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A thermochemical study of rare-earth bromide hydrates

Sun Tong-Shan* , Wang Feng-Lian, Xiao Yu-Mei

Department of Chemistry, Shandong University, Jinan 250100, China

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Abstract

The enthalpies of solution of $REBr_3nH_2O(n=7$ for $RE=La$, Ce, and Pr; $n=6$ for $RE=Nd$, Sm, Eu, Gd, Tb, Dy, Ho, Yb, and Y) in aqueous KCl solution and those of KBr in aqueous RECl₃ solution have been measured calorimetrically at 298.15 ± 0.1 K. By means of a suitable thermochemical cycle, the standard molar enthalpies of formation for these twelve rareearth bromide hydrates were obtained, and their lattice energies and dehydration enthalpies calculated. The corresponding data of REB r_3 -6H₂O (RE=Pm, Er, Tm, and Lu) were estimated. The "double peak effect" during the property changes of the lanthanide elements and the probability that the effect will be applied for practice have been discussed. \odot 1998 Elsevier Science B.V.

Keywords: Bromide hydrates; Formation enthalpies; Lattice enthalpies and energies; Enthalpies of dehydration; Rare-earth metals

1. Introduction

In the field of studying the thermochemical and thermodynamic properties of rare-earth halides, Spedding et al. $[1-4]$ reported the thermochemistry of rareearth chlorides. Khanaev [5,6], Rezukhina [7] and Kim [8] reported the standard molar formation enthalpies of rare-earth fluorides. Hurtgen [9], Wang [10], Bettonville [11] and Schumm [12] reported the standard molar formation enthalpies of rare-earth bromides and iodides. The standard molar formation enthalpies of rare-earth bromide hydrates have not been reported in the literature.

We now report results of the determination of the standard molar enthalpies of formation for rare-earth bromide hydrates and the estimated results of their lattice enthalpies, lattice energies and standard enthalpies of dehydration.

2. Experimental

2.1. Reagents and synthesis procedures

The purities of RE_2O_3 were 99.99% (Shanghai Yue Long Chem. Fact., China). Tris-(hydroxy-methyl)- $\text{amino-methane}(Tris)$ was laboratory reagent (B.D.H., England). Tris was dried at 78° C for 2.5 h after being ground, and dried at 78° C for 1.5 h after being ground again. Treated tris was titrated by 0.1 mol 1^{-1} HCl (G.R. grade) with chlorophenol red as indicator. Finally, the purity of treated tris was 99.92%. KCl was G.R. grade. All other chemicals were A.R. grade.

^{*}Corresponding author.

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 $REBr₃·nH₂O$ and $RECl₃·nH₂O$ were prepared according to reported methods [16,17].

2.2. Component analysis of compounds

The rare-earth metal contents in these compounds were determined by EDTA titration [18]. The $Br⁻$ and Cl^- contents were determined by the Volhard method [19]. The difference between the totality and the contents of other entire elements RE^{3+} and Br^- or Cl^- were the H₂O contents. Analytical data for $REBr₃·nH₂O$ are listed in Table 1.

2.3. Calorimeter and calorimetric procedures

A modified RD-1 model heat-conducting automatic calorimeter (Sci. Instr. Fact. of Sichuan Univ., China) was used for the calorimetric measurements. Its thermoelectric pile of calorimetric component was composed of 144 pairs of nichrome-constantan thermocouples connected in series. Heat changes up to 2 J could be exactly measured. Details of the apparatus, principles and calorimetric procedures of the calorimeter have been described previously [20,21].

The reliability of the calorimetric system was assessed by measuring the enthalpy of reaction of tris (ca. 0.1 g) and HCl $(0.1003 \text{ mol l}^{-1}, 20.00 \text{ ml})$ at 298.15 \pm 0.1 K.The measured value of $-29.75\pm$ 0.09 kJ mol⁻¹, agrees very well with the recommended value of -29.771 ± 0.032 kJ mol⁻¹ [22].

Table 1 Analytical data for $REBr_2nH_2O$ (calculated values in parentheses)

The uncertainty of the calorimetric data is twice the standard deviation of the mean of at least five determinations.

