Solution Thermochemistry of CuO and Entropy of the Aqueous Cupric Ion

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The heats of reaction of $CuO-Cu(OH)_2-H_2O$ samples with aqueous $HClO_4$ have been obtained as a function of concentration. Extrapolated to the normal standard state, the values are $\Delta H^\circ_{298} = -15.0_0$ and -15.3_7 kcal. per mole for CuO and $Cu(OH)_2$, respectively. These data are consistent with thermochemical paths based on data in the literature. The entropy of $Cu^{2+}(aq)$ has been determined as -21.5 ± 1.5 cal. per mole °K. No evidence was obtained for stable "hydrates" of CuO in the H_2O/CuO range 0 to 1.25.

MAH *et al.* (*8*) reviewed the literature data for the thermodynamics of formation of Cu_2O and CuO, and presented new heat capacity, heat content, and heat of combustion data. They also selected what they consider the best values for the various thermochemical quantities. Bidwell (*2*) reported high-temperature cell data from which some of the same information can be obtained. The authors' interests have been in the solution thermochemistry of CuO and $Cu(OH)_2$, and in the thermodynamic properties of the aqueous Cu^{2+} ion, with concomitant investigation of the stability of phases in the $CuO-Cu(OH)_2-H_2O$ system as precipitated from aqueous media. Sillen and Martell (*13*), in their compilation of stability constants, cite solubility products for $Cu(OH)_2$, and for "active" and "inactive" forms of CuO. They conclude that only the latter is stable in contact with alkaline solutions containing $Cu^{2+}(aq)$ ion.

The data to be presented are heats of reaction of various compositions in the system, $CuO-Cu(OH)_2-H_2O$, with aqueous perchloric acid. The data have been obtained as a function of concentration and extrapolated to the conventional standard state for use in thermochemical cycles involving the $Cu^{2+}(aq)$ ion.

EXPERIMENTAL

Table II contains the analyses of the calorimetric samples. Those samples designated I, II, and III were prepared by dehydration of precipitates formed by sodium hydroxide addition to cupric sulfate solutions. Those designated IVA and VA were prepared after the method suggested by Weiser *et al.* (*15*). Samples IVB-F and VB are partial dehydrations of IVA and VA, respectively. Qualitative analyses for anions from possible double salts were negative. Analyses for compositions within the system were performed by an x-ray diffraction method described below.

Composition Analyses. Determination of the relative thermodynamic stabilities of metal oxides and hydroxides often requires composition analyses for ternary mixtures containing the oxide, the hydroxide, and "free" water, adsorbed onto one or both of the solid phases. The quantitative analyses are usually obtained from the sample mass, the total mass of metal, and the mass of free water.

Complications arise for a number of systems for which the standard techniques (*9*) for the determination of free water yield inconclusive results. The system $CuO-Cu(OH)_2-H_2O$ is one such system. Because $Cu(OH)_2$ decomposes at 82.5° C. (*2*), oven-drying to obtain the water content is unsuitable. Vacuum-drying at lower temperatures is extremely slow. Karl Fischer Analysis, seemingly the best method for water determination, is unsatisfactory because of the reaction of the Karl Fischer Reagent (KFR) with $Cu(OH)_2$. Nor is this last observation useful, because the reaction with KFR is not quantitative. Several modifications of the Karl Fischer method involving the extraction of free water from the mixture with one or more solvents were attempted in this laboratory and by a commercial testing laboratory. While improvement was obtained, the results were still of insufficient precision for composition analysis.

All x-ray measurements were made using a wide range goniometer equipped with a scintillation detector and auxiliary x-ray generating equipment, and a Mark II data processor manufactured by the Norelco Division, Phillips Electronic Instrument Co. Samples were pressed to a constant density in a custom-made spring-loaded press. Copper hydroxide was prepared by a procedure described by Weiser *et al.* (*15*). Copper oxide was prepared by the thermal decomposition of the hydroxide at 120° C. Phase purities were verified by comparison of x-ray diffraction patterns with data in the ASTM files (*12*).

Table I. Typical X-Ray Data: Sample Contains 80.69% $Cu(OH)_2$

19–22°2θ			23–5°2θ			26–9°2θ		
Seconds	Counts	Counts per sec.	Seconds	Counts	Counts per sec.	Seconds	Counts	Counts per sec.
179.851	12055	67.0	120.057	13216	110.1	179.814	10715	59.6
179.958	12098	67.2	120.350	13122	109.0	179.947	10813	60.1
180.095	12202	67.8	119.999	13064	108.9	179.790	10794	60.0
179.785	12105	67.3	119.978	13151	109.6	179.993	10819	60.1
		av. 67.3			av. 109.4			av. 60.0

