Chemistry. — *"On the Phenomenon after Anodic Polarisation."* II. By Prof. A. Smits, G. L. C. La Bastide, and Th. de Crauw. (Communicated by Prof. P. Zeeman).

(Communicated in the meeting of June 28, 1919).

1. It was shown in a preceding communication that the phenomenon that appears after anodic polarisation of iron in an iron salt solution is owing to this that during the anodic solution the iron gets surrounded by a liquid layer which is very rich in ferro-ions. As a rule the ratio $\dfrac{(Fe^{\cdot\cdot})}{(Fe^{\cdot\cdot\cdot})}$ will be greater in this liquid layer than outside it. After the current has been broken the ferri-ions will, therefore, diffuse from the surroundings into the boundary layer, whereas the ferro-ions pass outside, which causes the ratio $\dfrac{(Fe^{\cdot\cdot})}{(Fe^{\cdot\cdot\cdot})}$ to become again smaller in the boundary layer. In consequence of this change the potential of the iron, which was at first less negative or positive through the disturbance of the metal, passes through a minimum value after interruption of the current.

That the above explanation actually accounts for the phenomenon was proved by the fact that the phenomenon disappears altogether when the iron salt solution is previously heated in a hydrogen atmosphere with iron powder for some time. We then get a ferro salt solution which is in electromotive equilibrium with unary iron, so that in the boundary layer the ratio $\dfrac{(Fe^{\cdot\cdot})}{(Fe^{\cdot\cdot\cdot})}$ practically does not change when the iron is anodically dissolved.

2. In the above mentioned communication it was pointed out that the potential of Nickel after polarisation in a solution of $NiSO_4$ likewise passes through a minimum value, so that it was already supposed that this phenomenon would have to be explained in the same way as for iron.

To examine this the phenomenon for Nickel was first photographed when the metal was immersed in a solution of $NiCl_2$. In this the minimum shows itself very clearly, as the adjoined photo (fig. 1) sets forth.

