the molecule, through interference of the charge clouds of the lone pair electrons on the oxygen atoms, would result in a weakening of the peroxide bond by some 10 kcal. The present work corroborates a skew arrangement for $S_2F_{10}O_2$ and, on a basis of Walsh's work, there should be a general increase in stability of the molecule from the charge transfer over that of H_2O_2.

With respect to the formation of $S_2F_{10}O_2$ under the reaction conditions, it has been reported[18] that if any traces of water are present in the acid fluorides which are electrolyzed to obtain fluorine for the sulfur–fluorine reaction, especially during the initial period of electrolysis, they may introduce oxygen as an impurity in the fluorine, either as the element itself or as an oxygen fluoride. When the hydrogen atoms in H_2O_2 are replaced by such groups as $(CH_3)_3C$— or $(C_6H_5)_3C$— the peroxide is quite stable and it is postulated to form readily by a simple chain mechanism from the di-$\{(CH_3)_3C\}$ or di-$\{(C_6H_5)_3C\}$ compound and molecular oxygen. Since $(SF_5–SF_5)$ is obtained in the reaction mixture, it does not seem unreasonable that the peroxide $SF_5–O–O–SF_5$ could form in a similar fashion to those mentioned above, especially if molecular oxygen or oxygen fluoride molecules were present to react with (SF_5) groups.

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ITHACA, N. Y.

(18) "Symposium on Fluorine Chemistry," *Ind. Eng. Chem.*, **39**, 236 (1947). See especially R. C. Downing, A. F. Benning, F. B. Downing, R. C. McHarness, M. K. Richards and T. W. Tomkowit, *ibid.*, **39**, 259 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

The Equilibria of Crystalline Zinc Hydroxide in Dilute Hydrochloric Acid and Sodium Hydroxide at 25°. The First and Second Acidic Dissociation Constants of Zinc Hydroxide[1,2]

BY JAMES W. FULTON AND D. F. SWINEHART

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The solubility of orthorhombic zinc hydroxide has been determined at 25° in dilute hydrochloric acid and sodium hydroxide. The solubility product is found to be 7×10^{-18}. The solubility in dilute alkali is represented by one equation from 0.0004 to 1 *m* NaOH. From these data the bizincate ion is found to exist in appreciable concentrations and the first and over-all acid ionization constants of solid zinc hydroxide are calculated to be 1.20×10^{-17} and 2.20×10^{-30}, respectively. The free energies of formation of the bizincate and zincate ions are calculated to be −119,560 and −92,180 cal./mole, respectively.

Introduction

Although zinc hydroxide is one of the classical amphoteric hydroxides and solutions of this substance in acids and alkalies have been the subject of a large number of investigations, substantial disagreement exists in the literature concerning the identification of the ionic species in solution and the values of the equilibrium constants involved. In particular there is disagreement as to the existence of an acid zincate ion and no data exist for the independent determination of the first and second acidic dissociation constants of zinc hydroxide. This paper is written to present data on the solubility of crystalline zinc hydroxide in very dilute sodium hydroxide and hydrochloric acid. From these data it is possible to show the existence of the acid zincate ion and to calculate values of the first and second acid dissociation constants of zinc hydroxide separately.

Previous results for the solubility in water[3–7] lie between 1.3×10^{-5} and 5.2×10^{-5} mole per liter at temperatures between 18 and 25° while values of the solubility product[4,8–13] lie between 1.69×10^{-21} and 1.0×10^{-15}.

Evidence for the existence of the bizincate ion has been obtained from polarographic data by Bernheim and Quintin.[14] Solid sodium bizincate, $NaHZnO_2 \cdot H_2O$ has been reported as the stable solid phase between 13.5 and 19.6 *m* NaOH by Scholder and Hendrich.[15]

The over-all acid dissociation constant of zinc hydroxide is estimated by Latimer[16] from the data of Dietrich and Johnston[4] to be of the order of 1×10^{-29}.

Experimental

Preparation of Materials.—Crystalline zinc hydroxide was prepared by precipitation of the flocculent hydroxide from a zinc sulfate solution with ammonia followed by

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(1) Taken from the master's thesis of James W. Fulton.

