Thermodynamics of the formation of oxosulfides of rare-earth elements

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The enthalpies of solution of several oxosulfides of rare-earth elements and the high-temperature enthalpies of oxosulfides and oxosulfates of lanthanum and yttrium were measured using solution calorimetry and high-temperature microcalorimetry techniques. Standard enthalpies of formation and some thermodynamic properties of oxosulfides and oxosulfates were calculated.

Key words: oxosulfides, oxosulfates of lanthanides; formation enthalpies, high-temperature entalpies, calorimetry.

Oxosulfides of composition Ln_2O_2S and their solid solutions are known as efficient anti-Stokes luminophores used as ceramics, single crystals, films, and powders. Apart from this, oxosulfides are formed in the desulfurization of metallurgical melts. There are no reliable experimental data on the thermodynamics of oxosulfides necessary to optimize their technology and use. In the present work, a thermochemical study of oxosulfides has been undertaken to determine their fundamental thermodynamic constants: their enthalpies of formation and their high-temperature enthalpies.

Experimental

Oxosulfides of La, Pr, Nd, Sm, Eu, and Gd were obtained by reduction of the sulfates of the corresponding lanthanides by a nitrogen—hydrogen mixture at 900 °C.[1] According to the chemical analysis data (a complexonometric analysis for the Ln^{3+} ions and a gravimetric analysis for their sulfates after oxidation of the sulfidic sulfur with bromine), the composition of oxosulfides was determined as $Ln_2O_2S_{1.00+0.01}$. The presence of only one phase for the compounds synthesized was established by X-ray phase analysis (a DRON-0.5 diffractometer, Cu cathode, Cu-Kα radiation). Then the crystal lattice parameters were calculated, the picnometric densities were measured, and the molar volumes were determined (Table 1). Oxosulfates of La and Y were obtained by calcination of their sulfates,[2] and their composition ($Ln_2O_2SO_4$) was established from the data of gravimetric and chemical (complexonometric determination of Ln^{3+} ions) analyses.

To determine the standard enthalpies of formation of Ln_2O_2S, the quantitative oxidation of oxosulfides in acid solutions under conditions identical to those of the reactions in the calorimeter cell was studied using a solution calorimeter.[3] Based on the data of preliminary experiments, sulfuric solutions of cerium(IV) sulfate and potassium permanganate were chosen from a number of oxidants capable of oxidation of sulfidic sulfur. In this case the rate of the oxidation of sulfidic sulfur was found to decrease in the series of oxosulfides. It was established in an analytical study of the oxidation of oxosulfides of lanthanum and samarium by sulfuric solutions of cerium(IV) sulfate that the sulfidic sulfur (a sample of mass ~1 g) is oxidized to elemental sulfur by solutions of cerium sulfate (of normality $N \geq 0.05$) containing not less than 10% sulfuric acid in 5—6 min. The quantitative compositions of the reaction products were determined from the data of the chemical analysis for the Ce^{4+} ions (iodometry) and those of the gravimetric analysis of the elemental sulfur, which, according to the X-ray phase analysis data, forms its orthorhombic modification. The amount of elemental sulfur (13 experiments with La_2O_2S and 12 experiments with Sm_2O_2S) determined from the results of the analysis for the Ce^{4+} ions coincides

Table 1. Physical properties of oxosulfides of rare-earth elements

Ln	Unit cell parameters /Å			$\rho \cdot 10^{-3}$ /kg m^{-3}	$V_m \cdot 10^{-6}$ /m^3 mol^{-1}
	a (±0.004)	c (±0.006)	c/a		
La	4.040	6.920	1.72	5.82	58.7
Pr	3.950	6.810	1.72	6.25	55.4
Nd	3.935	6.795	1.73	6.47	54.5
Sm	3.888	6.715	1.73	6.89	53.0
Eu	3.860	6.680	1.73	7.07	52.0
Gd	3.843	6.665	1.73	7.38	51.3
Tb	3.812	6.617	1.74	7.61	50.2

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Table 2. Enthalpies of reactions of Ln_2O_2S according to Eqs. (1)—(3)

