CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

A Calorimetric Study of Germanium Dibromide

L. N. Zelenina, T. P. Chusova, Yu. G. Stenin, and G. A. Berezovskii

Nikolaev Institute of Inorganic Chemistry, Siberian Division, Russian Academy of Sciences, pr. Akademika Lavrent'eva 3, Novosibirsk, 630090 Russia

> *E-mail: zelenina@che.nsk.su* Received November 25, 2005

Abstract—The temperature dependence of the heat capacity of germanium dibromide was studied over the temperature range 8.3-314 K by adiabatic calorimetry. The enthalpy of formation of solid germanium dibromide was determined by solution calorimetry. Scanning calorimetry was used to obtain the thermodynamic characteristics of fusion of GeBr₂. The thermodynamic characteristics of the Ge–Br system studied by us earlier were used to consistently calculate the consistent standard enthalpies of formation and absolute entropies of germanium bromides in the solid, liquid, and gaseous states.

DOI: 10.1134/S0036024406120077

INTRODUCTION

Germanium halides are currently the main initial material for the preparation of high-purity germanium or compounds based on it. Reliable thermodynamic data are necessary for selecting process schemes and optimizing these processes. In [1], we reported such data for the Ge–I system. The purpose of this work was to obtain consistent thermodynamic information about the properties of germanium bromides.

EXPERIMENTAL

Germanium dibromide was synthesized according to the procedure suggested in [2]. The initial substances were GPZ os. ch. (special purity) germanium single crystals (the concentration of residual impurities $2 \times$ 10^{-12} at./cm³) and bromine of kh. ch. (chemically pure) grade (the content of the major component 99.99%) purified additionally by vacuum sublimation. The carrier gas was TU 6-21-12-79 argon (no less than 99.998% argon and no more than 0.0003% moisture) additionally purified from water by concentrated sulfuric acid. The reaction gave a mixture of GeBr₂, Ge, and GeBr₄, which was dissolved in a water-free diethyl ether preliminarily dried by distillation over sodium metal. The solution was prepared in a dry box filled with argon and filtered from germanium particles. Ether and germanium tetrabromide were removed by heating the transparent solution obtained on a water bath in a vacuum. The remaining dry residue was pale yellow GeBr₂ crystals. The product was identified by chemical, x-ray powder, and spectral analyses. According to the chemical analysis data, it contained (wt %) Ge, 31.0 ± 0.5 and Br, 68.37 ± 0.45 ; calculated for GeBr₂ (wt %): Ge, 31.24 and Br, 68.76. According to the atomic absorption spectrophotometry data, the sample contained 6×10^{-3} wt % silicon, and the contents of the other impurities (23 elements) were at the level of or below their detection limits (10^{-2} – 10^{-6} wt %). The diffractograms of the samples only contained reflections characteristic of germanium dibromide [3]. The above analytic data allow us to claim that our physicochemical measurements were performed for single-phase germanium dibromide with the total content of impurities lower than 0.1 wt %.

The samples were transferred into calorimetric ampules and weighing bottles for analyses in a dry box filled with argon; phosphorus pentoxide was used as the drying agent.

The temperature dependence of the isobaric heat capacity of GeBr_2 was measured by adiabatic vacuum calorimetry; the characteristics of the unit and procedure for measurements were described in [4]. The calorimeter was calibrated by measuring the heat capacity of benzoic acid. The results showed that the error in heat capacity measurements was 1% at 5–50 K and 0.2% at 50–300 K.

Scanning calorimetry was used to determine the thermodynamic characteristics of compound fusion ($T_{\rm fus}$ and $\Delta_{\rm fus}H^{\circ}$). Calorimetric measurements were performed on a Setaram DSC 111 scanning calorimeter at heating rates of 1–3 K/min. Sample weights were of 20–30 mg. During measurements, the substance was in evacuated glass ampules. The limiting error in heat effects was 0.9% (estimated in calibration against reference substances, KNO₃ and Sn).

