COMPONENTS:	EVALUATOR:
(1) Copper(II) oxide; CuO; [1317-38-0]	T. P. Dirkse
	Department of Chemistry
(2) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]	Calvin College
	Grand Rapids, Michigan 49506, U.S.A.
(3) Water; H_2O; [7732-18-5]	October 1984

CRITICAL EVALUATION:

       For the bipositive oxidation state of copper there is both a solid oxide, CuO, and a solid hydroxide, $Cu(OH)_2$. However, in some environments the hydroxide is metastable with respect to the oxide. Such situations are discussed later in this Critical Evaluation. The hydroxide has been referred to as a hydrous oxide whose properties depend on the temperature of precipitation, the amount of alkali used, and the age of the precipitate. The degree of hydration of the precipitate decreases with increasing concentration of alkalies (1).

       In addition to the metastability of the hydroxide, the possibility of the presence of colloidal CuO or $Cu(OH)_2$ must also be considered in evaluating the solubility data. Measurements of conductance (2) and viscosity (3) indicate that the hydroxide is at least partially peptized in solutions of NaOH and NH_4OH.

<div align="center">Solubility in water</div>

       There are a few reports that give numerical values for the solubility of CuO or $Cu(OH)_2$ in water, but the values were determined at different temperatures.

Copper oxide. Remy and Kuhlmann (4) used conductance measurements as the experimental approach to measuring the solubility of CuO in water at 293 K. The values were obtained by a conductimetric titration and by a measurement of the specific conductance of a saturated solution. The latter value was used together with accepted values for the ionic conductance of Cu^{2+} and OH^- ions to arrive at a solubility value. The average of the values obtained by these two methods was 6.8×10^{-5} mol dm^{-3}. This information was repeated in a later report (5) but no new solubility information was then given.

       The solubility of CuO in water was also measured at 298 K (6). The solubility value, 2.9×10^{-5} mol dm^{-3}, was obtained by chemical analysis of a saturated solution. This value is the better of the two just mentioned because it was determined by direct analysis. However, the value is classed as tentative because of lack of supporting work and because the authors had difficulty preparing saturated solutions that contained no colloidal CuO.

Copper hydroxide. The solubility of $Cu(OH)_2$ in water is reported to be 3×10^{-6} mol dm^{-3} (7). This value was obtained in the course of a study of the treatment of sewage and industrial wastes. It is marred by the fact that there is a lack of precision in the work and no temperature is specified. This is true also of other reports. The solubility of $Cu(OH)_2$ in distilled water is said to be about 4×10^{-6} mol dm^{-3} at room temperature. The article (8), however, gives practically no experimental details and presents the data only in graphical form.

       Makarov, et al. (9) determined the solubility of $Cu(OH)_2$ in solutions of hydrogen peroxide and, as an extension of that work, report a value of 2.9×10^{-6} mol kg^{-1} for the solubility of $Cu(OH)_2$ in water at 273 K. But, again, very few experimental details are given.

       Another report on solubility (10) merely uses information already in the literature at that time and presents no new experimental data.

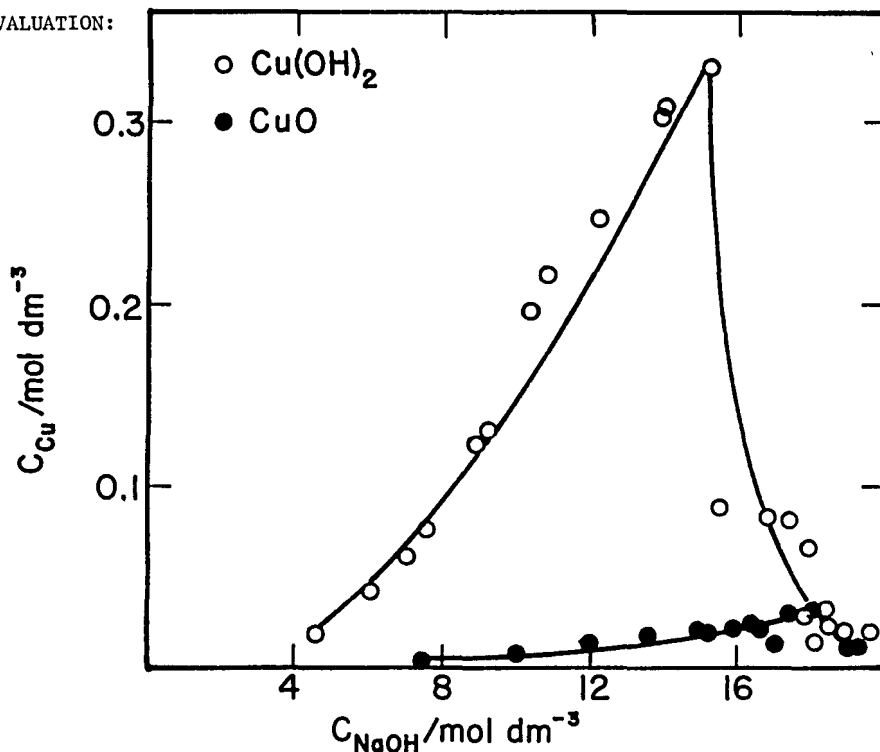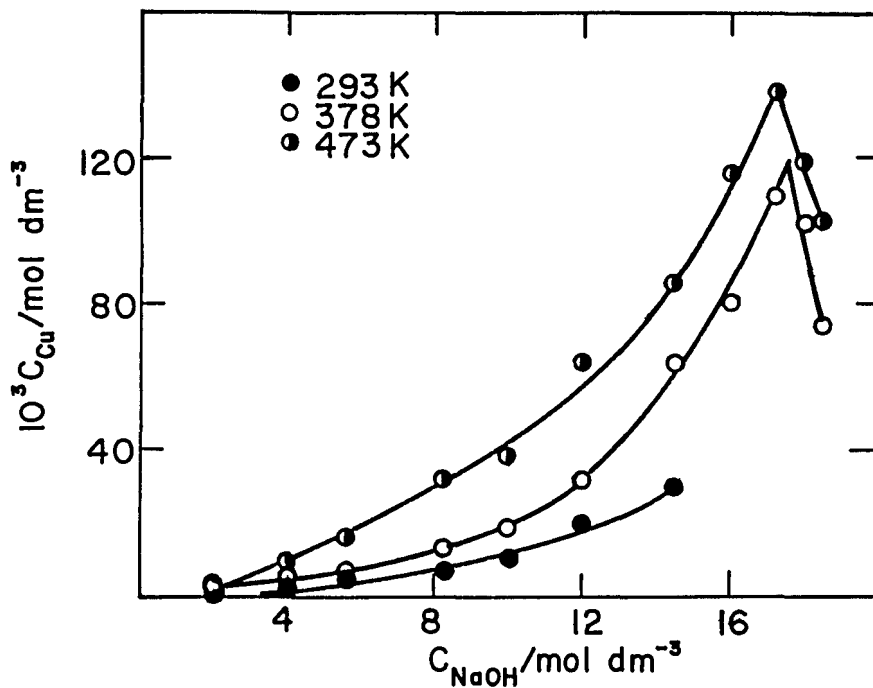| COMPONENTS:	EVALUATOR:
(1) Copper(II) oxide; CuO; [1317-38-0] (2) Copper(II) hydroxide; Cu(OH)$_2$; [20427-59-2] (3) Water; H$_2$O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. October 1984

