Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

Chemistry. — *"The zincates of sodium. Equilibriums in the system*
Na_2O-ZnO-H_2O". By Dr. F. Goudriaan. (Communicated by
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The data we find in the literature about the influence of the
strong bases of light metals on the insoluble weak hydroxides of
heavy metals, are extremely contradictory and ill-defined. So it is
generally assumed that the hydroxides of zinc, aluminium, lead and
tin display an amphoteric character, so that in an excess of strong
base they "dissolve" under the formation of salts. It is supposed on
the other hand that the hydroxides of numerous other heavy metals
do not show any propensity to form similar salts and by this the
stronger electro-positive character of these metals is thought to
reveal itself And yet it is a fact that the hydroxides of the so-
called strong electro-positive metals can likewise in some circum-
stances display an amphoteric character; nay even cuprum hydroxide
can dissolve in a concentrated solution of NaOH or KOH. Hence
the differences occurring with the metalhydroxides are probably only
of a quantitative nature and it will be worth while to investigate
to what extent the different hydroxides show this phenomenon and
what compounds arise in this process. This is in the first place of
importance for analytic chemistry, where numerous separations are
due to the difference in solubility of the hydroxides; next investi-
gations about this subject can give us a more definite insight into
the mutual affinity of the metaloxides and metal-hydroxides.

Up till now it has not yet been ascertained what compounds are
formed under the influence of hydroxides on strong bases and under
what circumstances they are stable. In a pure state they are not
isolated and accurately delineated. We are still quite in the dark
about the nature of the hydroxides themselves. For as a rule we
obtain these substances as voluminous, gelatinous products, and the
question arises whether we are to consider these as solid phases of
a constant or variable composition or as liquid ones of a great
viscosity. The great difficulties which the procuring of these substances
in a pure state, involves, are probably the cause of the very few
exact data we have about the subject under discussion.

In the following lines we shall now state the results of experiments made with a view to get more closely acquainted with the compounds formed in "dissolving" zinchydroxide in NaOH i. e. the zincates of sodium, and accurately to determine their range of existence. Similar investigations concerning the correspondent compounds of some other metals are in progress.

We shall now briefly summarize the data known up till now concerning the sodium-zincates:

By means of solving ZnO in a hot NaOH-solution, followed by the addition of alcohol, COMEY and LORING JACKSON [1]) obtained two products, to which they ascribe respectively the formulae:

$H_3 Na_4 Zn_3 O_3 17 H_2 O$ and $HNa ZnO_3 \frac{1}{2} H_2 O$. The first compound has a melting-point of 100°, the second proved not to melt even at 300°.

FÖRSTER and GÜNTHER [2]) found only one compound viz. the formula

$$Zn \underset{\diagdown O.Na}{\overset{\diagup OH}{<}} 3 H_2 O.$$ It formed white silky-glossy needles.

HERZ [3]) precipitated a solution of Zn SO$_4$ of known concentration with a KOH-solution and then investigated how much base is required once more to solve the Zn (OH)$_2$ that is formed. It appeared that to 1 gram equivalent of Zn, 6 gram equivalents of OH were required.

HANTZSCH [4]) denies the existence of sodium-zincates on the ground of conductivity measurements and attributes the solution of Zn (OH)$_2$ in NaOH to the forming of a colloidal solution.

JORDIS [5]) observes that in the long run, crystals of the composition: Zn (ONa)$_2$ arise in the cupron-element, in which zinc is found as a negative pole in a solution of NaOH.

Finally it should be mentioned, that RUBENBAUER [6]) and WOOD [7]) have determined the proportion of the number of gramatoms Zn and Na in a solution of Zn (OH)$_2$ in NaOH; these observations can teach but little regarding the existence of definite compounds.

We see from these data of the literature how vague our knowledge about such comparatively simple compounds still is.

The equilibriums that may arise in an aqueous solution between

[1]) Amer. Chem. Journ. 11, 145 (1889); Ber. d. deut. Chem. Ges. 21, 1589 (1888)
[2]) Zeitschr. f. Elektroch. 6, 301 (1899).
[3]) Zeitschr. f. anorg. Chem. 28, 474 (1901).
[4]) Ibid. 30, 289 (1902).
[5]) Zeitschr. f. Elektroch. 7, 469 (1900).
[6]) Zeitschr. f. anorg. Chem. 30, 332 (1902).
[7]) Journ. Chem. Soc. 97, 886 (1910).

