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THERMODYNAMIC CHARACTERISTICS OF ZIRCONIUM AND HAFNIUM HYDROXIDES IN AQUEOUS SOLUTION

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Abstract

The enthalpies of dissolution of $ZrCl_4$, $ZrBr_4$, $HfCl_4$ and $HfBr_4$ in water in weakly acidic and alkaline solutions were measured at 25°C in a calorimeter provided with an isothermal cover. The standard enthalpies of formation of $Zr(OH)_4$ and $Hf(OH)_4$ in solution were measured. The thermodynamic characteristics of the reactions which resulted in the formation of tetrahydroxy complexes of Zr and Hf in aqueous solution were also determined.

Keywords: complexes, entropies, hafnium, hydroxides, standard enthalpies of formation, standard Gibbs energy of formation, zirconium

Introduction

There are no references on the standard enthalpies of formation of Zr(IV) and Hf(IV) hydroxy complexes in the literature [1]. There is some information concerning the dissolution heats of Zr and Hf tetrahalides in water and alkaline solutions. Beck [2] measured the heat of interaction of $ZrCl_4$ with NH_4OH solution. Turnbull [3] calculated the heats of dissolution of $ZrCl_4$, $HfCl_4$, $ZrBr_4$ and ZrI_4 in water and in aqueous NaOH solution at a molar ratio of 1:1500. The values obtained can not be used in further calculations because only single measurements were carried out, control of the pH of the solutions was not done and the content of Hf in the Zr preparations exceeded 2.5%. On the basis of the temperature dependence of the solubility of crystalline HfO_2 in water [4], the standard enthalpy of formation $\Delta_f H^\circ$ ($Hf(OH)_4$, 298.15 K$=-1701.01\pm1.67$ kJ mol^{-1} was calculated.

Interpretation of the thermochemical properties of Zr and Hf compounds in solution is complicated, because of the tendency of Zr^{4+} and Hf^{4+} to undergo hydrolysis and polymerization. The compositions and stabilities of the species formed depend greatly on pH and temperature. The literature data relating to investigations of the ions in aqueous solution [5, 6] and the stability constants of

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their hydroxy complexes [7, 8] revealed that $M(OH)_4$ is the predominant species in solution if the metal concentration $C_{Hf,Zr}$ is less than $1\cdot10^{-3}$ mol l^{-1}. Thus, it is possible to calculate the standard enthalpies of formation of the hydroxy complexes in aqueous solution from the thermal data crystalline the Zr(Hf) halides, whose enthalpies of formation are well known.

Experimental

To measure the dissolution heat effects, a calorimeter provided with an isothermal cover and automatic recording of the calorimetric curve were used [9]. 54.64 or 58.05 ml of aqueous solution with pH 3.0, 4.0 or 9.0, or distilled water, was placed into the reaction flask of the calorimeter. The pH of the solutions was checked with a 340 pH-meter to an accuracy of ±0.05 pH units. The precisely weighed preparations of Zr or Hf tetrahalide was placed into a glass ampoule. The initial $ZrCl_4$, $ZrBr_4$, $HfCl_4$ and $HfBr_4$ preparations were pure white and did not give insoluble precipitates in solutions of mineral acids. Spectral analysis showed the content (on a metal basis) of Hf in the Zr preparations to be 0.12–0.14%, and the content of Zr in the Hf preparations to be 0.38–0.41%. As the sum of the other admixtures did not exceed 0.01%, no corrrections for the compositions of the tetrahalides were made. The desired pH of the initial solutions was adjusted with $HClO_4$ and KOH solutions. All solutions were prepared with doubly distilled water. The procedure for placing the weighed preparations of Zr and Hf tetrahalides into the glass ampoules and the method of carrying out the calorimetric experiment were as described earlier [9]. The experimental data on the dissolution heats of $ZrCl_4$, $ZrBr_4$, $HfCl_4$ and $HfBr_4$ at the given pH values, together with the calculated values, are given in Tables 1 and 2.

Results and discussion

After the calorimetric experiments, control of the pH demonstrated that dissolution of the crystal halides of Zr and Hf leads to an increased acidity of the solution. Thus, the process of dissolution can be presented as follows:

$$MX_4(c)+4H_2O(l)=M(OH)_4(sol;\,H_2O)+4HX(sol;\,H_2O) \qquad (1)$$

Experimentally measured and calculated final pH values are given in Tables 1 and 2. The balanced concentrations of OH^- were calculated by the RRSU program [10], taking into account the processes of hydrolysis and ionization. The calculated and experimental pH values coincide within the limits of error. This testifies to the correctness of dissolution scheme (1).

The dissolution heats of the tetrachlorides and tetrabromides of Zr and Hf in water (pH~6.5) were also measured in a wider range of concentrations. In the concentration range $1\cdot10^{-4}$–$1\cdot10^{-3}$ mol l^{-1} the dissolution heat remains practically constant. The mean values of the dissolution heats in this concentration range are

$$-221.71\pm0.5\ \text{kJ mol}^{-1}\ (ZrCl_4);\ -260.91\pm1.13\ \text{kJ mol}^{-1}\ (ZrBr_4);$$
$$-238.47\pm0.46\ \text{kJ mol}^{-1}\ (HfCl_4);\ -271.48\pm1.63\ \text{kJ mol}^{-1}\ (HfBr_4)$$

The error was checked according to the Student coefficient at the level of 95% correctness.

