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**Chemistry.** — “*On the Periodic Passivity of Iron, II*”. By Prof. A. SMITS and C. A. LOBRY DE BRUYN. (Communicated by Prof. P. ZEEMAN).

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*Periodic passivity in experiments with sealed-in iron electrodes.*

In a previous communication <sup>1)</sup> on this subject we have shown how we have succeeded in calling forth the phenomenon of periodic passivity on anodic polarisation of iron in a solution of 0,473 gr. mol Fe SO<sub>4</sub> + 0,023 gr. mol Fe Cl<sub>2</sub> per litre. In these experiments we made use of an iron electrode 0.3 cm. long with an area of  $\pm 0.3$  cm<sup>2</sup>, which was sealed into the short leg of a U-shaped tube by means of shellac. The considerations that led us to these investigations were the following. During the anodic solution of iron in a solution of Fe SO<sub>4</sub> the internal equilibrium in the metal surface above a certain density of current, can be disturbed so greatly that passivity appears. When into the solution Cl, Br., or I-ions are introduced in a sufficient concentration, which need, however, be only exceedingly small, activation of the iron suddenly makes its appearance. It follows from this that for a definite density of current, given by the velocity of solution of the iron, it must be possible to find a halogen-ionconcentration, for which at a definite moment the chance that the iron remains passive, is equally great as the chance that it becomes active.

When at this moment the density of current is slightly diminished, the transition passive-active is sure to take place.

The iron anode in the passive state will dissolve only exceedingly little, the iron, which has now become active, will, however, go very greatly into solution.

In consequence of this the contact of the halogen-ions with the iron will diminish, and as the iron is now almost entirely withdrawn from the catalytic influence of the halogen-ions, it can again pass into the passive state.

Since, however, as has been said, the passive iron dissolves very little, and the processes which now take place at the anode consist

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<sup>1)</sup> These Proc.

of the discharge of the  $\text{SO}_4^{--}$ -ions with the subsequent  $\text{O}_2$ -generation, and further of a concentration increase of the halogen-ions, activation will again make its appearance through this latter process at a given moment etc.

This surmise was perfectly confirmed, and using Dr. MOLL's excellent galvanometer, we photographed some exceedingly regular periodic curves, the maxima and minima of which differed 1.74 Volt in situation. These graphs were, however, still incomplete in so far that the lines of time still failed.

In our further researches we made use of a photographic registration arrangement with time-signal-apparatus manufactured at this laboratory, so that also the time-lines are visible on the new photos, and accordingly a better idea of the regularity of the phenomenon can be formed.

We intend to answer several other questions by means of this arrangement, but before proceeding to do so we will first give a photographic representation of the phenomenon of the periodic passivity, under about the same circumstances as before, but now with registration of the time.

This photograph is given in Fig. 1. The potential difference again ranges here from about  $-0,3$  Volt with respect to the 1 norm. calomel electrode in the active state, to about  $+1,4$  Volt, in the passive state, the current density retrogressing from  $33$  m.Amp. to  $28$  m.Amp. per  $\text{cm}^2$ . Since the time-lines, which are at a distance of  $3,3$  seconds from each other, are now also drawn, the regularity of the phenomenon can be much better observed than before. The maxima lie  $6,15$  seconds apart. Fig 1 shows further that the iron was only a short time active, and comparatively long passive. The electrode was sealed in as before, and  $1,5$  cm. long, and the siphon of the auxiliary electrode was halfway of the height of the electrode. The solution contained  $0,72$  gr. mol.  $\text{FeSO}_4$  and  $\pm 0,014$  gr. mol.  $\text{FeCl}_2$  per litre solution.

The content of  $\text{FeCl}_2$  was, therefore, much smaller than before, hence the periodicity appeared here already at a smaller current density. Fig. 2 refers to an experiment with the same electrode, but taken with a slightly smaller current density, viz.  $30-25$  m.Amp. As is very apparent from this photograph, this has caused the periods to become longer, and the time during which the iron was in active state to become about equally long as the time in which the iron was passive.

It is remarkable that when we endeavour to proceed in the same direction, and try to make the active state last still longer

by diminishing the current density still more, this can only be maintained for a short time, and a state soon sets in again as reproduced here.

*Periodic passivity in experiments with iron electrodes that were not sealed in.*

The following experiment was made with an electrode that was not sealed in, but in which an iron electrode was simply immersed 1.5 cm. deep into the electrolyte, the siphon of the auxiliary electrode being placed quite at the bottom against the iron electrode. In this case there was always an activating influence, starting from the iron at the height of the liquid level, but in preliminary experiments we had already found that this activating influence did not, however, prevent the iron at the bottom of the electrode, which was 1.5 cm. long, from exhibiting pretty regular periodic passivity.

