Available online at www.sciencedirect.com

SCIENCE DIRECT®

International Journal of Thermal Sciences 42 (2003) 657–664

International Journal of Thermal Sciences

www.elsevier.com/locate/ijts

Thermodynamic investigation of crystalline $K_2Cr_2O_7$ and aqueous $K_2Cr_2O_7$ solution

Zhaodong Nan [a,*], Xiao-Zheng Lan [b], Li-Xian Sun [b], Zhi-Cheng Tan [b]

[a] *Department of Chemistry, Qufu Normal University, Qufu 273165, People's Republic of China*
[b] *Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China*

Received 13 May 2002; accepted 18 July 2002

Abstract

The molar heat capacities ($C_{\mathrm{p,m}}$) of crystalline potassium dichromate ($K_2Cr_2O_7$ (cr)) and aqueous $K_2Cr_2O_7$ solution (0.1699 mol·kg^{-1}) were measured in the temperature range from 100 to 390 K and from 80 to 370 K by an automatic adiabatic calorimeter equipped with a small cell of internal volume of 6 cm^3, respectively. No phase transition took place in the temperature range from 100 to 390 K for $K_2Cr_2O_7$ (cr). The relationships of $C_{\mathrm{p,m}}$ of $K_2Cr_2O_7$ (cr) with respect to T were established to be $C_{\mathrm{p,m}} = 177.53 + 161.92X - 138.14X^2 - 209.67X^3 + 160.35X^4 + 137.44X^5 - 41.291X^6$ and $C_{\mathrm{p,m}} = 177.52 + 171.66X - 149.59X^2 - 246.17X^3 + 194.79X^4 + 167.30X^5 - 64.368X^6$ ($X = (T - 245.00)/145.00$) for Series 1 and Series 2 experiments, respectively. No phase transition took place for the solution from 80 to 270 K. The function of $C_{\mathrm{p,m}}$ of the solution with respect to T was established to be $C_{\mathrm{p,m}} = 0.137T + 2.5068$ [J·K^{-1}·mol^{-1}]. A fusion transition at $T_{\mathrm{fus}} = 272.19$ K was found from the $C_{\mathrm{p,m}}$–T curve of the solution. The molar enthalpy and entropy of the phase transition were calculated to be 6.115 kJ·mol^{-1} and 22.47 J·K^{-1}·mol^{-1}, respectively. The molar heat capacities of the solution are about a constant in the temperature range from 275 K to 370 K, $C_{\mathrm{p,m}} = 76.75 \pm 1.12$ [J·K^{-1}·mol^{-1}]. The thermodynamic data of $K_2Cr_2O_7$ (cr) and the solution were derived from the heat capacity data and the relationship of thermodynamic functions.

Keywords: Heat pipe; Working fluid; Potassium dichromate; Aqueous solution; Heat capacity; Thermodynamic function; Adiabatic calorimetry

1. Introduction

The heat pipe is a thermal device, which affords efficient transport of thermal energy by use of an intermediate heat transfer fluid named working fluid. Structure of a heat pipe and its mechanism of heat transfer have been extensively studied [1–5]. Water as the most convenient working fluid has been widely investigated [1,6–8]. Aqueous electrolyte solutions of $K_2Cr_2O_7$ as one of the components of a working fluid have attracted interest in recent years [9,10]. The thermodynamic data of this kind of working fluid are very needed in order to investigate the mechanism of heat transfer of this kind of working fluid. Hepler and co-workers studied the thermodynamic data of $K_2Cr_2O_7$ (cr) and aqueous $K_2Cr_2O_7$ solution at 298 K only [11,12]. Other thermodynamic data have not been reported about $K_2Cr_2O_7$ (cr) and aqueous $K_2Cr_2O_7$ solution as we know.

The aim of the present investigation is to gain the thermodynamic data of this kind of working fluid by measurements of the low temperature heat capacities.

2. Experimental

2.1. Experimental materials

The potassium dichromate used for calorimetric study was purchased from Shenyang Chemical Agent Factory, and its purity was 99.8%. The water used for preparing the aqueous $K_2Cr_2O_7$ solution was deionized and distilled twice. The concentration of the aqueous $K_2Cr_2O_7$ solution investigated in this paper is to be 0.1699 mol·kg^{-1} as in Ref. [9].