CRITICAL EVALUATION:

Because of the lack of experimental details, and the few values reported, the solubility of Cu(OH)$_2$ in water can only be given as about 10^{-6} mol dm^{-3} in the temperature range 273-300 K.

Solubilities in acids

Aqueous HF. Only one report is available for this system (11). The solubility values were measured at 298 K, but they cannot be considered reliable because there is practically no information about the experimental details of this investigation.

Aqueous HNO$_3$. There has been one investigation of the solubility of CuO in aqueous HNO$_3$ (12). The temperature varied from 298 to 301 K and only a few dilute solutions of HNO$_3$ were used. The values reported can only be classified as tentative because of the absence of corroborating work.

Aqueous H$_3$BO$_3$. Only one paper (13) gives information on the Cu(OH)$_2$-H$_3$BO$_3$-H$_2$O system but the interest in the study was to determine the nature and composition of the solid phases that were present in this system at room temperature. No solubility data are included.

Solubilities in alkalies

Aqueous NaOH. Early in this century it had been shown that Cu(OH)$_2$ was slightly soluble in aqueous NaOH or KOH solutions without the presence of other substances (14). However, such solutions were shown to be metastable (15). A thorough investigation of this system was made by Muller. In two preliminary publications he verified the metastability and noted that the solubility of Cu(OH)$_2$ was dependent on the method used for the preparation of the Cu(OH)$_2$ (16), and he presented a phase diagram for the system (17). He later published a more complete account of the results of his investigations (18). The conclusion of this thorough investigation was that Cu(OH)$_2$ does dissolve to a significant extent in aqueous NaOH and the solubility increases markedly with increasing concentration of NaOH, Figure 1. However, these solutions are metastable. The copper content decreases on standing and the undissolved solid phase undergoes a change in color. The chemically-bound water content (or the Cu(OH)$_2$ content) of the solid phase is dependent on the copper concentration in the solution phase. In no instance did the chemically-bound water content become zero, i.e., the solid phase did not change completely to CuO. On the other hand, CuO had a lower solubility in the aqueous NaOH solutions than did the solutions of Cu(OH)$_2$ after they had ceased to decrease in copper content on standing. That is, with Cu(OH)$_2$ dissolved in aqueous NaOH, the solid phase approached but did not reach the composition CuO. Likewise, the solution decreased in copper content but the value did not reach the value of a saturated solution of CuO in aqueous NaOH. Thus, on the basis of the work of Muller, a solubility value for a saturated solution of Cu(OH)$_2$ in aqueous NaOH (or KOH) is meaningless. The most that can be said for such values is that they are minimum values. This agrees with earlier work (15).

The metastability of solutions of Cu(OH)$_2$ in aqueous NaOH has also been noted at 298 K by others (19). This group found that the solubility of

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CRITICAL EVALUATION:

Figure 1. Solubility of Cu(OH)$_2$ and CuO in aqueous NaOH at 291 K, ref. (18).

Figure 2. Solubility of Cu(OH)$_2$ in aqueous NaOH, ref. (20).

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CRITICAL EVALUATION:

$Cu(OH)_2$ decreased with aging. They also found that the amount of $Cu(OH)_2$ dissolved in a 7.5 mol dm^{-3} solution of NaOH increased for about the first hour after the components were mixed, but then decreased over the period of a month. No equilibrium solubility values are given in this paper. The solubility values recorded after a month of standing are about 10% of those shown on Figure 1. The data obtained by some members of this research group (20) are shown on Figure 2. The solubility of $Cu(OH)_2$ increases with increasing temperature and shows the same variation with increasing NaOH concentration as do the results on Figure 1, but the solubility values given on Figure 2 are much smaller than those shown on Figure 1. This may be due to the preparation of $Cu(OH)_2$ that was used (19).

In larger concentrations of NaOH (above 16 mol dm^{-3}) the solubility of $Cu(OH)_2$ and of CuO decrease markedly. This is due to the fact that the solid phase changes to Na_2CuO_2.

The difference in solubility of $Cu(OH)_2$ and CuO in aqueous NaOH was noted by Feitknecht (21) who presented no new solubility data but observed that the free energy content of CuO is about 1.62 kcal mol^{-1} less than that of $Cu(OH)_2$. Another report (22) mentions that freshly precipitated $Cu(OH)_2$ is more soluble in aqueous solutions of alkalies than is CuO, but no numerical solubility data are given.

