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Bureau of Mines Report of Investigations/1984

High-Temperature Relative Enthalpies of CuBr

By M. J. Ferrante and R. R. Brown



UNITED STATES DEPARTMENT OF THE INTERIOR

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Library of Congress Cataloging in Publication Data:

Ferrante, M. J. (Michael John), 1930-

High-temperature relative enthalpies of CuBr.

(Report of investigations ; 8917)

Bibliography: p. 9-10.

Supt. of Docs. no.: I 28.23:8917.

1. Cuprous bromide—Thermal properties. 2. High temperatures.
I. Brown, R. R. (Robert R.), II. Title. III. Series: Report of investigations (United States. Bureau of Mines) ; 8917.

TN23.U43 [QD181.C9] 622s [546'.6522] 84-600 175

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cal	calorie	h	hour
cal/mol·K	calorie per mol per degree kelvin	J	joule
cm ³	cubic centimeter	K	kelvin
deg	degree	kcal/mol	kilocalorie per mol
g	gram	pct	percent
g/cm ³	gram per cubic centimeter		

HIGH-TEMPERATURE RELATIVE ENTHALPIES OF CuBr

By M. J. Ferrante¹ and R. R. Brown¹

ABSTRACT

Relative enthalpies of CuBr from 298.15 to 1,301 K were measured at the Bureau of Mines to provide thermodynamic data needed for the advancement of mineral technology. The temperatures of transition were measured by differential scanning calorimetry (DSC) and the standard enthalpies of transition (ΔH_{tr}°) by drop calorimetry. The combined results gave reversible transitions at 657 K with $\Delta H_{tr}^{\circ} = 1.10$ kcal/mol, at 741 K with $\Delta H_{tr}^{\circ} = 0.51$ kcal/mol, and at 759 K with an enthalpy of fusion (ΔH_m°) of 1.22 kcal/mol. An anomalous increase in heat capacity preceded the first crystal transition at 657 K. Tabulated values are listed for the standard relative enthalpy, heat capacity, entropy, and Gibbs energy function from 298.15 to 1,500 K. Standard relative enthalpies are also given in equation form and combined with thermodynamic data from the literature to derive values of standard enthalpies of formation and Gibbs energies of formation.

INTRODUCTION

The Bureau of Mines determined the relative enthalpies of cuprous bromide (CuBr) to provide reliable thermodynamic data needed for the correction of some of the problems of copper technology described by Schroeder (1).² The present investigation is part of a continuing program by the Bureau to determine the thermodynamic properties for important copper compounds such as those reported by Beyer (2) and Ferrante (3). In addition, a monograph on the thermodynamic properties of copper and its inorganic compounds was compiled by King (4).

No reliable high-temperature thermodynamic data for CuBr could be found in the literature. Experimental measurements of heat capacities or relative enthalpies above 298.15 K reported by Carré (5), Hoshino (6), and Nölting (7) could not be adequately interpreted because they were only shown graphically. The enthalpy data given by Carré were scattered, and one of the phases was not represented by an equation. Le-Van-My (8) listed only the temperature and enthalpy of transition for the phase changes. None of these investigators presented standard enthalpies of formation or Gibbs energies of formation. Complete thermodynamic data are reported in the present investigation, and these reliable results consist of relative enthalpies measured with a copper-block calorimeter and transition temperatures determined with a differential scanning calorimeter/thermogravimetric analyzer (DSC/TGA). The DSC

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

investigation was also made to clarify the anomalous rise in heat capacity before the first crystal transition.

Unless designated otherwise, CuBr refers to the stable α -phase that exists from 0 to 657 K and has a face-centered cubic structure as shown on the Powder Diffraction File (PDF) card 6-292. The β -phase exists between 657 and 741 K and has a hexagonal structure as listed on PDF card 6-700. The γ -phase exists from 741 K to the melting point at 759 K and crystallizes in a body-centered cubic structure as given on PDF card 6-310.

ACKNOWLEDGMENT

The identification of the CuBr phase by X-ray powder diffraction analysis was made by Robert A. McCune, a research chemist with the Albany Research Center.

MATERIALS

The sample of CuBr was from the same batch used by Ko (9) to measure the standard enthalpy of formation. Since Ko gave details of the preparation of cupric bromide (CuBr₂), which was decomposed to CuBr by heating at 523 K under a flow of argon, only analyses of the CuBr are presented here. Chemical analyses of the powdered product showed 44.26 pct Cu and 55.69 pct Br compared with the stoichiometric composition of 44.30 and 55.70 pct, respectively. No metallic impurities were detected by optical emission spectroscopy. X-ray powder diffraction analysis showed that the pattern matched the α -form of CuBr.