(2) Presented at the Pacific Northwest Regional Meeting of the American Chemical Society, Seattle, Washington, June 8, 1951.

(3) G. Bodländer, *Z. physik. Chem.*, **27**, 66 (1898).

(4) H. G. Dietrich and J. Johnston, THIS JOURNAL, **49**, 1419 (1927).

(5) Dupre, Jr., and J. Bialas, *Z. angew. Chem.*, **16**, 55 (1903).

(6) W. Herz, *Z. anorg. Chem.*, **23**, 227 (1900).

(7) H. Remy and A. Kuhlmann, *Z. anal. Chem.*, **65**, 161 (1925).

(8) G. C. Bauer, *Iowa State Coll. J. Sci.*, **13**, 37 (1938).

(9) H. J. de Wijs, *Rec. trav. chim.*, **44**, 663 (1925).

(10) W. Feitknecht, *Helv. Chim. Acta*, **16**, 1302 (1933).

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(12) A. I. Nikuroskin, *J. Gen. Chem. (U.S.S.R.)*, **8**, 1463 (1938).

(13) W. Feitknecht and E. Haberli, *Helv. Chim. Acta*, **33**, 922 (1950).

(14) P. Bernheim and M. Quintin, *Compt. rend.*, **230**, 388 (1950).

(15) R. Scholder and G. Hendrich, *Z. anorg. allgem. Chem.*, **241**, 76 (1939).

(16) W. M. Latimer, "Oxidation Potentials," Second Edition, Prentice-Hall, Inc., New York, N. Y., 1952, p. 170.

thorough washing by decantation with water and dilute ammonia until the precipitate was free of sulfate. Twenty washings were required over a period of a week or two. Concentrated ammonia was then saturated with the resulting semi-crystalline product and pure zinc hydroxide crystals were allowed to grow by slowly removing the ammonia by diffusion through air in a closed system into 90% sulfuric acid. This growth was carried out in a polythene beaker since, when it was carried out in a Pyrex beaker, the crystals adhered tenaciously to the glass and contained an appreciable amount of silica. The product was analyzed for water by loss in weight on ignition and for zinc by titration with ferrocyanide using the Dead Stop end-point.[17] Average values obtained were 18.21% (±0.05) water and 65.56% (±0.10) zinc (theoretical 18.13% water and 65.77% zinc). Analyses of the solid phases remaining after the equilibrium measurements showed that no change in solid phase had occurred during the equilibration.

X-Ray powder photographs of the product[18] showed that it was orthorhombic zinc hydroxide with lattice constants $a_0 = 8.53$, $b_0 = 5.16$, $c_0 = 4.92$. These values agree with the data of Corey and Wyckoff.[19]

Sodium Hydroxide.—Reagent sodium hydroxide pellets were dissolved in an equal weight of water in a polythene bottle and the sodium carbonate allowed to settle. Samples of the clear supernatant solution were diluted with water freshly boiled and cooled under nitrogen.

Water was distilled from Pyrex and had a conductivity less than 1×10^{-6} mho.

Other reagents were Reagent Grade used without further purification. Hydrochloric acid solutions used in equilibrations were boiled and cooled under nitrogen.

Samples for equilibration containing an excess of zinc hydroxide were sealed off in nitrogen-filled Pyrex flasks using an oxy-hydrogen flame to obviate the introduction of carbon dioxide. Samples were made up in pairs for each concentration of acid and base. One sample of each pair was stirred at 36° for two days after which the temperature was regulated at 25 ± 0.05° for a further eight days. The second of each pair was equilibrated at 25 ± 0.05° for the entire ten days; so equilibrium was approached from undersaturation and supersaturation, check results being taken as a criterion of the attainment of equilibrium. The samples were sedimented at 25 ± 0.05° until clear of a Tyndall beam. The samples most dilute in alkali required two weeks sedimentation.