2.2. Adiabatic calorimeter

Heat-capacity measurements were carried out in a high-precision automatic adiabatic calorimeter described in detail

---

[*] Corresponding author.
E-mail address: zdnan65@hotmail.com (Z. Nan).

1290-0729/03/$ – see front matter © 2003 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.
doi:10.1016/S1290-0729(03)00031-0

Nomenclature

$C_{p,m}$	molar heat capacity	$J{\cdot}K^{-1}{\cdot}mol^{-1}$
T	temperature	K
$H_{(T)}$	enthalpy at T K	$kJ{\cdot}mol^{-1}$
$H_{(298.15\ K)}$	enthalpy at 298.15 K	$kJ{\cdot}mol^{-1}$
$S_{(T)}$	entropy at T K	$J{\cdot}K^{-1}{\cdot}mol^{-1}$
$S_{(0\ K)}$	entropy at 0 K	$J{\cdot}K^{-1}{\cdot}mol^{-1}$
$G_{(T)}$	Gibbs free energy at T K	$kJ{\cdot}mol^{-1}$
$G_{(298.15\ K)}$	Gibbs free energy at 298.15 K	$kJ{\cdot}mol^{-1}$
T_{fus}	fusion temperature	K

Subscripts

m	molar
p	constant pressure
fus	fusion

elsewhere [13]. The principle of the calorimeter is based on the Nernst stepwise heating method. The calorimeter mainly consists of a sample cell, an adiabatic (or inner) shield, a guard (outer) shield, a platinum resistance thermometer, an electric heater, two sets of chromel-copel thermocouples and a high vacuum can. The sample cell was made of gold-plated copper and had an inner volume of 6 cm^3. Four gold-plated copper vanes of 0.2 mm thickness were put into the cell to promote heat distribution between the sample and the cell. The platinum resistance thermometer was inserted into the copper sheath which was soldered at the bottom of the sample cell. The heater wire was wound on the surface of the cell. The lid of the cell with a copper capillary was sealed to the sample cell with cycleweld after the sample was loaded in it. The air in the cell was pumped out and a small amount of helium gas (0.1 MPa) was introduced into it to enhance the heat transfer in the cell. The capillary was pinched off and the resultant fracture was soldered with a little amount of solder to ensure the cell sealing. The evacuated can was kept within ca. 1×10^{-3} Pa during the heat-capacity measurements so as to eliminate the heat loss due to gas convection. Liquid nitrogen was used as the cooling medium. One set of chromel-copel thermocouples was used to detect the temperature difference between the sample cell and the inner shield. Likewise, the other set of thermocouples were installed between the inner and outer shields. The temperature difference between them was kept to be 0.5 mK during the whole experimental process. The sample cell was heated by the standard discrete heating method. The temperature of the cell was alternatively measured. The temperature increment in a heating period was 2–4 K, and temperature drift was maintained at about 10^{-3} $K{\cdot}min^{-1}$ in equilibrium period. All the data were automatically picked up through a Data Acquisition/Switch Unit(Model: 34970A, Aglient, USA) and processed by a computer.

To verify the reliability of the adiabatic calorimeter, the molar heat capacities for the reference standard material α-Al_2O_3 and water were measured. The deviations of our experimental results from the recommended values of the National Bureau of Standards [14] were within ±0.2% in the temperature range of 80–400 K for α-Al_2O_3. The plot of molar heat capacities of water as a function of temperature was given in Fig. 1. In order to compare the results of water heat capacities measured in our laboratory with Ref. [15], the data of heat capacities gained from Ref. [15] are given in Fig. 1 as well. From Fig. 1, it can be shown that the molar heat capacities reported in this paper are in excellent agreement with the data cited from Ref. [15].