EXPERIMENTAL WORK AND RESULTS

Enthalpies relative to 298.15 K were measured with a copper-block calorimeter. In this method, a sample was heated in a furnace to a known temperature and dropped into a copper block of known heat capacity. The rise in temperature of the block determined the relative enthalpy of the sample. In order to provide a nearly isothermal region for heating of the sample, two furnaces were used with cylindrical heat sinks of silver or platinum. The temperature of the sample in the furnace was measured with a platinum versus platinum-10 pct rhodium thermocouple, which was frequently calibrated against the melting point of pure gold. Before and after a series of enthalpy measurements for a substance, the calorimeter was calibrated electrically and the entire system was checked for accuracy by measuring the enthalpy of periclase (MgO). These MgO measurements agreed within 0.1 pct with the values from 298 to 1,400 K given by Victor (10). Detailed descriptions of the construction and operation of the calorimeter and furnaces were given by Ferrante (11).

Experimental measurements of relative enthalpies were made with CuBr sealed in a capsule of pure silica (SiO₂). After the capsule was filled with powdered CuBr in a glove box that contained an atmosphere of dry nitrogen, it was transferred to a vacuum system without exposure to air. The neck of the evacuated capsule was sealed by fusion while the portion of the capsule containing the CuBr was immersed in ice water. The CuBr in the sealed capsule was melted by heating at 1,000 K for 1 h, and the melt was quenched on an aluminum block. Under these conditions, X-ray powder diffraction of the capsule contents disclosed only the room-temperature α -phase, which showed the reversibility of the phase transitions. Enthalpy measurements were then made with another sample of CuBr sealed and melted in a SiO₂ capsule as just described. For this sample, a mass of 12.00205 g of CuBr was sealed in 5.08443 g of SiO₂. This amount of SiO₂ contributed an average of 44 pct of the total enthalpy change measured for the CuBr and SiO₂ capsule. The enthalpy change of the empty SiO₂

capsule was measured in separate experiments. The empty capsule had an internal volume of 4.40 cm³. The volume of CuBr in the capsule was calculated to be 2.32 cm³ based on the density of 5.17 g/cm³. The mass of the filled capsule was periodically checked for constancy by weighing between enthalpy measurements. The molecular weight of 143.450 for CuBr conforms to the 1981 Table of Atomic Weights (12).

The relative enthalpies are expressed in terms of the thermochemical calorie where 1 cal = 4.1840 J. Enthalpy measurements for CuBr were conducted with a minimum furnace residence time of 1.5 to 2 h. Measurements made with double these residence times showed no increase in relative enthalpy. Therefore, the sample and capsule attained temperature equilibrium in the furnace at the minimum residence time, which was employed in 85 pct of the measurements. The results of experimental measurements were converted to kilocalories per mol and are listed in table 1 in order of increasing temperatures as standard enthalpies relative to 298.15 K (H°-H₂₉₈^o). Temperatures (T) refer to kelvin as defined by the International Temperature Scale of 1968 (13). Table 1 also shows the reversibility of phase transitions when the run numbers are arranged sequentially, as discussed later. In addition, table 1 shows the percent deviation between the experimental and smoothed values. Smoothed values are given in the "Discussion" section.

The temperatures and enthalpies of transition for CuBr were also measured by a DSC/TGA, Mettler³ model TA2000C. The temperature calibration of the instrument used the melting points of 429.75 K for indium and 1,337.58 K for gold. Both of these standards were better than 99.99 pct pure. This temperature calibration showed an accuracy of ±0.3 K for temperature measurements. The temperature calibration was confirmed by measuring the temperature of solid-solid and solid-liquid transitions of selected compounds and metals. The enthalpies of transition of these selected substances were also measured to establish the calorimetric sensitivity of the DSC sensor. Results of these measurements are listed in table 2 and are in good agreement with the values reported by Breuer (14), Rajeshwar (15), and Pankratz (16). Data by Breuer and by Rajeshwar were obtained by DSC measurements using Dupont thermal analyzers 1090 and 990, respectively. Table 2 also shows the temperatures of transition and enthalpies of transition measured for CuBr.

