

CHEMICAL THERMODYNAMICS  
AND THERMOCHEMISTRY

The Enthalpy of Formation of the Praseodymium Ion (3+)  
in an Infinitely Dilute Aqueous Solution

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**Abstract**—The enthalpy of reaction between praseodymium metal and 1.07 n HCl and the enthalpy of solution of praseodymium trichloride in 1.07 n HCl and water were measured in a swinging isoperibol calorimeter at 298.15 K. The results were used to calculate the enthalpy of formation of the praseodymium ion in the state of an infinitely dilute aqueous solution,  $\Delta_f H_{298.15}^\circ \text{Pr}^{3+}(\text{sln}, \infty \text{H}_2\text{O}) = -687.8 \pm 1.7 \text{ kJ/mol}$ .

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INTRODUCTION

This work is concerned with the determination of the enthalpy of formation of the praseodymium ion (3+) in an infinitely dilute aqueous solution. This is a key value in the thermochemistry of praseodymium compounds; it allows the standard enthalpies of formation of ionic compounds containing this rare-earth metal to be reliably calculated [1]. Data on the thermochemical properties of praseodymium compounds are in turn necessary for calculating the standard enthalpies of formation of new functional materials synthesized on their basis.

The enthalpies of formation of metal ions can be determined by various methods. The  $\Delta_f H_{298.15}^\circ \text{Pr}^{3+}(\text{sln}, \infty \text{H}_2\text{O})$  value can, however, be calculated from the data avail-

able only using the enthalpies of three reactions, those between praseodymium metal and hydrochloric acid, between praseodymium trichloride and hydrochloric acid, and between praseodymium trichloride and water. The enthalpies of these three reactions taken from the original works are listed in Table 1.

In addition to these basic reactions, the enthalpies of dilution of solutions of  $\text{PrCl}_3$  and HCl to infinite dilution are necessary for calculating the enthalpy of formation of the praseodymium ion. Note from the outset that these values are known from the literature with a high degree of reliability and are therefore not given in Table 1.

We stress that the basic reaction for calculating  $\Delta_f H_{298.15}^\circ \text{Pr}^{3+}(\text{sln}, \infty \text{H}_2\text{O})$  is the reaction between

**Table 1.** Literature data on the enthalpies of Pr and  $\text{PrCl}_3$  reactions with hydrochloric acid and solution of  $\text{PrCl}_3$  in water (kJ/mol)

Refs.	Pr and HCl (sln)	$\text{PrCl}_3$ in HCl (sln)	$\text{PrCl}_3$ in $\text{H}_2\text{O}$
[8]			-144.5 (1 : 1300)
[2]	-709.2, -732.2 (2.0 n)		
[3, 9]	$-723.4 \pm 13.5$ (0.12 n)	-141.8 (0.12 h)	-141.8 (1 : 4625)
[4]	$-687.9 \pm 21.1$ (1.5 n)		
[5, 10]	-704.1 (0.25 n)	$-142.2 \pm 7.6$ (0.25 h)	-146.6 (1 : 5344)
	-692.8 (1.47 n)	$-125.6 \pm 11.1$ (1.47 h)	
[11]			$-144.3 \pm 1.23$
[6]	$-687.9 \pm 3.8$ (1.0 n)		
[13]			<i>-148.4 ± 0.5</i>
[7]	$-692.2 \pm 1.7$ (2.0 n)		
[14]			<i>-147.7</i>
[12]			$-145.12 \pm 0.53$ (1 : 6168); <i>-147.46 ± 0.53</i>

Note: Values in parentheses are hydrochloric acid concentration (n) or salt concentration in water, 1 mol  $\text{PrCl}_3$  : x mol  $\text{H}_2\text{O}$ ; the  $\Delta H$  values for  $\text{PrCl}_3$  in  $\infty \text{H}_2\text{O}$  are given in italics; errors were calculated for a 95% confidence interval.

praseodymium metal and hydrochloric acid. The enthalpy of this reaction was measured in several works [2–7]. However, only in [7] was the metal thoroughly analyzed and quantitative data on both metallic and nonmetallic impurities in it were obtained. Quantitative elemental analysis data are absent in the other works.

