

Citation:

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of the theory of allotropy, as it necessarily led to the conclusion that the stable *red* or *violet* modification is really complex, and consists at least of two components, which greatly differ in volatility.

As the denomination *red* phosphorus is universally known, we will also apply this term to the stable modification, though, as was said before, this modification is violet in coarser crystalline state.

The adjoined figure represents the vapour pressure line, as it has been found by us after laborious study, and the table gives the vapour pressures at different temperatures, as they can be read from the vapour pressure line. In a following communication this investigation will be treated more fully.

Amsterdam, Sept. 25, 1914.

Anorg. Chem. Laboratory
of the University.

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

(Communicated in the meeting of Sept. 26, 1914).

Introduction.

The application of the theory of allotropy to metals necessarily led to the assumption that every metal that exhibits the phenomenon of phase allotropy, must contain different kinds of ions. As was already mentioned before, these kinds of ions can 1. differ in composition, the electric charge per atom being the same; 2. differ in valence with the same composition, and 3. differ in composition and charge per atom.

On extension of the said theory to the electromotive equilibria it was now demonstrated 1. that the unary electromotive equilibrium finds its place in a Δx figure of a pseudo system, 2. what can be the relation between the unary and the pseudo-binary system, and 3. what phenomena will have to appear when in case of electrolytic solution resp. separation of metals the internal equilibrium is noticeably disturbed. The phenomena of anodic and cathodic polarisation appeared by this in a new light and the passivity of metals revealed itself as a disturbance of the internal equilibrium in the metal surface in the direction of the noblest kind of ions¹⁾, which view seemed already to be confirmed by a preliminary investigation²⁾.

Thus we had arrived at the region of the passivity of metals, and

¹⁾ These Proc. XVI p. 699.

²⁾ These Proc. XVII p. 37. -

it became desirable to get acquainted with the immensely extensive literature on this phenomenon.

The most important hypotheses that have been proposed as an explanation of this phenomenon, and which have been collected by FREDENHAGEN ¹⁾ in an interesting summary, are the following:

1. The oxide theory of FARADAY, who assumes that passive metals are covered by a coat of oxide ²⁾).

2. KRÜGER FINKELSTEIN's ³⁾ valence theory which slightly modified is also adopted by MÜLLER ⁴⁾. In this it is assumed that the passivity consists in a change of the proportion between the components of different valence.

3. LE BLANC's velocity theory ⁵⁾, which supposes the phenomena of passivity to be due to the slight velocity with which the formation of metal ions would take place.

4. The velocity theory of FREDENHAGEN ⁶⁾, MUTHMANN, and FRAUENBERGER ⁷⁾, who start from the supposition that the passivity is caused by the slight reaction velocity between the anodically separated oxygen and the passifiable metal, which causes oxygen charges or solutions of oxygen in metal to originate.

5. The theory of GRAVE ⁸⁾, who assumes a retarded heterogeneous equilibrium metal-electrolyte which is under catalytic influences.

If we now consider the passivity which has arisen by an electrolytic way, it seems to us that too little attention has been paid to the *primary* character of the phenomenon.

First of all we should inquire to what it is owing that in case of anodic polarisation of base metals the potential difference is modified in such a way that the tension of separation for the O_2 is reached, and we should also question why in case of cathodic polarisation of base metals the potential difference changes in such a way that the tension of separation for the H_2 is reached.

¹⁾ Z. f. phys. Chem. 63, 1 (1908).

²⁾ FARADAY has not expressed himself so positively as is generally thought. In a letter to R. TAYLOR FARADAY writes explicitly [Phil Mag X 175. Jan. 21 (1837)]: "I have said (Phil. Mag. IX. 61 1837) that my impression is, that the surface of the metal is oxidized, or else, that the superficial particles of the metal are in such a relation to the oxygen of the electrolyte as to be equivalent to an oxidation, meaning by that not an actual oxidation but a relation..."

³⁾ Z. f. phys. Chem. 39, 104, (1902).

⁴⁾ " " " " 48, 577, (1904). Z. f. Electr. Chem. 11, 755, 823, (1905)

⁵⁾ Chem. News 109, 63 (1914).

⁶⁾ Z. f. phys. chem. 43, 1 (1903).

⁷⁾ Sitzber. K. Bayr. Akad. 34, 201 (1904).

⁸⁾ Z. f. phys. Chem. 77, 513 (1911).

