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THERMODYNAMIC INVESTIGATION OF SEVERAL NATURAL POLYOLS (II)

Heat capacities and thermodynamic properties of sorbitol

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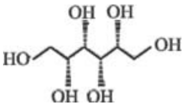
The low-temperature heat capacity $C_{p,m}$ of sorbitol was precisely measured in the temperature range from 80 to 390 K by means of a small sample automated adiabatic calorimeter. A solid–liquid phase transition was found at T=369.157 K from the experimental C_p–T curve. The dependence of heat capacity on the temperature was fitted to the following polynomial equations with least square method. In the temperature range of 80 to 355 K, $C_{p,m}$/J K^{-1} mol^{-1}=170.17+157.75x+128.03x^2–146.44x^3–335.66x^4+177.71x^5 +306.15x^6, x= [(T/K)–217.5]/137.5. In the temperature range of 375 to 390 K, $C_{p,m}$/J K^{-1} mol^{-1}=518.13+3.2819x, x= [(T/K)–382.5]/7.5. The molar enthalpy and entropy of this transition were determined to be 30.35±0.15 kJ mol^{-1} and 82.22±0.41 J K^{-1} mol^{-1} respectively. The thermodynamic functions [H_T–$H_{298.15}$] and [S_T–$S_{298.15}$], were derived from the heat capacity data in the temperature range of 80 to 390 K with an interval of 5 K. DSC and TG measurements were performed to study the thermostability of the compound. The results were in agreement with those obtained from heat capacity measurements.

Keywords: *DSC, heat capacity, phase transition, sorbitol, TG-DTG, thermodynamic properties*

Introduction

Polyhydroxy compounds and their properties are important in many areas of chemistry and biochemistry. Their polar nature and ability to participate in hydrogen bonding give them a high affinity for water and other polar solvents [1–3]. Sorbitol [(CH_2OH) $(CHOH)_4$ (CH_2OH), CAS No. 50-70-4] is an important natural polyol in food and pharmaceutical applications, as it is increasingly used to provide sweetness to various products or replaces sugar in confectionery. Its molecular formula is $C_6H_{14}O_6$ with molar mass of 182.17 g mol^{-1} and structural formula as follows:



Compared with the sucrose, the sorbitol has the characteristic sweet taste of sugars but the amount of energy (calories) in the products is reduced. Another important advantage is that it does not contribute to the development of dental caries. Moreover, it is suitable for diabetics, because it does not require insulin of glucose in their metabolism [2, 4]. In industrial applications, the state and phase transition of the sorbitol affects its molecular mobility and physicochemical properties [2, 5]. The heat capacity and phase transition data of sorbitol were reported in 1982 [6] and 1990 [7], respectively. Because it is very useful in food and pharmaceutical applications, in the present study, the heat capacity and phase transition were investigated in detail with precision adiabatic calorimetric and thermal analytic technique in a wide temperature range from 80 to 390 K.

Heat capacity is one of the most fundamental thermodynamic properties of substances and it closely related to other physical and chemical properties. Heat capacity determinations of various compounds have attracted many researchers. Adiabatic calorimetry is one of the most accurate method for obtaining the heat capacity, melting point and enthalpy of fusion of substances. In the present paper, low temperature heat capacity measurements were carried out with an adiabatic calorimeter over the temperature range from 80 to 390 K, and thermodynamic properties such as molar enthalpies and entropies of phase transition as well as chemical purity were determined based on the heat capacity measurements. The thermodynamic functions, [H_T–$H_{298.15}$] and [S_T–$S_{298.15}$], were calculated from heat capacity data in the temperature range of 80–390 K.

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Experimental

Sample

The sorbitol was purchased from YuanJu Bio-Tech Co. Ltd. Shanghai, in PR China with batch number 040603 and labeled purity >99.0% mass fraction. The sample was recrystallized and then purified by sublimation. It was handled in a dry N_2 atmosphere to avoid possible contamination by moisture.

Adiabatic calorimetry

Heat capacity measurements were carried out in a high-precision automated adiabatic calorimeter described in detail in literature [8, 9]. The calorimeter was established by Thermochemistry Laboratory of Dalian Institute of Chemical Physics, Chinese Academy of Sciences in PR China. It mainly consisted of a sample cell, a miniature platinum resistance thermometer, an electric heater, an inner and outer adiabatic shield, two sets of chromel-copel thermocouples and a high vacuum system. Its working temperature is from 80 to 400 K [10] with liquid nitrogen as cooling medium.

