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**Chemistry.** — “*The Electromotive Behaviour of Aluminium.*” I.  
By Prof. A. SMITS. (Communicated by Prof. H. A. LORENTZ.).

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1. *Introduction.*

As early as 1914<sup>1)</sup> we began to consider the behaviour of aluminium from the point of view offered by the new theory of the electromotive equilibria.

As regards its electromotive behaviour aluminium is a most interesting metal. It has generally not been inserted in the electromotive series, because no certainty has been attained as yet about its place. In alkaline solutions aluminium precipitates the zinc, but it does not do so in neutral or acid solutions. To this is added the very remarkable fact that the amalgamated aluminium does precipitate the zinc from neutral solutions, and acts with violent decomposition on water, that it further rapidly oxidizes when exposed to the air, and exhibits a character that indicates that aluminium in this condition must be placed directly after the metals of the alkaline earths, thus: Mg—Al—Mn—Zn.

In connection with this the conclusion was obvious that commercial aluminium is in a noble, less active condition, or in other words that it is in a state of passivity. This was decidedly a step in the right direction, but an explanation of the behaviour of aluminium had not yet been given.

Most handbooks and publications state that commercial aluminium is covered with a coat of oxide, and that its passivity is owing to this.

Also the anodic polarisation of aluminium has made the peculiar character of this metal evident. It was found before, that when an  $\text{Al}_2(\text{SO}_4)_3$ -solution was used, the density of the current,  $i/o$ , on anodic polarisation continually decreased, whereas the electric potential rose, which may be seen from the following table, which has already been published before.<sup>2)</sup> Here the potential has been measured with respect to another aluminium rod as auxiliary electrode.

<sup>1)</sup> SMITS, ATEN, These Proc. **22**, 1133 (1914).

<sup>2)</sup> SMITS, ATEN, Loc. cit.

Al-electrode in 1/2 N Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>

i/o	anode
0.8	+ 2.56
0.53	+ 3.48
0.46	+ 3.84
0.36	+ 4.13

It has been tried to account for this phenomenon by assuming the formation of an Al<sub>2</sub>O<sub>3</sub>-layer with great resistance, which supposition is, however, hardly tenable, for when the above-mentioned phenomenon presents itself, the aluminium-anode is *perfectly bright*. Besides when the current is reversed, the resistance has entirely disappeared.

When the tension is increased, there is actually formed a coat of Al<sub>2</sub>O<sub>3</sub>, Al(OH)<sub>3</sub> or of a basic salt. Then the density of the current is practically reduced to zero, but when the current is reversed, the potential of the aluminium-electrode is considerably smaller.

When the anode potential is carried up very high, e.g. to 200—500 V., the potential is reduced to from 1/10 to 1/50 on reversal of the current.

This property, the so-called *valve-action*, is used to transform an alternating current into a continuous one. With high current-densities the electric valve-action stops under ordinary circumstances owing to rise of temperature.

FISCHER<sup>1)</sup>, therefore, used as anode an aluminium tube, through which water flowed, and in this way he succeeded in getting coats of oxide of a thickness of some tenths of millimeters.

The most extensive researches on the valve-action of aluminium have been performed by SCHULZE<sup>2)</sup>. He assumes, that every newly-

<sup>1)</sup> Zeitschr. f. phys. Chem. **48**, 177 1904.

<sup>2)</sup> Ann. der Phys. **21**, 929. 1906.

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Zeitschr. f. Elektrochem. **20**, 307. 1914.

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formed aluminium-surface is immediately covered with a solid, not porous layer of oxide of molecular thickness. This layer, indeed, insulates, but according to him it can be pierced by the anions of the salt-solutions or by the  $O''$ -ion on anodic polarisation, and the oxygen formed then combines with the metal to  $Al_2O_3$ . The porous oxide layer offers an ever increasing resistance with increasing thickness, and at last the anions are almost exclusively discharged at the layer of oxide, and only very few succeed in traversing this layer, and reaching the metal, which he tries to prove by the fact that the quantity of generated oxygen is 96 % of the quantity of electricity transmitted.

When with a certain thickness of layer a definite potential gradient has been reached, sparking commences, which puts a stop to the increase of tension and the thickening of the oxide layer. This maximum tension is greatly dependent on the nature and the concentration of the anions; when this concentration increases, the maximum tension diminishes. It is remarkable that, when the current is reversed, no current passes below a certain potential, and that this minimum potential of the cathode is then many times smaller than the anodic-minimum-potential. Also the cathodic minimum potential depends greatly on the nature of the ions.

SCHULZE, and before him TAYLOR and INGLIS <sup>1)</sup> and GUTHE <sup>2)</sup>, thought that they could find the explanation of this peculiar phenomenon by assigning to the gas layer that is formed in the pores of the  $Al_2(OH)_6$ , the property of allowing the anions to pass less easily than the cations.

It is clear that this explanation is not entirely satisfactory, the more so because there are still a great many other exceedingly remarkable phenomena on which it does not throw any light. Two of them may be mentioned here, first the phenomenon that amalgamated aluminium does not show valve-action, and secondly that a chlor-ion concentration in the electrolyte of 0.2 % renders the valve-action quite impossible.

2. When aluminium is considered from the point of view of the theory of the electromotive equilibria, the conclusion is readily reached that this theory is able to account for the above-mentioned remarkable behaviour of aluminium by means of the same principles as the polarisation-phenomena in the other metals.

In the first place it may be pointed out that it can easily be

<sup>1)</sup> Phil. Mag. 5, 301, (1903).

<sup>2)</sup> Phil. Rev. 15, 327, (1902).