TABLE 1. — *System* Na_2O—ZnO—H_2O (Temperature 30,0° C.).

N°.	Composition of the solution.			Composition of the rest.			Solid phases.
	% Na_2O	% ZnO	% H_2O	% Na_2O	% ZnO	% H_2O	
1	11.8	2.6	85.6	10.1	22.2	67.7	ZnO
2	17.4	5.0	77.6	15.3	16.9	67.8	ZnO
3	24.6	12.6	62.8	20.2	29.1	50.7	ZnO
4	24.9	12.9	62.2	22.0	23.5	54.5	ZnO
5	23.7	11.3	65.0	19.1	31.2	49.7	ZnO
6	27.3	16.0	56.7	22.1	32.7	45.2	ZnO
7	27.8	16.5	55.7	—	—	—	$ZnO + Na_2O . ZnO . 4H_2O$
8	28.0	14.9	57.1	28.1	28.3	43.6	$Na_2O . ZnO . 4H_2O$
9	33.5	10.9	55.6	28.6	27.9	43.5	$Na_2O . ZnO . 4H_2O$
10	36.7	9.5	53.8	31.9	28.5	39.6	$Na_2O . ZnO . 4H_2O$
11	31.8	11.7	56.5	31.0	20.2	48.8	$Na_2O . ZnO . 4H_2O$
12	30.1	13.2	56.7	29.1	29.2	41.7	$Na_2O . ZnO . 4H_2O$
13	33.2	11.2	55.6	29.7	31.8	38.5	$Na_2O . ZnO . 4H_2O$
14	31.5	11.8	56.7	29.2	32.9	37.9	$Na_2O . ZnO . 4H_2O$
15	36.9	10.1	53 0	34.9	17.2	47.9	$Na_2O . ZnO . 4H_2O$
16	34.7	10.4	54.9	33.7	15.6	50.7	$Na_2O . ZnO . 4H_2O$
17	36.1	10.2	53.7	34.0	17.7	48.3	$Na_2O . ZnO . 4H_2O$
18	36.8	9.9	53.3	33.1	22.8	44.1	$Na_2O . ZnO . 4H_2O$
19	39.2	9.7	51.1	—	—	—	$Na_2O . ZnO . 4H_2O + Na_2O . 3H_2O$
20	39.4	9.0	51.6	42.6	7.0	50.4	$Na_2O . 3H_2O$
21	39.6	7.2	53.2	41.0	6.1	52.9	$Na_2O . 3H_2O$
22	40.7	2.0	57.3	42.0	1.8	56.2	$Na_2O . 3H_2O$
23	40.5	1.6	57.9	42.6	1.3	56.1	$Na_2O . 3H_2O$
24	40.9	1.1	58.0	42.7	0.4	56.9	$Na_2O . 3H_2O$
25	41.9	0.0	58.1	—	—	—	$Na_2O . 3H_2O$
26	24.6	12.5	62.9	23.6	15.2	61.2	ZnO
27	19.9	15.2	64.9	16.1	27.7	56.2	$Zn (OH)_2$
28	4.6	1.0	96.4	3.7	15.4	80.9	$Zn (OH)_2$
29	4.5	0.4	95.1	3.7	20.3	76.0	ZnO
30	13.7	7.2	79.1	9.3	30.4	60.3	$Zn (OH)_2$
31	10.1	4.7	85.2	6.2	32.7	61.1	$Zn (OH)_2$

NaOH, Zn(OH)$_2$ and their compounds if any, must be considered, as those in a ternary system with the components: Na_2O—ZnO—H_2O.

The solubility-diagram of this system could now be completely determined at a constant temperature. As starting-material for these determinations we used NaOH, prepared from sodium, the ZnO being obtained in the following manner: Pure crystallized zinc nitrate was precipitated with the required quantity of ammonia, thoroughly washed out with boiling water, the precipitate then being dried at 140°—150°. The oxide was also obtained by glowing precipitated zinc-carbonate, this oxide being less active, owing to the strong heating, it required a longer time to reach equilibrium. Both preparations showed equal solubility. For the preparing of the hydroxide, vide infra. The water had been distilled and boiled out before use. All the determinations were executed in a thermostat of 30,0° C.

