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Heat Capacity and Thermodynamic Functions of $TbBr_3$

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The heat capacity of solid $TbBr_3$ was measured by differential scanning calorimetry in the temperature range from 300 K up to the melting temperature. The polynomial heat capacity dependence on temperature was used to fit experimental data. Additionally, the temperature and enthalpy of fusion of $TbBr_3$ were also measured. By combination of these results with the literature data on the entropy at 298.15 K, $S^0_{\mathrm{m}}(\mathrm{TbBr_3, s, 298.15\ K})$, the standard molar enthalpy of formation, $\Delta_{\mathrm{form}} H^0_{\mathrm{m}}(\mathrm{TbBr_3, s, 298.15\ K})$, and the heat capacity of the liquid phase, $C^0_{\mathrm{p,m}}$ $(\mathrm{TbBr_3, l})$, the thermodynamic functions of terbium tribromide were calculated up to $T = 1300$ K.

Introduction

Nearly 20 years ago, a documented review from Oak Ridge National Laboratory[1] on the anhydrous rare-earth halides summarized the currently available data. Since a considerable fraction of these data were estimated values, it was concluded that “new and more accurate data will be needed if the chemistry of rare-earth halides is to have the increased significance that its intrinsic elegance suggests is possible”. In addition to their use for pyrochemical processes in nuclear industry, the rare-earth halides are attractive components in high-intensity discharge lamps[2,3] and new highly efficient light sources with energy-saving features.[4,6] They offer the opportunity when combined with other metal halides to design light sources with high efficacy and good color rendition. An assessment of their thermodynamic properties was conducted,[7] but even nearly 20 years after,[1] it was also concluded that the properties of the rare-earth halides are poorly characterized and also that the bromides have received even less attraction than the chlorides and iodides.

The aforementioned technological applications require prior knowledge of the micro- and macroscopic behavior of the related lanthanide compounds. To elucidate this behavior, systematic investigations of their thermodynamic,[8,9] electrochemical,[10] physicochemical,[11] and structural properties[12] are required. The present work is a continuation of these systematic investigations on lanthanide halides and their systems with alkali metal halides by a variety of experimental techniques, such as calorimetry, electrical conductivity and density measurements, and X-ray and neutron diffraction, coupled to numerical procedures by molecular dynamic simulations.[13]

It is concerned with the determination of the thermodynamic functions of terbium bromide $TbBr_3$. Very little is known on $TbBr_3$, and only the enthalpy of formation at 298 K,[14] the melting temperature, and enthalpy[15] were experimentally determined. This paper reports original heat capacity data on solid $TbBr_3$ obtained by differential scanning calorimetry (DSC) over the extended temperature range from 300 to 1100 K. Another technique, high-temperature Calvet microcalorimetry, was used to confirm the melting temperature and enthalpy, which were out of the DSC experimental range.

All these data were then used for the calculation of the thermodynamic functions up to 1300 K.

Table 1. Chemical Analysis of Terbium Tribromide

	mass %			
compound	Br_{exp}	Br_{theo}	Tb_{exp}	Tb_{theo}
$TbBr_3$	60.15	60.13	39.85	39.87

Experimental Section

Sample Preparation. Terbium bromide, $TbBr_3$, was prepared by sintering of terbium oxide Tb_4O_7 (Johnson Matthey, 99.9%) with ammonium bromide NH_4Br (POCh Gliwice, Poland). The terbium oxide−ammonium bromide mixture (molar ratio = 1:14) was heated slowly up to 570 K. After 3 h reaction at 570 K, the temperature was increased up to 650 K and unreacted ammonium bromide was sublimated. Finally the salt was melted at 1150 K, cooled, and transferred to the glovebox. Further purification of crude terbium bromide was obtained by distillation under reduced pressure (~0.1 Pa) at 1170 K.

The chemical analysis of the synthesized $TbBr_3$ was performed by titration methods for bromide (mercurimetric) and lanthanide (complexometric). These results are presented in Table 1.

All manipulations with $TbBr_3$ were performed in an argon glovebox with a measured volume fraction of water of about 2×10^{-6} and continuous gas purification by forced recirculation through external molecular sieves.