The enthalpy of solution of praseodymium trichloride in hydrochloric acid was measured in [3, 5]. These data can, however, only be considered estimates, because the enthalpies of the reaction are based on the results of only one or two measurements. The enthalpies of solution of praseodymium trichloride in water were obtained in [8–12]. The  $\text{PrCl}_3$  sample used was thoroughly analyzed and quantitatively characterized only in [12]. Note that, in [13, 14], the enthalpy of solution of praseodymium trichloride in water is only given for the infinitely dilute solution state, without mentioning how this value was obtained.

It follows that rigorous calculations of the key  $\Delta_f H_{298.15}^\circ \text{Pr}^{3+}(\text{sln}, \infty \text{H}_2\text{O})$  value from the available data cannot be performed. Since reliable enthalpies of formation of praseodymium compounds are necessary for thermodynamic calculations, we deemed it worthwhile to independently determine the enthalpy of formation of the praseodymium ion. For this purpose, we used a praseodymium metal sample characterized in detail and anhydrous praseodymium trichloride synthesized and analyzed by us. Measurements were performed on a precision calorimetric instrument with a leak-proof reaction vessel.

## EXPERIMENTAL

We used a praseodymium metal sample analyzed for both metallic and nonmetallic impurities. The impurity contents in the sample were (wt %): O, 0.042; N, 0.0018; H, 0.00058; C, 0.089; Fe < 0.01; Ca < 0.01; Cu < 0.01; Mo < 0.02; and La, Ce, Nd < 0.20.

The content of carbon was determined by burning samples in oxygen and analyzing outgoing carbon-containing gas on a coulometric analyzer. Analyses for oxygen and nitrogen were performed by vacuum melting with analyzing gases released on a chromatograph. The content of hydrogen was determined by heating samples in a flow of an inert carrier gas followed by chromatographing. Metallic impurities were determined spectroscopically.

Anhydrous praseodymium trichloride was prepared by chlorinating praseodymium oxide  $\text{Pr}_6\text{O}_{11}$  powder (the major component content 99.9%) with carbon tetrachloride (os. ch., special purity grade) vapor. The synthesis was conducted following the original procedure [15], according to which the initial substance was heated and held in  $\text{CCl}_4$  vapor at 950 K for 11 h, while the reactor was rotated. Reactor rotations accelerate chlorination and allow the reaction to be performed to completion because the area of the reaction surface increases as a result of reaction product granulation.

Note that the design of the reactor fully prevented sample contact with air moisture not only during chlorination but also when the container with the anhydrous product was removed from the reactor.

The product was identified by analyzing it for praseodymium and chlorine. The contents of praseodymium (determined by complexometric titration with Trilon B) and chlorine (determined gravimetrically in the form of  $\text{AgCl}$ ) were (wt %)  $56.90 \pm 0.15$  (calculated: 56.99) and  $43.01 \pm 0.12$  (calculated: 43.01), respectively. According to the X-ray powder patterns, the product was single-phase and corresponded to  $\text{PrCl}_3$  with a  $\text{UCl}_3$ -type structure.

Praseodymium trichloride is very hygroscopic. To prevent it from contact with air moisture, all operations with this substance were performed in a dry box in an inert atmosphere. Hydrochloric acid (1.07 n) used as a reacting liquid was prepared from concentrated hydrochloric acid of os. ch. grade (the total content of impurities was less than 0.002 wt %) and distilled water with specific conductivity  $6 \times 10^{-6} \text{ S cm}^{-1}$ .