3. Results and discussion

3.1. Standard molar enthalpies of formation of $REBr_3\cdot nH_2O$, $\Delta H_f^0(\text{REBr}_3 \cdot nH_2O, c)$

In order to obtain the value of ΔH_f^0 (REBr₃. nH_2O,c , a thermochemical cycle is presented for the derivation of the standard molar enthalpies of formation of rare-earth bromide hydrates in this paper. The cycle consists of four reaction shown as follows.

$$
REBr_3 \cdot nH_2O(c) + 3KCl \cdot 1500H_2O(aq)
$$

\n
$$
\xrightarrow{\Delta H_1} REBr_3 \cdot 3KCl \cdot (1500 + n)H_2O(aq) \quad (1)
$$

$$
RECl3(c) + (1500 + n)H2O(l)
$$

\n
$$
\xrightarrow{\Delta H2} RECl3 \cdot (1500 + n)H2O(aq)
$$
 (2)

$$
KCl(c) + 500H_2O(l) \stackrel{\Delta H_3}{\rightarrow} KCl \cdot 500H_2O(aq)
$$

$$
(3)
$$

$$
KBr(c) + 1/3[RECl_3 \cdot (1500 + n)H_2O](aq)
$$

\n
$$
\xrightarrow{\Delta H_4} 1/3[REBr_3 \cdot 3KC1 \cdot (1500 + n)H_2O](aq)
$$

$$
(\mathbf{4})
$$

Combining the Eqs. $(1)-(4)$ gives

Eq. (2) + 3 × Eq. (4) – Eq. (1) – 3
\n× Eq. (3) = Eq. (5)
\n
$$
RECl3(c) + 3KBr(c) + nH2O(1)
$$
\n
$$
\xrightarrow{\Delta H_5} REBr_3 \cdot nH_2O(c) + 3KCI(c)
$$
\n(5)

$$
\Delta H_5 = \Delta H_2 + 3\Delta H_4 - \Delta H_1 - 3\Delta H_3 \tag{6}
$$

$$
\Delta H_{\rm f}^{0}(\text{REBr}_{3} \cdot n\text{H}_{2}\text{O}, \text{c}) = \Delta H_{5}
$$

+
$$
\Delta H_{\rm f}^{0}(\text{RECl}_{3}, \text{c}) + 3\Delta H_{\rm f}^{0}(\text{KBr}, \text{c})
$$

+
$$
n\Delta H_{\rm f}^{0}(\text{H}_{2}\text{O}, \text{I}) - \Delta H_{\rm f}^{0}(\text{KCl}, \text{c})
$$
 (7)

where $n=7$ for RE=La, Ce, and Pr; and $n=6$ for RE=Nd, Sm, Eu, Gd, Tb, Dy, Ho, Yb and Y.

By substituting the values of the enthalpies of solution of $REBr₃·nH₂O$ in aqueous KCl solution $(KCl : H₂O=1 : 500 \text{ mol/mol}), \Delta H₁$, and those of KBr in aqueous RECl₃ solution (RECl₃: H₂O= $1:1507$ mol/mol for RE=La, Ce, and Pr; RECl₃: $H_2O=1$: 1506 mol/mol for RE=Nd, Eu, Gd, Tb, Dy, Ho, Yb, and Y), ΔH_4 , obtained in this work (see Table 2), the reported values of ΔH_3 of 17.56 kJ mol⁻¹ [15], ΔH_f^0 (H₂O, 1) of -285.83 kJ

Table 2

Thermochemical data (298.15 \pm 0.1 K) (enthalpies in kJ mol⁻¹)

mol⁻¹ [14], ΔH_f^0 (KBr,c) of -393.80 kJ mol⁻¹ [23], $\Delta H_{\rm f}^0$ (KCl,c) of -436.75 kJ mol⁻¹ [23], the values of ΔH_2 obtained by the described method in footnote of Table 2, and the values of ΔH_f^0 (RECl₃, c), taken from Ref. [13], into Eqs. (6) and (7), the values of ΔH_f^0 (REB r_3 · nH_2O ,c) in Table 3 are obtained.

