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THERMODYNAMIC INVESTIGATION OF ZIRCONIUM DISELENITE

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On the basis of calorimetric research of selenium dioxide, zirconium dioxide and zirconium diselenite dissolution reactions in the hydrofluoric acid solution under 298 K a standard enthalpy of $Zr(SeO_3)_2$ formation reaction from ZrO_2 and SeO_2 and a standard enthalpy of zirconium diselenite formation have been obtained. The value of enthalpy has been equal to –58.1±3.43 kJ mol^{-1} in $ZrO_{2(solid)}+2SeO_{2(solid)}\rightarrow Zr(SeO_3)_{2(solid)}$ reaction. The standard enthalpy of zirconium diselenite formation is equal to $\Delta H^0_{f,298}Zr(SeO_3)_{2(solid)}=-1603.2\pm3.8$ kJ mol^{-1}. The $\Delta H^0_{f,298}Zr(SeO_3)_{2(solid)}$ value has been determined for the first time.

Keywords: *calorimeter, dissolution, enthalpy, thermochemical cycle, thermodynamics, zirconium diselenite*

Introduction

Investigation of various physico-chemical properties of $Zr(SeO_3)_2$ zirconium diselenite is of great interest, because the indicated compound is presently a single reliably identified zirconium selenite that is important in chemical technology of zirconium and aluminium separation, as well as in chemical analysis [1–8]. At the same time the literature does not contain any experimental data on determination of thermodynamic zirconium diselenite properties.

The aim of the present research is to determine calorimetrically the standard enthalpy of the $Zr(SeO_3)_2$ formation reaction from ZrO_2 and SeO_2 and the standard enthalpy of the zirconium diselenite formation.

Experimental

In order to solve this problem it has appeared expeditious to use the dissolution method, because preliminary experiments have shown the possibility of rather quick ZrO_2, SeO_2 and $Zr(SeO_3)_2$ dissolution in sand acid with HF concentration not less than 10 mol L^{-1}. It has allowed to apply the indicated solvent as calorimetric liquid. Characteristics of the applied materials and brief description of calorimetric plant are given below.

Selenium dioxide has been prepared as a result of sublimation of SeO_2 reagent of P qualification according to [9]. Zirconium dioxide has been prepared by calcining corresponding hydroxide. Zirconium hydroxide precipitation has been executed from hot solution (~353 K) by quick infusion of concentrated (1.5 mol L^{-1}) zirconium oxychloride solution (of CP qualification) into double excess of 25% ammonia solution under intensive mixing. The prepared hydroxide has been washed by distilled water for many times, it has been dried under 378 and calcined under 773 K for 12 h. The roentgenogram of the prepared sample is identical to roentgenogram of tetragonal ZrO_2 [10, 11]. Absence of water and impurity of NH_4^+ ions have been determined by means of thermal analysis and IR-spectroscopy. Chemical analysis has revealed the absence of chlorine ions.

The hydrofluoric acid solution has been prepared from reagent of AP qualification by diluting distilled water in ratio 1:1 and it has had concentration 11.28 mol L^{-1} HF. Zirconium diselenite has been prepared similarly to [1–4] by mixing water solutions, namely: 0.1 mol L^{-1} zirconium oxychloride (of AP qualification) and 2.3 mol L^{-1} selenious acid. Selenious acid has been prepared by selenium dioxide dissolution in water (selenium dioxide was additionally decontaminated according to the above-mentioned description). In order to prevent basic zirconium selenite formation, solution of seleniuos acid has been taken in 10 times stoichiometric excess [4, 12]. The prepared sediment has been held in mother liquor on water bath during 2 h, then it has been washing on glass filter by 0.1 N HCl and then by distilled water until absence of selenium and chlorine ions in rinsing water, and after that it has been dried under 373 K for 18 h.

