Zinc Hydroxide: Solubility Product and Hydroxy-complex Stability Constants from 12.5–75 °C

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We have made atomic absorption measurements leading to the solubility of zinc hydroxide at 12.5, 25.0, 50.0, and 75.0 °C from $pH = 6.7$ to $pH = 13.8$. Results have been used for evaluation of the solubility product and stepwise constants for association of Zn^{2+}(aq) with OH^-(aq) to form solute species of type $Zn(OH)_i^{2-i}$(aq) with $i = 1$–4. Evidence is presented to support the reliability of the various equilibrium constants. Uncertainties in derived enthalpies are assessed.

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On a fait des mesures d'absorption atomique conduisant à la solubilité de l'hydroxyde de zinc à 12.5, 25.0, 50.0 et 75.0 °C, à des $pH = 6.7$ à 13.8. On a utilisé les résultats pour évaluer le produit de solubilité et les constantes successives pour l'association de Zn^{2+}(aq) avec OH^-(aq) pour former des espèces solutées du type $Zn(OH)_i^{2-i}$(aq) avec $i = 1$–4. On présente des données pour supporter la fiabilité de diverses constantes d'équilibre. On établit les incertitudes dans les enthalpies qui en dérivent.

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Introduction

It is well established that zinc hydroxide is slightly soluble in water, becoming more soluble as the pH is either lowered or raised. There are, however, substantial differences between solubilities at 25 °C reported by various investigators and we know of no solubility measurements that have covered a substantial range of temperature. As a result of these limitations on the available solubility data there are related uncertainties in the equilibrium constants for association of Zn^{2+}(aq) with OH^-(aq) and in the solubility product of zinc hydroxide. We have therefore measured (by atomic absorption spectrophotometry) the solubility of zinc hydroxide at 12.5, 25.0, 50.0, and 75.0 °C from p$H = 6.7$ to p$H = 13.8$. Results have been used for evaluation of the solubility product and stepwise equilibrium constants for association of Zn^{2+}(aq) with OH^-(aq).

Experimental

Zinc hydroxide was first precipitated from aqueous zinc sulfate solution by NH_3(aq), washed thoroughly to remove all sulfate, and then dissolved in a small excess of NH_3(aq) as described by Dietrich and Johnston (1). The resulting solution was then transferred to a polyethylene container (to avoid contamination of the product with silica) and placed in a vacuum oven maintained at 60 °C; crystals of zinc hydroxide were soon formed. This procedure leads to the orthorhombic form of $Zn(OH)_2$(c), sometimes called the ε phase.

Solubility determinations began by adding zinc hydroxide and either HCl(aq) or NaOH(aq) to polyethylene test tubes with care taken to exclude CO_2. The stoppered test tubes (containing N_2) were then shaken gently in constant temperature baths controlled to within $\pm 0.1°$ at 12.5 and 75 °C and to within $\pm 0.05°$ at 25 and 50 °C. Additional HCl(aq) or NaOH(aq) was added to many of the tubes after they had been in the baths for a few days. Samples of solution in contact with solid zinc hydroxide were removed periodically for analysis. It was found that the concentration of zinc in these solutions usually approached constancy in about 10 days. Solutions were then allowed to stand (without agitation) in the baths for 3 days, which permitted zinc hydroxide to settle, thus facilitating removal of supernatant liquid for analysis.

Zinc analyses were done with a Model 500 Jarrell Ash Atomic Absorption Spectrophotometer. Six standard solutions for calibration were prepared by weight, ranging from 0.01533 to $7.05 \times 10^{-5} m$ zinc sulfate. Further solutions for calibration were prepared by dilution of some of the original standard solutions, with final concentrations down to $1.41 \times 10^{-6} m$.

The pH of each solution (at the temperature of solubility measurement) was measured immediately after the supernatant liquid was removed for analysis for zinc. A Radiometer (Model 26) pH Meter with Corning multipurpose glass electrode and saturated KCl calomel reference electrode was used for these measurements. The system was calibrated with standard buffers described by Bower and Bates (2).