Solubility values for solutions of $Cu(OH)_2$ in NaOH solutions more dilute than those shown on Figure 1 have also been reported (23). The three papers (15, 18, 23) that report solubility values for $Cu(OH)_2$ in aqueous NaOH (all at approximately the same temperature) give different solubility values for the NaOH concentration range that is common to all of them. This is to be expected when dealing with a metastable system. Another set of solubility values for $Cu(OH)_2$ in aqueous NaOH at 298 K (24) resemble more nearly the solubility values for CuO that were reported by Muller (18).

Solubility values for solutions of CuO in aqueous NaOH (18) can be accepted as equilibrium values because such solutions were stable. Solubility values for this same system have also been reported by others (6) and are shown on Figure 3. There are differences that should be noted. In one report (6) the concentrations are given as mol kg^{-1} while in the other (18) they are given as mol dm^{-3}. The temperatures differ by 7 K. Yet, in spite of these differences the data support each other in the alkali concentration regions that are common to both. Furthermore, solubilities in NaOH and in KOH are about the same. The values of Akhmetov, et al. (24) are somewhat larger. There are too few data to recommend solubility values or an equation that expresses the solubility of CuO in aqueous NaOH. Therefore, for temperatures around room temperature the data on Figure 3 (6, 18) are classified as tentative, but there is no reason to doubt their validity. They are preferred to those of ref. (24) because in that work no information is given about the CuO that was used in making the measurements. A value of 4.2 x 10^{-3} mol dm^{-3} was mentioned as a solubility value of CuO in a 7.5 mol dm^{-3} NaOH solution at 298 K (19). This value was not reported as an equilibrium value but it is in good agreement with the values shown on Figure 3.

The solubility of CuO in aqueous NaOH at higher temperatures has also been reported (25) and is shown on Figure 4. The values are considerably

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(1) Copper(II) oxide; CuO; [1317-38-0] (2) Copper(II) hydroxide; Cu(OH)$_2$; [20427-59-2] (3) Water; H$_2$O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. October 1984

CRITICAL EVALUATION:
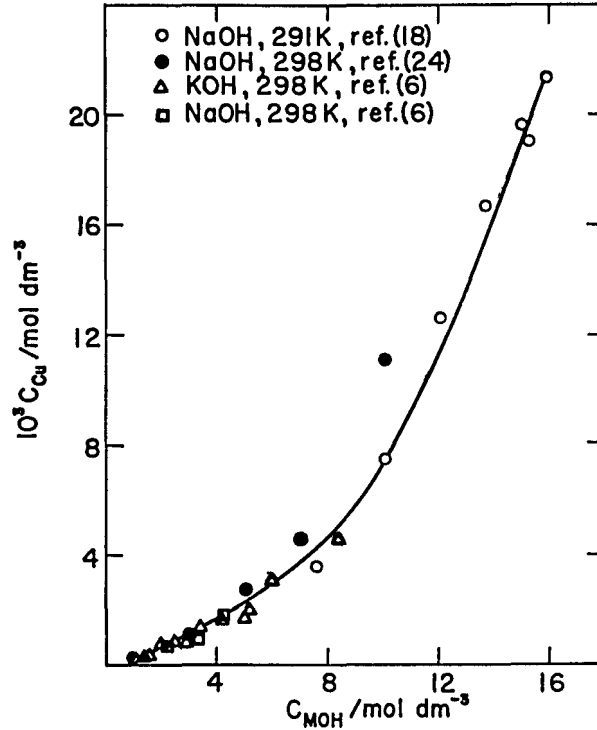
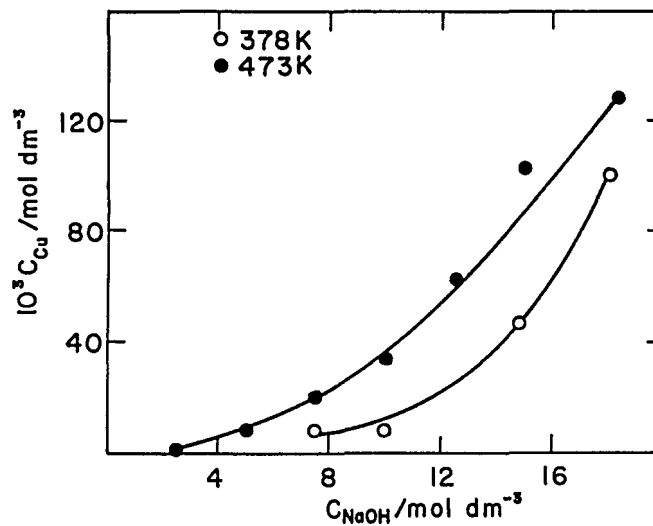Figure 3. Solubility of CuO in aqueous NaOH and KOH solutions. For ref. (6) the units on the axe are mol kg^{-1}.

Figure 4. Solubility of CuO in aqueous NaOH, ref. (25).

COMPONENTS:	EVALUATOR:
(1) Copper(II) oxide; CuO; [1317-38-0]	T. P. Dirkse Department of Chemistry
(2) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]	Calvin College Grand Rapids, Michigan 49506, U.S.A.
(3) Water; H_2O; [7732-18-5]	October 1984

CRITICAL EVALUATION:

larger than those shown on Figure 2. This may be due to the higher temperature, but these values can only be accepted tentatively until further work is reported.