These phenomena being only observed *above a certain current density*, it is clear that we have to do here with a disturbance which makes its appearance when the electric current is passed through with too great velocity.

We have, therefore, to do here with a *question of velocity*, and as an explanation of the primary character of the passivity phenomenon FARADAY'S oxide theory is to be rejected from the beginning.

With regard to GRAVE'S theory we may remark that it seemed very improbable already at a cursory examination. NERNST has namely demonstrated that in the phenomenon of solution equilibrium of saturation always prevails in the boundary layer solid-liquid. In connection with this we may, therefore, expect that this continues to hold for the phenomenon of solution by an electrolytic way. There is no reason at all to make an exception here.

With regard to the second theory it should be observed that the valence hypothesis, on which it is founded, is implied in the conclusions to which the application to metals of the theory of allotropy leads. This theory generally concludes, namely, as was already said before, to the existence of *different kinds of ions in the metal phases* and points out that *one of the possibilities* is this that the metal ions *with the same composition only differ in valence*.

The application of the theory of allotropy to the heterogeneous electrolytic equilibria has further shown that when the metal phase is *complex, apart from the nature of the difference between the ions*, the anodic and cathodic polarisation, and also the passivity of metals can be explained.

Diametrically opposed to this theory are the theories 3, 4 and 5, and it is now clear what will have to be decided. By an experimental way we must try to get an answer to the question as to whether the phenomenon polarisation and passivity resides in the boundary surface between metal and electrolyte, as the theories 3, 4 and 5 suppose, or in the metal surface itself, as the theory of allotropy has rendered probable.

For this purpose the investigation about the complexity is the obvious way. When experiment has proved the complexity, we can try to find out whether it possesses metal ions of different valence.

Experimental part.

1. To examine whether or no the phenomenon of polarisation and that of passivity resides in the metal surface, it seemed to us the simplest course to attack the metal surface by means of chemical reagents, and to see if it has changed its properties in consequence

of this. If a metal really contains different kinds of ions they will, as was stated before, differ in reactive power; hence an attack may result in a change of the concentration in the metal surface, in the sense of enobling. It is, however, to be seen beforehand that the investigation in this direction will be successful only when the internal equilibrium in the metal surface in contact with the electrolyte is established slowly enough. If this equilibrium is established with very great velocity, no disturbance will of course, take place, even though the ion-kinds differ greatly in reactivity.

It appeared in our previous investigation about polarisation that the metals *Ag*, *Ca*, *Pb* are exceedingly little polarisable, from which we inferred that these metals quickly assume internal equilibrium. Hence the etching of these metals promised little success. Quite in agreement with our anticipations it appeared that the potential difference metal- $\frac{1}{10}$ norm. salt solution was not to be changed for these metals by previous etching.

To examine this the electrode of the metal that was to be investigated, fastened to a platinum thread was etched with acid, and then quickly rinsed with water. Then this electrode was immersed in a $\frac{1}{10}$ norm. salt solution, and made to rotate, after which the potential with respect to a $\frac{1}{10}$ N. calomel-electrode was measured as quickly as possible.

When the above mentioned metals according to our anticipations had yielded a negative result, the metals *Co*, *Ni*, *Cr*, and *Fe* were examined with the following result:

Metal	Potential rise through etching	
Co	by HCl	0,108 V
	" H ₂ SO ₄	0,109 "
	" HNO ₃	0,107 "
Ni	by HCl	0,04 V
	" HNO ₃	0,10 "
	" Br-water	0,00 "
Cr	by HNO ₃	1,00 V
	" Br-water	0,60 "
Fe	by HNO ₃	above 1,00 V

It follows from this table that these metals about which it was derived from the phenomenon of polarisation that they assume their internal equilibrium much more slowly than *Ag* etc. really become *nobler* when etched with acid, as was expected.

This temporary change of the potential difference in the sense noble must find its origin in a change in the metal surface, and so it is perfectly clear that theories 3, 4, cannot be of any use here.

