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Enthalpies of Formation of Cupric and Cuprous Bromides

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Enthalpies of Formation of Cupric and Cuprous Bromides

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ENTHALPIES OF FORMATION OF CUPRIC AND CUPROUS BROMIDES

by

Hon-Chung Ko[1] and D. W. Richardson[2]

ABSTRACT

This Bureau of Mines report provides the enthalpies of formation of cupric bromide and cuprous bromide as determined by hydrochloric and hydrobromic acid solution calorimetry. At 298.15 K, the values are -33.10 ± 0.4 kcal/mole for $CuBr_2$, and -25.24 ± 0.25 kcal/mole for CuBr.

INTRODUCTION

Earlier Bureau of Mines investigations reported thermodynamic properties for some metallurgically important copper compounds: cupric oxide (CuO) and cuprous oxide (Cu_2O) (12),[3] cupric sulfate ($CuSO_4$) and cupric oxysulfate ($CuO \cdot CuSO_4$) (3), and chalcopyrite ($CuFeS_2$) and bornite (Cu_5FeS_4) (14). As part of a continuing thermodynamic program on compounds of copper, calorimetric studies were carried out in this Bureau of Mines research to determine the standard enthalpies of formation of cupric bromide ($CuBr_2$) and cuprous bromide (CuBr). Values reported in the literature vary by nearly 2 kilocalories for cupric bromide and by more than 1 kilocalorie for cuprous bromide. Therefore, the objective of this investigation was to improve the accuracy of the enthalpies of formation for these two compounds.

MATERIALS

The reference compounds used in this investigation were cupric oxide, cuprous oxide, sodium bromide, and sodium chloride. The sources and analyses of these compounds, as well as cupric bromide and cuprous bromide, are given in the following paragraphs.

Cupric oxide (CuO) was prepared by dissolving pure copper metal in concentrated nitric acid, heating to dryness, and then igniting at 750° C for 2 hours. The compound was then ground to minus 150 mesh. X-ray diffraction analysis showed the product to be cupric oxide. Chemical analysis showed

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[2] Research chemist (now retired).

[3] Underlined numbers in parentheses refer to items in the list of reference at the end of this report.

79.83 pct copper compared with the theoretical value of 79.88 pct. The only impurity detected spectrographically was titanium, present at less than 30 ppm.

Cuprous oxide (Cu_2O) was prepared by heating a portion of the cupric oxide at 925° to 985° C for 45 hours in a dry atmosphere of nitrogen. The resulting cuprous oxide was ground to minus 325 mesh and finally heated at 950° C for 2 hours. Analysis showed 88.83 pct copper. The theoretical copper content is 88.82 pct. Only cuprous oxide was detected by X-ray diffraction. Impurities detected spectrographically were less than 30 ppm silicon and 10 to 100 ppm titanium.

Cupric bromide ($CuBr_2$) was prepared by reacting a portion of the cupric oxide with hydrobromic acid. Water was removed by evaporation in vacuum over sulfuric acid. Analysis of the product showed 28.48 pct copper and 71.54 pct bromine. The theoretical amounts are 28.45 pct copper and 71.55 pct bromine. X-ray diffraction analysis confirmed the material to be cupric bromide. No significant impurities were detected spectrographically.

Cuprous bromide (CuBr) was prepared by thermodecomposition of cupric bromide at 250° C under a stream of argon. Analysis showed 44.26 pct copper and 55.69 pct bromine. The theoretical amounts are 44.30 pct copper and 55.70 pct bromine. Only cuprous bromide was detected by X-ray diffraction analysis. Only negligible amounts of impurities were found spectrographically.

Sodium bromide and sodium chloride were reagent-grade compounds that were used without further treatment except for drying at 110° C.

The solvents, $HCl\cdot 12.731H_2O$ (4.360 molal HCl) and $HBr\cdot 0.007Fe_2(SO_4)_3\cdot 50H_2O$ [1.110 molal HBr and 0.0078 molal $Fe_2(SO_4)_3$], were prepared from reagent-grade materials. Chemical analyses confirmed the compositions as given.

