COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(3) Water; H_2O; [7732-18-5]

EVALUATOR:

T. P. Dirkse
Department of Chemistry
Calvin College
Grand Rapids, Michigan 49506, U.S.A.
June 1984

CRITICAL EVALUATION:

So far as the stable oxides and hydroxides are concerned, zinc exists only in the dipositive form. ZnO is a stable material but there are also indications that metastable forms of ZnO exist, depending on the method of preparation. The rate of solubility, and to some extent the solubility itself, of ZnO in an alkali solution was found to be dependent on the previous history of the ZnO (1). There is also mention of seven solid phases of ZnO (2). A rather extensive review of the literature showed that the values of many physical characteristics of ZnO depend on the method of preparation or the previous history of the material (3), and, consequently, there is much discrepancy in the values reported in the literature. The so-called "active zinc oxides" had lower densities and higher catalytic activities than the "stable zinc oxides," yet all had the same X-ray diffraction pattern. A study of the effect of particle size on the solubility showed that the solubility product of ZnO as determined by solubility measurements in 1 mol NaOH dm^{-3} did increase as the particle size decreased and as the surface area of the ZnO increased (4).

Zinc hydroxide, on the other hand, is a substance whose purity and stability have often been called into question. Zinc hydroxide is frequently prepared by adding an alkali to a solution of a zinc salt. Hantzsch (5) noted that the use of $ZnSO_4$ did not give a pure $Zn(OH)_2$. Feitknecht (6) observed that the addition of NaOH to a solution of a zinc salt produced a basic salt rather than $Zn(OH)_2$. This was confirmed later (7) when it was shown that the addition of alkalies to a solution of $Zn(NO_3)_2$ did not produce a pure $Zn(OH)_2$ but, rather, a product contaminated with the anions of the zinc salt.

Zinc hydroxide has also been considered to be unstable (8, 9). Thermodynamic calculations are said to show that $Zn(OH)_2$ is unstable with respect to ZnO (8). It has also been observed that $Zn(OH)_2$ undergoes a change on standing, especially in the presence of alkalies (10). This change is a decrease in solubility and is often ascribed to a loss of water. The rate of this change may be affected by the previous history of the preparation.

The instability of $Zn(OH)_2$ has also been observed in other work (11). In order to determine the free energy of formation of ZnO, the e.m.f. of the following cell was measured. The e.m.f. was constant after 48 hours and then

$$H_2(g)|\text{dil. } Ba(OH)_2|ZnO(s) + Zn$$

remained constant for some time. However, when $Zn(OH)_2$ was substituted for ZnO in the above cell, the e.m.f. showed a continual drift. The conclusion of this work was that $Zn(OH)_2$ is metastable with respect to ZnO at 298 K but that the free energy driving force is small.

Pure $Zn(OH)_2$ appears to have been produced by a method described by Dietrich and Johnston (12). The calculated amount of NH_4OH is added to a solution of $ZnCl_2$ or $ZnSO_4$. The precipitate that is formed is separated by filtration and washed thoroughly. The washed precipitate is then dissolved in the requisite amount of concentrated NH_4OH and the NH_3 is gradually removed from solution by absorption from the vapor phase by concentrated H_2SO_4. After about a week crystals of $Zn(OH)_2$ begin to precipitate. The $Zn(OH)_2$ so produced is stable when kept under water at 338 K. At higher temperatures the crystals begin to decompose.

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In view of all these questions about the character of $Zn(OH)_2$ it is not surprising that there have been references to different kinds of $Zn(OH)_2$. Klein (13) maintained that there are three kinds of $Zn(OH)_2$ varying in solubility and in stability. His article contains no useful solubility data. Experimental details are meager, no temperature is specified, and there is no certainty that equilibrium was attained in any of the measurements given. Feitknecht, as a result of extensive and intensive work with metal hydroxides (2) has identified six forms of $Zn(OH)_2$: amorphous-, α-, β-, γ-, δ- and ε-$Zn(OH)_2$. The conditions for the preparation of these are described and the X-ray diffraction patterns of each is also given. These various forms of $Zn(OH)_2$ vary in stability, with ε-$Zn(OH)_2$ being the most stable. The reactions used to prepare these forms of $Zn(OH)_2$ are: (a) the addition of an alkali to an aqueous solution of a zinc salt; and (b) the dilution of a solution of a zincate. By varying the concentration of reagents, the rate of mixing and stirring, the extent of dilution, etc., one or the other varieties of $Zn(OH)_2$ are precipitated. Although X-ray diffraction patterns are given, no chemical analyses are presented. Therefore, there is no certainty that the products were $Zn(OH)_2$ rather than basic salts or contaminated forms of $Zn(OH)_2$. Incidentally, no reference is made to the work of Dietrich and Johnston (12) which was published five years earlier and in which a procedure is described for producing a stable form of $Zn(OH)_2$. Further information about these various types of $Zn(OH)_2$ was published later (14, 15).

Thus, in evaluating solibility data for $Zn(OH)_2$ the most reliable, truly equilibrium, values are to be expected only when some time was allowed for equilibrium to be established. Results obtained from working with freshly precipitated $Zn(OH)_2$ are suspect and this includes much of the work which was used to calculate solubility product values.

There is one other consideration in evaluating the solubility data and that has to do with whether, in the experimental work, colloidal mixtures were present rather than, or in addition to, true solutions. The claim has been made that solutions of $Zn(OH)_2$ in aqueous KOH are partly in colloidal form (16). Others have maintained that the extent of peptization of $Zn(OH)_2$ in aqueous NaOH solutions depends on the amount of excess solid phase, but the solutions become optically clear at higher concentrations of NaOH (17). Most investigators of the solubility of ZnO or $Zn(OH)_2$ have been aware of these claims and have made certain that the solutions were optically clear, although it is possible that, even then, some colloidal material may have been present.

In addition to the solubility of ZnO and $Zn(OH)_2$ as reported on the accompanying data sheets, there is also literature data on so-called supersaturated zincate solutions. Such solutions have been prepared by dissolving ZnO in hot solutions of alkali. They have been prepared more commonly by treating a zinc electrode anodically in solutions of alkalies. However, such solutions have no definite quasi-equilibrium values but appear to be more accurately described as solutions in a steady-state condition. The amount of dissolved zinc species can be varied by controlling the conditions used to prepare the solutions. Furthermore, such solutions, when once prepared, undergo a gradual decrease in concentration of dissolved zinc species until the dissolved zinc content is the same as that for solutions in equilibrium with ZnO (18). This process is completed in about a year at room temperature. Because of the lack of equilibrium values for, and the

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T. P. Dirkse
Department of Chemistry
Calvin College
Grand Rapids, Michigan 49506, U.S.A.
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instability of the supersaturated zincate solutions, data for such systems have not been compiled and will not be evaluated.

Solubility in water

Zinc oxide. Five papers report a value for the solubility of ZnO in water. In one of these (19) electrical conductance was used as the experimental approach. Two methods were used: (a) a conductimetric titration; and (b) the measurement of specific conductance which was used together with available literature values for individual ionic conductances. The average of these determinations was 3.67 x 10^{-5} mol dm^{-3} at 293 K. Busch (20) used a potentiometric titration to establish the solubility. He found a value of (1.92 ± 0.15) x 10^{-5} mol dm^{-3} at 302 K. Both these values can only be considered tentative or approximate in view of the small differences involved in one case (19) and the shallowness of the titration curve in the other (20).

A value of 7.75 x 10^{-5} mol dm^{-3} was reported as a result of a direct determination of the solubility of ZnO in water (21). The temperature was not specified but it was probably 288 to 293 K. A much smaller value was reported in a more recent work (22). The value is 5.22 x 10^{-6} mol dm^{-3}. However, this result is not very reliable because the pH of the water that was used varied from 5.8 to 9.2, the temperature was not carefully controlled, and the average deviation of the individual results from the mean is about 30%. A maximum value of 3 x 10^{-4} mol dm^{-3} at 298 K has also been reported. It was obtained by extrapolation of solubility data in NaOH solutions to zero concentration of NaOH (23). No great confidence was placed in the extrapolation procedure, and values of the order of 10^{-5} mol dm^{-3} are more likely to be the true values.

Zinc hydroxide. Five papers report a value for the solubility of $Zn(OH)_2$ in water and in four of these the temperature was maintained at 298 K. One value given is 7.8 x 10^{-4} mol dm^{-3} (24). This value was not obtained by a solubility measurement but was obtained along with a study of the extent of hydrolysis of sodium zincate. A set of equations was derived on the assumption that one of the values for a hydrolysis product was the solubility of $Zn(OH)_2$ in water. Even then, in only one instance was a positive value calculated for this term. Consequently, this value is considered doubtful. Furthermore, the $Zn(OH)_2$ was formed by adding NaOH to aqueous $ZnSO_4$, and, in view of the discussion above, this casts doubt on the purity of the $Zn(OH)_2$ that was used in this work.

The use of an extrapolation method (12) gave a value of 2 x 10^{-5} mol kg^{-1}. This is considered to be a maximum value. A direct determination of the solubility of $Zn(OH)_2$ in water (25) gave a value of (100 ± 0.1) x 10^{-5} mol kg^{-1}. Herz (26) reports a value of (1.4 to 2.6) x 10^{-5} mol dm^{-3}. However, this value was obtained from calculations of equilibrium quotients for the $Zn(OH)_2$-NH_4^+-H_2O system.

In a work dealing with the solubility of $Zn(OH)_2$ in aqueous H_2O_2 solutions, values for the solubility of $Zn(OH)_2$ in water were determined to be 7.7 x 10^{-5} mol kg^{-1}, 2.2 x 10^{-4} mol kg^{-1} and 1.27 x 10^{-4} mol kg^{-1} at 273, 293 and 303 K, respectively(27). There is some question about the composition and purity of the $Zn(OH)_2$ used in this work.

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Because of these divergent values, about all that can be said about the solubility of $Zn(OH)_2$ in water at 298 K is that it is of the order of 10^{-5} mol dm^{-3}.

Solubility in aqueous solutions of varying pH.