For comparing the thermodynamic properties of $REBr₃·nH₂O(c)$ and $RECl₃·nH₂O(c),$ the values of $\Delta H_{\rm f}^0$ (RECl₃·nH₂O,c) obtained by Yin et al. [21] using the relationship (8) are also listed in Table 3.

$$
\Delta H_{\rm f}^{0}(\text{RECl}_{3} \cdot n\text{H}_{2}\text{O}, \text{c}) = \Delta H_{\rm s}^{0}(\text{RECl}_{3}, \text{c}) \n- \Delta H_{\rm s}^{0}(\text{RECl}_{3} \cdot n\text{H}_{2}\text{O}, \text{c}) + \Delta H_{\rm f}^{0}(\text{RECl}_{3}, \text{c}) \n+ n\Delta H_{\rm f}^{0}(\text{H}_{2}\text{O}, 1)
$$
\n(8)

where the values of ΔH_s^0 (RECl₃,c) and ΔH_f^0 (RECl_{3,} c), are taken from Ref. [13]; the values of ΔH_s^0 $(RECl_3 \cdot nH_2O,c)$ and ΔH_f^0 (H₂O,l), are taken from Ref. [4] and [14], respectively.

In Fig. 1, $-\Delta H_{\rm f}^0$ (REBr₃·nH₂O, c) and $-\Delta H_{\rm f}^0$ $(RECl₃·nH₂O,c)$ are plotted against the atomic numbers of the lanthanide elements. It is seen from Fig. 1 that $-\Delta H_{\rm f}^0$ (REBr₃·nH₂O,c) is smaller than $-\Delta H_{\rm f}^0$ (RECl₃·nH₂O,c) by ca. 123–153 kJ mol⁻¹ and a "double peak effect'' [24] is observed at the position of Eu

^a Ref. [13].

b Estimated values.

^c Example of the calculation of Φ_L (Φ_L (RECl₃) is the relative apparent molar enthalpy of RECl₃) in aqueous solution) [12]: $\Phi_L(RECI_3)_{0.03673} = 6990 \, m^{0.5} - 18851.9306 \, m + 56881.9234 \, m^{1.5} - 66921.7907 \, m^{1.75} + 25185.78432 \, m^2 - 700.23677 \, m^{2.75} = 874.8 \, \text{cal mol}^{-1} =$

3.66 kJ mol⁻¹ (*m* is the molality).
 $\Delta H_2 = \Delta H_s^0 + \Phi_L = \Delta H_f^0 (RE^{3+}, aq) + 3\Delta H_f^0 (Cl^-, aq) - \Delta H_f^0 (RECl_3, c) + \Phi_L (\Delta H_s^0$ is the standard enthalpy of solution; $\Delta H_f^0 (Cl^-, aq) =$ $167.08 \text{ kJ} \text{ mol}^{-1}$ [14]).

 $^{\rm a}$ Refs. [9-11].

b Estimated values.

Fig. 1. A plot of $-\Delta H_f^0$ (REBr₃·nH₂O, c) and $-\Delta H_f^0$ (RECl₃·nH₂O, c) vs. lanthanide atomic numbers ((\blacklozenge) Cl comp. = RECl₃·nH₂O; (\blacksquare) Br comp.= $REBr₃·nH₂O$).

and Yb on the two broken lines, i.e. the positions of Eu and Yb are the minimum among the values of $-\Delta H_f^0$ (REBr₃· nH_2O,c) and $-\Delta H_f^0$ (RECl₃· nH_2O,c). As Eu and Yb atoms do not have any 5d electrons, they have

thermodynamic stability of the half-filled $(4f^7)$ and filled $(4f¹⁴)$ valency shells. Their third electroionization energy and the total amount of the electroionization energies of the first, the second and the third are

Table 3

maximum in lanthanides. The greater the energy of electroionization, the more the energy consumed during the formation of some chemical bonds. Therefore, the releasing energy of the compounds of Eu and Yb decreases acutely when the compounds form so that the enthalpies of formation have the minimum.

The vast prospects of application of the "double" peak effect'' could be predicted: It could be used to separate and purify rare-earth compounds by using the specific characteristics of compounds of Eu and Yb so that we can separate superpurified rare-earth metals and compounds. It could be used to find and prepare particular function material of rare-earth metals because the properties of Eu and Yb compounds are fairly different from the remaining compounds of lanthnoids. It could be used to predict the properties and chemical thermodynamics data of compounds and complexes of rare-earth metals. Based on this information, we can use known data to predict unknown properties of some compounds.