The measurements were conducted by means of the standard method of intermittently heating the sample and alternately measuring the temperature. The temperature difference between the sample and adiabatic shield was automatically kept to be about 10^{-3} K during the whole experiment. The temperature increment for a heating period was 2–4 K, and temperature drift was maintained about 10^{-4} K min^{-1} during each equilibrium period. The data were automatically collected through a Data Acquisition/Switch Unit (Model: 34420, Agilent USA) and processed on line by a personal computer according to the program developed in our thermochemistry laboratory [11].

The sample amount used for the heat capacity measurement is 3.71682 g, which is equivalent to 20.403 m mol based on its molar mass of 182.17 g mol^{-1}.

DSC and TG analysis

A differential scanning calorimeter (Model: DSC141, SETARAM, France) was used to perform the thermal analysis of sorbitol under high purity nitrogen (99.999%) with a flow rate of 40 mL min^{-1} and heating rate of 10 K min^{-1}. The mass of the sample used in the experiment was 3.01 mg.

The TG measurements of the sample were carried out by a thermogravimetric analyzer (Model: Setaram setsys 16/18, SETARAM, France) under N_2 with a flow rate of 40 mL min^{-1} and heating rate of 10 K min^{-1}. The mass of the sample used in the experiment was 13.15 mg.

Results and discussion

Heat capacity

Experimental molar heat capacities of sorbitol measured by the adiabatic calorimeter over the temperature range from 80 to 390 K are listed in Table 1 and plotted in Fig. 1. From the Fig. 1, a phase transition was observed in the range of 360 to 375 K with a peak temperature of 369.157 K. According to its melting point 366.5 K [7], this transition corresponds to a solid–liquid phase change.

The values of experimental heat capacities can be fitted to the following polynomial equations with least square method:

For the solid phase over the temperature range (80 to 355) K:

$$C_{p,m}/\mathrm{J\ K^{-1}\ mol^{-1}}=170.17+157.75x+128.03x^2 -146.44x^3-335.66x^4+177.71x^5+306.15x^6 \quad (1)$$

where x is the reduced temperature $X=[T-(T_{max}+T_{min})/2]/[(T_{max}-T_{min})/2]$, T is the experimental temperature, thus, in the solid state (80 to 355 K), $x=[(T/\mathrm{K})-217.5]/137.5$, T_{max} is the upper limit (355 K) and T_{min} is the lower limit (80 K) of the above temperature region. The correlation coefficient of the fitting $R^2=0.9966$.

For the liquid phase over the temperature range (375 to 390) K:

$$C_{p,m}/\mathrm{J\ K^{-1}\ mol^{-1}}=518.13+3.2819x \quad (2)$$

where x is the reduced temperature, $x=[(T/\mathrm{K})-382.5]/7.5$, T is the experimental temperature, 382.5 is obtained from polynomial $(T_{max}+T_{min})$, 7.5 is obtained from polynomial $(T_{max}-T_{min})$. T_{max} and T_{min} are the upper (390 K) and lower (375 K) limit temperature respectively. The correlation coefficient of the fitting $R^2=0.9968$.

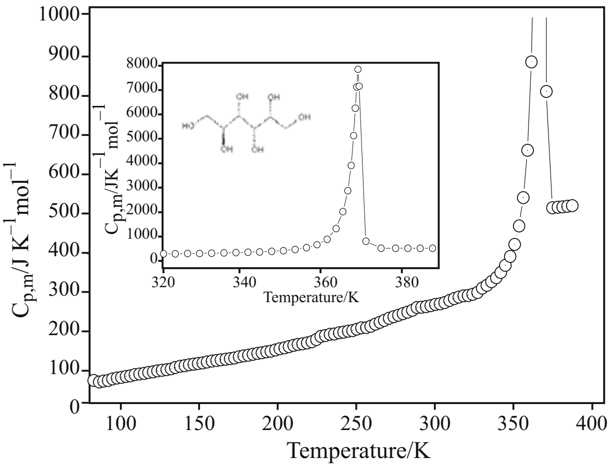

Fig. 1 Experimental molar heat capacity of sorbitol as a function of temperature

Table 1 Experimental molar heat capacity of sorbitol (M=182.17 g mol^{-1})

