[Contribution from the Sterling Chemistry Laboratory, Yale University]

EQUILIBRIUM BETWEEN CRYSTALLINE ZINC HYDROXIDE AND AQUEOUS SOLUTIONS OF AMMONIUM HYDROXIDE AND OF SODIUM HYDROXIDE

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The present investigation is primarily concerned with the preparation of crystalline zinc hydroxide, the evaluation of its solubility product, the determination of its solubility and its activity coefficient in a series of solutions of ammonium hydroxide and of sodium hydroxide, and the results that may be derived from such experimental observations. These results are, in general, in harmony with those published recently by Maier and co-workers.[2] Evidence is also presented as to the chemical nature of two basic salts of zinc, the formation of which was observed in the course of the experimental work on the preparation of the hydroxide.

I. Crystalline Zinc Hydroxide

Preparation.—Since many equilibrium measurements were to be made, the method of preparing a stable form of crystalline zinc hydroxide had to be one which would permit the ready formation of a large amount of definite crystalline product, a criterion which methods of former investigators[3] do not satisfy.

In the precipitation of a substance the size of grain obtained will depend upon, among other factors, the product of the activities of the ions of the substance precipitating, relative to the product of the activities of the same ions in a solution which, under the conditions of the experiment, is saturated with the substance; and this ratio must be such that the rate of deposition does not exceed a certain maximum characteristic of the particular crystal.[4] For the formation of crystalline zinc hydroxide, a low degree of virtual supersaturation can be maintained by having a large reservoir of the zinc ion in the form of a slightly ionized complex, and arranging conditions so that the various equilibria are disturbed very

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[1] From the dissertation presented in June, 1926, by Harold G. Dietrich to the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

[2] (a) Maier and Ralston, This Journal, **48**, 364 (1926). (b) Maier, Parks and Anderson, *ibid.*, **48**, 2564 (1926).

[3] (a) Runge, *Pogg. Ann.*, **16**, 129 (1829). (b) Schindler, *Mag. Pharm.*, **31**, 167 (1830); **36**, 43 (1831). (c) Nichols, *Ann. chim. phys.*, [3] **22**, 31 (1848). (d) Becquerel, *Compt. rend.*, **34**, 29 (1852). (e) Boedeker, *Ann.*, **94**, 358 (1855). (f) Malaguti and Sarzeau, *Ann. chim. phys.*, [3] **9**, 431 (1843). (g) Cornu, *Bull. soc. chim.*, [1] **5**, 64 (1863). (h) Ville, *Compt. rend.*, **101**, 375 (1885). (i) Klein, *Z. anorg. Chem.*, **74**, 157 (1912). (j) De Forcrand, *Ann. chim. phys.*, [7] **27**, 26 (1902). (k) Goudriaan, *Rec. trav. chim.*, **39**, 505 (1920). (l) Fricke and Ahrndts, *Z. anorg. allgem. Chem.*, **134**, 344 (1924); **136**, 48 (1924).

[4] Compare Johnston, This Journal, **36**, 16 (1914).

slowly. The zinc-ammonia complex readily adapts itself to this purpose, for by the gradual removal of ammonia from the solution the activity of the zinc ion is increased and a point eventually reached where the product of the activities of the zinc and hydroxyl ions exceeds that characteristic of zinc hydroxide, which thereupon precipitates. If the removal of ammonia is carried on very slowly, the degree of virtual supersaturation is kept sufficiently low and the rate of deposition is such that good crystals form.

In the actual preparation, gelatinous zinc hydroxide was first precipitated by the addition of the calculated amount of ammonia to a zinc sulfate (or chloride) solution of known strength, the precipitate separated by filtration, then washed thoroughly to remove as much of the adhering sulfate ion as possible. This precaution is very important; for, if the *unwashed* hydroxide is immediately dissolved in an excess of ammonia and subsequently treated as indicated above, the crystals separating will sooner or later be basic sulfate.[5] The moist, washed precipitate was then dissolved in the requisite amount of concd. ammonium hydroxide, and the ammonia gradually removed from solution by absorption from the vapor phase by concd. sulfuric acid. This operation was carried out under a bell jar, one beaker containing the ammoniacal solution, another the acid. Within a week there was obtained a large quantity of easily visible crystals, the crystallization rate of which was seemingly unaffected by the strength of the ammonium hydroxide or the amount of zinc present, but only by the removal of ammonia, the initial stages of which must be done slowly to achieve the best results. Only in this manner can colloid formation be avoided, and crystals with an average length of 0.5 mm. obtained.

