[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

# Low Temperature Heat Capacities of Inorganic Solids. XII. Heat Capacity and Thermodynamic Properties of Cuprous Bromide from 16 to 300°K.[1]

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The heat capacities of cuprous bromide have been measured in the temperature range 14 to 300°K., and the derived thermodynamic functions have been calculated and tabulated at integral values of the temperature over this range. The value of the entropy at 298.16°K. = 22.97 ± 15 e.u. The peculiar shape of the heat capacity curve has been explained in terms of a particular type of force field in which the copper ion moves. Third law is checked through cell measurements.

## Introduction

There is a great deal of similarity between the physical properties of silver iodide and cuprous bromide. Pitzer[2] found a very peculiar shape in the heat capacity curve of the former, which he explained by the assumption that there exists a certain type of potential of the force field, in which the silver ion moves within the relatively rigid tetrahedron of iodide ions. It was therefore thought desirable to measure the heat capacity of the cuprous bromide to see if the same peculiarity existed. No previous measurements have been made on CuBr at low temperatures.

## Apparatus and Materials

The cuprous bromide used was prepared as follows:[3] About 100 g. of cupric sulfate and 40 g. of ammonium bromide were dissolved in 1500 cc. of water, and treated with a stream of sulfur dioxide, forming small white crystals of cuprous bromide. These were filtered rapidly from the mother liquid, washed with sulfurous acid, exposed over potassium hydroxide *in vacuo* for several days and finally transferred into a desiccator with $P_2O_5$ as drying agent.

TABLE I

MOLAR HEAT CAPACITY OF CUPROUS BROMIDE

| Mean $T$, °K. | $\Delta T$ | $C_p$, cal. mole$^{-1}$ deg.$^{-1}$ | Mean $T$, °K. | $\Delta T$ | $C_p$, cal. mole$^{-1}$ deg.$^{-1}$ |
|---|---|---|---|---|---|
| 15.51 | 2.630 | 1.685 | 104.44 | 7.945 | 9.847 |
| 18.09 | 2.149 | 2.025 | 112.43 | 8.311 | 10.13 |
| 20.78 | 2.977 | 2.371 | 131.67 | 10.143 | 10.46 |
| 24.25 | 3.845 | 2.807 | 131.27 | 9.209 | 10.73 |
| 27.71 | 3.156 | 3.243 | 141.41 | 9.770 | 10.98 |
| 30.89 | 3.391 | 3.662 | 150.84 | 9.062 | 11.21 |
| 34.29 | 3.428 | 4.066 | 159.93 | 9.357 | 11.38 |
| 37.90 | 3.775 | 4.568 | 170.11 | 10.995 | 11.57 |
| 42.47 | 5.388 | 5.117 | 180.57 | 10.278 | 11.72 |
| 44.45 | 4.021 | 5.340 | 192.01 | 11.781 | 11.93 |
| 48.54 | 4.278 | 5.800 | 203.50 | 11.046 | 12.04 |
| 52.96 | 4.582 | 6.274 | 214.73 | 10.374 | 12.21 |
| 54.34 | 5.546 | 6.487 | 225.10 | 9.830 | 12.32 |
| 60.35 | 4.509 | 7.094 | 236.25 | 11.161 | 12.49 |
| 66.11 | 8.357 | 7.636 | 247.46 | 10.585 | 12.57 |
| 73.09 | 5.631 | 8.150 | 258.27 | 10.078 | 12.71 |
| 78.58 | 5.190 | 8.584 | 268.22 | 9.669 | 12.75 |
| 84.00 | 5.576 | 8.903 | 277.77 | 9.269 | 12.86 |
| 84.73 | 3.530 | 9.000 | 286.91 | 8.883 | 13.01 |
| 89.87 | 6.719 | 9.250 | 295.83 | 8.531 | 13.11 |
| 96.94 | 7.105 | 9.552 | | | |

The water used for washing the cuprous bromide had previously been boiled in a stream of nitrogen to expel dissolved oxygen which decomposes cuprous bromide. Its copper content was determined by electrolytic analysis and its bromine content was analyzed gravimetrically by precipitation as silver bromide. Assuming that the entire copper and bromine content was derived from cuprous bromide, the sample contained 99.92 and 99.93% of CuBr, respectively.

