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Chemistry. — „On Hydrogel of oxide of iron (ferric-oxide)“.

By Prof. J. M. VAN BEMMELEN.

In the Recueil des Travaux Chimiques des Pays-bas ¹⁾ Mr. SPRING stated some time ago that he had prepared a hydrate of oxyd of iron: d'une composition définie. He had got it by allowing to dry — by exposure to the air — the gelatinous precipitate produced by ammonia in a diluted ferri-solution and that after having washed it out. After 72 days the equilibrium became stable, and after 5 months it was found to be unchanged. It answered to the composition $\text{Fe}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$. Above sulphuric acid it lost water so that after 3 days the composition was $\text{Fe}_2\text{O}_3 \cdot 1.78\text{H}_2\text{O}$ (calculated by me).

Formerly, in 1888 ²⁾ and 1892, I have communicated, that the gelatinous oxide of iron had no stable composition, but was an absorption-alloy of Fe_2O_3 with water. I had also found the number $\pm 4,0\text{H}_2\text{O}$ in one of my preparations, but I considered it as an alloy, that only answered to a whole number by chance. The opinion that a fixed hydrate had been obtained, is contrary to the nature of hydrogels. For the composition is continuously dependent on: 1st. the structure of the colloïd, which in its turn depends upon the circumstances of the gel-formation; 2nd. the modifications that the structure has undergone by the further treatment; 3rd. the concentration of the gaseous phase, with which the gel co-exists; 4th. the temperature.

Owing to my having determined the composition only with a few vapour-tensions, SPRING's communication led me to determine the entire isotherm at 15° viz. of dehydration of rehydration and of redehydration and to examine carefully how the Hydrogel behaves when exposed to the air, the vapour-tension of which is continually changing.

Accordingly I prepared again a Hydrogel from a highly diluted ferric-solution ³⁾ and worked with it at once, while it was still quite fresh. Besides I determined the same curves for the preparation already investigated by me in 1882, which had now grown 16 years older (III); and in the third place for a preparation made in 1891, which had been under water for seven years (II). These determinations were made in the same manner as formerly for the hydrogel of SiO_2 and of CuO ⁴⁾. On the graphic sketch I have

¹⁾ 18.222 (1898).

²⁾ Recueil VII 106—114. J. f. prakt. Ch. 46—529.

³⁾ 1 Part Fe_2O_3 on 66 p. water = 1 Mol. Fe_2O_3 on 585 p. water.

⁴⁾ Vide Verslag Kon. Akad. of 28 Janr. 1893 and 29 June 1895. At present the equilibriums are determined at vapour-pressures of 12²—11⁶—10⁶—10—9¹—8¹—7²—6²—5—4³—2—0⁸ m.m. both for A and for Z ↓ and Z ↑.

made use of the same signs (see fig.) viz. $A \downarrow$ for the curve of dehydration of water, $Z \uparrow$ for that of the rehydration of water and $Z \downarrow$ for that of the redehydration of water. The equilibrium at a certain vapour-tension was only gradually approximated on $A \downarrow$, the more slowly in proportion to the latter's differing less from the tension of saturated vapour (12.7 m.m.). At 12² m.m. a loss in 1 month's time was still noticeable after 5 months; at 9 m.m. the loss in 1 month's time was no longer noticeable after 3 months; and at 0° m.m. after one week. On the contrary the equilibrium in $Z \uparrow$ and $Z \downarrow$ was obtained within 1—2 days, except on part of $Z \downarrow$ (from point O to O₁) where the phenomenon of Hysteresis showed itself again.

From the figure we see that the curves agree with those for the Cu O- and the Si O₂-hydrogel.