Properties.—The mean result (water, 18.08%; zinc oxide, 81.91%) of several concordant analyses[6] indicates that the crystalline product is pure zinc hydroxide (water, 18.12%; zinc oxide, 81.88%). The crystals always assumed the orthorhombic bipyramidal form, generally showing parallel extinction. They exhibit no cleavage planes, but a petrographic examination of the irregular fragments has led to the belief that the optical angle is large and the crystals are probably negative. The three indices of refraction lie very close to 1.57, thus accounting for the pronounced interference colors of even the thick crystals. Measurements of the facial angles confirmed those made by Morel.[7]

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[5] When in the ammoniacal solution the ratio of zinc to sulfate (or of zinc to chlorine) falls below about five, basic sulfate (or basic chloride) crystals may appear, as discussed later.

[6] Water content was determined by heating a definite quantity, previously dried over concd. sulfuric acid, at low red heat until weight became constant; zinc content, by electrometric titration against potassium ferrocyanide, reference to which is made later.

[7] Morel, *Bull. soc. franç. minéral.*, **15**, 9 (1892); *Z. Kryst. Mineral.*, **23**, 482 (1894).

The suitability of these crystals as solid phase for equilibrium measurements depends upon the conditions and the ease with which zinc hydroxide reverts to zinc oxide, a matter on which the statements in the literature are conflicting.[3j,k] That their transition rate is exceedingly slow at room temperatures is indicated by the fact that under ordinary laboratory conditions the crystals remain unchanged in composition for an indefinite period, and that in the presence of concd. sulfuric acid, or of lime, no loss in weight was observed in six months. With respect to the effect of temperature on the transition rate, no appreciable decomposition was noted when the crystals were kept under water at 65° for three weeks; at 75° for the same period the decomposition was less than 10%. At higher temperatures than this, however, the rate of decomposition under water increased rapidly, so that at 100° decomposition was complete in less than an hour.

The ease with which pure, crystalline zinc hydroxide may be prepared suggested its use in place of metallic zinc, which is difficult to purify and maintain pure, for the standardization of solutions requisite for zinc analyses. That this is entirely justified is shown by a comparison of the titer of a potassium ferrocyanide solution standardized with "pure" zinc[8] with that based on the hydroxide, for the difference, 0.1%, is no greater than the aggregate experimental uncertainty.

In the course of experiments on the preparation of the hydroxide, two crystalline basic salts of zinc appeared, the analysis and properties of which indicate definite compound formation.

II. Preparation and Properties of Two Basic Zinc Salts

If to an aqueous solution of zinc sulfate, ammonium hydroxide is added in quantity sufficient to redissolve the precipitate first formed, no intermediate separation from the mother liquor being made, and the ammonia then removed as indicated in the preparation of zinc hydroxide, there are obtained crystals which, after thorough washing, have the following composition, the mean of several concordant analyses: zinc oxide, 62.87%; sulfate (SO_3), 12.21%; water, 24.69%,[9] which corresponds closely to the formula $4ZnO.ZnSO_4.9H_2O$ (zinc oxide, 62.69%; sulfate 12.33%; water, 24.98%). Crystals of the same composition continued to form after the first crop had been removed; and identical crystals were obtained from a solution which, owing to the presence initially of insufficient sulfate, first yielded

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[8] The zinc, furnished by the New Jersey Zinc Co., and an analysis of the same, were obtained through the courtesy of Professor C. H. Mathewson of the Hammond Laboratory, Yale University. Impurities were: lead, 0.005%; iron, 0.003%; cadmium, 0.001%; arsenic, under 0.0001%.

[9] Zinc was determined by electrometric titration; sulfate, according to the method outlined by Johnston and Adams [THIS JOURNAL, **33**, 844 (1911)]; water, by heating a known weight of the crystals to constant weight.

crystals of the hydroxide. In this case the gelatinous product appearing upon addition of ammonium hydroxide to the zinc sulfate solution was, after filtration, dissolved *unwashed* in an excess of ammonium hydroxide. The formation of basic sulfate before crystallization has proceeded to any extent, due to failure to wash the gelatinous mass before solution in ammonium hydroxide, emphasizes the necessity, if the pure hydroxide is desired, of washing the colloidal material thoroughly before proceeding to redissolve it in ammonium hydroxide.

Since, in the preparation of the hydroxide, zinc chloride may be used as well as zinc sulfate, the possibility of the formation of a basic chloride was likewise investigated; a definite crystalline product again appeared, the composition of which as the average of several concordant results is: zinc 54.17%, chlorine 11.70%[10]—corresponding to the formula $4ZnO.ZnCl_2.8H_2O$ (zinc 53.95%, chlorine 11.73%).

