Thermodynamic Investigation of Electrolytes of the Vanadium Redox Flow Battery (II): A Study on Low-Temperature Heat Capacities and Thermodynamic Properties of $VOSO_4 \cdot 2.63H_2O(s)$

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The low-temperature heat capacities of $VOSO_4 \cdot 2.63H_2O(s)$ which is a key component in the electrolyte of the vanadium redox flow battery were measured by adiabatic calorimetry in the temperature range of (78 to 388) K, and the experimental values of the molar heat capacities in the temperature regions of (78 to 372) K were fitted to a polynomial equation. The polynomial fitted values of the molar heat capacities and fundamental thermodynamic functions of the compound relative to the standard reference temperature of 298.15 K were calculated at intervals of 5 K. Additionally, a dehydration process occurred in the temperature range of (372 to 382) K, and the peak temperature, $T_{de} = (378.895 \pm 0.309)$ K, molar enthalpy of dehydration, $\Delta_{de}H_m = (116.446 \pm 0.148)$ $kJ \cdot mol^{-1}$, and molar entropy of dehydration, $\Delta_{de}S_m = (307.329 \pm 0.141)$ $J \cdot K^{-1} \cdot mol^{-1}$, were determined in terms of the heat capacity curve.

1. Introduction

The vanadium redox flow battery (VRB) was first proposed and investigated by Skyllas-Kazacos et al.,[1,2] in which the V(II)/V(III) and V(IV)/V(V) redox couples were successfully employed as the negative and positive half-cell electrolytes. The VRB, as a promising large-scale energy storage system, has been investigated extensively since then.[3,4] The chemistry of vanadium has recently attracted considerable attention from industry and the academic community.[5,6] Reliable thermodynamic data are needed to provide clues to optimize the overall performance of the VRB. $VOSO_4$ is a key component in the positive electrolyte of the VRB. To our knowledge, no reports on low-temperature heat capacities and thermodynamic properties of $VOSO_4$ are at present available. As a continuation of our earlier work,[7] in this paper the heat capacities of $VOSO_4 \cdot 2.63H_2O(s)$ in the temperature range of (78 to 388) K were measured by an adiabatic calorimetry method. The thermodynamic functions, $(H_T - H_{298.15})$, $(S_T - S_{298.15})$, and $(G_T - G_{298.15})$ of $VOSO_4 \cdot 2.63H_2O(s)$, were calculated from heat capacity data in the temperature range of (80 to 370) K. The thermodynamic properties such as molar enthalpies and entropies of the thermal dehydration process of $VOSO_4 \cdot 2.63H_2O(s)$ were determined on the basis of the heat capacity measurements.

2. Experimental Section

2.1. Chemicals. $VOSO_4 \cdot nH_2O(s)$ (≥ 97 mass %, Shanghai Chemical Co.) was recrystallized twice from water.

2.2. Determination of the Value of n. The recrystallized $VOSO_4 \cdot nH_2O(s)$ was then dried under reduced pressure at 80 °C for an hour,[8] and the value of n ($n = 2.63$) was determined by thermogravimetric analysis (TG) (ThermoMax 700, Thermo Carhn, U.S.). The temperature range of the TG was (273 to 673) K with a heating rate of 20 $K \cdot min^{-1}$ in a nitrogen atmosphere.

2.3. Measurement of Heat Capacity. A precision automatic adiabatic calorimeter was used to measure heat capacities of $VOSO_4 \cdot 2.63H_2O(s)$ over the temperature range of $78 \le (T/K) \le 388$. The calorimeter was established in the Thermochemistry Laboratory of the Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China.[9–11] The calorimeter mainly comprised a sample cell, a platinum resistance thermometer, an electric heater, inner and outer adiabatic shields, two sets of six-junction chromel−constantan thermopiles installed between the calorimetric cell and the inner shield and between the inner and the outer shields, respectively, and a high vacuum can. A 100 Ω miniature platinum resistance thermometer (IPRT No. 2, Shanghai Institute of Industrial Automatic Meters, China) was applied to measure the temperature of the sample. The thermometer was calibrated on the basis of ITS-90 by the Station of Low-Temperature Metrology and Measurements, Academia Sinica. The electrical energy introduced into the sample cell and the equilibrium temperature of the cell after the energy input were automatically recorded by use of a data acquisition/switch unit (model 34970A, Agilent, U.S.) and processed online by a computer.