Fig. 3 shows the result obtained in this experiment. The phenomenon is, indeed, not quite so regular as with the sealed-in electrodes, but the difference is not great.

*Periodic passivity at different heights under the liquid level.*

We will now examine what is the behaviour of a non-sealed electrode at different heights under the liquid level.

For this purpose experiments were made with an electrode which was immersed much deeper, viz. more than 5 cm. under the liquid surface. When the auxiliary electrode was again placed quite at the bottom, a pretty regular periodicity was observed, just as in case of less deep immersion; this is shown by Fig. 4. When the auxiliary electrode was placed 1.5 cm. above the lower end against the iron electrode, the activating influence exerted from above, was already very clearly noticeable. Thus Fig. 4a shows that though the phenomenon is still regular, the character of the curve has been greatly modified. The periods are much shorter and the passive state lasts very short, and what is very remarkable, now a longer duration of the activity than of the passivity can be maintained.

In the following experiment we have placed the auxiliary electrode halfway up the immersed part, hence  $\pm 2.5$  cm. from the bottom, and under these circumstances still greater modifications were found, consisting in this that the iron did not always become equally strongly active, and that regularly two less active states were followed by a more active one, or that alternately a more active and a less active state followed, as is clearly shown by Fig.



Fig. 1. Sealed-in iron electrode 1.5 cm. long, of a diameter of 3 mm. Solution contains per Liter 0.72 gr. mol.  $\text{FeSO}_4 \pm 0.014$  gr. mol.  $\text{FeCl}_2$ . Potential measured halfway the height. Current density 28—33 milli-ampère/cm<sup>2</sup>. 1 period 6.15 seconds. Difference of the extreme values  $\pm 1.7$  Volt.



Fig. 2. Electrode, solution and arrangement siphon for potential measurement as in experiment in fig. 1. Current density 25—30 milli-ampère/cm<sup>2</sup>. 1 period 7.8 seconds.



Fig. 3. Electrode 1.4 cm. long, of a diameter of 3 mm., not sealed in, solution as in the experiment in fig. 1. Potential measured at the bottom of the electrode. Current density 32—36 milli-ampère/cm<sup>2</sup>. 1 period 5.25 sec.



Fig. 4. Electrode 5.1 cm. long of a diameter of 3 mm., not sealed in. Solution as in the experiment in fig. 1. Potential measured 1 mm. from the bottom. Current density 24—39 milli-ampère/cm<sup>2</sup>. 1 period  $\pm 5.1$  seconds.



Fig. 4a. Iron electrode 5.3 cm. long of a diameter of 3 mm. not sealed in. Solution as in the experiment in fig. 1. Potential measured 1.5 cm. from the bottom. Current density 38—43 milli-ampère/cm<sup>2</sup>. 1 period 2.7 seconds.



Fig. 5. Iron electrode 5.1 cm. long of a diam. of 3 mm. not sealed in. Potential measured halfway the height. Current density 30—34 milli-ampère/cm<sup>2</sup>. 1 period 2.2 seconds.



Fig. 5a. Electrode, solution and arrangement siphon for potential measurement as in fig. 5. Current density 28—32 milli-ampère/cm<sup>2</sup>.



Fig. 6. Electrode and solution as in fig. 5. Potential measured 1 mm. under the liquid level. Current density 47—53.5 milli-ampère/cm<sup>2</sup>. 1 period 3.65 seconds.



Fig. 7. Electrode  $\pm 60$  cm. long of a diameter of 3 mm. electrode spirally wound in 5 windings. Potential measured at the second winding from the top. Strength of the current regularly periodical at  $\pm 0.5$  ampère.

5 and 5a. The next figure 6 refers to the phenomenon that occurs when the auxiliary electrode is placed only 1 mm. under the liquid level against the iron electrode, and from this we see how greatly the activating influence issuing from the iron at the level of the liquid surface, disturbs the periodicity; the regularity now consists only in this that the most active state recurs at pretty regular times.

As might be expected the strength of the polarising current was perfectly regularly periodic.

*Influence of the area of the surface on the periodic passivity.*

In conclusion we have examined what is the influence of an enlargement of the immersed surface. For this purpose we have made an experiment with a spiral, of which 5 windings, with a joint length of 60 cm. were immersed into the electrolyte. The cathode was placed inside the windings, the auxiliary electrode being placed against the second winding from above. While the strength of the current was again regularly periodic, the potential difference exhibited very irregular oscillations, as Fig. 7 clearly shows. The irregularity was such that even the most active state did not recur regularly, and the whole curve, therefore, shows the periodicity under the influence of great disturbances. Hence it could be clearly perceived when observing the iron electrode, that this was never passive resp active throughout the whole area at the same moment, but that different parts were activated at different times.

This curve is a very fine demonstration of the fact observed by us already before that a piece of iron can be passivated with the more difficulty as the surface is greater.

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