Ln	Solvent	Number of experiments	$-\Delta H°_{298.15}$ /kJ mol^{-1}
La	$Ce(SO_4)_2 \cdot 50\ H_2SO_4 \cdot 5000\ H_2O$	8	725.1±3.4
Pr	$Ce(SO_4)_2 \cdot 50\ H_2SO_4 \cdot 5000\ H_2O$	8	718.0±2.9
Nd	$Ce(SO_4)_2 \cdot 50\ H_2SO_4 \cdot 5000\ H_2O$	8	713.8±2.1
Sm	$Ce(SO_4)_2 \cdot 50\ H_2SO_4 \cdot 5000\ H_2O$	8	717.6±2.5
La	$KMnO_4 \cdot 30\ H_2SO_4 \cdot 1000\ H_2O$	7	1274.4±2.9
La	$HCl \cdot 30\ H_2O$	12	325.1±11.7
Eu	$HCl \cdot 30\ H_2O$	8	295.8±2.5
Gd	$HCl \cdot 30\ H_2O$	8	293.3±2.5

with the data of its gravimetric analysis within the limits of 0.3—0.5%, *i.e.*, the sulfidic sulfur is quantitatively oxidized to elemental sulfur.

Results and Discussion

The main reaction of the thermochemical cycle can be written as:

$$Ln_2O_2S(cryst) + 2\ Ce(SO_4)_2(sol.\ A) + 100\ H_2SO_4(sol.\ A) = \\ = Ln_2(SO_4)_3(sol.\ B) + S(orthorhomb) + Ce(SO_4)_2(sol.\ B) + \\ + 2\ H_2O(sol.\ B) + 98\ H_2SO_4(sol.\ B), \qquad (1)$$

where solution A is $Ce(SO_4)_2 \cdot 50\ H_2SO_4 \cdot 5000\ H_2O$ and B is $Ln_2(SO_4)_3 \cdot Ce_2(SO_4)_3 \cdot 98\ H_2SO_4 \cdot 10002\ H_2O$.

The enthalpies of reaction (1) were determined for oxosulfides of La, Pr, Nd, and Sm. Lanthanum oxosulfide is oxidized by potassium permanganate in a solution of composition $KMnO_4 \cdot 30\ H_2SO_4 \cdot 1000\ H_2O$ according to the reaction:

$$5\ La_2O_2S(cryst) + 16\ KMnO_4(sol.) + 480\ H_2SO_4(sol.) = \\ = 5\ La_2(SO_4)_3(sol.) + 4\ K_2SO_4(sol.) + \\ 8\ MnSO_4(sol.) + 458\ H_2SO_4(sol.) + \\ + 22\ H_2O(sol.). \qquad (2)$$

The enthalpy of reaction (2) was obtained only for La_2O_2S because a solution of $KMnO_4$ is less stable than a solution of cerium(IV) sulfate (on the basis of the absorption spectrum, hydrated manganese peroxide forms in the solution 1 h after the calorimetric experiment). Oxosulfides of europium and gadolinium enter reaction (1) at a low rate, which is unsuitable for performing adequate calorimetric measurements. Therefore, the enthalpies of formation of the mentioned Ln_2O_2S were determined from the measurements of enthalpies of their reaction with a solution of HCl ($HCl \cdot 20\ H_2O$) saturated with hydrogen sulfide according to the following equation:

$$Ln_2O_2S(cryst) + 6\ HCl(sol.) = \\ = 2\ LnCl_3(sol.) + H_2S(g) + 2\ H_2O(sol.). \qquad (3)$$

The results of measurements of the enthalpies of reactions (1)—(3), processed using a t-distribution, are listed in Table 2. To formulate the thermochemical cycle and calculate the enthalpies of formation of oxosulfides, the enthalpies of solution of sulfates of La, Pr, Nd, Sm, Mn^{II}, K, and Fe^{III}, those of chlorides of La, Eu, and Gd, and that of $KMnO_4$ were additionally measured in the corresponding solvents as well as the enthalpy of the interaction of S(orthorhomb) with solution B. In addition, to determine the enthalpy of the transition $Ce^{IV} \rightarrow Ce^{III}$ (reaction (1)), the enthalpy of the oxidation of $FeSO_4$ by Ce^{IV} sulfate in a solution of sulfuric acid was also determined. The results of these measurements after statistical processing are listed in Table 3. The enthalpies of formation of crystalline sulfates of La, Pr, Nd, and Sm needed for calculations were obtained from analyzing data published previously[4,5] (Table 4). For the enthalpy of formation of neodimium sulfate, a weighted-mean value of the two results is given (see Ref. 5).