To verify the accuracy of the calorimeter, the heat capacities of a reference standard material (α-Al_2O_3) were measured over the temperature range of $78 \le (T/K) \le 400$. The mass of the sample was 1.7143 g, which was equivalent to 0.0168 mol on the basis of its molar mass, $M(Al_2O_3) = 101.9613$ $g \cdot mol^{-1}$. Deviations of the experimental results from those of the smoothed curve lay within ± 0.2 %, while the experimental error was ± 0.3 %, as compared with the values given by the former National Bureau of Standards[12,13] over the whole temperature range.

Heat-capacity measurements of $VOSO_4 \cdot 2.63H_2O(s)$ over the temperature range of $78 \le (T/K) \le 388$ were continuously and

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Table 1. Experimental Molar Heat Capacities of $VOSO_4 \cdot 2.63H_2O(s)$ ($M = 210.38\ g \cdot mol^{-1}$)

T	$C_{p,m}$	T	$C_{p,m}$	T	$C_{p,m}$
K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$	K	$J \cdot K^{-1} \cdot mol^{-1}$
78.212	100.219	200.631	182.711	326.529	232.149
79.813	101.752	202.649	183.736	329.174	233.212
82.179	103.584	204.667	184.723	331.957	234.356
84.058	105.051	206.825	185.747	334.811	235.399
86.425	106.453	208.843	186.810	337.664	236.625
88.582	107.985	210.861	187.702	340.518	237.728
90.670	109.518	212.880	188.666	343.301	238.934
92.967	111.204	214.898	189.585	346.016	239.813
95.054	112.847	216.707	190.571	348.660	240.815
96.794	114.380	218.795	191.425	351.166	241.816
99.230	116.372	220.605	192.450	353.532	242.961
101.596	118.190	222.623	193.343	355.829	243.921
103.893	119.942	224.641	194.131	358.056	244.923
106.259	121.737	226.242	194.841	360.144	245.904
108.556	123.511	228.678	195.774	362.162	246.864
110.644	125.000	230.696	196.601	364.041	247.968
112.940	126.555	232.575	197.455	365.850	248.969
115.098	128.394	234.385	198.257	367.590	249.705
117.186	129.839	236.472	199.058	369.191	250.502
119.343	131.834	238.560	199.860	370.583	251.769
121.431	133.365	240.579	200.648	371.766	252.117
123.589	134.876	242.458	201.436	372.810	253.869
125.537	136.540	244.476	202.133	373.645	257.810
127.695	137.832	246.494	203.000	374.411	269.197
129.643	139.628	248.373	203.709	375.107	281.752
131.522	140.942	250.531	204.550	375.733	293.869
133.471	142.345	252.549	205.247	376.220	307.372
135.489	143.745	254.706	206.048	376.568	323.431
137.299	144.905	256.933	206.889	376.916	340.511
139.317	146.307	258.743	207.651	377.264	354.526
141.405	147.469	260.900	208.413	377.473	370.292
143.145	148.854	262.919	209.162	377.751	388.832
145.372	150.258	265.215	210.042	377.960	407.372
148.225	151.909	267.303	210.988	378.099	428.540
150.383	153.504	269.391	211.566	378.238	444.453
152.471	154.908	271.618	212.539	378.378	460.073
155.742	156.692	273.845	213.353	378.517	476.058
159.013	158.780	276.003	214.247	378.586	498.102
162.562	160.886	278.369	215.140	378.826	480.201
164.789	162.309	281.361	216.034	378.973	462.911
167.503	163.885	284.215	216.888	379.091	448.073
170.217	165.403	287.068	217.847	379.239	433.112
173.140	166.921	289.922	218.898	379.356	415.822
175.020	168.326	292.775	219.968	379.500	395.956
176.968	169.559	295.629	221.039	379.704	378.666
178.987	170.565	298.482	222.018	379.883	362.969
180.935	171.723	301.335	223.010	380.117	349.051
182.814	172.918	304.328	224.088	380.326	331.022
184.833	174.114	307.181	225.191	380.465	314.380
186.712	175.196	310.104	226.164	380.700	295.279
188.521	176.258	312.819	227.188	380.966	274.555
190.539	177.188	315.394	227.924	381.788	259.717
192.418	178.365	317.760	228.660	385.059	261.434
194.437	179.371	319.917	229.585	387.912	263.028
196.455	180.509	322.005	230.269		
198.473	181.648	324.093	231.168		

automatically carried out by means of the standard method of intermittently heating the sample and alternately measuring the temperature. The heating rate and temperature increments were generally controlled at (0.1 to 0.4) $K \cdot min^{-1}$ and (1 to 3) K. The heating duration was 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were always kept within (10^{-3} to 10^{-4}) $K \cdot min^{-1}$ during the acquisition of all heat-capacity data. The data of heat capacities and corresponding equilibrium temperature have been corrected for heat exchange of the sample cell with its surroundings.[9] The sample mass used for calorimetric measurements was 1.65749 g.

