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FOR THE STUDY OF NICKEL HYDROXIDE ELECTRODES-- 1.
1. THROUGH NICKEL (II) HYDROXIDE HYDRATE

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FOR THE STUDY OF NICKEL HYDROXIDE ELECTRODES -- 1. THROUGH NICKEL (II) HYDROXIDE HYDRATE.

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Abstract

In a series of papers, experimental results leading to new understanding of reactions and reaction products on the nickel oxide electrode of the alkaline storage battery are reported. The first communication deals with a hitherto unknown compound of bivalent nickel, which is genetically similar to the oxidation products found on a charged nickel oxide electrode.

Although the nickel hydroxide electrode has been the object of chemical and electrochemical investigations for over 50 years (Ref.1), up to now there exists no contradiction-free picture concerning the reaction mechanism, nor any concerning the compounds present on the electrode in a charged (oxidized) and unchaged (reduced) state. Some investigations (Refs 2-6) show distinctly that the facts about the possible potassium content in the reaction products, as well as about the participation of water in the reaction, are not clear. Furthermore, there exist discrepancies concerning the thermodynamic data of the reaction. The values for the reaction enthalpy, free enthalpy, as well as entropy, respectively connected with the temperature coefficients of the reaction, show marked discrepancies in the reports of various researchers (Refs.,5, 7-9).

In a series of lectüres and reports (Refs 10-12) we have given information about some sections of our work in this area. A work of Tuomi (Ref.6) instigates us to present a summarized view with the experimental data, although our procedings are not completed in all respects.

Through the presentation of our results we would like to give as wide a basis as possible for further discussion of these problems.

The results of our procedings can be presented as follows:

1. The charge and discharge processe at a nickel hydroxide electrode cannot be represented by q single reaction equation, because there are several initial and final products.

2. X-ray and electrochemical findings made until now show that the reactions proceed heterogeneously.

3. Even at the smallest current densisities the reaction takes place at a higher potential than does the discharge process.

The differences in the voltages amount in one case to about 60 mv, and in the other two to about 100 mv. In thermodynamics this means that the reactions cannot be described by a reversible voltage, as may be done in the case of a $Cd/Cd(OH)_2$ or $PbO_2/PbSO$ electrode.

Systematology of the Phases and Nomenclature

A certain conclusion of the earlier investigations seemed to be the conversion equation presented by Glemser and Einerhand (Ref.13)

$$Ni(OH)_2 + OH^- = \beta\text{-}NiOOH + H_2O + e^-$$

The initial product on the left side of the equation is a hydroxide of bivalent nickel, a crystallizing compound (Refs 14, 15). In distinction from another hydroxide of bivalent nickel, described by us below, this well-characterized hydroxide will be designated in this work as $\beta\text{-}Ni(OH)_2$. This can be chemically or electrochemically oxidized into a nickel (III) oxide hydroxide, designated by Glemser as β-NiOOH.

The newly produced hydroxide of bivalent nickel has proved to be a hydrate of nickel (II) hydroxide with the formula $3Ni(OH)_2 \cdot 2H_2O$. It can be produced chemically and electrochemically, and is distinguished by a characteristic X-ray diagram. Feitknecht (Ref.16) has already described analogous compounds, although not of nickel, by similar X-ray diagrams. In distinction from the known C 6 type hydroxides he designated them as α -hydroxides. The designation α -hydroxide will also be used by us for the nickel hydroxide hydrate $3Ni(OH)_2 \cdot 2H_2O$ obtained by us.

This α -hydroxide can be converted by means of oxidation into a nickel hydroxide of higher value. In the course thereof two analytically different substances are obtained, however; the

X-ray diagrams are practically the same, differing only, as usual depending on the production process, with respect to line sharpness or the presence or absence of weak reflexes. The Debye diagrams correspond to γ-NiOOH of Glemser and Einerhand (Ref.17). One compound (A), which Glemser and Einerhand have produced through hydrolysis of $NaNiO_2$, is a nickel (III) oxide hydroxide hydrate

(A) $4NiOOH \cdot 3H_2O$

with the oxidation value of $NiO_{1.5}$; it contains water of hydration. The second substance (B) is obtained, as an electrolyte, through oxidation with potassiumhypobromite or electrochemically in potassium hydroxide. It contains potassium and has a higher oxidation value than $NiO_{1.5}$. It can be designated as potassium nickel (III,IV) oxide hydroxide. The compound with the highest oxidation value has the analytic composition $4NiO_{1,81} \cdot 2,25H_2O \cdot 0,5K_2O$. As it is discussed later, we derive from this the following structural formula