"Solid Calorimeter No. 6," of the group of seven vacuum calorimeters described in the first paper[4] of this series, was filled with 75.397 g. (0.5254 mole) of cuprous bromide for heat capacity measurements.

## Experimental Results

Experimental heat capacities are summarized in Table I. In Fig. 1 the experimental values are plotted along with the best fitting Debye–Einstein function, but the heat capacity of the cuprous bromide deviates appreciably from the latter.

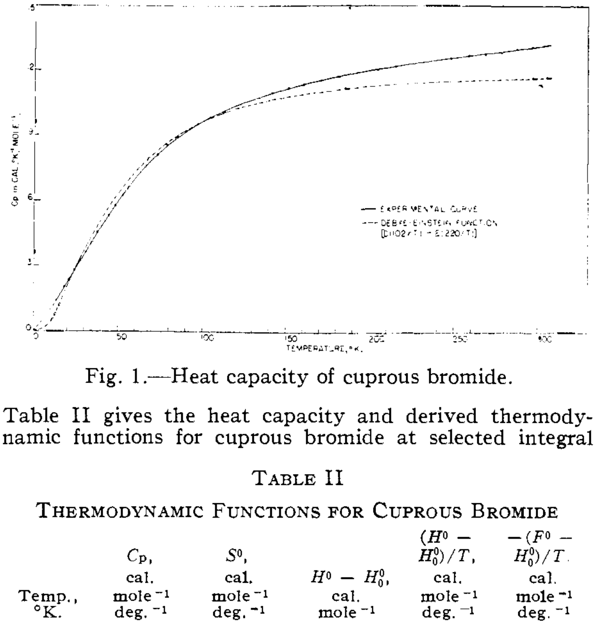

Fig. 1.—Heat capacity of cuprous bromide.

Table II gives the heat capacity and derived thermodynamic functions for cuprous bromide at selected integral

TABLE II

THERMODYNAMIC FUNCTIONS FOR CUPROUS BROMIDE

| Temp., °K. | $C_p$, cal. mole$^{-1}$ deg.$^{-1}$ | $S^0$, cal. mole$^{-1}$ deg.$^{-1}$ | $H^0 - H_0^0$, cal. mole$^{-1}$ | $(H^0 - H_0^0)/T$, cal. mole$^{-1}$ deg.$^{-1}$ | $-(F^0 - H_0^0)/T$ cal. mole$^{-1}$ deg.$^{-1}$ |
|---|---|---|---|---|---|
| 16 | 1.732 | 0.8772 | 9.761 | 0.6101 | 0.2671 |
| 25 | 2.192 | 1.8975 | 30.730 | 1.2292 | 0.6683 |
| 50 | 5.969 | 4.8747 | 142.53 | 2.8506 | 2.0241 |
| 75 | 8.335 | 7.7754 | 323.47 | 4.3129 | 3.4625 |
| 100 | 9.672 | 10.378 | 550.44 | 5.5044 | 4.874 |
| 125 | 10.555 | 12.634 | 803.63 | 6.4290 | 6.205 |
| 150 | 11.180 | 14.617 | 1075.8 | 7.1720 | 7.445 |
| 175 | 11.642 | 16.376 | 1361.3 | 7.7789 | 8.597 |
| 200 | 12.019 | 17.957 | 1657.3 | 8.2865 | 9.670 |
| 225 | 12.337 | 19.391 | 1961.7 | 8.7187 | 10.672 |
| 250 | 12.616 | 20.706 | 2273.8 | 9.0952 | 11.611 |
| 275 | 12.864 | 21.920 | 2592.3 | 9.4265 | 12.494 |
| 298.16 | 13.084 | 22.969 | 2892.8 | 9.7022 | 13.267 |
| 300 | 13.100 | 23.050 | 2916.9 | 9.7230 | 13.327 |

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(2) K. S. Pitzer, THIS JOURNAL, **63**, 516 (1941).