Fragments of the basic sulfate aggregates have a rectangular, micaceous, plate-like appearance, exhibiting parallel extinction. Two indices of refraction have been determined, 1.59 and 1.58. The basic chloride crystals under microscopic examination appear as pentagonal and hexagonal micaceous plates, one of the indices of refraction being 1.600–1.605.

The facts that both products are certainly crystalline, that in each case all preparations, although obtained under differing sets of conditions, remained unaltered both as to composition and indices of refraction, indicate that these basic salts are true definite compounds. Both appear to be sparingly soluble in water; when dissolved in ammonium hydroxide, they form incongruent solutions, that is, upon removal of the ammonia through the vapor phase, crystals of zinc hydroxide, and not of the basic salt, appear. This fact is of importance in the preparation of the hydroxide in that, to prevent the possibility of contamination with basic salt, the ratio of zinc to sulfate or chlorine in the solution should not fall too far below 5 to 1; failure to observe this probably accounts for many of the discrepancies in solubility data of former investigators.[11]

According to Mellor,[12] of the large number of basic zinc salts reported in the literature, the majority are unstable and of indefinite composition. An examination of the formulas of those reported reveals the prevalence of the figure 5 in the ratio of metal oxide to acid anhydride.[13] It is note-

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[10] Chlorine was determined according to the procedure in Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, **1915**, vol. 2, p. 320; water analysis was impossible, inasmuch as the crystals decomposed even at low temperatures with some loss of chlorine.

[11] For example, Bonsdorff, *Z. anorg. Chem.*, **41**, 132 (1904).

[12] Mellor, "Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, **1923**, vol. 4, 625, 645.

[13] Pickering [*J. Chem. Soc.*, **91**, 1981 (1907)] notes the repetition of the figure 5 in his work on basic metal sulfates other than zinc.

worthy that this same ratio of 5 to 1 appears in the formulas ascribed to the definite basic salts just described, namely, $4ZnO.ZnSO_4.9H_2O$ and $4ZnO.ZnCl_2.8H_2O$.

III. Solubility of Zinc Hydroxide in Ammonium Hydroxide and in Sodium Hydroxide

The data of former investigators[3k,11,14] show no agreement, a fact to be expected when one considers that in most cases the exact nature of the solid phase is open to question. In those cases in which solubility measurements were carried out at different temperatures, there is such a wide divergence in the results of independent investigations not attributable to temperature alone, that further experimental work was necessary. Accordingly, we determined the molality of zinc in solutions of (1) aqueous ammonia, (2) sodium hydroxide, saturated with zinc hydroxide at 0, 25 and 35°, in a series of concentrations of alkali ranging from 0 to 5 molal.

For the preparation of aqueous ammonia of the desired molality, commercial C. P. ammonium hydroxide was distilled into a Pyrex flask containing laboratory-distilled water, a rough determination of the strength of the resulting solution made, and a portion diluted to the approximate concentration desired. One hundred twenty-five cc. of this solution, together with more than sufficient zinc hydroxide crystals for saturation, was placed in four Pyrex glass-stoppered bottles of 160 cc. capacity. Sodium hydroxide of the desired molality was prepared by proper dilution of a 1:1 solution, made up and freed from carbonate as described by Clark.[15]

Equilibrium in the solutions was established within 24 hours, as determined by successive analyses, by rotation in a water thermostat, constant to ±0.02°. For the temperature 0° the thermostat was filled with a slushy mixture of ice and snow, and a side compartment filled with ice, through which the water circulated. Equilibrium in two bottles was approached from supersaturation as well, by removing these at the end of the first 24 hours, keeping them for eight hours with frequent agitation at such a temperature that supersaturation with respect to the original temperature occurs,[16] then rotating them in the thermostat for 24 hours more, at the end of which two samples were withdrawn from each bottle for analysis.

Each sample, withdrawn by forcing some of the solution through a

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[14] For ammonium hydroxide, (a) Herz, *Z. anorg. Chem.*, **30**, 280 (1902). (b) Euler, *Ber.*, **36**, 3400 (1903). For sodium hydroxide, (c) Rubenbauer, *Z. anorg. Chem.*, **30**, 332 (1902). (d) Wood, *J. Chem. Soc.*, **97**, 878 (1910).

[15] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, **1922**, p. 101.

