Now it is certainly very remarkable that this correction is of the same sign and the same order of magnitude as the planetary precession derived from the attraction of SEELIGER's ellipsoids. It must however be kept in mind that it is very well possible to explain the discrepancy between the determinations of the constant of precession from right-ascensions and from declinations (or from m and from n) by the hypothesis of systematic proper motions of the stars. Thus HOUGH and HALM (M. N. Vol. LXX page 586) have from the hypothesis of unequal distribution of the stars over the two streams derived a systematic difference which is equivalent (for NEWCOMB) [1] to a correction

$$\Delta \lambda = + 0'' 56.$$

As the effect of the attraction of SEELIGER's ellipsoids on the motion of the moon Mr. WOLTJER finds a secular motion of both the perigee and the node. Both of these are due chiefly to the inner ellipsoid and are thus not much altered if SEELIGER's hypothesis is replaced by either of the hypotheses A or C. We find

SEELIGER	$\dfrac{d\tilde{\omega}}{dt} = + 2''.11$	$\dfrac{d\mathcal{S}b}{dt} = - 2''.50$
A	$+ 2 .04$	$- 3 .30$
C	$+ 2 10$	$- 2 .06$

All these quantities are well within the limits of uncertainty of the observed values.

Chemistry. — "*The application of the theory of allotropy to electromotive equilibria.*" II. By Dr. A SMITS and Dr. A. H. W. ATEN. (A preliminary communication). (Communicated by Prof. J. D. VAN DER WAALS).

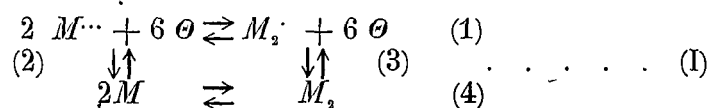(Communicated in the meeting of April 24, 1914).

1. In the first communication [2] under the above title it has been demonstrated that the theory of allotropy applied to the electromotive equilibrium between metal and electrolyte, teaches that a metal that exhibits the phenomenon of allotropy and is therefore built up of different kinds of molecules immersed in an electrolyte, will emit different kind of ions.

The different kinds of ions assumed by the theory of allotropy, need not be per se different in size, as was remarked before. They

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[1] For STRUVE's stars the correction would be $+ 0''.77$. For Boss the corresponding computation has of course not been executed by HOUGH and HALM.

[2] These Proc. Dec. 27, 1913, XVI. p. 699.

may be equal in size, but different in structure. There can, however, be another difference besides, viz. in electrical charge. In the preceding communication the molecule kinds M and M_2 were assumed, and for simplicity's sake the circumstance that part of these molecules are electrically charged also in the metal, was not mentioned. This circumstance need not be taken into account, because the electrical charge of the atom M in one ion M_2) was put equal to that in the other ion ($M^{\cdots}$). If it had then been our intention to indicate the total equilibrium in the metal, we might have drawn up the following scheme :

$$2\ M^{\cdots} + 6\ \Theta \rightleftarrows M_2^{\cdot} + 6\ \Theta \quad (1)$$
$$(2) \quad \updownarrow \qquad \quad \updownarrow \quad (3) \qquad \cdots \cdots \quad (I)$$
$$2M \quad \rightleftarrows \quad M_2 \qquad (4)$$

from which follows that the system would then be pseudoquaternary.

For an explanation of the electromotive disturbances of the equilibrium mentioned in the preceding communication, a consideration of the equilibrium (1) or '(4) sufficed. Then equation (4) was chosen and $2M$ and M_2 were therefore called the pseudo components, though of course we might as well have taken $2M^{\cdots} + 6\Theta$ and $M_2^{\cdot} + 6\Theta$.

Now it is clear that when in the metal ions of equal structure occur, but of different value, the scheme of equilibrium can be as follows.

$$M^{\cdots} + 2\ \Theta \rightleftarrows M^{\cdots} + 3\ \Theta \qquad (1)$$
$$(2) \ \searrow \quad M \quad \nearrow\ (3) \qquad \cdots \cdots \quad (II)$$
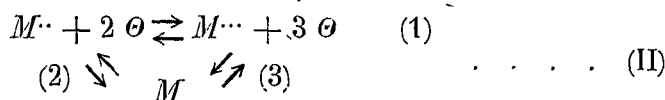
The system is then pseudo ternary, but in most of the cases it will be sufficient to consider the pseudo binary system, indicated by equation (1), and assume $M^{\cdots} + 2\ \Theta$ and $M^{\cdots} + 3\ \Theta$ as pseudo components. A similar equilibrium will have to be assumed, when the metal can go in solution with different valency under different circumstances. This case is probably of frequent occurrence.