DISCUSSION

High-temperature enthalpies were computer fitted with smooth curves by a least squares technique. This fitting process was used to smoothly merge the high-temperature data with the low-temperature values between 250 and 298.15 K given by Hu (17). These low-temperature values were given more weight than the high-temperature data near 400 K, where the precision of the measurements is significantly less than it is above 500 K, owing to the small amount of heat measured. The fitting process used polynomial functions with up to 10 terms, as described by Justice (18), to derive smooth values of relative enthalpies at the temperatures of the experimental measurements. These smoothed enthalpies were compared with the experimental values to calculate the deviations shown in table 1. The average deviation of the 24 valid experimental measurements was 0.06 pct. This average deviation does not include the 0.49 pct for the test at 403.1 K.

³Reference to specific brand names does not imply endorsement by the Bureau of Mines.

TABLE 1. - Standard relative experimental enthalpies of CuBr(c,l) measured by drop calorimetry

T, K	H°-H° ₂₉₈ , kcal/mol	Deviation, ¹ pct	Run	T, K	H°-H° ₂₉₈ , kcal/mol	Deviation, ¹ pct	Run
403.1	1.404	-0.49	1	744.2	8.885	0.06	12
451.2	2.080	.17	2	751.5	8.973	-.09	14
503.2	2.812	-.02	3	757.4	9.070	.08	16
555.7	3.600	-.05	4	763.8	10.379	.01	20
602.0	4.398	.02	7	770.3	10.475	-.01	15
628.1	4.944	-.10	9	784.9	10.692	-.03	17
652.7	5.618	.03	5	803.1	10.962	-.04	18
667.6	6.588	NAP	10	902.7	12.413	-.01	21
677.0	7.194	-.15	8	1,002.4	13.813	-.01	22
686.1	7.377	.17	19	1,104.6	15.236	.18	23
703.0	7.664	.05	6	² 1,106.5	15.220	-.09	24
723.7	8.025	.03	11	² 1,199.6	16.470	-.07	25
737.5	8.264	.00	13	² 1,300.8	17.823	.00	26

NAP Not applicable.

¹Deviation, pct = 100 (experimental enthalpy - smoothed enthalpy)/experimental enthalpy.

²Furnace with platinum heat sink used, while other measurements used furnace with silver heat sink.

TABLE 2. - Temperatures of transition and standard enthalpies of transition measured by DSC

Substance	Transition ¹	T, K		ΔH_{tr}° , kcal/mol	
		Literature ²	This investigation	Literature ²	This investigation
In.....	MP	430.15	429.8	0.784	ND
Sn.....	MP	505.15	505.1	1.718	1.692
KClO ₄	ss	573.15 (15)	572.6	3.393 (15)	3.478
Cd.....	MP	594.15	594.0	1.484	1.458
CuBr(α-β)..	ss	³ 658-665	656.8	³ 0.64-2.125	1.030
Zn.....	MP	692.15	692.7	1.697	1.694
Ag ₂ SO ₄	ss	699.15	700.1	3.800	3.800
CuBr(β-γ)..	ss	³ 742-753	741.1	³ .32- .370	.454
CsCl.....	ss	749.15	740.2	.693	.659
CuBr(γ-δ)..	MP	³ 760-769	759.1	³ 1.08-1.715	1.133
Al.....	MP	933.61 (16)	934.3	2.580 (16)	2.723
K ₂ CrO ₄	ss	941.15	943.6	1.623	1.622

ND No data.

¹MP = Melting point; ss = solid-solid transition.

²All data by Breuer (14) unless otherwise noted by a reference number.

³See "Discussion" section.

The polynomials from the computer program were also used to derive the smoothed values as shown in table 3 for enthalpy ($H^\circ - H_{298}^\circ$), heat capacity (C_p°), entropy (S°), and Gibbs energy function [$-(G^\circ - H_{298}^\circ)/T$]. Smoothed values in tabular form are arbitrarily given to three decimal places to maintain internal consistency among the values, even though experimental precision does not warrant this exactness. The values of ΔH_{tr}° were rounded to the nearest 10 cal. The smoothed enthalpies of table 3 are estimated to have an absolute uncertainty of ± 0.3 pct. The standard deviation of the experimental enthalpies from the smoothed values was 0.09 pct, not including the measurement at 403.1 K. The standard deviation was calculated from the following

TABLE 3. - High-temperature thermodynamic properties of CuBr(c,&)