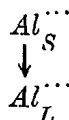
demonstrated that it is erroneous to assert that commercial aluminium is covered with a coating of oxide. It was shown before that when the bottom of a vessel with an  $\text{Al}_2(\text{SO}_4)_3$  solution is covered with a layer of mercury, and when through the solution an aluminium rod is immersed in the mercury layer, the aluminium rod immediately assumes the potential of the mercury, from which follows that the aluminium rod was not covered with an insulating layer of  $\text{Al}_2\text{O}_3$ , but was in direct contact with the mercury <sup>1)</sup>.

Now that this fact has been established, and the initial condition is uncovered metal, it is clear that it must be explained why on anodic polarisation the potential of the metal becomes so strongly positive already with very small current densities that the tension of separation of the oxygen is reached. It is seen that here the same question presents itself as in the case of anodic polarisation of other inert metals. It was pointed out before that in the first place the most essential, the *primary* phenomenon, should be explained, viz. the change of the potential in noble direction; the oxygen, separation and the subsequent oxide formation are *secondary* phenomena.

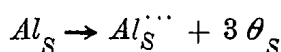
The strong ennobling of the potential of aluminium on anodic polarisation must be explained by this, that while the withdrawal of electrons from the metal which is represented by



is immediately followed by aluminium-ions going into solution



because this heterogeneous equilibrium is instantaneously established, the homogeneous reaction



proceeds with very small velocity, so that the metal becomes poorer in ions and electrons. In consequence of this the potential of the metal becomes less negative or more positive, as appears from the equation:

$$E = - \frac{0,058}{v} \log \frac{L_M}{(M_L^v)} - 2,8$$

because in this case  $L_M$  becomes smaller.

This phenomenon is, therefore, primary, and if the metal is inert,

<sup>1)</sup> SMITS, ATEN. l.c.

as it is here, the potential of separation of the oxygen will soon be reached, and oxygen generation will set in, which under certain circumstances may lead to the formation of an adherent coating of oxide or hydroxide round the metal. Of course this coating gives rise to a certain resistance, which may rise to considerable amounts with increasing thickness. The assumption, however, that the resistance of such a coating should be different for different directions of current is not justifiable, so that there can be no doubt that the sudden decrease of the resistance on reversal of the current, must be owing to some other cause.

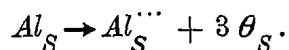
So far there is no reason to doubt that oxygen and hydrogen are negative catalysts for the setting in of the internal metal equilibrium. Hence the slight quantities of oxygen absorbed by the metal on anodic polarisation have a greatly retarding effect (Fe, Co, Ni).

Most probably this is likewise the case for aluminium, and to this it will have to be attributed that such a strong anodic polarisation has been observed in aluminium.

Accordingly this fact leads to the assumption that the metal is disturbed here to a great extent, i. e. that the metal surface becomes very poor in ions and electrons, or in other words, that the metal passes at its surface into a state which agrees with a metalloid in this that it possesses an exceedingly small electric conductivity.

On this strong anodic disturbance the aluminium surface becomes, therefore, a metal coating of great resistance, and this coating is in its turn surrounded by another of  $Al_2O_3$ .

As the study of the phenomenon of polarisation in other metals has taught, the disturbance that has arisen by anodic polarisation, stops immediately through reversal of the current. This behaviour must be explained by the fact that hydrogen, just as oxygen, though in a different degree, is a negative catalyst for the establishment of the internal metal equilibrium, and can yet apparently act positively catalytically, when it separates on a metal surface that has previously absorbed oxygen, as both negative catalysts then disappear amidst formation of water. The small quantity of oxygen absorbed then enhances the disturbance of the aluminium on anodic polarisation; hence the removal of this negative catalyst will immediately stop the disturbance, and the strongly metastable state of the aluminium surface will be transformed with great velocity in the direction of the state of internal equilibrium. This transformation changes the metal coating of great resistance suddenly into another of smaller resistance, which must, therefore, be attributed to the great velocity of the reaction:



Hence the resistance that remains when aluminium is made from anode to cathode, is chiefly the resistance of the coating of  $Al_2O_3$ .

In the earlier paper cited here a great resistance was simply assigned to the solid solution of oxygen in aluminium, and too little stress was laid on the fact that the strong disturbance of the aluminium may lead to the formation of an aluminium surface that is very poor in ions and electrons.

Since 1914 researches on the electromotive behaviour of aluminium have been made in my laboratory, first by Miss RIWLIN, and afterwards continued by Mr. DE GRUYTER, both as regards commercial aluminium and amalgamated aluminium.

Working with very pure commercial aluminium, the polarisation and the curves of activation in different aluminium-salt solutions, have been determined, in which again, just as with iron, the strongly positively catalytic influence of halogen-ions came to light.

A closer examination of the valve action is in progress, and also the thermic and electromotive investigation of the system mercury-aluminium. In connection with this investigation there are other thermic and electromotive investigations being made on systems mercury-metal, as mercury-magnesium, mercury-tin etc. As a peculiarity it may be mentioned here that, as was already found by DE LEEUW<sup>1)</sup> in tin, mercury exerts an accelerating influence on enantiotropic conversions, so that, where a point of transition in the pure metal is not, or hardly, to be observed, this is generally very clearly seen on addition of a little mercury.

A good example of this is furnished by aluminium, for which a point of transition at  $\pm 580^\circ$  was found with great clearness from the investigations of amalgams rich in aluminium.

Also with a view to this the investigation mercury-metal with other important metals will be continued.

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*Amsterdam, Jan. 30, 1920.*

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