T/K	$C_{p,m}$/J K^{-1} mol^{-1}	T/K	$C_{p,m}$/J K^{-1} mol^{-1}	T/K	$C_{p,m}$/J K^{-1} mol^{-1}
82.726	75.56	192.708	147.5	303.367	270.5
86.246	70.52	195.520	149.5	306.351	273.7
89.038	73.43	198.401	152.8	309.384	278.5
91.898	75.11	201.345	155.5	312.388	283.6
94.668	78.50	204.261	158.5	315.356	287.6
97.529	81.64	207.152	161.4	318.309	290.2
100.456	83.40	210.016	164.5	321.256	291.6
103.318	85.35	212.859	166.9	324.199	294.7
106.117	87.08	215.768	168.5	327.190	299.3
108.990	89.64	218.735	170.8	330.193	310.1
111.937	91.63	221.666	174.4	333.153	317.3
114.826	93.47	224.562	179.3	336.136	326.4
117.663	95.46	227.408	186.8	339.129	337.2
120.451	97.23	230.258	189.9	342.067	350.3
123.318	99.47	233.175	192.9	344.995	368.5
126.255	101.2	236.113	194.0	347.949	390.9
129.150	103.0	238.997	196.4	350.841	421.9
132.003	104.7	241.854	198.5	353.684	468.4
134.810	107.8	244.712	200.8	356.464	540.8
137.702	111.1	247.567	202.3	359.101	661.2
140.666	113.1	250.398	205.8	361.565	886.5
143.592	114.9	253.298	208.9	363.769	1321
146.482	116.6	256.257	209.7	365.493	2022
149.338	118.2	259.184	212.9	366.677	2874
152.162	119.9	262.100	218.3	367.485	3908
155.061	122.4	264.997	223.3	368.082	5134
158.032	123.9	267.875	228.1	368.528	6257
160.970	125.7	270.808	233.2	368.866	7127
163.878	127.4	273.797	236.9	369.157	7854
166.756	129.3	276.766	241.0	369.458	7160
169.609	131.1	279.715	244.9	371.133	811.0
172.432	132.7	282.640	248.6	374.834	515.1
175.323	135.5	285.612	253.9	378.420	516.4
178.287	137.4	288.617	260.7	381.464	517.6
181.223	139.2	291.579	261.7	384.500	519.1
184.132	141.3	294.523	262.8	387.530	520.3
187.013	143.7	297.489	265.7		
189.872	145.7	300.435	269.2		

The published papers in literature [12–14] have used the same method to treat the $C_{p,m}$ data around the phase change temperature.

The temperature, enthalpy and entropy of solid–liquid phase transition

The molar enthalpies and entropies of the solid–liquid phase transition $\Delta_{fus}H_m$ and $\Delta_{fus}S_m$ of the compound were derived according to the following Eqs (3), (4):

$$\Delta_{\mathrm{fus}}H_{\mathrm{m}}=\frac{Q-n\int_{\mathrm{T_i}}^{\mathrm{T_m}}C_{\mathrm{p,m}}(s)\mathrm{d}T-n\int_{\mathrm{T_m}}^{\mathrm{T_f}}C_{\mathrm{p,m}}(l)\mathrm{d}T-\int_{\mathrm{T_i}}^{\mathrm{T_f}}H_0\mathrm{d}T}{n} \qquad (3)$$

$$\Delta_{\mathrm{fus}}S_{\mathrm{m}}=\frac{\Delta_{\mathrm{fus}}H_{\mathrm{m}}}{T_{\mathrm{m}}} \qquad (4)$$

where T_{i} is a temperature slightly lower than the solid-liquid transition temperature, T_{f} a temperature slightly higher than the solid–liquid transition temperature, Q the total energy introduced into the sample cell from T_{i} to T_{f}, H_0 the heat capacity of the sample cell from T_{i} to T_{f}, $C_{\mathrm{p,m}}$ (s) the heat capacity of the sample in solid phase from T_{i} to T_{m}, $C_{\mathrm{p,m}}$ (l) the heat capacity of the sample in liquid phase from T_{m} to T_{f} and n is molar amount of the sample. The heat capacity polynomials mentioned above were used to calculate the smoothed heat capacities, and were numerically integrated to obtain the values of the standard thermodynamic functions above T= 298.15 K. The calculated results are listed in Table 2.

