COMPONENTS:	EVALUATOR:
(1) Cadmium oxide; CdO; [1306-19-0] (2) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. October 1983

CRITICAL EVALUATION:

Cadmium, like zinc, ordinarily appears only in the dipositive form in its compounds. Therefore, with respect to its oxide and hydroxide we have to consider only CdO and $Cd(OH)_2$. However, like zinc, the hydroxide, which is usually produced by adding OH^-ions to an aqueous solution of a cadmium salt, is not of uniform composition. Analysis of the products obtained shows an impurity of at least 0.5%. The impurity usually consists of the anion of the cadmium salt that was used in the preparation. This raises the question whether we are dealing with a randomly contaminated $Cd(OH)_2$ or a $Cd(OH)_2$ together with some basic salt. This question will arise again as we discuss the solubility values reported for $Cd(OH)_2$.

Solubility in water. Three papers deal with the solubility of CdO in water. In two of these the values were obtained from electrolytic conductance measurements, either by a conductimetric titration or from specific conductance values (using literature values for individual ionic conductances). In each of these papers (1, 2) concern was expressed about the possible influence of dissolved CO_2 and how to correct for it. The one author (2) was critical of the work of the others (1) with respect to the method used to correct for the presence of the dissolved CO_2. The temperature was controlled at 298 K in one instance (2) but was allowed to vary in the range 291-293 K in the other work (1). More recently, the solubility of CdO in H_2O at 298 K has been determined by chemical analysis as part of a study dealing with the effect of $(NH_4)_2SO_4$ on the solubility of CdO in water (3). Here the solubility of CdO in water at 298 K was determined to be 9 x 10^{-5} mol dm^{-3}. A minimum of experimental detail is given. Consequently, only a tentative value of 5.4 x 10^{-5} mol dm^{-3} at 298 K can be given. This is an average of the two values reported (2,3).

Six papers report a value for the solubility of $Cd(OH)_2$ in water. The results range over about an order of magnitude. This is, in some cases, a reflection of the purity or impurity of the $Cd(OH)_2$ and of the method used to make the solubility measurement. It may also be a reflection of the age of the precipitate (4).

In one paper the solubility was determined using several samples of $Cd(OH)_2$ (2). Each sample was prepared by a different method. A significant difference in the solubility values was found, although, in each case the order of magnitude was the same, i.e., 10^{-5} mol dm^{-3}. This value is very similar to that for the solubility of CdO reported above.

The recommended value for the solubility of $Cd(OH)_2$ in water at 298 K is 1.5 x 10^{-5} mol/kg H_2O as determined by Gayer and Woontner (5). Piater (2) reported a value of 1.2 x 10^{-5} mol dm^{-3} at 298 K, but this value may be in error because of impurities in the $Cd(OH)_2$ and the imprecision of the experimental work. There are two other values reported for the solubility of $Cd(OH)_2$ at 298 K. One of these is 1.75 x 10^{-5} mol dm^{-3} (6). (This value is taken from Chemical Abstracts. The original article was not available to us.) The other value is 8.5 x 10^{-6} mol dm^{-3} (7), but this value cannot be accepted because of the meager amount of information dealing with the way in which this value was obtained. The method involved the potentiometric titration of an aqueous solution of a cadmium salt with NaOH, so that the nature and purity of the precipitating phase is suspect. In one other paper the solubility of $Cd(OH)_2$ in water is given as a limiting (or extrapolated) value in which the solubility of $Cd(OH)_2$ was studied as a function of H_2O_2 concentration (8). However, it appears that the results reported are in error because calculations from the data reported show a solubility of the order of 10^{-4} mol dm^{-3} at both 273 and 293 K. This is 10 times the solubility at 298 K. It is possible that the column labelled "wt %" should be "g CdO/kg". This would give results in agreement with the work reported by others and discussed above. Because of this uncertainty the results reported in ref. (8) cannot be considered as reliable.

A value of 7.2 x 10^{-6} mol dm^{-3} has also been reported for the solubility of $Cd(OH)_2$ in water (9). The temperature was not controlled, but in some 40 samples it varied from 290 to 295 K. These results are not considered reliable for the following reasons:

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CRITICAL EVALUATION:

(a) the pH of the water used varied from 5.9 to 9.0; (b) the values were dependent on the type of filtering medium that was used; (c) the $Cd(OH)_2$ was apparently a commercially available material and no information is given as to its purity; and (d) the average deviation of the individual results from the mean is about 33%.

In summary, the review of the solubilities of CdO and $Cd(OH)_2$ in water strongly suggests that these values are identical at 298 K.

The solubility product of $Cd(OH)_2$ has been evaluated by means of a variety of methods, and a wide range of values has been reported. Schindler (4) maintained that the value obtained depends on the age of the precipitate. He analyzed the saturated solutions over a period of time and found that only after about 100 hours did the solubility product value become constant. Up to this time the solid phase undergoes some subtle changes. The freshly precipitated $Cd(OH)_2$ and a sample of $Cd(OH)_2$ that had been in contact with the solution (an "aged sample") gave the same X-ray diffraction pattern, so the process of aging is not a matter of a change in crystal structure. Perhaps it is a change in particle size. Others (10) had noted this same phenomenon and suggested that perhaps during the aging process the crystallinity of the precipitate becomes more perfect. Schindler also pointed out that solubility product values that had been determined by using "aged" samples of $Cd(OH)_2$ were in general agreement with each other while solubility product values determined with the use of freshly precipitated $Cd(OH)_2$ tended to be widely scattered.