[16] A lower temperature for ammonium hydroxide; a higher temperature for sodium hydroxide.

cotton filter into a pipet, was delivered into a known weight of standard hydrochloric acid solution, the weight of the sample determined by reweighing; the excess of hydrochloric acid was then titrated against standard sodium hydroxide solution, all titrations being made by weight, with sodium alizarin sulfonate as indicator. The neutralized sample was then acidified with 3 cc. of concd. hydrochloric acid, diluted to 200 cc., and the zinc content determined by electrometric titration against potassium ferrocyanide, in accordance with the procedure recommended by Willard and Fenwick.[17] This procedure was chosen because it appears to be more accurate and more feasible, in view of the large number of analyses that had to be made, than other methods of zinc analysis. In all titrations the ferrocyanide solution was added to the zinc solution, although preliminary experiments indicate that no difference exists if the titration is performed in the other way. During titration the zinc solution was kept at about 80°, as this increases the speed of operation. The middle of the break of the curve of e.m.f. of the solution plotted against ferrocyanide added was taken as the end-point, exactly as in the repeated titration of the ferrocyanide solution with pure zinc or crystalline zinc hydroxide. This solution, prepared for standardization by dissolving about 10 g. of the trihydrate ($K_4Fe(CN)_6.3H_2O$) per liter of distilled water, was kept under hydrogen to avoid any change in concentration through oxidation.

Solubility measurements at 35 and 0° were made in the same manner, except that only two bottles were used for each concentration, one for approaching the equilibrium from undersaturation and the other from supersaturation; and three samples were withdrawn from each bottle.

From the analytical data the solubility of zinc hydroxide was determined in terms of the number of moles of this and of alkali per 1000 g. of water. In order to facilitate the interpolation of solubility values, the logarithm of $1000R$, R being the mean ratio of the number of moles of zinc hydroxide per mole of alkali for a given sample, has been plotted against the molality of alkali, and the points so plotted lie on a smooth curve. Each point, the experimental values for which are given in Table I, is the mean of from four to six separate results. The average deviation from R is in general below 0.5% for concentrations of alkali above 1 M; below this molality the deviation is somewhat higher, owing to the presence of much less zinc hydroxide in the solution and, therefore, the greater relative error involved in its determination.

The product of the value of R, as derived by interpolation for a selected concentration of alkali, and the molality of alkali represents the solubility of zinc hydroxide in the alkali of the chosen concentration. The

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[17] (a) Willard and Fenwick, THIS JOURNAL, **44**, 2504, 2516 (1922). (b) Van Name and Fenwick, *ibid.*, **47**, 9 (1925).

TABLE I

AVERAGE EXPERIMENTAL RESULTS ON THE SOLUBILITY OF CRYSTALLINE ZINC HYDROXIDE IN A SERIES OF SOLUTIONS OF AMMONIUM HYDROXIDE AND OF SODIUM HYDROXIDE IN TERMS OF 1000*R*, WHERE *R* IS THE NUMBER OF MOLES OF ZINC HYDROXIDE PER MOLE OF ALKALI

NH_4OH, *M*	1000*R*	NaOH, *M*	1000*R*	NH_4OH, *M*	1000*R*	NaOH, *M*	1000*R*
			Temp., 25°				
0.1569	4.916	0.1554	7.513	1.265	29.44	1.395	65.52
.2402	7.584	.3416	16.50	1.697	34.06	2.700	125.3
.5527	15.32	.5430	25.39	2.416	42.85	3.364	150.4
.6468	17.64	.8641	40.17	3.753	51.55	6.69	279.7
1.088	26.11	1.167	55.21	5.086	55.90		
			Temp., 0°				
0.5099	20.07	0.5652	22.29	1.739	43.14	2.398	89.37
1.152	32.78	1.204	47.02	2.455	52.13	3.003	114.2
1.517	40.73	1.781	68.94	3.344	62.32		
			Temp., 35°				
0.4781	12.55	0.5679	29.60	1.753	31.18	1.710	86.54
.5049	13.11	.9618	49.32	2.432	37.68	2.456	122.9
1.035	22.58	1.383	68.84				

results of such interpolation for 25° appear in Table IV. It is to be noted that the solubility of zinc hydroxide in sodium hydroxide is greater than in ammonium hydroxide and, furthermore, increases more rapidly with change in concentration of alkali. With rise in temperature, however, the solubility in sodium hydroxide increases, whereas in aqueous ammonia it decreases. Even in this a point of similarity exists in that in each case a constant ratio exists between the solubility at 25° and that at 0° and at 35°. These constants, given in Table II, were evaluated by determining the slopes of the straight lines obtained when the solubility at either temperature is plotted against the solubility at 25°.