The standard enthalpies of formation of oxosulfides calculated from the data of Tables 2 and 3 and those of Refs. 4 and 5 are listed in Table 4. Since three methods were used to determine the enthalpy of formation of La_2O_2S, the weighted-mean value, $\Delta_f H°_{298.15}$ =

Table 3. Enthalpies of reactions of sulfates and chlorides with HCl and sulfate solutions of $Ce(SO_4)_2$ and $KMnO_4$

Compound	Solvent	Number of experiments	$\Delta H°_{298}$ /kJ mol^{-1}
$LaCl_3 \cdot 7\ H_2O$	$HCl \cdot 30\ H_2O$	5	11.42±0.33
$EuCl_3 \cdot 6\ H_2O$	$HCl \cdot 30\ H_2O$	8	13.77±0.59
$GdCl_3 \cdot 6\ H_2O$	$HCl \cdot 30\ H_2O$	9	15.86±0.38
$La_2(SO_4)_3$	$Ce_2(SO_4)_2 \cdot 98\ H_2SO_4 \cdot 1000\ H_2O$	8	120.0±0.7
$Pr_2(SO_4)_3$	$Ce_2(SO_4)_2 \cdot 98\ H_2SO_4 \cdot 1000\ H_2O$	8	106.3±1.3
$Nd_2(SO_4)_3$	$Ce_2(SO_4)_2 \cdot 98\ H_2SO_4 \cdot 1000\ H_2O$	8	134.3±1.3
$Sm_2(SO_4)_3$	$Ce_2(SO_4)_2 \cdot 98\ H_2SO_4 \cdot 1000\ H_2O$	5	144.0±0.8
$Fe_2(SO_4)_3$	$Ce_2(SO_4)_2 \cdot 98\ H_2SO_4 \cdot 1000\ H_2O$	8	124.8±0.9
$FeSO_4$	$Ce(SO_4)_2 \cdot 50\ H_2SO_4 \cdot 5000\ H_2O$	8	105.9±2.1
$La_2(SO_4)_3$	$Ce(SO_4)_2 \cdot 50\ H_2SO_4 \cdot 5000\ H_2O$	5	119.7±0.8
$MnSO_4+K_2SO_4$	$8KMnO_4 \cdot 458\ H_2SO_4 \cdot 16022\ H_2O$	5	20.5±0.2
$KMnO_4$	$8KMnO_4 \cdot 458\ H_2SO_4 \cdot 16022\ H_2O$	8	32.1±0.6

Table 4. Standard enthalpies of formation of the initial chlorides and sulfates, and thermodynamic properties of oxosulfides of rare-earth elements

Ln	Main reaction	$Ln_2(SO_4)_3$ or $LnCl_3 \cdot nH_2O$, $-\Delta_fH^\circ_{298}$/kJ mol^{-1}	Ln_2O_2S $-\Delta_fH^\circ_{298}$ (kJ mol^{-1})	$-\Delta_fG^\circ_{298}$ (kJ mol^{-1})	S°_{298} /J mol^{-1} K^{-1}
La	(3)	3179.2±0.9	1660.2±11.9	—	—
La	(2)	3947.7±13	1674.3±13.4	—	—
La	(1)		1673.0±14.8	1539	137.7
Pr	(1)	3920.8±20	1639.7±23	1515	143.0
Nd	(1)	3938.0±4.2	1646.9±5.0	1523	142.6
Sm	(1)	3885.7±6.7	1642.6±9.5	1518	142.3
Eu	(3)	2788.8±4.2	1469.0±4.0	1339	160.7
Gd	(3)	2865.1±1.4	1644.9±4.0	1520	160.7

−1670.4±7.6 kJ mol^{-1}, is recommended as the most reliable value.

Using the approximately calculated values of S°_{298} [6,7] and the experimental values of the enthalpy of formation we estimated the standard Gibbs energies of formation of oxosulfides (see Table 4).

The study of the high-temperature enthalpies of oxosulfides and oxosulfates was carried out by using high-temperature calorimeters in the intervals from 298.15 to 673 K (Ln_2O_2S) and from 298 to 923 K ($Ln_2O_2SO_4$) in air,[8] and in the interval from 865 to 1350 K under an N_2 atmosphere,[9] because oxosulfides are oxidized in air at temperatures above 770 K. Both calorimeters were calibrated against the values of the high-temperature enthalpies of single-crystal samples of α-Al_2O_3 by the mixing method. The results of processing the experimental data (4—8 runs for each substance) are listed in Table 5.