Of course the metal phase is already complex, when metal ions occur by the side of uncharged molecules, but this complexity does not suffice to explain the peculiar electromotive behaviour of the metals, whereas schemes I and II are competent to do so.

In connection with the foregoing considerations it could be shown that the unary electromotive equilibrium finds its proper place in the Δ, x figure of a pseudo system, which can clearly appear under certain circumstances, when we namely succeed in bringing the metal out of the state of internal equilibrium. Thus it was e.g. shown

that when a metal is brought to solution by an electrolytic way, so when it is made into an anode, the internal equilibrium will be disturbed, and the metal will become superficially enobled, at least when the velocity of solution is greater than the velocity with which the internal equilibrium sets in. In this case therefore the dissolving metal will have to become positive with respect to an auxiliary electrode of the same metal which is superficially in internal equilibrium. If reversely the metal is made to deposit electrolytically, the reverse will take place, and the separating metal will be less noble and therefore negative with respect to the auxiliary electrode.

The anodic disturbance of equilibrium being attended with a diminution of the more active kinds of molecules, this process will bring about a diminution of the chemical activity. This is therefore the reason that this anodic state of disturbance is a more or less passive state of the metal.

At the cathode the disturbance lies exactly in the other direction, and a more active state will be brought about.

The degree in which a metal is thrown out of its state of equilibrium in case of electrolytic solution or deposition, will depend on the current density at constant temperature, and it was therefore of importance to study the discussed phenomenon at different current densities.

What may be expected is this that the internal equilibrium will generally be able to maintain itself for very small current densities. Then the tension with respect to the auxiliary electrode will be zero, both when the metal is anode and cathode. With greater current densities the metal will get superficially more and more removed from the state of internal equilibrium on increase of the current density, and the tension with respect to the auxiliary electrodes will greatly increase.

As the metal surface gets further removed from the state of internal equilibrium, so becomes more metastable, the velocity of reaction which tries to destroy the metastability, increases however in consequence of the change of concentration in the homogeneous phase; and we may therefore expect that the potential difference between metal and auxiliary electrode will vary with the current density in the way indicated in Fig. 1.

When the velocity with which the internal equilibrium sets in, is small, the part ab will lie at exceedingly small current densities, and if the measurements are not exceedingly delicate, we shall get the impression that this piece is entirely wanting.

It is clear that the tension which is represented here as function

of the current density means the tension with respect to the auxiliary electrodes. This tension, which is also called polarisation tension, is
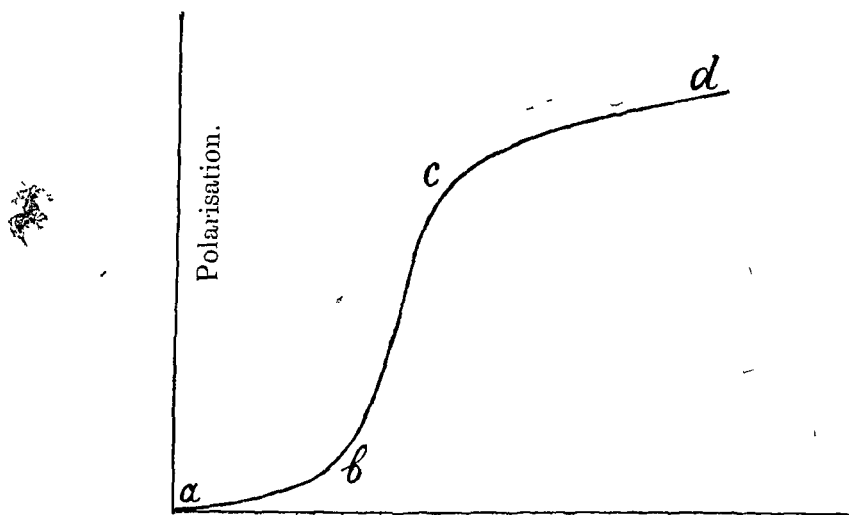

Fig. 1.

positive when the metal is anode, and negative, when it is used as cathode.

Further this possibility was still to be foreseen that when the metal assumes internal equilibrium very slowly a distinct change of the potential difference would have to be demonstrated even after the current had been interrupted.