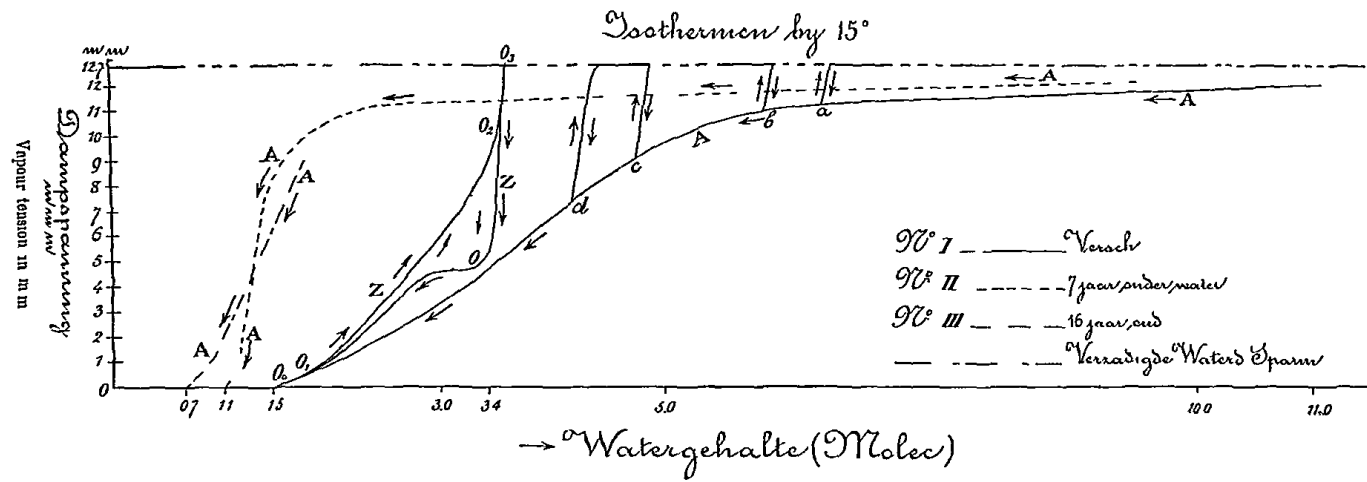
The proportion of water at 15° is greater than that of these two (I only give here that at 12² and at 0 m.m. vapour-tension).

	12 ² m.m.	0° m.m.
Fe ₂ O ₃	± 9.5	1.5 ¹
Cu O	± 7	1.1
Si O ₂	± 6	0.2 ⁵

but is equally continuously dependent on the vapour tension.

Point O, which shows a break in the continuity in silicic acid (in consequence of a transformation in the gel and the diminution of the power of absorption resulting therefrom) and at the same time the turnpoint of the process of de-hydration, this point is not so clearly seen in the hydrogel of Fe₂ O₃. But it betrays itself in the following manner. If the gel, arriving in any point of the line $A \downarrow$, is provided again with water from this point (by the exposition to a higher vapour-tension up to 12⁷ m.m.) it only absorbs ± 0,2 H₂O; comp. for this on fig. 1 the lines $A \uparrow$, starting from the points a, b, c, d. This rule however only holds good if the proportion of ± 3,5 H₂O is not yet reached; below this the gel absorbs in case of rehydration so much water, that the proportion in tension of saturated vapour amounts to ± 3,6⁵. It is therefore about here that the possibility of reversing the further process of the dehydrations begins, and there is a point which answers in that respect to the turningpoint O in silicic acid. At the end of the dehydration in point O₀ (vapour-tension = 0° m.m.) the appearance of air-bubbles

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Isothermen by 15° = Isotherms at 15°

Versch = fresh
7 jaar onder water = 7 years under water
16 jaar oud = 16 years old
Verzadigde Waterspann = { tension of saturated vapour

Watergehalte (molec) . = Molecules Water

on the immersion in water is only observed in a slight degree¹⁾. It must therefore be inferred that but few cavities are formed during the dehydrations on the branch $O-O_0$. This phenomenon is however much better noticed in the gel II (see below). The final curve of the rehydration $Z \uparrow$ again has the points O_1 and O_2 , which appear at the rehydration of water as in the case of silicic acid. For the rehydration curve $Z \downarrow$ does not converge, neither with $Z \uparrow$ nor with $A \downarrow$. It is true that the difference for the branches $O_3 O_2$ and $O_1 O_0$ is slight, but just as with silicic acid, the branch $O_2 O$ is vastly divergent from $O_1 O_2$. The same hysteresis-phenomenon appears. Line $Z \uparrow$, especially the branch $O_1 O_2$ can only be realized in the direction \uparrow (rehydration), the line $O O_1$ in the direction \downarrow (dehydration). An intensified power of absorption is created on $Z \uparrow$, that leaves its influence on $Z \downarrow$. At the rehydration ($Z \downarrow$) a point O appears, showing the same phenomena as in silicic acid. Starting from this point O_1 the equilibrium is obtained very slowly on the branch $O O_1$; a weakening of the power of absorption takes place, that leaves its influence behind, so that at the rehydration it is not the branch $O O_1$ that is run back, but the branch $O_1 O_2$. As a result, here as with silicic acid return-curves may be realized within the figure $O O_1 O_2 O$, if rehydration or redehydration takes place, starting from a point on the line $O O_1$ or on the line $O_1 O_2$. Two of these intermediate curves, one of the dehydration \downarrow and one of the rehydration \uparrow , are indicated in the figure by dotted lines.

Modifications. The modification caused by time, by which the power of absorption is weakened, is also the same as with silicic acid. The figure shows this for a Gel, that has grown 16 years older (curve $A \downarrow$ of III). The proportions are lower again than were found before, when the same substance was seven years older than at the first determination. The fact of the Gel having been under water for seven years has also weakened the power of absorption (curve $A \downarrow$ of II). For the sake of clearness the curves $Z \uparrow$ and $Z \downarrow$ have been omitted. They differ very little from the $A \downarrow$ line, and only diverge from it at higher vapour-tensions (at about 10—11 m.m.), as is shown in the following table:

¹⁾ In silicic acid many cavities are formed, which condensate a considerable volume of air. Vide Verslag Kon Akad. of April 6, 1898, p. 498—506.