The composition of the precipitate also is a significant factor in determining the solubility product of $Cd(OH)_2$. One study (10) showed that $Cd(OH)_2$ formed by adding NaOH or KOH to a cadmium salt solution is generally contaminated with the anion of the cadmium salt. There was less contamination when the salt selected was $Cd(NO_3)_2$. This was a confirmation of earlier work (11) but even so the $OH^-:Cd^{2+}$ ratio in the precipitate was 1.96 rather than 2.

Another factor affecting the value of the solubility and the solubility product of $Cd(OH)_2$ is the total ionic strength of the solution. For example, the solubility product constant expressed as a concentration product was 1.66×10^{-14} $mol^3\ dm^{-9}$ when the total ionic strength was 0.042 mol dm^{-3} while it was 7.60×10^{-15} $mol^3\ dm^{-9}$ when the total ionic strength was 0.0025 mol dm^{-3} (10).

Thus, there are at least four factors that determine the value of the solubility and solubility product of $Cd(OH)_2$ in aqueous solutions. These factors are: temperature, purity of the precipitate, age of the precipitate, and total ionic strength of the solution. In most papers the temperature is specified and was controlled. However, in many papers very little, if anything, is said specifically about the other factors. This, doubtless, accounts for the wide range of values reported in the literature.

Three papers report a thermodynamic value for the solubility product. In one of these (10), this value was arrived at by extrapolation to zero ionic strength and also by the use of the Debye-Huckel equation for activity coefficients. This value for an "aged" precipitate is given as 5.9×10^{-15} at 298 K. Unfortunately, this paper does not give the experimental data from which the calculations and extrapolations were made. Consequently, while this value is in good agreement with other reported results, it cannot be accepted as a recommended value. In another work (12) the activity product of $Cd(OH)_2$ was determined incidentally to a study of the basic cadmium bromides. The activity of Cd^{2+} was determined with a dropping cadmium amalgam electrode. No numerical experimental data are given but it is merely stated that the activity product at 298.1 K is 8.1×10^{-15} as determined from a solution to which the quantities of Cd^{2+} and OH^- ions that had been added were equivalent to those needed for the formation of $Cd(OH)_2$. The precipitate was aged by heating it at 373 K for one hour. However, no investigation was made of the precipitate so there is some possibility that the precipitate may not have been a pure $Cd(OH)_2$.

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In a somewhat similar work (13) the activity product at 291.0 K is given as -log $K°_{so}$ = 14.5820. This was arrived at by determining the activity product of $Cd(OH)_2$ in a series of $CdSO_4$ solutions and then extrapolating to $[Cd^{2+}] = 0$. But again no analysis was made of the precipitate. Consequently, this value can at present only be considered a tentative value.

So far as thermodynamic values for the solubility product of $Cd(OH)_2$ are concerned only the following tentative values can be given at this time: 2.6×10^{-15} at 291 K (13), and 5.9×10^{-15} at 298 K (10).

There are several papers which report the solubility product as a concentration product. On the basis of calculations involving semiempirical relationships, Maijs (14) suggests a value of 10^{-14} mol^3 dm^{-9}. However, no experimental data are given nor is a temperature specified. Marcus (15) titrated solutions of cadmium salts with NaOH and measured the pH at which the first precipitate occurred. This was done at 298.1 K in solutions of constant ionic strength = 3 mol dm^{-3}. Because of imprecision in the pH data the only conclusion is a lower limit to the value of the solubility product. This lower limit is given as pK_{so} = 15.6.

From results reported in a study of the solubility of CdO in aqueous $(NH_4)_2SO_4$, a hybrid solubility product $[c_{Zn^{2+}} \cdot (a_{OH^-})^2]$ at 298 K is calculated to be 2.26×10^{-14} mol^3 dm^{-9} (3). Another value for this hybrid or "conventional" (10) type of solubility product is 3.1×10^{-14} mol^3 dm^{-9} at 298 K (11). Both these values may be a little large. It is not stated whether the $Cd(OH)_2$ was freshly precipitated when the measurements were made or whether the $Cd(OH)_2$ had been allowed to age first. Therefore, the recommended values for the solubility product expressed in concentration units are: log $K_{so} = -14.41 > 0.05$ at 298 K in 3 mol $NaClO_4$ dm^{-3} (4), and log $K_{so} = -14.6$ (s=>0.1) at 298 K in 1 mol $NaClO_4$ dm^{-3} (16). In the latter work the precipitate was allowed to stand about a week before measurements were made.

Where it appears that a freshly precipitated $Cd(OH)_2$ was used as the solid phase the values for the solubility product are somewhat larger than those given above. This is consistent with the general observation that the solubility of the precipitate decreases during the aging process (4,10). Such reported values (expressed as concentration products) are: 3.1×10^{-14} mol^3 dm^{-9} (11), 5.0×10^{-15} mol^3 dm^{-9} (2).