In table 1 and the accompanying diagram 1 a survey of the results is given. All the number-values represent weight percentages of the saturated solution. As it proved extremely difficult to accurately isolate the solid phases, we determined the composition in nearly all cases according to SCHREINEMAKERS's rest-method.

In determining the curve AB we added ZnO as solid phase [1]; the solubility of this substance appears rapidly to increase with growing NaOH-concentration. As appears from the second curve BC of the isotherm, the sodium-zincate of the formula: $Na_2OZnO4H_2O$ precipitates from the solution, while constantly the NaOH-concentration is increasing. The curve CD, where solutions are saturated by the monohydrate of sodium-hydroxide: $NaOH.H_2O$ [$Na_2O.3H_2O$] is immediately joined to BC. According to the melting-diagram NaOH—H$_2$O determined by PICKERING [2] this hydrate is the only stable compound of NaOH with water at 30°.

Consequently only one stable zincate arises at 30°, *having the formula:* $Na_2O.ZnO.4 H_2O$. *All the other zincates described in the literature, must be considered either as metastable or as not existing at all.*

The opinion of HANTZSCH [3] concerning the colloidal nature of the solutions, does not hold true either, as will appear still more decidedly later on.

Properties, preparation, etc. of the sodium-zincate
$$Na_2O.ZnO.4H_2O.$$

The diagram referred to already shows that the sodium-zincate

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[1] Except in the numbers 26 and 29 (vide infra).

[2] Journ. Chem. Soc. 63, 890 (1893).

[3] Loc. cit.

belongs to those salts that form the so-called incongruent solutions. On adding water, these salts do not yield a simple solution, but one of the components, from which we can imagine the salt to 'be formed, separates on the addition of water. Many instances of this are already known. With the zincate of sodium this' phenomenon is specially pronounced. Not only will the addition of water to the solid salt effect a separation of ZnO, hence a decomposition of the compound, but diluted solutions of NaOH will likewise produce the same effect. From the isotherm we may infer, that solutions below a concentration of 33,3 Gr. NaOH to 100 Gr. solution (hence 1 part NaOH to 2 parts of water) will cause a separation of ZnO from the solid salt, i e. the concentration of the NaOH-solution will have to be raised beyond this boundary in order to obtain pure zincate crystals The inadequate attention paid to this circumstance is probably the cause of the manifold contradictions in the literature, hardly anywhere do we find the concentration of the solutions indicated, thus obtaining in many cases mixtures of zincate crystals and ZnO, the possibility for this being very great as appears from the situation of the solubility-curves. In analysing these mixtures investigators attributed the incorrect composition of a compound to them. This occurred among others with the experiments of Comey and Loring Jackson [1]), who prepared zincates by solving ZnO in a hot, concentrated NaOH-solution, they then added alcohol to the liquid and in this way obtained two products: one from the layer of water by shaking out so long with alcohol till crystals appeared and one from the alcoholic liquid.

I have repeated this method and in doing so I started from 50 Gr. of water, to which 50 Gr. NaOH was added. After introducing 17 Gr. ZnO in small quantities at a time, the zincate crystallized out in an appreciable quantity. According to our diagram we are in the centre of the saturation-region of the zincate. With the necessary precautions the crystal agglomerate was sucked out without any access of air and carbonic acid, and was then dried on porous earthenware. Of course the remaining liquor could not be altogether removed in this way, but washing-out without simultaneous decomposition is impossible. The analysis of the crystals produced:

$Na_2O...29.8\%$, $ZnO...37.8\%$, $H_2O...32,4\%$.

(Theoretically for $Na_2O . ZnO. 4H_2O... Na_2O...28,9\%$, $ZnO...37,6\%$, $H_0O...33,5\%$). On microscopic inspection the product appeared to be perfectly homogeneous, the crystals showed as long bars with a