APPARATUS AND PROCEDURE

The solution calorimeter employed in this investigation and the method of operation were described by Mrazek (<u>13</u>). A few changes were made as follows:

1. The resistance of the nickel thermometer was measured by means of a guarded potentiometer-nanovolt galvanometer combination, which also was used to measure the current and voltage across the heater during electrical calibration. The measurement unit has a resolution of 0.01 to 0.02 μv when the six-dial potentiometer (maximum 1 volt) is set at x 1 scale and the galvanometer is set for the 1 μv range. The thermometer has a sensitivity of approximately 1,000 μv/deg.

2. The stopwatch previously used for timing during electrical calibration was replaced by a precision electronic timer.

3. A precision constant direct current source was incorporated in the calibration circuit to replace lead storage batteries.

The solution media were 2,131.1 g of $HCl\cdot 12.731H_2O$ and 2,110.0 g of $HBr\cdot 0.007Fe_2(SO_4)_3\cdot 50H_2O$ for the cupric bromide and cuprous bromide systems, respectively. The temperature of operation was 298.15 K. All measured heat values are expressed as defined kilocalories (1 kcal = 4,184.0 joules). Weighings were corrected to vacuum, and molecular weights are in accordance with the 1969 table of atomic weights.

Throughout this report, precision uncertainties were assigned to measured and derived heat values as follows: (1) When several individual heat values were measured for a reaction, the precision uncertainty was taken as twice the standard deviation of the mean; (2) when the heats of two or more reactions were combined, the uncertainty of the resulting reaction was taken as the square root of the sum of squares of the individual uncertainties.

ENTHALPIES OF FORMATION

Cupric Bromide

The reaction scheme for obtaining the enthalpy of formation of cupric bromide is given in table 1. The symbols s, l, and sol denote substances that are crystalline, liquid, and in solution, respectively. The reactions are written in an abbreviated form sufficient to show that stoichiometry was maintained. Table 1 also lists the average measured heat values and precision uncertainties for the individual reactions. A quantity of 0.010 g-mole of cupric bromide was used as the weight basis for this scheme and other substances conformed stoichiometrically with this quantity.

TABLE 1. - Reaction scheme for $CuBr_2$

Reaction	ΔH, kcal	Uncertainty, kcal
(1) $26.462H_2O(l) = 26.462H_2O(sol)$.....................	-2.01	0
(2) $2NaCl(s) = 2Na^+(sol) + 2Cl^-(sol)$..................	3.86	0.02
(3) $CuBr_2(s) = Cu^{+2}(sol) + 2Br^-(sol)$..................	-2.72	.02
(4) $2[HCl\cdot 12.731H_2O](l) = 2H^+(sol) + 2Cl^-(sol) + 25.462H_2O(sol)$..................................	0	.02
(5) $2NaBr(s) = 2Na^+(sol) + 2Br^-(sol)$..................	1.36	.02
(6) $CuO(s) + 2H^+(sol) = Cu^{+2}(sol) + H_2O(sol)$..........	-12.57	.04

$$\Delta H_7 = \Delta H_4 + \Delta H_5 + \Delta_6 - \Delta H_1 - \Delta H_2 - \Delta H_3$$

(7) $2[HCl\cdot 12.731H_2O](l) + 2NaBr(s) + CuO(s) = 26.462H_2O(l) + 2NaCl(s) + CuBr_2(s)$

$$\Delta H_7(298.15) = -10.34 \pm 0.06 \text{ kcal}$$

Reactions 1, 2, and 3 were measured consecutively in 2,131.1 g of solvent, $HCl\cdot 12.731H_2O$. Reactions 4, 5, and 6 were measured consecutively in a fresh portion of 2,131.1 g of solvent. Reaction 4 was measured by Coughlin (1) who reported the heat of this reaction to be 0 ± 0.010 kcal/mole. The experimental heats of solution for reactions 1, 2, 3, 5, and 6 are given in table 2 with their mean values and uncertainties listed on the bottom line.