Much of the earlier work dealing with the solubility of ZnO or $Zn(OH)_2$ was motivated by the desire to determine the extent to which these substances showed acidic and basic characteristics. In this section we will be concerned with solubilities in aqueous solutions of alkalies and acids and the information this gives about the acidic and basic character of ZnO and $Zn(OH)_2$. ZnO is recognized as the more stable of these two substances.

Solubility of ZnO in aqueous NaOH. There are several papers that deal with the solubility of ZnO in aqueous NaOH solutions. Some preliminary work was done by Huttig and Steiner (1). (This work was done with aqueous KOH rather than with aqueous NaOH.) They studied the effect of various factors on the rate of solubility of ZnO in aqueous KOH solutions. One of the concerns was the effect of the amount of the solid phase on the rate of solubility. There were at that time numerous statements in the literature that the solubility of $Zn(OH)_2$ in aqueous alkali solutions did depend on the amount of solid phase present. But Huttig and Steiner found this to be an unimportant factor in the solubility of ZnO. In their work they arbitrarily assumed the equilibrium solubility to be the solubility after 90 minutes of stirring at a constant rate. Using this definition they found that the temperature to which $ZnCO_3$ has been heated to produce the ZnO did have a bearing on the solubility value. The solubility decreased as the decomposition temperature increased to a value of 773 K. Above this temperature there was no dependence of solubility on the decomposition temperature of the $ZnCO_3$. As expected, they also found that the solubility increased with decreasing particle size. In view of this work it is obvious that in evaluating the solubility data of ZnO in aqueous alkalies it is important to know the previous history of the ZnO. Furthermore, a sufficient time should be allowed for equilibration in order to minimize the effect of particle size.

Goudriaan (28) determined the phase diagram of the Na_2O-ZnO-H_2O system at 303 K. He observed that ZnO, $Na_2ZnO_2\cdot 4H_2O$ and $NaOH\cdot H_2O$ were the solid phases, Figure 1. A later work (29) repeated that part of the system for which ZnO is the solid phase and was in very good agreement with the earlier work (28). A still later investigation (30) at 298 K gave solubility values slightly larger than those reported earlier for 303 K (28). They also found $NaZn(OH)_3$ to be the solid zincate phase rather than a form of $Na_2Zn(OH)_4$ as reported by Goudriaan (28).

Deshpande and Kabadi (31) measured the solubility of ZnO in aqueous NaOH over a temperature range of 308-348 K. The results do not show a correlation of solubility with temperature. It appears that the solubility of ZnO in aqueous NaOH is not temperature-dependent, but there is too much scatter in the data to verify this statement. Furthermore, there is a question about the accuracy of the concentration of NaOH in these data. This value was determined by back-titrating with NH_4OH after excess acid had been added. The solutions apparently still contained zinc which could react with the NH_4OH and thus give smaller values for the NaOH concentration. This suspicion is borne out by the

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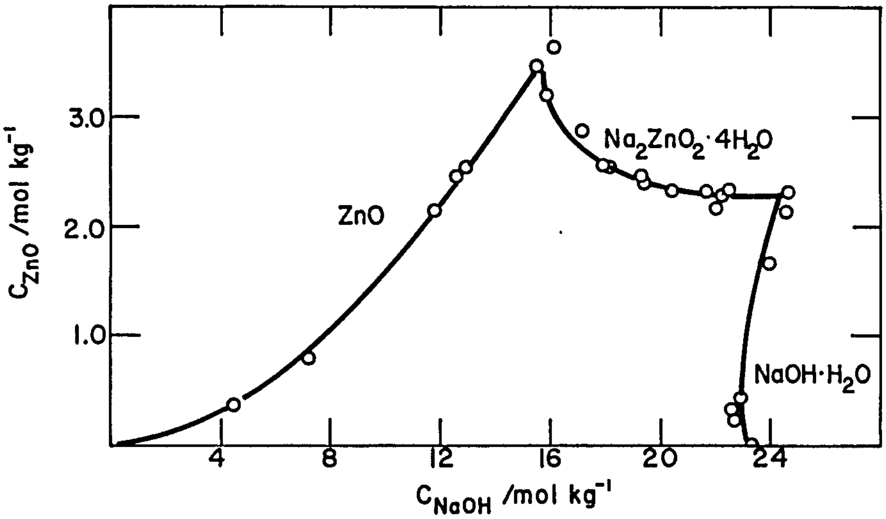

Figure 1. The Na_2O-ZnO-H_2O system at 303 K, ref. (28).

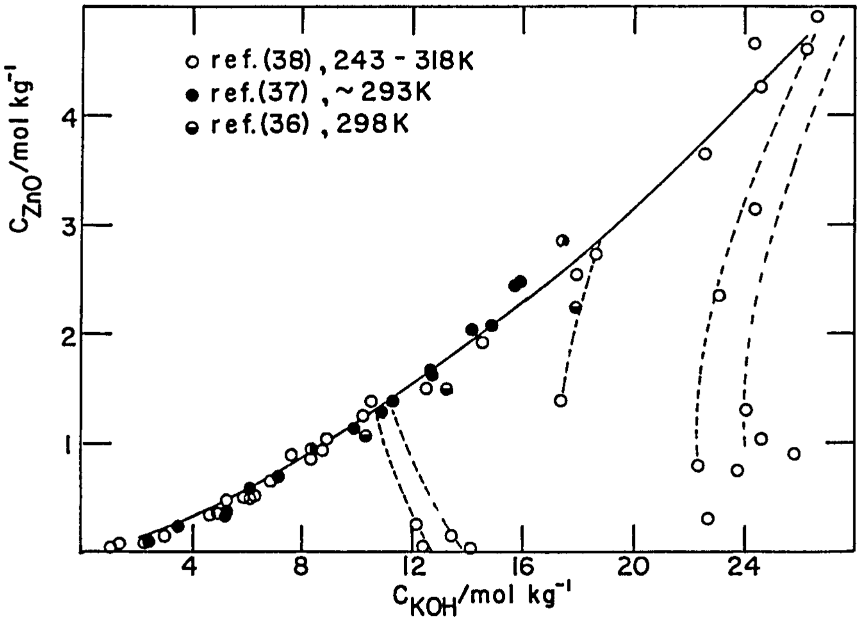

Figure 2. Solubility of ZnO in KOH solutions. The solid line is equation (5) and ZnO is the solid phase. Along the dashed lines the solid phase is a hydrate of KOH.

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fact that the results agree fairly well with those of Goudriaan (28) at the lower concentrations of dissolved zinc but deviate increasingly as the concentration of dissolved ZnO increases.

A few solubility values were obtained by extrapolation of rate of dissolution data in concentrations of NaOH 1-4 mol dm^{-3} (32). The solubility values are smaller than those reported by others (29) for the same temperature.

Urazov, et al., determined solubility values in this system at 298 and 348 K (33). Their results agree well with those of Goudriaan (28) up to NaOH concentrations of 12 mol kg^{-1}. However, they report $Zn(OH)_2$ rather than ZnO to be the equilibrium solid phase for these solutions. This difference cannot be resolved because of lack of information about experimental details and the method of analysis in the one paper (33). In larger concentrations of NaOH other solid phases appear and the analytical results become less reproducible. The solubility of ZnO in aqueous NaOH is significantly larger at 348 than at 298 K (33).

A review of the data for the solubility of ZnO in aqueous NaOH solutions indicates that there are significant differences in the values reported. The disagreement does not appear to be due primarily to differences in temperature. A possible reason for the discrepancy is that in the reports we have been discussing, relatively large concentrations of NaOH were used, probably because of a common interest of the investigators to determine whether sodium zincates could be prepared and, if so, under what conditions. In some investigations there apparently was more interest in determining the composition of the solid phases than that of the solutions. While occasional statements are made about temperature control, no details are given about the control of the analytical or other procedures. In view of the work reported by Huttig and Steiner (1), more reliance can be placed on work in which the ZnO has been heated to at least 770 K. This, apparently was done in the work of some (28, 29, 32) but not in others (30), and it is a fact that the results of the former agree fairly well with each other while the results of the latter are larger--as would be expected from a ZnO that had not been heated to such a high temperature (1). Therefore, the solubility results of the former (28, 29, 32) are considered to be the most reliable and acceptable for the solubility of ZnO in NaOH solutions of concentrations up to 16 mol dm^{-3}.

But the above data are not suitable for determining the acidic constants of ZnO because the NaOH concentrations were too large to use theoretical relationships. Some data obtained in more dilute NaOH solutions have been used to evaluate such constants (23). No other solubility data have been reported for such dilute NaOH solutions. The treatment of the data followed the procedure described by others (34). Extrapolation of a plot of solubility data of ZnO vs NaOH concentration gave a value of about 3×10^{-4} mol dm^{-3}. This should be the value for the solubility of ZnO, or $Zn(OH)_2$, in water, but it is only an approximate value because extrapolation was made from a line of changing slope. This value is about 10 times the value reported by others and discussed earlier. However, it is not to be preferred because similar work in KOH solutions gave a value of approximately zero for this concentration of ZnO or $Zn(OH)_2$ in water.

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The acidic character of ZnO can be represented by equations (1) and (2).

$$ZnO(s) + OH^- + H_2O = Zn(OH)_3^- \qquad (1)$$

$$ZnO(s) + 2OH^- + H_2O = Zn(OH)_4^{2-} \qquad (2)$$

The corresponding equilibrium constants are:

$$K_1^\circ = a_{Zn(OH)_3^-}/a_{OH^-} \qquad (3)$$

$$K_2^\circ = a_{Zn(OH)_4^{2-}}/(a_{OH^-})^2 \qquad (4)$$

The treatment of these results in dilute NaOH solutions (23) gives $K_1^\circ = 6 \times 10^{-4}$ and $K_2^\circ = 6 \times 10^{-3}$. Values for these same constants based on other experimental work will be given and discussed later.