At the same time they throw a peculiar light on GRAVE's theory. GRAVE thinks that the heterogeneous equilibrium metal-electrolyte can be easily retarded, but that the hydrogen exerts a positively catalytic influence on the heterogeneous equilibrium. According to him iron would become passive by extraction of the dissolved hydrogen, which would take place on anodic polarisation. Now specially in ion-state hydrogen is certainly a catalyst for the transition passive \rightarrow active, but it is quite unpermissible to derive from this that hydrogen catalyses the heterogeneous equilibrium. It is of importance to state emphatically that according to GRAVE's theory it could by no means be expected that an *enobling* of the metal surface would be brought about when it was etched with HCl or H_2SO_4 , in which the metal can absorb hydrogen. We have to do here with a phenomenon that cannot be counteracted by the positively catalytic influence of the hydrogen on the internal transformations in the metal surface.

Further we made the following in our opinion very important experiment with iron. An iron electrode forged to a platinum wire was made passive one time through anodic polarisation, another time through immersion in strong nitric acid. Both times the potential of these passive states of the iron electrode immersed in $\frac{1}{10}$ N. $FeSO_4$ solution, was measured with respect to $\frac{1}{10}$ norm. calomel, in which the following appeared.

The potential difference of the passive iron, both after anodic polarisation and after etching with strong HNO_3 at first decreases pretty rapidly, then remains constant for a time, and then descends again rapidly. We now compared the temporarily constant potential difference of the quickly rotating electrode in the two cases, and then found what follows:

Observations	Tension of the constant part of the potential of passive iron
Passivity arisen by anodic polarisation	+0,20 V with respect to $\frac{1}{10}$ Norm. Calomel electrode
Passivity arisen on attack of strong HNO_3	+0,205 V with respect to $\frac{1}{10}$ Norm. Calomel electrode

From this experiment the important conclusion could, therefore, be drawn that the two passive states are the same.

At the end of this series of experiments we may finally already conclude that from the fact that where anodic enobling was observed, also ore enobling could be demonstrated, follows that the two phenomena must be explained from one and the same point of view, as the theory of allotropy makes possible.

2. As the course followed bade fair to lead to success, we have changed our mode of procedure so that we could expect still greater effects.

Our purpose was now to attack the metals while they were immersed in the salt-solutions, and measure the potential with respect to the calomel-electrodes at the same time.

Very effective in this respect is bromic water, with which in some cases enormous effects were obtained, and a catalytic influence was also discovered of Br-ions for Ni.

Nickel.

The first experiment was made with a screwshaped Ni-electrode, which was kept in rapidly rotatory motion by a motor, and served therefore at the same time as stirrer. The result was as follows.

Ni-electrode in 100 cm³ $\frac{1}{10}$ N. Ni(NO₃)₂-solution.

Observations	Potential of the Ni-electrode with respect to $\frac{1}{10}$ Norm. Calomel-electrode
Initial value	+ 0,15 V
with one drop of Br-water	+ 0,44 "
" 3 drops " "	+ 0,51 "
" 5 " " "	+ 0,64 "
" 7 " " "	+ 0,67 "
" 3 cm ³ " "	+ 0,80 "
	Now a pretty abrupt descent of the potential set in. After 4 minutes the potential is constant
	+ 0,42 V
At last 2 drops of pure Br. are added	} + 0,428 "

It follows from this table in the first place that addition of bromic water makes the potential of the nickel rise at first by about 0,65 Volt. Then a maximum is reached, after which a considerable decrease takes place. We further see that when after the potential did not change any more, the bromic concentration was raised to saturation by the addition of three drops of bromine, the potential of the Ni changed only exceedingly little.

This very remarkable result ¹⁾ led us to suspect that the disturbance of the internal equilibrium caused by the action of the bromine, is catalytically influenced by Br⁻-ions which had arisen when the metal was etched. With certain Br⁻-ion-concentration the positive catalytic action of the Br⁻-ions is so great that it can just compensate the disturbing action of the bromine, and the Br⁻-ion-concentration increasing continually, a considerable decrease will then have to set in. If now the bromine concentration is increased considerably, both the disturbing action and the catalytic action is greatly increased, after which the condition *can* become pretty well stationary, and addition of more bromine has little or no influence. To test this supposition the potential of the Ni was first carried up by bromine water, and then KBr was added with the following result:

Ni-electrode in 100 cm³ $\frac{1}{10}$ Norm. Ni(NO₃)₂-solution.

Observations	Potential of the Ni-electrode with respect to $\frac{1}{10}$ Norm. Calomel-electrode
Initial state	+ 0,07 V
With 5 drops of Br-water	+ 0,52 "
" 10 " " "	+ 0,64 "
" 2 cm ³ N.KBr solution	+ 0,24 "
" 2 drops of pure Br	+ 0,35 "
After this a slight decrease takes slowly place.	

