

*Citation:*

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**Chemistry.** — “*On the Phenomenon of Anodic Polarisation.*” II.

By Prof. A SMITS. (Communicated by Prof. P. ZEEMAN).

(Communicated in the meeting of March 29, 1919).

1. In this communication will be discussed the peculiar phenomenon that was mentioned in the first communication with the above title. As was already stated there I observed the described phenomenon for the first time with Mr. LOBRY DE BRUYN for iron and nickel more than two years ago, but I did not publish it, because I thought it necessary to study the phenomenon first more closely.

Afterwards the same phenomenon was found by Mr. ATEN <sup>1)</sup> for chromium, but most probably he has not interpreted it correctly.

*Explanation of the Phenomenon.*

2. It has appeared from the preceding communication that the “phenomenon” appeared for iron when this was polarized anodically in a solution of ferro-sulphate or ferro-chloride, which had, indeed, been freshly prepared, but had not beforehand been heated with iron-powder.

We have already pointed out before that iron in the state of internal equilibrium can only coexist with a solution which practically possessed no ferri-ions. It is further known that a solution in which ferri-ions occur, clearly disturbs iron, and the more strongly as the ferri-ion-concentration is greater. As we communicated already before we have even succeeded in making iron passive by simply immersing it in a concentrated solution of ferri-nitrate.

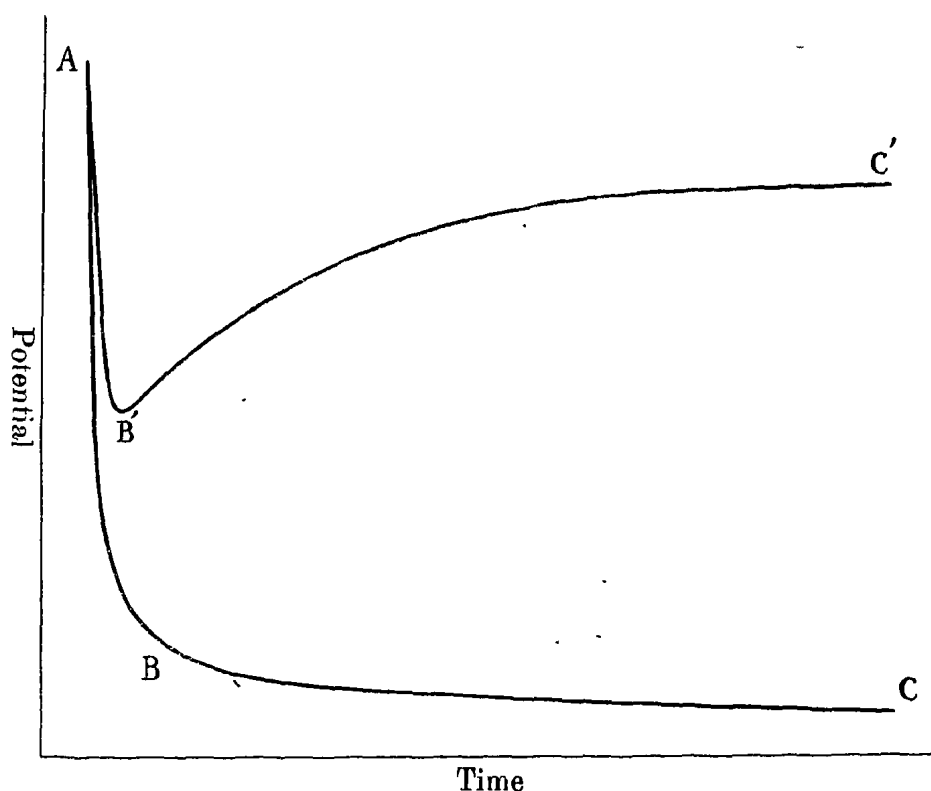
Hence the potential of the iron is less negative in a solution that contains ferri-ions than in a solution that coexists with unary iron, which latter solution is practically free from ferri-ions. In the solution with which the “phenomenon” was obtained the iron accordingly did not present the potential of internal equilibrium, but the potential was less negative.

When now iron in such a liquid is anodically brought to solution, the electrolyte will undergo a change in the neighbourhood of the iron, because iron when it is not passive, certainly goes into solution practically exclusively as ferro-ion. The iron is disturbed during this anodic dissolving, as appears from the less negative potential of the iron during the passage of the current, and at the same time the iron gets surrounded by a liquid layer that is poorer in ferri-ions

<sup>1)</sup> These Proc. XX, p. 1121.

than the other part of the solutions. After the current has been broken the iron surface is transformed with pretty great velocity in the direction of the internal equilibrium, and as it is surrounded by a solution that contains fewer ferri-ions than the solution outside the boundary layer, the potential of the iron will now be more negative than before the anodic polarisation. This state can, however, last only a very short time, for the ferri-ions diffuse from outside into the boundary layer, in consequence of which the potential must again become less negative, and will rise to the original value.

For a right understanding of the matter it is useful to study the subjoined diagram.



The line  $ABC$  represents the course of the potential of iron after anodic polarisation, when it is immersed in the solution of a ferro-salt, which is practically free from ferri-ions. Immediately after the anodic polarisation the iron is pretty greatly disturbed, but this disturbance diminished at first with great velocity, and afterwards more slowly. The curve  $AB'C'$  also indicates the course of the potential of iron after anodic polarisation, but now after a small quantity of a ferri-salt has been added to the preceding solution. At first the potential descends rapidly, to below the final value. If the liquid in the boundary layer had been entirely free from ferri-

ions and if it had remained so, the potential would have followed the curve *ABC*, but now the iron is, indeed, in a liquid layer that is poorer in ferri-ions than the liquid outside the boundary layer, but the ferri-ions present prevent the iron from assuming internal equilibrium, hence the potential cannot reach such a great negative value as when the ferri-ions were present, as in the first experiment.

Besides continually more ferri-ions diffuse into the boundary layer, which causes the disturbance of the iron to increase again and in consequence of which the potential becomes again less negative. When we imagine fig. 10 placed under fig. 2 of the former publication, we get the schematic figure indicated just now.

In this way the phenomenon for iron must be explained, and very probably it will have to be explained in the same way for nickel and chromium.

That for iron the minimum appears sooner and is more pronounced, must be attributed to the great rapidity with which iron, so long as it is not yet passive, tries to re-establish equilibrium after a disturbance. Nickel is much more inert in a  $\text{NiSO}_4$ -solution than in a  $\text{NiCl}_2$ -solution, and this shows itself also again in this phenomenon <sup>1)</sup>.

3. When it now appears on continued research, as is to be expected, that the discussed phenomenon can also be made to disappear for nickel and chromium by beforehand heating the electrolytes with the metals in the form of powder for a long time in a current of hydrogen, then it is sure that the solutions of nickel sulphate and chromo-sulphate used up to now contain a second kind of ions, and this in a concentration different from that prevailing in the liquid that coexists with the metal which is in internal equilibrium.

For nickel we are then confronted by the interesting question what is the second nickel-ion here.

Thus it will probably appear that the found phenomenon furnishes an excellent expedient to decide whether a solution contains different kinds of ions of a same element or whether it does not.

In conclusion I will point out that it is very well possible that as it were the reflected image of the found phenomenon can present itself after cathodic polarisation; this has, however, not been found by us as yet. The results published by RAHTERT would prove this possibility for nickel, but in our opinion these results are not correct.

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<sup>1)</sup> This will clearly appear in a following communication.