

Specific molar heat capacity and thermodynamic properties of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$

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ABSTRACT

Using hydrothermal synthesis, $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ was obtained and studied by X-ray diffraction, thermogravimetric analysis and infrared spectroscopy. It was found that the compound had orthorhombic symmetry (*Fddd*) and unit cell parameters $a=25.8700 \text{ \AA}$, $b=5.5300 \text{ \AA}$, $c=11.5900 \text{ \AA}$, $\alpha=\beta=\gamma=90.00^\circ$. Absorption bands characteristic for the valence and deformation vibrations of the water molecules, as well as for the valence vibrations of the bidentate sulfate anion coordinated with the hafnium atom were registered in the IR spectra. The thermogravimetric analysis carried out up to 850°C did not end with formation of solid HfO_2 residue but with formation of dihafnyl sulfate $\text{Hf}_2\text{O}_3(\text{SO}_4)$. Using the experimental data obtained from the differential scanning calorimetry (DSC), the specific heat capacities ($C_{p,m}$) and the thermodynamic values ($\Delta_T^T \cdot S_m^0$, $\Delta_T^T \cdot H_m^0$, $-\Delta_T^T \cdot G_m^0 / T$) of all the intermediate phases by the dehydration and decomposition of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ were calculated. The temperature dependences of their molar heat capacities were determined by regression analysis. © 2016 Trade Science Inc. - INDIA

KEYWORDS

Heat capacity;
Thermodynamic properties;
Entropy;
Enthalpy and Gibbs energy.

INTRODUCTION

The studies on the structure and properties of hafnium compounds fill in information in an important field of the inorganic chemistry such as the chemistry of hafnium which is still not thoroughly studied^[1,2]. Many of the hafnium compounds are used in different industries. Some of them have specific catalytic activities, others are important components for preparation of optical glasses with specific properties used in optoelectronics, nuclear technology and medicine. There are perspectives for their application in radioceramic industry as dielectric materi-

als. In particular, hafnium sulfate is applied in textile industry for treatment of cloth to make it water impermeable, fire resistant and heavier^[2-4].

Many authors have studied the synthesis of compounds in the system $\text{Hf}(\text{SO}_4)_2-\text{H}_2\text{O}$ to find that all the phases are isomorphic to the phases in the system $\text{Zr}(\text{SO}_4)_2-\text{H}_2\text{O}$ ^[5]. It was reported for a great number of hafnium sulfates obtained from mixtures of HfO_2 and sulfuric acid in the concentration range of 50–95 wt% heated to the boiling point; their structure and thermal properties were then studied^[6].

The $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ synthesized in the present work was studied by XRD to confirm that it is

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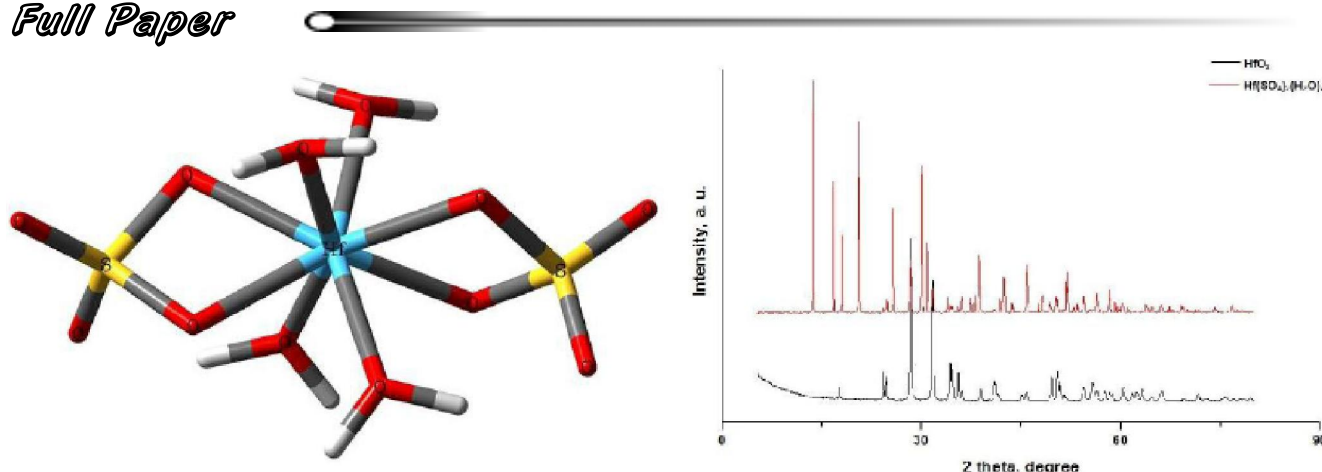