Thermodynamic functions of the compound

The thermodynamic functions of the sorbitol relative to the reference temperature 298.15 K were calculated in the temperature range (80–390) K with an interval of 5 K, using the polynomial equation of heat capacity and thermodynamic relationships as follows:

Before melting,

$$H_{\mathrm{T}}-H_{298.15}=\int_{298.15}^{\mathrm{T}}C_{\mathrm{p,m}}(s)\mathrm{d}T \qquad (5)$$

$$S_{\mathrm{T}}-S_{298.15}=\int_{298.15}^{\mathrm{T}}\frac{C_{\mathrm{p,m}}(s)}{T}\mathrm{d}T \qquad (6)$$

After melting,

$$H_{\mathrm{T}}-H_{298.15}=\int_{298.15}^{\mathrm{T}}C_{\mathrm{p,m}}(s)\mathrm{d}T+\Delta_{\mathrm{fus}}H_{\mathrm{m}}+\int_{298.15}^{\mathrm{T}}C_{\mathrm{p,m}}(l)\mathrm{d}T \qquad (7)$$

$$S_{\mathrm{T}}-S_{298.15}=\int_{298.15}^{\mathrm{T}}\left[\frac{C_{\mathrm{p,m}}(s)}{\mathrm{T}}\right]\mathrm{d}T+\frac{\Delta_{\mathrm{fus}}H_{\mathrm{m}}}{T_{\mathrm{m}}}+\int_{298.15}^{\mathrm{T}}\frac{C_{\mathrm{p,m}}(l)}{\mathrm{T}}\mathrm{d}T \qquad (8)$$

where T_{i} is the temperature at which the solid-liquid phase transition started; T_{f} is the temperature at which the solid–liquid phase transition ended; $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ is the molar enthalpy of fusion; T_{m} is the temperature of solid-liquid phase transition.

The thermodynamic functions, H_{T}–$H_{298.15}$, S_{T}–$S_{298.15}$, are listed in Table 3.

The result of TG and DSC analysis

From the DSC curve in Fig. 2, a sharply endothermic peak corresponding to melting process was observed, with the peak temperature of 372.39 K and the enthalpy of 30.66±0.31 kJ mol^{-1}, which are consistent with the values (369.157 K, 30.35±0.15 kJ mol^{-1}) observed from the adiabatic calorimetric measurements. The results were listed in Table 2, from which, it can be seen that the thermodynamic parameters obtained from adiabatic calorimetry and DSC in the present research are in accordance with each other and slightly higher than those reported in literature [7].