Solution calorimetry was used to determine the standard enthalpy of formation of germanium dibromide. The heats of solution were measured in a liquid isothermic-shell calorimeter [5]. The reliability of the calorimetric system was checked by measuring the heat of solution of KCl in water. The mean enthalpy of solution was in agreement with the value accepted as the international standard (17.524 \pm 0.007 kJ/mol) [6] to

Т, К	C_p°	Т, К	C_p°	<i>Т</i> , К	C_p°	Т, К	C_p°
Series 2		217.92	82.38	108.04	65.05	12.40	6.86
135.01	70.08	222.34	83.41	112.81	66.10	14.11	8.93
139.50	71.21	226.72	84.13	117.41	67.23	15.05	9.93
144.17	72.32	231.06	84.87	121.86	68.58	16.24	11.25
149.00	72.23	240.55	86.79	126.61	69.51	17.70	12.84
153.76	73.31	245.30	86.41	Series 4		19.43	14.72
158.42	74.25	250.00	87.92	304.40	93.54	21.14	16.75
163.26	75.11	254.66	88.45	309.97	94.96	22.98	18.78
168.27	76.52	259.28	89.13	314.70	96.65	25.40	21.34
173.20	77.87	263.88	89.65	Seri	es 5	28.13	24.03
178.06	77.53	268.44	90.66	275.36	91.91	31.11	26.90
182.85	77.55	272.97	91.04	279.81	93.59	34.45	29.90
Series 1		277.49	90.23	285.06	93.47	38.36	33.08
186.25	77.50	281.97	90.97	295.51	97.10	43.71	37.07
190.51	78.35	Seri	es 3	290.30	95.91	49.83	41.01
195.19	78.92	83.82	56.79	Seri	es 6	55.76	44.75
199.83	79.39	88.18	59.11	8.32	2.78	61.85	47.88
204.41	80.43	92.88	60.64	8.97	3.36	68.39	51.03
208.95	81.19	97.84	61.18	9.77	4.01	75.35	54.10
213.46	81.52	103.07	63.36	11.00	5.13		

Table 1. Experimental heat capacities of $\text{GeBr}_2(s)$ (C_p° , J/(mol K))

within 0.1%. The heats of solution were measured at 301 K, because the temperature of fusion of GeBr_4 equaled 299.35 K.

The solvent used was distilled benzene bromide (C_6H_5Br) of ch. (pure) grade. The enthalpy of formation of GeBr₂ was calculated from the heats of the calorimetric reactions

$$Br_2(l) + sln I \longrightarrow sln II + \Delta H_1,$$
 (1)

$$\text{GeBr}_2(s) + \sin II \longrightarrow \sin III + \Delta H_2,$$
 (2)

$$\operatorname{GeBr}_4(1) + \operatorname{sln} I \longrightarrow \operatorname{sln} \operatorname{III} + \Delta H_3,$$
 (3)

where $sln I = 21.5Br_2 + 4.2GeBr_4 + 2025C_6H_5Br$.

The concentrations of the calorimetric solutions used ensured a fairly high rate of reactions on the one hand (Br_2 and $GeBr_4$ were dissolved in 5–10 min and $GeBr_2$ in 20–30 min) and the independence of the heats of reactions (1)–(3) from changes in the concentrations of the substances to be dissolved.

RESULTS AND DISCUSSION

The heat capacity of germanium dibromide was measured over the temperature range 8.3-314 K. The weight of the sample was 4.890 g, the molecular weight of GeBr₂ being 232.418. The results of 73 calorimetric experiments are presented in Table 1. The mean deviations of the experimental values from the smoothed

 $C_p(T)$ curve were 1.5, 0.3, and 0.15% over the temperature ranges 8–16, 16–35, and 35–275 K, respectively. The accuracy of the calculated values was estimated with the inclusion of both errors in calorimeter calibration against benzoic acid and the spread of experimental heat capacity values over the whole temperature interval.

The smoothed $C_p(T)$ dependence was used to calculate the absolute entropy S° , the enthalpy of heating $H_T^\circ - H_0^\circ$, and the reduced Gibbs energy $\Phi^\circ = S^\circ - [H_T^\circ - H_0^\circ]/T$. Their values at the selected temperatures are listed in Table 2.

Scanning calorimeter measurements were performed over the temperature range 273–500 K. To within the sensitivity of the method, the substance studied was a pure phase. The only phase transition observed over the temperature range of measurements was fusion.