TABLE 2. - Experimental heat of solution data at 298 K, kcal/mole

$H_2O(l)$, reaction 1	$NaCl(s)$, reaction 2	$CuBr_2(s)$, reaction 3	$NaBr(s)$, reaction 5	$CuO(s)$, reaction 6
-0.0762	1.939	-2.715	0.6716	-12.565
-.0760	1.930	-2.763	.6828	-12.628
-.0760	1.944	-2.708	.6689	-12.509
-.0760	1.924	-2.705	.6726	-12.615
-.0761	1.931	-2.729	.6794	-12.540
-.0762	-	-2.726	.6893	-12.586
-0.0761 ±0.0001	1.93 ±0.01	-2.72 ±0.02	0.68 ±0.01	-12.57 ±0.04

The final solution after conducting consecutive reactions 1, 2, and 3 is the same as that after conducting consecutive reactions 4, 5, and 6. Therefore, these reactions and their heats can be combined to give the overall calorimetric reaction 7 and a value of -10.34 ± 0.06 kcal for ΔH_7 at 298.15 K.

The enthalpy of formation of cupric bromide is obtained by combining the heat of reaction 7 with the enthalpies of formation of cupric oxide, sodium bromide, $HCl\cdot 12.731H_2O$, sodium chloride, and water at 298.15 K.

$$Cu(s) + 1/2O_2(g) = CuO(s)$$
$$\Delta H_8 = -37.20 \pm 0.10 \text{ kcal/mole;} \tag{8}$$

$$Na(s) + 1/2Br_2(l) = NaBr(s)$$
$$\Delta H_9 = -86.38 \pm 0.10 \text{ kcal/mole;} \tag{9}$$

$$1/2H_2(g) + 1/2Cl_2(g) + 12.731H_2O(l) = HCl\cdot 12.731H_2O(l)$$
$$\Delta H_{10} = -38.82 \pm 0.04 \text{ kcal/mole;} \tag{10}$$

$$Na(s) + 1/2Cl_2(g) = NaCl(s)$$
$$\Delta H_{11} = -98.26 \pm 0.08 \text{ kcal/mole;} \tag{11}$$

$$H_2(g) + 1/2O_2(g) = H_2O(l)$$
$$\Delta H_{12} = -68.315 \pm 0.010 \text{ kcal/mole.} \tag{12}$$

The enthalpy of formation for cupric oxide was from King, Mah, and Pankratz (11). The enthalpy changes for reactions 9 and 11 were from the JANAF tables (2). The enthalpy changes for reactions 10 and 12 were from Wagman (19). Combination of reactions 7, 8, 9, 10, 11, and 12 gives the formation reaction 13 for cupric bromide.

$Cu(s) + Br_2(l) = CuBr_2(s)$

$\Delta H_{13} = \Delta H_7 + \Delta H_8 + 2\Delta H_9 + 2\Delta H_{10} - 2\Delta H_{11} - \Delta H_{12}$

$\Delta Hf°(298.15) = -33.10 \pm 0.30$ kcal/mole. (13)

Cuprous Bromide

The solution medium was $HBr \cdot 0.007Fe_2(SO_4)_3 \cdot 50H_2O$. The presence of $Fe_2(SO_4)_3$ insured the oxidation of Cu^{+1} to Cu^{+2} ions in solution. Tests demonstrated qualitatively that no Cu^{+1} ions were present after CuBr was dissolved in this solvent. The reaction scheme for obtaining the enthalpy of formation of cuprous bromide is given in table 3. A quantity of 0.020 g-mole of cuprous bromide was used as the weight basis for this scheme, and other substances conformed stoichiometrically with this quantity. Also listed in table 3 are the average measured heat values and precision uncertainties for the individual reactions.

TABLE 3. - Reaction scheme for CuBr

Reaction	ΔH, kcal	Uncertainty, kcal
(14) $50.5H_2O(l) = 50.5H_2O(sol)$...........................	-0.22	0.01
(15) $CuBr(s) + Fe^{+3}(sol) = Cu^{+2}(sol) + Fe^{+2}(sol) + Br^-(sol)$..	2.32	.02
(16) $HBr \cdot 50H_2O(l) = H^+(sol) + Br^-(sol) + 50H_2O(sol)$......	.01	.01
(17) $1/2Cu_2O(s) + Fe^{+3}(sol) + H (sol) = Cu^{+2}(sol) + Fe^{+2}(sol) + 1/2H_2O(sol)$..............	-8.19	.11

$\Delta H_{18} = \Delta H_{16} + \Delta H_{17} - \Delta H_{14} - \Delta_{15}$

(18) $HBr \cdot 50H_2O(l) + 1/2Cu_2O(s) = 50.5H_2O(l) + CuBr(s)$

$\Delta H_{18}(298.15\ K) = -10.28 \pm 0.11$ kcal

Reactions 14 and 15 were measured consecutively in 2,110.0 g of solvent, $HBr \cdot 0.007Fe_2(SO_4)_3 \cdot 50H_2O$. Reactions 16 and 17 were measured consecutively in a fresh portion of 2,110.0 g of solvent. The experimental heats of solution for reactions 14, 15, 16, and 17 are given in table 4 with their mean values and uncertainties listed on the bottom line.