We see from this that addition of KBr made the potential of Ni really decrease greatly, but then it was necessary in order to get more certainty about the signification of the phenomenon to examine in how far Ni behaved here as a Bromine electrode.

¹⁾ The same result was obtained with a Ni-electrode glowed in *vacuo*, from which follows that possibly dissolved hydrogen exerts no influence on the phenomenon.

For this purpose besides a Ni-electrode, also a Pt-electrode covered with Pt-black was placed in the same Ni-nitrate-solution, and then after addition of Br-water the potential of the Ni- and of the Bromine-electrode was determined.

Then the following was found :

Ni and Pt-electrodes immersed in 100 cm³ N. Ni(NO₃)₂-solution.

Observations	Potential of the Ni-electrode with respect to $\frac{1}{10}$ N. Calomel electrode	Potential of the Br-electrode with respect to $\frac{1}{10}$ N. Calomel electrode
Initial value	- 0,33 ¹⁾ V rise	- 0,03 V rise
With 10 drops of Br-water	+ 0,27 " > 0,60 V	+ 0,82 " > 0,85 V
" 1 cm ³ " "	+ 0,58 " > 0,31 "	+ 0,84 " > 0,02 "
" 3 " " "	+ 0,62 " > 0,04 "	+ 0,83 " > -0,01 "
" 1 " N. KBr-solution	+ 0,46 " > -0,16 "	+ 0,79 " > -0,04 "
" 4 " " "	+ 0,41 " > -0,05 "	+ 0,75 " > -0,04 "
" 1 " Na-thiosulphate	- 0,43 " > -0,84 "	- 0,04 " > -0,79 "

Of an unassailable metal which behaves as bromine electrode it may be expected according to the formula :

$$V_{met.} - V_{sol.} = \Delta = \Delta_0 + 0,058 \log^{10} \frac{\sqrt{C_{Br_2}}}{C_{Br'}}$$

that the addition of the first small quantity of bromine will give rise to a considerable increase of the potential difference, while a subsequent increase of the bromine concentration must exercise a much smaller influence. Our bromine electrode very clearly exhibited this behaviour; the first 10 drops of brominewater made the potential rise 0,85 Volt, whereas the subsequent addition of 1 cm³ resp. 3 cm³ of bromine water no longer practically changed the potential. Increase of the Br'-ion-concentration must lower the potential difference of the bromine electrodes again, and this too was observed. By the addition of 1 cm³ of N.KBr-solution the potential fell 0.04 Volt. That this lowering is not greater is owing to this that during the action of Bromine on nickel bromine ions had already been formed.

In conclusion we removed all the bromine by addition of Na-

¹⁾ This negative value must be attributed to the catalytic influence exerted by KBr in the preceding experiment.

thiosulphate, and then the potential fell to $-0,04$ V., which was about the initial value. If we now compare the behaviour of the Ni-electrode with this behaviour, we notice that the addition of the *first* quantity of bromine has a smaller influence than for the bromine-electrode, and that the addition of more bromine has a much greater influence here than for the bromine-electrode.

While the potential of the bromine electrode *no longer* changes on further addition of Bromine up to 3 cm^3 ., it increased for the nickel-electrode by an amount of $0,34$ V., so that the total rise amounted to $0,95$ V.

And we see further that while the addition of KBr brought about a decrease of only $0,04$ V. for the bromine-electrode, it came to *four times* the amount, viz. to $0,16$ V. for the nickel-electrode.

All this suggests that the nickel-electrode does not behave at all as a bromine-electrode in the experiments mentioned here, which is, indeed, not astonishing, as the Br pretty strongly attacks the Ni-electrode.

It is, therefore, clear that we have to do *here* with a very particular behaviour of the metal itself, and that the explanation, as was already surmised, must be this that during the action of bromine on nickel a disturbance of the internal equilibrium takes place in the metal surface, in the nobler sense, and that this disturbance is counteracted by addition of Br-ions, from which follows that bromine ions execute a positively catalytic action. The result is that we have observed here a great disturbance of the internal equilibrium in the metal surface caused by chemical action, which proceeds *continuously*, in the same direction as was found in case of anodic polarisation. The electrolytical solution of metals is, however, very certainly the most efficient means to disturb the internal equilibrium in the metal, and thus in this way an anodic polarisation of $1,88$ V. was observed for Ni, which after the current had been broken off still amounted to $0,95$ V., a value which is in fairly good agreement with that found now. The disturbance brought about by Br during the rinsing of the electrode with water being again neutralized, the previous etching experiments with Br had a negative result.