(B) $[Ni_4O_4(OH)_4]O_{1,5}(OH)_{0,5}K.$

The potassium ion can be replaced by Ba^{2+} as well as by Na^+, and probably also by H_3O^+, but, on the contrary, not by Rb^+ or Cs^+ ions. The incorporatuin of Li^+ could occur differently. It is not known if substance (A) occurs at all in a practical battery; on the other hand, the potassium-containing highly oxidized phase (B) can be demonstrated by prolonged overcharges (Feitknecht (Ref.2), Salkind and Bruins (Ref.5)). The designation γ-form must be reserved for compound (B). A substance originating at overcharge has been designated by Tuomi (Ref 6) as the -phase. This nomenclature should, however, be avoided, since Glemser and Einerhand (17) have proposed the designation α-NiO(OH) for another oxidized nickel hydroxide.

The genetic relationships of the nickel hydroxide are presented in the following diagram:

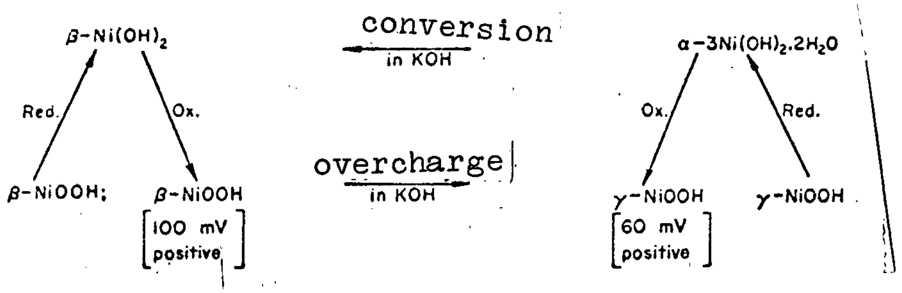


Diagram 1.

The significance of these raction series to the behavior of the nickel hydroxide electrodes in the alkali accumulator will be the subject of this study and the succeeding works.

EXPERIMENTAL PART

Production of $3Ni(OH)_2 \cdot 2H_2O$.

For the electrochemical production of α hydroxide, a nickel foil (sized 60 x 40 x 0.1 mm) is connected as a cathode to two homogeneous anode plates at an interval of 3 to 4 cm. An 0.1 n nickel nitrate solution (Merck, purest), the pH value of which is maintained at 4.8 by means of the addition of nitric acid, serves as the electrolyte. The electrolysis takes place at a current density of 0.1 m/cm^2, at room temperature and without stirring of the electrolyte. After about half an hour, approximately 1 mg

α hydroxide is precipitated on the cathode. The electrode with the precipitation is washed free of nitrate, and is dried in a vacuum exsiccator over P_2O_5. After this, the preparation can be scraped off the sublayer.

For the chemical production of α hydroxide, 100 ml/0.01 n nickel solution is added dropwise to 1 liter of 0.001 n KOH with stirring and the constant application of CO_2-free nitrogen gas. The formation of basic nickel nitrates is prevented by the constantly present surplus of leveling solution. After precipitation, the product is filtered, the precipitate is washed free of nitrate and alkali, and is then dried in a vacuum over P_2O_5. The use of leveling solutions diluted to such an extent hinders the production of large quantities of purified α hydroxide.

Larger substance quantities can be more easily obtained by another process. For production, $Ni(OH)_2$ is diluted to saturation in an approximately 8 n ammonia solution. The blue solution is filtered into a polyethelyne tumbler of appropriate size, which is held in an exsiccator over concentrated sulphuric acid. After one or two weeks the solution is fully evaporated, the α hydroxide precipitating as a dry, generally well-crystallized powder.

For analysis of the preparations, a nickel determination and a total water determination is prepared. The nickel content muct be recalculated in terms of $Ni(OH)_2$, and the remainder of the total water must be recalculated in terms of water of hydration. The pycnometric density is determined with waterless petroleum (boiling point 150-200°)used) as a sealing fluid. The pycnometric density of well crystallized, waterless β-$Ni(OH)_2$ obtained by the three day heating of a normally precipitated product in autoclave at 270°, is 3.85 g/cm^3; the X-ray density is 3.97 g/cm^3. Some data are compiled in Table I.

