

Citation:

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the ascending branch of (Z_n) and in fig. 6 on the returning branch of curve (Z) and on the descending branch of curve (Z_n).

As we have found now the P, T -diagrams, we may easily deduce the corresponding concentration-diagrams with the aid of those.

I shall not enter into this subject any further and leave this deduction to the reader.

Leiden, Inorg. Chem. Lab.

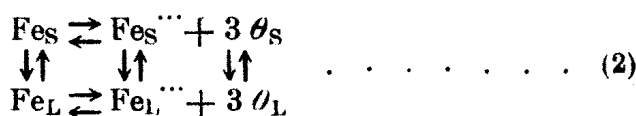
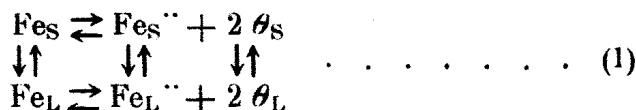
(To be continued.)

Chemistry. — “*A New Method for the Passivation of Iron.*”

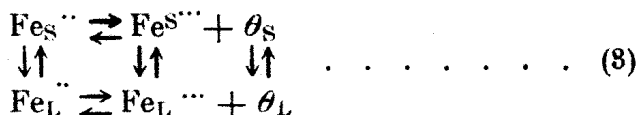
By Prof. A. SMITS and C. A. LOBRY DE BRUYN. (Communicated by Prof. P. ZEEMAN).

(Communicated in the meeting of Dec. 21, 1916).

I. If iron is immersed in an electrolyte, we have to deal with the following complex equilibria:

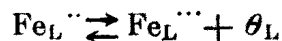


from which follows:



Those of these equilibria that are indicated by vertical arrows except the equilibrium between the uncharged ironatoms in the solid phase and the electrolyte refer to that part of the heterogeneous equilibrium that governs the potential difference.

Now it has been pointed out before that the iron, which is in internal equilibrium, can be in electromotive equilibrium only with a solution which contains almost exclusively ferro-ions, so that under these circumstances the equilibrium:



in solution lies almost entirely to the left.

If we now add ferri-ions, a consequence of this will be that ferro-ions and electrons from the iron go into solution, which disturbs the equilibrium in the iron surface.

This disturbance can now cease again, as a result of the reaction



taking place in the iron surface, and it will therefore entirely depend on the velocity with which this ionisation takes place, whether a disturbance, i. e. in this case an ennobling of the metal surface and attending it a decrease of the negative potential difference, occurs.

Now we had found already two years ago ¹⁾ that it is indeed possible to disturb the internal equilibrium in the iron surface in the way indicated here, and it has further appeared that as was to be expected, the degree of the disturbance depends 1. on the velocity with which the liquid is stirred; 2 on the concentration of the ferri-ions, and 3 on the temperature.

When this had been ascertained, we have made attempts to carry the disturbance through a solution of a ferri-salt so far that the iron became passive. As a ferri-salt we chose ferri-nitrate, because it had appeared to us that the nitrate ion exercises a negative catalytic influence on the setting in of the internal equilibrium.

Experiments made at the ordinary temperature with iron electrodes cemented with sealing wax in a glass tube, at first gave a negative result with a single exception. In the meantime we heard from Messrs. ORNSTEIN and MOLL, who, induced by our research, had also occupied themselves for some time with the passivity of iron, that they had succeeded in making a thin iron wire fused into glass, passive by immersing it in a solution of $\text{Fe}(\text{NO}_3)_3$.

On continuation of the investigation it now appeared that our negative result up to then was probably owing to our cementing the iron electrode, and that when the cement does not perfectly exclude from all contact the part of the iron covered by this material including all capillary rifts and cracks, a passification probably fails to take place in a solution of $\text{Fe}(\text{NO}_3)_3$, in consequence of seeding originating from the non-passive parts which are all the same in contact with the solution. By bestowing the greatest care on the cementing we succeeded accordingly in obtaining iron-electrodes which become almost instantaneously passive on immersion in a solution of $\text{Fe}(\text{NO}_3)_3$ at the ordinary temperature.

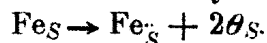
This result may also be reached by fusing the iron in, as Messrs. ORNSTEIN and MOLL did. Then use must be made of enamel, because else no perfectly isolating fusing can be brought about on account of the great difference in expansion coefficient between glass and iron.

This method of passifying iron also succeeds with iron electrodes of greater dimensions. Then the iron is suspended on a platinum

¹⁾ Versl. Nat. en Geneesk. Congres Amsterdam April 1915. Z. f. phys. chem. 40, 723 (1915).

wire or, to make the experiment more rigorous, on a hook of glass¹⁾.

2. When we now apply our new views to what has been discussed here, we immediately see that the disturbance of iron brought about by a solvent, will depend on two circumstances. 1 of the velocity of attack, and 2 of the velocity of the reaction



Hence it is clear that the disturbance will increase with the concentration of the $\text{Fe}(\text{NO}_3)_3$ -solution and that when the same $\text{Fe}(\text{NO}_3)_3$ -solution is used, a slighter disturbance will be found when the influence of the temperature on the homogeneous reaction $\text{Fe}_S \rightarrow \text{Fe}_S'' + 2\theta_S$ is greater, than on the velocity of attack, which is a heterogeneous reaction.