Analyses.—The clear solutions were forced under nitrogen pressure through a fine sintered glass filter and analyzed for zinc by two methods. Those solutions lowest in zinc concentrations were analyzed by a modified dithizone method[20] in which the zinc was extracted from a buffer 0.1 *m* NH_4OH, 0.1 *m* NH_4Cl, *p*H 9.25, into a solution of dithizone in carbon tetrachloride. Most of the dithizone was extracted into the aqueous phase while the zinc dithizonate was left undecomposed in the carbon tetrachloride. Absorption measurements were made in a one-cm. cell in a Lumetron colorimeter using a 515-millimicron filter. Samples higher in zinc content were titrated with ferrocyanide using the Dead Stop end-point.[17]

Results

Water Solubility.—The water solubility was more erratic than the remainder of the results. Six results gave an average of 1.0 (±0.1) $\times 10^{-5}$ moles per 1000 g. of H_2O, several results varying by a factor of two from this average being rejected.

Solubility in Dilute Hydrochloric Acid.—The solubility in hydrochloric acid for twelve pairs in the acid concentration range 0.000645 to 0.0350 *m* was stoichiometric in the sense of reaction 4 below within the limits of error of the analyses (±1% except for two samples at the lowest concentration of HCl which were 2% low in zinc). The *p*H of each solution was measured as quickly as possible after filtration using a Gamma *p*H meter and glass electrode standardized *vs.* 0.05 *m* potassium acid phthalate at *p*H 4.00. These results are shown in Fig. 1. Attempts to improve these results by measurements with a hydrogen electrode in a closed system gave no greater reproducibility.

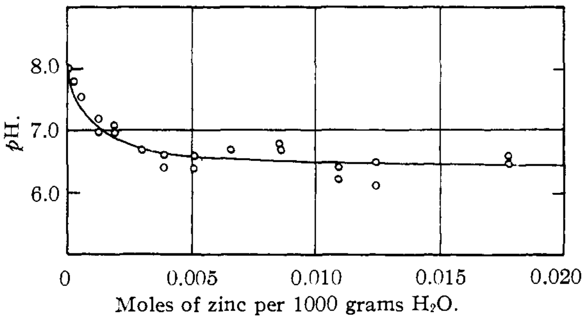

Fig. 1.—*p*H of solutions of HCl saturated with $Zn(OH)_2$.

Solubility in Dilute Sodium Hydroxide.—These data are shown in Table I and in Figs. 2 and 3.

TABLE I

SOLUBILITY[a] OF $Zn(OH)_2$ IN DILUTE NaOH

Equilibrium *m* of NaOH	*m* of Zinc × 10^6	$\gamma_{\pm NaOH}$	Calcd. solubility $S \times 10^6$
0.000413	5.83	0.980	4.50
.000858	6.07	.971	5.05
.00182	5.49	.958	6.25
.00452	9.05	.935	9.93
.00721	13.7	.919	14.0
.00986	19.5	.907	18.4
.0186	36.6	.876	36.2
.0311	75.7	.847	71.0
.0386	107	.834	97.4
.0497	151	.818	145
.0669	247	.799	239
.102	509	.771	512
.190	1610	.731	1720
.1554	1168[b]	.743	1153
.3416	5636[b]	.700	5655
.5430	13790[b]	.690	14280
.8641	34710[b]	.681	36460
1.167	64430[b]	.676	66960

[a] Each value is the average of a pair of samples, one approaching equilibrium from supersaturation and one from undersaturation. [b] Calculated from the data of Dietrich and Johnston.[4]

Discussion

Presumably the data may be accounted for by several of the following reactions

$$Zn(OH)_2(s) = Zn(OH)_2\ (\text{dissolved}) \tag{1}$$

$$Zn(OH)_2(s) = Zn^{++} + 2OH^- \tag{2}$$

$$Zn(OH)_2(s) + H^+ = Zn(OH)^+ + H_2O \tag{3}$$

$$Zn(OH)_2(s) + 2H^+ = Zn^{++} + 2H_2O \tag{4}$$

$$Zn(OH)_2(s) + OH^- = HZnO_2^- + H_2O \tag{5}$$

$$Zn(OH)_2(s) + 2OH^- = ZnO_2^= + 2H_2O \tag{6}$$

the ions being written in the anhydrous form since their states of hydration are not known although

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[17] D. F. Swinehart, *Anal. Chem.*, **23**, 380 (1951).