Aqueous KOH. Traube (26) has reported some solubility values for solutions of $Cu(OH)_2$ in aqueous KOH containing polyhydroxy compounds. These data were not entered on a data sheet because no temperature was specified and there is no information about the source and purity of the materials that were used. The solubility data are expressed as ratios. The main objective of the work was not to measure solubilities but to ascertain the mechanism whereby $Cu(OH)_2$ dissolves in such mixtures. The discussion of the mechanism of dissolution was continued in two later reports (27, 28) but no additional solubility information was given.

<div align="center">Solubility constants</div>

The dissolution of $Cu(OH)_2$ and CuO in aqueous solutions may proceed by one or more of reactions (1) to (4).

$$Cu(OH)_2(s) \qquad = Cu(OH)_2(sln) \qquad\qquad (1)$$

$$CuO(s) + H_2O \qquad = Cu(OH)_2(sln) \qquad\qquad (1a)$$

$$Cu(OH)_2(s) \qquad = Cu^{2+} + 2OH^- \qquad\qquad (2)$$

$$CuO(s) + H_2O \qquad = Cu^{2+} + 2OH^- \qquad\qquad (2a)$$

$$Cu(OH)_2(s) + OH^- = Cu(OH)_3^- \qquad\qquad (3)$$

$$CuO(s) + H_2O + OH^- = Cu(OH)_3^- \qquad\qquad (3a)$$

$$Cu(OH)_2(s) + 2OH^- = Cu(OH)_4^{2-} \qquad\qquad (4)$$

$$CuO(s) + H_2O + 2OH^- = Cu(OH)_4^{2-} \qquad\qquad (4a)$$

Reactions (1) and (1a) have received practically no attention. In a review containing values for a variety of constants and reactions (29), the value of the equilibrium constant for reaction (1) is given as 3.3×10^{-5} at 298 K. However, this value was deduced from thermodynamic data found in the literature, but no indication is given as to the source of this information. On the other hand, the solubility of undissociated $Cu(OH)_2$ in aqueous solutions was estimated to be about 10^{-9} mol dm^{-3} at 298 K (6). The solubility is too small to be determined precisely, and its contribution to the total solubility of $Cu(OH)_2$ is considered to be negligible.

Reactions (2) and (2a) represent the solubility product reaction, for which the equilibrium constants are:

$$K_2^o = K_{so}^o = (a_{Cu^{2+}}) \cdot (a_{OH^-})^2 \qquad\qquad (5)$$

$$K_{2a}^o = K_{so}^o = (a_{Cu^{2+}}) \cdot (a_{OH^-})^2/(a_{H_2O}) \qquad\qquad (5a)$$

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CRITICAL EVALUATION:

In spite of the fact that the solubility of $Cu(OH)_2$ in aqueous solutions of alkalies is indeterminable because of the instability of the system, there are many reports in which K_2^o has been evaluated. Two attempts have been made to evaluate this constant by measuring the e.m.f. of an appropriate cell (30, 31). A value of 1.7×10^{-13} mol^3 dm^{-9} was obtained as a concentration product at 292 K (30) and 1.0×10^{-19} mol^3 dm^{-9} was reported at 290 K (31). In neither investigation was the reproducibility very good, because of the instability of the $Cu(OH)_2/Cu$ electrode.

In four investigations the experimental method consisted of a potentiometric titration of a copper salt with aqueous NaOH or LiOH, but slightly different temperatures were used. A concentration product of 3.72×10^{-10} mol^3 dm^{-9} was reported at 293 K (32). However, there is a legitimate doubt whether equilibrium was established in this work. A value of 1.3×10^{-20} was reported for K_2^o at an unspecified temperature (22), although the data were probably obtained at room temperature. Oka (33) reported values of 1.1×10^{-19} and 9.3×10^{-19} mol^3 dm^{-9} at 298 K, depending on whether the copper salt was $Cu(NO_3)_2$ or $CuCl_2$, respectively. However, these values are rejected because of insufficient information about the experimental details and the method of treating the experimental data. An approximate value of 3.9×10^{-19} mol^3 dm^{-9} for a concentration product was reported at 298 K (34).

In two investigations the pH of a saturated solution of $Cu(OH)_2$ was measured and the copper concentration in the solution was determined by analysis. The nature of the solid phase is uncertain in one of the reports (35). Little information is given about the experimental procedure and the author's calculations could not be reproduced. In the other report (36) the saturated solution of $Cu(OH)_2$ was prepared by pouring a 0.2 mol dm^{-3} solution of $NaClO_4$ through a column containing $Cu(OH)_2$. A value of 4.78×10^{-20} was obtained for K_2^o at 298 K. This value is the most reliable of those reported but it is classified as tentative because of the instability of the $Cu(OH)_2$-alkali system and because there is no other work to substantiate it.

In a somewhat similar approach, solid $Cu(OH)_2$ was dissolved in solutions of $CuSO_4$ at 291 K (37). The pH of the resulting solutions was measured and an analysis was made for copper content (no analytical method is mentioned). On the basis of these measurements a value of K_2 was calculated for each solution. The K_2 values for the most dilute $CuSO_4$ solutions were then extrapolated to zero ionic strength. The extrapolated value, 1.31×10^{-20}, was proposed as a value for K_2^o at 291 K. One assumption implicit in this method is that the copper content of the solution is assumed to be completely in the form of Cu^{2+} ions. This has not been substantiated and, therefore, the value suggested must be accepted with some reservations.

Values for K_2^o have been calculated on the basis of theoretical considerations, such as thermodynamic values. A value of 1.6×10^{-19} at 291 K was derived in one work (21). Maijs (38) suggested that the value is between 10^{-12} and 10^{-20}, but no temperature was specified. The values suggested by Maijs are rejected because of lack of information as to the basis on which the values were calculated.