Table I

$Ni(OH)_2$	H_2O	$Ni(OH)_2$	H_2O	density
%	%	Mol	Mol	g/cm^3
89,90	10,43	1	0,60	2,52 (pykn.)
89,00	10,94	1	0,63	
89,00	11,97	1	0,69	
89,90	10,12	1	0,58	2,48 (pykn.)
compiled for $3Ni(OH)_2 \cdot 2H_2O$				
88,50	11,45	1	0,67	2,62 (röntg.)

α-nickel hydroxide cannot be differentiated by color from the nromal green β-$Ni(OH)_2$. In a dry state, it is stable. On the other hand, with escape of the water of hydration it changes in alkali solutions to β-$Ni(OH)_2$ and, furthermore, it does so all the faster, the higher the temperature and the more concentrated the alkali solution. With a strong alkali (about 6 to 9 n), the change transformation is completed in a few hours at 90°C. On the other hand, in a 0.1 to 1 n alkali at room temperature, the substance remains unchanged for several days. The process is not reversible.

Stabilization of α-hydroxide can be achieved by the addition of certain admixtures to the precipitation solutions during the production process. In this connection, OH groups containing substances such as glucose, boric acid, mannitol, etc., have a particularly stabilizing effect. It is true that under these conditions a nonstoichometric quantity of the additive is also precipitated and is incorporated into the α-hydroxide. These products can be characterized by means of X-ray diagrams as α forms (appearance of a line with d = 8.1 Å).

During the thermogravimetric investigation, the α hydroxide releases the water of hydration at about 150°, but is not converted into β-$Ni(OH)_2$.

Concerning other α-hydroxides.

Nickel-zinc mixed hydroxide hydrates of the form $3(Ni,Zn)(OH)_2 \cdot 2H_2O$ are particularly stable. They can be obtained by the same methods as α nickel hydroxide. Nickel-zinc hydroxides are considerably stable, so that pure α hydroxides can be obtained with precipitation in 0.5 n alkali. Here is, therefore, possible to produce larger quantities of a α-hydroxide. These mixed hydroxide hydrates have the X-ray diagram of α nickel hydroxides. The zinc content can be varied without structural change over a wide range. Mixed hydroxides, as well as pure α $Zn(OH)_2$, have already been produced by Feitknecht (R.16). Well crystallized substances are obtainable with medium zinc concentrations. For this, some analysis data are presented in Table 2. The production of pure α cobalt hydroxide is much more difficult since it converts much more easily into the β-form and, in addition is easily oxidized by atmospheric oxygen. On the other hand, this example is especially interesting because the forms differ in color: α-$3Co(OH)_2 \cdot 2H_2O$ is intensely blue, and β-$Co(OH)_2$ is pink.

Table 2

$Ni(OH)_2$	$Zn(OH)_2$	H_2O	$Ni,Zn(OH)_2$	H_2O	Pycnometric density
%	%	%	Mol	Mol	g/cm^3
58,10	29,30	12,54	1	0,75	—
61,50	27,40	11,10	1	0,66	2,69
62,00	29,30	8,97	1	0,52	2,78

In electrochemical precipitation from a 0.1 n cobalt solution, the pure blue α form is obtained at the cathode. It is instantly converted into pink-colored $Co(OH)_2$ by immersion into dilute alkali. Therefore, the washing and drying process following the precipitation must be performed very rapidly, the air must be exxluded also. In the course of this process, blue preparations are at first obtained which change to a green-spotted coloration under the slightest influence of oxygen. The total water content of these substances is always somewhat lower than that, which corresponds to the above formula. In the presence of stabilizing additived, chemical precipitation yields blue preparations(according to Feitknecht (R.16). These additives are incorporated into the precipitates and affect the analytical composition of the α hydroxide. But densities, and especially X-ray photographs, permit to be recognized the identity of the blue cobalt hydroxide and the α nickel hydroxide: the density of a cathode-precipitated blue cobalt hydroxide $D_{pycn} = 2.89\ g/cm^3$; the density of a product stabilized by glucose $D_{pycn} = 2.27\ g/cm.^3$ The deviations of the pynometric density from the X-ray density are due to the fact that a small part of the cathode precipitated is converted into the pink-colored β-$Co(OH)_2$ ($D = 3{,}79$ g/cm³) while the chemically precipitated blue cobalt hydroxide contains a certain percentage of glucose.