$$r = \frac{109.4 - 63.7}{63.7} = 0.717$$

Standard samples were prepared by grinding weighed quantities of previously analyzed $Cu(OH)_2$ and CuO in an agate mortar until the mixture was of uniform color. The samples were then pressed into the holders supplied with the goniometer, and counts per unit time were recorded over the ranges 2θ = 19–22°, 23–5°, and 26–9°. The data for the lower and upper ranges, which contain neither an oxide nor a hydroxide peak, were used to assess the background radiation. The range 2θ = 23–5° includes the strongest $Cu(OH)_2$ peak that does not overlap a CuO peak. The goniometer was set at a scan speed of 1° per minute; CuK_α radiation was used; and a pulse height analyzer was used to exclude as much of the background as possible. Six standard samples were prepared with a range of [moles $Cu(OH)_2$/total moles Cu] between 0.00 and 1.00. At least four determinations were made for each sample. The average of counting rates in counts per second over the two background ranges was assumed to represent the background in the range of the $Cu(OH)_2$ peak. A separate series of runs over a region not containing any peaks indicated that the background is a linear function of 2θ over a limited range (*ca.* 10°). Data for a typical run are given in Table I.

The ratio

$$r = \frac{(\text{counting rate, 23–5°}) - (\text{average background})}{(\text{average background})}$$

was a linear function of [moles $Cu(OH)_2$/total moles Cu] for the standard samples. These data were fitted to the least squares straight line, [moles $Cu(OH)_2$/total moles Cu] = 0.0022 + 1.121r, with an r.m.s. deviation of ±0.008. Assumption that the background is a linear function of 2θ would require that the constant term in the least squares straight line be zero. These data bear this out within the experimental uncertainty.

The *particular* straight line represented by the equation above is valid for the authors' method of grinding and pressing the sample, and for their diffraction apparatus. The method, however, is general, requiring only the establishment of uniform sample-handling procedures and the preparation of a laboratory standard curve.

Calorimetry. Heats of solution of the solid samples were determined in 1.10M $HClO_4$(aq) to avoid the aqueous complexes formed by Cu^{2+}(aq) and the hydrohalic acids. The acid concentration was chosen as a compromise in minimizing both the time required for dissolution, typically 4 to 5 minutes, and calculational difficulties in extrapolation to infinite dilution. The calorimetric system has been described previously (*14*).

An exhaustive series of measurements involving sample VA was performed to determine the concentration-dependence of the heat of reaction data. Variations involving final Cu^{2+}(aq) concentrations between 0.0018 and 0.010m and acid strengths between 0.11 and 1.10M resulted in 25 data points that were fitted, by least squares, to the relationship

$$\Delta H = -14.78 + 0.524\,M^{1/2}\,[1 + (m/M)]\ \text{kcal. per mole}$$

with an r.m.s. deviation of ±0.11 kcal. per mole. This empirical relationship was assumed valid in extrapolating data for all samples to infinite dilution. The limiting slope, 0.524, is comparable to the limiting heats of dilution of 1 to 1 electrolytes (*10*).

The extrapolated molar heats of reaction, ΔH°_{298}, are also presented in Table II. Each entry represents the mean of from three to seven identical determinations. The final copper concentrations in all cases, other than those from sample VA discussed above, were the same. Thus, any errors in extrapolation become negligible when the results for two or more samples are compared.

The heats of reaction are also depicted in Figure 1 as a function of the ratio (moles H_2O/mole Cu), where the moles H_2O include water present in a bound hydrate—e.g., 1 H_2O in $Cu(OH)_2 = CuO\cdot H_2O$—and unbound water. The heats of reaction corresponding to values of the ratio of 0 and 1 are the heats of reaction of CuO and $Cu(OH)_2$, respectively.

$$CuO(c) + 2H^+(aq) = Cu^{2+}(aq) + H_2O(liq)\ \Delta H^\circ = -15.0_0\ \text{kcal. per mole}$$

$$Cu(OH)_2(c) + 2H^+(aq) = Cu^{2+}(aq) + H_2O(liq)\ \Delta H^\circ = -15.3_7\ \text{kcal. per mole}$$

The authors estimate uncertainties of 0.25 kcal. per mole in these extrapolated quantities.

Table II. Compositions and Heats of Reaction

Sample	X_{CuO}	$X_{CuO(OH)_2}$	n_{H_2O}	ΔH°, Kcal. per Mole
I	1.000	0.000	0.033	−15.06
II	1.000	0.000	0.245	−15.41
III	0.691	0.309	0.290	−16.02
IVA	0.000	1.000	0.170	−14.98
IVB	0.073	0.927	0.164	−15.44
IVC	0.580	0.420	0.210	−15.99
IVD	0.649	0.351	0.279	−16.16
IVE	1.000	0.000	0.212	−16.82
IVF	1.000	0.000	0.027	−15.47
VA	0.000	1.000	0.223	−14.94
VB	0.282	0.718	0.183	−15.47