(3) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 3, Longmans, Green and Co., New York, N. Y., 1923, p. 192.

(4) H. L. Johnston and E. C. Kerr, THIS JOURNAL, **72**, 4733 (1950).

values of the temperatures. The entropy at 298.16°K. is 22.97 e.u., of which 0.88 e.u. is contributed by extrapolation below 16°K. Our estimate of the uncertainty in the entropy is ±0.15 e.u., of which ±0.10 e.u. is due to that of the extrapolation.

## Discussion

While the crystal structure of cuprous bromide is cubic[5] (zincblende type), and that of silver iodide is of the wurtzite type,[2] both the silver ion in the latter and the cuprous ion in the former are surrounded tetrahedrally by the respective halide ions; both are ionic conductors[6] with the metallic ions as the sole carrier; and both crystals undergo modifications at high temperatures.[7]

Pitzer[2] explains the odd shape of the heat capacity curve of silver iodide by the assumption that the probable potential energy function for the silver ion has a single minimum at the center of the relative rigid iodide tetrahedron, which rises much more rapidly in the direction of one iodide ion than in the opposite direction toward the hole between the other three.

It is reasonable to expect, therefore, that, since similar potential energy functions exist for both these compounds, the unusual shape of the heat capacity curve of the cuprous bromide may thus also be explained.

## Third Law Check through Cell Measurements

**(a).**—The free energy and heat of formation of cuprous bromide may be calculated from free energies and heats of reaction by the equations

$$\begin{array}{ll}
\text{Cu-amalgam} + \text{AgBr} = \text{Ag} + \text{CuBr} & \Delta F_1,\ \Delta H_1 \\
\text{Cu} = \text{Cu-amalgam} & \Delta F_2,\ \Delta H_2 \\
\text{Ag} + {}^1/_2\text{Br}_2(\text{l}) = \text{AgBr} & \Delta F_3,\ \Delta H_3 \\
\hline
\text{Cu} + {}^1/_2\text{Br}_2(\text{l}) = \text{CuBr(s)} & \Delta F,\ \Delta H,\ \Delta S
\end{array}$$

John-Held and Jellinek[8] have obtained $\Delta F_1 = -633$ cal., $\Delta H_1 = 97$ cal. through the measurements of the cell

$$\text{Cu-amalgam, CuBr} \mid \text{HBr } (0.1\ N) \mid \text{AgBr, Ag}$$

Oku[9] has studied the cell

$$\text{Cu} \mid \text{Cu}^{++} \mid \text{Cu-amalgam}$$

His results are: $E_{298.16} = 0.00512$ volt, $\mathrm{d}E/\mathrm{d}T = -0.0000737$ volt/deg. (0–40°). From which it has been derived $\Delta F_2 = -236$ cal., $\Delta H_2 = -1250$ cal.

Jones and Baeckstrom[10] have obtained $\Delta F_3 = -22{,}940$ cal. through the measurements of the cell

$$\text{Pt, Br}_2(\text{l}) + \text{KBr, KBr, AgBr, Ag}$$

Bertram and Roth[11] give the most probable value of $\Delta H_3$ to be $-23{,}710$ cal. from their own measurements and a consideration of all early data. The uncertainty is estimated to be about 50 cal.

We obtain, finally, $\Delta F = -23{,}809 \pm 20$ cal.; $\Delta H = -24{,}860 \pm 90$ cal. and $\Delta S = -3.52 \pm 0.40$ e.u.

If we substitute the entropies of copper (7.97 ± 0.02)[12] and of bromine (36.8 ± 0.4)[12] into the equation for entropy of formation, we have $S^\circ$ CuBr, 298.16 = 22.85 ± 0.6 e.u. which differs only by 0.12 e.u. from our calorimetric value (22.97 ± 0.15).