The thermodynamic characteristics of fusion obtained from the differential scanning calorimeter data were $\Delta_{fus}H^{\circ}(GeBr_2) = 11.6 \pm 0.1 \text{ kJ/mol}, T_{fus} = 409.15 \pm 0.5 \text{ K}, \text{ and } \Delta_{fus}S^{\circ} = 28.3 \pm 0.5 \text{ J/(mol K)}.$

Solution calorimetry measurements for bromine and germanium bromides gave the following enthalpies of reactions (1)–(3) (kJ/mol): $\Delta_{r1}H^{\circ}_{301} = -4.25 \pm 0.49$, $\Delta_{r2}H^{\circ}_{301} = -185.12 \pm 1.40$, and $\Delta_{r3}H^{\circ}_{301} = 0.98 \pm 0.025$.

The errors specified correspond to a 95% confidence level. For each reaction, five measurements were performed, and the weights of solute samples were (g) 0.09–0.16 for Br₂, 0.15–0.27 for GeBr₂, and 0.22–0.37 for GeBr₄. The mean cooling constant value in our experiments was 41×10^{-4} s⁻¹. The correction for heat exchange calculated by the Regnault–Pfaundler method was no larger than 7% of the overall temperature rise on average.

The $\Delta_f H^{\circ}(\text{GeBr}_4, 1)$ value obtained from our data (see below) and enthalpies of reactions (1)–(3) can be used to calculate the standard enthalpy of formation of solid germanium dibromide,

$$\Delta_{\rm f} H^{\circ}({\rm GeBr}_2, {\rm s}) = \Delta_{\rm f} H^{\circ}({\rm GeBr}_4, {\rm l}) -\Delta H_1^{\circ} - \Delta H_2^{\circ} + \Delta H_3^{\circ}.$$
(4)

The enthalpy of formation of liquid germanium tetrabromide ($\Delta_f H^{\circ}(\text{GeBr}_4, 1)$) was determined from the thermodynamic information about the Ge–Br system obtained by us in [7–12]. The static method for vapor pressure measurements allowed us to determine the thermodynamic characteristics of reactions with the participation of the gas phase [7, 8],

$$GeBr_4(s) = GeBr_4(g), \tag{5}$$

$$GeBr_4(l) = GeBr_4(g), \tag{6}$$

$$GeBr_4(g) = GeBr_2(g) + Br_2(g), \tag{7}$$

$$Ge(s) + GeBr_4(g) = 2GeBr_2(g).$$
(8)

The entropies and heat capacities of gaseous germanium bromides were determined using the statistical method for thermodynamic function calculations in the rigid rotator-harmonic oscillator approximation [9, 10]. The temperature dependence of the heat capacity of condensed germanium tetrabromide was measured by adiabatic calorimetry over the temperature range 5– 315 K [11] and drop calorimetry over the temperature range 303–427 K [12]. To summarize, the following thermodynamic data were obtained for the Ge–Br system (S° and C_p in J/(mol K) and ΔH° in kJ/mol) [12]:

$$C_p^{\circ}(\text{GeBr}_4, \text{s}) = 561.375 - 0.6842T - 6.67 \times 10^4 T^{-1}$$

(273–299 K), (9)

$$S^{\circ}(\text{GeBr}_4, \text{ s}, 298.15) = 247.4 \pm 0.2,$$
 (10)

$$\Delta_{\rm fus} H^{\circ}({\rm GeBr}_4, 299.27) = 12.85 \pm 0.03,$$
 (11)

$$C_p^{\circ}(\text{GeBr}_4, 1) = 157.15 \pm 1.5,$$
 (12)

$$C_p^{\circ}(\text{GeBr}_2, \text{s}) = 126.5 - 0.0197T - 9654.8T^{-1}$$

(230-409 K), (13)