Now it should be noted here·that when a base metal has become noble during its use as anode, and the difference of potential between the metal and electrolyte has risen to the tension of liberation of the oxygen, at the anode two processes will begin to proceed side by side; besides the going in solution of the metal we get also the discharge of the OH'-ions and the possible formation of oxide skins, the influence of which should be examined.

We get something of the same kind at the cathode. When viz. the difference of tension metal-electrolyte at the cathode has become greater than the tension of liberation of the hydrogen, besides discharge of metal ions, also discharge of H'-ions will take place there.

Method of Investigation.

The measurement of the polarisation tensions took place in the following way (see Fig. 2). Two electrodes of the metal that is to be investigated, in the shape of wire or rods, were placed in a solution

of a salt of the metal, generally the nitrate. The two electrodes were connected by a variable resistance and an Ampèremeter with a number of accumulators, so that the strength of the polarizing current is easily changed and measured. To measure the tension of polarisation at one of the electrodes a beakshaped bent glass tube was brought into the solution, whose capillary point was placed as close as possible against the polarized electrode. In this glass tube a third (auxiliary) electrode of the same metal was brought. This auxiliary electrode, which is currentless, exhibits the normal potential difference with respect to the solution. As there is no loss of tension in the liquid of the auxiliary electrode, and its point is close against the polarized electro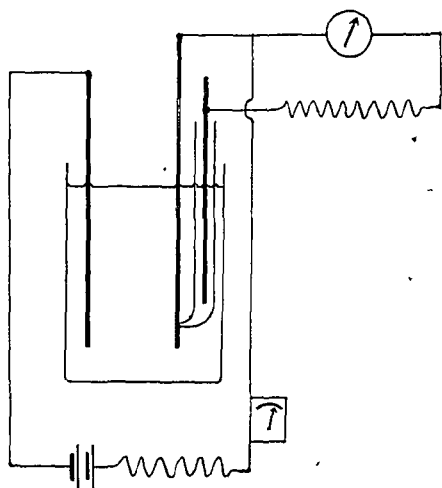de, the potential difference between the auxiliary electrode and the polarized electrode gives directly the deviation which the potential difference of the polarized electrode presents from the normal potential difference, so the *polarisation tension.* The measurement of this potential difference took place by reading the deviation which was obtained by connecting the auxiliary electrode and the polarized electrode by means of a resistance of some meg. ohms with a galvanometer. The value of the scalar divisions in Volts was determined by connecting the galvanometer with a normal element.

Fig. 2.

Silver, Copper, Lead.

2. The investigation of different metals, undertaken in this direction, has shown us that as was to be expected, they represent the most different types.

There are metals which in contact with an electrolyte, assume internal equilibrium very quickly, there are those that do so very slowly, and there are those that lie between these extremes.

Beginning with the metals which quickly assume internal equilibrium, we may first mention the metals: *silver, copper* and *lead.*

The result of the investigation of these metals is found in the following tables.

After the current had been interrupted, no potential difference with the auxiliary electrode was to be perceived.

In the first column the current density is found expressed in milliampères per cm². In the second column the potential difference with the auxiliary electrode is indicated in Volts, the metal serving as *anode* (anodic polarisation tension); and in 'the third column the same is given for the case that the metal served as *cathode* (cathodic polarisation tension).

TABLE I.

Silver electrode immersed in ¹/₂ N. Ag NO₃-solution.

$\dfrac{i}{0} = \dfrac{m.A}{cm^2}$	V-anode	V-cathode
25	+ 0.03	— 0.006
50	+ 0.03	— 0.012
100	+ 0.04	— 0.014
200	+ 0.05	— 0.015
300	+ 0.05	— 0.016
400	+ 0.06	— 0.018
750	+ 0.09	— 0.020

It is seen from this table that the silver is not materially nobler during the solution, and not materially baser during the deposition than the auxiliary electrode, which is entirely in internal equilibrium. The polarisation is therefore exceedingly slight here, from which we may deduce that the metal silver very quickly assumes internal equilibrium. Under these circumstances it is of course out of the

TABLE 2.

Copper electrode in ¹/₂ N . Cu (NO₃)₂-solution.

$\dfrac{i}{0} = \dfrac{m.A}{cm^2}$	V-anode	V-cathode
14	+ 0.016	— 0.016
29	+ 0.026	— 0.026
57	+ 0.032	— 0.035
114	+ 0.048	— 0.063
171	+ 0.048	— 0.082
230	+ 0.050	— 0.088

question that a potential difference could still be demonstrated after the current had been broken, which accordingly was by no means the case.