Additional results are available concerning compounds of the $3(Ni, Cd)(OH)_2$ and $3(Ni, Fe)(OH)_2 \cdot 3H_2O$ type. Because of the special significance of these compounds in battery engineering, they will be dealt with in a separate report.

Discussion

The nickel hydroxide formed in the course of cathode deposition has a Debye photograph which differs from that of normal $Ni(OH)_2$ (compare also Briggs and Wynne-Jones (Ref.18)). Since the pH value increases at the cathode during electrolysis it should also be possible to precipitate this form of nickel hydroxide from alkali solutions with relatively small pH values. Precipitations from millinormal solution of potassium hydroxide yields products for which the same X-ray diagram never appears with cathode deposition. These compounds also originate from ammonia-containing hexamine volute salt solutions which we designate as α forms.

The Debye diagrams of the α hydroxide described in the experimental part are shown in Figures 1-4, together with 2 other powder diagrams of nickel hydroxides of the β type. The discovery of this substance group dates back to Feitknecht (R.16). He interpreted the structure of the α hydroxide as a double-layer lattice, consisting of ordered hydroxide layers of the corresponding C-6 type (as in the case of β-$Ni(OH)_2$) in which "unarranged material" by which in this case is meant "amorphous $Ni(OH)_2$) is incorporated as the c-axis is enlarged. But this conception would lead to a substantially higher density, approximately close or equal to the density of β-$Ni(OH)_2$.

In connection with our investigations, waterof hydrogenation is to be considered as an essential compound ingredient of the α hydroxides, and because of this we would like to make the following structural proposal. The α hydroxides form a layer lattice consisting of Brucite type hydroxide layers, the layer interval of which is widened through the internal formation of a water interlayer. For this proposed model which corresponds to the observed one (compare Table I), This proposal can be unequivocally proven through a complete structural analysis of single crystals, the production of which, however, could raise serious difficulties since in this group of substances we are dealing with one-dimensionally disordered compounds (Ref. 16).

Table 3

α-$3Ni(OH)_2 \cdot 2H_2O$			β-$Ni(OH)_2$		
d_{hkl}	hkl	J_0	d_{hkl}	hkl	J_0
8,07	001	s-st			
			4,60	001	st
4,05	002	st			
2,65	100	st	2,70	100	st
			2,30	002	s
2,02	004	s			
1,54	110	m-st	1,56	110	st
1,333	200	m	1,349	200	m
			1,148	004	s
1,010	210	m	1,022	210	s-m
0,893	300	m	0,900	300	m

The following features are valid for the derivation of this structural proposal. The X-ray diagram of α nickel hydroxide has considerably fewer lines thandoes that of β-$Ni(OH)_2$ (as can be seen in Figures 1 and 2). It can, however, be indicated as this hexagonal, with the result that only the cross-lattice reflexes (hk0) and the basic reflexes are present. The latter show an increase of the c-axis corresponding to the built-in water. Pyramidal reflexes are not observed. In Table 3, all the prism and unit cell reflexes of β-Ni(OH)$_2$ are again presented next to all reflexes which have been observed in α nickel hydroxide. With a like indication the lattice constants result in:

$a = 3{,}08$ and $c = 8{,}09$ Å for α-3Ni(OH)$_2$·2H$_2$O
$a = 3{,}12$ and $c = 4{,}60$ Å for β-Ni(OH)$_2$.

While the a axis is only slightly contracted, the c axis is considerably increased.

With the above lattice constants and with formula uniformity in the elementary cell a density of 7.85 g/cm^3 would be yielded.

Under the assumption that the pycmometrically calculated density is 2.52 g/cm^3, the cell must be three times larger. In a hexagonal system this can be attained either through the choice of a setup turned 90° ($P\bar{3}m1$-$P\bar{3}1m$), or through the choice of a rhombohedral space group. Since the prism reflexes permit a precise follow-through of the hexagonal indication) no deviations are allowed in the rhombohedron condition), a new a-axis will be chosen with a value of $a = 5.34 = 3.08\sqrt{(3)}$ Å With this value and $c = 8.09$Å, an X-ray density of 2.62 g/cm^3 will be calculated.