Measurements. The heat capacity of pure $TbBr_3$ was measured with a Setaram DSC 121 differential scanning calorimeter. The apparatus and the measurement procedure were described in details in refs 11 and 16. Samples of (from 300 to 500) mg were contained in vacuum-sealed quartz ampules (about 6 mm diameter, 15 mm length). The sidewalls of ampules were grounded in order to fit the cells snugly into the heat-flow detector.

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Table 2. Experimental Molar Heat Capacity of $TbBr_3$

T/K	$C^0_{\mathrm{p,m}}/\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$	T/K	$C^0_{\mathrm{p,m}}/\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$	T/K	$C^0_{\mathrm{p,m}}/\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$	T/K	$C^0_{\mathrm{p,m}}/\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$
305	95.25	504	102.99	703	96.70	902	101.94
310	96.04	509	102.18	708	97.79	907	97.88
315	96.89	514	100.27	713	99.85	911	97.43
320	96.99	519	96.88	717	99.17	916	100.85
325	97.03	524	98.84	722	99.02	921	97.21
330	96.84	529	97.84	727	99.08	926	100.73
335	97.05	534	99.15	732	99.98	931	95.04
340	97.06	539	97.79	737	99.41	936	99.59
345	98.47	543	97.70	742	101.93	941	98.67
350	98.03	548	97.62	747	100.10	946	99.44
354	96.27	553	98.93	752	104.88	951	102.23
359	96.56	558	98.58	757	100.82	956	103.73
364	95.16	653	99.85	762	101.00	961	99.70
369	95.49	568	98.34	767	101.85	966	98.27
374	95.66	573	98.95	772	102.41	971	101.79
379	94.73	578	98.65	777	103.20	976	102.55
384	96.58	583	99.14	782	102.71	981	97.92
389	94.78	588	98.88	787	101.90	986	104.37
394	96.69	593	100.12	792	101.02	991	100.42
399	97.48	598	98.39	797	101.52	996	107.17
404	97.16	603	99.23	802	101.51	1001	105.67
409	97.43	608	100.21	807	99.68	1006	110.34
414	96.37	613	99.21	812	103.05	1011	102.11
419	97.26	618	100.47	817	103.73	1016	100.99
424	96.24	623	100.62	822	102.94	1021	106.91
429	97.60	628	99.41	827	103.83	1026	105.87
434	98.83	633	99.03	832	99.83	1031	112.44
439	98.92	638	100.94	837	98.83	1036	99.98
444	98.73	643	100.90	842	101.98	1041	101.71
449	100.77	648	106.81	847	103.78	1046	101.91
454	101.24	653	102.18	852	103.32	1051	106.32
459	102.68	658	101.21	857	99.15	1056	110.86
464	101.53	663	102.10	862	102.98	1061	111.70
469	101.69	668	99.19	867	101.94	1066	119.25
474	101.67	673	98.90	872	105.24	1071	138.60
479	101.42	678	101.61	877	101.33	1076	140.70
484	102.61	683	98.15	882	103.27	1081	180.28
489	102.50	688	99.94	887	97.19	1086	329.82
494	101.69	693	98.07	892	97.82	1091	622.78
499	102.17	698	97.98	897	98.26	1096	1622.99

The so-called "step method" used for C_p measurements has been already described.[17−20] In this method, small heating steps are followed by isothermal delays, when thermal equilibrium of the sample is achieved. Two correlated experiments should be carried out to determine the heat capacity of the sample. The first one, with two empty cells (containers) with identical mass, and the second with one of these cells loaded with the sample. The heat flux is recorded as a function of time and of temperature in both runs. The difference of heat flux in both runs is proportional to the amount of heat (Q_i) necessary to increase the temperature of the sample by a small temperature increment ΔT_i. Therefore, the heat capacity of the sample is equal to

$$C^0_{\mathrm{p,m}} = (Q_i M_s)/(\Delta T_i m_s)$$

where m_s is the mass of the sample and M_s is the molar mass of the sample.

The same operating conditions (e.g., initial and final temperatures, temperature increment, isothermal delay, and heating rate) are required for the two experimental runs. The original SETARAM program performs all necessary calculations.