There is one report of a value of K_2^o for 348 K (39). The value is 1.26×10^{-20}. The article contains many curves for potentiometric titrations and it
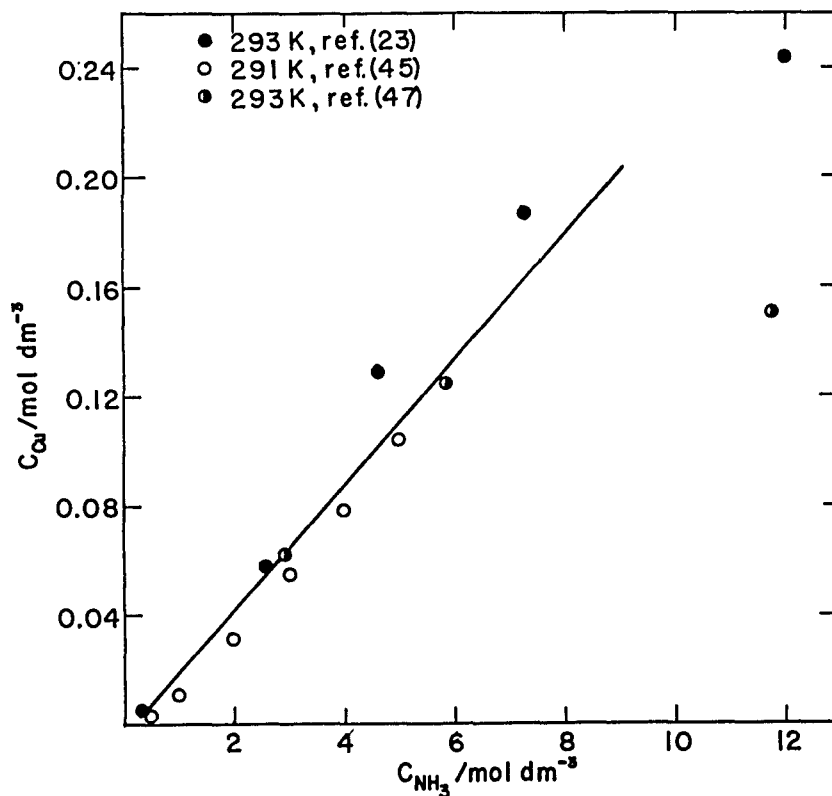
COMPONENTS:	EVALUATOR:
(1) Copper(II) oxide; CuO; [1317-38-0]	T. P. Dirkse
	Department of Chemistry
(2) Copper(II) hydroxide; Cu(OH)$_2$; [20427-59-2]	Calvin College
	Grand Rapids, Michigan 49506, U.S.A.
(3) Water; H$_2$O; [7732-18-5]	October 1984

CRITICAL EVALUATION:

is not clear exactly which experiments led to the value reported. The work may have been carried out in a way very similar to that of Akselrud and Fialkov (37). pH and copper content values for the solutions are given and apparently were manipulated in the same way. The value for K_2^o is subject to the same reservations as those expressed for the work of Akselrud and Fialkov (37). Because of the uncertainties that have been expressed, the work was not entered on a data sheet.

Because of the instability of the Cu(OH)$_2$-alkali system all values for K_2 or K_2^o are considered to be of questionable merit. More reliable values are to be expected for K_{2a}^o because reaction (2a) reaches a stable equilibrium condition. The value of K_{2a}^o is expected to be smaller than that for K_2^o because CuO is less soluble than Cu(OH)$_2$. Feitknecht (21) calculated a value of 1.0×10^{-20} at 291 K on the basis of free energy data. This is to be compared with the value of 1.6×10^{-19} calculated for K_2^o by the same author.

In one investigation (12) a value for K_{2a}^o was calculated from measurements of the solubility of CuO in HNO$_3$ solutions at a temperature of about 300 K. An average value of 1.5×10^{-20} was reported but the individual values of K_{2a}^o decreased as the concentration of HNO$_3$ increased.

The earliest reported value for K_{2a} at 298 K, based on solubility measurements, was 2.24×10^{-20} mol^3 dm^{-9} (40). The value was obtained by measuring the pH of saturated solutions in equilibrium with both CuO and basic copper(II) perchlorate. The K_{so}^o of the basic copper(II) perchlorate had been evaluated in a separate work. The total ionic strength of the solutions varied from 0.009 to 0.058 mol dm^{-3}. Later a value of 3.09×10^{-20} mol dm^{-3} was reported for K_{2a} at 298 K in solutions having a total ionic strength of 0.2 mol dm^{-3} (36). The use of activity coefficients led to a value of 4.47×10^{-21} for K_{2a}^o at 298 K.

In a third investigation (41) the solubility of CuO was measured in solutions containing NH$_3$ and varying in pH. The total ionic strength of all solutions was 1.0 mol dm^{-3}. The value of K_{2a} at 298 K calculated from these results was 7.94×10^{-20} mol^3 dm^{-9}.

The above results are all consistent with each other. The value of K_{2a} increases with increasing total ionic strength. The one value of K_{2a}^o at 298 K must, however, be considered tentative because no other work has attempted to duplicate it.

No values, based on solubility data, have been reported for the equilibrium constant of reaction (3).

A value of 10.3×10^{-6} has been suggested for K_{3a}^o at 298 K (6), but the authors considered the copper-containing anion to be HCuO$_2^-$ rather than Cu(OH)$_3^-$.

$$K_{3a}^o = (a_{Cu(OH)_3^-})/(a_{H_2O}) \cdot (a_{OH^-}) \qquad (6)$$

The only other value reported for K_{3a}^o at 298 K is 1.2×10^{-4} (24). This value, however, was based on the solubility of Cu(OH)$_2$ (not CuO) in NaOH solutions. Therefore, the value of McDowell and Johnston (6) is to be preferred and is accepted tentatively.