A polarographic study of the cadmium amalgam electrode in a saturated solution of $CdSO_4$ as a function of pH has been made (17). The shift in half-wave potential with pH above pH = 11 was considered to be due to control of the Cd^{2+} ion concentration at the surface of the dropping electrode by the solubility product relationship. The author says that as a result of this treatment the K_{so} for $Cd(OH)_2$ is 1.6×10^{-13} mol^3 dm^{-9} at 298 K. However, the necessary numerical data for making such a calculation are not included in the article.

De Wijs (18) studied the composition and stability of cadmium-ammonia complex ions by measuring the pressure of NH_3 in equilibrium with such solutions. Occasionally only a precipitate of $Cd(OH)_2$ was formed from such solutions. In those cases the measurements were used to calculate the solubility product constant. Again, no data are given in the article, but the author says the data she collected lead to a value of 2.5×10^{-14} mol^3 dm^{-9} for the solubility product constant of $Cd(OH)_2$ at 298 K.

An exception to the above generalization is the value 2×10^{-20} mol^3 dm^{-9} (19). This latter value was estimated from an ion exchange study using ^{109}Cd and assumed that Cd was present in solution only as $Cd(OH)^-_3$. However there is no other work in the literature that reports a value near this one.

Solubility in acid and alkaline aqueous solutions. The following reactions may represent the process of dissolution of $Cd(OH)_2$ in aqueous solutions.

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CRITICAL EVALUATION:

$$Cd(OH)_2(s) + 2\ H^+ = Cd^{2+} + 2\ H_2O \tag{1}$$
$$Cd(OH)_2(s) + H^+ = CdOH^+ + H_2O \tag{2}$$
$$Cd(OH)_2(s) = Cd(OH)_2(sln) \tag{3}$$
$$Cd(OH)_2(s) = Cd^{2+} + 2\ OH^- \tag{4}$$
$$Cd(OH)_2(s) + OH^- = Cd(OH)^-_3 \tag{5}$$
$$Cd(OH)_2(s) + 2\ OH^- = Cd(OH)_4^{2-} \tag{6}$$

The corresponding concentration ratios or products are:

$$K_1 = C_{Cd^{2+}}/(C^{H+})^2 \tag{7}$$
$$K_2 = C_{CdOH^+}/C_{H^+} \tag{8}$$
$$K_3 = C_{Cd(OH)2} \tag{9}$$
$$K_4 = C_{Cd^{2+}} \cdot (C_{OH^-})^2 \tag{10}$$
$$K_5 = C_{Cd(OH)_3^-}/C_{OH^-} \tag{11}$$
$$K6 = C_{Cd(OH)_4^{2-}}/(C_{OH^-})^2 \tag{12}$$

Reaction (4) is the solubility product reaction which has been discussed above. The ions $Cd(OH)^-{}_3$ and $Cd(OH)^{2-}{}_4$ are sometimes written in a dehydrated form as $HCdO^-{}_2$ and $CdO^{2-}{}_2$, respectively.

Reactions (1) to (4) are the predominant ones in acidic and neutral solutions. Only one paper gives solubility data in acid solutions (5). The acid range was very limited because of the basicity of the $Cd(OH)_2$. As the acidity of the solvent increased it was difficult to maintain a solid phase of $Cd(OH)_2$ in equilibrium with the solution. As a result, there are no solubility data from which K_1 can be evaluated.

In the region of slight acidity the solubility of $Cd(OH)_2$ decreased with decreasing H^+ ion concentration (or increasing OH^- ion concentration). This decrease in solubility also continued on into the alkaline region until a minimum in solubility was reached in a slightly alkaline solution. This decrease in solubility can be explained by assuming that reaction (2) is the dominant one in this pH region. On the basis of this assumption the limited amount of data of Gayer and Woontner (5) gives a value of 1.5×10^4 at 298 K. for K_2. One other paper (16) contains information from which a value of K_2 can be calculated. However, this information does not consist of solubility data found in the paper but of a calculated formation constant for the ion $CdOH^+$. This value, $10^{4.7}$, was derived by solving several equations simultaneously. These equations were based on data (not given in the paper) for the solubility of $Cd(OH)_2$ in NaOH solutions. Using the value of this formation constant, K_2 is calculated to be 1.3×10^4. This is in good agreement with the value based on the data of Gayer and Woonter (5).

One other paper gives data for the solubility of $Cd(OH)_2$ in the very dilute alkaline region approaching the solubility minimum (20). The data are reported for a temperature of 297.5 K. The data are not numerous but a value for K_2 calculated from them is 3.4×10^5. This is ten times the values given above. The discrepancy between the data of Gayer and Woontner (5) and of Ryan, et al. (20) lies in the solubility values reported for $Cd(OH)_2$ in the very dilute NaOH region. While the values of Gayer and Woontner are larger than those of Ryan, et al., at most concentrations of NaOH, Figures 1 and 2, yet in the very dilute solutions (too dilute to show up on Figure 2) the values of Gayer and Woontner are the lower ones. The difference cannot be ascribed to the 0.5 K temperature difference. A possible explanation is that by maintaining a constant ionic strength (by the addition of perchlorate ions), the solubility of $Cd(OH)_2$ was increased due to the increased total ionic concentration.

