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THE VAPOR PHASE HYDROLYSIS OF LANTHANIDE(III) BROMIDES
III: HEAT AND FREE ENERGY OF THE REACTION
$SmBr_3(s) + H_2O(g) \overset{K_p}{\rightleftharpoons} SmOBr(s) + 2HBr(g)$

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Summary

The equilibrium constant K_p for the hydrolysis of solid samarium tribromide by water vapor was measured as a function of temperature in the range 860–699 K. The standard method of Cunningham and Koch in the improved version developed by Weigel and Wishnevsky was used. The following thermodynamic data were obtained: $\Delta H_{298}^\circ = 61.05$ kJ mol^{-1} and $\Delta H_{785}^\circ = 54.66$ kJ mol^{-1}; $\Delta S_{298}^\circ = 113.6$ J mol^{-1} K^{-1} and $\Delta S_{785}^\circ = 100.9$ J mol^{-1} K^{-1}; $\Delta G_{298}^\circ = 27.22$ kJ mol^{-1} and $\Delta G_{785}^\circ = -24.56$ kJ mol^{-1}. The heat of formation of SmOBr was calculated to be $\Delta H_{298}^\circ(\mathrm{SmOBr}) = -965.3 \pm 2.1$ kJ mol^{-1}.

1. Introduction

In the first paper of this series [1] we reported the measurement of the equilibrium constant K_p of the reaction

$$LnBr_3(s) + H_2O(g) \overset{K_p}{\rightleftharpoons} LnOBr(s) + 2HBr(g) \quad (1)$$

(Ln ≡ Nd). The equilibrium constant K_p is defined by

$$K_p = p_{HBr}^2 / p_{H_2O} \quad (2)$$

where p_{HBr} and p_{H_2O} are the partial pressures of gaseous HBr and H_2O respectively. In the second paper of the series [2] we reported similar measurements for Ln ≡ Pr and Gd. In a continuation of our systematic investigations of the corresponding bromide systems we report the results of the measurements for Ln ≡ Sm in this paper.

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2. Experimental details

2.1. Apparatus

The apparatus used for all bromide–oxybromide systems has been described in detail elsewhere [1, 3] and therefore no description is given here. Because the same apparatus had been used for measurements on radioactive samples of plutonium and americium [4] and is to be used for similar measurements of promethium in the future, it was installed in a Berkeley-type piano-box.

2.2. Reagents

The following reagents were used: samarium oxide (Sm_2O_3) (purity, 99.9%; Auer-Remy KG, Hamburg); hydrogen bromide (commercial grade, Linde, Höllriegelskreuth); hydrobromic acid (47% HBr solution; analytical grade, Merck); NaOH asbestos (analytical grade, Merck); magnesium perchlorate (analytical grade, Merck); nitrogen (purified nitrogen; commercial grade, Linde, Höllriegelskreuth).

2.3. Preparation and identification of $SmBr_3$ and SmOBr

A small apparatus outside the glove-box was used to confirm that only the bromide and oxybromide (in our case $SmBr_3$ and SmOBr) were formed during the hydrolysis reaction. $SmBr_3$ and SmOBr were prepared by the following reactions under the same conditions as in our hydrolysis apparatus:

$$Sm_2O_3 \xrightarrow[60\,\text{min},\,600\,^\circ\text{C}]{\text{HBr}} SmBr_3$$

$$SmBr_3 \xrightarrow[60\,\text{min},\,600\,^\circ\text{C}]{N_2\text{–}H_2O} SmOBr$$

X-ray samples were taken after the completion of each step and the reaction products were identified from their powder patterns. No oxide was formed under the hydrolysis conditions used. The hydrolysis reaction could be reversed by using HBr or HBr–N_2 in the second step instead of N_2–H_2O. Thus it can safely be assumed that the entire hydrolysis process takes place between $SmBr_3$ and SmOBr.