TABLE 4. - Experimental heat of solution data at 298 K, kcal/mole

$H_2O(1)$, reaction 14	CuBr(s), reaction 15	$HBr\cdot50H_2O(1)$, reaction 16	$Cu_2O(s)$, reaction 17
-0.0043	2.331	0.0165	-16.362
-.0043	2.348	.0020	-16.515
-.0046	2.297	.0083	-16.015
-.0041	2.312	.0201	-16.686
-.0044	2.289	.0132	-16.536
-	-	-	-16.148
-0.0043 ±0.0002	2.32 ±0.02	0.01 ±0.01	-16.38 ±0.21

Combination of reactions 14, 15, 16, and 17 and their respective reaction heats gives the overall calorimetric reaction 18 and a value of -10.28 ± 0.11 kcal for ΔH_{18} at 298.15 K. The standard enthalpy of formation of cuprous bromide is obtained by combining the heat of reaction 18 and the enthalpies of formation of cuprous oxide, $HBr\cdot50H_2O$, and water.

$$2Cu(s) + 1/2O_2(g) = Cu_2O(s)$$
$$\Delta H_{19} = -40.80 \pm 0.20 \text{ kcal/mole;} \quad (19)$$

$$1/2H_2(g) + 1/2Br_2(g) + 50H_2O(1) = HBr\cdot50H_2O(1)$$
$$\Delta H_{20} = -28.719 \pm 0.050 \text{ kcal/mole;} \quad (20)$$

$$H_2(g) + 1/2O_2(g) = H_2O(1)$$
$$\Delta H_{12} = -68.315 \pm 0.010 \text{ kcal/mole.} \quad (12)$$

The enthalpy change for reaction 19 was from King, Mah, and Pankratz (11), and the enthalpy changes for reactions 12 and 20 were from Wagman (19). Combination of reactions 12, 18, 19, and 20 gives the formation reaction 21 for cuprous bromide:

$$Cu(s) + 1/2Br_2(1) = CuBr(s)$$
$$\Delta H_{21} = \Delta H_{18} + 1/2\Delta H_{19} + \Delta H_{20} - 1/2\Delta H_{12}$$
$$\Delta Hf^\circ(298.15) = -25.24 \pm 0.16 \text{ kcal/mole.} \quad (21)$$

DISCUSSION

Considering the high purities of the compounds used in this study, no impurity corrections were found necessary in the derivations of standard enthalpy-of-formation values. However, larger uncertainties than the calculated ones were allowed in the final values to include uncertainties associated with calibration measurements and auxiliary thermodynamic data. The final values for enthalpies of formation of cupric bromide and cuprous bromide are -33.10 ± 0.40 and -25.24 ± 0.25 kcal/mole, respectively.

There are a few reported data for enthalpies of formation of cupric bromide and cuprous bromide in the literature. Paoletti (15), Thomsen (18), Sabatier (16-17), Hammer (4), Hilden (5), and Jackson (7) reported either directly the enthalpy of formation of cupric bromide or data which could be used to derive the desired values, by calorimetric or vapor pressures studies. Kapustinsky (10), Jellinek (9), Jahn-Held (8), Thomsen (18), and Ishikawa (6) reported enthalpy of formation of cuprous bromide or relevant data. King, Mah, and Pankratz (11) reviewed data from these authors and made recalculations wherever necessary. They showed values ranging from -32.37 to -34.25 kcal/mole for cupric bromide and -24.35 to -25.54 kcale/mole for cuprous bromide. The "best" values chosen by weighted averages were -33.4 ($CuBr_2$) and -25.0 (CuBr) kcal/mole. The results obtained by the present investigation agree well with the selections of these compilers and serve to firmly establish the standard enthalpies of formation of the two compounds.

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