Chromium.

Of all the metals which we have investigated up to now, chromium is nearest akin to Ni.

The following table represents the result obtained when bromine was added to a rotating chromium-electrode immersed in a $\frac{1}{10}$ N. CrCl_3 -solution.

Cr-electrode in 100 cm³ 1/10 norm. CrCl₃-solution.

Observations	Potential of the Cr-electrode with respect to 1/10 norm. Calomelelectrode
Initial state with active chromium ¹⁾	— 0,26 V
with 3 drops of Br-water	— 0,08 „
	then slowly descends to
	— 0,24 V
with 1 cm ³ of Br-water	+ 0,62 „
	rises in a few minutes to
	+ 0,79 V
with 2 cm ³ of Br-water	+ 0,79 „
with 1 cm ³ of N. KBr solution	+ 0,78 „

Then the preceding experiment was repeated with a solution of Cr(NO₃)₃ with the following result:

Observations	Potential of the Cr-electrode with respect to 1/10 Norm. Calomelelectrode
Initial state	— 0,35 V
with 9 drops of Br-water	+ 0,73 „
„ 1 cm ³ of N. KBr-solution	+ 0,74 „

In the first place we see from this that the chromium electrode undergoes an exceedingly strong enobling, in which the metal becomes *passive*, as could be demonstrated. By 1 cm³. of bromine water the potential rises more than 1 Volt. Further we see that addition of KBr has no influence on the Cr-potential, which proves both that chromium does *not* behave here as bromine electrode, and that Br⁻-ions do not exert a catalytic influence on the setting in of the metal equilibrium. The metals *Co*, *Al* gave a smaller rise of the potential when attacked by Bromine.

We shall revert to this behaviour later on.

¹⁾ The commercial chromium is passive, and can as HITTORF states, be activated by heating with strong HCl. Z. f. phys. Chem. **25**, 729 (1898) and **30**, 481 (1889).

Iron.

The metal iron yielded a remarkable result. The potential of a rotating iron electrode immersed in 100 cm³. of $\frac{1}{10}$ NFeCl₃, could be affected neither by addition of bromine up to saturation, nor by addition of a solution of N.KBr.

This remarkable result must be explained in the following way. As we shall soon see, iron is strongly attacked by a solution of FeCl₃, and when acted on in this way iron becomes *nobler*. Now Br. also attacks iron pretty strongly, and this attack would undoubtedly also lead to an enobling of the iron surface. Evidently, however, the disturbance called forth on attack by Br, is slighter than that caused by FeCl₃, on account of which the addition of Br could of course have no influence in the just mentioned experiment. What is further most convincingly proved here is this that the iron *absolutely* cannot behave as bromine electrode in consequence of the attack.

This is quite in accordance with what has now been found by us, that namely an enobling of the potential of a metal-electrode caused by addition of bromine, must be attributed to a disturbance of the internal metal equilibrium, at least when the metal is attacked by bromine.

Chlorine acting more strongly on iron than bromine, it was expected that when the former experiment was repeated with chlorine instead of with bromine, a marked rise of the iron potential would be found. As the following table shows, this was actually the case.

Fe-electrode in 100 cm³ of N.FeCl₃-solution.

Observations	Potential of the Fe-electrode with respect to $\frac{1}{10}$ Norm. Calomel electrode
Fe in Norm. FeCl ₃ -solution	— 0,292 V
In a current of chlorine.	— 0,184 „ > 0,108 V

We may be sure that the iron which is strongly attacked by chlorine, cannot have behaved here as chlorine electrode, and that this experiment therefore proves that we have succeeded also for iron in disturbing the internal equilibrium in the surface.

Another phenomenon which is in perfect harmony with this view, and which had already been observed by FINKELSTEIN ¹⁾, is the elec-

¹⁾ Z. f. phys. Chem. **39**, 91 (1901).

tromotive behaviour of iron with respect to solutions containing a varying ferro- and ferri-ion content, as appears from the following table.