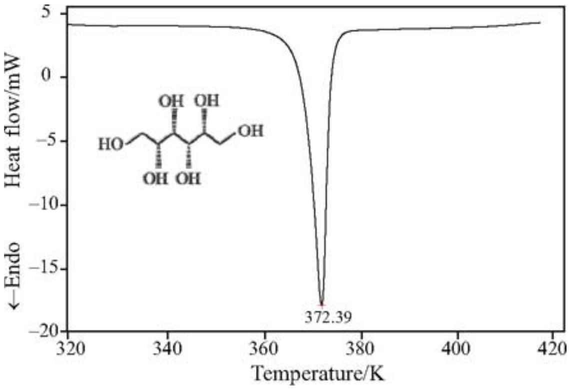

Fig. 2 DSC curve of sorbitol under high purity nitrogen

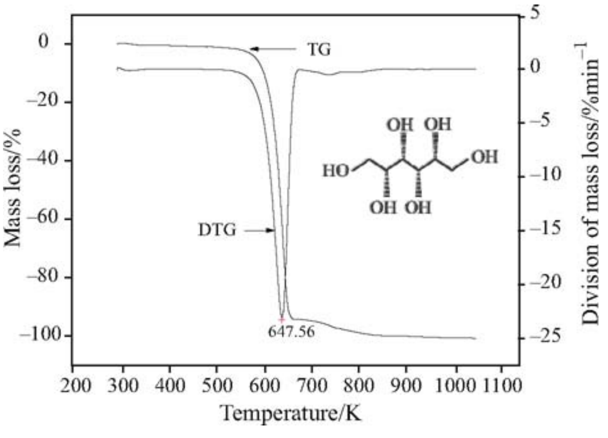

Fig. 3 TG-DTG curve of sorbitol under high purity nitrogen

Table 2 Thermodynamic parameters of sorbitol

Thermodynamic properties		Melting point T_{m}/K	$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$/kJ mol^{-1}	$\Delta_{\mathrm{fus}}S_{\mathrm{m}}$/J mol^{-1} K^{-1}
Present work	Adiabatic calorimetry	369.157	30.35±0.15	82.22±0.41
	DSC	372.39	30.66±0.31	82.34±0.82
Barone. G. *et al.* [7]		366.5	30.20	82.50

Table 3 Calculated thermodynamic functions of sorbitol

T/K	$C_{p,m}$/ J K^{-1} mol^{-1}	H_T–$H_{298.15}$/ kJ mol^{-1}	S_T–$S_{298.15}$/ J K^{-1} mol^{-1}
80	79.67	–33.88	–178.0
85	76.12	–33.49	–173.6
90	75.36	–33.11	–169.3
95	76.68	–32.73	–165.2
100	79.48	–32.34	–161.0
105	83.28	–31.94	–157.0
110	87.67	–31.51	–152.9
115	92.36	–31.06	–148.8
120	97.10	–30.59	–144.8
125	101.7	–30.09	–140.8
130	106.1	–29.57	–136.7
135	110.2	–29.03	–132.7
140	114.0	–28.47	–128.7
145	117.5	–27.89	–124.7
150	120.6	–27.29	–120.7
155	123.6	–26.68	–116.8
160	126.4	–26.06	–112.8
165	129.1	–25.42	–108.9
170	131.9	–24.77	–105.0
175	134.7	–24.10	–101.1
180	137.6	–23.42	–97.28
185	140.8	–22.72	–93.43
190	144.3	–22.01	–89.59
195	148.2	–21.28	–85.76
200	152.4	–20.53	–81.92
205	157.0	–19.76	–78.06
210	162.0	–18.96	–74.20
215	167.3	–18.13	–70.30
220	173.1	–17.28	–66.38
225	179.1	–16.40	–62.42
230	185.4	–15.49	–58.42
235	191.9	–14.55	–54.37
240	198.6	–13.57	–50.28
245	205.2	–12.56	–46.14
250	211.8	–11.52	–41.96
255	218.3	–10.45	–37.73
260	224.5	–9.338	–33.45
265	230.5	–8.200	–29.14
270	236.2	–7.033	–24.79
275	241.5	–5.839	–20.42
280	246.4	–4.619	–16.02
285	251.0	–3.375	–11.62
290	255.4	–2.109	–7.202
295	259.6	–0.8219	–2.784
298.15	262.3	0	0
300	263.9	0.4867	1.635
305	268.5	1.817	6.056
310	273.8	3.173	10.48
315	280.1	4.557	14.93
320	288.0	5.977	19.41
325	298.2	7.441	23.95
330	311.3	8.963	28.59
335	328.3	10.56	33.38
340	350.1	12.25	38.38
345	378.1	14.07	43.67
350	413.4	16.05	49.34
355	457.7	18.22	55.53
360	\	\	\
365	\	\	\
370	\	\	\
375	514.9	48.57	137.8
380	517.0	51.15	144.6
385	519.2	53.74	151.4
390	521.4	56.35	158.1

From the TG-DTG curve in Fig. 3, it can be seen that the mass loss of the sample was completed in a single step. The sample keeps thermostable below 500 K. It begins to lose mass at 529.50 K, reaches the maximum rate of mass loss at 647.56 K and completely loses its mass when the temperature reaches 764.50 K.