	III (16 years old).		II 7 years under water.	
	Z ↑	Z ↓	Z ↑	Z ↓
m.m.	Mol H ₂ O		Mol H ₂ O	
9	1.5 ⁶	1.5 ⁶	1.5	1.5
10	1.6 ⁴	1.6 ⁵	1.6 ⁶	1.7 ¹
10 ⁷	1.7 ⁴	1.7 ⁷	1.8 ⁵	1.9 ⁶
11 ⁶	2.2 ¹	2.4 ⁷	3.0 ²	4.5
12 ³	3.3 ⁵	3.5 ⁷	6.7	7.9 ⁶
12 ⁷ saturated	± 8.5 ¹⁾		8.6 ²⁾	
	¹⁾ Obtained in the course of some months.		²⁾ After 8 days.	

The same phenomenon presents itself as with silicic acid. The more it is modified, the more water it can absorb at the higher vapour-tensions. The hysteresis is removed to that region. The Gels II and III at rehydration can absorb up to more than 8 Mol. H₂O, while I can come no further than to ± 3.6⁵.

It is highly remarkable that III requires months for it, II only days. This too points to a difference in structure. Now it is very remarkable that Gel III does not show any air-bubbles escaping at the point O₀, when immersed in water, while Gel II does. In Gel II there appear immediately on the surface and at the rims of the transparent (so exceedingly thin) films at numerous places smaller and larger air-bubbles. Consequently the gel contains cavities, but their joint volume is not by far so great as in silicic acid. In connection herewith seems to be that II absorbs pretty quickly a considerable amount of aqueous vapour at a vapour-tension of 12 m.m., while III, which contains no cavities, does this so extremely slowly.

It results from the above that no chemical hydrate can be obtained by drying the Gel by exposure to the air, and that moreover the composition must change with the change in the vapour-tension of the air. This was also proved by daily weighing a quantity of I exposed to the air (freshly prepared and pressed between two porous plates) for half a year. In the beginning it contained ± 18 Molec. H₂O on 1 Molec. Fe₂O₃ and contained therefore much water inclosed. With decreasing velocity the proportion had fallen after 9 days to 5.4 H₂O; from that period it came sensibly under the influence of the changes in the vapour-tension of the air, so that it decreased irregularly in weight and sometimes increased. After 1½ month the

proportion had fallen to 4,64 H_2O , and for the next three months this proportion varied according to the vapour-tension of the air, between 4,64 and 4,55 H_2O . Unaltered weight, rising or falling were found to agree with the indications of the hygrometer (of KLINKERFUES). Meanwhile a little decline was observable. If the vapour-tension of the air, which in that time varied between 10 and 8 m.m. had fallen to 7 m.m. and had remained stationary for some time, the composition $\pm 4 \text{H}_2\text{O}$ would have been attained. For this amount has been obtained in the Gel I after some months at *that* vapour-tension. That composition would have risen but little if the vapour-tension of the air had become again greater.

That the composition depends on the temperature, that the power of absorption is weakened by heating to higher temperatures, and is destroyed at incandescence, all this I have already communicated before ¹⁾.

Dr. KLOBBIE and I have only succeeded in observing the transition of colloidal ferric oxide to a crystalloidal chemical hydrate in case of monohydrate²⁾, by the influence of water at 15° on the hexagonal crystals of the chemical compound $\text{Fe}_2\text{O}_3 \cdot \text{Na}_2\text{O}$, in which Na_2O is gradually replaced by H_2O without the crystalline structure (form, transparency, power of polarisation) being modified. Nature provides us with the crystalline Monohydrate: Göthit, that can bear heating to $\pm 280^\circ$ without losing water and without passing into the amorphous state ³⁾.

Chemistry. — MR. VAN BENMELEN presents in the name of MR. B. DE BRUIJN a paper on an investigation held in the Inorganic Chemical Laboratory of the University of Leyden, concerning: „*The equilibrium of systems of three substances, in which two liquids occur*”.

In systems of three components, in which two liquid phases occur, the following cases may be distinguished:

1st. the components A and B form together two liquid phases; equally so the components A and C and B and C.

2nd. the components A and B and A and C form two liquid phases, but the components B and C do not, at least in stable conditions.

¹⁾ Recueil **7**. 111—113. Zeitschr. anorg. Ch. **18**. 24.

²⁾ J. f. pr. Ch. **46** 523—529.

³⁾ J. f. pr. Ch. **46**. 521.