For *copper* the following values were found. (See table 2 p. 42).

This is, therefore, the same result as was obtained for silver, and lead behaves in an analogous way, as appears from the following table.

TABLE 3.

Lead electrode in $^1/_2$ N . Pb $(NO_3)_2$-solution.

$\dfrac{i}{0} = \dfrac{\text{m.A}}{\text{cm}^2}$	V-anode	V-cathode
36	+ 0.010	— 0.006
140	+ 0.033	— 0.010
280	+ 0.046	— 0.013
570	+ 0.082	— 0.017
1000	+ 0.126	— 0.020

After the current had been interrupted no potential difference with the auxiliary electrode could be demonstrated.

Nickel.

3. A splendid example for an internal equilibrium setting in very slowly is furnished by *nickel*, as appears from the following result.

TABLE 4.

Nickel electrode immersed in $^1/_2$ N . Ni $(NO_3)_2$-solution.

$\dfrac{i}{0}$	V-anode	V-cathode
27 —	+ 1.61	— 0.95
45 —	+ 1.64	— 1
90 —	+ 1.68	— 1.25
180 +	+ 1.77	— 1.40
360·	+ 1.83	— 1.66
540	+ 1.88	— 1.77

Nickel shows therefore an enormous anodic and cathodic polarisation, which we must ascribe to the very slow setting in of the internal equilibrium, the more so, as we found that even *after the*

current had been interrupted a great potential difference with the auxiliary electrode could still be demonstrated viz. an anodic polarisation tension of 0,95 Volt. and a cathodic polarisation tension of 0,5 Volt. These tensions decreased with diminishing velocity to 0, as a proof that the metal assumes internal equilibrium by the aid of the electrolyte. As on account of the oscillations of the mirror of the galvanometer the said tensions could not be observed quickly enough after the current had been interrupted, the above values give the tensions some seconds after the interruption of the current. Immediately after the interruption they will have been + 1,88 V resp. — 1,77 V. Hence nickel, used as anode, becomes superficially a metal nobler than platinum as we know it.

Cadmium.

4. *Cadmium* is a metal lying between silver, copper, and lead on one side and nickel on the other side with regard to the velocity with which its internal equilibrium sets in.

For this metal we found what follows:

TABLE 5.
Cadmium electrode in $^1/_2$ N. Cd $(NO_3)_2$-solution.

$\dfrac{i}{0}$	V-anode	V-cathode
21	+ 0.093	— 0.127
72	+ 0.186	— 0.186
144	+ 0.290	— 0.220
286	+ 0.380	—· 0.220
428	+ 0.507	— 0.220

Besides that the polarisation is smaller here than for nickel, it is noteworthy that while for nickel the anodic and cathodic polarisation tension differ little, this difference becomes pretty considerable for cadmium, at least for large current densities. This peculiarity may be explained in a simple way by means of the Δ,x-figure given in the preceding communication. (See Fig. 3.[1])

Suppose that with unary electromotive equilibrium at the given temperature the electrolyte L and the metal phase S coexist, then the

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.[1]) Here the potential difference of the metal with respect to the electrolyte has been given.

metal phase in case of anodic polarisation will move from S to b, and over this range $\dfrac{d\Delta}{dx}$ is great.
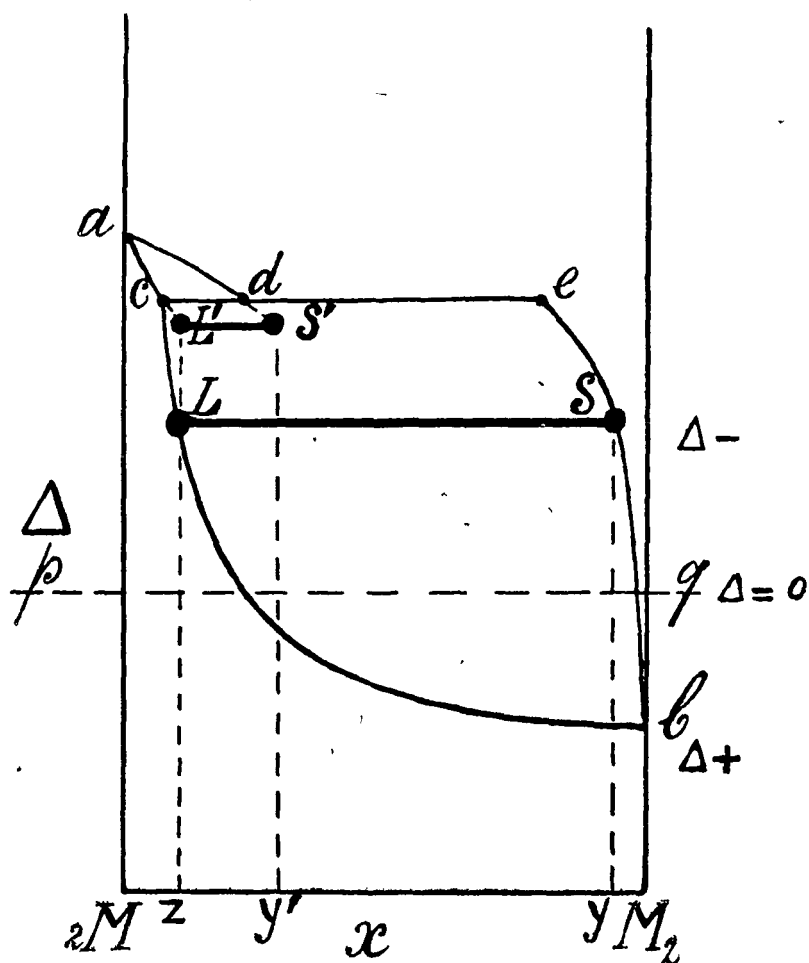