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The only value for K^o_{4a} based on solubility data is 81 x 10^{-6} at 298 K (6) but here the copper-containing anion is assumed to be CuO_2^{2-} rather than

$$K^o_{4a} = (a_{Cu(OH)_4^{2-}})/(a_{H_2O}) \cdot (a_{OH^-})^2 \qquad (7)$$

$Cu(OH)_4^{2-}$. Feitknecht (16) arrived at a value of 1.6 x 10^{-4} at 291 K. The value was calculated from free energy data and was not based on solubility measurements. A value of 7.6 x 10^{-5} has also been reported for 298 K (24), but this value was based on solubility of the Cu(OH)$_2$-aqueous NaOH system and not for the CuO-aqueous NaOH system. Therefore, the value of 81 x 10^{-6} (6) is to be preferred because it was based on solubility measurements for CuO. The value can only be classified as tentative, at best.

The cation CuOH$^+$ has also been considered to be a solute species in solutions of CuO or Cu(OH)$_2$ in aqueous alkalies. Evidence for this ion was found at 298 K but not at 323 K (42). Its presence has also been suggested by others (22, 43), but in both these reports the experimental evidence for this conclusion is not given in adequate detail.

Solubility in aqueous NH$_3$

Copper(II) hydroxide. An early attempt to measure the solubility of Cu(OH)$_2$ in solutions of NH$_4$OH failed to give reproducible results (44). The explanation given was that the solid Cu(OH)$_2$ was not a pure compound but possibly a mixture. Shortly after this attempt a report on the solubility of Cu(OH)$_2$ in NH$_4$OH solutions was published (45). There is no indication as to the reproducibility of the results, which were obtained at 291 K. The effect of (NH$_4$)$_2$SO$_4$ and Na$_2$SO$_4$ on the solubility of Cu(OH)$_2$ in NH$_4$OH was also measured and it was observed that the addition of these salts increased the solubility of Cu(OH)$_2$. The addition of NaOH and Ba(OH)$_2$ either singly or together was found to decrease the solubility of Cu(OH)$_2$ in a given concentration of NH$_4$OH. Later, Arkhipov and co-workers published several papers dealing with the solubility of Cu(OH)$_2$ in aqueous NH$_3$, generally at 292-293 K. In one paper (23) a wide range of NH$_3$ concentrations was used and the solubility values reported are larger than those reported by Dawson (45), Figure 5. In another paper (46) the effect of a series of polyhydroxy compounds on the solubility of Cu(OH)$_2$ in aqueous NH$_3$ was discussed but no numerical solubility data were given. In the first paper of this series (47) the objective was to ascertain the effect of a variety of compounds, e.g., alcohols, salts, amines, sugars, etc., on the solubility of Cu(OH)$_2$ in aqueous ammonia. The values do not agree with the values reported later (23), Figure 5. The divergence increases as the concentration of NH$_3$ increases. Arkhipov summarized much of this work in a later paper (48) but presented no new solubility information. The solubility of Cu(OH)$_2$ in aqueous ammonia was investigated by one other group (49), but the results are admittedly qualitative. No numerical data are given nor is any temperature specified.

In summary, there are no reliable data for the solubility of Cu(OH)$_2$ in aqueous ammonia. All the results that have been reported can only be classified as doubtful.

Copper(II) oxide. There are fewer reports on the solubility of CuO in aqueous NH$_3$ in spite of the fact that CuO is a more stable phase than is Cu(OH)$_2$. One

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CRITICAL EVALUATION:

Figure 5. Solubility of $Cu(OH)_2$ in aqueous NH_3.

COMPONENTS:	EVALUATOR:
(1) Copper(II) oxide; CuO; [1317-38-0] (2) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. October 1984

CRITICAL EVALUATION:

study was made at 298 K but no numerical solubility data are included in the report (50). This is also true of the report of Ganz, et al., (51). Only two reports give numerical solubility data for this system (41, 52). The solubility of CuO is much less than that of $Cu(OH)_2$. The solubility was measured at 298 K and is a function of the pH of the solution as well as of the concentration of NH_3 (41). There is one reservation about the pH values reported. The values were obtained by the use of a glass electrode and there is no indication whether corrections were made for the high alkalinity or whether a special high-alkaline glass electrode was used. No data sheet has been made for the work reported in ref. (52) because no temperature is specified and no information is given about the experimental procedure nor about the quality of the materials that were used.

There are no other numerical data for the solubility of CuO in aqueous ammonia. Therefore, the data of Gubeli, et al. (41) can only be classified as tentative.

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Solubility in acidic oxides

Chromium oxides. Three investigations have been reported on these systems, but in none of them is any numerical solubility data given. Knoche (53) studied the effect of $Cr(OH)_3$ on the induced solubility of insoluble metal hydroxides in solutions of alkalies. $Cu(OH)_2$ was included in this study and was found to be peptized under these conditions. Hayek (54) investigated the $CuO-CrO_3-H_2O$ system at 313 K. However, his interest was to identify the basic salts that were formed. The study was made in alkaline solutions. This same system has been studied in acidic solutions at 303 K (55). The interest here was primarily in the solid phases that separate from such a system. Some solubility data are given but there is no assurance that the solutions were saturated with respect to CuO.

Phosphorus(V) oxide. Only two investigations have been made of this system. One of these (56) reports a study of the system at 291 and 333 K. The report discusses the solid phases that were formed, but no solubility data are presented. In the other investigation (57) the system was studied at 298 K, but it was studied by using copper phosphate as the solid phase and not CuO or $Cu(OH)_2$. Thus, there is no assurance that the solutions were saturated with respect to either CuO or $Cu(OH)_2$.

Selenium oxides. One investigation was made of the $Cu(OH)_2-SeO_2-H_2O$ system, but only at 373 K (58). The values are classified as tentative because there are no other values with which they can be compared. Baroni (59) studied the $CuO-SeO_3-H_2O$ system at 303 K, but the solubility data are expressed as ratios, e.g., mol H_2O:mol SeO_3, and not as absolute values. Therefore, a solubility table cannot be compiled.