 $S^{\circ}(\text{GeBr}_2, \text{ s}, 298.15) = 153.2 \pm 0.2,$ (14)

$$\Delta_{\rm fus} H^{\circ}({\rm GeBr}_2, 409.15) = 11.6 \pm 0.2, \tag{15}$$

$$C_p^{\circ}$$
 (GeBr₄, g) = 128.26 - 0.244 × 10⁻¹T

Table 2. Main thermodynamic functions of GeBr₂(s) $(C_p^{\circ}(T), S^{\circ}(T), \text{ and } \Phi^{\circ}(T) \text{ in } J/(\text{mol } K) \text{ and } H^{\circ}(T) - H^{\circ}(0) \text{ in } J/(\text{mol})$

<i>Т</i> , К	$C_p^{\circ}(T)$	$ \begin{array}{c} H^{\circ}(T) \\ - H^{\circ}(0) \end{array} $	$S^{\circ}(T)$	$\Phi^{\circ}(T)$
5.00	(0.702)	(0.887)	(0.236)	(0.059)
10.00	4.14	11.9	1.63	0.438
15.00	9.27	45.1	4.25	1.24
20.00	14.8	105	7.67	2.41
25.00	20.2	193	11.6	3.85
30.00	25.2	307	15.7	5.47
35.00	29.8	444	19.9	7.24
40.00	34.0	604	24.2	9.09
45.00	37.8	784	28.4	11.0
50.00	41.3	982	32.6	13.0
60.00	47.20	1425	40.67	16.91
70.00	52.10	1923	48.32	20.85
80.00	56.22	2465	55.56	24.74
90.00	59.75	3045	62.39	28.55
100.00	62.79	3658	68.84	32.26
120.00	67.76	4966	80.75	39.37
140.00	71.54	6361	91.49	46.06
160.00	74.68	7824	101.26	52.36
180.00	77.40	9345	110.21	58.29
200.00	80.01	10920	118.50	63.91
220.00	82.94	12550	126.26	69.23
240.00	86.06	14240	133.61	74.29
260.00	89.15	15990	140.62	79.12
280.00	92.11	17800	147.34	83.76
298.15	94.59 ± 0.2	19500 ± 50	153.20 ± 0.2	87.81 ± 0.2
300.00	94.83	19670	153.79	88.21
314.70	96.66	21080	158.37	91.38

 $-6507T^{-1} + 0.1594 \times 10^{6}T^{-2} + 0.946 \times 10^{-5}T^{2}$ (16) (298.15–1500 K),

$$S^{\circ}(\text{GeBr}_4, \text{ g}, 298.15) = 396.1 \pm 5,$$
 (17)

$$C_p^{\circ}$$
 (GeBr₂, g) = 66.24 - 1.109 × 10⁻²T

$$-2450T^{-1} + 0.459 \times 10^{5}T^{-2} + 0.514 \times 10^{-5}T^{2}$$
(18)
(298.15–1500 K).

$$S^{\circ}(\text{GeBr}_2, \text{g}, 298.15) = 318.2 \pm 3,$$
 (19)

$$\Delta_{\rm sub}H^{\circ}({\rm GeBr}_4, 298.15) = 58.6 \pm 1.2, \tag{20}$$

$$\Delta_{\rm sub}S^{\circ}({\rm GeBr}_4, 298.15) = 145.6 \pm 3.8, \tag{21}$$

$$\Delta_{\rm vap} H^{\circ}({\rm GeBr}_4, 299.27) = 46.6 \pm 0.3, \qquad (22)$$

$$\Delta_{\rm vap} S^{\circ}({\rm GeBr}_4, 299.27) = 104.6 \pm 0.8, \qquad (23)$$

RUSSIAN JOURNAL OF PHYSICAL CHEMISTRY Vol. 80 No. 12 2006



Deviations of experimental pressures from values calculated using the consistent set of thermodynamic characteristics (Table 3) for reaction (8) in the Ge–Br system for three series of measurements.

