THERMODYNAMIC PROPERTIES OF PURE SUBSTANCES

The Enthalpies of Formation of Praseodymium Halides PrCl₃, PrBr₃, and PrI₃ in the Crystalline State and Aqueous Solution

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Abstract—The enthalpies of solution of praseodymium tribromide and triiodide in water were measured at 298.15 K in a hermetic isothermic-shell swinging calorimeter. The data obtained and the $\Delta_f H^{\circ}(Pr^{3+}, sln, \infty H_2O, 298 \text{ K})$ value found earlier were used to calculate the enthalpies of formation of three praseodymium halides (PrCl₃, PrBr₃, and PrI₃) in the crystalline state and aqueous solution.

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INTRODUCTION

This work is concerned with the determination of the enthalpies of formation of praseodymium halides (PrHal₃, Hal = Cl, Br, and I) in the crystalline state and aqueous solution. The enthalpies of formation of these compounds can be obtained from the enthalpies of formation of the Pr³⁺, Cl⁻, Br⁻, and I⁻ ions in aqueous solution at infinite dilution and the enthalpies of solution of praseodymium halides in water to infinite dilution. The enthalpies of formation of halogen anions have been determined fairly reliably [1]. The $\Delta_{\rm f} H^{\circ}(\rm Pr^{3+}, \ sln, \ \infty H_2O, 298.15 \ K)$ value was found by us in [2]. The enthalpy of solution of praseodymium trichloride in water at a finite concentration (1 : 6327H₂O) and infinite dilution was also obtained in [2].

The enthalpy of solution of praseodymium tribromide was measured in an acidified (10⁻³ N HCl) aqueous solution only in [3]. Praseodymium tribromide used in [3] was obtained from praseodymium metal (purity 99.99 wt %) and liquid bromine purified by preliminary degassing. The synthesis of PrBr₃ was performed at 773 K in a quartz reactor loaded in a dry box under nitrogen. The product was purified by sublimation at 1173–1273 K immediately before calorimetric measurements. All operations with synthesized PrBr₃ were performed in a dry box under nitrogen. The substance was analyzed gravimetrically for Pr³⁺ and Br⁻. Found (wt %): Pr³⁺, 37.00 and Br⁻, 62.85. Calculated for PrBr₃ (wt %): Pr^{3+} , 37.02 and Br^- , 62.98. According to the X-ray data, the sample was single-phase. The enthalpies of solution were measured at 298.15 K in an LKB 8700-1 calorimeter. Five experiments were performed to find that the enthalpy of solution of praseodymium tribromide was -177.8 ± 2.2 kJ/mol at a 1 : $27400H_2O$ dilution.

The enthalpy of solution of praseodymium triiodide was also measured in one work only [4]. Praseody-

mium triiodide was prepared by the reaction between praseodymium trichloride and a mixture of hydrogen iodide and hydrogen at ~870 K. The content of I⁻ in the sample was determined by potentiometric titration; no analytic data were, however, reported in [4]. The enthalpy of solution of praseodymium triiodide in water was measured at 293 K in a nonhermetic liquid calorimeter (the volume of the liquid was 450 ml). According to the results of two experiments, its value was -208.8 kJ/mol at a 1 : 10000H₂O dilution.

It follows from an analysis of the literature data that only the results obtained in [3] for the enthalpy of solution of crystalline praseodymium tribromide can be used in thermochemical calculations. The error in enthalpy obtained in [3], 2.2 kJ/mol, is, however, a bit too large for this class of compounds. There is virtually no data on the determination of the enthalpy of solution of praseodymium triiodide in water, because the samples used in [4] were not characterized quantitatively, and the recommended enthalpy of solution was obtained from the results of only two measurements. We considered it expedient to perform new precision measurements of the enthalpy of solution of praseodymium triiodide in water and refine the enthalpy of solution of praseodymium tribromide reported in [3]. The data obtained in this work and reported by us in [2] were used to calculate the standard enthalpies of formation of praseodymium halides ($PrCl_3$, $PrBr_3$, and PrI_3) in the crystalline state and aqueous solution.

EXPERIMENTAL

Anhydrous praseodymium tribromide was synthesized in two stages. At the first stage, $PrBr_3 \cdot nH_2O$ crystal hydrate was obtained in the reaction between praseodymium oxide Pr_6O_{11} (99.9%) and hydrobromic acid of ch. d. a. (pure for analysis) grade. At the second stage, $PrBr_3 \cdot nH_2O$ was dehydrated in a vacuum in a quartz reactor of a special shape with a section for collecting sublimed substances. The reactor with crystal hydrate was heated to ~480 K at a reduced pressure $(5 \times 10^{-1} \text{ Pa})$. The temperature was then increased to 1300 K, and the system was held at this temperature for 4 h. The stage of dehydration was followed by the stage of sublimation, and both were performed in one reactor. The sublimed substance was prevented from contacting with the atmosphere.