Figure 1 : Calculated geometry of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ and the experimental data from the XRD analysis

isostructural to the corresponding zirconium sulfate^[7]. The compound has orthorhombic symmetry (*Fddd*) and unit cell parameters $a = 25.8700 \text{ \AA}$, $b = 5.5300 \text{ \AA}$, $c = 11.5900 \text{ \AA}$, $\alpha = \beta = \gamma = 90.00^\circ$. The IR spectrum of the complex contained absorption bands characteristic for the water molecules (3410 cm^{-1} II 1640 cm^{-1}) which are two by two structurally unequal while the bands at 1055 cm^{-1} and 1201 cm^{-1} correspond to the vibrations of the bidentate sulfate ion coordinated with the Hf^{4+} ion. The vibration frequencies observed in the IR spectra of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ were reported in^[8,9]. Using Gaussian03^[10] and the density functional theory, the lengths and angles of the bonds were calculated, as well as their order and the electrostatic potential of the $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ molecule^[11]. Figure 1 shows the calculated geometry of the tetraaqua complex of hafnium sulfate and the experimental data obtained from the XRD analysis of the initial HfO_2 and the complex synthesized.

Knowing the thermodynamic properties of hafnium compounds such as the specific molar heat capacity ($C_{p,m}$), enthalpy ($\Delta_T^T H_m^0$), entropy ($\Delta_T^T S_m^0$) and Gibbs energy ($-\Delta_T^T G_m^0/T$) is essential for the studies on the possibilities of its application. Hafnium sulfate is comparatively well studied but no detailed thermodynamic data were found in the available literature. The aim of present work is to calculate the specific molar heat capacities and the thermodynamic values of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ and the intermediate phases $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})$ and $\text{Hf}(\text{SO}_4)_2$ obtained during the process of decomposition of the initial tetraaqua

complexes.

EXPERIMENTAL

The initial $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ was obtained from 1g HfO_2 (Merck) and 5 cm^3 96-98% H_2SO_4 (Merck) by hydrothermal synthesis in 15 cm^3 metal-teflon autoclaves at 300°C for 6 h. the white crystalline phase obtained was washed with ethanol and dried at 100°C ^[12].

The experimental data on the specific molar heat capacity $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ were registered on an apparatus for differential thermal analysis STA-TG-DSC/DTA F3 UPITER, product of NETZSCH, Germany, in air and in the temperature interval $30\text{--}850^\circ\text{C}$ at heating rate of $10^\circ\text{C}/\text{min}$. Sample weight was 13,8 mg and it was placed in a platinum crucible with lid.

The experimental results on $C_{p,m}$ were processed by the least squares method^[13-17]. By regression analysis, the coefficients a , b and c in the polynomial

$$C_p = c + bT + aT^2, \quad (1)$$

Were determined to find the minimum of the function $-C_{p,m}$:

$$C_{p,m} = f(T, a, b, c) \quad (2)$$

After finding the coefficients in eq.(1), the equation was checked for adequacy as the predicted values should correspond the experimentally measured ones^[16]. The goodness of fit of the model was estimated by the coefficient of linear regression - R^2 calculated from the scattering of the values of the