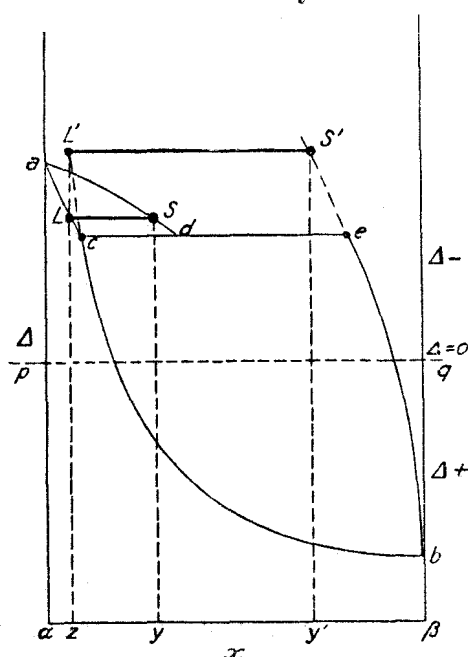
Fe-electrode in solutions with varying ratio $\frac{\text{ferrosalt}}{\text{ferrisalt}}$	
Observation	Potential of the Fe-electrode with respect to $\frac{1}{10}$ of N. Calomel electrode
Fe-electrode in 1 N. Ferrosulphate	— 0,622 V
„ $\frac{1}{2}$ N. Ferro + $\frac{1}{2}$ N. Ferrisalt	— 0,400 „
in 1 N. Ferrisulphate	— 0,292 „

As was said in the introduction, the complexity must first be proved, and then we may try and decide whether the ions differ in valence.

The theory of allotropy already considered the anodic polarisation phenomenon of iron a clear experimental proof, and now the attack experiments have furnished in our opinion the first irrefutable proof.

And now that this stage is reached the electromotive behaviour of iron with respect to solutions with varying ferro- and ferri-ion content appears in a new light.

Now that we namely know that iron must contain different metal



ions, it was natural to try if the observed phenomena may be accounted for from the new point of view on the assumption that iron contains ions of different valence. And really, for so far as we can now survey the region of the observations, this attempt is entirely successful.

If we construct a Δ, x figure for the system Fe-electrolyte in the way as was already indicated by one of us, the connection between the pseudo-binary and the unary system drawn in fig. 1 harmonizes well with the experimental facts.

The stable unary electromotive two-phase equilibrium is indicated

by the solution L and the solid phase S . This solid phase, therefore, contains very much of the less noble pseudo component α . The metastable unary electromotive two-phase equilibrium is indicated by the solution L' and the solid phase S' .

As was set forth before, on anodic polarisation the metal phase S will move down along Sd , hence become nobler, whereas the metal surface will move upward along Sa on cathodic polarisation, hence become less noble.

The stable unary electromotive equilibrium requires an electrolyte which contains only exceedingly few ferri-ions (β) by the side of the ferro-ions (α). When iron is immersed in a solution of ferri-chloride, the system tends to assume unary electromotive equilibrium, in which we may assume the metal phase to send ferro-ions into solution, whereas ferri-ions are deposited from the solution on the metal.

As follows from the Δ, x -figure, a solution containing many ferri-ions could only be in pseudo-electromotive equilibrium with the iron for much less negative potential of the iron. Hence there will be a tendency to make the electrolyte richer in ferro-ions, and the metal in ferri-ions, but until the unary equilibrium concentration has been reached, the iron potential will possess a too small negative value, as was also observed.

It is further to be seen that the negative value of the iron potential will have to increase in a solution of ferro-sulphate, when during the measurement the ferri-ions are precipitated as much as possible.

This follows, indeed, from the following table.

Initial potential of Fe in $\frac{1}{10}$ N. FeSO_4 -solution ¹⁾				= -0,538 V
Potential	"	idem	" with a little NH_4CNS	= -0,578 "
"	"	idem	" " " H_3PO_4	= -0,569 "
"	"	idem	" " " NH_4 oxalate	= -0,555 "

The removal of the ferri-ions makes the iron clearly baser.

It is here the place to point out that in the just mentioned etching experiments with chlorine, this substance has only indirectly caused etching. It is namely very well possible that the action of the chlorine has consisted in this that the ferro-ion emitted by the iron is immediately converted into the ferri-ion, in consequence of which the electrolyte remains as far as possible from the concentration of the unary electromotive equilibrium, and that this gives to the electrolyte its maximum etching action with respect to the iron electrode.