The first solubility measurements were made at 50 °C. The same solid samples were then successively equilibrated at 25 and 12.5 °C. A new set of samples was made up and equilibrated at 75 °C. Subsequent measurements were made by equilibrating separately prepared samples at each temperature. Uncertainties in our experimental solubilities (Table 1) are ~5%.
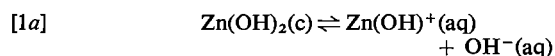
TABLE 1. Solubility* of zinc hydroxide

12.5 °C		25.0 °C		50.0 °C		75.0°C	
pH	$S(\times 10^5)$	pH	$S(\times 10^5)$	pH	$S(\times 10^5)$	pH	$S(\times 10^5)$
13.80	327	13.19	178	12.50	261	12.22	1029
13.71	216	12.97	67.3	12.24	88.7	11.95	319
13.51	91.8	12.77	28.3	11.99	33.7	11.68	104
13.34	45.1	12.52	11.2	11.76	14.8	11.35	29.1
13.18	25.2	12.29	5.74	11.55	8.03	11.14	12.6
12.85	6.12	11.05	0.54	11.25	2.92	10.85	5.27
12.21	1.68	10.84	0.46	10.99	2.14	10.54	3.06
11.51	0.50	10.14	0.31	10.75	1.38	10.22	2.14
11.50	0.31	9.43	0.38	10.25	0.92	10.01	2.06
11.10	0.24	9.18	0.54	10.02	0.84	9.71	1.84
9.83	0.23	8.97	0.61	9.55	0.76	9.54	1.76
9.49	0.23	8.91	0.92	9.08	0.87	8.93	1.68
9.27	0.31	8.72	0.84	8.77	0.99	8.55	1.84
9.14	0.38	8.67	1.22	8.52	1.15	8.38	2.06
8.99	0.46	8.41	1.30	8.27	1.45	8.08	2.06
8.55	1.33	7.90	4.74	8.04	1.84	7.89	1.99
7.96	13.2	7.63	17.2	7.82	2.43	7.65	2.37
7.70	48.3	7.44	32.1	7.54	4.97	7.18	7.22
7.32	265	7.31	49.7	7.26	10.7	6.94	13.1
7.22	415	7.00	204	7.05	19.6		
7.06	844			6.75	53.4		

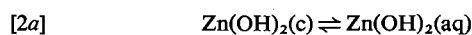*S represents the solubility expressed in mol of zinc per kg of water.

Results and Calculations

Results of our solubility determinations are summarized in Table 1, where S represents the total molality of dissolved zinc. Earlier investigations have been cited by Sillén and Martell (3, 4) and Schindler (5). Our results at 25 °C generally agree with those of earlier investigators, although there are significant differences, particularly near the high and low ends of the pH range. There are no earlier solubility data available for higher temperatures to compare with our results.
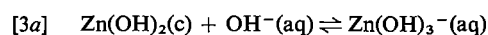
We begin by interpreting our solubility results in terms of $Zn(OH)_2(c)$ in equilibrium with saturated solution that can contain species that we represent by $Zn^{2+}(aq)$, $Zn(OH)^+(aq)$, $Zn(OH)_2(aq)$, $Zn(OH)_3^-(aq)$, and $Zn(OH)_4^{2-}$ (aq). It is convenient to relate these species to one another and to our solubility data by way of the following equilibria and corresponding equilibrium constants:

[1a] $Zn(OH)_2(c) \rightleftharpoons Zn(OH)^+(aq)$
$+ OH^-(aq)$

[1b] $K_1 = [Zn(OH)^+][OH^-]$

[2a] $Zn(OH)_2(c) \rightleftharpoons Zn(OH)_2(aq)$

[2b] $K_2 = [Zn(OH)_2]$

[3a] $Zn(OH)_2(c) + OH^-(aq) \rightleftharpoons Zn(OH)_3^-(aq)$

[3b] $K_3 = [Zn(OH)_3^-]/[OH^-]$

[4a] $Zn(OH)_2(c) + 2OH^-(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq)$

[4b] $K_4 = [Zn(OH)_4^{2-}]/[OH^-]^2$

[5a] $Zn(OH)_2(c) \rightleftharpoons Zn^{2+}(aq)$
$+ 2OH^-(aq)$
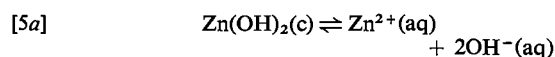
[5b] $K_{sp} = [Zn^{2+}][OH^-]^2$

The square brackets above 'should' indicate thermodynamic activities of the enclosed species, but we have used molalities instead, which means that the equilibrium constants we have evaluated might better be called equilibrium quotients. Consequences of the approximation $a \cong m$ are discussed later in this paper.