TABLE II

RATIOS OF THE SOLUBILITY (*m*) OF ZINC HYDROXIDE AT 0 AND 25°, AND AT 35 AND 25°, IN SOLUTIONS OF AMMONIUM HYDROXIDE AND OF SODIUM HYDROXIDE

Alkali	m_0/m_{25}	m_{35}/m_{25}
NH_4OH	1.21	0.87
NaOH	0.84	1.10

Owing to the different methods of expressing concentration, a quantitative comparison with the data of former investigators[3k,11,14] cannot be made. The evidence, however, indicates that, but for two exceptions,[18] the analytical results given in Table I are the lowest recorded and, therefore, pre-

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[18] Bonsdorff (Ref. 11) presents one set of data, based on experimental work in which the nature of the solid phase is questionable, which indicates a lower solubility for the hydroxide in aqueous ammonia than we observed. Wood (Ref. 14 d) offers data on the solubility of the hydroxide in sodium hydroxide less than 1 *M* which show surprising agreement with the analytical results in Table I.

sumably the most reliable. Goudriaan,[3k] when working with a crystalline form of the hydroxide at 30°, published measurements of solubility in sodium hydroxide solutions which are greater than those interpolated for 30° from our data. A reason for this may lie in the fact that the crystalline form which he used has been shown to be metastable[31] toward the orthorhombic form, the form which we have used. No evidence was obtained during the course of experimental observations on any one solution, which extended in some cases over a period of five days, of a change in the character of the solid phase in equilibrium with the solution, although a transition has been reported by Rubenbauer[14c] and Goudriaan[3k] for solutions of zinc hydroxide in sodium hydroxide.

IV. The Zinc Hydroxide Electrode

The possibility of setting up a reversible zinc hydroxide electrode which shall yield a definite electromotive force depends upon the stability at 25° of the hydroxide used and upon the reproducibility of solubility measurements in alkaline solutions. These conditions are fulfilled by our material, as is shown also by the fact that the observed e.m.f. of any one cell remained unchanged for hours; whereas Maier, Parks and Anderson[2b] state that their hydroxide cells "showed a more or less continued drift, probably due to slow decomposition of the hydroxide form." The electromotive force of a cell of the type $Zn(s), Zn(OH)_2(s) \mid$ dilute alkali solution $\mid HgO(s), Hg(l)$ determines directly the thermodynamic solubility product (that is, in terms of activities instead of concentrations) of zinc hydroxide; the e.m.f. of such a cell is given by the expression $E_{\text{cell}} = \overset{\circ}{E}_{\text{Zn}} - \overset{\circ}{E}_{\text{Hg}} - (RT/2\text{F})\ ln\ (a_{\text{Zn}^{++}}\, a^2_{\text{OH}^-})$, in which the logarithmic term is the thermodynamic solubility product (K) of the hydroxide. Upon assumption of the standard electrode potentials for zinc and mercury, as given by Lewis and Randall,[19] the expression reduces to $E = 0.8565 - 0.029575 \log K$. The electromotive force of the cell is independent of the concentration of alkali, but depends somewhat on the difference in the activity of water on the two sides of the cell; this, however, becomes negligible at low concentrations of sodium hydroxide.

Zinc was prepared in a fine state of subdivision[20] by the electrolysis of a zinc sulfate solution, with an anode of stick zinc and a platinum cathode; the zinc obtained at the cathode was then made the anode in a new solution and the process repeated, the product thoroughly washed, and kept under water until used. Crystalline zinc hydroxide was prepared as described in Part I. Pure, distilled mercury was treated repeatedly with chloride-free, concentrated nitric acid followed by evaporation to

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[19] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, **1923**, pp. 408, 420.

[20] As proposed by Richards and Lewis [*Proc. Am. Acad. Arts Sci.*, **34**, 87 (1898); *Z. physik. Chem.*, **28**, 1 (1899)] for constancy and reproducibility.

dryness; the nitrate was then converted to oxide by adding sodium hydroxide, boiling for some time, filtering, washing and drying on the hot-plate.

Two portions of the same solution of sodium hydroxide, prepared by proper dilution of a solution obtained by the action of water on sodium, were saturated with zinc hydroxide and mercuric oxide, respectively, by rotation in a thermostat at 25° (±0.02°) for 24 hours. Each solution was then placed in contact with its metal and the hydroxide or oxide in a half-cell so constructed that, after bridging with an alkaline solution of the same concentration as that used in the half-cells, nine combinations are possible. Carbon dioxide was excluded, and the potential differences were measured after equilibrium at 25° had been established. These became uniform in a few hours after making up the cells and remained constant for 24 hours. Each electromotive force recorded is the average of nine measurements, since nine combinations were possible; the greater part of the deviation from the average is due to the lesser reproducibility of the zinc hydroxide electrodes, as the mercuric oxide electrodes were reproducible to less than 50 microvolts. The data are presented in Table III.