The enthalpies of reactions were measured in a swinging isoperibol leak-proof calorimeter at 298.15 K. A detailed description of the unit and the procedure for measurements can be found in [16, 17]. A calorimetric titanium vessel ( $V = 80 \text{ cm}^3$ ) was filled with hydrochloric acid (1.07 n,  $55.000 \pm 0.003 \text{ g}$ ) and sealed. Temperature rise in experiments was measured by a copper resistance thermometer ( $R_{298.15} = 223.90 \Omega$ ,  $1 \Omega = 1.05 \text{ K}$ ) using a bridge scheme. The null instrument was an F-116/2 microvoltmicroammeter connected to a KSP-4 self-balancing potentiometer, which recorded calorimeter temperature changes during the whole experiment. The thermometric sensitivity of the unit was  $3 \times 10^{-5} \text{ K/mm}$  recorder scale. Water temperature in the shell was controlled automatically with an accuracy of  $5 \times 10^{-3} \text{ K}$ .

The energy equivalent of the calorimeter was determined electrically with an accuracy to several hundredths of a percent. The voltage on the heater and reference coil ( $R = 1.0000_5 \Omega$ ) was measured by an R-363-2 high-resistance potentiometer of accuracy class 0.002%. The time of current passage was determined using an F-5080 frequency meter-chronometer with an accuracy of 0.002 s. The energy equivalent of the calorimeter ( $W$ ) was measured in six experiments and was found to be  $344.55 \pm 0.25 \text{ J}/\Omega$ . Here and throughout, confidence intervals correspond to a 95% probability.

Prior to calorimetric experiments, the substances to be studied were placed into glass ampules and sealed in a dry box in an inert atmosphere. The praseodymium metal surface was preliminarily polished to glitter. The samples were weighed on a Sartorius balance with an accuracy of 0.00002 g.

**Table 2.** Results of enthalpy measurements for the reaction between Pr and 1.07 n HCl at 298.15 K

$\Delta R, \Omega$	$g, g$	$g(\text{Pr}), g$	$Q, J$	$Q', J$	$-\Delta U, \text{kJ/mol}$	$-\Delta H, \text{kJ/mol}$
0.76544	0.05382	0.05318	263.73	262.07	694.39	690.67
0.79913	0.05647	0.05580	275.34	273.59	690.89	687.17
0.87894	0.06191	0.06118	302.84	300.92	693.07	689.35
0.93123	0.06563	0.06485	320.86	318.83	692.75	689.03
0.80391	0.05677	0.05610	276.99	275.23	691.31	687.59
1.04564	0.07378	0.07290	360.28	358.00	691.97	688.25
1.58408	0.11148	0.11016	545.79	542.33	693.70	689.98

Note:  $\Delta R$  is the temperature rise corrected for heat exchange,  $g$  is the sample mass,  $g(\text{Pr})$  is the mass of praseodymium corrected for impurities,  $Q$  is the heat effect,  $Q'$  is the heat effect corrected for impurities,  $\Delta U$  and  $\Delta H$  are the changes in the internal energy and enthalpy in the reaction;  $\Delta H_{\text{av}} = -688.86 \pm 1.17 \text{ kJ/mol}$ .

**Table 3.** Results of enthalpy measurements for the reaction between  $\text{PrCl}_3$  and 1.07 n HCl at 298.15 K

$\Delta R, \Omega$	$Q, J$	$g, g$	$-\Delta H, \text{kJ/mol}$	
			experimental	$\text{PrCl}_3 : 121.24 \text{ HCl} \cdot 6327.54 \text{ H}_2\text{O}$
0.20340	70.081	0.12462	139.05	138.89
0.20236	69.723	0.12230	140.97	140.80
0.19962	68.779	0.12152	139.95	139.76
0.20676	71.239	0.12665	139.08	138.91
0.18701	64.434	0.11326	140.67	140.50
0.18510	63.776	0.11181	141.04	140.89

Note: See Table 2 for notation;  $\Delta H_{\text{av}} = -139.96 \pm 0.96 \text{ kJ/mol}$ .