The data of Gubeli and Taillon (16) serve as another indication of the difficulty in determining precise solubility values in the vicinity of pH = 7-12. While their values

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

EVALUATOR:

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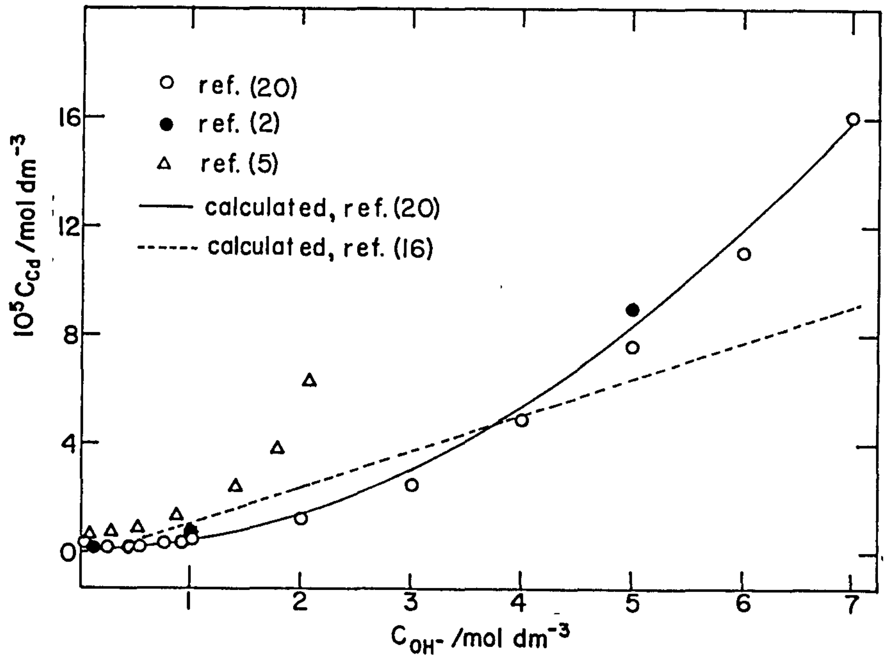

Figure 1. Solubility of $Cd(OH)_2$ in alkaline solutions at 298 K.

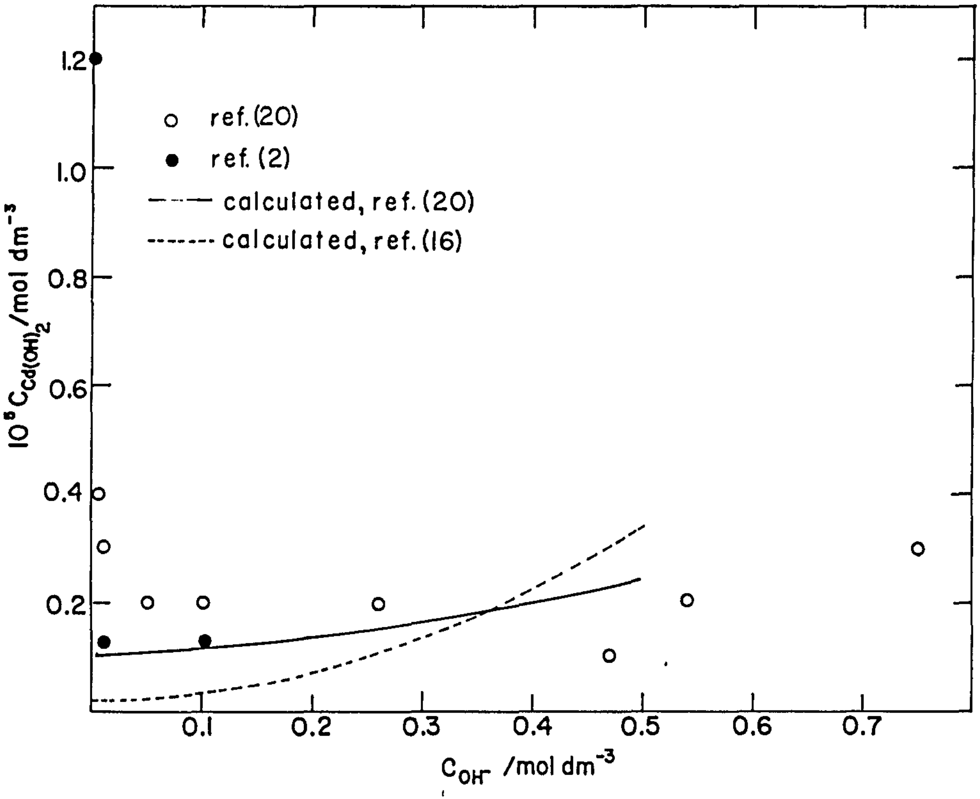

Figure 2. Solubility of $Cd(OH)_2$ in dilute alkaline solutions at 298 K.

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CRITICAL EVALUATION:

are lower at the solubility minimum, yet below pH = 9 their values tend to become at least ten times larger than those reported by others.

The tentative value for K_2 at 298 K is 1.3×10^{-4} (16) because the results in this work agree best with the tentative value for the minimum solubility to be discussed next.

