RI 7851

Bureau of Mines Report of Investigations/1974

Enthalpy of Formation of Malachite $[Cu_2(CO_3)(OH)_2]$

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 7851

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UNITED STATES DEPARTMENT OF THE INTERIOR
Rogers C. B. Morton, Secretary

BUREAU OF MINES
Thomas V. Falkie, Director

This publication has been cataloged as follows:

Richardson, Dale W

Enthalpy of formation of malachite [$Cu_2(CO_3)(OH)_2$], by D.W. Richardson and R.R. Brown. [Washington] U.S. Bureau of Mines [1974]

5 p. table. (U.S. Bureau of Mines. Report of investigations 7851)

Includes bibliography.

1. Malachite. I. U.S. Bureau of Mines. II. Brown, Robert R., jt. auth. III. Title. (Series)

TN23.U7 no. 7851 622.06173

U.S. Dept. of the Int. Library

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ENTHALPY OF FORMATION OF MALACHITE [$Cu_2(CO_3)(OH)_2$]

by

D. W. Richardson[1] and R. R. Brown[1]

ABSTRACT

This Bureau of Mines publication provides the enthalpy of formation of malachite [$Cu_2(CO_3)(OH)_2$] as determined by hydrochloric acid solution calorimetry. At 298.15 K the enthalpy of formation from the component oxides is -15.10±0.30 kcal/mole and from the elements, -251.9±0.5 kcal/mole.

INTRODUCTION

Malachite [$Cu_2(CO_3)(OH)_2$] and azurite [$Cu_3(CO_3)_2(OH)_2$] are the two mineral copper carbonates having commercial importance. Of the two, malachite is the more abundant. As part of a continuing thermodynamic program on compounds of copper, this paper presents the results of a calorimetric investigation on the enthalpy of formation of a synthetic sample of malachite.

Earlier Bureau of Mines investigations reported thermodynamic properties for other metallurgically important copper compounds: CuO and Cu_2O (5);[2] $CuSO_4$ and $CuO{\cdot}CuSO_4$ (1); and $CuFeS_2$ and Cu_5FeS_4 (7).

MATERIALS

Malachite

The synthetic malachite sample used in this investigation was obtained by partially dehydrating analytical grade basic cupric carbonate in a stream of carbon dioxide. The basic carbonate was heated first at 110° to 118° C for 80 hours and then at 130° to 150° C for 60 hours.

Analysis of the product gave 71.93 pct CuO, 8.48 pct H_2O, and 19.71 pct CO_2. The theoretical composition is 71.95 pct CuO, 8.15 pct H_2O, and 19.90 pct CO_2. Analysis by emission spectroscopy showed that there were no impurities present in significant amounts. For calorimetric purposes, the sample was assumed to be composed of 98.93 pct malachite, 0.81 pct $Cu(OH)_2$, and 0.26 pct H_2O.

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

The X-ray diffraction pattern agreed closely with the standard pattern given by NBS (11).

Cupric Oxide

Reagent-grade CuO that had been ignited at 800° C was used as the reference compound for copper. Chemical and spectrographic analyses combined to show the composition to be 99.94 pct CuO and 0.06 pct H_2O. Other impurities were present in negligible amounts. The sample was assumed to be composed of 99.68 pct CuO and 0.32 pct $Cu(OH)_2$.

ENTHALPY OF FORMATION

The solution calorimeter employed in the investigation and its method of operation were described by Mrazek and coworkers (6). They closely followed the design and methods given by Southard (9). A slight modification was made so that carbon dioxide could be introduced into the reaction solution. The solution was saturated with CO_2 prior to each solution determination and a CO_2 atmosphere was thereafter maintained above the solution so as to assure constant solution saturation.

The solution medium was 2,132.2 g of hydrochloric acid having the composition $HCl\cdot 12.731\ H_2O$. The temperature of operation was 298.15 K. All measured heat values are expressed as defined kilocalories (1 kcal = 4184.0 absolute joules). The atomic weights were taken from the 1969 table of atomic weights (3).

Precision uncertainties of the calorimetric measurements are given as twice the standard deviation of the mean. Absolute uncertainties include, in addition to precision uncertainties, uncertainties associated with the measurements, energy calibrations, impurity corrections, carbon dioxide evolution, and auxiliary thermodynamic data.

The reaction scheme used for obtaining the enthalpy of formation of malachite is given in table 1. The symbols s, l, g, and sol denote substances that are crystalline, liquid, gaseous, and in solution, respectively. A weight of 2.2112 g of malachite served as the weight basis for the calorimetry. The other substances conformed stoichiometrically with this quantity. The table also contains the heat values and absolute uncertainties for the individual reaction steps.

TABLE 1. - Calorimetric reaction scheme

Reaction	ΔH_{298}, kcal	Uncertainty, ±kcal
(1) $Cu_2(CO_3)(OH)_2(s) + 4H^+(sol) = 2Cu^{++}(sol) + CO_2(g) + 3H_2O(sol)$........................	-10.54	0.20
(2) $H_2O(l) = H_2O(sol)$..........................	-0.076	0
(3) $2CuO(s) + 4H^+(sol) = 2Cu^{++}(sol) + 2H_2O(sol)$..	-25.56	0.10
$\Delta H_4 = -\Delta H_1 + \Delta H_2 + \Delta H_3$ (4) $2CuO(s) + H_2O(l) + CO_2(g) = Cu_2(CO_3)(OH)_2(s)$.	-15.10	0.30

Reaction 1 represents the solution of malachite in acid solution that has been saturated with CO_2. By this procedure all of the CO_2 resulting from the solution process will be in the gaseous state. Five determinations were made of the heat. The values before making various corrections were -10.32, -10.48, -10.69, -10.53, and -10.43 kcal for 223.514 g of sample containing 1 mole of malachite plus impurities. The mean is -10.49 kcal with a precision uncertainty of ±0.13 kcal.