2.4. Measurements

Because of the reactivity of the commercial Sm_2O_3 available to us we were able to use it without any additional treatment as a starting material rather than using oxide freshly formed by the decomposition of the oxalate for each measurement. 2–3 mg of Sm_2O_3 were placed in the pan of a Salvioni quartz cantilever balance which was mounted in the reaction tube of the vapor phase hydrolysis apparatus. On heating to 560–600 °C in an HBr stream the oxide was converted to the tribromide; the furnace was then adjusted to the temperature necessary for the particular measurement and the hydrolysis experiment was performed as described in ref. 1.

3. Evaluation

The temperature dependence of K_p was measured as described in detail in ref. 1. The experimental ΔG_T° values (ΔG_T°(obs)) were calculated from the equation

$$\ln \bar{K}_p = -\frac{\Delta G_T^\circ}{RT} \tag{3}$$

where

$$\bar{K}_p = \frac{(K_p)_{\max} + (K_p)_{\min}}{2}$$

They were then fitted to the theoretical equation

$$\Delta G_T^\circ = I_H - I_S T - 1.372 \times 10^{-2}(T - T \ln T) - 4.5 \times 10^{-8} T^2 - 63 T^{-1} \tag{4}$$

where ΔG_T° is in kilojoules per mole, which was derived from the equation

$$\Delta C_p = -13.72 + 9 \times 10^{-5} T + 1.26 \times 10^5 T^{-2} \tag{5}$$

where ΔC_p is in joules per mole per kelvin.

The thermodynamic values of the enthalpy ΔH_T°, the entropy ΔS_T° and the Gibbs energy ΔG_T° as functions of temperature are as follows:

$$\Delta H_T^\circ = I_H - 1.372 \times 10^{-2} T + 4.5 \times 10^{-8} T^2 - 126 T^{-1} \tag{6}$$

$$\Delta S_T^\circ = I_S - 1.372 \times 10^{-2} \ln T + 9 \times 10^{-8} T - 63 T^{-2} \tag{7}$$

$$\Delta G_T^\circ = I_H - I_S T - 1.372 \times 10^{-2}(T - T \ln T) - 4.5 \times 10^{-8} T^2 - 63 T^{-1} \tag{8}$$

where ΔH_T° and ΔG_T° are in kilojoules per mole and ΔS_T° is in kilojoules per mole per kelvin. The constants I_H and I_S in eqns. (4), (6), (7) and (8) are obtained as the axis intersection and slope respectively.

The evaluation method has been slightly changed compared with that used in the earlier work [1, 2, 4] in order to facilitate the programming and to improve the calculation of the standard deviation which is the best criterion for the reliability of the results. All the calculations were performed using an HP-97 calculator which was programmed for this purpose. Comparison of the results obtained using the new and the old methods showed that the difference between them was much less than the standard deviations of both programs and was therefore negligible for all practical purposes. The integration constants I_H and I_S obtained using the new method were evaluated by a modified linear regression procedure. The standard deviations and the correlation r^2 were calculated by standard methods. A value of 0.99993 was obtained for r^2 which shows that there is excellent agreement between eqn. (4) and the experimental data.

The heat of formation of SmOBr was calculated from the equation

$$\Delta H_{f\,298}^\circ(\mathrm{SmOBr}) = \Delta H_{f\,298}^\circ(\mathrm{SmBr_3}) + \Delta H_{f\,298}^\circ(\mathrm{H_2O}) - 2\,\Delta H_{f\,298}^\circ(\mathrm{HBr}) + \Delta H_{298}^\circ \tag{9}$$

The values of the general parameters used in eqn. (9) are summarized in Table 1.

