followed, at intervals of 3 minutes. At a slightly higher *C.D.* the metal was permanently passive, whilst it remained active at *C.D.*'s below 50 milliamp./cm.^{2}.

Experiments in Other Solutions.—In solutions of caustic soda or of potassium cyanide iron became passive at the lowest *C.D.*'s, whilst in hydrochloric acid solutions the highest available *C.D.* did not induce the passive state. In solutions of ammonium sulphate or sodium sulphate, the main product was ferrous hydroxide, which fell continuously from the anode. Although at higher *C.D.*'s passivity set in, the anode remained passive until the circuit was broken, and an intermediate oscillating condition was not realised.

Cobalt Anode.

Experiments in Sulphuric Acid Solutions.—In 100 and 80% sulphuric acid, a brown film readily formed over the anode and oxygen was evolved. Periodicity was observed in 50, 40, 30, 25, 20, 15, 10, 5, and 1% solutions, and the effect was far more striking than in the corresponding experiments with iron. The effects produced vary to some extent with the concentration.

In a 50% solution, cobaltous sulphate was formed below 70 milliamp./cm.^{2}. Immediately this *C.D.* was reached, however, the *P.D.* rose from 1·2 to 2·6 volts, and continued to oscillate regularly and rapidly (about one wave per second) between these two values, oxygen being evolved at the high potential. This periodicity was observed over a wide range, but above a *C.D.* of 250 milliamp./cm.^{2} the cobalt remained permanently in the passive state, oxygen being evolved continuously. The cobalt continued to dissolve when in the passive state, but formed a dark green solution of cobaltic sulphate. The surface of the metal appeared black throughout. The green colour did not appear in solutions weaker than this.

In 40% sulphuric acid, periodic passivity appeared at a *C.D.* of 105 milliamp./cm.^{2}, the *P.D.* oscillating between 1·1 and 2·8 volts in periods of 30 seconds' duration. In this system, it appeared that increase of *C.D.* *increased* the frequency—the reverse of what has been observed in all other systems. In solutions of concentration 30% and less, the effects were similar, except that a higher critical *C.D.* was required with increasing dilution and the periods were slower. 20 and 15% Solutions were best for observing changes in the state of the electrode, which correspond exactly with those recorded for iron. At the end of each passive period, during which the cobalt was lustrous, oxygen evolution ceased and the metal became dull; immediately before the next passive period a dark grey film travelled up the anode and peeled off as the oxygen evolution began afresh.

Experiments in Other Solutions.—In hydrochloric acid (from 20 to 0·05%), nitric acid (100 to 0·5%), ammonium sulphate (10 to 1%), and sodium sulphate (10 to 2%) a cobalt anode did not become passive; on the other hand, in sodium hydroxide (8%) and potassium cyanide (20%) it became passive immediately and remained so after the circuit had been broken.

Nickel Anode.

Experiments in Sulphuric Acid Solutions.—The behaviour of nickel was similar to that of iron and cobalt. In 100 and 80% solutions, the *P.D.* soon rose to a high value, due to the formation of difficultly soluble nickel sulphate. Periodic passivity was observed in 60, 40, 30, 20, 10, and 5% solutions. The effect was less striking than in the foregoing instances, however, the amplitude being generally of the order of 0·2 volt.

As in the previous cases, oxygen was evolved during the passive periods and a dark film travelled up the metal immediately prior to its becoming passive.

Although the periods can be produced in the direct way by cautiously raising the *C.D.*, they are more easily started in the case of nickel by rendering the metal passive and then lowering the *P.D.* slightly. Thus in 5% sulphuric acid a nickel anode became passive at a *C.D.* of 102 milliamp./cm.^{2}, the *P.D.* rising from 1·4 to 2·9 volts. On lowering the *C.D.* to 70 milliamp./cm.^{2}, continuous oscillations between 2·3 and 2·5 volts followed at intervals of 5 seconds.

Experiments in Other Solutions.—In nitric acid (100, 75%), nickel did not appear to become passive, although it did so in more dilute solutions (25, 20, 10, and 5%). Periodicity was not observed in these solutions, however. In solutions of hydrochloric acid (30, 15, 5, 2, 0·5, and 0·1%) and of ammonium chloride (5, 2, 1, and 0·5%), the anode remained active at all current densities. Solutions of caustic soda (8%) and potassium cyanide (20, 10, 5, and 2·5%) caused passivity immediately, and ammonium sulphate (10, 5, and 2%) produced the passive state very readily. Periodic phenomena were not encountered in these systems.

Aluminium Anode.

Experiments in Nitric Acid Solutions.—Aluminium was used as an anode in 100% nitric acid at 30°. The metal dissolved continuously at low *C.D.*'s, but at 50 milliamp./cm.^{2} the *P.D.* oscillated regularly between 1·2 volts and 14·0 volts in periods of 20 seconds.