Table 1 Enthalpies of dissolution of $ZrCl_4$ at 25°C

pH_{init}	$Mass_{ZrCl_4}$/ g	$C_{ZrCl_4}\cdot10^4$/ mol l^{-1}	$-\Delta_{sol}H$/ kJ mol^{-1}	pH_{fin}	
				exp.	calc.
3.0	0.00811	6.371	221.33	2.50	2.45
	0.00783	6.151	220.96	2.59	2.46
	0.00623	4.893	220.92	2.64	2.53
	0.00533	4.187	221.08	2.68	2.57
	0.00472	3.708	220.75	2.70	2.60
	0.00340	2.671	220.92	2.78	2.68
	0.00303	2.380	220.71	2.81	2.71
			220.95±0.19		
4.0	0.00861	6.763	221.79	2.60	2.57
	0.00725	5.695	220.83	2.63	2.64
	0.00716	5.624	220.92	2.73	2.65
	0.00677	5.318	220.75	2.74	2.67
	0.00673	5.287	221.04	2.81	2.67
	0.00568	4.462	220.71	2.84	2.75
	0.00354	2.781	221.00	2.98	2.95
			221.01±0.34		
9.0	0.00820	6.441	221.33	2.63	2.59
	0.00788	6.190	221.33	2.64	2.61
	0.00686	5.389	220.92	2.80	2.67
	0.00632	4.964	221.12	2.83	2.70
	0.00489	3.841	221.42	3.00	2.82
	0.00364	2.859	221.38	3.10	2.94
	0.00340	2.671	220.92	3.21	2.98
	0.00280	2.199	221.08	3.35	3.06
			221.19±0.17		

Table 2 Enthalpies of dissolution of $HfCl_4$ at 25 °C

pH_{init}	$Mass_{HfCl_4}$/ g	$C_{HfCl_4}\cdot10^4$/ mol^{-1}	$-\Delta_{sol}H$/ kJ mol^{-1}	pH_{fin}	
				exp.	calc.
3.0	0.00832	4.755	237.88	2.69	2.54
	0.00647	3.698	237.86	2.76	2.61
	0.00629	3.595	237.99	2.77	2.61
	0.00585	3.343	237.86	2.78	2.63
	0.00478	2.732	238.03	2.68	2.68
	0.00445	2.543	238.17	2.85	2.70
	0.00287	1.640	237.73	2.80	2.78
			237.93±0.13		
4.0	0.00865	4.943	237.73	2.68	2.68
	0.00811	4.639	237.90	2.76	2.71
	0.00806	4.606	237.90	2.77	2.71
	0.00747	4.269	238.78	3.00	2.74
	0.00668	3.818	238.40	2.96	2.79
	0.00554	3.166	238.61	2.88	2.86
	0.00453	2.589	238.74	3.07	2.94
	0.00451	2.577	237.94	3.17	2.94
	0.00312	1.783	237.99	3.24	3.09
			238.24±0.34		
9.0	0.00823	4.703	238.78	2.81	2.73
	0.00692	3.955	238.15	3.01	2.80
	0.00640	3.658	238.04	2.95	2.84
	0.00565	3.229	238.99	3.02	2.89
	0.00407	2.326	238.32	3.08	3.04
	0.00354	2.023	238.86	3.28	3.10
			238.52±0.42		

The standard enthalpies of formation of $Hf(OH)_4$ and $Zr(OH)_4$ can be calculated in the following way according to Eq. (1):

$$\Delta_f H^\circ(M(OH)_4\text{, sol; }H_2O\text{, stand. st., hyp.non-diss., 298.15 K})=$$
$$\Delta_f H^\circ(MX_4\text{, c, 298.15 K})+4\Delta_f H^\circ(H_2O\text{, l, 298.15 K})-4\Delta_f H^\circ(HX\text{, sol;}$$
$$\infty H_2O\text{, 298.15 K})+\Delta_{sol}H \qquad (2)$$

The values:

$$\Delta_f H^o(\mathrm{ZrCl_4}, \mathrm{c}, 298.15\ \mathrm{K}) = -979.77 \pm 1.17\ \mathrm{kJ\ mol^{-1}};$$

$$\Delta_f H^o(\mathrm{ZrBr_4}, \mathrm{c}, 298.15\ \mathrm{K}) = -760.7 \pm 3.8\ \mathrm{kJ\ mol^{-1}};\ \Delta_f H^o(\mathrm{HfCl_4}, \mathrm{c}, 298.15\ \mathrm{K}) = -990.19 \pm 1.21\ \mathrm{kJ\ mol^{-1}};\ \Delta_f H^o(\mathrm{HfBr_4}, \mathrm{c}, 298.15\ \mathrm{K}) = -766.63 \pm 1.97\ \mathrm{kJ\ mol^{-1}};$$