Purity determination of the sample

Adiabatic calorimetry provides an accurate way for determining the purity of a substance. Here, we suppose that the impurity resolves ideally in the liquid phase of the sample and does not resolve at all in the solid phase. The total amount of impurities does not exceed a couple of mole%. According to the ideal solution law, the relation between the mole fraction N (N<<1) of a small amount of impurities in the sample and its melting-point depression is as follows:

$$N=\frac{\Delta H_m (T_0-T_1)}{RT_0^2} \qquad (9)$$

where T_0 is the melting point of an absolutely pure substance; T_1 the melting point of the given sample, ΔH_m the heat of fusion of the sample and R is molar gas constant. As for the liquid solution formed by a part of the sample melted, given that N' is the mole fraction of the impurities and T is the melting point of the solution, then

$$N'=\frac{\Delta H_{\mathrm{m}}\,(T_0-T)}{RT_0^2} \tag{10}$$

If it is assumed that the impurities are solid-insoluble and all of the impurities are transferred completely into the liquid phase when the melting started, the relative amount of the sample in the liquid phase will be increasingly more in the process of the melting; on the other hand, since the total amount of the impurities remains constant, the mole fraction of the impurities in the liquid phase will gradually decrease. Given: F is the ratio of the amount of the sample in the liquid phase to the total amount of the sample, then

$$F=q/Q \tag{11}$$

where F is also designated as the fraction melted, its value being the ratio of the heat required to melt a part of the sample (q) to the total heat required to melt the whole sample (Q). Obviously, F is inversely proportional to the mole fraction of the impurities in the liquid phase, that is,

$$N'=\frac{1}{F}N \tag{12}$$

Substituting Eqs (9) and (10) into (12), we have

$$T_0-T=\frac{1}{F}(T_0-T_1) \tag{13}$$

From (13) it may be observed that the relation between the melting point, or the equilibrium melting temperature T and $1/F$ is linear. The purity of the sample was determined by a set of equilibrium melting temperatures (T) and melting fractions (F) corresponding to these temperatures [15–17]. The calculated results are shown in Table 4. A plot of the equilibrium melting temperature (T) *vs.* the reciprocal of the melting fractions ($1/F$) is a straight line, as shown in Fig. 4. The T_0 is the temperature when $1/F$ is 0 and T_1 is the temperature when $1/F$ equals to 1. From Fig. 4, the T_0=370.12 K and T_1=369.90 K were obtained, respectively. Thus, we calculated the mol percentage of impurities, N=5.924·10^{-3} mol fraction from Eq. (9), and the purity of the sample amounted to $1-N$=0.9941 mol fraction.

Table 4 Experimental values of melted fraction (F) and equilibrium temperature (T) of sorbitol

$F=q/Q$	$1/F$	T/K
0.0259	38.66	361.565
0.0485	20.63	365.493
0.0871	11.48	367.485
0.140	7.15	368.528
0.210	4.77	369.157

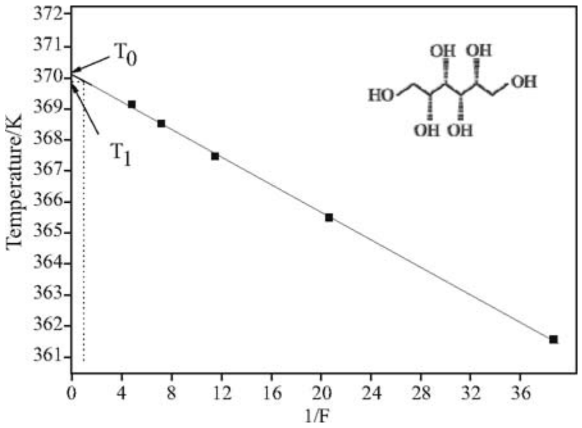

Fig. 4 Melting curve of sorbitol with temperature plotted *vs.* reciprocal of the melting fraction (T_0=370.12 K, T_1=369.90 K)

Conclusions

The heat capacities of sorbitol were measured in the temperature range from 80 to 390 K by a high precision automated adiabatic calorimeter. From the results of heat capacity experiment, the thermodynamic properties of fusion were completely studied, and the thermodynamic functions [H_T–$H_{298.15}$] and [S_T–$S_{298.15}$] were derived in the range from 80 to 390 K with temperature interval of 5 K. The melting temperature, standard molar enthalpy and entropy of this transition were determined to be 369.157 K, 30.35±0.15 kJ mol^{-1} and 82.22±0.41 J K^{-1} mol^{-1}, respectively. The chemical purity was calculated to be 0.9941 mol fraction according to the Van't Hoff equation.

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