Fig. 3.

In case of cathodic polarisation the metal phase moves from S upwards along the line SC, but here we see now that the quantity $\dfrac{d\Delta}{dx}$ will continually decrease and can become very small in consequence of the ever increasing curvature of the line SC, which can be even a great deal more pronounced than has been drawn here.

It now follows from the observations that the metal cadmium assumes internal equilibrium pretty rapidly, and in harmony with this is the fact that after the current had been broken the polarisation had soon entirely vanished.

It was besides noticed in this investigation that the metal which

served as anode, was gradually covered with a skin of basic salt. It was, however, easy to demonstrate that this skin could not have caused the observed phenomena through increase of the resistance, for the phenomena remained the same also when this skin, which could be very easily removed, was taken away during the electrolysis. Moreover it appeared that when this metal with skin was made to cathode, the cathodic polarisation was the same as in the absence of this skin. The formation of the skin is therefore a secondary phenomenon, as was also expected (see under 1).

Bismuth.

5. Bismuth is a metal that very clearly seems to be catalytically influenced, as appears from the following table.

TABLE 6.

Bismuth in $1/2$ N Bi $(NO_3)_2$-solution.

$\dfrac{i}{0}$	V-anode	V-cathode
35	+ 0.02	— 0.02
60	+ 0.04	— 0.03
133	+ 0.05	— 0.03
260	+ 1.14	— 0.03

The anodic polarisation presents this particularity that though it is exceedingly small up to a current density of 133 milli Ampères per cm², as for silver, it becomes pretty considerable for a current density of 260 milli Ampères. Now it is worthy of note that the anodic polarisation was at first also small for a current density of 260, but it increased slowly, so that it amounted to + 1.14 volts after a few minutes. For smaller current densities, however, no rise of the polarisation tension took place in course of time. The explanation of the observed phenomenon is probably as follows. The Bismuth, which gets positively charged in the used solution, assumes internal equilibrium very quickly at first. At the greatest density of current, however, this internal equilibrium is no longer able to maintain itself, and then generation of oxygen seems to take place, which oxygen evidently exercises a negative, catalytic influence, which renders the metal still nobler. This phenomenon being attended with the formation

of a white skin (probably of basic salt) we have again examined
what influence this skin exercises on the phenomenon. For this pur-
pose the current was suddenly reversed, after a thick layer of the
basic salt had formed, in which however, only a cathodic polarisation
of 0,18 Volt was observed as a proof that this skin, indeed, increased
the resistance somewhat, as was expected, but that this could have
been only of slight influence on the amount of the anodic polarisation
tension [1]). What the negative catalytic influence here consists in,
cannot be said with certainty, but as has been stated, it seems
probable to us that the oxygen, dissolved in the metal to an exceed-
ingly slight degree, retards the setting in of the internal equilibrium.

Iron.

6. If we now proceed to the metal iron we meet again with
phenomena, and very pronounced ones too, which in our opinion
point to catalytic influences.

We found the following result:

TABLE 7.

Iron electrode immersed in $\frac{1}{2}$ N.FeSO$_4$-solution.