$$\Delta_{\rm r7} H_{298}^{\circ} = 250.3 \pm 6.1, \tag{24}$$

$$\Delta_{\rm r7} S_{298}^{\circ} = 160.5 \pm 5.0, \tag{25}$$

 $\Delta_{\rm r8} H_{298}^{\circ} = 152.6 \pm 1.2, \tag{26}$

$$\Delta_{\rm r8} S_{298}^{\circ} = 209.6 \pm 1.7. \tag{27}$$

These data allowed us to calculate the thermodynamic characteristics of gaseous germanium dibromide and germanium tetrabromide in all states of aggregation with the use of various thermodynamic cycles. Because of the redundancy of information contained in (9)-(27), we obtained several sets of the thermodynamic characteristics of germanium bromides. To select a unique set of consistent characteristics, the maximum likelihood principle in terms of estimating parameters of a system with several dependent variables was used [13]. The deviations of the experimental data from the results of calculations with the use of the unique consistent set of characteristics for all the reac-

Table 3. Consistent standard enthalpies of formation and absolute entropies of germanium bromides

Compound	$-\Delta_{\rm f} H^{\circ}(298.15),$ kJ/mol	<i>S</i> °(298.15), J/(mol K)
GeBr ₂ (s)	162.0 ± 4.4	153.2 ± 0.5
GeBr ₂ (l)	$140.0 \pm 4.5*$	$210.6 \pm 0.5*$
$GeBr_2(g)$	76.8 ± 6.2	317.5 ± 2.6
GeBr ₄ (s)	365.3 ± 4.1	247.41 ± 0.2
GeBr ₄ (l)	352.4 ± 4.1	290.27 ± 0.3
GeBr ₄ (g)	306.0 ± 5.8	394.6 ± 0.95

Note: The asterisked values correspond to $T_{\text{fus}} = 409.15$ K.

tions studied did not exceed the limiting measurement errors, which was evidence of the absence of serious systematic errors in our experiments. By way of example, such deviations are shown in the figure for reaction (8).

The enthalpy of formation of liquid germanium tetrabromide obtained when consistency was attained was used to calculate the enthalpy of formation of solid germanium dibromide according to (4). Equation (13) was used to determine the enthalpy of formation and absolute entropy of liquid germanium dibromide at the temperature of fusion.

The consistent standard enthalpies of formation and absolute entropies of germanium bromides are listed in Table 3.

ACKNOWLEDGMENTS

This work was financially supported by the "State Program for Support of Leading Scientific Schools," project NSh no. 1042 2003.3.

REFERENCES

- 1. L. N. Zelenina, V. A. Titov, T. P. Chusova, et al., J. Chem. Thermodyn. **35**, 1601 (2003).
- 2. M. D. Curtis and P. Wolbert, Inorg. Chem. **11** (2), 431 (1972).
- R. C. Rouse, D. R. Peacor, and B. R. Maxim, Z. Kristallogr. 145, 161 (1977).
- G. A. Berezovskii, K. S. Sukhovei, T. P. Chusova, et al., Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim., No. 5, 88 (1979).
- L. N. Zelenina, T. P. Chusova, Yu. G. Stenin, and T. D. Karpova, Khim. Interesah Ustoich. Razvit., No. 8, 97 (2000).
- 6. M. V. Kilday, J. Res. Natl. Bur. Stand. 85 (6), 449 (1980).
- L. N. Zelenina, T. P. Chusova, and Yu. G. Stenin, Zh. Fiz. Khim. **78** (4), 1 (2004) [Russ. J. Phys. Chem. **78** (4), 499 (2004)].
- L. N. Zelenina, A. A. Titov, and T. P. Chusova, Zh. Fiz. Khim. **79** (1), 51 (2005) [Russ. J. Phys. Chem. **79** (1), 43 (2005)].
- G. Y. Schultz, J. Tremmel, and I. Hargittai, J. Mol. Struct. 82, 107 (1982).
- R. S. H. Clark and P. D. Mitchell, J. Chem. Soc., Faraday Trans. 72, 69 (1975).
- G. A. Berezovskii, L. N. Zelenina, T. P. Chusova, and I. E. Paukov, Zh. Fiz. Khim. **73** (8), 1504 (1999) [Russ. J. Phys. Chem. **73** (8), 1347 (1999)].
- L. N. Zelenina, Candidate's Dissertation in Chemistry (Inst. Neorg. Khim. Sib. Otd. Ross. Akad. Nauk, Novosibirsk, 2001).
- 13. D. M. Himmelblau, *Process Analysis by Statistical Methods* (Wiley, New York, 1970).