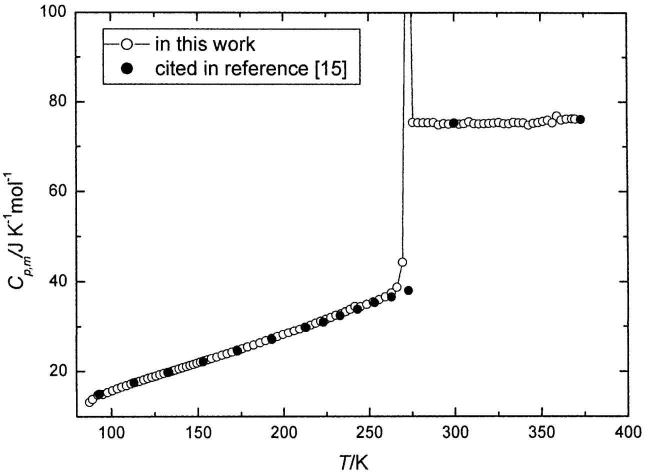

Fig. 1. Molar heat capacities of H_2O as a function of temperature.

The mass of $K_2Cr_2O_7$ and aqueous $K_2Cr_2O_7$ solution (0.1699 $mol{\cdot}kg^{-1}$) used for heat-capacity measurements was 8.1548 g and 4.0975 g, respectively.

3. Result and discussion

3.1. Molar heat capacity of $K_2Cr_2O_7$ (cr)

The molar heat capacities of $K_2Cr_2O_7$ (cr) were determined by using the adiabatic calorimeter in the temperature range of 100–390 K. Two series of calorimetric measurements experiments of heat capacities of $K_2Cr_2O_7$ (cr) were carried out. The results of the molar heat capacities of $K_2Cr_2O_7$ (cr) are shown in Table 1 and Fig. 2. From Fig. 2 it can be seen that the reproducibility of heat capacity measurements is good. No thermal anomaly was observed or no phase transition took place in the temperature range of 100–390 K.

The values of molar heat capacities were fitted in the following polynomial expressions with least square method.

Table 1
The experimental molar heat capacities of crystalline $K_2Cr_2O_7$ ($C_{p,m}$) in the temperature range of 98–390 K

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}]
Series 1		250.621	180.080	171.448	93.721
		254.857	191.811	175.339	95.211
98.654	71.501	259.059	195.601	179.153	96.729
101.704	73.033	263.232	198.721	181.365	102.108
104.587	72.727	267.374	201.672	182.896	101.321
107.396	72.099	271.470	203.313	186.573	103.622
110.144	71.227	275.546	207.121	190.190	102.890
112.812	72.108	279.579	207.911	193.757	107.521
115.429	72.391	283.588	208.692	197.287	109.967
117.985	73.544	287.600	208.613	200.782	114.422
120.502	74.043	291.520	209.182	204.252	118.192
122.982	74.541	295.422	209.042	207.699	122.002
125.423	75.162	299.321	209.413	211.100	132.083
127.832	75.911	303.170	209.051	214.470	132.090
130.219	75.561	306.993	209.512	217.850	141.231
132.580	74.183	310.791	210.041	221.237	145.078
134.911	76.712	314.565	209.213	224.586	148.902
137.211	76.581	318.307	208.591	227.871	161.113
139.482	77.294	322.669	208.913	234.901	166.489
141.726	78.550	327.725	209.523	239.135	173.302
143.945	79.510	332.676	209.081	243.291	178.051
146.149	80.342	337.563	210.042	247.419	181.042
148. 328	81.323	342.475	210.324	251.482	186.409
150.493	82.466	347.139	209.802	255.495	192.522
152.637	84.001	351.766	211.494	259.477	197.091
154.766	84.995	356.281	210.613	263.427	198.720
156.880	86.802	360.688	212.931	267.343	199.409
158.975	88.785	365.007	213.722	271.204	206.302
161.056	90.089	369.252	216.202	275.039	208.621
163.128	91.010	373.429	219.589	278.834	208.692
165.185	91.631	377.538	225.331	282.635	210.030
167.238	92.089	381.575	229.603	286.409	210.078
169.277	92.899	385.539	235.951	290.131	210.054
171.309	94.421	Series 2		293.847	210.071
173.347	94.631			297.586	210.242
175.346	95.410	100.679	71.522	301.311	210.063
177.361	96.703	104.107	72.223	305.046	210.310
179.371	99.041	107.442	72.181	308.780	209.801
183.354	99.012	110.883	72.682	312.512	209.603
185.332	105.202	114.194	73.053	316.244	210.060
187.305	106.720	117.341	73.781	319.971	210.029
189.268	105.211	120.386	74.525	323.689	208.623
191.222	107.491	123.368	75.814	327.376	209.411
193.426	109.913	126.294	76.621	331.020	208.892
195.851	112.802	129.181	77.309	335.277	209.021
199.656	114.478	132.023	77.911	340.175	209.312
205.078	120.509	134.826	78.582	344.959	208.930
209.950	128.922	137.595	79.122	349.665	209.611
214.780	136.578	140.330	80.731	354.335	210.039
219.567	145.807	143.030	80.672	358.922	210.920
224.232	150.071	145.700	82.201	363.429	213.231
228.807	161.911	148.340	83.413	367.852	216.752
231.937	165.243	153.959	85.980	372.190	218.621
235.206	170.070	157.402	86.802	376.403	223.940
237.685	175.720	160.674	88.281	380.561	230.081
242.018	175.712	163.825	88.838		
246.342	179.532	167.437	92.144		