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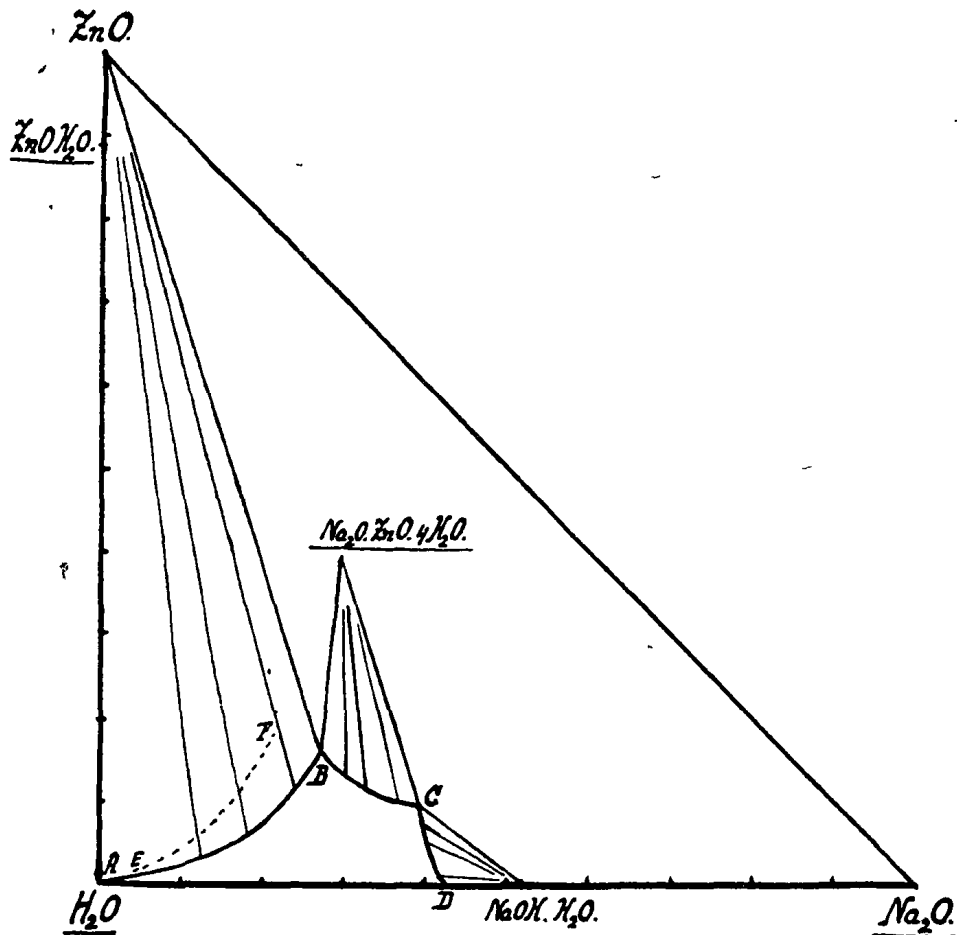[1]) Loc. cit. c.f. also Gmelin-Kraut's Handbuch.

Fig. 1.

blunt extremity. They are faintly double-refractive. Amorphous particles could not be ascertained. The crystals which had formed in the experiments N°s 8—18 were likewise microscopically examined; they appeared entirely to correspond with those obtained in the above-mentioned manner.

A specimen of the crystals treated with alcohol of 96 °/$_0$ showed a complete change. A superficial examination already teaches us in this case, that under the influence of the alcohol the crystals gradually disappear, while amorphous particles precipitate from the liquid. Microscopically too it appears that in these circumstances the crystals cannot exist, but separate out amorphous particles ZnO (or Zn(OH)$_2$)· Even alcohol of 96 °/$_0$ has a hydrolyzing influence on the zincate, and it is not surprising that the above-mentioned investigators obtained products of an improbable composition. Proportional to the quantity of the alcohol and the duration of the operation, a

mixture will be obtained containing a greater or smaller quantity of zincate-crystals. The formulae for such products are devoid of sense and should consequently disappear from the literature.

Stability, preparation, etc. of zinc hydroxide.