T, K	cal/mol·K			$H^\circ - H_{298}^\circ$, kcal/mol
	C_p°	S°	$-(G^\circ - H_{298}^\circ)/T$	
298.15	13.084	22.969	22.969	0
300	13.100	23.050	22.969	.024
350	13.462	25.093	23.130	.687
400	13.746	26.911	23.491	1.368
450	13.930	28.540	23.963	2.060
500	14.414	30.029	24.496	2.766
550	15.590	31.450	25.064	3.512
600	18.919	32.921	25.656	4.359
650	30.309	34.794	26.282	5.533
¹ 657	33.288	35.135	26.375	5.755
657	17.500	36.809	26.375	6.855
700	17.500	37.918	27.050	7.607
² 741	17.500	38.914	27.679	8.325
741	13.900	39.602	27.679	8.835
750	13.900	39.770	27.823	8.960
³ 759	13.900	39.936	27.966	9.085
759	15.136	41.543	27.966	10.305
800	14.862	42.332	28.682	10.920
850	14.556	43.224	29.512	11.655
900	14.283	44.048	30.297	12.376
950	14.041	44.814	31.041	13.084
1,000	13.831	45.528	31.748	13.781
1,050	13.652	46.199	32.420	14.468
1,100	13.506	46.830	33.061	15.147
1,150	13.391	47.428	33.673	15.819
1,200	13.308	47.996	34.258	16.486
1,250	13.257	48.538	34.818	17.150
1,300	13.237	49.058	35.356	17.812
1,350	(13.249)	(49.557)	(35.873)	(18.474)
1,400	(13.293)	(50.040)	(36.370)	(19.138)
1,450	(13.369)	(50.508)	(36.850)	(19.804)
1,500	(13.477)	(50.963)	(37.312)	(20.475)

¹ α - β transition.

² β - γ transition.

³ Melting point.

NOTE.--Values in parentheses are extrapolations.

equation, where d is the percent deviation of a measurement and n is the total number of measurements:

$$\text{Standard deviation, pct} = \left(\frac{\sum d^2}{n-2} \right)^{0.5}.$$

Although the DSC is a more precise technique for measuring temperatures of transition than drop calorimetry, the DSC is not as precise for determining enthalpies of transition, except for slow solid-solid transitions. Thus, the transition temperatures were established by the DSC, and enthalpies of transition by the drop calorimeter. Enthalpies of transition that were determined by the DSC served to substantiate those measured by the drop calorimeter. Of particular concern was the enthalpy of transition for the α - to β -crystal transition, which showed an anomalous increase in heat capacity below the transition temperature.

Three reversible transitions were shown by the thermal behavior of CuBr. Temperatures of transition were measured by the DSC at 656.8 ± 0.3 , 741.1 ± 0.3 , and 759.1 ± 0.3 K. These temperatures were rounded to the nearest degree for the derivation of thermodynamic quantities from enthalpy measurements. Accordingly, the transitions at 657, 741 and 759 K are illustrated graphically in figure 1, which depicts the relationship between the smoothed and experimental enthalpies as the mean heat capacity, $(H^\circ - H_{298}^\circ)/(T - 298.15)$, versus T . The ΔH_{tr}° of all phase transitions measured by the drop calorimeter and the DSC were in agreement and are discussed below. Thus, all phase transitions occurred rapidly and reversibly. The reversibility of the phase transitions and the reproducibility of the enthalpy measurements were also verified when measurements made at temperatures above and then below the transitions again fell on the smooth curve of the mean heat capacity (see sequential order of runs in table 1 and then figure 1).

The first solid-solid transition of CuBr was established at 657 K after rounding the temperature measured by the DSC at 656.8 ± 0.3 K. Enthalpy data at 657 K gave a ΔH_{tr}° of 1.10 kcal/mol, which was substantiated by the DSC measurement of $\Delta H_{tr}^\circ = 1.03$ kcal/mol. An anomalous increase in heat capacity starting about 150 deg below the transition temperature of 657 K was found; however, the bulk of the heat absorption occurred isothermally at the transition