Solubility of ZnO in aqueous KOH solutions. The solubility of ZnO in aqueous KOH solutions is characterized by being temperature-independent over a wide range of temperatures. The solubility of ZnO in 36.3 mass % KOH is constant over the range 211 to 299 K (35). The temperature independence may extend up to 418 K, but not enough data have been reported to warrant a categorical statement to this effect (36). There is good agreement in the solubility values reported in the temperature range 243 to 318 K, Figure 2. The data for that Figure are taken from 3 different sources (36, 37, 38). Equation (5) was developed to describe the line drawn through those data points on Figure 2 for which ZnO is the solid phase. The equation has a standard deviation of C_{ZnO}

$$C_{ZnO} = -0.145 + 0.0941(C_{KOH}) + 0.0036(C_{KOH})^2 \qquad (5)$$

about the regression line of s = 0.1355. It is a strictly empirical equation with concentration values expressed as mol/kg H_2O. In these concentrated KOH solutions such an equation can hardly be derived, or interpreted, on the basis of theoretical considerations.

Some of the data that have been reported (35, 39, 40) express the concentrations in terms of mol dm^{-3}. A few of the data agree well with equation (5), e.g., (35). Other reports (39) give larger solubility values than those shown on Figure 2. But no information is given as to how these data were obtained so they can be rejected. In other work (40) the analytical method has already been evaluated above in connection with ref. (31). There is no solubility-temperature pattern in these data and at the higher concentrations of ZnO the values of the KOH concentration are too low as would be expected from the analytical method that was used. These values, therefore, are considered doubtful, and the recommended values are those expressed by equation (5) for at least the temperature range 243 to 318 K.

The solubility of ZnO in more dilute solutions of KOH has been reported in two papers (1, 23). The results agree very well with each other. In one paper (23) the data have been used to evaluate K_1° and K_2°. The values for these constants are reported to be 6×10^{-4} and $(100 \pm 2) \times 10^{-4}$, respectively, at 298 K.

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Solubility of $Zn(OH)_2$ in aqueous NaOH solutions. Although there are several papers giving solubility values for $Zn(OH)_2$ in aqueous NaOH, most of these values may be considered questionable in view of the discussion given above in the introduction to this Critical Evaluation, i.e., there are questions about the stability of the $Zn(OH)_2$ that was used, and with respect to the time allowed for equilibration. Because of the effect of particle size of the $Zn(OH)_2$ on its nature and stability, at least a few weeks should have been allowed for the equilibration process.

The effect of the nature of the solid $Zn(OH)_2$ on its solubility in aqueous NaOH is brought out in a few of the papers. In Goudriaan's work (28) the solid $Zn(OH)_2$ had changed to ZnO when standing in contact with NaOH solutions of concentrations 1.53 and 12.6 mol kg^{-1} for two to three weeks. Later (29) somewhat similar work showed that in NaOH solutions of concentrations up to 7.15 mol dm^{-3} the solid $Zn(OH)_2$ did not change during a two-week period, while in concentrations of 9.87 mol dm^{-3} the $Zn(OH)_2$ did change physically during this same two-week period. This change is called aging. It is sensitive to a variety of experimental conditions, it manifests itself by a decrease in solubility, and is generally considered to be due to a loss of water from the solid $Zn(OH)_2$. These changes were also noted and recorded by others (31, 41). Deshpande and Kabadi (31) prepared the solid $Zn(OH)_2$ by two different methods. The solubility of the one type was lower than that of the other type at all temperatures, and the difference in solubility appeared to increase with increasing NaOH concentrations. The solubility values are subject to the same reservations expressed above with respect to the solubility of ZnO reported by these same authors. Nevertheless, the differences observed between the two types of $Zn(OH)_2$ may be real. The transition of $Zn(OH)_2$ to ZnO while standing in contact with aqueous NaOH is said to take place more rapidly as the concentration of NaOH is increased but often the time required for the transition is of the order of 150 days (30).

In the light of the observations just recorded it is not surprising that the various results reported for the solubility of $Zn(OH)_2$ in aqueous NaOH solutions show considerable variation, Figure 3. Some of these results (42, 43) are questionable because the solid $Zn(OH)_2$ probably was not pure or stable. No temperature is reported either although it appears that the results were obtained at room temperature. The results reported for a temperature of 293 K (30, 44) are in fair agreement with each other. Only one set of results is reported for a temperature of 298 K (12). These results appear to be quite reliable although only one day was allowed for equilibration. However, we can only consider these results to be tentative until other solubility work is reported at this temperature.

In more dilute NaOH solutions there is additional work reported at 298 K (24) and these few data agree well with the other work reported for this temperature (12). Some careful work in rather dilute NaOH solutions (25) also appears to corroborate these data but there is only one NaOH concentration that is common to the concentration ranges used by these two groups of investigators. The latter work (25) appears to be a reasonable extension of the former work (12), but, in view of the fact that there are no other data to corroborate any of these values they are at present to be considered as tentative.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(3) Water; H_2O; [7732-18-5]

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T. P. Dirkse
Department of Chemistry
Calvin College
Grand Rapids, Michigan 49506, U.S.A.
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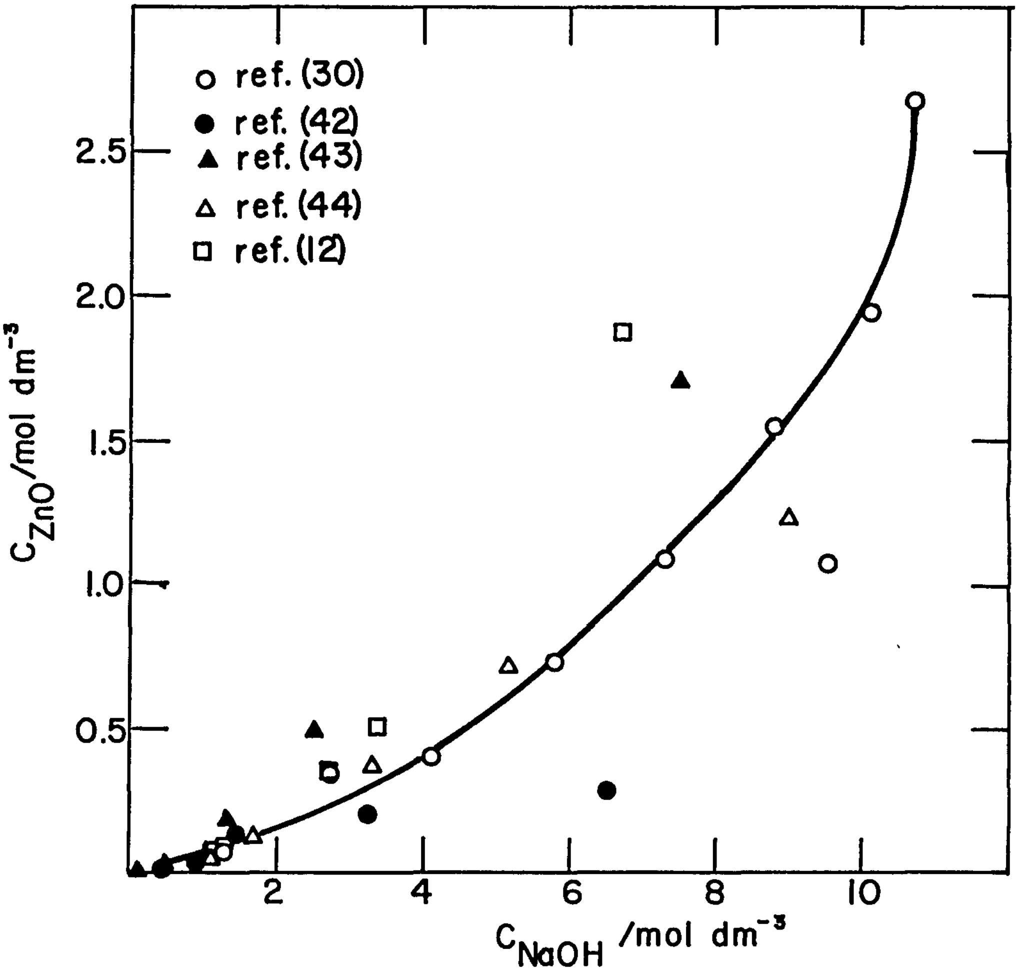

Figure 3. Solubility of $Zn(OH)_2$ in NaOH solutions.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(3) Water; H_2O; [7732-18-5]

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T. P. Dirkse
Department of Chemistry
Calvin College
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Only two papers present solubility data at different temperatures and, here again, the results are at variance with each other. In work covering the temperature range 293-373 K (30) there appears to be very little temperature effect, Figure 4. The main differences at 293 and 313 K are at NaOH concentrations greater than 13 mol dm^{-3} where $Zn(OH)_2$ or ZnO is no longer the equilibrium solid phase, but some type of zincate begins to precipitate instead. At 373 K the solid phase has become ZnO so that these results are really solubility data for ZnO rather than for $Zn(OH)_2$. On the other hand, there are data that appear to show a temperature dependent solubility in the range 273-313 K (12), Figure 5.

The solubility of $Zn(OH)_2$ in solutions of varying pH was studied at 285.5 to 348 K (45). Solutions in the alkaline range were produced by the addition of NaOH. The solubility of $Zn(OH)_2$ was reported as a function of pH. The pH was measured with a glass electrode, and there is no indication that any correction was made for this in the alkaline region. Therefore, there is a question about the absolute values in the higher pH region. However, even so, the results do show a slight temperature dependence for the solubility of $Zn(OH)_2$ in the pH range 9 to 12.

The variances and discrepancies just discussed with respect to the solubility of $Zn(OH)_2$ in aqueous NaOH likely have their origin in the non-uniformity of the materials designated as $Zn(OH)_2$. Because of this, all the solubility data for this system can, at best, be considered as tentative.

Solubility of $Zn(OH)_2$ in aqueous KOH solutions. Only four papers give data on this system (37, 40, 43, 46) and, again, there are discrepancies in the values reported. Reservations about the work in one paper (40) have already been discussed earlier in this Critical Evaluation. The $Zn(OH)_2$ was prepared by two different methods and, while the absolute values are subject to question, the results showed that the one preparation (b) had a smaller solubility at all temperatures. The solubility was studied in the temperature range 308 to 348 K but no temperature-dependence is apparent. A summary of the results reported by the others is given on Figure 6. There are differences in the results and this again is related to the uncertainties with respect to the solid $Zn(OH)_2$ that was used. As in the case of the $Zn(OH)_2$-NaOH-H_2O system, the results that have been reported can only be considered tentative, perhaps even doubtful.