$\frac{i}{0}$	V-anode
50	0.026
100	0.038
130	0.044
160	0.064
190	0.075
250	0.113
300	0.164
400	2.25
600	2.47
800	2.53

from which it appears that in this transition of a current density
from 300 to 400 the iron has suddenly become very noble. This

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[1]) For it can hardly be assumed here that the skin offers a different resistance to
currents of different direction.

phenomenon, which has been already often observed, and is called the becoming passive of iron, has not been accounted for in a satisfactory way.

In the light of these new considerations the explanation, as was already observed, is not difficult [1] The iron, which shows this sudden increase of the anodic polarisation, is entirely free from so-called annealing colours and perfectly reflecting, so that an oxide skin is out of the question.

If we, however, assume that the metal dissolves a little oxygen, and this oxygen retards in a high degree the setting in of the internal equilibrium, the sudden considerable enobling of the metal is explained in a simple way.

Up to now it has been lost sight of too much that the phenomenon of passivity, arisen by an electrolytic way, and that called into existence by a purely chemical way, must be explained from one and the same point of view. By a purely chemical way iron is made passive by being simply immersed in strong nitric acid for a few moments. If then the iron is put in a solution of copper sulphate, the copper does not deposit. By a slight shake, the application of a magnetic field etc. this passive state can, however, at once be destroyed, and the iron is covered with a coat of copper.

If we consider the passive iron to be iron that is superficially very far from the state of internal equilibrium, in which superficially the easily reacting molecules are practically entirely wanting, and assume that this state can be maintained for some time on account of the negative catalytic action of oxygen under certain circumstances, which state, however, outside the cell, can be destroyed by vibrations, a magnetic field etc., the phenomenon of passivity of iron becomes less unintelligible. [2]

Returning to the experiment, we will show in the first place what was found when smaller current densities were worked with after the iron had become "passive" at higher current density.

This table exhibits therefore the great difference between the passive and the active iron. As appears from the last table but one, the active iron yields a difference of tension with the auxiliary electrode of 0,026 Volts for a density of current of 50, the passive iron yields a difference of tension of 2,18 Volts for the same current density.

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[1] Smits, These Proc January 25, 1913. XVI. p. 191.

[2] We have probably to do here with metal ions of different valency. (We shall return to this later on)

TABLE 8.

Iron electrode, immersed in $1/2$ $NFeSO_4$-solution.

$\dfrac{i}{0}$	V-anode	V-cathode
800	2.53	0 50
600	2.47	0.47
400	2.40	0.44
200	2.30	0 42
100	2.24	0.37
50	2.18	0.27

It is now remarkable that, as -has also been found by others, contact with hydrogen can annihilate the passivity. When we reversed the current and made the passive anode the cathode for a moment, and then reversed the current again at a density of 400 m.A., the difference of tension with the auxiliary electrode amounted at first only to 0,12 Volt, but this tension rose at first rather slowly to 0,6 Volt and then rapidly to 2,27 Volts.

It therefore appears from this experiment that hydrogen is a positive catalyst for the setting in of the internal equilibrium of iron, which also accounts for the fact that the cathodic polarisation, as appears from the last table, is extremely small in comparison with the anodic polarisation. The difference between anodic and cathodic polarisation is therefore so great here, because for the anodic polarisation a negative catalyst, and for the cathodic polarisation a positive catalyst come into play.

That for nickel the anodic and the cathodic polarisation are about the same proves that the oxygen and the hydrogen do not act noticeably catalytically on this metal.

It should finally still be pointed out that when at the moment that the passive iron had reached an anodic tension of polarisation of 2.27 Volts, the current was broken, still a tension of polarisation was observed of 1,07 Volts, which tension, however, pretty quickly fell to 0. So it appeared just as for nickel that the iron without passage of the current soon assumes internal equilibrium by the aid of the electrolyte, and becomes active. We see from -this that the negative catalytic action is maintained by the current; when the current is broken the active iron above the liquid will, however,

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promote the setting in of the internal equilibrium in the at first passive part, and this will be the explanation of the fact that the iron becomes active after the current has been broken.

Also after the use of the iron electrodes as cathode the current was broken, and as was to be expected, the much smaller cathodic polarisation tension of $\pm$ 0,15 appeared to run very rapidly back to 0.

Aluminium.

7. As far as its electromotive behaviour is concerned, aluminium is undoubtedly one of the most interesting metals. For anodic polarisation the current density decreased regularly, and the tension increased, as is shown in the following table.

TABLE 9.

Aluminium electrode in $\frac{1}{2}$ NAl$_2$ (SO$_4$)$_3$-solution.