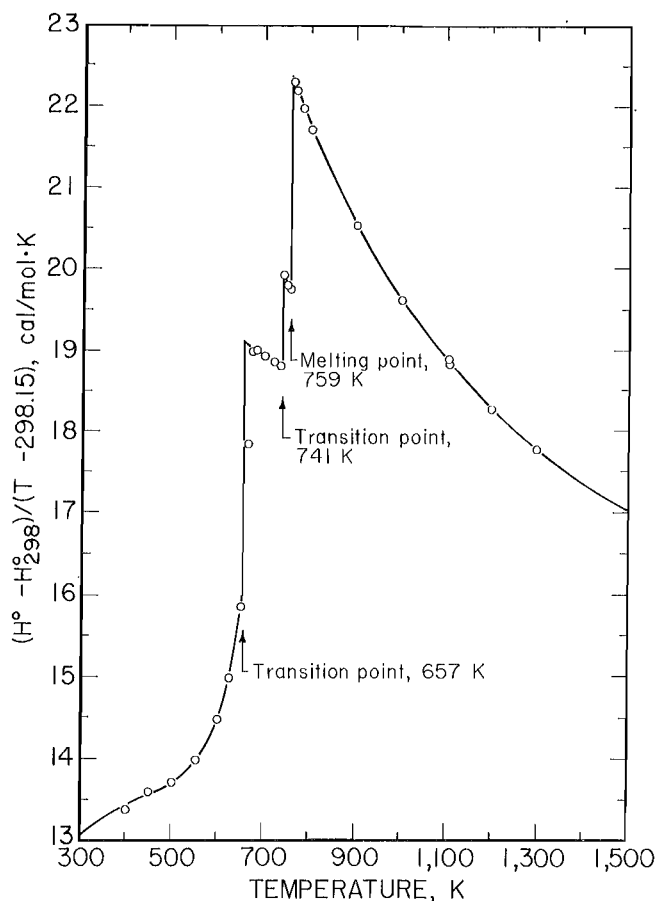


FIGURE 1. - Variation of mean heat capacity with temperature for CuBr(c,l).

temperature. This anomaly for the crystal transition was also found by heat capacity measurements made with the adiabatic calorimeters of Nölting (7) and Hoshino (6). Nölting gave a transition temperature of 658 K from measurements conducted between 305 and 765 K. Hoshino studied the temperature range from 530 to 659 K and reported a transition temperature of 658 K with an estimated ΔH_{tr}° of 1.4 kcal/mol. Both Hoshino and Nölting showed their experimental measurements of heat capacity only graphically, and their data could not be satisfactorily evaluated. Le-Van-My (8) reported a ΔH_{tr}° of 0.64 kcal/mol at 667 K from measurements made between 298 and 850 K by differential thermal analysis (DTA). Carré (5) measured transition temperatures with a DTA and relative enthalpies with a copper-block calorimeter between 298 and 854 K; however, his experimental enthalpies were scattered and were only depicted graphically. He gave a temperature of 665 K with $\Delta H_{tr}^{\circ} = 2.125$ kcal/mol. His enthalpy data for some of the CuBr phases were represented by equations. Enthalpy values calculated from the equation representing the data given by Carré from 507 to 663 K were from 7 pct above to 12 pct below the data of the present investigation.

Experimental enthalpy measurements showed that the second crystal transition of CuBr was between 737.5 and 744.2 K, and the selected transition temperature of 741 K was established from rounding the DSC measurement at 741.1 ± 0.3 K. Enthalpy data at the rounded temperature gave $\Delta H_{tr}^{\circ} = 0.51$ kcal/mol, which was verified by the DSC measurement of 0.45 kcal/mol. Temperatures and/or enthalpies of transition reported by other investigators were 742 K by Nölting, 753 K and 0.32 kcal/mol by Le-Van-My, 743 K and an estimated 0.7 kcal/mol by Hoshino, and 743 K and 0.370 kcal/mol by Carré. The relative enthalpies calculated from the equation representing the data of Carré from 663 to 743 K were from 0 to 8 pct below the values of the present investigation.

The measurements for the third transition of CuBr from the solid to liquid phase established a melting point at 759 K from the DSC and a ΔH_m° of 1.22 kcal/mol from the drop calorimeter. A fusion temperature of 759.1 ± 0.3 K with $\Delta H_m^{\circ} = 1.13$ kcal/mol was actually measured by the DSC. The fusion temperature from the DSC was verified by drop calorimeter measurements that showed the temperature was between 757.4 and 763.8 K. The work of Le-Van-My gave a melting point of 769 K with $\Delta H_m^{\circ} = 1.08$ kcal/mol. Carré listed 761 K with $\Delta H_m^{\circ} = 1.715$ kcal/mol. Carré did not give an enthalpy equation for the solid γ -phase just below the liquid phase. The equation representing the data of Carré for the liquid phase from 761 to 854 K gave relative enthalpies from 4 pct below to 2 pct above those of the present investigation.