The compound prepared in such a way has been investigated by means of chemical analysis, thermal analysis and IR-spectroscopy. The zirconium has been analysed by gravimetric (precipitation by ammonia) and volumetric (chelatometry) methods and the selenium has been analysed iodometrically. As a result of chemical analysis it has been found out (mass%): Zr – 26.43; Se – 45.75. Calculation of $Zr(SeO_3)_2$ for-

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Table 1 Graduation of the calorimeter by KCl dissolution in water at 298 K

Sample of KCl, *a*/g	Mass of water in a cell/g	ΔR/ohm	$W=(\Delta H^0_m a/\Delta R M_{KCl})$/J ohm^{-1}	ΔH^0_m/J mol^{-1} [15]
3.5080	169.6	3126	0.2644	
3.5055	174.9	3060	0.2699	
3.3978	170.6	3013	0.2661	17577
3.5024	170.0	3073	0.2686	
3.5028	170.0	3080	0.2678	
			average: 0.2674±0.0029	

1	$ZrO_{2(solid)}+nHF\cdot mH_2O\rightarrow H_2ZrF_6\cdot(n-6)HF\cdot(m+2)H_2O$	ΔH_1	(1)
2	$SeO_{2(solid)}+nHF\cdot mH_2O\rightarrow SeO_2\cdot nH\cdot mH_2O$	ΔH_2	(2)
–1	$Zr(SeO_3)_{2(solid)}+3(nHF\cdot mH_2O)\rightarrow H_2ZrF_6\cdot 2SeO_2\cdot(3n-6)HF\cdot(3m+2)H_2O$	ΔH_3	(3)
1	$H_2ZrF_6\cdot(n-6)HF\cdot(m+2)H_2O+2(SeO_2\cdot nHF\cdot mH_2O)\rightarrow H_2ZrF_6\cdot 2SeO_2\cdot(3n-6)HF\cdot(3m+2)H_2O$	ΔH_4	(4)

Reactions (1)–(4)

mula has given the following values 26.43 and 45.76, respectively, that indicates the excellent accordance of the prepared product composition and its formula. The data of thermography and IR-spectroscopy have shown that zirconium diselenite contained only trace amount of adsorbed water.

The calorimetric plant has represented an isoperibolic calorimeter of dissolution and it did not differ principally from the classic calorimeter of the Skuratov design [13]. The difference was in selection of structural materials, which are stable in concentrated HF solutions, and a calorimetric thermometer. So, silvered copper calorimetric cup of 200 mL capacity, additionally covered by fluoroplastic-epoxy LFE-26x lacquer, and propeller teflon stirrer have been used. In order to add the studied reagent into calorimetric liquid a specially designed teflon container has been applied [14].

Measurement of temperature inside a calorimetric cell has been taken with the help of a thermistor of the MX-168 brand and direct-current R-329 of bridge with checking unbalance by a self-recording KSP-4 potentiometer with a scale from 0 up to 1 mV. With the purpose to increase reproducibility of thermistor observations its artificial ageing has been carried out at 473 K, with electrical current change in the bridge during the process. A calorimetric cell has been put in a thermostat (isothermal shell), where temperature of 298 K with accuracy ±0.02° was maintained.

Results and discussion

In order to determine calorimeter calorific value its graduation (*W*) has been done on heat of potassium chloride dissolution in water, which is recommended to be used as a calorimetric standard [15]. The results of calorimeter graduation done with the help KCl are presented in Table 1.

Average value out of five experiments which is equal to 0.2674±0.0029 J ohm^{-1} has been taken as *W* index used for calculation of unknown heat effects. In order to exclude any mistake due to difference in heat capacities of KCl and HF solutions in water, amount of HF solution in comparison with the mass of the KCl solution while conducting the experiments has been increased by value, which is proportional to difference of their heat capacities.

The results of experiments on calorimetric study of SeO_2, ZrO_2 and $Zr(SeO_3)_2$ dissolution reactions in HF solution under 298 K are given in the Table 2. The errors have been calculated with help of the known formulas of dispersional analysis [16] with confidence odds $\alpha=0.95$. The correction for heat exchange has been calculated in accordance with known the Renio–Pfaundler formula [13].

Heat of the zirconium diselenite formation from oxides can be calculated on the basis of the obtained data and collating of calorimetric reactions (1)–(4).