The continued investigation has now proved that this is really the case.

The best way to realize this is by consulting the following tables, which show besides that the temperature at which the passivity occurs is the higher, the greater the concentration of the ferri-nitrate-solution is.

Active iron-electrode put in a solution containing 0.14 grammolecules of $\text{Fe}(\text{NO}_3)_3$ per litre.

Temp. of the solution	Condition of the iron
20°	passive
30°	passive
35°	active
31°	passive
34°	active
30°	passive
Solution containing 0.11 grammol. $\text{Fe}(\text{NO}_3)_3$ per litre.	

Temp. of the solution	Condition of the iron
10°	passive
19°	passive
23°	active
20.5°	passive
22°	active
20°	passive
limit 31°—34°	
limit 20.5°—22	

¹⁾ When we take a platinum wire the experiment is not conclusive because then an element is formed, in which the iron forms the negative electrode, and this is continually polarized.

Solution containing 0.06 grammol. $\text{Fe}(\text{NO}_3)_3$ per litre.

Temp. of the solution	Condition of the iron
9°	active
3°	passive
5°	passive
7°	passive
10°	active
8°	passive

3. Though the possibility of the here observed phenomenon had been predicted on the ground of our views, more experiments had to be made before we could see a firm confirmation of the said considerations in the results obtained.

It is namely known that $\text{Fe}(\text{NO}_3)_3$ is partially hydrolytically split up; hence it had to be examined if the disturbing influence could possibly have been exerted by the nitric acid present in the solution used.

To ascertain this the experiment was repeated at room temperature with a solution of nitric acid, which was a slightly stronger acid than the ferri-nitrate solution used. The result was that the iron remained active. To make the result still more pronounced the nitric acid concentration was increased to 32% by weight of HNO_3 , but the result did not change, the iron remained active.

This indubious result showed therefore that the disturbing action of the ferri-nitrate solution with regard to iron is really owing to the ferri-ion, and that the obtained results may be accepted as convincing confirmations of the newer views about the electromotive processes and equilibria between a metal and an electrolyte.

S U M M A R Y.

Through the above described investigation it has therefore been proved with certainty that, in perfect agreement with the supposition pronounced already before, the disturbance in the iron surface by a solution of ferri-nitrate must be attributed to this that the unary iron can be in electro-motive equilibrium only with a solution which contains only exceedingly few ferri-ions by the side of ferro-ions, so that iron put in a ferri-solution will emit ferro-ions and electrons.

If the internal equilibrium in the metal sets in less rapidly than the metal goes into solution, the internal equilibrium in the iron-surface will be disturbed in the noble direction, i.e. the surface will become richer in ferri-ions, and poorer in electrons.

This case actually presents itself here, and the said disturbance increases with quicker stirring and also through increase of the ferri-ion concentration, and fall of temperature. Owing to the negative catalytic influence of the nitrate ion, the iron could easily be passified in this way.

It could be established with certainty that not the hydrolytically split off nitric acid effects this disturbance, for even a nitric acid solution of 32% by weight of NHO_3 was not able to make the iron passive.

Amsterdam, Dec. 16, 1916.

Anorg. Chem. Laboratory of
the University.

Physics. — EINSTEIN'S *theory of gravitation and HERGLOTZ'S mechanics of continua*'. By GUNNAR NORDSTRÖM. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of November 25, 1916).

In a way somewhat different from that used by LORENTZ and HILBERT, EINSTEIN has recently deduced his gravitation theory from HAMILTON'S principle¹⁾. In doing this he divides HAMILTON'S function \mathfrak{H}^* into two parts:

$$\mathfrak{H}^* = \mathfrak{G}^* + \mathfrak{M} \quad \dots \quad (1)$$

in this way that the first part \mathfrak{G}^* depends on the $g^{\mu\nu}$'s only and their first derivatives with respect to the coordinates $g^{\mu\nu}_\alpha$ while the second part \mathfrak{M} contains the $g^{\mu\nu}$'s only and besides certain variables $q(q)$, which determine the state, and the derivatives of these $q(q)$'s.

By varying the $g^{\mu\nu}$'s EINSTEIN obtains the equations for the gravitation field in the form

$$\sum_x \frac{\partial}{\partial x_x} \left(\frac{\partial \mathfrak{G}^*}{\partial g^{\mu\nu}_x} \right) - \frac{\partial \mathfrak{G}^*}{\partial g^{\mu\nu}} = \frac{\partial \mathfrak{M}}{\partial g^{\mu\nu}}, \quad \dots \quad (2)$$

¹⁾ A. EINSTEIN. HAMILTONSches Prinzip und allgemeine Relativitätstheorie, Berliner Sitzungsberichte 1916. p. 1111.