TABLE 1
General parameters used in the calculations

Parameter	*Numerical value at 298 K* (kJ mol^{-1})	*Reference*
$\Delta H_f°(H_2O)$	-241.814 ± 0.042	[5, 6]
$\Delta H_f°(HBr)$	-36.38 ± 0.17	[5, 6]
$\Delta H_f°(SmBr_3)$	-857.3 ± 2.0	[7]

4. Results

The experimental values of K_p obtained in our measurements of the vapor phase hydrolysis of $SmBr_3$ are summarized in Table 2. We used eqns. (6)–(8) and the data from Table 2 to calculate the thermodynamic data for reaction (1) which are compiled in Table 3. These data and the general parameters of Table 1 were used to calculate the heat of formation of SmOBr from eqn. (9):

$$\Delta H_{298}°(SmOBr) = -965.3 \pm 2.1 \text{ kJ mol}^{-1}$$

5. Discussion

The vapor phase hydrolysis data are shown as a function of temperature in Fig. 1. Comparison with the results of Weigel *et al.* for the neodymium [1] and gadolinium [2] systems shows that the values obtained are within the range expected; the $SmBr_3$ hydrolysis line is below that of $GdBr_3$ and above that of $NdBr_3$. As already mentioned, there is excellent agreement between $\Delta G_T°$(obs) and $\Delta G_T°$(calc) for the system studied.

The $\Delta S_{298}°$ values are compared with the values predicted by Latimer [8]. It should be noted, however, that Latimer's data for the entropy contribution of Br^- ions in connection with trivalent positive ions (as in the case of $SmBr_3$ and SmOBr) are given in parentheses and therefore have to be treated as a rough approximation only (ref. 8, p. 363). The value of $\Delta S_{298}°$(est) for our system is obtained in the following manner:

$\Delta S_{298}°(SmOBr)$	98.7 J mol^{-1} K^{-1}
$+\Delta S_{298}°(2HBr)$	397 J mol^{-1} K^{-1}
$-\Delta S_{298}°(SmBr_3)$	172 J mol^{-1} K^{-1}
$-\Delta S_{298}°(H_2O)$	188.7 J mol^{-1} K^{-1}
$\Delta S_{298}°$(est)	135 J mol^{-1} K^{-1}

(10)

Since according to Latimer the entropy of a compound is the sum of the entropy contributions of its positive and negative ions, eqn. (10) can be reduced to the following formula which is valid for all lanthanides:

$$\Delta S_{298}°(\text{est}) = \Delta S_{298}°(O^{2-}) + \Delta S_{298}°(2HBr) - \Delta S_{298}°(2Br^-) - \Delta S_{298}°(H_2O) \quad (11)$$

TABLE 2

Equilibrium constants for the reaction $SmBr_3(s) + H_2O(g) \rightleftharpoons SmOBr(s) + 2HBr(g)$

T (K)	T^{-1} ($\times 10^3$ K^{-1})	p_{H_2O} (mmHg)	p_{HBr} (mmHg)	$(K_p)_{max}$	$(K_p)_{min}$	$\bar{K}_p$	G_T°(obs) (kJ mol^{-1})	G_T°(calc) (kJ mol^{-1})	*Deviation*
860	1.163	2.885	449.88	92.30		89.72	−32.15	−32.08	+0.07
		2.802	430.72		87.13				
838	1.193	2.649	388.67	75.04		73.82	−29.97	−29.88	+0.09
		2.582	377.47		72.60				
815	1.227	2.804	355.69	59.36		57.96	−27.51	−27.58	−0.07
		2.749	343.78		56.56				
800	1.250	2.098	288.11	52.06		50.25	−26.05	−26.07	−0.02
		2.203	284.79		48.44				
780	1.282	2.064	259.35	42.88		40.00	−23.92	−24.05	−0.13
		2.332	256.49		37.12				
758	1.319	1.952	221.49	33.07		31.50	−21.74	−21.83	−0.09
		2.085	217.77		29.93				
720	1.389	2.589	204.35	21.22		20.41	−18.05	−17.96	+0.09
		2.841	205.72		19.60				
699	1.431	2.359	167.15	15.58		15.34	−15.87	−15.81	+0.06
		2.280	161.76		15.10				