The point of minimum solubility of $Cd(OH)_2$ in aqueous solutions is at a pH slightly alkaline to the pH of neutrality. However, because of the low concentrations involved it is difficult to determine exactly where the solubility minimum is. At 298 K it was found between 0.01 and 0.1 mol NaOH dm^{-3} (2) or between 10^{-4} and 10^{-2} mol NaOH dm^{-3} (5). Gubeli and Taillon (16) located the minimum solubility between pH = 11-13, or about 10^{-1} to 10^{-3} mol NaOH dm^{-3}. They present data only in graphical form but they apparently collected much more data in this region than did the others. At 297.5 K the minimum is said to be between 0.05 and 0.1 mol NaOH dm^{-3} (20). These latter investigators determined this minimum at two different total ionic strengths: 1 and 7 mol dm^{-3}. There was little difference in solubility values at these two total ionic strengths. The solubility of $Cd(OH)_2$ at this minimum is given as 1×10^{-6} mol dm^{-3} (20), 1.3×10^{-6} mol dm^{-3} (2), 3.5×10^{-6} mol dm^{-3} (5), and about 4.3×10^{-7} mol dm^{-3} (16).

A lower value of the solubility of CdO at the minimum was obtained in work at constant ionic strength of 3 mol-dm^{-3} (ionic strength was maintained by adding $NaClO_4$) at 298 K (21). The method of Schindler (4) was modified by using a solubility column (22). The data are presented only in the form of a graph from which it appears that the minimum solubility is about $10^{-6.7}$ mol dm^{-3} at pOH = 1.2 to 3.7. The authors consider the data of Schindler (4) to be the norm and admit that their data do not agree completely with his, possibly because of a slight contamination of the solid $Cd(OH)_2$ phase. In both refs. (16) and (21) there are many experimental data points around the minimum solubility. The results of these two investigations are in fairly good agreement considering the differences in total ionic strength, the small values involved, and the difficulty of interpolation from a fairly small graph. Therefore, in summary, the tentative value for the minimum solubility of $Cd(OH)_2$ is 3×10^{-7} mol dm^{-3} at 298 K and occurs in the region pH = 10 to 13.

A common assumption is that at the solubility minimum the main solute species is undissociated $Cd(OH)_2$. Consequently, the minimum solubility will be the value of K_3. This value is tentatively given as 3×10^{-7} mol dm^{-3} at 298 K.

Four papers give numerical data for the solubility of $Cd(OH)_2$ in NaOH solutions. In two of these (2, 5) the temperature was maintained at 298 K, in another (20) it was 297.5 K, and in a third (23) it was not specified. A summary of these results is given on Figures 1 and 2. The data from ref. (23) are not included on these Figures because insufficient information is given about the experimental procedure used in obtaining these values. A difference in total ionic strength (20) caused very little difference in solubility. The solubility values of Gayer and Woontner (5) are significantly higher than those in the other two papers. Therefore, in the subsequent calculations the data of ref. (20) will be used even though the temperature is 297.5 rather than 298 K.

As the alkalinity of the solvent increases beyond the point of minimum solubility, reactions (5) and (6) become more prominent. One paper (16) does not consider the $Cd(OH)_3^-$ ion to be present to any significant extent and therefore has no calculations with respect to any of its characteristics. Gayer and Woontner (5) used their experimental data to calculate equilibrium constants for different reactions and found that only reaction (5) gave a constant value for the equilibrium constant in the range 0.1 to 1 mol NaOH dm^{-3}. The value of K_5 calculated from their data is 2.1×10^{-5} at 298 K (this is a concentration ratio). However, as noted above, the solubility results reported in that paper are higher than those reported by others in the same region, see Figure 1.

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The data of ref. (20) in this same region give a value of 1.2×10^{-6} for K_5 (also a concentration ratio). This value is based on a value for a coefficient in an equation that was developed to fit the solubility data. An analysis of these data using a method described previously (24) gives a value of 2.5×10^{-6} for K_5. This value is 1/10 of that calculated by Gayer and Woontner (5), and reflects the higher solubility data reported in ref. (5). The suggested tentative value for K_5 is 2×10^{-6} at 298 K (this is a concentration ratio). The difficulty with this and other equilibrium constant values for reactions involving CdO or $Cd(OH)_2$ is the paucity of experimental data reported in the literature. This, in turn, may be a reflection of the experimental and analytical difficulties associated with this system.

Apparently reaction (6) becomes prominent only at NaOH concentrations above 1 mol dm^{-3}. The only data available here are those at 297.5 K (20). These are really insufficient on which to base a conclusion as to the value of K_6.

Two attempts have been made to develop an equation to describe the solubility of $Cd(OH)_2$ in NaOH solutions (16, 20). In each of these there is one coefficient from which a value for K_6 can be extracted. One such value is 1.3×10^{-5} mol^{-1} dm^3 (16). The other is 3.1×10^{-6} mol^{-1} dm^3 (20). An analysis of the data in the latter paper using a method described previously (24) gives a value of 1.4×10^{-6} mol^{-1} dm^3. The best tentative value for K_6 at 298 K is 2×10^{-6} mol^{-1} dm^3 based on the presumably better solubility data of ref. (20).