[18] X-Ray data by courtesy of the U. S. Bureau of Mines, Albany, Oregon.

[19] R. B. Corey and R. W. G. Wyckoff, *Z. Krist.*, **86**, 8 (1933).

[20] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, N. Y., 1944, pp. 449–460.

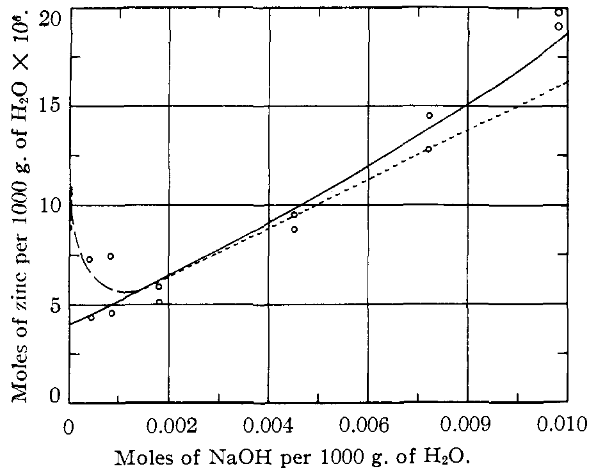

Fig. 2.—Solubility of $Zn(OH)_2$ in dilute sodium hydroxide. The plotted points are individual samples. The solid line is the calculated solubility, *S*. The straight broken line is the sum of the contributions of dissolved $Zn(OH)_2$ and bizincate ion. The difference is the contribution of the zincate ion.

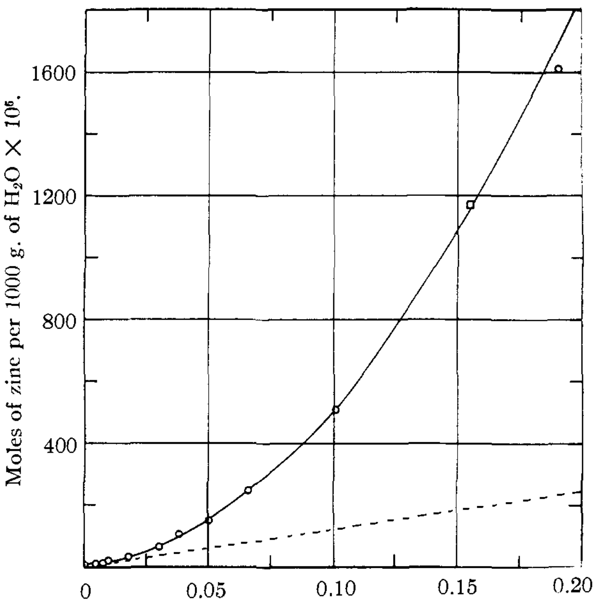

Fig. 3.—Solubility of $Zn(OH)_2$ in sodium hydroxide. The plotted points are averages of a pair of samples. The solid curve is the calculated solubility, *S*. The broken line is the sum of the contributions of dissolved $Zn(OH)_2$ and bizincate ion. The difference is the contribution of the zincate ion.

presumably zinc has a coördination number of four in each of these ions.[21]

The data in acid indicate that reaction 4 accounts quantitatively for the dissolved zinc and that reaction 3 does not make a measurable contribution. This agrees with the results of Kolthoff and Kameda[22] who estimate that in a neutral solution the ratio of Zn^{++} to $Zn(OH)^+$ concentrations is 1000 to 1.