Solubility in dilute solutions of mineral acids. There are no reports on the solubility of ZnO in such solutions and only two reports on the solubility of $Zn(OH)_2$ (25, 45). Both of these reports deal with the solubility in dilute HCl solutions. The one paper (25) presents the data only in graphical form. The other paper (45) presents the data as pH vs $C_{Zn(OH)_2}$ at temperatures ranging from 285.5 to 348 K. This latter report appears to present somewhat larger solubility values in the vicinity of pH = 8. Both papers show that the solubility of $Zn(OH)_2$ has a minimum value above pH = 8. It appears to be located more precisely at pH = 9 to 10 and the solubility at the minimum increases with increasing temperature.

Acidic and basic characteristics of ZnO and $Zn(OH)_2$. The dissolution of $Zn(OH)_2$ and ZnO in aqueous solutions may proceed by one or more of the following reactions. Reactions (1) and (2) correspond to (10) and (11), respectively.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(3) Water; H_2O; [7732-18-5]

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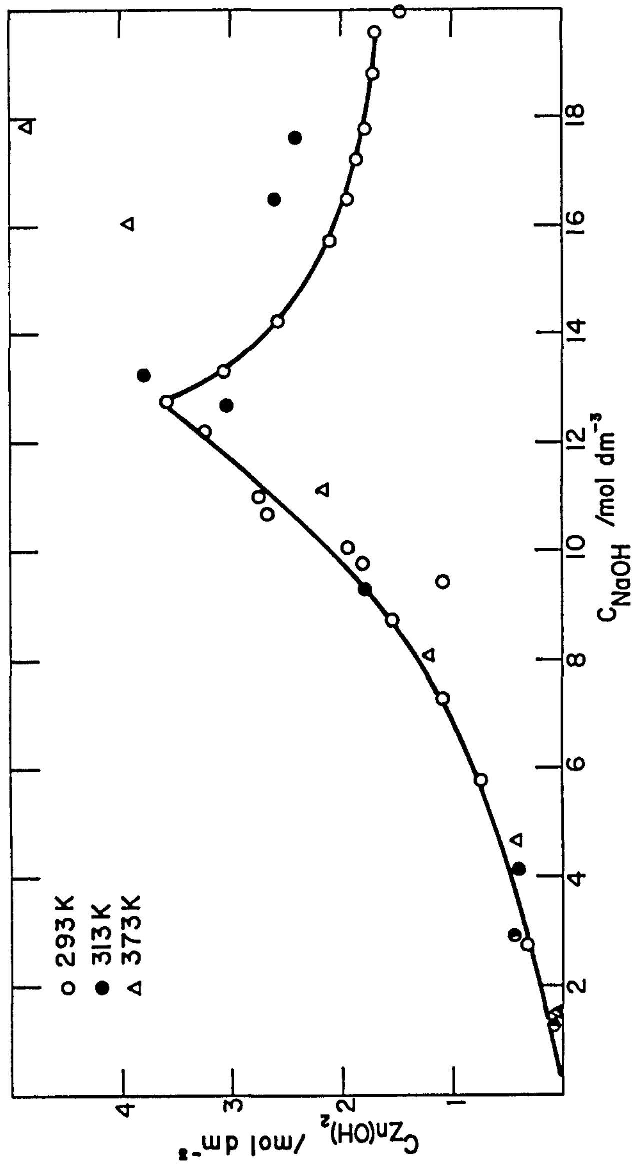

Figure 4. Solubility of $Zn(OH)_2$ in aqueous NaOH (30).

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

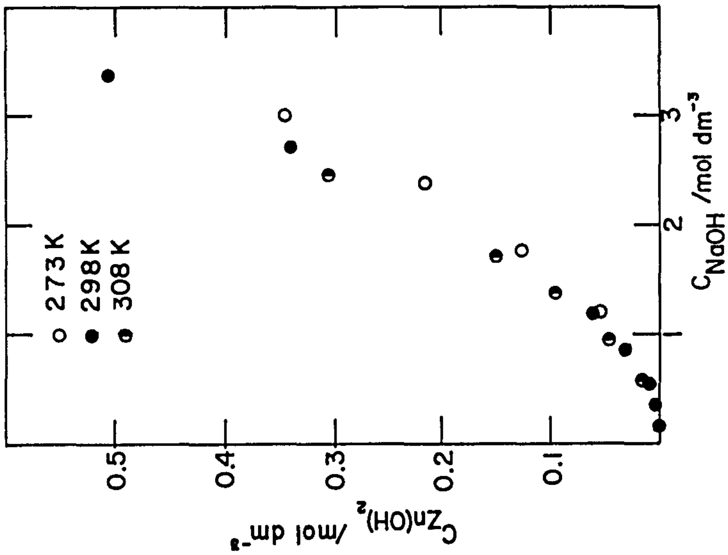

Figure 5. Solubility of $Zn(OH)_2$ in NaOH solutions (12).

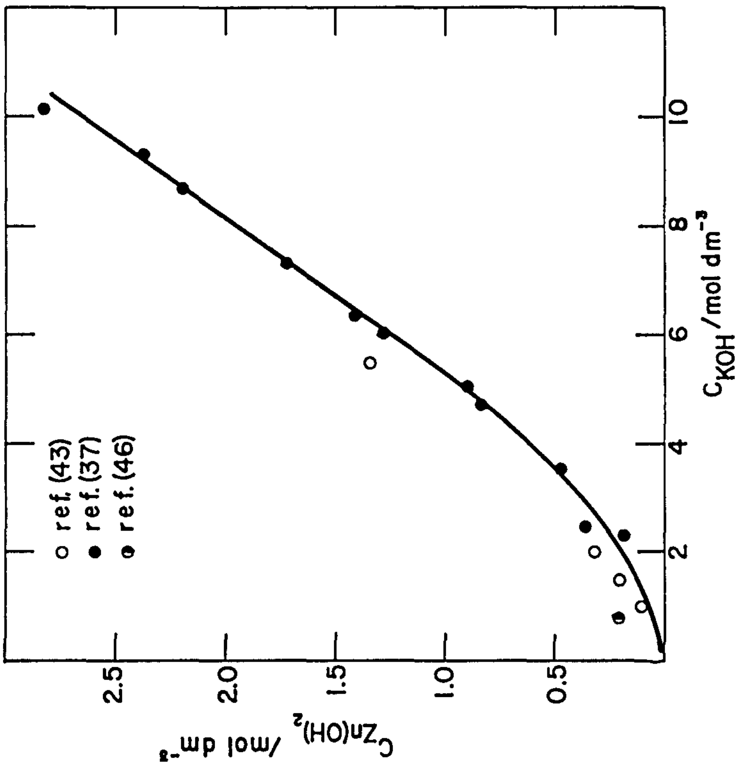

Figure 6. Solubility of $Zn(OH)_2$ in KOH solutions.

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

$$Zn(OH)_2(s) + 2\,H^+ = Zn^{2+} + 2\,H_2O \qquad (6)$$

or

$$ZnO(s) + 2\,H^+ = Zn^{2+} + H_2O \qquad (6a)$$

$$Zn(OH)_2(s) + H^+ = ZnOH^+ + H_2O \qquad (7)$$

or

$$ZnO(s) + H^+ = ZnOH^+ \qquad (7a)$$

$$Zn(OH)_2(s) = Zn(OH)_2(sln) \qquad (8)$$

or

$$ZnO(s) + H_2O = Zn(OH)_2(sln) \qquad (8a)$$

$$Zn(OH)_2(s) = Zn^{2+} + 2\,OH^- \qquad (9)$$

or

$$ZnO(s) + H_2O = Zn^{2+} + 2\,OH^- \qquad (9a)$$

$$Zn(OH)_2(s) + OH^- = Zn(OH)_3^- \qquad (10)$$

$$Zn(OH)_2(s) + 2\,OH^- = Zn(OH)_4^{2-} \qquad (11)$$

Reaction (8) or (8a) is considered to be the reaction at the point of minimum solubility. The value of the minimum solubility is most easily determined by extrapolation of solubility curves in the very dilute acid and alkaline regions. Such extrapolation gives a value of 4×10^{-6} mol kg^{-1} (25) and 2.6×10^{-6} mol kg^{-1} (45) at 298 K. Because of the small values involved and the fact that the procedure admittedly "concentrates most of the uncertainties (in the value of K_8)" (45), the value of K_8 is tentatively given as 3×10^{-6} mol kg^{-1} at 298 K. Although this is strictly speaking an equilibrium quotient it should be very close to the true equilibrium constant K_8° or K_{8a}°.

$$K_8^{\circ} = a_{Zn(OH)_2} \qquad (12)$$

In acid solutions reactions (6), (6a), (7) and (7a) should be the main ones for the dissolution process. Equations (13)-(16) represent the equilibrium constant expressions for these processes.

$$K_6^{\circ} = (a_{Zn^{2+}})\cdot(a_{H_2O})^2/(a_{H^+})^2 \qquad (13)$$

$$K_{6a}^{\circ} = (a_{Zn^{2+}})\cdot(a_{H_2O})/(a_{H^+})^2 \qquad (14)$$

$$K_7^{\circ} = (a_{ZnOH^+})\cdot(a_{H_2O})/(a_{H^+}) \qquad (15)$$

$$K_{7a}^{\circ} = (a_{ZnOH^+})/(a_{H^+}) \qquad (16)$$

There is only one paper that attempts to evaluate K_6° (25). The assumption here is that equation (6) adequately describes the solubility behavior of $Zn(OH)_2$ in dilute HCl solutions. Using solubility data and the Debye-Huckel

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

limiting law, K_6^o is calculated to be 7×10^{10} at 298 K. However, this value is based on the further assumption that $a_{H_2O} = 1$. Because there is no corroborating work, this value is to be considered a tentative one. With the assumptions made by the authors (25) the value of K_6^o and of K_{6a}^o should be the same. In view of the assumption made about the activity of the water, these values must, however, be considered as approximate values.