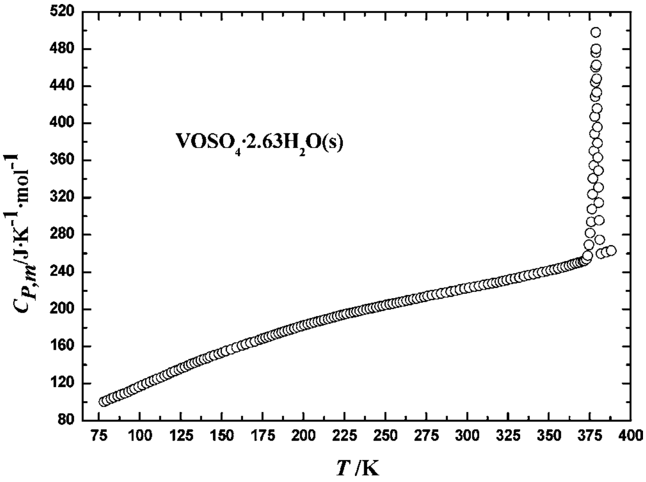

Figure 1. Curve of experimental molar heat capacities against the temperature ($C_{p,m} \sim T$) of $VOSO_4 \cdot 2.63H_2O(s)$.

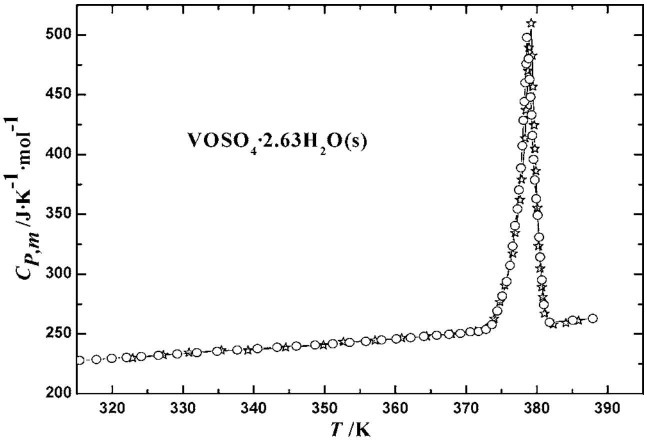

Figure 2. Curve of experimental molar heat capacities of the dehydration process against the temperature ($C_{p,m} \sim T$) of $VOSO_4 \cdot 2.63H_2O(s)$. ○, the first series; ☆, the second series of heat capacity measurements.

3. Results and Discussion

3.1. Low-Temperature Heat Capacities. The experimental molar heat capacities of $VOSO_4 \cdot 2.63H_2O(s)$ are listed in Table 1 and plotted in Figure 1. The heat capacities of $VOSO_4 \cdot 2.63H_2O(s)$ increase slowly in the temperature range of (78 to 372) K, which shows that the structure of $VOSO_4 \cdot 2.63H_2O(s)$ is stable in this temperature region, that is, no thermal decomposition occurs. The accelerated rise of the experimental heat capacities after $T = 372$ K results from dehydration of $VOSO_4 \cdot 2.63H_2O(s)$. All of the experimental points in the temperature range between $T = 78$ K and $T = 372$ K were fitted by means of a least-squares method, and a polynomial equation of the experimental molar heat capacities ($C_{p,m}$) versus reduced temperature (X), $X = f(T)$, was obtained

$$C_{p,m}/(J \cdot K^{-1} \cdot mol^{-1}) = 194.1129 + 65.14856X - 26.3759X^2 + 11.0306X^3 + 8.19886X^4 \quad (1)$$

where $X = (T - 225)/147$. The coefficient of determination for the fitting is $R^2 = 0.99997$. The standard deviations of experimental molar heat capacities from the smoothed heat capacities calculated through the polynomial equation are within ± 0.4 %.