The total solubility S can be represented as the sum of molalities of all zinc-containing solute species

[6] $S = [Zn^{2+}] + [Zn(OH)^+] + [Zn(OH)_2]$
$+ [Zn(OH)_3^-] + [Zn(OH)_4^{2-}]$

Substitution of [1b], [2b], [3b], [4b], and [5b] in [6] leads to

[7] $S = \dfrac{K_{sp}}{[OH^-]^2} + \dfrac{K_1}{[OH^-]} + K_2$
$+ K_3[OH^-] + K_4[OH^-]^2$

TABLE 2. Equilibrium constants derived from solubilities

t (°C)	$K_{sp}(\times\ 10^{17})$	$K_1(\times\ 10^{11})$	$K_2(\times\ 10^6)$	$K_3(\times\ 10^3)$	$K_4(\times\ 10^2)$
12.5	1.42	1.13	1.66	1.12	5.70
25.0	1.74	2.54	2.62	1.32	6.47
50.0	2.34	7.70	7.02	2.56	7.92
75.0	3.16	20.2	15.0	2.74	8.99

Now there are several ways to proceed with evaluation of the various equilibrium constants in [7]. One way is to begin with consideration of our solubilities at relatively low pH where Zn^{2+}(aq) and $Zn(OH)^+$(aq) are likely to be the only important solute species so that we need use only the first two terms on the right hand side of [7]. We thus obtain

[8] $\qquad S[OH^-] = (K_{sp}/[OH^-]) + K_1$

that is suitable for graphical evaluation of K_{sp} and K_1. Using pK_w = 14.44, 14.00, 13.28, and 12.71 from Olofsson and Hepler (6) for t = 12.5, 25.0, 50.0, and 75.0 °C to obtain [OH$^-$] values from our pH values (Table 1), we have constructed graphs of $S[OH^-]$ vs. 1/[OH$^-$] and derived the values of K_{sp} and K_1 that are listed in Table 2.

Next we have limited our attention to solubilities at high pH where only $Zn(OH)^-$(aq) and $Zn(OH)_4^{2-}$(aq) are likely to be important solute species. Taking only the last two terms on the right hand side of [7], we obtain

[9] $\qquad S/[OH^-] = K_3 + K_4[OH^-]$

and from graphs of $S/[OH^-]$ vs. [OH$^-$] we find the values of K_3 and K_4 that are listed in Table 2.

Now we solve [7] for K_2 in terms of S, [OH$^-$], and various K values already obtained by way of [8] and [9]. Because $Zn(OH)_2$(aq) is relatively most important at the minimum in solubility, we use the minimum solubility at each temperature with the corresponding pH and other equilibrium constants (Table 2) to obtain the K_2 values that are listed in Table 2.

It should be recognized that the evaluation procedure we have used effectively concentrates most of the uncertainties in all of our work in the reported values of K_2 rather than the other K values.

We have used K values in Table 2 to calculate the fraction f of Zn(II) that exists as Zn^{2+}(aq), $Zn(OH)^+$(aq), $Zn(OH)_2$(aq), $Zn(OH)_3^-$(aq), and $Zn(OH)_4^{2-}$(aq) as pH is varied. Results for 25 °C
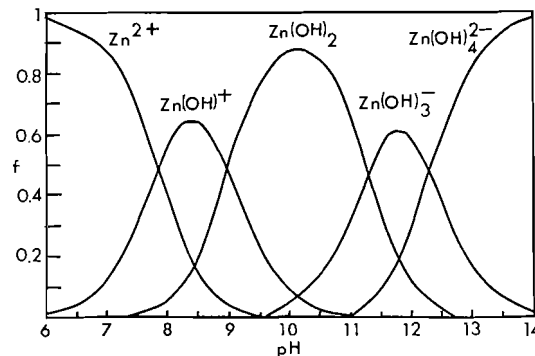
FIG. 1. Graph of fraction f of Zn(II) existing as Zn^{2+}(aq), $Zn(OH)^-$(aq), $Zn(OH)_2$(aq), $Zn(OH)_3^-$, and $Zn(OH)_4^{2-}$(aq) over a range of pH at 25 °C.

are displayed in Fig. 1. Ranges of satisfactory validity of [8] and [9] can be deduced from Fig. 1, or by using data in Table 1 for making appropriate graphs of $S/[OH^-]$ vs. 1/[OH$^-$] and [OH$^-$].