Slow evolution of gas occurred during these periods, but the surface of the electrode appeared to be unchanged. If, however, a very thin oxide film had formed periodically, it would probably have escaped observation, being transparent. Aluminium was not rendered passive in 80% nitric acid.

Experiments in Caustic Soda Solutions.—In an 8% solution, an anode of aluminium dissolved smoothly at moderate *C.D.*'s, hydrogen being evolved simultaneously when the current was sufficiently low. Hydrogen evolution ceased at about 60 milliamp./cm.^{2}. At 70 milliamp./cm.^{2}, a brass-coloured film appeared on the anode, and at 75 milliamp./cm.^{2} the *P.D.* oscillated in regular periods of 25 seconds between 1·65 and 2·0 volts, and a few bubbles, presumably of oxygen, were evolved. Above 110 milliamp./cm.^{2}, the *P.D.* remained constant. When a very small anode was employed, giving a high *C.D.* (roughly 10,000 milliamp./cm.^{2}), vigorous evolution of oxygen occurred and the metal remained bright. Periodic phenomena were observed also in 4% caustic soda.

Experiments in Other Solutions.—Solutions of hydrochloric, sulphuric, and orthophosphoric acids, sodium carbonate, and ammonium chloride were unsuitable for the production of periods.

The Conditions for Periodicity.

From the examination of a large number of periodic anodic reactions (Hedges, *loc. cit.*) it appears that when an anode can exist in one of two states, *e.g.*, with or without a film, then there exists a range of conditions (sometimes very narrow) in which the electrode is given more or less equal opportunities of being in either state, and the result is that it passes alternately from one to the other. The apparent truth of this generalisation has been demonstrated both in the case of anodes undergoing dissolution and in the case of film formation by deposition at an unattackable anode.

The experiments now described tend to show that periodic passivity is simply a special case, for it seems that periodicity ensues wherever the anode is given simultaneous opportunities of existing in the active or passive state. In order to test this point further, special experiments were devised in which a passivated anode was progressively activated, the idea being that at some stage, when activity and passivity were almost equally probable, the system would alternate continuously between the two states.

The progressive activation was effected in three ways: (*a*) By raising the temperature of the system, (*b*) by dilution of the reagent, (*c*) by addition of some agent favouring the active state.

(a) *Raising the temperature.* The system aluminium–100% nitric acid was used. At 20°, passivity readily set in and was permanent. At 30°, the periods which have been described were produced. At 40°, the system still alternated between the two states, but very rapidly, the amplitude being only from 1·0 to 7·0 volts. At 60°, the aluminium remained active.

(b) *Dilution of the reagent.* The same system was taken and 0·5 c.c. of water was added to the nitric acid at 20°. Still the passivity was permanent when it developed. Further small additions of water were made until 2 c.c. had been added; oscillations between 1·7 and 13·4 volts with a 30-second period were then produced. An excess of water caused the aluminium to become completely active. In the experiments at 20°, a gelatinous, white, transparent film peeled off the anode; in one case, the solution was allowed to become warm and this film apparently dissolved in the acid at the higher temperature.

FIG. 1.

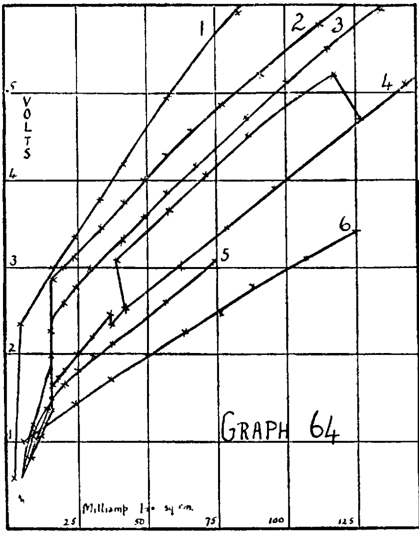
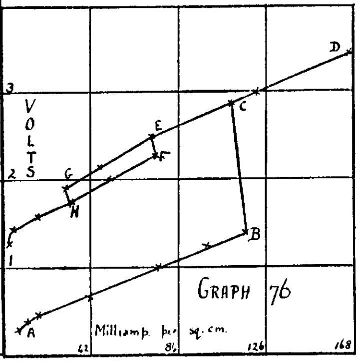


FIG 2.



(c) *Addition of an agent favouring activity.* A nickel anode immediately becomes passive in 5% ammonium sulphate solution, as shown by the steep portion of Curve 1 (Fig. 1) where potential is plotted against current density; on the other hand it remains active in 5% ammonium chloride solution (Curve 6, Fig. 1). The behaviour of a nickel anode was examined in ammonium sulphate solutions containing progressively increasing quantities of ammonium chloride, in the expectation that a state would be reached at which the activating and passivating influences (whatever they may be) balance each other, so that the electrode would alternate continually from one state to the other.