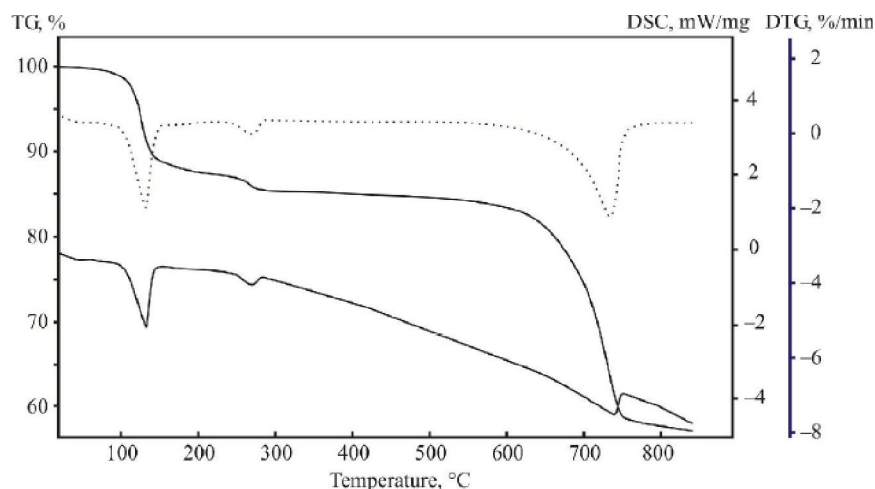


Figure 2 : TG/DTA/DSC curves of decomposition of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$

TABLE 1 : Experimental data on $C_{p,m}$ of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$, $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})$ and $\text{Hf}(\text{SO}_4)_2$

T, K	$C_{p,m}, \text{J K}^{-1} \text{mol}^{-1}$ $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$	T, K	$C_{p,m}, \text{J K}^{-1} \text{mol}^{-1}$ $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})$	T, K	$C_{p,m}, \text{J K}^{-1} \text{mol}^{-1}$ $\text{Hf}(\text{SO}_4)_2$
304.65	574				
309.65	578	423.65	326	513.65	1082
314.65	605	425.65	338	517.65	1271
319.65	638	427.65	349	521.65	1498
324.65	664	429.65	358	525.65	1769
329.65	686	431.65	364	529.65	2090
334.65	699	433.65	365	533.65	2468
339.65	704	435.65	364	537.65	2911
344.65	701	437.65	363	541.65	3429
349.65	692	439.65	365	545.65	4033
354.65	694	441.65	366	549.65	4734
359.65	712	443.65	364	553.65	5542
364.65	747	445.65	361	557.65	6457
369.65	801	447.65	357	561.65	7442
374.65	867	449.65	352	565.65	8276
379.65	953	451.65	345	568.65	8494
384.65	1058	453.65	339		
389.65	1191				
393.65	1439				

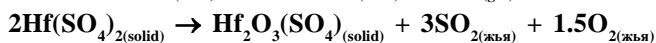
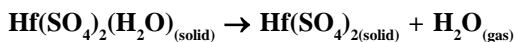
specific molar heat capacity ($C_{p,m}$) around its mean value^[16,17]. If R^2 value tends to zero then the regression model does not describe well the influence of temperature on the specific molar heat capacity. Values of R^2 close to unity (as with our results) indicates that the model adequately describes the dependence^[14,15]. the same approach was used for the determination of the thermodynamic properties of the tellurites of Cu(II), Hg(II)^[18] and rare earth elements^[19,20].

RESULT AND DISCUSSION

The behavior of hafnium sulfate on decomposition has been studied by many authors^[2,6,21]. The present work showed that the tetraaqua complex of hafnium sulfate decomposes along the following sequence:

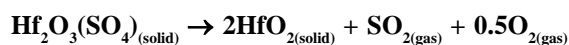


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The dehydration of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$ started at 130°C with the release of three water molecules and the fourth one coordinated with Hf^{4+} was released at 270°C. The decomposition of the anhydrous hafnium sulfate occurred in the temperature interval 580–780°C and the mass loss theoretically calculated from the TG curve corresponded to the experimental one for the formation of solid residue of $\text{Hf}_2\text{O}_3(\text{SO}_4)$. If the process is continued to tempera-

tures higher than 1000°C, the dihafnium sulfate will fully decompose to HfO_2 along the reaction:



The formation of the individual phases is clearly indicated in the TG/DTA/DSC curves shown in Figure 2.