Another approach has been to use all of our solubility–pH data at each temperature for computer calculations leading to overall 'best' fits of [7] and hence the desired K values. Different weighting procedures lead to slightly different K values, but all of the K values obtained in this way are in good agreement with those already listed in Table 2. For some further calculations and comparisons with results of earlier investigators, we will take the values listed in Table 2 to be the best ones that can be derived from our solubilities in combination with our neglect of activity coefficients.

Whether our K values do or do not have the significance we ascribe to them, use of these K values in [7] does lead to calculated solubilities that agree well with the experimental values in Table 1 over the whole range of temperature and pH. In this sense, our K values have uncertainties of a few percent.

Our measurements and calculations have led to K_{sp} = 1.74 × 10^{-17} at 25 °C. Because this K_{sp} was evaluated from our solubilities in solu-

tions of relatively low pH, all of which were quite dilute, it is appropriate to take this value to be nearly equal to the thermodynamic solubility product in spite of our neglect of activity coefficients. This value can be compared with results of previous investigators as follows.

Reported solubility products at or near 25 °C range from 10^{-13} to 10^{-21}. Here we consider only a few of what appear to be the best of these earlier investigations. Fulton and Swinehart (7) have found $K_{sp} = 0.7 \times 10^{-17}$. Schindler et al. (8) have reported $K_{sp} = 3.39 \times 10^{-17}$. Davies and Staveley (9) have reported $K_{sp} = 3.80 \times 10^{-17}$. Each of these thermodynamic (activity coefficients have been considered) solubility products applies to the orthorhombic (ε) modification of zinc hydroxide and can therefore be compared with our value. Our assessment of all of these investigations leads us to suggest that $K_{sp} = 3.5 \times 10^{-17}$ is the 'best' value. The discrepancy between this 'best' value and our result corresponds to a difference of 0.4 kcal mol^{-1} in ΔG^0 for [5a].

Application of d ln $K_{sp}/dT = \Delta H^0/RT^2$ to our results leads to $\Delta H^0 = 2.5$ kcal mol^{-1} for the reaction represented by [5a]. We know of no published K_{sp} values at several temperatures that permit calculation of a ΔH^0 value to compare with our result above, but calorimetric measurements have led to ΔH_f^0 values listed in ref. 10 that correspond to $\Delta H^0 = 7.02$ kcal mol^{-1} for [5a]. More recently, Davies and Stavely (9) have made new calorimetric measurements that lead to $\Delta H^0 = 7.92$ kcal mol^{-1} for this same reaction. It is nearly certain that this last ΔH^0 is the best one available for this reaction.

The difference between our ΔH^0 and the calorimetric value (10) is much larger than can be accounted for on the basis of statistical analysis of 'reasonable' uncertainties in the various experimental results. It seems to us most likely that the source of the discrepancy lies in the interpretation of our solubilities in terms of [1a], [2a], [3a], [4a], and [5a] and/or the assumption that the solid phase remains pure Zn(OH)$_2$(c,ε) at temperatures above 25 °C.

Sillén and Martell (3, 4) have reviewed some evidence for dinuclear species in the Zn^{2+}–OH$^-$ system and much evidence for a variety of di- and polynuclear species in other M^{2+}–OH$^-$ systems. Experience with other systems (3, 4) suggests that neglect of small concentrations of these species would lead to only small errors in our

K_{sp} values, but to substantially greater errors in the ΔH^0 obtained by differentiation and thence magnification of all experimental and interpretive errors.

The work of Schindler et al. (8) has shown that Zn(OH)$_2$(c,ε) is unstable with respect to ZnO(c) and H$_2$O(liq) and also with respect to Zn(OH)$_2$-(amorph), with further evidence that conversion between the various forms of Zn(OH)$_2$ and ZnO is often slow. Since these conversions might be expected to proceed faster at higher temperatures, it is possible that the solid phase in apparent equilibrium with our saturated solutions above 25 °C was some phase other than Zn(OH)$_2$ (c,ε) or was a mixture of phases, which might also account for the error in our calculated ΔH^0 for [5a].