There has been some disagreement whether the solute species $Cd(OH)_3^-$ or $HCdO_2^-$ exists in any significant amount in solution. Ichikawa and Sato (19) measured the distribution coefficients of ^{109}Cd between an anion exchange resin and NaOH solutions. From their results they concluded that only the univalent ion existed in NaOH solutions less concentrated than 3 mol dm^{-3}. The temperature was not specified but it apparently was room temperature. On the other hand, Gubeli and Taillon (16) assumed that this ion did not exist in any appreciable quantities. Their argument was based on the values of the slopes of the solubility curve. However, these slopes were all measured in the region of minimum solubility where the concentration of $Cd(OH)_3^-$ is not significant compared to that of $Cd(OH)_2$. All the other papers dealing with solutions of CdO or $Cd(OH)_2$ in alkaline solutions consider $Cd(OH)_3^-$ to be one of the solute species present.

One equation that fits the solubility data of two papers (2, 20) in NaOH concentrations greater than 0.5 mol dm^{-3} is as follows (20).

$$[Cd]_{tot} = 1.0 \times 10^{-6} + 1.2 \times 10^{-6}[OH^-] + 3.1 \times 10^{-6}\,[OH^-]^2 \qquad (13)$$

The numerical terms on the right hand side of the equation are: concentration of undissociated $Cd(OH)_2$, K_5, and K_6, respectively. This curve is shown on Figures 1 and 2 and fits the data well for NaOH concentrations greater than 0.5 mol dm^{-3}.

Another equation was developed to fit the data in the vicinity of the minimum solubility (16). This equation is:

$$[Cd]_{tot} = \frac{2.5 \times 10\text{-}15}{[OH^-]^2} + \frac{1.3 \times 10^{-10}}{[OH^-]} + 1.6 \times 10^{-7} + 1.3 \times 10^{-5}[OH^-]^2 \qquad (14)$$

The terms on the right hand side of the equation represent the concentration of Cd^{2+}, $CdOH^+$, $Cd(OH)_2$, and $Cd(OH)_4^{2-}$, respectively. The line calculated from this equation is also shown on Figures 1 and 2. It does not fit the data very well except in the vicinity of the solubility minimum. This, no doubt, is due, at least in part, to the neglect of the presence of $Cd(OH)_3^-$ ions.

The question of whether or not polynuclear ionic species exist in solutions should also be considered. Three papers from the Department of Inorganic Chemistry, Royal

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Institute of Technology in Stockholm, Sweden, address this issue. Each of these papers (15, 21, 25) is a study of the hydrolysis of Cd^{2+} ions. Two of these papers (15, 21) state specifically that no evidence was uncovered for the existence of polynuclear species. The third paper (25) suggested that two polynuclear species existed: Cd_2OH^{3+} and $Cd_4(OH)_4^{4+}$. However, these species were said to become evident only when the total cadmium ion concentration exceeded 0.1 mol dm^{-3}. Such a concentration is not reached or exceeded in the solubility data discussed up to this point.

In one paper (26) results are given for the solubility of $Cd(OH)_2$ in NaOH solutions at 373 K. The purpose of this work was to determine whether $Cd(OH)_2$ had significant acidic characteristics, i.e., whether it would form cadmates which could be isolated. Therefore, concentrated NaOH solutions were used: 6.8 to 18.4 mol dm^{-3}. The results showed that in NaOH solutions less concentrated than 14.2 mol dm^{-3} the only solid phase was $Cd(OH)_2$. At concentrations greater than this, the solid phase appeared to be $Na_2[Cd(OH)_4]$. Similar work at 353 K gave additional solid phases but these are not described precisely. There is only one concentration of NaOH in which there are solubility data at 297.5 K (20) and 373 K (26). A comparison shows that at the higher temperature the solubility is about ten times as great.

Solovieva, et al., measured the solubility of both CdO and $Cd(OH)_2$ in concentrated NaOH solutions at elevated temperatures (27, 28). They also found that at the lower concentrations of NaOH the solid phase was $Cd(OH)_2$ but beyond a point of maximum solubility (which varies with the temperature) the solid phase changed and was probably a cadmate, $Na_2[Cd(OH)_4]$. According to their results the solubility of $Cd(OH)_2$ was significantly lower than that of CdO at comparable temperature and NaOH concentration. However, their results for the solubility of $Cd(OH)_2$ at 378 K are also lower than the results reported for 373 K (26), see Figure 3. Until more results are reported under these conditions, the results of Scholder and Staufenbiel (26) are considered the more reliable. The reason for this is that not enough is known about the experimental conditions under which the results of Solevieva, et al., (27, 28) were obtained.

Solubility in solutions containing ammonia and ammonia derivatives. Four papers deal with solutions of $Cd(OH)_2$ in aqueous ammonia solvents (16, 18, 29, 30). Only one of these papers (29) reports numerical solubility data. The solubility studies were made at 283, 293 and 303 K, but no attempts were made to determine the nature or stability of the cadmium-ammonia complex ions formed in such solutions. Furthermore, no information is given as to the purity of the materials used, nor to the reproducibility of the various experimental measurements and procedures. Nor is there any indication of the pH of the solutions. Consequently, it is not possible to develop an equation to express the solubility of $Cd(OH)_2$ in the aqueous ammonia solvents, and the results that are given must be considered as incomplete and tentative. Some of the first data on the solubility of $Cd(OH)_2$ in aqueous NH_3 solutions at 293 K (31) were not included in the Data sheets because the reproducibility was admittedly not very good and the $Cd(OH)_2$ samples used were not of uniform composition.