Sulfur oxides. While there are many reports that discuss systems involving CuO or $Cu(OH)_2$ in aqueous solutions of sulfur oxides, they contain very little information about solubility values. Only one paper discusses the system that involves SO_2 (60). This investigation was carried out in connection with a

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(3) Water; H$_2$O; [7732-18-5]	October 1984

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study of the leaching of metallic ores. Only a small phase diagram is included. It shows increasing solubility of CuO with increasing concentration of SO$_2$.

The studies of the CuO-SO$_3$-H$_2$O system were motivated primarily by a desire to determine the composition of the solid phases that precipitated from this system. Bell and Taber studied the system at 298 K (61), but the analytical methods are not described nor is there any information about the composition of the original mixtures. Furthermore, no solubility data are included. This same system was studied in the temperature range of 322-473 K (62). The interest, again, was in the composition of the solid phases that were produced, but a few solubility data are also given. Additional solubility data were given in a later paper (63). All the data are shown on Figure 6. Another study of this system was made at 295 K (64). In this study Cu(OH)$_2$ was used as the copper compound rather than CuO. When the SO$_3$ was introduced as CuSO$_4$ rather then as H$_2$SO$_4$, the solubility of Cu(OH)$_2$ was practically unaffected, Figure 7. These results are all consistent with each other. The main difference is the extent of the hydration of the solid phases. This difference is probably related to the relatively imprecise methods of analysis. The values in refs. (62, 63, 64) serve to complement each other. They do not duplicate each other. Therefore all the values in these reports are accepted tentatively.

Solubility in sea water

In spite of the fact that copper compounds are used in marine anti-fouling paints, there are practically no data for the solubility of CuO or Cu(OH)$_2$ in sea water. On the basis of calculations (not on a solubility study) the solubility of Cu(OH)$_2$ in sea water is said to be 2.1 x 10^{-7} mol dm^{-3} and that of CuO is 1.4 x 10^{-8} mol dm^{-3} (65). These calculations assumed a value of 5.6 x 10^{-20} for the solubility product constant of Cu(OH)$_2$, and a value of 0.63 mol dm^{-3} for the ionic strength of sea water. The experimental measurement of the solubility of CuO in Baltic Sea water (66) gave a value of 1.3 x 10^{-6} mol dm^{-3} at about 290 K. Apparently, the solubility of Cu(OH)$_2$ or CuO in sea water is so small that it is difficult to measure precisely, and the values that have been suggested are not to be considered as reliable.

Solubility under hydrothermal conditions

The solubility of CuO in water under hydrothermal conditions has been measured in connection with a study of the cause of deposits on a high-pressure turbine used in an electric power generator (67). The amounts of CuO that dissolved were very small and there is no information about the analytical procedure that was used to measure these small quantities. In another study of this system (68) lower temperatures and higher pressures were used. The analytical method was described. Hearn, et al. (68) state that their results are almost ten times those of Pocock and Stewart (67). This is difficult to ascertain because the conditions of temperature and pressure are not exactly duplicated in the two papers. Neither set of data can be recommended but that of Hearn, et al. (68) is tentatively accepted at this time because in that work more attention was paid to experimental detail and reproducibility of results.

Marshall and co-workers have investigated complex systems involving CuO-SO$_3$ and other metal oxides, such as NiO (69) and UO$_3$ (70) at elevated

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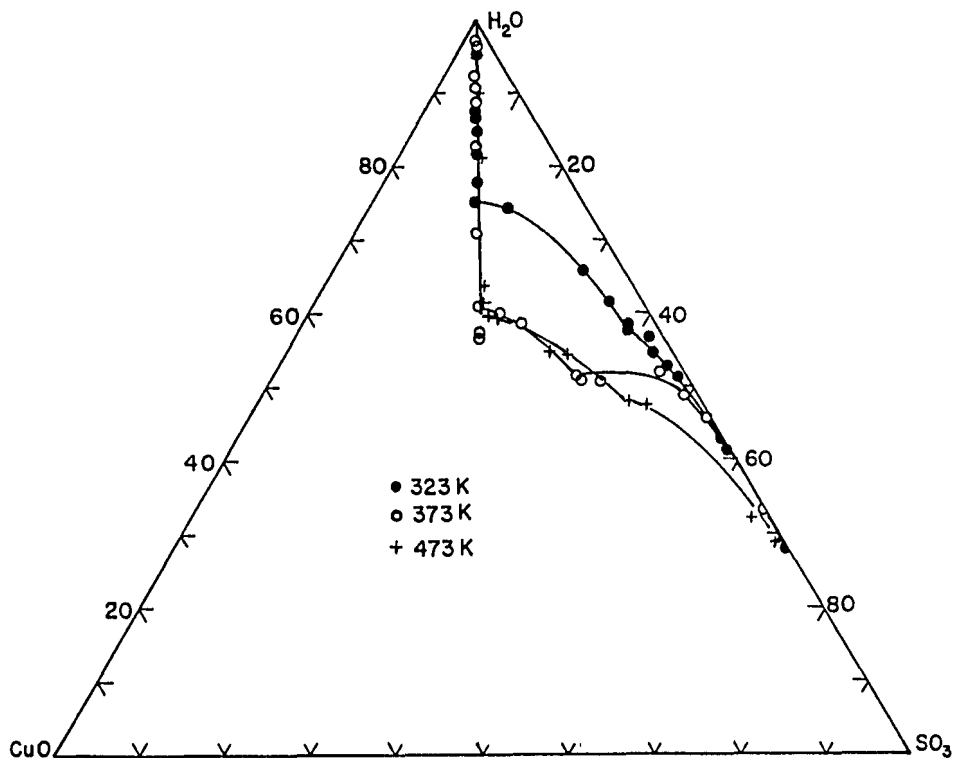
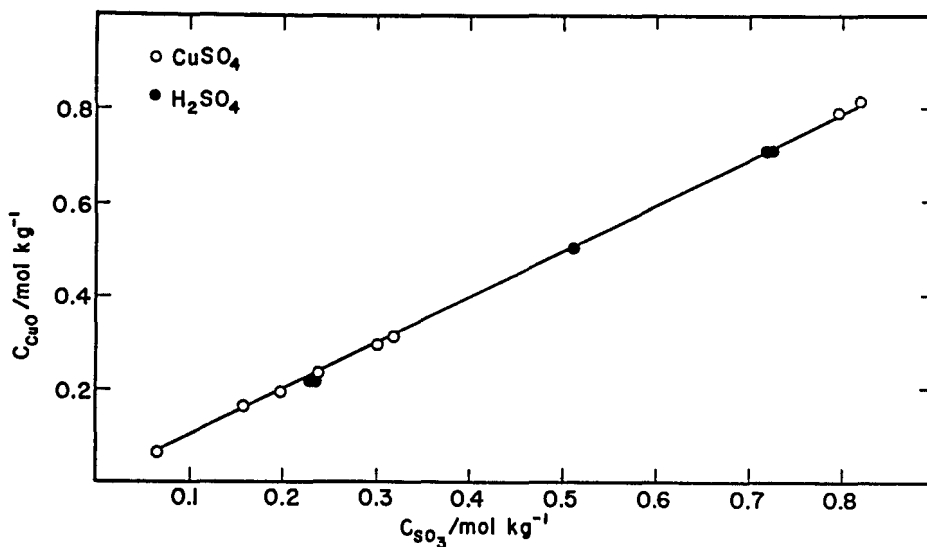Figure 6. The CuO-SO$_3$-H$_2$O system, refs. (62, 63). The scale units are in mass %.