Anhydrous praseodymium triiodide was synthesized in the reaction between praseodymium metal (99.8%) and iodine of os. ch. (special purity) grade in a two-section quartz reactor. The reactor was preliminarily degassed in a vacuum at 1200 K to remove impurities. Praseodymium metal filings were loaded into a quartz crucible in the left reactor section; the filings were prepared beforehand from an ingot in a dry box under argon. Powdered crystalline iodine taken in an excess twofold by weight was loaded into the first reactor section to provide constant boiling conditions. The reactor was then evacuated to 5×10^{-1} Pa. The temperature of the section with iodine was maintained constant (~490 K) during the whole synthesis time. The temperature of the section with metal was gradually (during 6 days) increased to 950 K with isothermal intervals. These temperature conditions prevented praseodymium and then praseodymium triiodide interactions with the container and ensured reaction completion,

(2/3)Pr + I₂ = (2/3)PrI₃.

The reactor was cooled starting with the section with iodine (the furnace for the section with iodine remained switched on during cooling). Next, the furnace for the section with iodine was switched off. After complete cooling, the reactor was transferred into a dry box and accurately broken in such a way that the quartz crucible with the product remained intact. The product was in the sintered but not molten state and could be easily removed from quartz crucible walls. The salt was removed from the crucible, ground in a mortar, and transferred into a Pyrex ampule, which was evacuated for 6 h at a 5×10^{-1} Pa pressure and 500 K to remove adsorbed iodine and then sealed for storage.

The praseodymium halide samples were identified by quantitative chemical analyses for praseodymium (complexonometric titration with Trilon B) and halogen (gravimetry). The chemical analysis data are listed in Table 1.

According to X-ray diffraction, the samples were single-phase and corresponded to PrI_3 (a $PuBr_3$ -type structure) and $PrBr_3$ (a UCl_3 -type structure). Praseodymium halides are strongly hygroscopic, and all operations with them were performed in a dry box in an inert atmosphere to prevent the substances from contact with air moisture.

Hydrochloric acid (1.07 N) used as a reacting liquid was prepared from concentrated hydrochloric acid of

Table 1. Chemical analysis data on praseodymium halides,at %

Halide	Foi	Calculated		
	Pr	Hal	Pr	Hal
PrBr ₃	37.00 ± 0.09	62.93 ± 0.04	37.02	62.98
PrI ₃	26.98 ± 0.11	72.92 ± 0.05	27.01	72.99

os. ch. grade (the total content of impurities less than 0.002 wt %) and distilled water with a specific conductivity of $6 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$.

The enthalpies of solution were measured in a hermetic isothermic-shell swinging calorimeter at 298.15 K. A detailed description of the unit and procedure for measurements can be found in [5, 6]. The calorimetric vessel ($V = 112 \text{ cm}^3$) made of titanium was filled with $80.000 \pm 0.003 \text{ g}$ H₂O and hermetically closed. Temperature rise was measured with a platinum resistance thermometer ($R_{298.15} = 401.32$, 1 $\Omega = 0.94 \text{ K}$) using a bridge scheme. An F-116/2 microvoltmicoammeter connected to a KSP-4 automated recording potentiometer was used as a null instrument. The potentiometer recorded calorimeter temperature variations during measurements. The thermometric sensitivity of the unit was $3 \times 10^{-5} \text{ K/mm}$ recorder scale. The temperature of water in the shell was maintained constant automatically with an accuracy of $5 \times 10^{-3} \text{ K}$.

The energy equivalent of the calorimetric system was determined electrically with the use of a potentiometric scheme to within several thousandths of a percent. The voltage on the heater and reference coil $(R = 1.0000_5 \ \Omega)$ was measured by an R-363-2 highresistance potentiometer of the accuracy class 0.002%. The duration of current passage was measured by an F-5080 frequency meter-chronometer with an accuracy of 0.002 s. The energy equivalent of the calorimeter $(W = 322.62 \pm 0.23 \ J/\Omega)$ was found in a series of 10 measurements. Here and throughout, the confidence intervals were calculated with a 95% probability.

Prior to calorimetric measurements, the substances were placed into glass ampules and sealed in a dry box in an inert atmosphere. The samples were weighed on a Satorius balance with an accuracy of 0.00002 g.