In addition to 221.116 g of malachite, the sample contained 1.817 g of $Cu(OH)_2$ and 0.581 g H_2O for which corrections must be made. The correction for $Cu(OH)_2$ is based on the following reactions:

$$CuO(s) + 2H^+(sol) = Cu^{++}(sol) + H_2O(sol)$$

$$\Delta H_5 = -12.78 \text{ kcal}, \quad (5)$$

$$Cu(OH)_2(s) = CuO(s) + H_2O(1)$$

$$\Delta H_6 = 0.400 \text{ kcal}, \quad (6)$$

and

$$H_2O(1) = H_2O(sol)$$

$$\Delta H_7 = -0.076 \text{ kcal}. \quad (7)$$

The heat ΔH_5 is one-half of that in reaction 3 in table 1. The heat for reaction 6 is from King, Mah, and Pankratz (4). Stuve, Pankratz, and Richardson (10) determined ΔH_7.

Correction for the heat of solution of $Cu(OH)_2$ impurity was evaluated as -12.46 kcal/mole or -0.1277 kcal/g from the summation of reactions 5, 6, and 7. The heat of solution correction for excess water was evaluated as 0.324 kcal/mole or 0.018 kcal/g based on an assumed binding energy of 0.4 kcal/mole and the measured heat of solution (reaction 2). When the corrections for $Cu(OH)_2$ and H_2O are applied, the heat of solution of 1 mole of malachite becomes -10.272 kcal.

A correction also was needed for the H_2O vaporization caused by the evolution of CO_2 gas during solution. It was assumed that the CO_2 coming out of the solution was saturated with H_2O. Fritz and Fuget (2) report the vapor pressure of HCl solutions. Their data give 19 torr as the partial pressure of H_2O at 298 K. Taking the heat of vaporization of H_2O, also from Fritz and Fuget (2), to be 10.6 kcal/mole, the vaporization correction for H_2O is 0.27 kcal/mole of CO_2 evolved. The heat effect from the vaporization of HCl is a negligible quantity.

When the vaporization heat is applied, the final value for the heat of solution of malachite as given by reaction 1 becomes -10.54 kcal/mole with an uncertainty estimated to be ±0.20 kcal/mole. The uncertainty includes allowances for the several corrections.

Reaction 2 represents the solution of liquid H_2O. This heat was determined previously under nearly identical conditions by Stuve and coworkers (10) of this laboratory to be -0.076±0 kcal/mole.

Reaction 3, the solution of cupric oxide, was conducted in the solution resulting from reaction 2. Six determinations of the heat gave -12.76, -12.81, -12.78, -12.81, -12.93, and -12.75 kcal for a sample containing 1 mole of CuO and 0.259 g of $Cu(OH)_2$. The mean value is -12.81 kcal with a precision uncertainty of ±0.05 kcal. Proceeding as before, the combination of reactions 5 through 7 gives 0.033 kcal as the solution heat of 0.259 g of $Cu(OH)_2$. The heat of solution of 1 mole of CuO then becomes -12.78 kcal. The absolute uncertainty is 0.10 kcal/mole CuO.

Combination of reactions 1 through 3 in the manner indicated in the table gives the enthalpy of formation of malachite from its component oxides, as follows:

$$2CuO(s) + H_2O(l) + CO_2(g) = Cu_2(CO_3)(OH)_2(s)$$

$$\Delta H_{298} = -15.10 \pm 0.30 \text{ kcal.} \qquad (8)$$

Calculation of the formation from the elements requires values for the standard enthalpies of formation of CuO(s), $CO_2(g)$, and $H_2O(l)$. The following value for CuO is from King and coworkers (4):

$$Cu(s) + 1/2\ O_2(g) = CuO(s)$$

$$\Delta H_{298} = -37.2 \pm 0.15 \text{ kcal.} \qquad (9)$$

The values for CO_2 and H_2O from Wagman and coworkers (12) are as follows:

$$C\ (\text{graphite}) + O_2(g) = CO_2(g)$$

$$\Delta H_{298} = -94.054 \pm 0.01 \text{ kcal,} \qquad (10)$$

and

$$H_2(g) + 1/2\ O_2(g) = H_2O(l)$$

$$\Delta H_{298} = -68.315 \pm 0.01 \text{ kcal.} \qquad (11)$$

The combination of reactions and their enthalpies,

$$\Delta H_8 + 2\Delta H_9 + \Delta H_{10} + \Delta H_{11},$$

gives $2Cu(s) + C\ (\text{graphite}) + H_2(g) + 5/2\ O_2(g) = Cu_2(CO_3)(OH)_2(s)$, (12)

for which $\Delta H_{298} = -251.9 \pm 0.5$ kcal.

Roth and coworkers (8) reported -13.78 kcal for the enthalpy of formation of malachite from its component oxides. They also employed the method of solution calorimetry. The present work provides -15.10 kcal (reaction 8). The difference of approximately 9 percent may be attributable to sample composition. Roth reported only a combined analysis for CO_2 and H_2O, whereas in the present investigation there were separate analyses. Therefore, the value of the enthalpy of formation of -251.9±0.5 kcal/mole as determined in this work is considered more reliable.

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[3] Titles enclosed in parentheses are translations from the language in which the article was published.

INT.-BU.OF MINES,PGH.,PA. 18992