The apparatus was calibrated by the Joule effect. Additionally, some test measurements with NIST 720 α-Al_2O_3 standard reference material have been carried out separately prior to investigation of the terbium bromide. According to this test, which gave $C^0_{\mathrm{p,m}}$ values consistent with standard data for Al_2O_3 (difference in all temperature range less than 1%), the step method may be considered as suitable for heat-capacity measurements.

In our experiments, each heating step of 5 K was followed by a 400-s isothermal delay. The heating rate was 1.5 K·min^{-1}. All experiments were started at 300 K and were performed up to 1100 K. The mass difference of the quartz cells in a particular experiment did not exceed 1 mg (the mass of the cells were (from 400 to 500) mg). The mass of the samples was (from 300 to 500) mg.

Fusion temperature and enthalpy values of $TbBr_3$ were determined with a Calvet high-temperature microcalorimeter described in details.[18] Two samples of $TbBr_3$ (3.0550 and 2.5110 g) sealed under vacuum in quartz ampules (12 mm diameter) were used in these determinations.

Results and Discussion

Enthalpy of Fusion and Heat Capacity of $TbBr_3$. Temperature and enthalpy of fusion of pure $TbBr_3$ were determined by high-temperature Calvet microcalorimetry because of the temperature limitation of DSC. It was found that fusion occurs at 1103 K with the corresponding enthalpy of 37.4 ± 0.5 kJ·mol^{-1}. The results obtained are in excellent agreement with literature data giving the same temperature of fusion and enthalpy of 37.7 kJ·mol^{-1}.[15]

Our experimental heat capacity values of $TbBr_3$ are presented in Table 2 and plotted against temperature in

Table 3. Thermodynamic Functions of $TbBr_3$ at Selected Temperatures (from 298.15 to 1300) K

T / K	$C^0_{p,m}(T)$ / $J\cdot mol^{-1}\cdot K^{-1}$	$S^0_m(T)$ / $J\cdot mol^{-1}\cdot K^{-1}$	$-(G^0_m(T) - H^0_m(298.15K)$ / $J\cdot mol^{-1}\cdot K^{-1}$	$[H^0_m(298.15K)/T]$ / $kJ\cdot mol^{-1}$	$\Delta_{form} H^0_m(T)$ / $kJ\cdot mol^{-1}$	$\Delta_{form} G^0_m(T)$ / $kJ\cdot mol^{-1}$
298.15	97.28	194.00	194.00	0.00	−843.5	−811.4
300	97.30	194.60	194.00	0.18	−843.6	−811.2
331	97.60	204.18	194.51	3.20	−845.0	−807.8
331	97.60	204.18	194.51	3.20	−889.3	−807.8
400	98.20	222.72	197.83	9.96	−888.3	−791.5
500	99.03	244.72	205.09	19.82	−886.8	−768.1
600	99.83	262.85	213.25	29.76	−885.3	−745.0
700	100.62	278.30	221.46	39.78	−883.9	−722.2
800	101.40	291.79	229.43	49.89	−882.6	−699.6
900	102.17	303.77	237.03	60.06	−881.5	−677.1
1000	102.95	314.58	244.26	70.32	−880.4	−654.7
1100	103.72	324.43	251.10	80.65	−879.4	−632.5
1103	103.74	324.71	251.30	80.96	−879.4	−631.8
1103	145.00	358.61	251.30	118.36	−847.9	−631.8
1200	145.00	370.83	260.04	132.43	−843.1	−613.8
1300	145.00	382.44	268.60	146.93	−838.4	−595.6

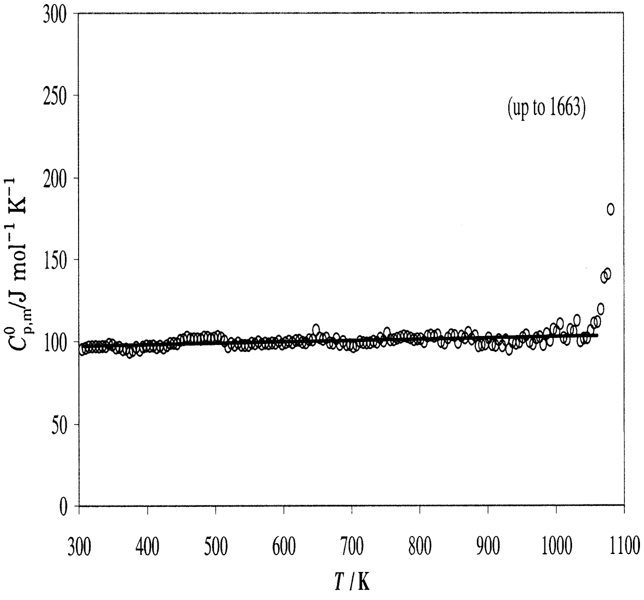

Figure 1. Molar heat capacity of $TbBr_3$: ○, experimental results; solid line, polynomial fitting of experimental results.