The other three papers dealing with this system (16, 18, 32) are primarily concerned with the composition and stability of the cadmium-ammonia complex ions. Only one of these papers (16) reports any solubility data but that is presented only in graphical form.

The reactions of interest are of the type

$$Cd(NH_3)_n^{2+} = Cd^{2+} + n\ NH_3. \qquad (15)$$

There is no unanimity as to the composition of these ions, i.e., the value of n. That may reflect the different conditions that were used. De Wijs (18) found evidence at 298 K for only two such ions: $Cd(NH_3)_2^{2+}$ and $Cd(NH_3)_4^{2+}$. The stability constants for

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CRITICAL EVALUATION:

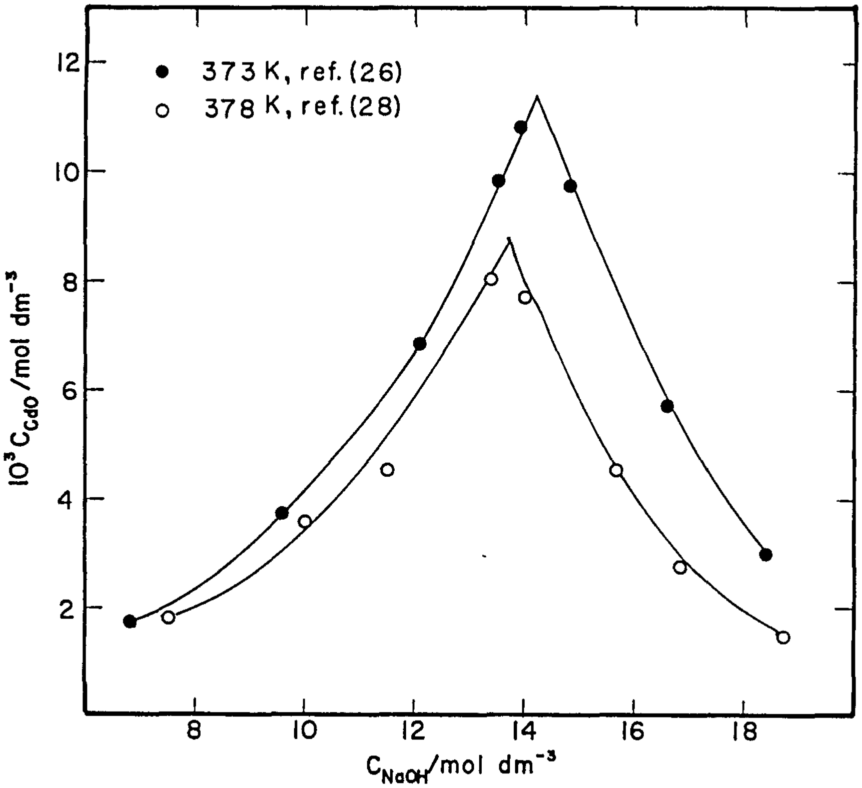

Figure 3. Solubility of $Cd(OH)_2$ in NaOH solutions at elevated temperatures.

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these ions are given as 2.7×10^{-5} mol^2 dm^{-6} and 2.5×10^{-7} mol^4 dm^{-12}, respectively. However, other authors reach different conclusions as to which complex ions are present and the value of the stability constant for each, Table I.

Table I

Reported stability constants for cadmium-ammonia complex ions.

Source	$Cd(NH_3)^{2+}$	$Cd(NH_3)_2^{2+}$	$Cd(NH_3)_3^{2+}$	$Cd(NH_3)_4^{2+}$
ref. (18)	---------	2.7×10^{-5}	---------	2.5×10^{-7}
ref. (16)	7.9×10^{-4}	6.3×10^{-6}	3.2×10^{-7}	1.6×10^{-8}
ref. (32)	2.2×10^{-3}	1.6×10^{-5}	3.3×10^{-8}	2.8×10^{-10}

It is difficult to determine which, if any, of these values are to be accepted. In view of the differences it seems best to consider all these values doubtful.

One paper (3) reports a few values for the solubility of CdO in aqueous $(NH_4)_2SO_4$ at 298 K. There is no other similar study reported and the solid phase is described only in general terms. Consequently, these values can only be considered as tentative.

Danilov, et al. (30) measured the solubility of CdO or $Cd(OH)_2$ in aqueous solutions containing 2-aminoethanol or 2,2'-iminodiethanol. The solubility data are reported at several temperatures, but it is impossible to evaluate the precision of the data from the meager amount of information given in the paper. The conclusions reached by the authors are: in aqueous solutions of 2-aminoethanol more concentrated than 3 mol dm^{-3} the solid phase contains 2 mol of the 2-aminoethanol per mol of $Cd(OH)_2$ while in aqueous solutions of 2,2'-iminodiethanol at concentrations up to 8 mol dm^{-3} the solid phase is $Cd(OH)_2$. In both types of solutions the solubility decreases with increasing temperature. The authors do present an equation for the total solubility of CdO in such solutions. The terms in the equation include the following factors: solubility product of $Cd(OH)_2$, mean ionic activity coefficient of $Cd(OH)_2$, ligand concentration, activity coefficient of the ligand, and the activity of water. According to the calculations of the authors this equation gives satisfactory results for aqueous solutions of 2-aminoethanol and 2,2'-iminodiethanol in which $Cd(OH)_2$ is the solid phase. However, insufficient data are included in the paper to enable one to check these calculations. Furthermore, there are no other results in the literature dealing with these systems. Consequently, the data and the conclusions can only be considered tentative, at best.