$$\Delta_f H^o(\mathrm{H_2O}, \mathrm{l}, 298.15\ \mathrm{K}) = -285.8295 \pm 0.0402\ \mathrm{kJ\ mol^{-1}};\ \Delta_f H^o(\mathrm{HCl}, \mathrm{sol};$$

$$\infty\mathrm{H_2O}, 298.15\ \mathrm{K}) = -167.11 \pm 0.04\ \mathrm{kJ\ mol^{-1}}\ \Delta_f H^o(\mathrm{HBr}, \mathrm{sol}; \infty\mathrm{H_2O}, 298.15\ \mathrm{K}) = -121.42 \pm 0.04\ \mathrm{kJ\ mol^{-1}}$$

are taken from a reference book [1]. Table 3 shows the values obtained.

Table 3 Standard enthalpies of formation of $Zr(OH)_4$ and $Hf(OH)_4$

Initial condition	$\Delta_f H^o$(298.15 K)/kJ mol^{-1}			
	pH_{init}=3.0	pH_{init}=4.0	pH_{init}=9.0	water (pH~6.5)
$ZrCl_4$	1675.60±1.18	1675.66±1.22	1675.84±1.18	1676.36±1.27
$ZrBr_4$	–	–	–	1679.25±3.96
$HfCl_4$	1703.00±1.22	1703.31±1.26	1703.59±1.28	1703.61±1.24
$HfBr_4$	–	–	–	1695.73±2.56
HfO_2	–	–	–	1701.01±1.67

*Calculated from [4].

It can be seen that the values obtained are in good agreement within the error limits, and for $Hf(OH)_4$ they coincide with the calculated values [4]. With the allowance of a constant error in the standard enthalpies of formation of the crystal salts, the following are considered to be the most probable mean values:

$$\Delta_f H^o(\mathrm{Zr(OH)_4}, \mathrm{sol}; \mathrm{H_2O}, \mathrm{stand.\ st.}, \mathrm{hyp.non\text{-}diss.}, 298.15\ \mathrm{K}) = -1676.54 \pm 1.79\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta_f H^o(\mathrm{Hf(OH)_4}, \mathrm{sol}; \mathrm{H_2O}, \mathrm{stand.\ st.}, \mathrm{hyp.non\text{-}diss.}, 298.15\ \mathrm{K}) = -1700.82 \pm 1.87\ \mathrm{kJ\ mol^{-1}}$$

The concentrations of the reaction products (1) did not exceed $1\cdot10^{-3}$ mol l^{-1}, and corrections connected with the value of the ionic strength were therefore not made; further, the values of the standard enthalpies of formation on dissolving HX in 50 000 H_2O and in ∞H_2O, which can be found in [1], practically do not differ.

The thermodynamic characteristics of the reactions of $Zr(OH)_4$ and $Hf(OH)_4$ formation were calculated according to the scheme

$$\mathrm{M^{4+}} + 4\ \mathrm{OH^-} = \mathrm{M(OH)_4}\ (\mathrm{sol}; \mathrm{H_2O}) \qquad (3)$$

In order to eliminate the errors in the values of standard Gibbs energies of formation of the ion, the corresponding ΔG° changes were calculated according to the equation

$$\Delta G^\circ = -RT\ln\beta^\circ \tag{4}$$

where β° is the formation constant of the corresponding tetrahydroxy complex (Table 4).

Table 4 Thermodynamic characteristics of reaction (3) at 25°C

M/	$\log\beta^\circ$	ΔH°/kJ mol^{-1}	ΔS°/J mol^{-1} K^{-1}
Zr	55.93	−148.99±2.53	571.02
Hf	54.78	−151.85±2.33	539.43

The values of the stability constants of the hydroxy complexes of Zr and Hf that are considered to be the most reliable were taken from [6, 7]. The calculated values are given in Table 4.

Standard thermodynamic characteristics of formation of the hydroxy complexes (Table 5) were calculated by using the ΔS° values of reaction (3), the data on the entropies of the corresponding ions, and the values of the standard Gibbs energy of formation of $Hf(OH)_4$ and $Zr(OH)_4$ [1].

Table 5 Standard thermodynamic characteristics of $Zr(OH)_4$ and $Hf(OH)_4$ formation in aqueous solution

Condition	$\Delta_f H^\circ$(298.15 K)/	$\Delta_f G^\circ$(298.15 K)/	S°(298.15 K)/ J mol^{-1} K^{-1}
	kJ mol^{-1}		
$Zr(OH)_4$ (sol., H_2O, stand. st., non-diss.)	−1676.54±1.79	−1466.9	18.27
$Hf(OH)_4$ (sol., H_2O, stand. st., non-diss.)	−1700.82±1.87	−1459.8	30.28

The highly charged Zr^{4+} and Hf^{4+} are strongly hydrated in aqueous solution. As a result of the formation of $Me(OH)_4$, there is a substantial increase in the number of the species in the system at the expense of the evolution of free water molecules from the Zr^{4+} or Hf^{4+} hydration shells. This leads to a large positive change in entropy.

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