Figure 1. These are original data obtained for the first time in this work. The classical heat-capacity dependence on temperature

$$C^0_{p,m}/J\cdot mol^{-1}\cdot K^{-1} = a + b \times 10^{-3}(T / K) + c \times 10^5(T/K)^{-2} \quad (1)$$

was already used by Barin et al.[21] for the purpose of representing data on lanthanide halides. This same equation was also employed in the present work. However, because of the strong C_p increase when approaching melting, only those data corresponding to a smooth heat-capacity dependence on temperature were used. The standard deviation of fitting was found as 2.56 $J\cdot mol^{-1}\cdot K^{-1}$. Because of the temperature limitation of apparatus, we could not do measurements for liquid phase of $TbBr_3$.

Thermodynamic Functions of $TbBr_3$. The thermodynamic functions of $TbBr_3$ were calculated up to 1300 K using our experimental melting temperature and enthalpy together with the heat capacity data. We determined the $C^0_{p,m}(TbBr_3, s, 298.15\ K) = 97.28\ J\cdot mol^{-1}\cdot K^{-1}$ by extrapolation of our results to 298.15 K.

The estimated values of standard entropy, $S^0_m(TbBr_3, s, 298.15\ K) = 194.00\ J\cdot K^{-1}\cdot mol^{-1}$, and of heat capacity of the liquid phase, $C^0_{p,m}(TbBr_3, l) = 145.00\ J\cdot mol^{-}1\cdot K^{-1}$, were taken from literature.[7]

The $C^0_{p,m} = f(T)$ equation was then used to calculate enthalpy increments $H^0_m(T) - H^0_m$ (298.15 K) in $kJ\cdot mol^{-1}$, entropy $S^0_m(T)$, and Gibbs energy functions $(G^0_m(T) - H^0_m(298.15))/T$ in $J\cdot mol^{-1}\cdot K^{-1}$ both for solid as well as liquid $TbBr_3$. The corresponding equations are given below. The results of the above calculations for selected temperatures are presented in Table 3.

$TbBr_3$(s), 298.15 K < T < 1103 K.

$$C^0_{p,m}/J\cdot mol^{-1}\cdot K^{-1} = 95.32 + 7.66 \times 10^{-3}(T/K) - 0.28 \times 10^5(T/K)^{-2}$$

$$H^0_m(T) - H^0_m(298.15\ K)/kJ\cdot mol^{-1} = 95.32 \times 10^{-3}(T/K) + 3.83 \times 10^{-6}(T/K)^2 + 0.28 \times 10^2(T/K)^{-1} - 28.85$$

$$S^0_m(T)/J\cdot mol^{-1}\cdot K^{-1} = 95.32 \ln(T/K) + 7.66 \times 10^{-3}(T/K) + 0.14 \times 10^5(T/K)^{-2} - 351.51$$

$$\{-(G^0_m(T) - H^0_m(298.15))/T\}/J\cdot mol^{-1}\cdot K^{-1} = 95.32 \ln(T/K) + 3.83 \times 10^{-3}(T/K) - 0.14 \times 10^5(T/K)^{-2} + 28853(T/K)^{-1} - 446.83$$

$TbBr_3$(l), 1103 K < T < 1300 K.

$$C^0_{p,m}/J\cdot mol^{-1}\cdot K^{-1} = 145.00$$

$$H^0_m(T) - H^0_m(298.15\ K)/kJ\cdot mol^{-1} = 145.00 \times 10^{-3}(T/K) - 41.571$$

$$S^0_m(T)/J\cdot mol^{-1}\cdot K^{-1} = 145.00 \ln(T/K) - 657.23$$

$$\{-(G^0_m(T) - H^0_m(298.15))/T\}/J\cdot mol^{-1}\cdot K^{-1} = 145.00 \ln(T/K) + 47541\ (T/K)^{-1} - 807.64$$

Having the thermodynamic functions for $TbBr_3$, one can calculate the thermodynamic functions of its formation as a function of temperature.