There is also only one paper (45) that allows K_7^o to be evaluated. The method used is to write an equation for the total solubility of $Zn(OH)_2$ in aqueous solutions in terms of the various zinc-containing species listed in equations (6)-(11). On the basis of reasonable assumptions about the relative concentrations of these solute species in different pH ranges, the equation for total solubility is simplified by neglecting certain terms, and the solubility data are then used to solve the equation and evaluate various constants. Using one of the derived values together with the ion product constant of water, the value of K_7^o is calculated to be 2.54×10^3 at 298 K. This is a tentative and approximate value because the assumptions are made that concentrations can be substituted for activities in the dilute solutions that were used. Furthermore, the activity of water is assumed to be unity.

No direct evaluation of K_{7a} is reported.

Many attempts have been made to evaluate the equilibrium constant for reaction (9), i.e., the solubility product constant. It has frequently been determined by titrating a solution of a zinc salt with aqueous NaOH or KOH and measuring the pH of the solution when a precipitate begins to form. The resulting equilibrium constant is then expressed as

$$K_9 = K_{so} = (c_{Zn^{2+}})\cdot(a_{OH^-})^2 \qquad (17)$$

so that it is a hybrid between a concentration product and a true thermodynamic equilibrium constant. There are several reservations about the legitimacy of this procedure. First, it assumes that the dissolved $Zn(OH)_2$ is completely dissociated in solution and that all the zinc is present as Zn^{2+} ions. Second, the precipitate formed is usually not $Zn(OH)_2$ but is a basic salt (47). Third, measurements are made with a freshly precipitated substance and, therefore, probably do not deal with a true equilibrium condition. In fact, it has been observed (48) that the pH of such solutions decreases on standing and the precipitate also undergoes a change with time. This is especially true with respect to $Zn(OH)_2$ because of the variety of forms reported and the instability of most of these. Therefore, it is not surprising that there is a wide variety of values reported for K_9 or K_{so}. The values obtained by the above method are (all in $mol^3\ dm^{-9}$ at 298 K): 7.3×10^{-17} (49); 3.4×10^{-16} (50); 1×10^{-17} (47) which was recalculated by others (6) to be 1.6×10^{-17}; and 2.6×10^{-16} (51). One paper (48) gives values of 3.9×10^{-16} to 6.0×10^{-17} depending on the form of $Zn(OH)_2$ and the total ionic strength of the solution. An attempt was made by others (58) to repeat the work of Kolthoff and Kameda (47). The attempt was unsuccessful because of inability to reproduce the pH values. The suggestion was made that the $ZnSO_4$ used by Kolthoff and Kameda may have been contaminated with basic zinc sulfate.

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

Another method commonly used to evaluate K_9 or $K_{s}o$ is to measure the pH of a solution in equilibrium with solid $Zn(OH)_2$ and then determine the zinc content of the solution by chemical analysis. The values obtained are substituted in equation (17) and have the units $mol^3\ dm^{-9}$. This method also is subject to the criticism that the assumption is made that all the zinc in solution is present as Zn^{2+} ions. The values obtained by this method (all at 298 K unless otherwise indicated) are: 1.69×10^{-21} (52); 5.25×10^{-17} in 0.2 mol KNO_3 dm^{-3} (53); 1.7 to 3.9×10^{-16} at 296 K (54); 2.0×10^{-15} to 2.24×10^{-16} in 0.2 mol KNO_3 dm^{-3} (55); 2.24×10^{-16} in 0.2 mol KNO_3 dm^{-3} (56); and 1.74×10^{-17} (57).

Both the above described experimental methods assume that $Zn(OH)_2$ is a strong base and completely dissociated in solution. There is experimental evidence (47) that $Zn(OH)_2$ is a strong base with respect to the first step in its ionization but that the second step, equation (18), is rather weak. Thus, all the values reported above are questionable. The objection to these methods

$$ZnOH^+ = Zn^{2+} + OH^- \qquad (18)$$

has been met to some extent in the work of Reichle, et al. (45). In their treatment of the solubility data they arrived at a value of 1.74×10^{-17} for K_9 or $K_{s}o$ at 298 K. However, other work which appears to be equally valid (25) leads to a value of 7×10^{-18} for K_9 at 298 K. These two values have been derived from solubility data. However, there is a difference. The latter value was, in effect, derived from solubility data in dilute HCl solutions while the former were derived from solubility data in dilute NaOH solutions. There was more scatter in the data for the HCl solutions and, thus, the value 1.74×10^{-17} mol dm^{-3} suggested by Reichle, et al., (45) is to be preferred.

A third method that has been used to evaluate K_9 derives this value from the e.m.f. measurement of a suitably chosen cell (12). The values so derived are thermodynamic values. The only reported value derived from this method is 3×10^{-17} and it is tentatively accepted as the $K_s^o o$ value for $Zn(OH)_2$ at 298 K. It is classed as tentative only because there is no report of other work similar to it.

Other values reported for K_9 or $K_{s}o$, but rejected for lack of experimental details are 10^{-13} to 10^{-17} (59); 10^{-14} (60); 1.69×10^{-21} (52). Also rejected are: (1) a value of 6.3×10^{-21} at 293 K was determined by Tyndallometry (61) and is rejected because it obviously was a measurement made with a freshly precipitated product; (2) a value of 1.29×10^{-17} (62) is rejected because it was based on a pH measurement obtained when aqueous $ZnCl_2$ was titrated with NaOH. The pH values were not reproducible and the value of K_9 decreased markedly with decreasing zinc content; (3) a value of 10^{-18} was based on data obtained by measuring the pH and $c_{Zn^{2+}}$ at the moment of precipitation when aqueous $Zn(NO_3)_2$ was titrated with NaOH (65). However, recalculating this value from the experimental data presented in the paper gave a value of 10^{-19}.

Because of the uncertainty as to the composition and stability of the zinc hydroxide used in all these investigations, attention should also be given to solubility product measurements made by using a stable or inactive form of ZnO.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(3) Water; H_2O; [7732-18-5]

EVALUATOR:

T. P. Dirkse
Department of Chemistry
Calvin College
Grand Rapids, Michigan 49506, U.S.A.
June 1984

CRITICAL EVALUATION:

The reaction is given in equation (9a). All the reported results are in the form given by equation (17) and these are subject to the same reservations expressed above. A value of 10^{-17} mol^3 dm^{-9} at 298 K was obtained by an extrapolation of rate of dissolution data (60). There are no solubility data presented in this article. Another value, determined by extrapolation of data from the solubility of ZnO in aqueous $ZnSO_4$ solutions, is 1.97 x 10^{-17} mol^3 dm^{-9} at 291 K (63). Feitknecht and Haberli (48) report a value of 2.75 x 10^{-18} mol^3 dm^{-9} at 298 K but in their work the concentration of Zn^{2+} was sometimes determined by analysis, and at other times by a calculation assuming certain reactions to have occurred. Other values are 2.5 to 3.8 x 10^{-17} mol^3 dm^{-9} at 296 K (54) and 9.77 x 10^{-17} mol^3 dm^{-9} at 298 K in 0.2 mol KNO_3 dm^{-3} (55). In a research which studied the solubility of ZnO at 298 K as a function of molar surface area and particle size a maximum value of 10^{-16} was given for K_{so} (4).

No data are reported for a thermodynamic solubility product constant based on equation (9a). However, a treatment of values obtained from equation (17) by the method of Davies (64) gives pK^o_{so} = 16.82 ± 0.04, or K^o_{so} = 1.5 x 10^{-17} (4). Therefore, all that can be given is a concentration product, and at 298 K the best value appears to be K_{so} = 9.8 x 10^{-17} mol^3 dm^{-9} in a solution having a total ionic strength of 0.2 mol dm^{-3}. At zero ionic strength the value will be smaller. Tentatively, a value of 1.5 x 10^{-17} is suggested for K^o_{9a} at 298 K.

The identity of the solute species in solutions of $Zn(OH)_2$ or ZnO in aqueous alkalies has been to some extent a matter of dispute. Some have claimed that $Zn(OH)_3^-$ or $HZnO_2^-$ is the main solute species in aqueous NaOH solutions (9, 66) while, more recently, $Zn(OH)_4^{2-}$ or ZnO_2^{2-} is considered to be also a prominent solute species in these solutions. Some (66) based their contention that $Zn(OH)_3^-$ is the main solute species on data obtained by titrating aqueous solutions of zinc salts with a dilute NaOH solution. Others (9), present no experimental data on which to base this conclusion.

Two papers present data for K^o_{10} and K^o_{11} at 298 K (25, 45).

$$K^o_{10} = a_{Zn(OH)_3^-}/a_{OH^-} \qquad (19)$$

$$K^o_{11} = a_{Zn(OH)_4^{2-}}/(a_{OH^-})^2 \qquad (20)$$

The values for K^o_{10} are: 1.32 x 10^{-3} (45) and 1.20 x 10^{-3} (25). The recommended value at 298 K is 1.3 x 10^{-3}. The values for K^o_{11} are: 2.20 x 10^{-2} (25) and 6.47 x 10^{-2} (45). There is one reservation about this latter value. It was derived from data in the pH region of about 13 and this pH was measured with a glass electrode. No mention is made of a correction to this value for the effect of NaOH on the glass. Consequently, there is some uncertainty about the higher pH values. A tentative value of K^o_{11} = 4 x 10^{-2} is suggested.

The fact that the values of K^o_{10} and K^o_{11} are within a factor of 10 has been suggested (25) as the reason why pH titrations may have failed to give evidence of both $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ in solutions of alkalies (66).

Only one report (23) deals with reactions (1) and (2), which may be considered as as reactions (10a) and (11a), respectively. Values for K^o_1 and

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CRITICAL EVALUATION:

K^o_2 have been reported earlier in this Critical Evaluation. The tentative values at 298 K are: $K^o_1 = 6 \times 10^{-4}$ and $K^o_2 = 10^{-2}$.