TABLE III

ELECTROMOTIVE FORCE OF THE CELL ZN, $ZN(OH)_2$ | NaOH(*m*) | HgO, HG

NaOH, *m*	E.m.f., volts	Deviation, millivolts	Soly. product $Zn(OH)_2$, $K \times 10^{17}$
0.075	1.3453	0.2	2.97
.159	1.3443	.06	3.21
.361	1.3429	.2	3.58
.417	1.3433	.1	3.47
1.0 (approx.)	1.3434	.4	3.44
Av.	1.3438 ± 0.0008 volts		3.33

Upon substitution in the expression for the electromotive force of the cell the mean value for E_{cell} (1.3438 volts), K (solubility product of zinc hydroxide) becomes 3.3×10^{-17}. This value is markedly smaller than that obtained by calculation from measured solubility values of the hydroxide in water[21] on the obviously erroneous assumption that the zinc hydroxide in solution is completely dissociated. The value does, however, correspond favorably with that derived indirectly by de Wijs,[22] 7.4×10^{-17}, from determination of the formulas and stability constants of the complex zinc-ammonia ions by experimental measurements of the partial pressures of ammonia above solutions containing such ions. Thermodynamic calculations, presented later, further sub-

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[21] (a) Bodländer, *Z. physik. Chem.*, **27**, 66 (1898), 1.25×10^{-5}. (b) Herz, *Z. anorg. Chem.*, **23**, 222 (1900), 1.3×10^{-5}. (c) Dupré and Bialas, *Z. angew. Chem.*, **16**, 54 (1903), 5.2×10^{-5}. (d) Remy and Kuhlmann, *Z. anal. Chem.*, **65**, 161 (1924/1925), 3.7×10^{-5}.

[22] de Wijs, *Rec. trav. chim.*, **44**, 663 (1925).

stantiate the value which we have derived for the solubility product of zinc hydroxide.

Stoichiometric Activity Coefficients of Zinc Hydroxide

Since the activity of zinc hydroxide (a_2) for saturated solutions is its solubility product, and since this has been evaluated for 25°, and the actual solubility (m) of the hydroxide in solutions of ammonium and of sodium hydroxide have been determined, the stoichiometric mean activity coefficient (γ) of zinc hydroxide may be calculated from the expression for a bi-univalent electrolyte:[23] $\gamma = (a_2)^{1/3}/(2)^{2/3}m$. Values of γ are given for round concentrations in Table IV; they must fall on a smooth curve since the data for the solubility of zinc hydroxide have been interpolated from a smooth curve. Attention is directed to the exceedingly small value of γ for the hydroxide even in the dilute solutions of alkali (of the order of 0.001 for 0.25 M ammonium hydroxide and less than this for 0.25 M sodium hydroxide); this serves as an indication that nearly all of the zinc in these solutions is present as complexes.

The activity coefficient of zinc hydroxide in pure water has been estimated by extrapolating to zero concentration of alkali the two curves which are obtained when the logarithms of the activity coefficients are plotted against the square root of molality of alkali. The extrapolation was made on a large scale over that part of each curve which, because of the method of plotting, is very nearly a straight line. The value so derived, which must be the same in each case, is approximately 0.1, a value which is in harmony with the idea that zinc hydroxide is a weak electrolyte. Upon substitution of this value and the value for the solubility product in the expression, already given, for the activity coefficient of zinc hydroxide, the solubility of this compound in water may be calculated, a value of 2×10^{-5} mole per 1000 g. water being obtained. As this value is based upon extrapolation, it is merely an approximation which, owing to the method of extrapolation, is to be considered as a maximum value. Values given in the literature for the solubility of the hydroxide in water vary from 1.25 to 5.2×10^{-5} mole per liter.[21]

V. Thermodynamic Calculations

A knowledge of the electromotive force of the cell, $Zn(s), Zn(OH)_2(s), | NaOH(m) | HgO(s), Hg(l)$, has permitted the evaluation of the solubility product (K) of zinc hydroxide. Since this is the equilibrium constant for the reaction $Zn(OH)_2 \longrightarrow Zn^{++} + 2OH^-$, the standard free-energy change (ΔF°) of which is given by the expression $\Delta F^\circ = RTlnK$, ΔF°_{298} becomes 22,490 cal.

The standard free-energy change for the cell reaction, $Zn(s) + HgO(s) + H_2O(l) \longrightarrow Zn(OH)_2(s) + Hg(l)$, may also be evaluated, for each of

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[23] Ref. 19, p. 328.

the substances is in its standard state and E_{cell} is therefore $E°$; since $\Delta F^{\circ}_{298} = -NFE°$, $\Delta F^{\circ}_{298} = -62{,}014 \pm 40$ cal.