The equilibrium constant of reaction 4 is

$$K_4 = \frac{m_{Zn^{++}}\gamma_{Zn^{++}}a^2_{H_2O}}{a_{H^+}{}^2 a_{Zn(OH)_2(s)}}$$

Values of $\gamma_{Zn^{++}}$ were calculated from the Debye–Hückel limiting law.[23] With $a_{H_2O} = a_{Zn(OH)_2(s)} = 1$ and a_{H^+} taken from the smooth curve in Fig. 1, values of K_4 varied from 15 to 3.9 and back to 5.5×10^{10} as the concentration increased, yielding an average

$$K_4 = 7 \times 10^{10}$$
$$\Delta F^0_{298} = -15000 \text{ cal./mole}$$

If it is assumed that the activity coefficients are unity, the electroneutrality condition for solutions in pure water reduces to[24]

$$pH = (^1/_3)\log (2K_4/K_w) = 8.4$$

in fair agreement with Fig. 1. The solubility product of $Zn(OH)_2$ is K_2.

$$K_2 = a_{Zn^{++}}a_{OH^-}{}^2/a_{ZnOH_2(s)}$$
$$= K_4\, K^2_w = 7 \times 10^{-18}$$

If zinc hydroxide is a strong base the solubility product should be $4m_{Zn^{++}}{}^3$ where $m_{Zn^{++}}$ is the solubility in pure water. This calculation yields $K_2 = 4 \times 10^{-15}$ from which we conclude that $Zn(OH)_2$ is not a strong base.

The solubility of zinc hydroxide in dilute alkali has a minimum at approximately 1×10^{-3} *m* NaOH. The solubility curve extrapolates into the axis of ordinates at 4×10^{-6} *m* zinc (Fig. 2). Accordingly we write

$$K_1 = m_{Zn(OH)_2} \text{ (dissolved)} = 4 \times 10^{-6}$$
$$\Delta F^0_{298} = 7000 \text{ cal./mole}$$

The equilibrium constants of 5 and 6 are

$$K_5 = \frac{m_{HZnO_2^-}\gamma_{HZnO_2^-}a_{H_2O}}{m_{OH^-}\gamma_{OH^-}a_{Zn(OH)_2(s)}}$$

$$K_6 = \frac{m_{ZnO_2^=}\gamma_{ZnO_2^=}a_{H_2O}{}^2}{m_{OH^-}{}^2\gamma_{OH^-}{}^2 a_{Zn(OH)_2(s)}}$$

Neither of these two expressions alone fits the data for the solubility in NaOH, the former varying over a factor of 8 and the latter over a factor of 1000 when K_5 and K_6, respectively, are fitted alone. In dilute solutions the ratio $\gamma_{HZnO_2^-}/\gamma_{OH^-}$ may be taken as unity. Then

$$m_{HZnO_2^-} = K_5 m_{OH^-}$$

Applying the Debye–Hückel limiting law in the manner of McDowell and Johnston,[25] $\gamma_{ZnO_2^=}/\gamma_{OH^-}{}^2$ may be shown to be equal to $\gamma_{\pm NaOH}{}^2$. The expression for K_6 yields

$$m_{ZnO_2^=} = K_6(m_{OH^-}{}^2/\gamma_{\pm NaOH}{}^2)$$

The total solubility in NaOH is then given by

$$S = m_{Zn(OH)_2\text{(dissolved)}} + m_{HZnO_2^-} + m_{ZnO_2^=}$$
$$= K_1 + K_5 m_{OH^-} + K_6\frac{m_{OH^-}{}^2}{\gamma_{\pm NaOH}{}^2}$$

By successive approximations the experimental data were fitted empirically with this equation using values of $\gamma_{\pm NaOH}$ interpolated graphically from the data of Harned and Hecker[26] to obtain the

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[21] L. P. Hammett, "Solutions of Electrolytes," McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 86.

[22] I. M. Kolthoff and T. Kameda, This Journal, **53**, 832 (1931).

[23] P. Debye and E. Hückel, *Physik. Z.*, **24**, 185, 305, 334 (1923).

[24] Suggested by the referee.

[25] L. A. McDowell and H. L. Johnston, This Journal, **58**, 2009 (1936).

[26] H. S. Harned and J. C. Hecker, *ibid.*, **55**, 4838 (1933).