TABLE 3

Thermodynamic parameters for the vapor phase hydrolysis of $SmBr_3$

Parameter	*Value*
I_H (kJ mol^{-1})	65.56±0.5
I_S (J mol^{-1} K^{-1})	192.4±0.6
ΔG_{785}° (kJ mol^{-1})	−24.56±0.5
ΔH_{785}° (kJ mol^{-1})	54.66±0.5
ΔS_{785}° (J mol^{-1} K^{-1})	100.9±0.6
ΔG_{298}° (kJ mol^{-1})	27.22±0.7
ΔH_{298}° (kJ mol^{-1})	61.05±0.5
ΔS_{298}° (J mol^{-1} K^{-1})	113.6±0.6

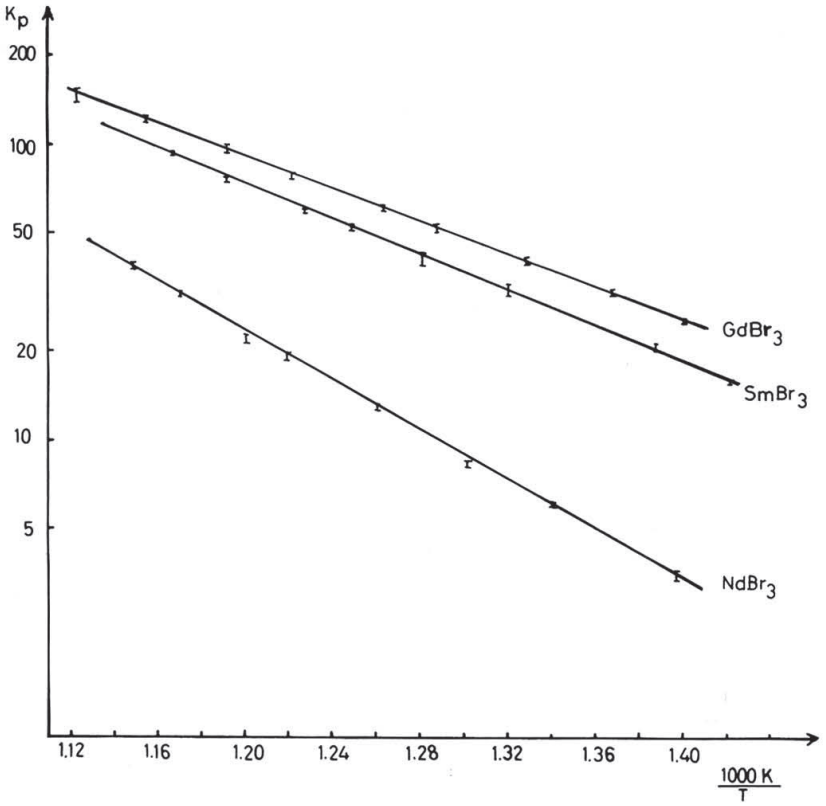

Fig. 1. Comparison of vapor phase hydrolysis data for $NdBr_3$ [1], $SmBr_3$ (this work) and $GdBr_3$ [2].

Using Latimer's data we obtain (all values in joules per mole per kelvin)

$$\Delta S_{298}^\circ(\text{est}) = 2.1 + 397 - 75.3 - 188.7 = 135.1 \text{ J mol}^{-1} \text{ K}^{-1}$$

(In our previous paper [2] the ΔS_{298}° values for the praseodymium and gadolinium systems were erroneously given as 128 J mol^{-1} K^{-1} and 127 J mol^{-1} K^{-1} respectively. In both cases the value is 135 J mol^{-1} K^{-1}.)

When the entropy data for the samarium system are compared with our previous results [1, 2] it can be seen that the ΔS_{298}° values increase with increasing atomic weight of the element involved. The ΔS_{298}° values were 138 J mol^{-1} K^{-1} for the praseodymium system, 137 J mol^{-1} K^{-1} for the neodymium

system and 114 J mol^{-1} K^{-1} for the samarium and gadolinium systems compared with Latimer's theoretical value of 135 J mol^{-1} K^{-1}. More data, particularly for the heavier lanthanides, are necessary in order to clarify the effect of the lanthanide contraction and of the $LnBr_3$ crystal structures on this phenomenon.

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