The summary equation:

$$ZrO_{2(solid)}+2SeO_{2(solid)}\rightarrow Zr(SeO_3)_{2(solid)}\ \Delta H_5 \quad (5)$$

According to the thermochemical cycle:

$$\Delta H_5=\Delta H_1+2\Delta H_2-\Delta H_3+\Delta H_4$$

Hydrofluoric acid solution of the given dilution is marked by the $nHF\cdot mH_2O$ formula and $H_2ZrF_6\cdot(n-6)HF\cdot(m+2)H_2O$, $SeO_2\cdot nHF\cdot mH_2O$ and $H_2ZrF_6\cdot 2SeO_2\cdot(3n-6)HF\cdot(3m+2)H_2O$ formulas mark solutions formed from zirconium dioxide, selenium dioxide and zirconium diselenite in the sand acid excess. The equation of the reaction (4) corresponds to the process of the solution mixing, which are formed according to the reactions (1) and (2) – solutions 1

Table 2 Experimental data on $ZrO_{2(solid)}$, $SeO_{2(solid)}$ and $Zr(SeO_3)_{2(solid)}$ dissolution in 11.28 mol L^{-1} HF under 298 K (W=0.2674±0.0029 J ohm^{-1})

Sample of matter/g		Mass of 11.28 mol L^{-1} HF in a cell/g	ΔR/ohm	ΔH^0_m/kJ mol^{-1}
$ZrO_{2(solid)}$	0.4806	185.6	1918	–131.4
	0.4780	185.1	1933	–133.1
	0.4795	185.5	1920	–131.8
	0.4797	185.5	1896	–130.1
				average: –131.8±1.97
$SeO_{2(solid)}$	0.9946	185.5	155	4.6
	1.4955	185.6	213	4.2
	1.9940	185.5	282	4.2
	1.9970	185.5	154	4.6
				average: 4.4±0.38
$Zr(SeO_3)_{2(solid)}$	1.0002	185.5	718	–66.1
	0.9980	185.5	695	–64.4
	0.6080	185.3	425	–64.4
	0.8980	185.6	630	–64.9
				average: –64.9±1.30

and 2, respectively – with preparation of the solution, formed on reaction (3) – a solution 3. So ΔH_4 enthalpy is an enthalpy of the 1 and 2 solutions mixing. In view of the high stability of ZrF_6^{2-} ion (pK=23.45 [17]) chemical interaction of dissolved selenium dioxide with fluorzirconate ion is unlikely, therefore ΔH_4 mixing enthalpy is possible to be neglected. Consequently, within inaccuracy of the experiment error the solution 3 can be considered as thermochemically identical to mixture of solutions 1 and 2 taken in equivalent ratio according to reaction (4). In our case it is also possible to neglect the corrections on diluting HF solutions due to high excess of the solvent ($n \geq 480$, $m \geq 2120$).

Conclusions

According to the thermochemical cycle experimental results have made it possible to obtain ΔH_5 enthalpy value of reaction (5). Taking into consideration the above arguments, the following enthalpy value of reaction (5) has been determined:

$$\Delta H_5 = -131.8 + 2 \cdot 4.4 - (-64.9) = -58.1 \pm 3.43 \text{ kJ mol}^{-1}$$

Taking into account literary data [18] on enthalpies of the zirconium dioxide ($\Delta H^0_{f,298} ZrO_{2(solid)} = -1094.1$ kJ mol^{-1}) and selenium dioxide ($\Delta H^0_{f,298} SeO_{2(solid)} = -225.5$ kJ mol^{-1}) formation and, ΔH_5 value, standard enthalpy of zirconium diselenite formation is equal to:

$$\Delta H^0_{f,298} Zr(SeO_3)_{2(solid)} = -1094.1 + 2(-225.5) + (-58.1) = \\ = -1603.2 \pm 3.8 \text{ kJ mol}^{-1}$$

This $\Delta H^0_{f,298} Zr(SeO_3)_{2(solid)}$ value has been determined for the first time.

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