The experimental data on the specific molar heat capacity ($C_{p,m}$) of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$, $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})$ and $\text{Hf}(\text{SO}_4)_2$ in the temperature interval of formation are presented in TABLE 1.

The experimental data in TABLE 1 are shown at

TABLE 2 : Standard molar entropy $\Delta_{0'}^{T'} S_m^0$, standard molar enthalpy $\Delta_{0'}^{T'} H_m^0$ and coefficients of regression a, b, c

Compound	$\Delta_{0'}^{T'} S_m^0, \text{J K}^{-1} \text{mol}^{-1}$	$\Delta_{0'}^{T'} H_m^0, \text{J mol}^{-1}$	a	b	c	R^2
$\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$	955.16	3610.2	0.0003	-0.1802	30.6069	0.8964
$\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})$	388.16	2752.8	-0.0004	0.3331	-72.2139	0.9475
$\text{Hf}(\text{SO}_4)_2$	199.16	2467.0	0.0058	-5.9525	1515.69	0.9981

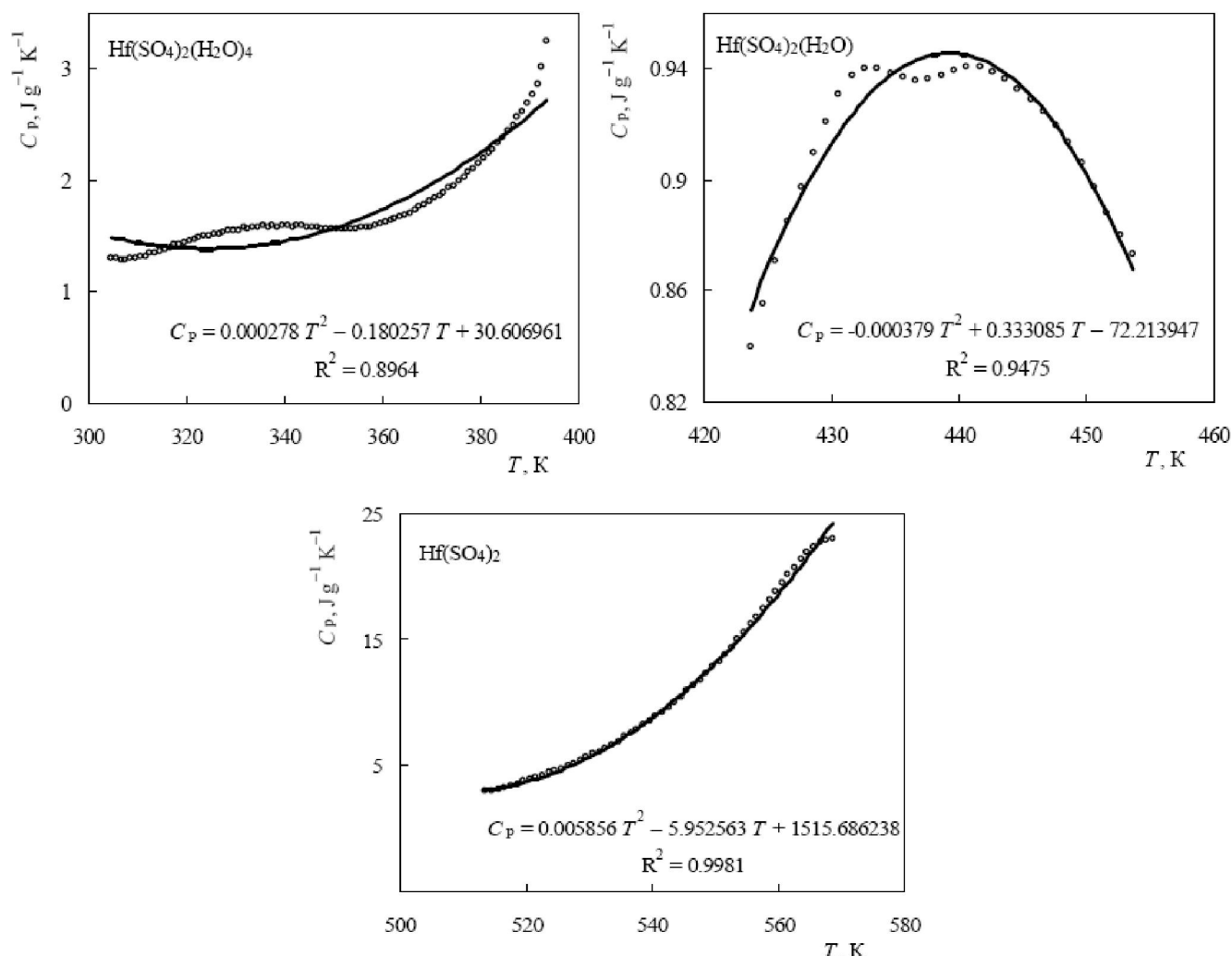


Figure 3 : Dependence of the C_p experimental values of temperature for $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$, $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})$ and $\text{Hf}(\text{SO}_4)_2$.