It is generally known, that as a rule zinc hydroxide is obtained as a gelatinous, voluminous mass. Now it was essential for the present investigation to determine whether this phase has a constant or a variable composition and to find out its stability regarding ZnO. There are many indications to be found in the literature that the hydroxides obtained in varying ways do not possess the same composition. EULER[1]) prepared from the nitrate hydroxides which proved to have a varying solubility in ammonia. HERZ[2]) and HANTZSCH[3]) point out the great difficulties involved in obtaining $Zn(OH_2$ in a pure state and specially the tenacity with which it retains sulphate-ions. It seems, that it is easier to obtain a pure hydroxide from the chloride or nitrate than from the sulphate. With the experiments made to confirm this statement, I proceeded from pure ZnO, which was dissolved in hydrochloric acid and nitric acid, upon which the hydroxide was precipitated by means of the addition of the quantity of ammonia calculated. If this precipitate is washed out with boiling water it almost immediately becomes more gritty, heavier and less gelatinous. After washing out a few times and following it up by desiccation at 100°, the product appeared to contain only 0,6 °/₀ water. In conseqence of the washing-out the hydroxide is converted into oxide already at 100°. *Hence $Zn(OH)_2$ at 100° is no longer stable.*

We then tried to achieve a pure hydroxide by washing out at room-temperature. It appeared however, that even after prolonged and continued extraction the products were still chloridic or nitritic. During the first hours of the extraction we observe a considerable decrease in the concentration of the adsorbed ion, afterwards it falls but very slowly. The following figures will further illustrate this statement:

Hence it is practically impossible in this way to obtain a pure hydroxide from the chloride. The products from sulphate and nitrate yielded similar results and though it is stated in the literature, that the nitrate-ion is much less strongly absorbed than the other ions, we determined that even after an extraction continued for days the

[1]) Ber. d. deutsch. Chem. Ges. **36**, 3400 (1903).
[2]) Zeitschr. f. anorg. Chem. **30**, 280 (1902); **31**, 357 (1902).
[3]) Loc. cit.

TABLE 2.

Duration of extraction in hours.	Cl' degree in % after drying at 100°.
0	0 59
4	0.36
8	0.35
16	0.34
48	0.30

products were still nitritic. Yet I performed with the gelatinous zinc-hydroxide some measurements concerning the solubility in NaOH, not because the values determined can have an absolute significance, but exclusively with the purpose to investigate whether this hydroxide reveals a higher solubility than ZnO, and consequently must be considered as metastable towards the latter. This proves indeed to be so, as the subjoined numbers demonstrate; the points found lie considerably above the curve of solubility (*AB*) of ZnO. At the same time it appears that the solubility decreases in proportion as the hydroxide is kept for a longer time. This too is in favour of the statement, that these products must be considered *as metastable phases inclining to stabilisation to ZnO*.

TABLE 3.

Time, given in hours, since the preparation of the hydroxide.	Composition of the solution.	
	% ZnO	% Na$_2$O
1	10.5	11.3
10	9.3	11.4
24	8.2	11.3
72	7.0	11.3

For the solubility of ZnO with a Na$_2$O concentration of 11,3 % we find by interpolation 2,3 %, hence considerably lower.

Crystallized zinc hydroxide.

It may be concluded from the above that we must consider the amorphous, gelatinous hydroxides as phases of varying water-percentage, they besides being extremely difficult to purify. There now

was a possibility that under special circumstances, a crystallized hydroxide of a constant composition could be obtained. There are some intimations in the literature, that $Zn(OH)_2$ sometimes seems to arise in a crystallized form. Thus BECQUEREL[1] states that he obtains the crystallized hydroxide by placing a zinc bar wound round with a copper-wire in a solution of sicilic acid in caustic lye. In this process isometric octahedrons were formed, to which he ascribed the formula $Zn(OH)_2$. Various similar indications are found in the older literature though the observers do not agree as regards the composition of the crystals[2]. Of late years the zinchydroxides have been newly examined among others by KLEIN[3]. He distinguishes three forms of the hydroxide; form A is most strongly soluble in NaOH and arises by adding drop by drop $ZnSO_4$-solution to a NaOH-solution. The analysis of the product dried at a normal temperature yielded: $2ZnO.H_2O$. In course of time the forms B or C separate out from the saturated solutions of A; both would have the composition: $ZnO.H_2O$, but B is sometimes obtained in fine crystals, whereas C is always amorphous.

It is clear from the preceding that we need not demonstrate that a constant composition of the amorphous hydroxides is out of the question. The water-percentage of these substances depends on all kinds of factors: preparation, duration of keeping, etc.; hence a definite formula for them is valueless.