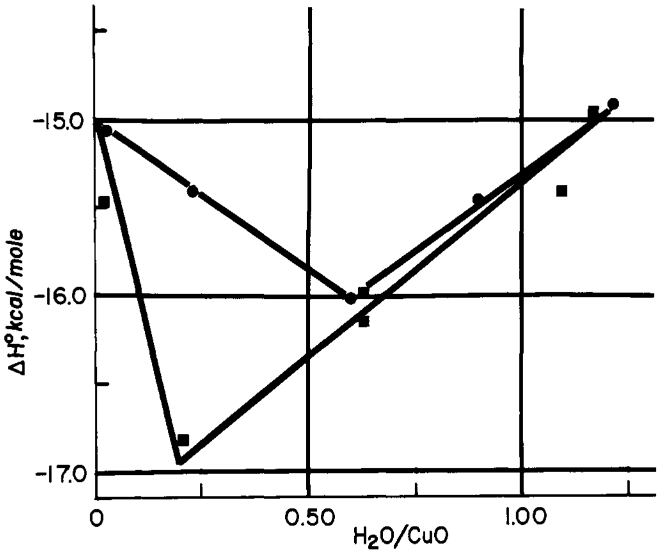

Figure 1. Heats of reaction of CuO samples with $HClO_4$

■ Samples IVA-IVF

● Other samples

Figure 1 is somewhat unusual in appearance, with the apparent preparation-dependent minimum in the heat of reaction. Support for this behavior can be obtained from reports in the literature. Sabatier (*11*), in 1897, reported heats of reaction of CuO and "brown" and "blue" $Cu(OH)_2$ with "dilute" nitric acid as −16.2, −16.4, and −15.9 kcal. per mole, respectively. If one associates his "brown" $Cu(OH)_2$ with the authors' samples at 0.6 H_2O/Cu (brown in color), there are similar minima in the two studies. De Forcrand (*3*), in 1913, reported heats of reaction of successively "drier" $Cu(OH)_2$ samples with nitric acid. These became more endothermic with increasing water content, similar to the behavior shown by the present systems. His result for "CuO" was, however, considerably more exothermic than that for any hydrated sample. Fricke *et al.* (*4*), in 1938, reported heats of reaction of oven-dried CuO with hydrochloric acid. The results became more endothermic as the oven temperature was increased. If one assumes that higher drying temperatures decreased the water content, this behavior is similar to the authors' results at low H_2O/Cu ratios.

Because of differences in solvent, concentrations, temperatures, etc., it is difficult to make a direct comparison of these literature values with the present work. The most logical comparison is for the heat of hydration of CuO to $Cu(OH)_2$(c, "blue"), i.e.,

$$CuO(c) + H_2O(liq) = Cu(OH)_2(c) \cdot \Delta H^\circ_{298}$$

The values in kcal. per mole are: 0.3 (Sabatier), 1.7 (De Forcrand), 0.6 to 2.1 (Fricke *et al.*), and 0.3_8 (this work).

An alternate path to this ΔH° value is available. Sillen and Martell (*13*) compiled data from which we calculate $\Delta G^\circ_{298} = 2.3_2$ kcal. per mole. Latimer's (*7*) method of estimating entropies can be used to give $\Delta S^\circ_{298} = -7 \pm 1$ cal. per mole °K., leading to $\Delta H^\circ_{298} = 0.2_4 \pm 0.3$ kcal. per mole—certainly in accord with the present experimental value.

Mah *et al.* (*8*) give $\Delta H^\circ_f = -37.23$ kcal. per mole of CuO, and the data of Bidwell (*2*) permit calculation of −37.23 kcal. per mole for the same quantity. These values and the present heats of reaction lead to $\Delta H^\circ_f = 16.1 \pm 0.3$ kcal. per mole for $Cu^{2+}(aq)$. Latimer (*7*) cites $\Delta G^\circ_f = 15.53$ kcal. per mole. Combination of these last two values leads to a partial molal entropy of $\bar{S}^\circ_2 = -21.5 \pm 1.5$ cal. per mole °K. for $Cu^{2+}(aq)$. Ko and Hepler (*5*) list -20.4 ± 1.0 cal. per mole °K. for this value, based on their calculations involving older literature data.

If Latimer's (*1, 7*) estimate that the entropy of bound water is approximately 9.3 cal. per mole °K. (*1*) is adopted, then ΔG°_f values calculated from these new heats of reaction show that no stable phases of $CuO \cdot nH_2O$ exist in the range $n = 0$ to $n = 1.2$. This finding is in accord with the relative solubility products for CuO and "$Cu(OH)_2$". For the latter species—i.e., $n = 1$—$\Delta H^\circ_f = -105.1$ kcal. per mole and $\Delta G^\circ_f = -84.8$ kcal. per mole, with an estimate of $\bar{S}^\circ_2 = 20$ cal. per mole °K.

A more recent study (*6*) gives $\Delta H^\circ_f = -15.7$ kcal. per mole and $\bar{S}^\circ_2 = -23.6 \pm 1.3$ cal. per mole °K. for $Cu^{2+}(aq)$, as based on the solution thermochemistry of $CuSO_4$ hydrates. Until the experimental uncertainties can be reduced, the authors suggest adoption of $\Delta H^\circ = 15.9$ kcal. per mole and $\bar{S}^\circ = -22.5$ cal. per mole °K. for Cu^{2+} (aq).

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