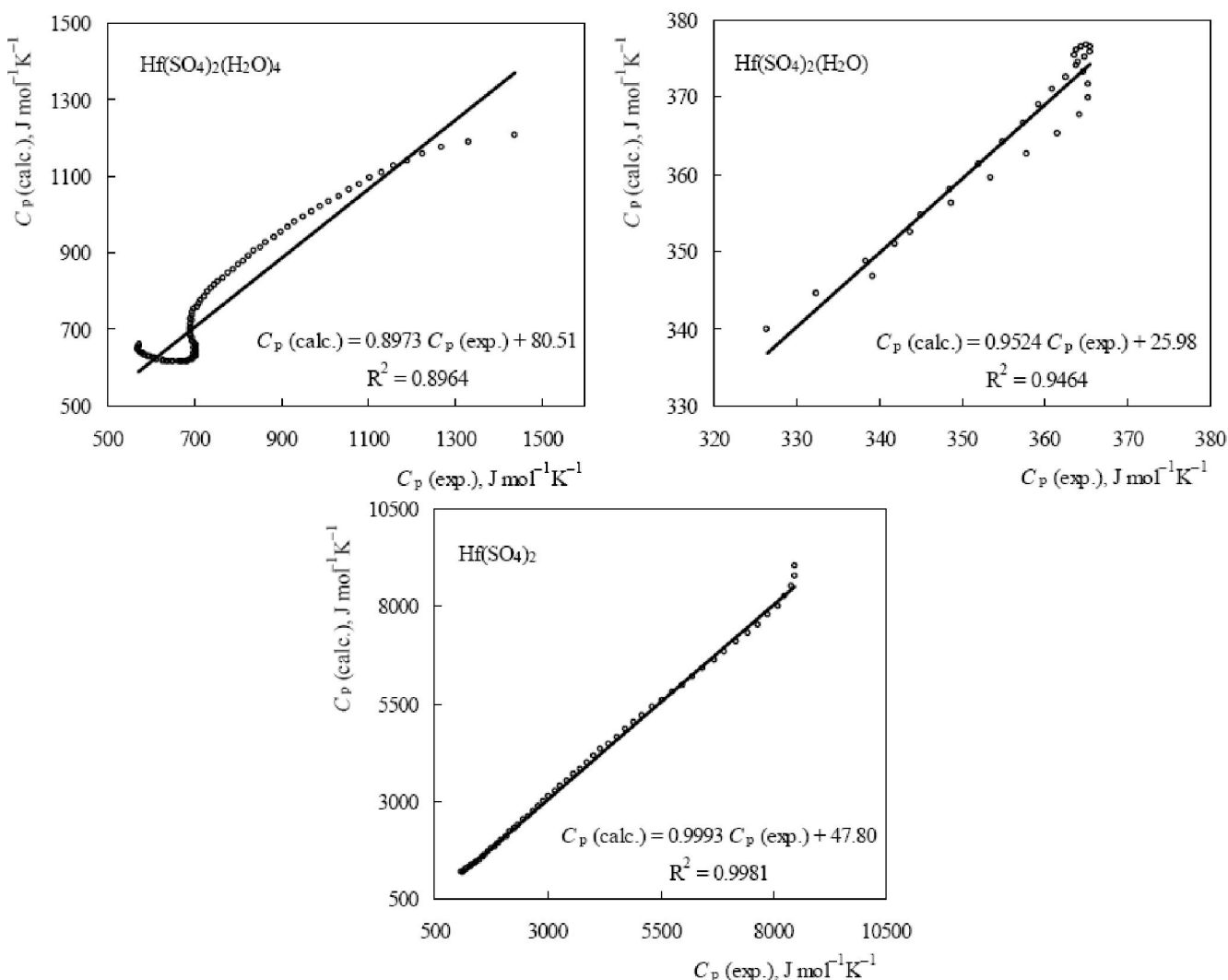


Figure 4 : Comparisons between the experimentally measured values of the specific molar heat capacities of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$, $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})$ and $\text{Hf}(\text{SO}_4)_2$ and these calculated by the regression analysis

intervals of 5, 2 and 4 K for $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$, $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})$ and $\text{Hf}(\text{SO}_4)_2$, respectively. The values were computer processed by the method of linear regression and empiric equations were derived for every phase according to the calculated values of the coefficients a , b and c in eq.(1). Using the method of Koumouk^[17], the standard molar entropies $\Delta_0^T S_m^0$ and enthalpies $\Delta_0^T H_m^0$ of the three compounds were calculated. TABLE 1 shows the values of the corresponding parameters, as well as the calculated coefficient of linear regression R^2 .

Figure 3 graphically shows the dependencies of the experimentally measured values of C_p on temperature and the empiric equations derived for the three phases $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$, $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})$ and

$\text{Hf}(\text{SO}_4)_2$.

Comparisons between the experimentally measured values of the specific molar heat capacities of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$, $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})$ and $\text{Hf}(\text{SO}_4)_2$ and these calculated by the regression analysis are presented in Figure 4.