The free energy of formation of zinc hydroxide from zinc oxide and water may now be evaluated as follows.

$$\begin{array}{llcll}
\text{(a)} & \mathrm{Zn(s)} + \mathrm{HgO(s)} + \mathrm{H_2O(l)} & \longrightarrow & \mathrm{Zn(OH)_2(s)} + \mathrm{Hg(l)} & \Delta F^{\circ} = -62{,}014 \text{ cal.} \\
\text{(b)} & \mathrm{Hg(l)} + {}^1/_2\mathrm{O_2} & \longrightarrow & \mathrm{HgO(s)} & \Delta F^{\circ} = -13{,}808 \text{ cal.}^{24} \\
 & \mathrm{ZnO(s)} & \longrightarrow & \mathrm{Zn(s)} + {}^1/_2\mathrm{O_2} & \Delta F^{\circ} = 75{,}930 \text{ cal.}^{2b} \\
\hline
\text{(sum)} & \mathrm{ZnO(s)} + \mathrm{H_2O(l)} & \longrightarrow & \mathrm{Zn(OH)_2(s)} & \Delta F^{\circ}_{298} = +108 \text{ cal.}
\end{array}$$

This result indicates that at 25° zinc hydroxide is essentially at equilibrium with water and zinc oxide. By combination of (a) and (b) with the free energy of formation of water from its elements,[24b] the free-energy change at 25° for the reaction $\mathrm{Zn(s)} + 2\mathrm{H_2O(l)} \longrightarrow \mathrm{Zn(OH)_2(s)} + \mathrm{H_2(g)}$ is —19,262 cal. This is in harmony with the value, —19,100 cal., obtained directly by Maier, Parks and Anderson[2b] from measurements of the e.m.f. of the cell $\mathrm{Zn(s)}, \mathrm{Zn(OH)_2(s)} \mid \mathrm{Ba(OH)_2} \mid \mathrm{H_2(g)}$, measurements which, however, were not considered very satisfactory on account of the continual drift observed.

Dissociation Constant of the Zincate Ion

On the basis that the zinc content of solutions of zinc hydroxide in sodium hydroxide is distributed between the zinc ion, the acid zincate ion ($\mathrm{HZnO_2^-}$), and the zincate ion ($\mathrm{ZnO_2^{=}}$), we outline a method whereby the dissociation constant of the zincate ion may be approximately evaluated. The expression for this constant is $a_{\mathrm{Zn}^{++}}a^4_{\mathrm{OH}^-}/a_{\mathrm{ZnO_2}^{=}} = K_1$. If the activity of the zincate ion may be considered to be proportional to the total concentration of zinc present, this may be written $(a_{\mathrm{Zn}^{++}}a^2_{\mathrm{OH}^-})a^2_{\mathrm{OH}^-}/m_{\mathrm{Zn(OH)_2}} = K_1$. The quantity in parentheses is the thermodynamic solubility product of zinc hydroxide and has been evaluated. The saturation concentration in the denominator has been determined for a series of concentrations of sodium hydroxide. By means of certain assumptions which seem plausible, the activity of the hydroxyl ion in each of the solutions may be estimated.

On the assumption that in a solution of potassium chloride the activities of the potassium and chloride ions are equal,[25] since these ions have about the same mobility and atomic weight, and on the basis of the further assumption that in dilute solutions of potassium chloride, sodium chloride and sodium hydroxide the principle of ionic strength as stated by Lewis and Randall[19] holds, and that, therefore, the activity of the chloride ion is the same in potassium and in sodium chloride solutions of the same ionic strength and that the activity of the sodium ion is the same for solutions of sodium chloride and sodium hydroxide of the same ionic strength, the following expression is derived for the activity of the hydroxyl ion

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[24] (a) Ref. 19, pp. 607; (b) 485.

[25] MacInnes, THIS JOURNAL, 41, 1086 (1919).

in solutions of sodium hydroxide: $a_{OH^-} = \gamma^2_{NaOH}\gamma_{KCl}m_{KCl}/\gamma^2_{NaCl}$, γ denoting a mean activity coefficient, m, molality. With the aid of data on the activity coefficients of sodium hydroxide by Harned,[26] and on the chlorides by Scatchard,[27] the activity of the hydroxyl ion in solutions of sodium hydroxide ranging up to 3 M has been approximately evaluated, as presented in Table IV.