RESULTS AND DISCUSSION

The results obtained in measuring the enthalpies of solution of praseodymium bromide and iodide in water are listed in Tables 2 and 3. We use the following notation: ΔR is the temperature rise corrected for heat exchange, g is the sample weight, Q is the thermal effect of measurements, and ΔH is the enthalpy of the reaction. The enthalpies of solution were calculated with corrections ΔH_r for reduction to a temperature of 298.15 K. There is no literature data on the temperature coefficients for the enthalpies of solution of praseody-

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Table 2. The results of measurements of the enthalpy (kJ/mol) of solution of PrBr₃ in water at 298.15 K (ΔH_1 is the enthalpy at the temperature of measurements, and ΔH_2 is the enthalpy reduced to 298.15 K)

$\Delta R, \Omega$	<i>g</i> , g	$\Pr Br_3 \cdot nH_2O, \\ mol$	<i>Q</i> , J	$-\Delta H_1$	$-\Delta H_{298}$
0.23722	0.16241	10400	76.532	179.36	179.19
0.22544	0.15550	10868	72.731	178.02	177.94
0.22463	0.15460	10931	72.470	178.42	178.28
0.21069	0.14445	11699	67.973	179.11	(178.97)
0.20939	0.14410	11728	67.553	178.43	178.36
0.20304	0.13957	12108	65.505	178.64	178.58
0.18910	0.13016	12984	61.007	178.40	(178.27)
0.18543	0.12687	13320	59.823	179.47	179.41
0.18266	0.12536	13481	58.930	178.92	178.92
0.17521	0.12033	14040	56.526	178.80	(178.80)
0.13672	0.09337	18100	44.108	179.80	179.66
0.09567	0.06584	25700	30.865	178.43	178.40

Note: The enthalpies of solution in a 0.001 N solution of HCl are given in parentheses; $\Delta H_{av} = -178.73 \pm 0.33$ kJ/mol.

Table 3. The results of measurements of the enthalpy (kJ/mol) of solution of PrI_3 in water at 298.15 K

$\Delta R, \Omega$	<i>g</i> , g	$\Pr \mathbf{I}_3 \cdot n\mathbf{H}_2\mathbf{O},\\ mol$	<i>Q</i> , J	$-\Delta H_1$	$-\Delta H_{298}$
0.21030	0.16989	13640	67.847	208.31	208.38
0.19749	0.15944	14526	63.714	208.45	208.52
0.18657	0.15434	15006	60.191	203.43	203.49
0.18222	0.14756	15695	58.788	207.81	(207.86)
0.16863	0.13915	16644	54.403	203.94	204.00
0.16261	0.13232	17500	52.461	206.81	206.88
0.15684	0.12797	18098	50.600	206.25	(206.33)
0.14581	0.11945	19389	47.041	205.42	205.49
0.13529	0.11051	20957	43.647	206.02	206.12
0.10805	0.08908	26000	34.859	204.12	204.23

Note: $\Delta H_{av} = -178.73 \pm 0.33$ kJ/mol; see Table 2 for notation.

Table 4. Enthalpies of formation of praseodymium trihalides in the crystalline state and aqueous solutions $(-\Delta_f H_{298.15}^\circ, kJ/mol)$

State	PrCl ₃	PrBr ₃	PrI ₃
Crystal	1041.8 ± 1.8	871.6 ± 1.8	650.6 ± 2.2
sln, <i>n</i> H ₂ O	1186.9 ± 1.8	1050.3 ± 1.8	856.7 ± 2.6
sln, ∞H ₂ O	1189.1 ± 1.8	1052.0 ± 1.8	858.2 ± 2.6

Note: *n* = 6328, 14044, and 17503 for Hal = Cl, Br, and I, respectively.

mium tribromide and triiodide. It can, however, be expected that the $\partial \Delta H / \partial T$ values for praseodymium halides should be close to each other. For this reason, the correction ΔH_r for reduction to 298.15 K was calculated for PrBr₃ and PrI₃ using the temperature coefficient of the enthalpy of solution of PrCl₃ in water, $(\partial \Delta H/\partial T)_p = 0.538$ kJ/(mol K), found in [7], especially as the correction was small and did not exceed ~0.17 kJ/mol. To exclude the influence of the possible hydrolysis of the salts in water, several experiments with the solution of praseodymium halides in an acidified aqueous solution (0.001 N solution of HCl) were performed. The enthalpies of solution in water and acidified water coincided. The enthalpies of solution of praseodymium halides in water were measured over wide concentration ranges, from 1 : 10400 to 1 : 25700H₂O for PrBr₃ and from 1 : 13640 to 1 : 26000 for PrI₃. The heat effect of solution was independent of solution concentration over the concentration range studied (see Tables 3 and 4). For this reason, the mean enthalpies of solution were assigned to the mean concentrations, $1: 14040H_2O$ for PrBr₃ and $1: 17500H_2O$ for PrI₃.

Note that the enthalpy of solution of $PrBr_3$ in water obtained in this work coincides with the data reported in [3] to within measurement errors, but the error of measurements performed in this work is much smaller.