As can be seen from Figure 4, the experimentally measured and the calculated values of the specific molar heat capacities had values of R^2 close to unity which indicated that the calculation procedure used was accurate and correct one. On this basis, it is possible to calculate the values of C_p at temperatures where there are no experimental data.

The specific molar heat capacity calculated by eq.(1) allows determining the values of the temperature dependencies of the change of entropy

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$(\Delta_T^T S_m^0)$, enthalpy $(\Delta_T^T H_m^0)$ Gibbs energy $(-\Delta_T^T G_m^0 / T)$ by the following equations:

$$\Delta_T^T S_m^0 = \Delta_0^T S_m^0 + \int_{T'}^T (C_{p,m} / T) . dT \quad (3)$$

$$\Delta_T^T H_m^0 = \Delta_0^T H_m^0 + \int_{T'}^T C_{p,m} . dT \quad (4)$$

$$(-\Delta_T^T G_m^0 / T) = \Delta_T^T S_m^0 - \Delta_T^T H_m^0 / T \quad (5)$$

The results obtained from the calculation of the

TABLE 3 : Molar thermodynamic functions of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$

T, K	$C_{p,m}$, $\text{J K}^{-1} \text{mol}^{-1}$	$(\Delta_T^T S_m^0)$, $\text{J K}^{-1} \text{mol}^{-1}$	$(\Delta_T^T H_m^0)$, J mol^{-1}	$(-\Delta_T^T G_m^0 / T)$, J mol^{-1}
304.65	660.89	969.26	7905.99	943.31
309.65	639.91	978.93	10969.15	943.50
314.65	625.08	987.94	13924.01	943.69
319.65	616.40	996.62	16862.83	943.87
324.65	613.88	1005.27	19877.89	944.04
329.65	617.50	1014.17	23061.47	944.21
334.65	627.28	1023.58	26505.84	944.37
339.65	643.21	1033.75	30303.29	944.53
344.65	665.29	1044.92	34546.07	944.69
349.65	693.52	1057.31	39326.49	944.98
354.65	727.90	1071.12	44736.80	945.12
359.65	768.44	1086.56	50869.28	945.26
364.65	815.13	1103.81	57816.22	945.39
369.65	867.97	1123.05	65669.88	945.52
374.65	926.96	1144.44	74522.54	945.65
379.65	992.10	1168.14	84466.49	945.77
384.65	1063.40	1194.30	95595.99	945.89
389.65	1140.84	1223.06	107997.31	945.90
393.65	1207.23	1248.04	118900.59	945.99