$\dfrac{i}{0}$	V-anode
0.8	+ 2.56
0,53	+ 3.48
0,46	+ 3.84
0,36	+ 4.12

Accordingly we find anodic polarisation tensions of about 4 Volts for this metal already at very small current densities, which points to the fact that here a layer of great resistance must have been formed.

Up to now it has been tried to explain this strong anodic polarisation for aluminium by the formation of an insulating skin of Al$_2$O$_3$. With greater densities of current the anode is really covered with an oxide skin, and it is therefore natural to assume the formation of this skin also for smaller densities of current, and attribute the observed phenomenon to this skin of Al$_2$O$_3$ with great resistance. There are however objections to adopting this explanation, for in our experiments no trace of annealing colours was to be observed, and the metal remained beautifully reflecting.

To ascertain whether in our experiments a skin of great resistance had formed round the anode, we made the following experiment.

The bottom of the vessel with the Al^2(SO$_4$)$_3$ solution was covered with a layer of mercury, and the aluminium electrode was anodi-

cally polarized. When this electrode was now covered with a skin of great resistance, an immersion of one extremity of the aluminium electrode in the mercury should not exert any influence on the difference of tension between the aluminium anode and the auxiliary electrode. If, however, this skin does not exist, the aluminium electrode will get into contact with the mercury during the just described manipulation, and the said difference of tension will be modified.

The result was that when *during* the anodic polarisation the aluminium anode was immersed in the mercury, and the current was then broken, the difference of tension with the auxiliary electrode was absolutely unchanged, which proved therefore that the aluminium electrode did not get in contact with the mercury, but was surrounded with a coat of electrolyte. This appeared to be no specific property of the anode, for the same thing was observed after cathodic polarisation. An unpolarized Al-wire, immersed from the electrolyte in the mercury layer, immediately assumed the potential of the mercury, from which therefore follows that the gas layer on the aluminium retains the electrolyte with great force.

In this way the question of the skin could therefore not be solved. What is remarkable is this that the skin formed during anodic polarisation, immediately seems to disappear again by cathodic polarisation. The assumption of a film of Al_2O_3 is attended with great difficulties, in the first place this oxide cannot be reduced under these circumstances by H in status nascens, and in the second place it appears, that nothing is to be perceived of this skin, at least with the naked eye, as no annealing colours are to be observed, and the metal remains clearly reflecting. It seems therefore not too hazardous to us to conclude in virtue of this that the skin cannot be an oxide layer, and the only thing left to us is to assume, as we did for iron, that the oxygen dissolves in the aluminium during anodic polarisation, and that this solution possesses a great electric resistance *for aluminium*. In this way we come to the assumption of a layer with great resistance, of which it is, however, to be understood, that it entirely disappears on cathodic polarisation to make room for a solution of hydrogen and aluminium. Accordingly this layer is metallic, and can amalgamate in course of time when in contact with mercury, through which the resistance disappears. The result at which we arrive is therefore this that the anodically measured tension is so extraordinarily great for aluminium, much greater than the liberation tension of O_2 can be here, because the dissolved oxygen not only retards the setting in of the internal equilibrium, but also a layer of great electric resistance is formed.

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At greater current densities Al_2O_3 can separate from this solutior of oxygen in aluminium, but then the electrode is no longer reflect ing, and it cannot be made reflecting again by cathodic polarisation This layer of Al_2O_3 can also possess a great resistance, but th primary feature of the phenomenon is in all cases the formation of solution of oxygen in aluminium, which possesses a great resistance

If we now proceed to the description of the experiments witl amalgamated aluminium, we will begin with stating that when ir the just described experiment the aluminium electrode was raisec out of the mercury, after amalgamation had set in, and the lowe opening of the auxiliary electrode was placed against the extremit of the aluminium wire, this part of the aluminium had undergon a great change, and had become negatively electrical with respec to the auxiliary electrode. The tension difference amounted to —0.5 Volt, and still increased slowly. At the place where the aluminiun had been in contact with the mercury, it had therefore becom much baser, and had visibly become somewhat amalgamated.

That amalgamated aluminium is baser than the non-amalgamated metal, was known, but the exact value of this difference in tensioi was not met with in the literature. To determine this difference ir tension, an aluminium electrode was amalgamated by immersion ir a solution of $HgCl_2$, after which this electrode was compared witl the auxiliary electrode. We found that the amalgamated Al obtained in this way was still baser than the just mentioned. Al, for the tension of this electrode with respect to the auxiliary electrode amounted now to —1.27 Volts.