The formation of $TbBr_3$ from the elements can be described by the reaction

$$Tb(s) + 1.5Br_2(l,g) = TbBr_3(s,l) \quad (2)$$

and the related thermodynamic functions of $TbBr_3$ formation depend on the thermodynamic functions of metallic Tb and bromine Br_2. The latter were calculated using literature data for $C^0_{p,m}$ and S^0_m(298.15 K).[22] The enthalpy of $TbBr_3$ formation at 298.15 K, $\Delta_{form}H^0_m$($TbBr_3$,s,298.15 K) = −843.5 kJ·mol^{-1}, also required in this calculation, was taken from Cordfunke and Konings recent work.[14]

Two phase changes occur in this system described by reaction 2: boiling of bromine at 331 K (enthalpy of 29.56 kJ·mol^{-1}) and melting of $TbBr_3$ at 1103 K. Accordingly, the formation enthalpy $\Delta_{form}H^0_m$ (kJ·mol^{-1}) and Gibbs formation energy $\Delta_{form}\,G^0_m$ (kJ·mol^{-1}) are described by the equations given below.

$TbBr_3$(s), 298.15 K < T < 331 K.

$$\Delta_{form}\,H^0_m/\mathrm{kJ{\cdot}mol^{-1}} = -35.06 \times 10^{-3}(T/\mathrm{K}) - 5.52 \times 10^{-6}(T/\mathrm{K})^2 + 6.30 \times 10^2(T/\mathrm{K})^{-1} - 834.7$$

$$\Delta_{form}\,G^0_m/\mathrm{kJ{\cdot}mol^{-1}} = -126.96 \times 10^{-3}(T/\mathrm{K}) + 5.52 \times 10^{-6}(T/\mathrm{K})^2 + 3.15 \times 10^2(T/\mathrm{K})^{-1} + 35.06 \times 10^{-3}(T/\mathrm{K})\ln(T/\mathrm{K}) - 834.7$$

$TbBr_3$(s), 331 K < T< 1103 K.

$$\Delta_{form}\,H^0_m/\mathrm{kJ{\cdot}mol^{-1}} = 22.50 \times 10^{-3}(T/\mathrm{K}) - 5.87 \times 10^{-6}(T/\mathrm{K})^2 + 4.35 \times 10^2(T/\mathrm{K})^{-1} - 897.4$$

$$\Delta_{form}\,G^0_m/\mathrm{kJ{\cdot}mol^{-1}} = 389.38 \times 10^{-3}(T/\mathrm{K}) + 5.87 \times 10^{-6}(T/\mathrm{K})^2 + 2.17 \times 10^2(T/\mathrm{K})^{-1} + 22.50 \times 10^{-3}(T/\mathrm{K})\ln(T/\mathrm{K}) - 98.4$$

$TbBr_3$(l), 1103 K < T< 1300 K.

$$\Delta_{form}\,H^0_m/\mathrm{kJ{\cdot}mol^{-1}} = 72.18 \times 10^{-3}(T/\mathrm{K}) - 9.69 \times 10^{-6}(T/\mathrm{K}) + 4.07 \times 10^2(T/\mathrm{K})^{-1} - 916.1$$

$$\Delta_{form}\,G^0_m/\mathrm{kJ{\cdot}mol^{-1}} = 744.78 \times 10^{-3}(T/\mathrm{K}) + 9.69 \times 10^{-6}(T/\mathrm{K})^2 + 2.03 \times 10^2(T/\mathrm{K})^{-1} - 72.18 \times 10^{-3}(T/\mathrm{K})\ln(T/\mathrm{K}) - 916.1$$

The results obtained at selected temperatures are presented in Table 3.

Summary

Temperature and enthalpy of fusion as well as heat capacity of solid $TbBr_3$ were experimentally determined. These data were used to calculate the whole set of thermodynamic functions up to 1300 K for solid and liquid terbium tribromide.

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