3.2. Thermodynamic Functions of the Compound. The smoothed molar heat capacities were calculated on the basis of the fitted polynomial equation. Thermodynamic functions of

Table 2. Smoothed Heat Capacities and Thermodynamic Functions of $VOSO_4 \cdot 2.63H_2O(s)$

T / K	$C_{p,m}$ / $J \cdot K^{-1} \cdot mol^{-1}$	$H_T - H_{298.15K}$ / $kJ \cdot mol^{-1}$	$S_T - S_{298.15K}$ / $J \cdot K^{-1} \cdot mol^{-1}$	$G_T - G_{298.15K}$ / $kJ \cdot mol^{-1}$
80	101.363	−37.35	−1.413	−37.23
85	105.360	−36.83	−1.371	−36.71
90	109.325	−36.29	−1.330	−36.17
95	113.256	−35.74	−1.289	−35.61
100	117.147	−35.16	−1.249	−35.04
105	120.994	−34.57	−1.209	−34.44
110	124.794	−33.95	−1.170	−33.82
115	128.542	−33.32	−1.132	−33.19
120	132.235	−32.67	−1.094	−32.53
125	135.871	−32.00	−1.056	−31.86
130	139.447	−31.31	−1.019	−31.17
135	142.960	−30.60	−0.9823	−30.47
140	146.407	−29.88	−0.9462	−29.74
145	149.787	−29.14	−0.9105	−29.00
150	153.099	−28.38	−0.8753	−28.25
155	156.339	−27.61	−0.8405	−27.48
160	159.508	−26.82	−0.8062	−26.69
165	162.605	−26.01	−0.7723	−25.88
170	165.628	−25.19	−0.7388	−25.06
175	168.578	−24.35	−0.7057	−24.23
180	171.453	−23.50	−0.6731	−23.38
185	174.255	−22.64	−0.6408	−22.52
190	176.984	−21.76	−0.6090	−21.65
195	179.639	−20.87	−0.5775	−20.76
200	182.223	−19.97	−0.5464	−19.86
205	184.736	−19.05	−0.5157	−18.94
210	187.180	−18.12	−0.4853	−18.02
215	189.556	−17.18	−0.4553	−17.08
220	191.866	−16.22	−0.4256	−16.13
225	194.113	−15.26	−0.3962	−15.17
230	196.299	−14.28	−0.3672	−14.20
235	198.426	−13.30	−0.3385	−13.22
240	200.499	−12.30	−0.3101	−12.22
245	202.519	−11.29	−0.2820	−11.22
250	204.491	−10.27	−0.2542	−10.21
255	206.418	−9.246	−0.2267	−9.188
260	208.304	−8.209	−0.1995	−8.157
265	210.155	−7.163	−0.1725	−7.117
270	211.973	−6.107	−0.1458	−6.068
275	213.765	−5.043	−0.1194	−5.010
280	215.534	−3.970	−0.09319	−3.943
285	217.288	−2.888	−0.06722	−2.868
290	219.030	−1.797	−0.04148	−1.785
295	220.768	−0.6972	−0.01597	−0.6925
298.15	221.863	0	0	0
300	222.507	0.4111	0.009338	0.4083
305	224.253	1.528	0.03444	1.517
310	226.014	2.654	0.05934	2.635
315	227.796	3.788	0.08405	3.762
320	229.607	4.932	0.1086	4.897
325	231.454	6.084	0.1330	6.041
330	233.345	7.247	0.1572	7.195
335	235.287	8.418	0.1812	8.357
340	237.289	9.600	0.2051	9.530
345	239.360	10.79	0.2288	10.71
350	241.509	11.99	0.2525	11.91
355	243.743	13.21	0.2760	13.11
360	246.074	14.43	0.2994	14.32
365	248.509	15.67	0.3226	15.55
370	251.060	16.92	0.3458	16.79

$VOSO_4 \cdot 2.63H_2O(s)$ relative to the standard reference temperature of 298.15 K, $(H_T - H_{298.15})$, $(S_T - S_{298.15})$, and $(G_T - G_{298.15})$, were evaluated according to the following thermodynamic equations,

$$(H_T - H_{298.15}) = \int_{298.15}^{T} C_p \, dT \tag{2}$$

$$(S_T - S_{298.15}) = \int_{298.15}^{T} C_p \cdot T^{-1} \, dT \tag{3}$$

$$(G_T - G_{298.15}) = \int_{298.15}^{T} C_{p,m} \, dT - T \cdot \int_{298.15}^{T} C_{p,m} \cdot T^{-1} \, dT \tag{4}$$

The polynomial fitted values of the molar heat capacities and fundamental thermodynamic functions of $VOSO_4 \cdot 2.63H_2O(s)$ relative to the standard reference temperature of 298.15 K are tabulated in Table 2 over the temperature range of (78 to 370) K at intervals of 5 K.