We have represented formation of Zn(OH)$^+$ (aq) by [1a] and have obtained $K_1 = 2.54 \times 10^{-11}$ at 25 °C for this reaction. By combining our K_1 with our K_{sp} we also obtain the equilibrium constant for the reaction

[10] $Zn^{2+}(aq) + OH^-(aq) \rightleftharpoons Zn(OH)^+(aq)$
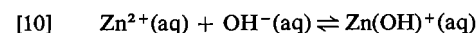
that we report as $\beta_1 = 1.46 \times 10^6$. Further combination of this β_1 with K_w leads to the equilibrium constant for the 'hydrolysis' or 'acid ionization' reaction that we represent by

[11] $Zn^{2+}(aq) + H_2O(liq) \rightleftharpoons Zn(OH)^+(aq) + H^+(aq)$
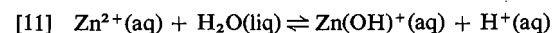
and $K_h = 1.46 \times 10^{-8}$. Because all of these values are based on solubilities in very dilute solutions, all are close to the thermodynamic constants in spite of our neglect of activity coefficients.

Sillén and Martell (3, 4) have reviewed many earlier investigations that have led to a wide range (10^{-3} to 10^3 times our values) of values for K_1, β_1, or K_h. We call particular attention to the $K_h = 1.10 \times 10^{-9}$ reported by Perrin (11) and the $\beta_1 = 2.04 \times 10^6$ reported by Gubeli and Ste-Marie (12) for 1.0 M NaClO$_4$ solution as the 'best' previous values for comparison with our results. It is seen that our K_h value is about 10 times that of Perrin (11) while our β_1 value is nearly the same as that of Gubeli and Ste-Marie (12).

Perrin's (11) K_h values at several temperatures from 15 to 42 °C have led him to $\Delta H^0 = 13.4$ kcal mol^{-1} (quoted as probably correct to within about 1 kcal mol^{-1}) for [11]. Combination of our $\Delta H^0 = 2.5$ kcal mol^{-1} for [5a] with our $\Delta H^0 = 8.9$ kcal mol^{-1} for [1a] (obtained from

d ln K_1/dT) and $\Delta H^0 = 13.3$ kcal mol^{-1} for ionization of water (6) leads to $\Delta H^0 = 19.7$ kcal mol^{-1} for [11]. Or we can combine our ΔH^0 for [1a] with ΔH^0 from Davies and Staveley (9) and ΔH^0 of ionization of water (6) to obtain $\Delta H^0 = 14.3$ kcal mol^{-1} for [11]. The former value is in poor agreement with Perrin (11), while the latter value is in good agreement with his results.

Formation constants for $Zn(OH)_i^{2-i}$(aq) species as in

[12] $\quad Zn^{2+}(aq) + iOH^-(aq) \rightleftharpoons Zn(OH)_i^{2-i}(aq)$
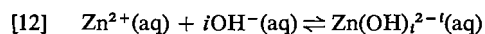
calculated from $\beta_1 = K_i/K_{sp}$ are as follows for 25 °C: $\beta_2 = 1.51 \times 10^{11}$, $\beta_3 = 7.59 \times 10^{13}$, and $\beta_4 = 3.72 \times 10^{15}$.

It is possible to calculate ΔH^0 values for reactions represented by [2b], [3b], and [4b] and thence for reactions of type [12] ($i = 2-4$) by way of d ln K/dT, but we decline to list the values so obtained. We have already discussed reasons for lack of confidence in related ΔH^0 values for [1a], [5a], [10], and [11]. Similar uncertainties apply to reactions of type [12] ($i = 2-4$). For these latter reactions and [2a], [3a], and [4a] there is also the increasingly significant error introduced by our neglect of activity coefficients.

Conclusions

The experimental work and subsequent calculations described here show that it is possible to use atomic absorption spectrophotometry to obtain reliable solubilities of sparingly soluble substances and then to derive reliable equilibrium constants (solubility products and stability constants) from these solubilities. Unfortunately, it also appears that the combination of experimental and interpretive uncertainties is sufficiently great that it is not possible to obtain entirely reliable enthalpies and entropies of reaction by way of d ln K/dT in this way.

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