The process is much quicker than when an $NiSO_4$ solution is used, in consequence of the positively catalytic action of the chlorine ions.
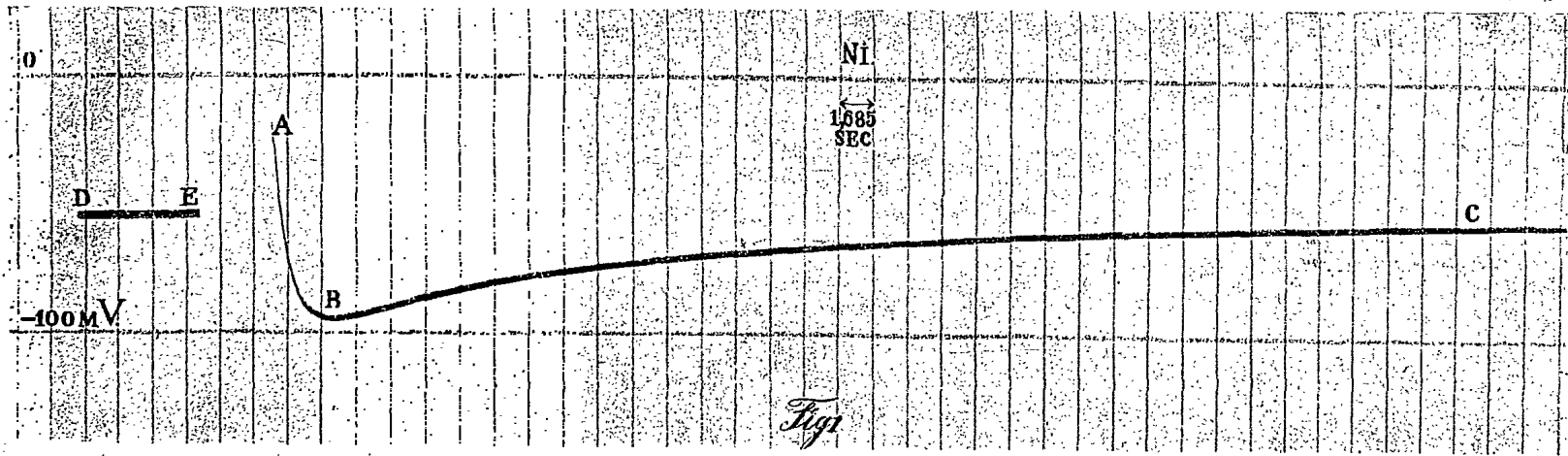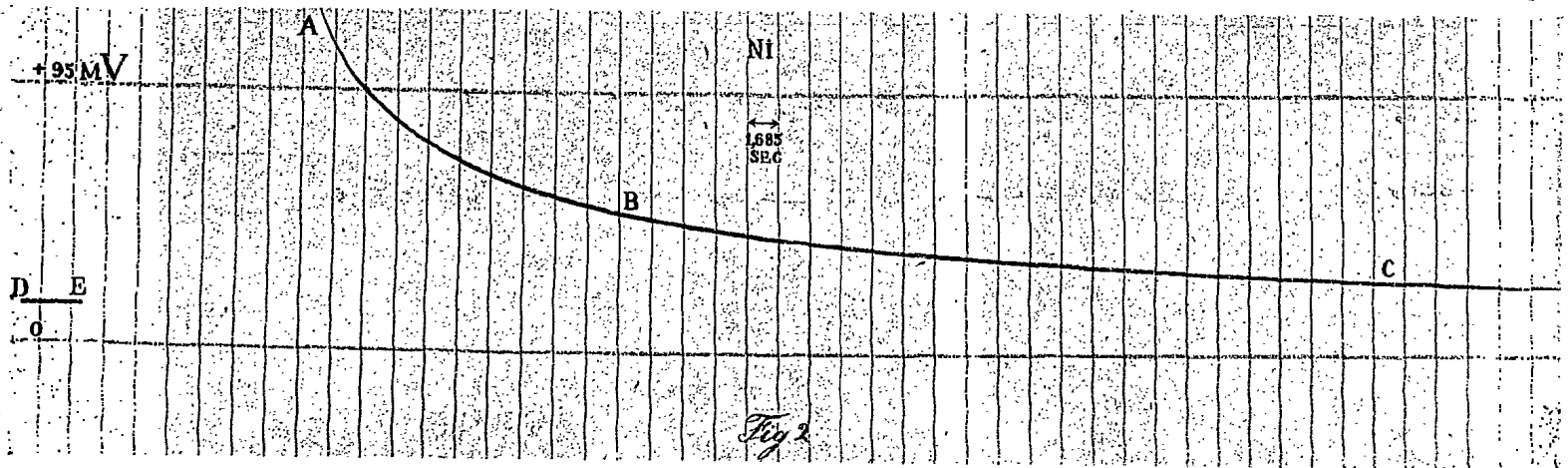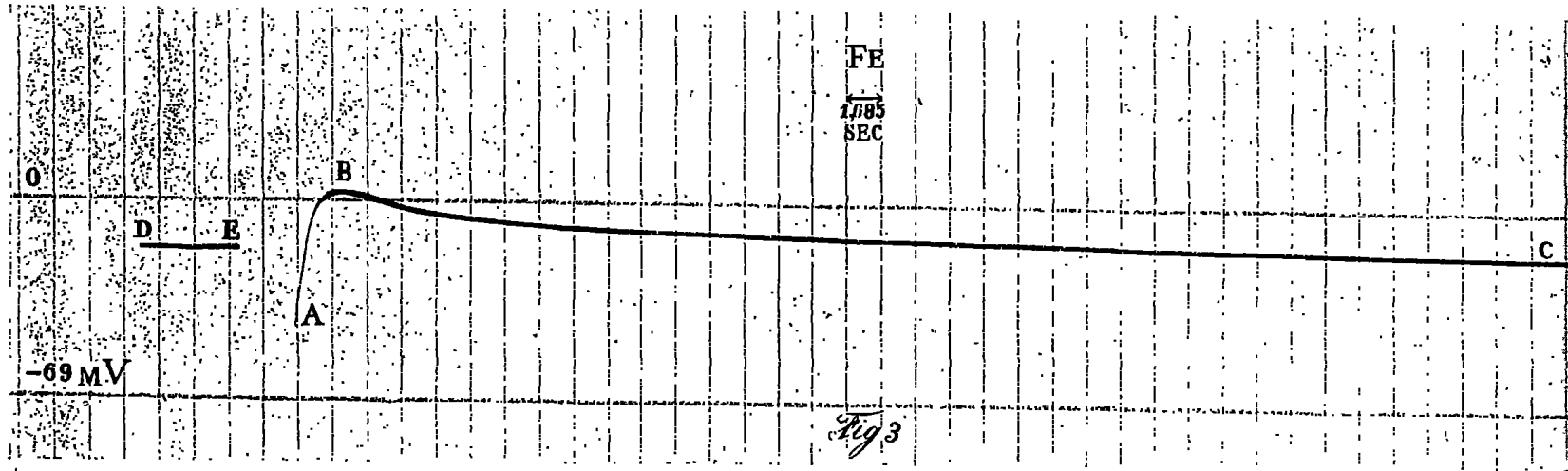
O