"best" fit over the whole range. The solid curves in Figs. 2 and 3 are those calculated with

$$K_5 = 1.20 \times 10^{-3} \text{ and, } K_6 = 2.20 \times 10^{-2}$$

The fit is excellent over the whole range of alkali concentrations. These two constants cannot be varied by more than 5% without destroying essential agreement at one or both ends of the curve. The straight broken lines in Figs. 2 and 3 show the sum of the contributions of dissolved $Zn(OH_2)$ and $HZnO_2^-$ ions to the total zinc concentration.

The equation for the solubility in alkali also fits the data of Dietrich and Johnson[4] within less than 5% up to an alkali concentration of 1 *m*. This equation satisfactorily accounts for the solubility of zinc hydroxide in alkali over an alkali concentration range of two thousand-fold. Thus

$$K_5 = 1.20 \times 10^{-3}$$
$$\Delta F^0_{298} = 3980 \text{ cal./mole}$$
$$K_6 = 2.20 \times 10^{-2}$$
$$\Delta F^0_{298} = 2260 \text{ cal./mole}$$

It is worthy of note that values of these constants have not appeared in the literature and they provide direct evidence for the existence of the bizincate ion and provide means for the quantitative calculation of its concentration as well as that of the zincate ion.

The first acid ionization reaction of zinc hydroxide is

$$Zn(OH)_2(s) = H^+ + HZnO_2^- \qquad (7)$$
$$K_7 = K_5K_w = 1.20 \times 10^{-17}$$
$$\Delta F^0_{298} = 23080 \text{ cal./mole}$$

The complete acid ionization reaction is

$$Zn(OH)_2(s) = 2H^+ + ZnO_2^= \qquad (8)$$
$$K_8 = K_6K_w^2 = 2.20 \times 10^{-30}$$
$$\Delta F^0_{298} = 40460 \text{ cal./mole}$$

This value is to be compared with the approximate value calculated by Latimer[16] of 1×10^{-29}

The second acid ionization reaction is

$$HZnO_2^- = H^+ + ZnO_2^= \qquad (9)$$
$$K_9 = K_8/K_7 = 1.83 \times 10^{-13}$$
$$\Delta F^0_{298} = 17380 \text{ cal./mole}$$

For comparison, the first ionization constant of dissolved zinc hydroxide is calculated from

$$Zn(OH)_2 \text{ (dissolved)} = H^+ + HZnO_2^- \qquad (10)$$
$$K_{10} = K_7/K_1 = 3 \times 10^{-12}$$
$$\Delta F^0_{298} = 16000 \text{ cal./mole}$$

Thus the second ionization constant is only one tenth as large as the first and for this reason it is not expected that the two ionizations could be detected as separate steps in a titration curve as reported by Hildebrand and Bowers[27] but could not be found by Britton.[28]

The solubility of carefully washed reagent grade zinc oxide in dilute alkali has been measured by Margetson.[29] His results were more erratic than those reported here for crystalline zinc hydroxide but his solubilities were uniformly lower than those for the crystalline hydroxide indicating that the oxide and not the hydroxide is the stable phase at room temperature. However, no change of phase to the oxide was observed in any of our equilibration runs.

Using the value of the free energy of formation of of $Zn(OH)_2(s)$ from Latimer,[16] *i.e.*, −132,640 cal./mole, the free energies of formation of acid zincate and zincate ions may be calculated.

	ΔF^0_{298}
$Zn(s) + H_2(g) + O_2(g) = Zn(OH)_2(s)$	−132,640
$Zn(OH)_2(s) = H^+ + HZnO_2^-$	23,080
$Zn(OH)_2(s) = 2H^+ + ZnO_2^=$	40,460
$Zn(s) + H_2(g) + O_2(g) = H^+ + HZnO_2^-$	−109,560
$Zn(s) + H_2(g) + O_2(g) = 2H^+ + ZnO_2^=$	− 92,180

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[27] J. H. Hildebrand and W. G. Bowers, THIS JOURNAL, **38**, 785 (1916).

[28] H. T. S. Britton, *J. Chem. Soc.*, **127**, 2120 (1925).

[29] R. G. Margetson, Unpublished Master's Thesis, University of Oregon, 1949.