Enthalpy measurements were discontinued when two glass capsules of SiO₂ devitrified and cracked open on heating at about 1,400 K. No vapor pressure correction was necessary even at the highest extrapolated temperature of 1,500 K because the data of Krabbes (19) showed the correction would be less than 0.01 pct.

The standard-form equations were derived from the smoothed enthalpies of table 3 by Kelley's method (20). These derived equations are expressed in kilocalories per mol. The temperature range of validity and the average deviation from the smoothed data are shown in parentheses after each equation:

$$\alpha: H^{\circ} - H_{298}^{\circ} = -12.428 \times 10^{-3}T + 24.670 \times 10^{-6}T^2 - 9.601 \times 10^2 T^{-1} + 4.733$$

(298-657 K; 2.4 pct)

$$\Delta H_{657}^{\circ}(\alpha - \beta) = 1.10.$$

$$\beta: H^\circ - H_{298}^\circ = 17.501 \times 10^{-3}T - 4.643$$

(657-741 K; <0.01 pct)

$$\Delta H_{41}^{\circ}(\beta-\gamma) = 0.51.$$

$$\gamma: H^\circ - H_{298}^\circ = 13.900 \times 10^{-3}T - 1.465$$

(741-759 K; <0.01 pct)

$$\Delta H_{59}^{\circ}(\gamma-\ell) = 1.22.$$

$$\ell: H^\circ - H_{298}^\circ = 10.983 \times 10^{-3}T + 0.417 \times 10^{-6}T^2 - 20.276 \times 10^2 T^{-1} + 4.400$$

(759-1,500 K; <0.02 pct).

These standard-form equations usually give less precise values than the smoothed enthalpies because they contain a maximum of 4 terms, compared with as many as 10 terms used to derive the smooth values. The average deviation of 2.4 pct for the equation of the α -phase is much higher than usual because of the anomalous increase in heat capacity before this transition. The average deviation of less than 0.01 pct for the β - and γ -phases shows that little accuracy is lost in using enthalpies calculated from the equations for the β - and γ -phases instead of the tabulated values. Even the equation for the ℓ -phase is a fairly good representation of the smoothed values because its average deviation is only 0.02 pct.

Standard enthalpies of formation (ΔH_f°), Gibbs energies of formation (ΔG_f°), and logarithms to the base 10 of the equilibrium constants of formation ($\log K_f$) were derived as functions of temperature for CuBr by combining relative enthalpies from the present investigation with supplementary data from the literature. The results of these calculations are listed in table 4. For CuBr, ΔH_f° was taken from Ko (9) and S_{298}° from Hu (17). The remaining data for Cu(c, ℓ) and Br₂(ℓ ,g) were obtained from Pankratz (16).

TABLE 4. - Formation data for Cu(c, ℓ) + 0.5 Br₂(ℓ ,g) = CuBr(c, ℓ)

T, K	kcal/mol		Log Kf	T, K	kcal/mol		Log Kf
	ΔH_f°	ΔG_f°			ΔH_f°	ΔG_f°	
298.15	-25.240	-24.302	17.814	⁴ 759	-24.752	-19.295	5.556
300	-25.243	-24.297	17.700	759	-23.532	-19.295	5.556
¹ 332.6	-25.299	-24.191	15.896	800	-23.370	-19.070	5.210
332.6	-28.831	-24.191	15.896	900	-23.026	-18.555	4.506
400	-28.615	-23.272	12.715	1,000	-22.747	-18.073	3.950
500	-28.269	-21.977	9.606	1,100	-22.524	-17.616	3.500
600	-27.747	-20.760	7.562	1,200	-22.352	-17.178	3.129
² 657	-26.968	-20.126	6.695	1,300	-22.224	-16.755	2.817
657	-25.868	-20.126	6.695	⁵ 1,357.6	-22.172	-16.515	2.659
700	-25.584	-19.759	6.169	1,357.6	-25.292	-16.515	2.659
³ 741	-25.315	-19.425	5.729	1,400	-25.252	-16.242	2.535
741	-24.805	-19.425	5.729	1,500	-25.149	-15.603	2.273

¹Boiling point of Br₂.

² α - β transition of CuBr.

³ β - γ transition of CuBr.

⁴Melting point of CuBr.

⁵Melting point of Cu.

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