To test the structure proposal derived here, an intensity calculation has been performed. The space group $D_{3d}^1 - P\bar{3}m$ was

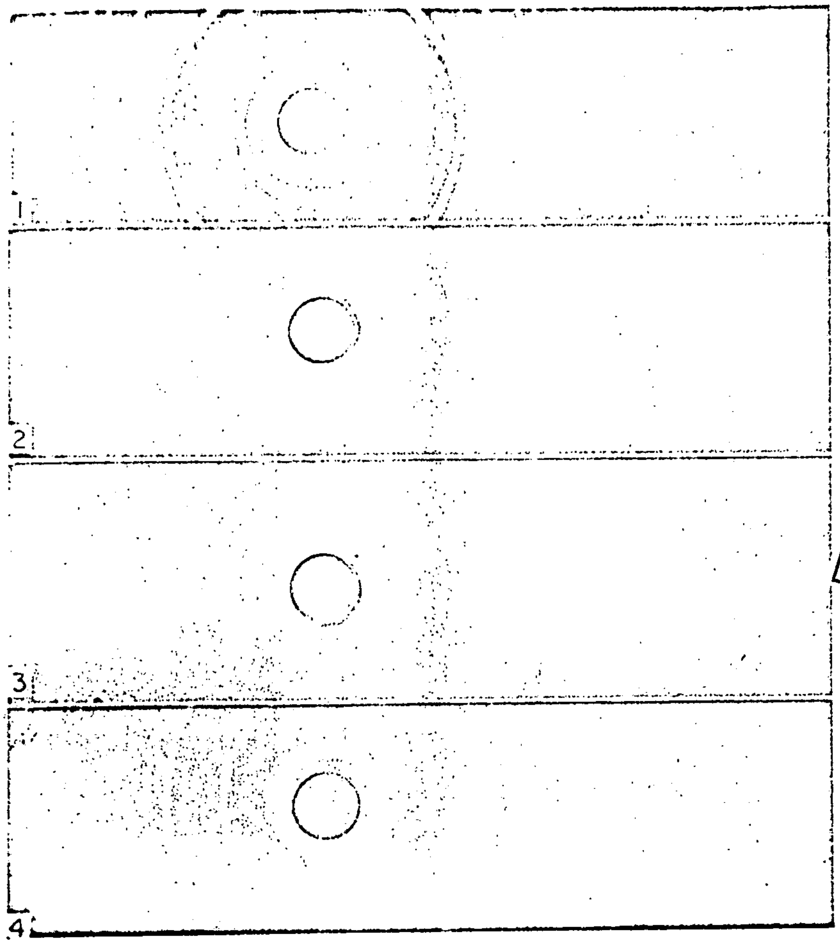


Fig. 1. β-$Ni(OH)_2$ recrystallized (CuKα)

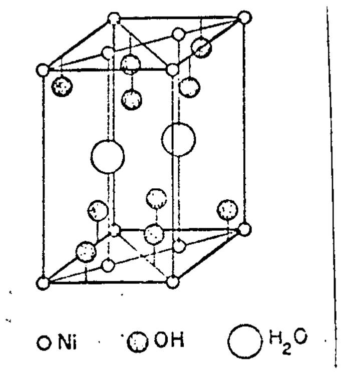
Fig. 2. α-$3Ni(OH)_2 \cdot 2H_2O$ (CuK$_\alpha$).

Fig. 3. α-$3(Ni,Zn)(OH)_2 \cdot 2H_2O$ (CuK$_\alpha$).

Fig. 4. α-$3Co(OH)_2 \cdot 2H_2O$ (blue) (FeK$_\alpha$).

(with traces of β-$Co(OH)_2$ (pink)) taken as a basis.

Position points (see Fig. 5):



: 3Ni (a): 000; (c): $\frac{1}{3}\,\frac{2}{3}\,0$
6OH (k): $x0z$ with $x = \frac{1}{3}$ and $z \sim \frac{1}{6}$
$2H_2O$ (d): $\frac{1}{3}\,\frac{2}{3}\,\frac{1}{2}$.

Figure 5. Lattice of $3Ni(OH)_2 \cdot 2H_2O$.

The result of the intensity calculation is compiled in Table 4. The indication is naturally altered so as to correspond to the larger cells.

We consider the fundamental correctness of the structure of α nickel hydroxide to be proven by the good agreement of the observed and calculated intensities.

Due to the choice of a larger cell, additional lines, approximately (100), (200), (210), etc., must be anticipated even with restriction prism reflexes, etc. The structural amplitudes of these reflexes are always very small, since neither the Ni nor the OH atoms contribute to their intensity; consequently it is understandable that they are not observed. For example, for the (100) reflex the intensity would (according to the above scale) be calculated as 0.2, whereas for the (200) reflex it would be only 0.02.