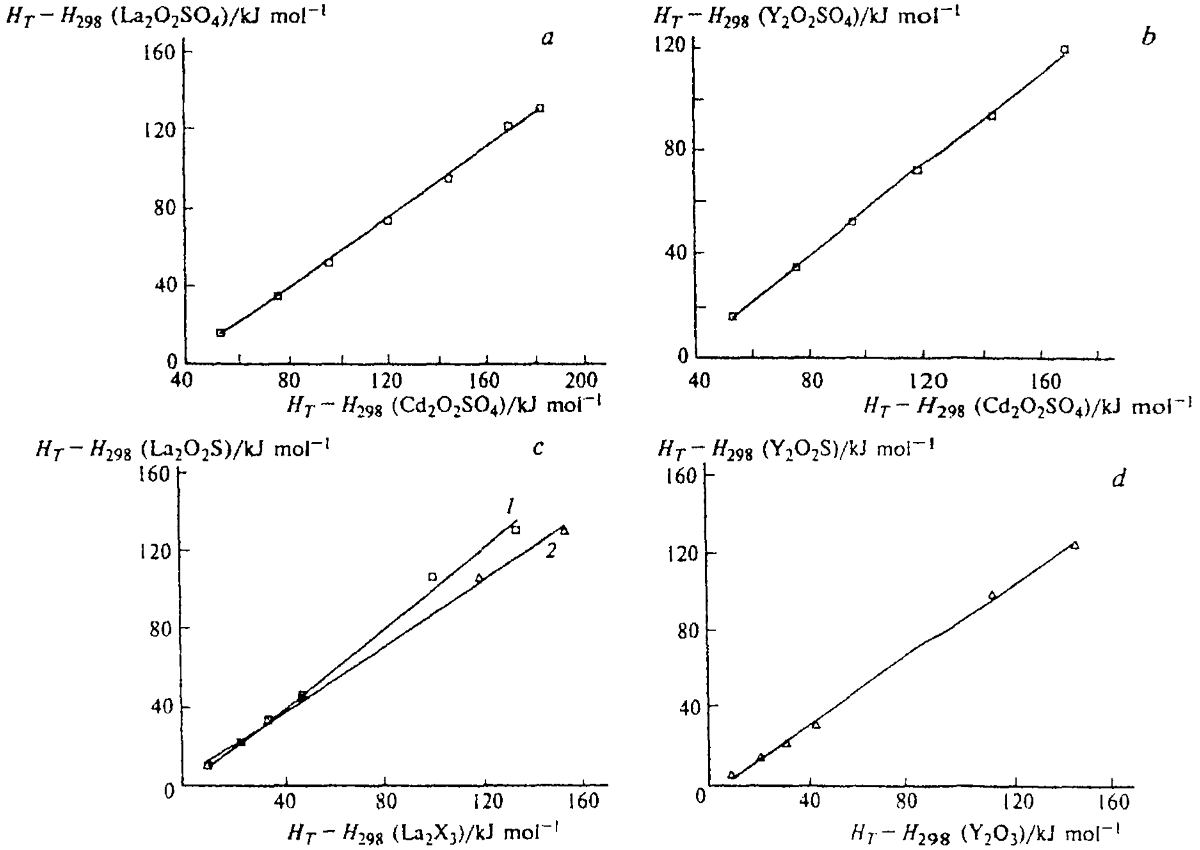

Fig. 1. Relationships between the high-temperature enthalpies of: *a*, oxosulfates of La^{2+} and Cd^{2+}; *b*, oxosulfates of Y^{3+} and Cd^{2+}; *c*, La^{3+} oxosulfate and La^{3+} oxosulfide (sulfide) (X = S(*1*), O(*2*)); *d*, Y^{3+} oxosulfate and Y^{3+} oxide.