Gigure 7. The Cu(OH)$_2$-SO$_3$-H$_2$O system at 295 K, ref. (64): open circles, SO$_3$ introduced as CuSO$_4$; closed circles, SO$_3$ introduced as H$_2$SO$_4$.

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temperatures, but they studied the solubility of complex copper compounds rather than CuO in these systems. The tabular data indicate the temperature at which liquid-liquid immiscibility appears but include no analysis of the liquid phases (71).

Because of an interest in the leaching and deposition of minerals in the earth, a study was made of the solubility of CuO in some salt solutions in contact with CO_2 at elevated pressures. The first report (72) contained very few data and there are inconsistencies between data in the text and in the Tables. A more complete report was published later (73). The data in this later report can only be accepted as tentative values because no other work similar to it has been reported.

There is a report of the solubility of $Cu(OH)_2$ in boiling water at 459 and 631 K (74). However, the data are presented only in graphical form and the article includes very few experimental details. The solubility decreases with increasing pH up to a value of pH = 7 and then is constant in the pH range 7 to 12. The solubility in this range is $17 - 25$ μg kg^{-1} when the temperature is 631 K and the pressure is about 1.9×10^7 Pa.

The solubility of CuO in aqueous NaOH was measured at temperatures up to 473 K (24). They are the only solubility data reported under such conditions. There is no reason to doubt these values, but because they have not been duplicated they must be classified as tentative. As a result of this work equations are given for the equilibrium constants of reactions (3a) and (4a). They are:

$$\log K_{3a} = \frac{691.74}{T/K} - 1.568 \qquad\qquad (8)$$

$$\log K_{4a} = -\frac{558.40}{T/K} - 2.257 \qquad\qquad (9)$$

Solubilities in aqueous salt solutions

One investigation has been made of the solubility of CuO in solutions of sodium citrate and sodium oxalate, with and without NaOH (75). The study was made at room temperature. The results that were reported were preliminary and qualitative. One conclusion of the study was that the rate and extent of the dissolution of CuO was controlled by the OH⁻ ions.

Lamure (76) investigated the $Cu(OH)_2$-$HgCl_2$-H_2O system in the temperature range 290 to 373 K. However, he merely reported the composition of the solid phases that were formed, and included no solubility data.

The system $Cu(OH)_2$-$CuCl_2$-H_2O was studied at 298 and 473 K by Walter-Levy and Goreaud (77, 78), but the only data given in the articles are about the solid phases. No data are given for the liquid phases.

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        A study has been made of the solubility of $Cu(OH)_2$ in solutions of NaCl and Na_2SO_4 (8) but no experimental details are given and the results are presented only in graphical form.

Solubility in other systems

Solutions of hydrogen peroxide. One report deals with this system and the primary interest appears to have been the isolation of copper(II) peroxides (9). The study was made over the temperature range 237 to 293 K but the copper content of the saturated solutions is given only for two temperatures: 253 and 273 K. Very few experimental details are included. Consequently, the results must be considered doubtful.

Solutions of 2, 2', 2''-nitrilotriethanol (triethanolamine). Only one report discusses this system (79). Only two data are given (for the solubility of CuO) but these are rejected because no temperature is specified, there is no assurance of saturation, and nothing is stated about the quality of the materials that were used.

Table I. Tentative values for equilibria at 298 K.

Reaction	Value
solubility of CuO in H_2O	2.9×10^{-5} mol dm^{-3}
$CuO(s) + H_2O = Cu^{2+} + 2OH^-$	$K_{2a}^o = 4.47 \times 10^{-21}$
$CuO(s) + H_2O + OH^- = Cu(OH)_3^-$	$K_{3a}^o = 10.3 \times 10^{-6}$
$CuO(s) + H_2O + 2OH^- = Cu(OH)_4^{2-}$	$K_{4a}^o = 81 \times 10^{-6}$
$Cu(OH)_2(s) = Cu^{2+} + 2OH^-$	$K_2^o = K_{s0}^o = 4.8 \times 10^{-20}$

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