The results were as expected and are shown in Curves 2, 3, 4, and 5 (Fig. 1). The effect of adding 0·1% of ammonium chloride to the 5% ammonium sulphate is depicted by Curve 2, which shows that passivation occurs, but there is a shift in the direction of the active state. Addition of 0·2% of ammonium chloride is represented by Curve 3. Here the degree of passivation is still less. In the presence of 0·5% of ammonium chloride (Curve 4), passivation occurs to a smaller extent, but at a *C.D.* of 38 milliamp./cm.^{2} the nickel becomes active once more. Between this value and 125 milliamp./cm.^{2}, the anode alternates regularly between the active and passive states in periods of 5—10 seconds with an amplitude having a mean value of 0·6 volt. These limits of periodicity are represented in the graph by the quadrilateral. At *C.D.*'s greater than 125 milliamp./cm.^{2}, the nickel became permanently active. An equally good region of periodicity (not shown) was found when the solution contained 0·3% of ammonium chloride. The solution containing 1·0% of ammonium chloride is beyond the region of periodicity, the nickel remaining active throughout (Curve 5).

The table below records the values of *P.D.* for a given *C.D.* of 50 milliamp./cm.^{2} with progressive increase in the amount of ammonium chloride. It illustrates the region of periodicity lying on the border-line between two states.

		% NH_4Cl added to 5%$(NH_4)_2SO_4$.					
Soln.	5%$(NH_4)_2SO_4$	0·1%	0·2%	0·3%	0·5%	1·0%	5%NH_4Cl
P.D.	4·6	4·0	3·65	3·4 $\rightleftharpoons$ 2·8	3·4 $\rightleftharpoons$ 2·8	2·5	2·05

Periodicity and Passivity.

It has been shown (Hedges, *loc. cit.*) that the limits of periodicity at the anode are defined by exactly the same conditions for film formation as for what is regarded as passivity. It may be concluded either that passivity is a special case of film formation or that a region of periodicity may be a feature of several systems capable of different types of change of state. There is nothing novel in the first suggestion, but the evidence in its favour cannot be regarded as conclusive.

The analogy between the experiments now described and those conducted with other metals is illustrated in Fig. 2. This is a current density–potential curve for a nickel anode in 5% sulphuric acid and should be compared with Graph 50 (this vol., p. 2581), which is a similar curve for a zinc anode in caustic soda. The line *AB* represents the rise of *P.D.* with increasing *C.D.* until the point represented by *B* is reached. At this critical *C.D.* the nickel becomes passive (or the zinc becomes enveloped in a film) and the *P.D.* rises to *C*, oxygen being evolved. Further increase in *C.D.* causes the *P.D.* to rise along the line *CD*. When the current is reduced, the *P.D.* retraces the same path to *C*, but continues as far as *E*. If the current density is reduced to those represented between *G* and *E*, the *P.D.* oscillates continuously between two values defined by the area *EGHF*, oxygen being evolved intermittently.

It is true that the nickel dissolves extremely slowly when passive, whereas the zinc in a similar state dissolves relatively rapidly, but that seems to be only a matter of degree—a change in the ratio of current employed in liberating oxygen to the current used in forming ions of the metal—which varies from metal to metal in any case.

On the other hand, the fact is now recorded for the first time (as far as the author is aware) that passivity is immediately preceded by the formation of a visible film, which disappears at the moment the electrode assumes the passive state. It will be recalled that in the experiments with a zinc anode in concentrated caustic soda solutions the film was flung from the metal each time oxygen was evolved, and it formed over the metal during the periods of lower potential.

No useful purpose would be served by drawing conclusions from these comparatively few experiments concerning a subject which has been controversial for almost a century, but it is hoped that the study of this type of periodicity may lead to a better understanding of the nature of passivity.

Summary.

Periodicity has been observed in the passivity of an iron anode in sulphuric, nitric, and phosphoric acids, a cobalt anode in sulphuric acid, a nickel anode in sulphuric acid, and an aluminium anode in nitric acid and in caustic soda. In each case, the effect is produced by so arranging conditions of concentration, current density, temperature, etc., that the electrode has approximately equal chances of being in the active or in the passive state. Under such conditions, the electrode oscillates regularly between the two states. Periodic phenomena may also be produced by electrolysis in a solution containing a mixture of passivating ions and activating ions, *e.g.*, by adding ammonium chloride to an ammonium sulphate solution in which a nickel anode has been made passive. The periodic passivity phenomenon does not seem to differ in any respect from the periodic film formation at other metallic anodes. Immediately before passivation of the anode a visible film forms over the

metal, but this disappears at the commencement of oxygen evolution. The bearing of these observations on the nature of passivity is considered.

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