Miscellaneous. One study has been made of the $CdO-As_2O_5-H_2O$ system (33). This was a phase study and intended to show that CdO does react with weakly acidic oxides at 298 K. Five solid phases were isolated and identified: $3CdO$©As_2O_5©$4H_2O$, $5CdO$©$2As_2O_5$©$5H_2O$, $2CdO \cdot As_2O_5 \cdot 2H_2O$, $CdO \cdot As_2O_5 \cdot 4H_2O$ and $CdO \cdot 2As_2O_5 \cdot 5H_2O$. The numerical data on which the phase diagram is based were not included in the paper but were supplied in a letter from Dr. N. Kbir-Arguib. These results should be considered as tentative until further work with this system is reported.

Another study is reported that deals with the reaction of CdO with hydrogen peroxide (8). The purpose of the work was to determine whether $Cd(OH)_2$, like $Zn(OH)_2$, would form peroxides. The solubility of $Cd(OH)_2$ in various H_2O_2 solutions is reported at 273 and 293 K. Besides $Cd(OH)_2$, four solid peroxides were reported to be equilibrium phases in this system: $CdO_2 \cdot 2H_2O$, $CdO_2 \cdot 1.5H_2O$, $CdO_2 \cdot H_2O$ and $CdO_2 \cdot 0.5H_2O$. Although it was stated that there is a question as to the structure of cadmium peroxides, yet the authors do not use their results to clarify this matter. There are no other solubility data reported for this aqueous hydrogen peroxide system. This fact, and the uncertainty of the results as mentioned earlier in discussing the solubility of $Cd(OH)_2$ in water, strongly indicate that these solubility results should be considered doubtful at the present time.

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One paper (34) deals with the effect of Na_2S on the solubility of CdO in water. Only one datum is given and there is no indication as to the purpose of this investigation. The one value given must be considered tentative until more work is done and reported on this system.

Solubility under hydrothermal conditions. Shlyapnikov and Shtern have presented two papers (35, 36) dealing with the effect of CO_2 and NaCl on the solubility of CdO under hydrothermal conditions. The data are rather few but, presumably, these papers are preliminary reports for a larger program of study dealing with the leaching and deposition of minerals in the earth.

In the earlier work (35) the solubility of CdO is reported for an aqueous solution containing 4 mol NaCl dm^{-3} at 293 K and under a CO_2 pressure of 50×10^5 Pa. In the later paper (36) solubility data are reported for several NaCl concentrations at two CO_2 pressures: 1×10^5 and 50×10^5 Pa. But the data in the two papers are not consistent with each other so far as can be checked. In the latter paper the solubility in a 4 mol NaCl dm^{-3} solution at 293 K and a CO_2 pressure of 50×10^5 Pa is twice that given in the earlier paper. The authors make no comment on this. Because there are no other data against which these results can be compared, the solubility data in refs. (35, 36) must be considered doubtful at the present time. However, the general conclusions are that the presence of NaCl in solution increases the rate at which CdO is converted to $CdCO_3$ under a pressure of CO_2. Furthermore, the solubility of CdO increases as the NaCl concentration increases and the CO_2 pressure increases. These phenomena are interpreted as due to the increasing formation of cadmium-chloride complexes and the formation of bicarbonates.

Several papers, e.g., (37-40) deal with the reaction of CdO with GeO_2 under hydrothermal conditions. However, these papers are primarily concerned with the formation and identification of cadmium germanates and present no numerical solubility data.

Table II

Summary of recommended values for the $CdO-H_2O$ system.

Solubility of $Cd(OH)_2$ in H_2O at 298 K	1.5×10^{-5} mol/kg H_2O
$\log K_{so}$ at 298 K in 3 mol $NaClO_4$ dm^{-3}	-14.41 ± 0.05
$\log K_{so}$ at 298 K in 1 mol $NaClO_4$ dm^{-3}	-14.6 ($\pm$ 0.1)

Table III

Summary of tentative values for the $CdO-H_2O$ system

Solubility of CdO in H_2O at 298 K	5.4×10^{-5} mol dm^{-3}
K^{o}_{so} at 291 K	2.6×10^{-15}
K^{o}_{so} at 298 K	5.9×10^{-15}
$Cd(OH)_2(s) + H^+ = CdOH^+ + H_2O$	$K_2 = 1.3 \times 10^{-4}$ at 298 K
$Cd(OH)_2(s) = Cd(OH)_2(sln)$	$K_3 = 3 \times 10^{-7}$ mol dm^{-3} at 298 K
$Cd(OH)_2(s) + OH^- = Cd(OH)^-_3$	$K_5 = 2 \times 10^{-6}$ at 298 K
$Cd(OH)_2(s) + 2\ OH^- = Cd(OH)^{2-}_4$	$K_6 = 2 \times 10^{-6}$ mol^{-1} dm^3 at 298 K

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(2) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2]

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

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