3.2. Standard enthalpies of dehydration of $REBr_3·nH_2O$, ΔH_0^0

The values of ΔH_d^0 were calculated according to reaction (9) and Eq. (10) ,

Table 4 Lattice energies ΔU_L^0 (REBr₃•nH₂O,c) (298.15 K) (in kJ mol⁻¹)

$$
REBr_3 \cdot nH_2O(c) \stackrel{\Delta H_0^0}{=} REBr_3(c) + nH_2O(1)
$$
\n(9)

where ΔH_d^0 is the standard enthalpy of dehydration, and

$$
\Delta H_d^0 = \Delta H_f^0(\text{REBr}_{3,c}) + n\Delta H_f^0(\text{H}_2\text{O}, l)
$$

-
$$
\Delta H_f^0(\text{REBr}_3 \cdot n\text{H}_2\text{O}, c)
$$
 (10)

where the values of $\Delta H_{\rm f}^0$ (REBr₃,c) were taken from Refs. [9-11]. The results of the calculation are listed in Table 3.

3.3. Lattice energies of $REBr_3 \cdot nH_2O$, ΔU_L^0

Setting $\Delta H_{\rm L}^{0}$ as the lattice enthalpy in forming the crystal REBr₃·nH₂O from RE³⁺(g), Br⁻(g) and $H_2O(g)$ at 298.15 K and ΔU_L^0 as the crystal lattice energies, we have

$$
RE3+(g) + 3Br-(g) + nH2O(g)
$$

\n
$$
\xrightarrow{\Delta H_1^0} REBr_3 \cdot nH_2O(c)
$$
 (11)

$$
\Delta H_{\rm L}^{0} = \Delta H_{\rm f}^{0}(\text{REBr}_{3} \cdot n\text{H}_{2}\text{O}, \text{c})
$$

$$
- \Delta H_{\rm f}^{0}(\text{RE}^{3+}, \text{g}) - 3\Delta H_{\rm f}^{0}(\text{Br}^{-}, \text{g})
$$

$$
- n\Delta H_{\rm f}^{0}(\text{H}_{2}\text{O}, \text{g}) \tag{12}
$$

^a Ref. [21]

b Estimated values

Fig. 2. A plot of $-\Delta U_{L}^{0}$ (REBr₃·nH₂O,c) and $-\Delta U_{L}^{0}$ (RECl₃·nH₂O,c) vs. lanthanide atomic numbers ((\blacklozenge) Cl comp.=RECl₃·nH₂O; and (\blacksquare) Br comp.= $REBr_3nH_2O$.

$$
\Delta H_{\rm L}^{0} = \Delta U_{\rm L}^{0} + \Delta n \text{RT}
$$
\n
$$
\Delta U_{\rm L}^{0} = \Delta H_{\rm f}^{0} (\text{REBr}_{3} \cdot n \text{H}_{2}\text{O}, \text{c})
$$
\n
$$
- \Delta H_{\rm f}^{0} (\text{RE}^{3+}, \text{g}) - 3 \Delta H_{\rm f}^{0} (\text{Br}^{-}, \text{g})
$$
\n
$$
- n \Delta H_{\rm f}^{0} (\text{H}_{2}\text{O}, \text{g}) - \Delta n \text{RT}
$$
\n(14)

where $\Delta n = -7$ for RE=La, Ce, and Pr; $\Delta n = -6$ for RE=Nd, Sm, Eu, Gd, Tb, Dy, Ho, Yb, and Y; $R=8.314$ J mol⁻¹ K⁻¹; T=298.15 K; ΔH_f^0 (H₂O, g)= $-241.814 \text{ kJ mol}^{-1}$ [14]; ΔH_f^0 (Br⁻, g) = -233.89 kJ mol $^{-1}$ [23].

By substituting the above-mentioned data and the values of $\Delta H_{\rm f}^0$ (RE³⁺, g) taken from a previous study [21] into Eqs. (12)–(14), the values of $\Delta U_{\rm L}^0$ in Table 4 are obtained.

A plot of $-\Delta U_L^0$ (REBr₃·nH₂O,c) obtained in this work and $-\Delta U_{\rm L}^0$ (RECl₃·nH₂O,c) taken from Ref. [21], vs. the lanthanides atomic numbers is shown in Fig. 2.

It is seen from Fig. 2 that there is the same trend, namely $-\Delta U_{\text{L}}^0$ in proper order increase with increasing atomic number in two broken lines. This is due to the fact that the well-known lanthanide contraction causes an overall decrease in ionic radius so the lattice energies increase successively. In addition, $-\Delta U_{\rm L}^0$ $(REBr_3 \cdot nH_2O,c)$ is smaller than $-\Delta U_L^0$ (RECl₃. nH_2O,c) by ca. 125–133 kJ mol⁻¹ owing to the radius of Br^- being larger than that of Cl^- .

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