3.3. Molar Enthalpy of Dehydration and Entropy of Dehydration. To verify the repeatability of the dehydration process of the sample, two additional series of experiments in the dehydration process of $VOSO_4 \cdot 2.63H_2O(s)$ with different cooling rates were carried out. The cooling rate of series 1 was about 15 $K \cdot min^{-1}$ (liquid nitrogen as the coolant), and that of the series 2 was about 2.5 $K \cdot min^{-1}$ (ice water cooling). The results of two series of heat capacity measurements are listed in Table 3 and plotted in Figure 2.

It can be concluded from Figure 2 that C_p values during the dehydration process of the repeated experiments are in agreement with each other. The dehydration process basically exhibited good repeatability, though there were some slight differences in heights and widths of peaks corresponding to each series of the experiment. In addition, different cooling rates do not affect the experimental results.

The molar enthalpy of dehydration, $\Delta_{de}H_m$, in the $C_{p,m} - T$ curve was evaluated in terms of eq 5, and the molar entropy of dehydration, $\Delta_{de}S_m$, was calculated with the thermodynamic eq 6:

$$\Delta_{de}H_m = [Q - n\int_{T_i}^{T_{de}} C_{p(i)} \, dT - n\int_{T_{de}}^{T_f} C_{P(f)} \, dT - \int_{T_i}^{T_f} H_0 \, dT]/n \ (J \cdot K^{-1} \cdot mol^{-1}) \tag{5}$$

$$\Delta_{de}S_m = \Delta_{de}H_m / T_{de} \ (J \cdot K^{-1} \cdot mol^{-1}) \tag{6}$$

where T_{de} is the peak temperature of the dehydration process of the sample; T_i is a temperature slightly below the starting dehydration temperature; T_f is a temperature slightly higher than the finishing dehydration temperature; $C_{p,(s)}$ is the average heat capacity at the temperature $(T_i + T_{de})/2$; $C_{p,(f)}$ is the average heat capacity at the temperature $(T_{de} + T_f)/2$; Q is the total heat quantity introduced to the calorimeter from temperature T_i to T_f; n is the mole number of the sample; H_0 is the heat capacity of the empty sample cell. Values of Q and H_0 are calculated with the program stored in the computer linked with the adiabatic calorimetric system and printed along with experimental results of heat capacities. The results of the dehydration process obtained from every series of repeated experiments are listed in Table 3.

Table 3. Results of Dehydration Process Obtained from Two Series of Repeated Experiments of $VOSO_4 \cdot 2.63H_2O(s)$

thermodynamic properties	m / g	T_{de} / K	$\Delta_{de}H_m$ / $kJ \cdot mol^{-1}$	$\Delta_{de}S_m$ / $J \cdot K^{-1} \cdot mol^{-1}$
series 1 x_i	1.64582	378.586	116.297	307.188
series 2 x_i	1.65749	379.204	116.594	307.470
mean value ($\bar{x}$)		(378.895 ± 0.309)	(116.446 ± 0.148)	(307.329 ± 0.141)

4. Conclusions

The molar heat capacities of $VOSO_4 \cdot 2.63H_2O(s)$ were measured by an adiabatic calorimeter in the temperature range of (78 to 388) K and were fitted to a polynomial equation. The thermodynamic functions, $(H_T - H_{298.15})$, $(S_T - S_{298.15})$, and $(G_T - G_{298.15})$, were calculated on the basis of the heat capacity measurements in the temperature range of (80 to 370) K at intervals of 5 K. In addition, a dehydration process of $VOSO_4 \cdot 2.63H_2O(s)$ was observed in the range of (372 to 382) K with the peak temperature of (378.895 ± 0.309) K; the molar enthalpy and entropy of the dehydration process were determined in terms of the heat capacity results.

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