In order to determine the enthalpies of formation of praseodymium trihalides in the crystalline state, we calculated the enthalpies of solution of praseodymium tribromide and triiodide in water at infinite dilution. There are no literature data on the enthalpies of dilution of aqueous solutions of praseodymium bromide and iodide. In [8], the enthalpies of dilution of aqueous solutions of virtually all rare-earth metal chlorides were determined. It was found that the experimental enthalpies of dilution of aqueous solutions of lanthanide salts determined with high reliability coincided with the values calculated by the Debye-Hückel law (the second approximation) in the concentration range of our measurements $(1 : 10000-1 : 26000H_2O)$. We therefore considered it possible to use the enthalpies of dilution of aqueous solutions of praseodymium trichloride from the concentrations studied (1: 14040H₂O for PrBr₃ and $1:17500H_2O$ for PrI₂) to infinite dilution. Note that the enthalpies of dilution of aqueous solutions of the praseodymium salts under consideration were $-1.40 \pm$ 0.06 and -1.50 ± 0.06 kJ/mol for PrI₃ and PrBr₃, respectively.

The enthalpies of solution of praseodymium trihalides to infinite dilution at 298.15 K were found to be (kJ/mol) ΔH_{sol}° (PrCl₃, ∞ H₂O) = -147.28 ± 0.33 [2], ΔH_{sol}° (PrBr₃, ∞ H₂O) = -180.39 ± 0.32, and ΔH_{sol}° (PrI₃, ∞ H₂O) = -207.56 ± 1.30. The enthalpies of formation

Table 5. Enthalpies of formation of praseodymium halides $(-\Delta_f H^\circ, \text{kJ/mol})$ according to our and literature data

Substance	This work	[9]	[10]	[11]
PrCl ₃	1041.8 ± 1.8	1057.7 ± 1.0	1056.9	1058.6 ± 1.5
PrBr ₃	871.6 ± 1.8	-	_	890.5 ± 4.0
PrI ₃	650.6 ± 2.2	-	654.4	664.7 ± 5.0

of praseodymium trihalides at 298.15 K were calculated by the equation

$$\Delta_{\rm f} H^{\circ}({\rm PrHal}_3,{\rm cr}) = \Delta_{\rm f} H^{\circ}({\rm Pr}^{3+},{\rm sln},\infty{\rm H}_2{\rm O})$$

+
$$3\Delta_{\rm f}H^{\circ}({\rm Hal}^{-}, {\rm sln}, \infty {\rm H}_2{\rm O}) - \Delta H^{\circ}_{\rm sol}({\rm PrHal}_3, \infty {\rm H}_2{\rm O}),$$

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where $\Delta_{\rm f} H^{\circ}({\rm Pr}^{3+}, \sin, \infty {\rm H}_2{\rm O}) = -687.8 \pm 1.7 \text{ kJ/mol is}$ the enthalpy of formation of the praseodymium ion determined in our work [2], the $\Delta_{\rm f} H^{\circ}({\rm Hal}^-, \sin, \infty {\rm H}_2{\rm O})$ values are the enthalpies of formation of the corresponding halide ions taken from reliable sources [1],

and the ΔH_{sol}° (PrHal₃, ∞ H₂O) values are the enthalpies of solution of praseodymium trihalides in water at infinite dilution obtained in this work.

The enthalpies of formation $\Delta_{\rm f} H^{\circ}({\rm Hal}^-, {\rm sln}, \infty {\rm H}_2{\rm O})$ were, in conformity with CODATA recommendations [1], taken to be -167.08 ± 0.10 , -121.41 ± 0.15 , and -56.78 ± 0.05 kJ/mol for Hal = Cl, Br, and I, respectively. The enthalpies of formation of praseodymium trihalides in the crystalline state and aqueous solutions calculated this way are listed in Table 4.

To summarize, we refined the key values of the enthalpies of formation of praseodymium trichloride and tribromide reported earlier and virtually for the first time determined the enthalpy of formation of praseodymium triiodide. These values differ from those recommended in fundamental handbooks [9, 10] and the review paper on the thermochemical properties of rareearth metal compounds published in 2001 [11] (see Table 5). Note that the $\Delta_{f}H^{\circ}(PrHal_{3}, cr, 298.15 \text{ K})$ values reported in the literature were calculated from the enthalpies of reactions between praseodymium metal and acids, which require refinement, and the ensuing enthalpy of formation of the praseodymium ion in an infinitely dilute aqueous solution, which therefore also needs to be refined. In the calculations performed in this work, we used the new $\Delta_{f}H^{\circ}(Pr^{3+}, sln, \infty H_{2}O)$ value obtained in [2].

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