The case is otherwise with the crystallized hydroxide. I really found it possible, to isolate *the zinchydroxide as a crystallized* phase of a constant composition. In doing so, I set about it in the following manner: to 50 c.c. of a normal solution of KOH, I added a normal solution of zinc sulphate in drops from a burette. At the outset the hydroxide forming immediately dissolves, but finally a point is reached at which the liquid remains slightly turbid when shaken. On vigorous shaking and especially on scratching the glasswall and allowing to stand for a few minutes a heavy, sandy precipitate arises. Grafting with crystals already obtained, appeared greatly to accelerate the separation. On microscopic examination the product gives an altogether homogeneous impression and it appears to consist of very small, drawn-out bar-shaped crystals. They filtrate very easily and contrary to the amorphous product, the crystals can

[1]) Lieb. Ann **94**, 358 (1855).

[2]) Cf. among others BÖDEKER. Lieb. Ann. **94**, 358 (1855); VILLE, Comp. Rend. **101**, 375 (1885).

[3]) Zeitschr. f anorg. Chem. **74**, 157 (1912). See also WOOD, Journ. Chem. Soc. **97**, 886 (1910).

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be washed out very rapidly. On drying at 40°—50° the analysis yielded:

18,06 % H_2O; 81,91 % ZnO (Theoretically for $Zn(OH)_2$....18,11 % H_2O 81,89 % ZnO.

The concentration of the KOH-solution was varied between the limits of 4,0 and 0,1 normal; the concentration of the zinc sulphate solution likewise; the crystals formed always were of the same shape and composition.

Stability of crystallized zinc hydroxide towards zinc oxide.

The experiments N[os] 26—31 of Table 1 give an insight into the stability-relation of the crystallized $Zn(OH)_2$ and ZnO. With No. 26 the solid phase was added as crystallized $Zn(OH)_2$; the mass was kept for over a fortnight in the thermostat at 30°. It then appeared that the crystalline $Zn(OH)_2$ had been entirely converted and *the solid phase consisted of ZnO*. This was confirmed by the analysis of the solution and remainder, the point found falls on the curve *AB*. So it appears from this, that at 30° *the crystallized zinc hydroxide is metastable towards ZnO*.

With a shorter equilibrium-adjustment *it proved possible to determine the metastable solubility curve of Zn* $(OH)_2$. No. 27 was set in with crystallized Zn $(OH)_2$ and after ± 24 hours the solution was analysed; the solid phase appeared to consist even then of crystallized hydroxide. Conformable to this the zinc percentage of the solution (c. f. table) was considerably higher than corresponds to the curve *AB*. Numbers 30 and 31 have been executed in a similar manner, here again crystallized Zn $(OH)_2$ was added as a solid phase, the solution being analysed after ± 24 hours. The determined compositions of the solution again lie considerably above curve *AB*. The points representing these solutions form together the metastable solubility curve *EF* of the crystallized zinc hydroxide.

Finally the determinations N[os] 28 and 29 have been carried out in the same solution, to which crystals $Zn(OH_2$ were added as a solid phase. After about ± 24 hours the solution yielded the composition N°. 28, $Zn(OH)_2$ being present as a solid phase. Whereas after one day these crystals still appeared to be present, the solution still being of the same composition, we found three weeks later on the composition N°. 29. All the $Zn(OH)_2$ crystals had disappeared; the point now found lies on *AB*, while the analysis of the rest indicated too, that ZnO was present as a solid phase. Other circumstances being equal the solubility of crystallized $Zn(OH)_2$ is considerably higher than that of ZnO.

SUMMARY.

1. The solubility-isotherm in the system Na_2O-ZnO-H_2O was completely determined at 30°.

2. We found that the following substances appeared as stable, solid phases: zinc-oxide ZnO, zincate of sodium Na_2O-ZnO-$4H_2O$, the monohydrate of sodium hydroxide $NaOH$-H_2O.

3. The sodium zincate forms very strongly incongruent solutions, by solutions below a concentration of 1 part of NaOH to 2 parts of water it is decomposed while separating out ZnO.

4. The amorphous, gelatinous zinchydroxide must be considered as a phase of a varying water-percentage; it cannot possibly be cleaned of adsorbed ions. It is metastable as regards crystallized zinchydroxide.

5, Under special circumstances zinchydroxide is obtainable as a crystalline phase of the constant composition $Zn(OH)_2$.

6. This crystallized hydroxide is metastable at 30° as regards ZnO.

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