**Table 4.** Results of enthalpy measurements for the reaction between  $\text{PrCl}_3$  and water at 298.15 K

$\Delta R, \Omega$	$Q, J$	$g, g$	$\text{PrCl}_3 \cdot x\text{H}_2\text{O}$	$-\Delta H, \text{kJ/mol}$	
				experimental	1 : 6327.54
0.36109	116.49	0.19777	5551	145.64	145.60
0.30226	97.515	0.16617	6607	145.11	144.96
0.29404	94.863	0.16074	6830	145.93	145.76
0.26104	84.217	0.14374	7638	144.87	144.63
0.25889	83.523	0.14225	7718	145.18	144.93
0.25749	83.071	0.14127	7771	145.40	145.15
0.25377	81.871	0.13981	7853	144.80	144.53
0.22473	72.502	0.12312	8917	145.61	145.26
0.19268	62.162	0.10545	10411	145.76	145.32

Note: Experiments were performed using a platinum resistance thermometer,  $R_{298.15} = 401.32 \Omega$ ,  $1 \Omega = 0.94 \text{ K}$ ; heat value  $W = 322.62 \pm 0.23 \text{ J}/\Omega$ ;  $\Delta H = -145.15 \text{ kJ/mol}$ , obtained in 0.001 n HCl;  $\Delta H_{\text{av}} = -145.13 \pm 0.32 \text{ kJ/mol}$ ; see Table 2 for notation.

## RESULTS AND DISCUSSION

The results of reaction enthalpy measurements are listed in Tables 2–4.

The enthalpy of reaction between praseodymium metal and hydrochloric acid was calculated with corrections for impurities on the assumption that metallic

impurities were present in the form of free elements (copper was considered inert under experimental conditions) and carbon, nitrogen, oxygen, and hydrogen as  $\text{PrC}_2$ ,  $\text{PrN}$ ,  $\text{Pr}_2\text{O}_3$ , and  $\text{PrH}_3$ , respectively. The corrections were introduced using the enthalpies of reactions taken from [18].

**Table 5.** Thermochemical cycle for calculating the enthalpy of formation of the praseodymium ion

No.	Reaction	$\Delta H(i)$ , kJ/mol
(1)	$\text{Pr}(\text{cr}) + 124.24\text{HCl}(\text{sln}, \text{HCl} \cdot 50.93\text{H}_2\text{O}) = \text{PrCl}_3(\text{sln}, \text{PrCl}_3 \cdot 6327.54\text{H}_2\text{O} \cdot 121.24\text{HCl}) + 121.24\text{HCl}(\text{sln}, \text{HCl} \cdot 52.19\text{H}_2\text{O} \cdot 0.00825\text{PrCl}_3) + (3/2)\text{H}_2(\text{g})$	$\Delta H(1) = -688.86 \pm 1.17$ [this work]
(2)	$\text{HCl}(\text{sln}, \text{HCl} \cdot 50.93\text{H}_2\text{O}) + (\infty\text{H}_2\text{O}) = \text{HCl}(\text{sln}, \text{HCl} \cdot \infty\text{H}_2\text{O})$	$\Delta H(2) = -1.785 \pm 0.004$ [19]
(3)	$\text{HCl}(\text{sln}, \text{HCl} \cdot 52.19\text{H}_2\text{O}) + (\infty\text{H}_2\text{O}) = \text{HCl}(\text{sln}, \text{HCl} \cdot \infty\text{H}_2\text{O})$	$\Delta H(3) = -1.760 \pm 0.004$ [19]
(4)	$\text{PrCl}_3(\text{cr}) + (6327.54\text{H}_2\text{O}) = \text{PrCl}_3(\text{sln}, \text{PrCl}_3 \cdot 6327.54\text{H}_2\text{O})$	$\Delta H(4) = -145.13 \pm 0.32$ [this work]
(5)	$\text{PrCl}_3(\text{sln}, \text{PrCl}_3 \cdot 6327.54\text{H}_2\text{O}) + (\infty\text{H}_2\text{O}) = \text{PrCl}_3(\text{sln}, \text{PrCl}_3 \cdot \infty\text{H}_2\text{O})$	$\Delta H(5) = -2.15 \pm 0.06$ [20]
(6)	$\text{PrCl}_3(\text{cr}) + 121.24\text{HCl}(\text{sln}, \text{HCl} \cdot 52.19\text{H}_2\text{O}) = \text{PrCl}_3(\text{sln}, \text{PrCl}_3 \cdot 6327.54\text{H}_2\text{O} \cdot 121.24\text{HCl})$	$\Delta H(6) = -139.96 \pm 0.96$ [this work]
(7)	$\text{Pr}(\text{cr}) + 3\text{HCl}(\text{sln}, \text{HCl} \cdot \infty\text{H}_2\text{O}) = \text{PrCl}_3(\text{sln}, \text{PrCl}_3 \cdot \infty\text{H}_2\text{O}) + (3/2)\text{H}_2(\text{g})$ or $\text{Pr}(\text{cr}) + 3\text{H}^+(\text{sln}) = \text{Pr}^{3+}(\text{sln}) + (3/2)\text{H}_2(\text{g})$ $\Delta H(7) = \Delta_f H_{298.15}^\circ(\text{Pr}^{3+}, \text{sln}) = \Delta H(1) - 124.24\Delta H(2) + 121.24\Delta H(3) + \Delta H(4) + \Delta H(5) - \Delta H(6)$	$\Delta H(7) = -687.79 \pm 1.70$ [this work]