**(b). Another Third Law Check Through Cell Measurements.**—The free energy of formation can also be calculated from the free energies of reaction of the equations

$$\begin{array}{ll}
\text{Cu-amalgam} + \text{HBr } (a = 1) = {}^1/_2\text{H}_2(\text{g}) + \text{CuBr} & \Delta F_1 \\
\text{Cu} = \text{Cu-amalgam} & \Delta F_2 \\
{}^1/_2\text{H}_2 + {}^1/_2\text{Br}_2(\text{l}) = \text{HBr } (a = 1) & \Delta F_3 \\
\hline
\text{Cu} + {}^1/_2\text{Br}_2(\text{l}) = \text{CuBr} & \Delta F
\end{array}$$

Ishikawa, Yamazaki and Murooka[13] have studied the cell

$$\text{Cu-amalgam, CuBr} \mid \text{HBr(m)} \mid \text{H}_2,\ \text{Pt}$$

By using Harned, Keston and Donelson's[14] values of activity coefficient of hydrobromic acid at various values of molarity and the relation $E^\circ = E + 0.1183 \log m\gamma$, we find $E^\circ_{298.16} = -0.0435$ volt. From which $\Delta F_1 = 1003$ cal. and $\Delta F_2 = -236$ cal. For $\Delta F_3$, let us consider the reactions

$$\begin{array}{ll}
\text{Ag} + \text{HBr } (a = 1) = {}^1/_2\text{H}_2 + \text{AgBr} & \Delta F_4 \\
\text{Ag} + {}^1/_2\text{Br}_2(\text{l}) = \text{AgBr} & \Delta F_5
\end{array}$$

Harned, Keston and Donelson[14] have measured the cell

$$\text{Pt, H (1 atm)} \mid \text{HBr(m)} \mid \text{AgBr, Ag}$$

From their data, we find that $\Delta F_4 = 1638$ cal.; $\Delta F_5 = -22{,}940$ cal.[10] which we have already used in (a); $\Delta F_3 = \Delta F_5 - \Delta F_4 = -24{,}578$ cal. Thus $\Delta F = -23{,}811$ cal.

The heat of formation can be calculated as

$$\begin{array}{ll}
\text{Cu-amalgam} + \text{HBr } (0.1\ m) = \text{CuBr} + {}^1/_2\text{H}_2 & \Delta H_1 \\
\text{Cu} = \text{Cu-amalgam} & \Delta H_2 \\
{}^1/_2\text{H}_2 + {}^1/_2\text{Br}_2(\text{g}) = \text{HBr} & \Delta H_3 \\
\text{HBr (g)} = \text{HBr } (0.1\ m) & \Delta H_4 \\
{}^1/_2\text{Br}_2(\text{g}) = {}^1/_2\text{Br}_2(\text{l}) & \Delta H_5 \\
\text{Cu} + {}^1/_2\text{Br}_2(\text{l}) = \text{CuBr(s)} & \Delta H
\end{array}$$

From the results of Ishikawa, Yamazaki and Murooka,[13] and of Oku,[9] we have $\Delta H_1 = 4838$ cal.; $\Delta H_2 = -1250$ cal.

For $\Delta H_3$, $\Delta H_4$, and $\Delta H_5$, we choose: $\Delta H_3 = -12{,}100$ cal.[14]; $\Delta H_4 = -20{,}000$ cal.[15] and $\Delta H_5 = +3670$ cal.[16] Thus $\Delta H = -24{,}824$ cal.

From the values of $\Delta F$ and of $\Delta H$ at 298.16°K., we have $\Delta S_{298\cdot16} = -3.40$ e.u. as entropy of formation of cuprous bromide.

By substituting entropies of copper[13] and of bromine[13] as we have done in (a), we find $S^\circ_{\text{CuBr},\ 288\cdot16} = 22.97 \pm 0.8$ e.u.

The exact agreement with our calorimetric value is of course more than expected.[17]

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