Values for formation constants have also been derived from solubility data. These values are listed in Table I. They are submitted as thermodynamic constants. The agreement is fairly good for the formation constants of $ZnOH^+$ and $Zn(OH)_2$, but the discrepancy is significant for $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$. A reason for this lies in the solubility data. The data of Gubeli and Ste-Marie (57) were obtained from solutions of constant ionic strength at 1 mol dm^{-3} while the ionic strength was not controlled in the other work (45). As a result, the solubility values are larger in the one work (57) and this difference increases at the higher pH values, Figure 7. The formation constant for $ZnOH^+$ was also reported to be 2.3×10^4 based on a study of the hydrolysis of zinc ions (47). This work was later criticized by others (58) who could not reproduce the pH values that were reported. Dietrich and Johnston (12) determined the formation constant of $Zn(OH)_4^{2-}$ from solubility data and derived a value of 2.8×10^{15} from solutions in which the total ionic strength was not controlled. This is in reasonable agreement with the value in Table I that was obtained under comparable circumstances (45). The values reported in Table I are to be considered as tentative.

Table I. Formation constants for $Zn(OH)_x^{2-x}$ ions at 298 K.

	ref (45)	ref (57)
$Zn^{2+} + OH^- = ZnOH^+$	1.46×10^6	2×10^6
$Zn^{2+} + 2OH^- = Zn(OH)_2(sln)$	1.51×10^{11}	1.5×10^{11}
$Zn^{2+} + 3OH^- = Zn(OH)_3^-$	7.59×10^{13}	2×10^{14}
$Zn^{2+} + 4OH^- = Zn(OH)_4^{2-}$	3.72×10^{15}	5×10^{17}

Table II. Values for equilibrium constants at 298 K.

Reaction	Value	evaluation[a]
$ZnO(s) + H_2O + OH^- = Zn(OH)_3^-$	$K^o_1 = 6 \times 10^{-4}$	t
$ZnO(s) + 2OH^- + H_2O = Zn(OH)_4^{2-}$	$K^o_2 = 10^{-2}$	t
$Zn(OH)_2(s) + 2H^+ = Zn^{2+} + 2H_2O$	$K^o_6 = 7 \times 10^{10}$	t
$Zn(OH)_2(s) + H^+ = ZnOH^+ + H_2O$	$K^o_7 = 2.54 \times 10^3$	t
$Zn(OH)_2(s) = Zn(OH)_2(sln)$	$K^o_8 = 3 \times 10^{-6}$ mol kg^{-1}	t
$Zn(OH)_2(s) = Zn^{2+} + 2OH^-$	$K^o_9 = 3 \times 10^{-17}$	t
$ZnO(s) + H_2O = Zn^{2+} + 2OH^-$	$K^o_{9a} = 1.5 \times 10^{-17}$	t
	$K_{9a} = 9.8 \times 10^{-17}$ mol^3 dm^{-9}	t
$Zn(OH)_2(s) + OH^- = Zn(OH)_3^-$	$K^o_{10} = 1.3 \times 10^{-3}$	r
$Zn(OH)_2(s) + 2OH^- = Zn(OH)_4^{2-}$	$K^o_{11} = 4 \times 10^{-2}$	t

[a] t = tentative; r = recommended.

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CRITICAL EVALUATION:

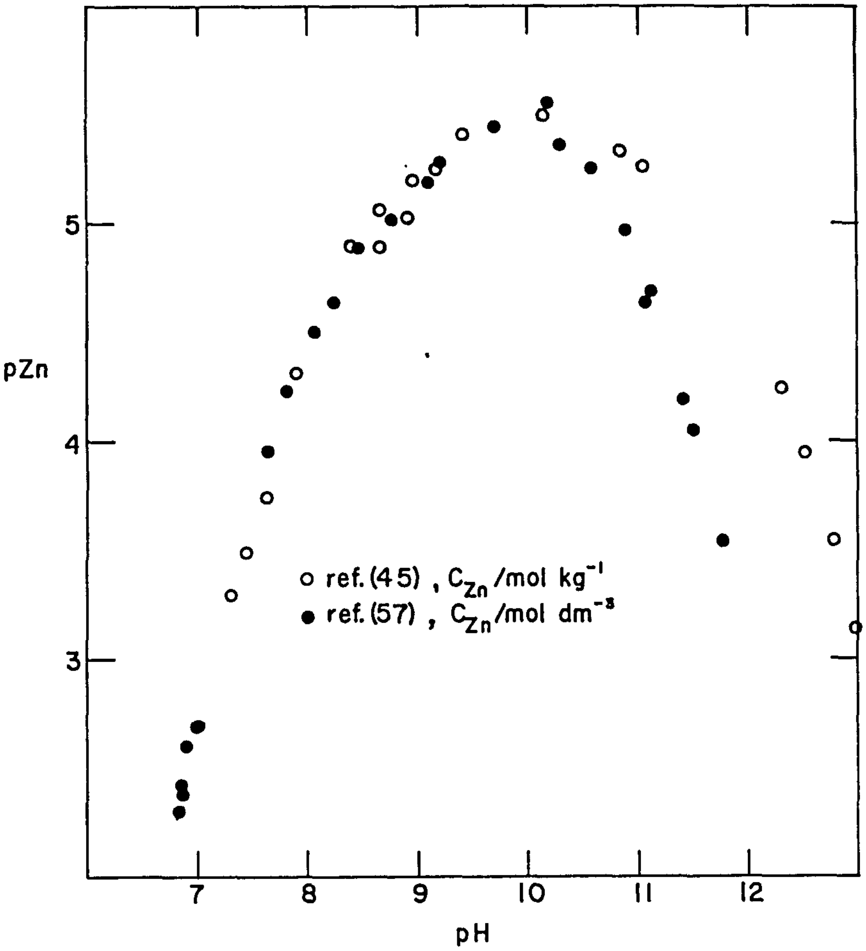

Figure 7. Solubility of ZnO as a function of pH at 298 K. Open circles, total ionic strength was not controlled; closed circles, total ionic strength kept at 0.1 mol dm^{-3}.

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

Solubility in aqueous solutions of acidic oxides.

Solubility measurements of ZnO or $Zn(OH)_2$ in aqueous solutions of acidic oxides appear, in most instances, to be incidental to the main purpose of the investigation. The purpose usually was to determine which zinc salts could be formed. Emphasis was placed on the structure of these salts and the conditions under which they could be formed. Therefore, in several papers, the solubility data are presented only in a graphical form. The studies in this area are rather scattered and in only a few instances was a given system studied by more than one investigator. Consequently, it is sometimes impossible to make comparisons and the resulting solubility data must, perforce, be regarded as tentative.

Solutions of arsenic(V) oxide. This system has been the subject of two separate studies. In one report (67) the data are presented only in the form of a phase diagram with no temperature specified, but presumably in the vicinity of 303 K. The solid phases reported are: $ZnHAsO_4 \cdot H_2O$ and $Zn(H_2AsO_4)_2$. In the other study (68) the temperature was held at 293 K. The solubility curve of ZnO in aqueous As_2O_5 appears to be very similar in both papers although more than 5 solid zinc arsenates were identified in the second paper (68). No further comparison of the work in these two papers is possible because one paper (67) contains no numerical solubility data.

Solutions of boron(III) oxide. The $ZnO-B_2O_3-H_2O$ system has been discussed by Bondareva and co-workers in several papers, e.g., (69), but the emphasis is on identifying and determining the crystal structure of the zinc borates that can be formed. The borates have generally been formed under hydrothermal conditions. Most of the tabular data deals with values determined by X-ray diffraction, but none of it has to do with solubility data. The Figures given in these papers are mainly drawings of the crystalline structure of the borates. Only occasionally is there a phase diagram. Therefore, no data sheets have been prepared from any of these papers.

Solutions of chromium(VI) oxide. Three papers present solubility data for the $ZnO-CrO_3-H_2O$ system. Two of these (70, 71) present data for 298 K while the other (72) reports data at 308 K. The interest in each of these papers is on the types of zinc chromates that are formed and, in one paper (71), their use as corrosion inhibitors. The data in these papers are quite consistent with each other, Figure 8, even though the concentrations are expressed in different units. The concentration range of CrO_3 was extensive in one paper (71) but rather limited in the others (70, 72). While the solubility data are in agreement there is hardly any agreement as to the composition of the solid phases in equilibrium with these solutions. The solubility of ZnO appears to be influenced but little by the temperature, Figure 9. Equation (21) was derived empirically to fit the data presented in these papers. The

$$C_{ZnO} = 0.0073 + 0.517 \cdot C_{CrO_3} - 0.0001 \cdot (C_{CrO_3})^2 \qquad (21)$$

concentrations are expressed as mol/kg H_2O. Equation (21) is recommended to express the solubility of ZnO in this system.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(3) Water; H_2O; [7732-18-5]

EVALUATOR:

T. P. Dirkse
Department of Chemistry
Calvin College
Grand Rapids, Michigan 49506, U.S.A.
June 1984

CRITICAL EVALUATION:

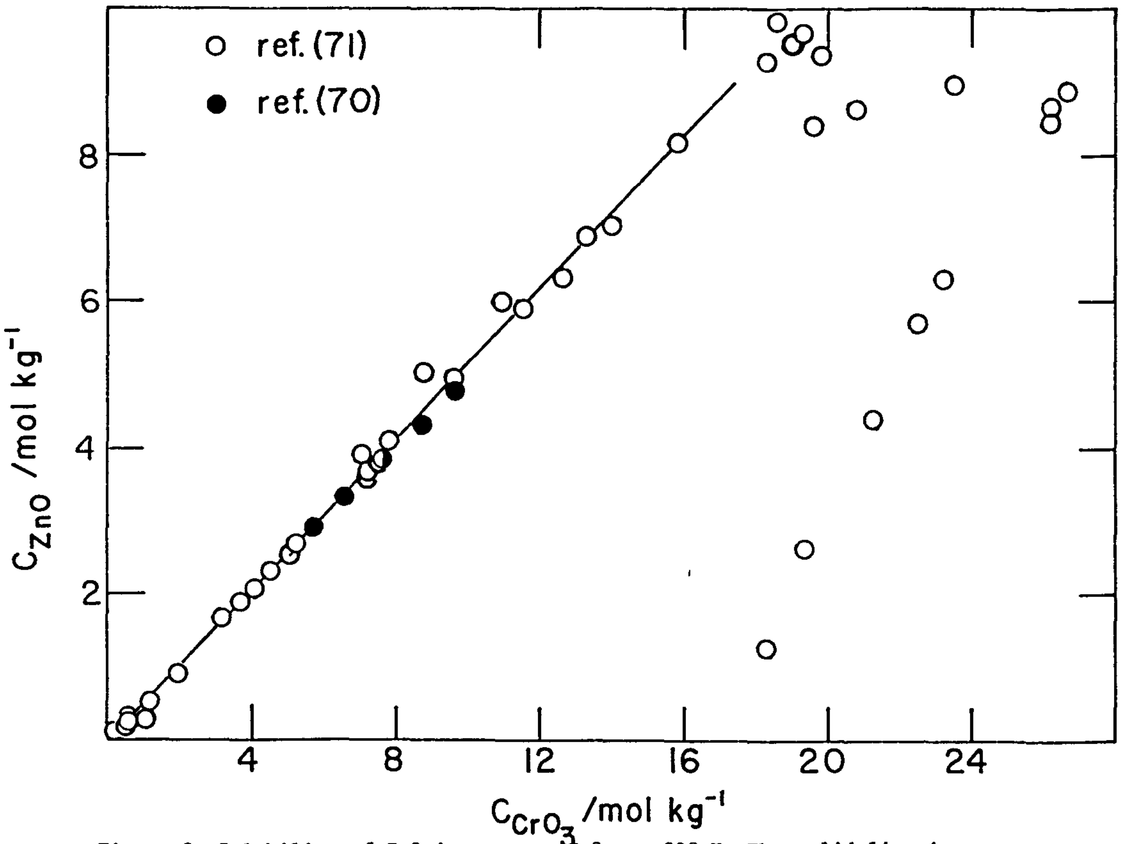

Figure 8. Solubility of ZnO in aqueous CrO_3 at 298 K. The solid line is equation (2]). For ref. (70) the concentration units are mol dm^{-3}.

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

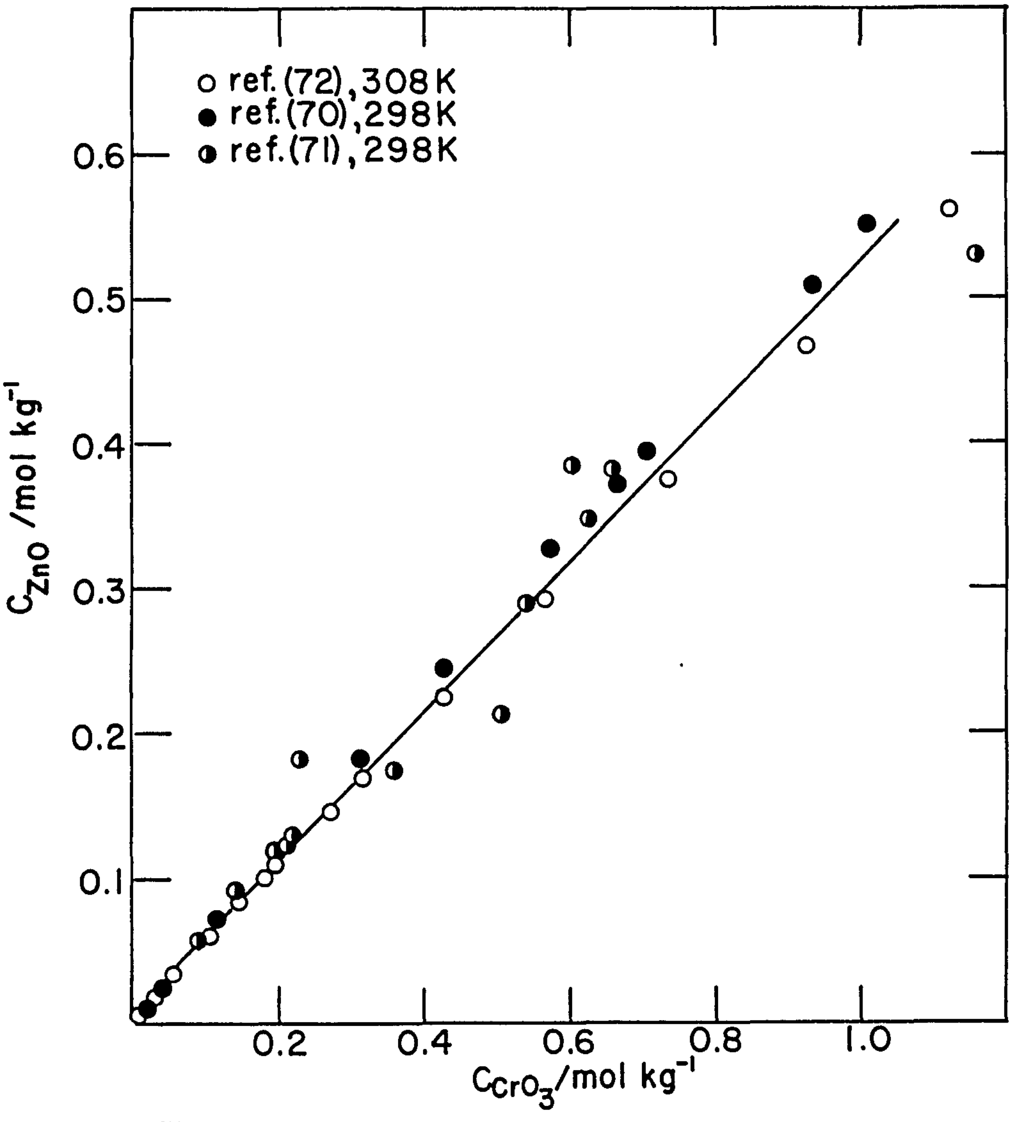

Figure 9. Solubility of ZnO in aqueous CrO_3. The solid line is equation (21). For refs. (70) and (72) the concentration units are mol dm^{-3}.

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

Solutions of phosphorus(V) oxide. Three papers report solubility data for this system. One (73) presents data for 298 and 310 K. Solubilities were measured only in P_2O_5 concentrations up to 55 mass%. The interest of the authors was to identify the zinc phosphates that precipitated from these solutions. A later paper (74) presented the solubility data for this system at 273, 298 and 333 K, and extended the solubility determinations to systems containing up to 65 mass% P_2O_5. As a result, an additional solid phase, $Zn(H_2PO_4)_2 \cdot 2H_3PO_4$ was observed at the higher concentrations of P_2O_5. No numerical solubility data are given in the paper but the results at 298 K appear to duplicate those of Eberley, et al. (73), except in the region of 35-45 mass% P_2O_5. More recently, another paper (75) has appeared with solubility data for this system at 298 K. The solubility was determined up to P_2O_5 concentrations of 65 mass%. Most of the data for the phase diagram were obtained by measuring the solubilities of the corresponding zinc phosphates rather than that of ZnO or $Zn(OH)_2$. Interestingly, experimental data are missing in the range of 35-45 mass% P_2O_5. This is the range in which there is disagreement between the other two papers (73, 74). All three papers agree on the solid phases present at 298 K with the exception of the phase, $ZnHPO_4 \cdot H_2O$ which Eberley, et al. (73) find at 310 K but not at 298 K. Only one paper (73) contains numerical solubility data at 298 K. The other papers appear to agree with these data, but they cannot be considered to be corroborative because either the numerical data are not given (74) or were not obtained by measuring the solubility of ZnO or $Zn(OH)_2$. Consequently, the data presented by Eberley, et al. (73) are to be considered tentative at this time.

Solutions of sulfur dioxide. One study of this system (76) was carried out in conjunction with a study of the feasibility of using the system for leaching zinc from its ores. The study was made at 288 and 298 K. The graphical presentation of the data show that the solubility of ZnO increases with increasing concentration of SO_2, but at 298 K a solubility maximum is reached. The solid phase is said to be $ZnSO_3 \cdot 2.5H_2O$. No data sheet was prepared for this article because of the absence of numerical solubility data and because very few experimental details were given in the article.

This system was also studied at 293 K (77). The solubility of ZnO appears to increase linearly with the concentration of SO_2. The solid phase, in all but 2 instances, was $ZnSO_3 \cdot 2.5H_2O$, in agreement with the earlier work (76), but there was no evidence for a solubility maximum within the experimental limits of the work. The two articles (76, 77) express the solubilities differently, so no comparison can be made. The data of Jager (77) are considered as tentative values. At present there is no reason for rejecting them or for considering them to be doubtful.

Solutions of sulfur trioxide. There is only one paper (78) that deals with the $ZnO-SO_3-H_2O$ system. The data were collected as a supplement to a rather thorough study of the $ZnSO_4-H_2SO_4-H_2O$ system. The data were collected at 298 K. Up to SO_3 molalities of about 3 mol kg^{-1} the ZnO and SO_3 appear to be dissolved in a 1:1 ratio, leading to the formation of $ZnSO_4$. However, the solid phase that precipitates from these solutions is a basic zinc sulfate, $3Zn(OH)_2 \cdot ZnSO_4 \cdot 4H_2O$. At larger molalities of SO_3 the 1:1 relationship breaks down and a hydrated zinc sulfate begins to precipitate from the solutions. The data in this paper appear to be reliable but they cannot be accepted as definitive until further work on this system is reported.

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

Solubility in aqueous solutions of NH_3 and its derivatives.

Zinc oxide. The solubility of ZnO in aqueous NH_3 has been reported in three papers. Euler (79) presents only two data at 294 K, but no experimental details are supplied. Kononov, et al. (80) report measurements at 298 K but the data are given only in graphical form. The interest in that paper appears to be the effect of dissolved $(NH_4)_2SO_4$ on the solubility of ZnO in aqueous NH_3. The effect is to decrease the solubility of ZnO (probably by precipitation) only after the molar ratio of $(NH_4)_2SO_4$ to ZnO exceeds one. The third paper (81) also uses aqueous NH_3 with dissolved $(NH_4)_2SO_4$ as the solvent. The investigation was motivated by an interest in the leaching of zinc from its ores. Only three numerical data--none for the solubility of ZnO in aqueous NH_3 alone--are given and no comparison is possible with the work reported in the other papers.