Note:  $\Delta_f H_{298.15}^\circ \text{H}^+(\text{sln}, \infty\text{H}_2\text{O}) = 0$ ; errors in the enthalpies of formation were calculated as  $\sigma = (\sum \sigma_i^2)^{1/2}$ , where  $\sigma_i$  is the error in intermediate values.

Corrections for the heat of solution of hydrogen released in the reaction between praseodymium and acid, changes in the internal energy of hydrogen  $(\partial U/\partial p)_T$ , heat effect of water vaporization into free volume, and heat of breaking calorimetric ampoules were negligibly small and were not introduced. The enthalpies of solution of  $\text{PrCl}_3$  in hydrochloric acid and water were reduced to 298.15 K, and the temperature coefficient of solution was taken from [13].

The enthalpy of formation of the praseodymium ion in an infinitely dilute solution was calculated using the thermochemical cycle from Table 5. The following assumptions were made in the calculations. The compositions of the final solutions in different experiments performed to determine the enthalpies of Pr reaction with hydrochloric acid were slightly different. The enthalpy of reaction is, however, independent of the ratio between reaction ingredients (Table 2), and its mean value was therefore assigned to reaction (1). Likewise, the mean  $\Delta H$  value for the solution  $\text{PrCl}_3$  in hydrochloric acid was attributed to reaction (6), and the enthalpy of solution of  $\text{PrCl}_3$  in water (4) was reduced to the concentration 1 : 6327.54  $\text{H}_2\text{O}$  using the reliable data on the enthalpies of dilution of aqueous solutions of praseodymium chloride from [20]. With  $\Delta_f H_{298.15}^\circ \text{H}^+(\text{sln}, \infty\text{H}_2\text{O}) = 0$ , the enthalpy of formation of the praseodymium ion in an infinitely dilute aqueous solution was found to be  $-687.8 \pm 1.7$  kJ/mol.

Fundamental handbooks *Thermal Constants of Substances* [18] and *Selected Values of Chemical Thermodynamic Properties* (National Bureau of Standards, United States) [21] give the values  $-705.0 \pm 1.1$  and  $-704.6$  kJ/mol, respectively, for the enthalpy of formation of the  $\text{Pr}^{3+}$  ions in the state of an infinitely dilute aqueous solution. These values were selected on the basis of the data reported in [5].

Review [22] of the thermochemical properties of lanthanide compounds, including the enthalpies of formation of ions, was published in 2001. The value recommended in this review,  $-705.7 \pm 2.0$  kJ/mol, was also based on the results obtained in [5], where the enthalpies of metal and anhydrous praseodymium trichloride reactions with hydrochloric acid were measured, and [13], where the enthalpy of solution of  $\text{PrCl}_3$  in  $\text{H}_2\text{O}$  was reported. As has been mentioned above, the data reported in [5] can only be considered approximate. We therefore recommend the value  $\Delta_f H_{298.15}^\circ \text{Pr}^{3+}(\text{sln}, \infty\text{H}_2\text{O})$  obtained in this work for use in thermodynamic calculations.

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