Ni

1.685
SEC

A

D ▬▬▬ E

C

B

−100 M V

Fig 1

A

+95 M V

Ni

1.685
SEC

B

D ▬ E

C

O

Fig 2

O

B

FE

1.085
SEC

D E

A

−69 MV

C

Fig 3

Then the $NiCl_2$ solution was heated for some time in a hydrogen atmosphere with finely divided Nickel that had been prepared by reduction of NiO at relatively low temperature, after which the experiment was repeated. As the following photo shows (fig. 2), the phenomenon had now entirely disappeared.

3. If was already pointed out in the preceding communication, that as it were, the *reflected image of the phenomenon* was to be expected, when e.g. iron immersed in a ferro-ferri-salt-solution is made cathode. The ratio $\dfrac{(Fe^{\cdot\cdot})}{(Fe^{\cdot\cdot\cdot})}$ will be greatest at the iron surface, because the iron by sending $Fe^{\cdot\cdot}$-ions into solutions, strives to bring such a change in the boundary layer that in case of unary behaviour, it can be in equilibrium with it. Hence the farther the liquid layer is from the iron, the smaller will be the ratio $\dfrac{(Fe^{\cdot\cdot})}{(Fe^{\cdot\cdot\cdot})}$. When therefore iron, immersed in the supposed solution, is made cathode for a moment, the iron will be deposited from the boundary layer, and the ions from the following layer will diffuse into the boundary layer, and as the ratio $\dfrac{(Fe^{\cdot\cdot})}{(Fe^{\cdot\cdot\cdot})}$ is smaller in this following layer, the iron after cathodic polarisation comes in contact with a liquid layer in which the ratio $\dfrac{(Fe^{\cdot\cdot})}{(Fe^{\cdot\cdot\cdot})}$ is smaller than before the cathodic polarisation, which causes a stronger disturbance in noble direction, hence a less negative potential. After interruption of the current the said ratio will now increase again through the solution of the iron, so that the potential of the iron becomes again more negative. As on cathodic polarisation the iron gets covered with a layer of iron, which at first deviates from the unary iron in base direction, *a phenomenon after cathodic polarisation* was really to be expected also here, which would have to consist in this, that after interruption of the current the potential of the iron, after cathodic polarisation, passes through a maximum value. [1])

As the photo on fig. 3 shows, this supposition is confirmed. The maximum B lies about 30 m.V. less negative than the initial potential indicated by the line DE.

It will now be examined whether the same phenomenon can also be observed for Nickel.

Amsterdam, June 27, 1919.   *Laboratory for General and Anorganic Chemistry of the University.*

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[1]) Through diminution of the total ion concentration the potential becomes more negative in a small degree, so that this circumstance still slightly counteracts the phenomenon under consideration.

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