If the further assumption is made that for solutions of sodium hydroxide of low concentration saturated with zinc hydroxide, the activity of the hydroxyl ion is the same as for the alkali alone at the same molality, the dissociation constant of the zincate ion may be evaluated. Justification for this assumption lies in the fact that the ratio of sodium hydroxide to zinc hydroxide is increasing with great rapidity with decrease in molality of sodium hydroxide at low concentrations and, therefore, these solutions are approaching more and more the properties of pure sodium hydroxide solutions of the same molality. It should then be possible to obtain a correct value for the dissociation constant of the zincate ion by extrapolation to zero concentration of alkali. The values as given in Table IV are sufficiently consistent for concentrations below 1 M sodium hydroxide, that the average value of these can be taken as the value at zero concentration of alkali. Thus, in round numbers K_1 = 3.6×10^{-16}. The concordance of the values vindicates the assumptions made in the course of their calculation.

TABLE IV

INTERPOLATED VALUES OF THE SOLUBILITY AT 25° OF CRYSTALLINE $Zn(OH)_2$ IN NH_4OH AND IN NaOH TOGETHER WITH CALCULATED ACTIVITY COEFFICIENTS OF $Zn(OH)_2$ AND THE DISSOCIATION CONSTANT OF THE ZINCATE ION

Alkali M	$m_{25°}$ in NH_4OH	$\gamma \times 10^6$ in NH_4OH	$m_{25°}$ in NaOH	$\gamma \times 10^6$ in NaOH	a_{OH^-} for NaOH	$K_{ZnO_2^=} \times 10^{16}$
0[a]	0.00002	10^5	0.00002	10^5		3.6
0.2	.00130	1559	.00206	983.8	0.147	3.49
.3	.00275	737.0	.00444	456.5	.221	3.66
.4	.00468	433.1	.00760	266.7	.291	3.71
.5	.00705	287.5	.0115	176.2	.359	3.73
.75	.0147	137.9	.02625	77.2	.519	3.41
1.0	.0246	82.4	.0468	43.3	.694	3.43
1.5	.0496	40.9	.1042	19.4	1.104	3.89
2.0	.0790	25.6	.1832	11.1	1.523	4.22
2.5	.1105	18.3	.2845	7.1	1.981	4.59
3.0	.1428	14.2	.4065	5.0	2.487	5.07
3.5	.1757	11.5	.5470	3.7		
4.0	.2096	9.7	.7032	2.9		
5.0	.2785	7.3	1.0740	1.9		

[a] By extrapolation.

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[26] Harned, THIS JOURNAL, **47**, 682 (1925).

[27] Scatchard, *ibid.*, **47**, 654, 656 (1925).

A large difference exists between the mean value (3.6×10^{-16}) and that reported by Kunschert,[28] 4×10^{-13}, upon which no stress can be placed inasmuch as its calculation is based upon electromotive-force measurements of cells containing zinc electrodes of poor reproducibility and having large liquid-junction potentials.

Summary

Crystalline zinc hydroxide has been prepared in quantity, and its stability and crystallographic properties were investigated. When crystallization is carried too far, basic zinc salts appear. Two such salts, $4ZnO.ZnSO_4.9H_2O$ and $4ZnO.ZnCl_2.8H_2O$, have been obtained as definite chemical compounds in crystalline form.

Its solubility at 25, 0 and 35°, in solutions of ammonia and of sodium hydroxide up to 5 M has been determined; the data indicate that a constant ratio exists between the solubility at 25° and at each of the other temperatures.

From measurements of the electromotive force at different alkali concentrations of the cell, $Zn(s), Zn(OH)_2(s) \mid NaOH(m) \mid HgO(s), Hg(l)$, there have been computed (a) a value, 3.3×10^{-17}, for the solubility product of zinc hydroxide; (b) the activity coefficients of this compound at 25° in solutions of ammonia and of sodium hydroxide; by extrapolation, a maximum value of this activity coefficient in water has been estimated and from this has been derived an upper limiting value of the solubility of zinc hydroxide in water at 25°; (c) the following standard free-energy changes at 25°: $Zn + HgO + H_2O(l) \longrightarrow Zn(OH)_2 + Hg(l)$, $\Delta F^\circ = -62{,}014$ cal.; $Zn(OH)_2 \longrightarrow Zn^{++} + 2OH^-$, $\Delta F^\circ = 22{,}490$ cal.; by combination with other recent data: $ZnO + H_2O(l) \longrightarrow Zn(OH)_2$, $\Delta F^\circ = 108$ cal.

With the adoption of certain assumptions it has been possible to derive a value, 3.6×10^{-16}, for the dissociation constant of the zincate ion from a knowledge of the solubility-product constant of zinc hydroxide and its solubility in solutions of sodium hydroxide at 25°.

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[28] Kunschert, *Z. anorg. Chem.*, **41**, 346 (1904).