¹⁾ This solution contained traces of ferri-salt.

In this case the chlorine would, therefore, indirectly bring about an increase of the disturbance of the internal equilibrium. What is not improbable for iron, may also be true for nickel in the experiment with bromine, when namely the nickel possesses ions of different valence, but this cannot yet be stated with certainty.

Besides this figure accounts for the discontinuous course of the potential, when passive iron immersed in an iron-salt solution, passes into the active form.

Iron which has passed into the passive state by anodic polarisation or by attack with strong HNO_3 , is greatly enobled superficially, and the potential possesses even a positive value. The concentration of the surface of passive iron, therefore, corresponds to a point on the line eb , and that below the line $\Delta = 0$.

When this passive iron is immersed in a solution of ferro-sulphate, transformations will take place, in consequence of which the unary electromotive equilibrium is approached, and while the potential is falling, the metal surface moves upward along be , till it has arrived in e . Here a second metal phase must occur, viz. d , and as long as the two metal phases occur side by side, the potential of the metal remains constant. The phase e must be entirely converted to d , and when this has taken place, the potential descends further, till the unary electromotive equilibrium has been reached, and the metal phase has been superficially transformed into S .

This is exactly the behaviour that has been observed by many others and also by us. According to our measurements the three-phase equilibrium cde must lie at $+0,20$ V. with respect to $\frac{1}{10}$ N. calomel electrode. The place of the dotted line $\Delta = 0$ is therefore not correct here; it must be thought between LS and cde .

We too found that the transition passive-active is accelerated by H-ions, and we are therefore obliged to assume that hydrogen is an accelerator for the internal transformations in the metal, as are also the ions of the halogens. On treatment with strong HNO_3 and on anodic polarisation the hydrogen is superficially removed, and this greatly promotes the internal transformation, so that the strongly metastable state which we call passive iron, is observed for some time.

Through the diffusion of the hydrogen from within towards the surface the passive iron, no longer subjected to the action of strong HNO_3 , or anodic polarisation, will soon again return to the active form.

Summarizing we come to the following conclusion.

1. FARADAY's oxide theory, which seemed already sufficiently refuted by others, cannot give an explanation of the *origin* of the

passivity. If a metal is once passive, it can undoubtedly be covered by an oxide coat on anodic polarisation, but the formation of this coat is a secondary phenomenon.

Leaving apart whether on anodic polarisation oxygen charges give rise to a certain rise of the potential, it should be borne in mind that it is exactly the *origin* of these gas charges that is to be explained. Only when the metal during the passage of the current undergoes a rise of the potential and the tension of generation of the O_2 is reached, these gas charges can arise, and so a theory which purposes to explain the phenomenon of passivity, will have to account for this potential rise.

It follows from this that the theories of FREDENHAGEN, MUTHMANN, FRAUENBERGER and others leave the essential part of the passivity phenomenon an open question.

3. Our experiments have proved that the phenomenon of passivity resides in the metal itself, and that though this phenomenon is decidedly a phenomenon of retardation, this retardation is not a retardation of the ion hydratation in the electrolyte, as LE BLANC thinks, but a retardation of the ion transformations in the metal-surface.

4. It is perfectly true, as GRAVE states, that hydrogen accelerates the setting in of the electromotive equilibrium. That the hydrogen would accelerate the setting in of the *heterogeneous* equilibrium metal-electrolyte, is an untenable supposition.

The hydrogen accelerates the establishment of the homogeneous internal equilibrium, but has often appeared to be inadequate to neutralize the disturbance of the equilibrium brought about by etching.

5. With regard to FINKELSTEIN's (KRÜGER's) view it might be said to be implied in the new conceptions to which the theory of allotropy has led, but that the said observers, not understanding the deeper signification and the drift of their assumption, were not able to embody their view in a theory.

6. W. J. MÜLLER's views, which are only distinguished from those of FINKELSTEIN (KRÜGER) by the assumption that the states of different valence formed different phases, are theoretically incorrect, and have therefore not led to any result either.

7. The trustworthy experimental data about passivity mentioned in the literature, just as the new results in this department described here, can all be easily explained by the application of the theory of allotropy to the electromotive equilibria.

Anorg. Chem. Lab. of the University.

Amsterdam, Sept. 25, 1914.