Zinc hydroxide. There are three papers that report the solubility of $Zn(OH)_2$ in aqueous NH_3, two at 298 K (12, 82) and one at 293 K (44). The understanding or interpretation of this system is complicated by the fact that both the OH^- ion and the NH_3 serve as ligands to the zinc ions in solution. Something of this complexity is illustrated by the pH vs pZn data for a few solutions of $Zn(OH)_2$ in aqueous NH_3 (82). In the most dilute NH_4OH solution used, 0.005 mol dm^{-3}, the solubility of $Zn(OH)_2$ passes through a minimum at about pH = 9.3. In more concentrated NH_4OH, 0.02 mol dm^{-3}, the data are more erratic and the solubility minimum is at pH = 8.5. In the most concentrated NH_4OH solutions that were used, 0.04 mol dm^{-3}, the solubility of $Zn(OH)_2$ shows a maximum at pH = 9.5 and then decreases to a minimum at pH = 10.5, after which the solubility again increases.

Where the solubility of $Zn(OH)_2$ is expressed in terms of the concentration of NH_4OH (12, 44), the results are fairly consistent. The solubility of $Zn(OH)_2$ increases with increasing NH_4OH concentration and, at 298 K, reaches a maximum in a solution having a NH_4OH concentration of about 8 mol dm^{-3}. The solubility decreases with increasing temperature. The data of Dietrich and Johnston (12) appear to be the best for this system but are considered tentative until additional work is reported.

In addition to the data in the above papers, some early solubility data at 294 K were reported (79) but these are rejected because of lack of experimental details and uncertainty as to the composition of the $Zn(OH)_2$ that was used.

Some of the interest in the $Zn(OH)_2$-NH_3-H_2O system has been motivated by a desire to determine the nature of the zinc-containing solute species, but there is no general agreement in this area, probably because of different experimental conditions. A study of the change of pH of aqueous NH_3 as it becomes saturated with either $Zn(OH)_2$ or ZnO (8) indicated to the authors that the solute species at 298 K in such solutions ranging in concentration from 1-12 mol dm^{-3} were: $Zn(OH)_2(NH_3)_2$, $Zn(OH)(NH_3)_3^+$, $Zn(OH)_3(NH_3)^-$ and $Zn(OH)_2(NH_3)$. No solubility values are given in the paper. Others (82) found evidence from the solubility data for $Zn(OH)_2$, $Zn(OH)_3(NH_3)^-$ and $Zn(NH_3)_4^{2+}$. The formation constants of these substances at 298 K as reported (82) cannot be confirmed by other work. De Wijs (49) measured the partial pressure of NH_3 in equilibrium with the ZnO-NH_3-H_2O system but reported no solubility measurements. On the basis of her

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results she reports the value of the formation constant of $Zn(NH_3)_4^{2+}$ at 298 K to be 1.02 x 10^9 mol^4 dm^{-12}. She also reported evidence for the presence of $Zn(NH_3)_2^{2+}$ with a formation constant value of 7.1 x 10^4 mol^2 dm^{-6}.

Derivatives of NH_3. The solubility of $Zn(OH)_2$ in aqueous solutions of NH_4Cl, NH_4NO_3 and $(NH_4)_2SO_4$ has been reported (26). However, no temperature is specified although the measurements appear to have been made at room temperature. Corrections were made for the degree of ionization of the zinc salts but there is no indication what these corrections were nor how they were made. Furthermore, no details of the analytical methods are given. Consequently, these solubility values are classified as doubtful.

There is one report (83) on the solubility of ZnO in aqueous solutions of 2,2',2''-nitrilotriethanol (triethanolamine). However, the paper contains values for only 3 experimental data points. There are no other data with which this work can be compared. Therefore, these values must be considered tentative, at best.

In another paper (84), the solubility of ZnO in aqueous glycine is reported. Because no other similar results have been reported these results, too, must be considered to be tentative.

Solubility in aqueous salt solutions.

Aqueous $ZnCl_2$. The earliest information dealing with the solubilities in this system was contained in a report to a meeting of the American Wood-Preservers' Association (85). Solutions of $ZnCl_2$ of concentrations suitable for timber injection would deposit a white sludge. The suggestion was made that the sludge may have been a basic zinc chloride and therefore the solubility of ZnO in aqueous $ZnCl_2$ solutions was investigated at 293, 313, 333 and 353 K. However, there is no indication as to the experimental procedure by which these results were obtained and the data, as presented, are difficult to interpret. The only clue to the concentration of $ZnCl_2$ is the specific gravity of the system, but there is no indication of the temperature at which the specific gravity was measured nor whether it was measured before or after the ZnO had dissolved in the solutions. Therefore, these data are not included in the data sheets. Qualitatively, the solubility of ZnO increases with increasing concentration of $ZnCl_2$ and with increasing temperature.

The other papers dealing with this system have as their main interest the identification of the solid phases associated with this system (86, 87, 88). Only one paper presents solubility data (86). In this paper the data are presented in the form of a smoothed square phase diagram, but the concentration units are not specified. If the data are plotted as c_{ZnO} vs c_{ZnCl_2} (both expressed as mol/kg H_2O) the data appear to have a great deal of scatter in them. Therefore, these data are not to be considered as realiable.

In another paper (87) the system was studied at 303 K. However, it is stated that the solubility of ZnO in the aqueous $ZnCl_2$ solutions was less than the experimental uncertainty and, therefore, these solubility determinations were not made.

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More recently, this system has again been investigated (88) in an effort to identify any solid zinc oxychlorides associated with the system, but no solubility data are presented in the paper.

Aqueous $MgCl_2$. There is only one report on this system (89). Solubility data for $Zn(OH)_2$ are given at 293, 313, 333 and 353 K for a limited range of $MgCl_2$ concentrations. The $Zn(OH)_2$ becomes more soluble as the concentration of $MgCl_2$ increases. The solubility also increases with increasing temperature. However, the values as given cannot be accepted as reliable because the solid phase was not shown to be $Zn(OH)_2$. It was prepared by mixing equivalent amounts of $ZnCl_2$ and NaOH. As pointed out earlier in this Critical Evaluation, such a procedure does not necessarily produce $Zn(OH)_2$ as a product of the reaction.

Solubility in aqueous hydrogen peroxide.

A study of this system was part of a larger program dealing with the formation of metal peroxides. The first paper (27) gives solubility data for the liquid phase while the second paper (90) is a study of the solid phases associated with the saturated solutions. It is difficult to evaluate the solubility data because there is no other work similar to it with which the data can be compared. It should be noted that the water solubility of $Zn(OH)_2$ at 293 and 303 K is reported to be of the order of 10^{-4} mol kg^{-1} which is about ten times the value suggested earlier in this Evaluation. The increased solubility may be due to the solid $Zn(OH)_2$ that was used. It was prepared by the addition of NH_4OH to an aqueous solution of $Zn(NO_3)_2$. No indication is given whether the $Zn(OH)_2$ was used immediately after preparation or whether it had first been allowed to age. Freshly precipitated $Zn(OH)_2$, as noted earlier in this Evaluation, will have a larger solubility. Because of this uncertainty, the solubility data given for this system must be considered doubtful at the present time.

Solubility in Sea Water

Only one paper reports work on this subject (21) and in this paper only the solubility of ZnO is measured in Baltic Sea water. No temperature is specified but it presumably was 288 or 291 K. The solubility values are sensitive to pH, as they are in water. There is no other work with which the values reported here can be compared. Much of the article discusses the analytical problems and the use of proper analytical procedures. Therefore, the values reported in this paper are accepted as tentative values.

Solubility under hydrothermal conditions

Although there are many papers that discuss the dissolution of ZnO under hydrothermal conditions, only two present numerical solubility data (91, 92). The authors of the other papers used hydrothermal conditions to prepare zinc germanates (93) or zinc borates (69, 94-97), but these papers all stress only the identification and characterization of the solid phases that are produced. They contain no solubility data.

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CRITICAL EVALUATION:

One paper (91) deals with the effect of CO_2 under pressure on the solubility of ZnO in aqueous NaCl. Only a few solubility values are given—not enough to establish the effect of the variables on the solubility of ZnO. The data apparently are preliminary values obtained in a larger program of research. Because of this, these data are to be considered tentative.

Two papers (92, 98) discuss the solubility of ZnO in solutions of alkalies. Numerical data are presented for very dilute solutions of NaOH at 373, 423 and 473 K (92). At each of these temperatures there is a solubility minimum in very dilute (10^{-2} to 10^{-4} mol dm^{-3}) solutions of NaOH. There is a good deal of uncertainty in most of the values. Because of this, and the fact that these are the only numerical results available, the data presented in this paper are considered tentative, but not very reliable. The other paper (98) discusses the solubility of ZnO in much more concentrated solutions of NaOH and KOH (6-9 mol kg^{-1}) and at temperatures upward from 473 K. Therefore, the data should be complementary to those of Khodakovskii and Yelkin (92), but only two numerical data are given. The graphs that are included in the paper show that the solubility of ZnO in the NaOH and KOH solutions increases linearly from 473-673 K. The slope of this line appears to be independent of the prevailing pressure.

Solubility in miscellaneous systems.

Only one value is reported for the solubility of ZnO in aqueous Na_2S solutions (99). Very little information is given about the experimental details. Furthermore, no other similar data have been reported. Therefore, this one value is classed as tentative, at best.

Some work has been reported on the solubility of ZnO in aqueous sodium tartrate solutions (100). No solubility data are given. The interest of the author, apparently, was in determining the nature of the zinc compound that is formed in this system. Others (101) have also studied the solubility of ZnO in tartrate solutions. The data for the solubility of ZnO in aqueous sodium potassium tartrate is presented only in the form of two small graphs. The authors state that the solubility of ZnO in such solutions decreases as the temperature is increased from 298 to 353 K. This temperature effect is also reported to be true for the solubility of ZnO in potassium oxalate solutions. In both these solutions, the solubility of ZnO varies linearly with the concentration of the tartrate or oxalate. The linear relationship also is reported for the solubility of ZnO in aqueous sodium citrate solutions but here the solubility is independent of the temperature in the range 298-353 K.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(3) Water; H_2O; [7732-18-5]

EVALUATOR:

T. P. Dirkse
Department of Chemistry
Calvin College
Grand Rapids, Michigan 49506, U.S.A.
June 1984

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