TABLE 4 : Molar thermodynamic functions of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})$

T, K	$C_{p,m}$, $\text{J K}^{-1} \text{mol}^{-1}$	$(\Delta_T^T S_m^0)$, J mol^{-1}	$(\Delta_T^T H_m^0)$, $\text{J K}^{-1} \text{mol}^{-1}$	$(\Delta_T^T G_m^0)$, J mol^{-1}
423.65	339.94	488.86	45415.64	381.66
425.65	348.65	492.59	47205.13	381.69
427.65	356.17	496.02	48877.05	381.72
429.65	362.52	499.11	50424.15	381.75
431.65	367.69	501.88	51839.35	381.78
433.65	371.68	504.30	53115.60	381.81
435.65	374.49	506.36	54245.82	381.84
437.65	376.13	508.05	55222.94	381.87
439.65	376.59	509.36	56039.89	381.90
441.65	375.87	510.29	56689.61	381.93
443.65	373.97	510.81	57165.02	381.96
445.65	370.89	510.92	57459.06	381.98
447.65	366.63	510.60	57564.66	382.01
449.65	361.20	509.86	57474.74	382.04
451.65	354.59	508.67	57182.25	382.07
453.65	346.80	507.03	56680.11	382.09

TABLE 5 : Molar thermodynamic functions of $\text{Hf}(\text{SO}_4)_2$

T, K	$C_{p,m}, \text{J K}^{-1} \text{mol}^{-1}$	$(\Delta_T^T \cdot S_m^0), \text{J mol}^{-1}$	$(\Delta_T^T \cdot H_m^0), \text{J K}^{-1} \text{mol}^{-1}$	$(\Delta_T^T \cdot G_m^0), \text{J mol}^{-1}$
513.65	1177.59	693.21	256237	194.00
517.65	1306.14	753.01	289166	194.39
521.65	1504.14	843.61	338643	194.43
525.65	1771.59	965.90	405503	194.43
529.65	2108.47	1120.73	490578	194.53
533.65	2514.80	1308.94	594701	194.54
537.65	2990.57	1531.33	718707	194.57
541.65	3535.78	1788.68	863428	194.61
545.65	4150.43	2081.74	1029698	194.64
549.65	4834.52	2411.26	1218349	194.67
553.65	5588.06	2777.95	1430216	194.70
557.65	6411.04	3182.51	1666132	197.74
561.65	7303.46	3625.60	1926929	194.77
565.65	8265.32	4107.89	2213441	194.80
568.65	9032.29	4495.71	2445702	194.82

thermodynamic functions by eqs.(3-5) are presented in TABLES 3-5.

From scientific point of view, the studies on the physicochemical properties of hafnium compounds is interesting since the enthalpy, entropy and Gibbs free energy are directly related to the strength of the chemical bonds in these compounds. The thermodynamic values established are important for the calculations of chemical reactions where some of these compounds take part. The thermodynamic data includes data on the aggregate and phase state in certain temperature interval, the enthalpy and entropy of formation and the phase transitions of the compounds studied.

CONCLUSION

$\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$, was obtained by the hydrothermal method and its composition was proved by X-ray diffraction and thermogravimetric analyses, as well as infrared spectroscopy. Processing the experimental data from the TG/DTG/DSC analysis for the specific molar heat capacity of $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})_4$, $\text{Hf}(\text{SO}_4)_2(\text{H}_2\text{O})$ and $\text{Hf}(\text{SO}_4)_2$, the coefficients in the polynomial $C_p = c + bT + aT^2$ were calculated. Based on these data and using the standard entropy of the initial compounds, the temperature dependencies of the change of entropy

$(\Delta_T^T \cdot S_m^0)$, enthalpy $(\Delta_T^T \cdot H_m^0)$ and Gibbs function $(-\Delta_T^T \cdot G_m^0/T)$.

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