Table 5. High-temperature enthalpies (kJ mol^{-1}) of oxosulfides and oxosulfates of lanthanum and yttrium

T/K	$H_T - H_{298}$/kJ mol^{-1}			
	La_2O_2S	Y_2O_2S	$La_2O_2SO_4$	$Y_2O_2SO_4$
383	10.2±0.05	7.2±0.03	16.4±0.2	16.0±0.1
483	22.2±0.2	16.1±0.1	35.0±0.2	34.8±0.2
573	33.3±0.3	22.5±0.1	52.1±0.3	52.4±0.2
673	45.3±0.2	31.8±0.2	74.1±0.5	72.5±0.3
773	—	—	95.2±0.5	93.8±0.4
865	—	74.5±3.0	—	—
873	—	—	122.8±1.0	119.5±1.3
923	—	—	131.1±1.0	—
1090	107.5±3.0	100.0±3.9	178.3±3.0	178.3±3.0
1350	131	126.3±3.0	—	—

Table 6. Enthalpies of oxidation of oxosulfides and standard enthalpies of formation of oxosulfates of lanthanides

Ln	ΔT	T_{av}	$-\Delta H^\circ_{T_{av}}(4)$	$-\Delta_f H^\circ_{298}$
	K		kJ mol^{-1}	
La	1000—1500	1250	457.87	
La		1200	459.2, 457.9	4679
La	1100—1500	1300	460.1	
Pr		1200	449.9	
Pr	1100—1400	1250	447.1	4566
Nd	930—1200	1070	452.77	4848
Nd	1170—1400	1285	451.76, 437.7	
Nd		1200	449.36	
	1100—1430	1265	452.0	
Sm	1050—1370	1160	453.4	4559
Sm		1200	447.32	
Eu	1020—1320	1170	447.2	4394
Eu		1200	444.0	
Gd		1200	443.69; 445.35	
Gd	1000—1280	1140	445.8	4559
Tb		1200	444.85	
Tb	1020—1280	1110	453.7	
Dy		1200	439.79	
Dy	1040—1180	1110	446.0	

Table 7. Comparison of standard enthalpies of formation of oxosulfides determined by different methods

Ln	$-\Delta H^\circ_{298}$/kJ mol^{-1}	
	Calorimetry	e.m.f. method
La	1670.4±7.6	—
Ce	—	1686.2
Pr	1639.7±23	—
Nd	1646.9±5.0	1643.9
Sm	1642.6±9.5	—
Eu	1469.0±4.0	—
Gd	1644.9±4.0	1680.6
Y	—	1770.5

The linear correlations (Fig. 1), which allow one to make a correct estimate of $H_T - H_{298}$ values of oxosulfides and oxosulfates up to the melting point, were obtained from a comparison of the high-temperature enthalpies of oxosulfides with the analogous characteristics of oxides of lanthanum and yttrium and lanthanum sulfide (in the case of oxosulfates with those of cadmium oxosulfate[10]).

Previously,[11—15] the equilibrium of oxidation of oxosulfides in the reaction

$$0.5\ La_2O_2S(\text{cryst}) + O_2(g) = 0.5\ La_2O_2SO_4(\text{cryst}) \qquad (4)$$

has been studied by the e.m.f. method with a solid electrolyte in the range from 950 to 1500 °C, and temperature dependences of the type $\Delta G^\circ = A + BT$ have been obtained. The enthalpies of oxidation for T_{av} ($\Delta H^\circ_{T_{av}}$) were calculated from these dependences (Table 6). To approximately calculate the standard enthalpies of formation of oxosulfates of lanthanides and yttrium, a set of quantities including the standard enthalpies of formation and the high-temperature enthalpies determined in this work, and the enthalpies of oxidation calculated from the literature data on thermodynamic properties of oxosulfides and oxosulfates[11—15] was used. As follows from the results given in Table 5, the values of the high-temperature enthalpies of oxosulfides or oxosulfates in the La—Y series are close at the same temperatures. Hence the $\Delta C_{p,298}$ values calculated using Kirchhoff's law for reaction (4) (the difference of close values) will depend only slightly on pairwise replacement of lanthanide in oxosulfide and oxosulfate. The assumption that the $\Delta C_{p,298}$ values are independent of the replacement of the rare-earth element in reaction (4) together with the standard enthalpies of formation of oxosulfides allowed us to make an estimate of the standard enthalpies of formation of oxosulfates (see Table 6). Using the data published previously[11—15] and the $H_T - H_{298}$ values we obtained, the standard enthalpies of formation were also calculated for several oxosulfides. A comparison of these values with those determined by calorimetric techniques (Table 7) showed that the maximum discordance between the two methods did not exceed 2.5%. Therefore, it is believed that the standard enthalpies of formation of oxosulfates were calculated with an error of ±3%.

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