According to the concepts derived above, the water molecules are arranged in the interlayer in even six-numbered ring groups. It still remains to be determined if this is correct, or if there takes place a statistical distribution in a (1 + 2) layer, (b) and (d). In the latter case this Feitknecht conception of an "unordered interlayer" (assumed by him to consist of $Ni(OH)_2$ postulated by us as water molecules) could have a certain justification. In any case in this only lightly bound interlayer, infrared photographs permit the assumption of weak hydrogen bridge-ring structures to be held responsible for the instability of this compound. The absence of pyramidal reflexes points to a one-dimensional disorder of the layer sets and could be explained by lattice imperfections, as for example, weak displacement of the hydroxide layers with respect to one another.

Table 4

$3Ni(OH)_2 \cdot 2H_2O$ $a = 5{,}34$ Å
$c = 8{,}09$ Å

hkl	$\sin^2\vartheta \cdot 10^{-3}$	J_o	J_c
001	9,1	60	62
002	36,1	7	8,3
110	84,5	10	8,9
004	145,8	0,5	1,3
300	250,8	6	4,2
220	334,7	1	0,9
410	580,8	1	0,8
330	746,3	1,5	0,9

The structure has analogies with some water-containing clay minerals; there we are also dealing with layer structures, although of a more complicated composition due to the presence of double or multiple layers, as for example in $Al_2Si_2(OH)_4$ with hexagonally arranged oxygen atoms, in ocahedronal and tetrahedral holes of the other atoms lie. The waterless substance built up from these layers is kaolin with $d_{001} = 7.15$ Å (analogous to β-$Ni(OH)_2$ with $d_{001} = 4.60$ Å, the water-containing form is hallosite $Al_2Si_2(OH)_4 \cdot 2H_2O$ with d_{ool} = 10.25 Å (analogous to α $3Ni(OH)_2$ with d_{ool} - 8.07 Å). When hallosite is heated, the total interlayer water evaporates at approximately 150°C just as in the case of α nickel hydroxide, without the hydroxide layer interval in metahallosyte being essentially diminished.

The transition from the α form when acted upon by alkali into the normal β form takes place only in one direction. This monotropic reaction process permits the assumption to be made that we are dealing with the transition of a thermodynamically unstable substance into a stable one.

In connection with these hydroxides, some data are available concerning the solubility products of the "active" and "inactive" forms (Ref 19):

$Ni(OH)_2$ (act.)	$\log K_0 = -14{,}7$	$Co(OH)_2$ (blue)	$\log K_0 = -14{,}2$
$Ni(OH)_2$ (inact.)	$\log K_0 = -17{,}2$	$Co(OH)_2$ (pink, inact)	$\log K_0 = -15{,}7.$

If it is assumed that the "active" hydroxides correspond to the α form for which the color of the cobalt hydroxides gives some support, it is possible to determine the free reaction enthalpy of the conversion

$$\alpha[Ni(OH)_2 \cdot \tfrac{2}{3}H_2O] \rightarrow \beta\text{-}Ni(OH)_2 + \tfrac{2}{3}H_2O$$

it shows that $\Delta G = -3{,}4$ Kcal/Mol, for the corresponding co-compounds $\Delta G = -2{,}0$ Kcal/Mol. Although the numerical values of the solubility products are somewhat uncertain, the sign of ΔG, shows that the reaction can take place only from α to β.

The remaining α- hydroxides also possess the structure of α- nickel hydroxide. For the blue cobalt hydroxide (Fig. 4) the lattice constants were found to be a = 5.40 Å and c = 9.08 Å, the X-ray density being $D_{roentg} = 2.56$ g/cm^3. The pycnometer densities, however, deviate from this for the above reasons expressed.

For a nickel-zinc mixed hydroxide hydrate $3(Ni, Zn)(OH)_2 \cdot 2H_2O$ Fig. 3) with 61.5% $Ni(OH)_2$ and 27.4% $Zn(OH)_2$, the following values were found:

$$a = 5{,}32\ \text{Å} \qquad c = 8{,}04\ \text{Å}$$

$$D_{\text{röntg.}} = 2{,}67\ \text{g/cm}^3 \qquad D_{\text{pykn.}} = 2{,}69\ \text{g/cm}^3.$$

For pure α-$Zn(OH)_2$, Feitknecht (Ref.16) indicates that a = 5.39 Å and c = 7.8 Å.

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