That the amalgamation for aluminium has a very particular effect follows moreover from this that amalgamated aluminium possesses a much greater chemical reactive power than the ordinary alumi- nium. Amalgamated aluminium immersed in water gives a very considerable generation of hydrogen, and it oxidizes so rapidly when exposed to the air that the metal is immediately covered with a layer of oxide, the liberated heat raising the temperature of the metal very noticeably.

In consideration of all this it seems more than probable to us that the action of mercury is here positively catalytic, and that mer- cury therefore, when dissolving in aluminium, brings the metal in internal equilibrium, which condition corresponds to a greater con- centration of the simpler, so more reactive kinds of molecules.

The anodic polarisation of the amalgamated state is almost as slight as for silver, as a proof that the internal equilibrium sets in

much more quickly here than for pure Al, but not yet so rapidly as for Ag.

Amalgamated   Aluminium.

i/o	V-anode	V-cathode
2	+ 0.03	
5	+ 0.07	— 0.05
17	+ 0.15	— 0.20
33	+ 0.18	— 0.33
47	+ 0.34	

That the amalgamated aluminium goes into solution much more rapidly than the non-amalgamated aluminium also appears from what follows. If a new aluminium electrode is put in the just mentioned mercury layer, which covers the bottom of the vessel with the $Al_2(SO_4)_3$-solution, this electrode assumes the mercury potential. The tension difference with the auxiliary electrode is then namely + 0,6 Volt, which tension difference is also found when a platinum electrode is used instead of an aluminium electrode. If the same experiment is, however, made with an amalgamated Al-electrode, the tension difference with the auxiliary electrode is — 0,78 Volt. It follows from this that if the ordinary aluminium partially immersed in mercury, failed entirely to maintain its potential difference with respect to the electrolyte in consequence of too slow solution, the amalgamated aluminium does not quite succeed in this either, but it almost succeeds, for instead of — 1,27 Volts its tension with respect to the auxiliary electrode has namely become — 0,78 Volt.

It is perhaps not superfluous to elucidate this phenomenon in a few words. With immersion of the aluminium electrode in the mercury a short circuited element aluminium-electrolyte-mercury is obtained, in which the aluminium is the negative pole, and therefore sends ions into solution. If now the setting in of the internal equilibrium took place with great rapidity, the aluminium would be able to maintain its unary potential difference, and in this case the tension of this electrode with respect to the auxiliary electrode would have remained — 1.27 Volts. Now we find — 0,78 Volt, proving that the state of internal equilibrium was disturbed to a certain extent after all, and the metal has become a little less base by dissolving. If, as was described, the same experiment is made with

ordinary aluminium, which is therefore an enobled state of aluminium, we get what fellows.

The ordinary aluminium is at first the negative pole with respect to the mercury. It becomes, however, noble by the dissolving, and it is soon as noble as mercury. Nobler'than mercury it can, howewer, not become then, since in this case, the current would be reversed, which would change the state of the aluminium again in the base direction. This is the reason that ordinary non-amalgamated aluminium immersed in mercury, assumes the potential of the mercury. This experiment can however not be continued for any length of time, because the aluminium in contact with mercury slowly amalgamates, as we have seen, in consequence of which finally also the part which is not in contact with the electrolyte, will become active, so that the same things will be observed as in case of well-amalgamated aluminium.

In a following communication the investigation of the other metals will be treated, after which a critical summary will be given of the theories which have been proposed by others up to now as an explanation of some of the facts discussed here.

SUMMARY.

In the foregoing pages the theory of allotropy was applied to the electromotive behaviour of the metals Ag, Cu, Pb, Ni, Cd, Bi, Fe, Al.

We have come to the conviction that the newly obtained point of view, as we hope to prove further, enables us to survey the widely divergent cases, and gives a deeper insight into the significance of the observed phenomena.

Anorg. Chem. Lab. of the University.
Amsterdam, April 23, 1914.

Chemistry. — *"The Allotropy of Cadmium."* II. By Prof. ERNST COHEN and W. D. HELDERMAN.

(Communicated in the meeting of April 24, 1914).

1. In our first paper on this subject[1]) we concluded from measurements with the pyknometer and the dilatometer that cadmium has a transition temperature at $64°.9$ and that this metal as we have known it until now, is a metastable system in consequence of the very strongly marked retardation which accompanies the reversible

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[1]) These Proc 16, 485 (1913). '