For Series 1,

$$\begin{aligned} C_{\mathrm{p,m}} = {} & 177.53 + 161.92X - 138.14X^2 - 209.67X^3 \\ & + 160.35X^4 + 137.44X^5 - 41.291X^6 \end{aligned} \quad (1)$$

For Series 2,

$$\begin{aligned} C_{\mathrm{p,m}} = {} & 177.52 + 171.66X - 149.59X^2 - 246.17X^3 \\ & + 194.79X^4 + 167.30X^5 - 64.368X^6 \end{aligned} \quad (2)$$

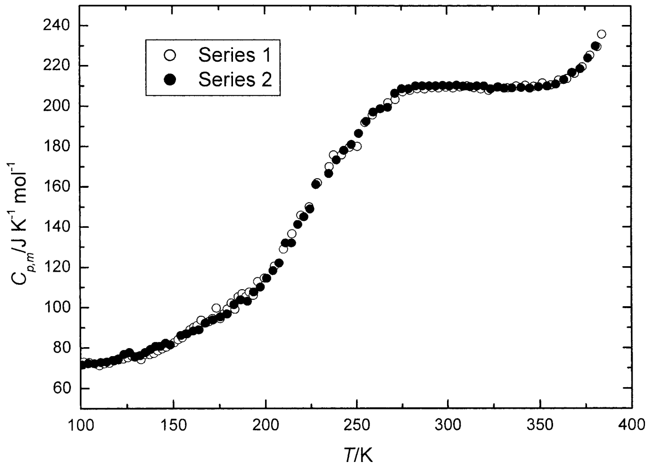

Fig. 2. Experimental molar heat capacities of crystalline potassium dichromate ($K_2Cr_2O_7$) as a function of temperature.

where $X = (T - 245.00)/145.00$, T [K] is temperature. The relative standard deviation is 2.56% and 2.55% for Series 1 and Series 2, respectively.

3.2. Thermodynamic data of $K_2Cr_2O_7$ (cr)

According to the relationship of thermodynamic functions and the function of molar heat capacity with respect to temperature [16], the thermodynamic data of $K_2Cr_2O_7$ (cr) were obtained and listed in Tables 2 and 3. The data of entropy were calculated from 0 K based on the data cited in reference [11].

3.3. Molar heat capacity of aqueous $K_2Cr_2O_7$ solution (0.1699 $mol{\cdot}kg^{-1}$)

The molar heat capacities of aqueous $K_2Cr_2O_7$ solution (0.1699 $\mathrm{mol{\cdot}kg^{-1}}$) were measured from 80 to 370 K and are presented graphically in Table 4 and Fig. 3.

Fig. 3 shows the variation in the molar heat capacity of the aqueous $K_2Cr_2O_7$ solution (0.1699 $\mathrm{mol{\cdot}kg^{-1}}$) with temperature increase. The curve of the molar heat capacities of the aqueous $K_2Cr_2O_7$ solution *vs* temperature presents smoothly from 80 to 270 K and 275 to 370 K, respectively. In other words, no thermal anomaly was observed in these

Table 2
Thermodynamic data of $K_2Cr_2O_7$ (cr) according to experimental Series 1

T [K]	$C_{\mathrm{p,m}}$ [J·K^{-1}·mol^{-1}]	$(H_{(T)} - H_{(298.15\ \mathrm{K})})$ [kJ·mol^{-1}]	$(S_{(T)} - S_{(0\ \mathrm{K})})$ [J·K^{-1}·mol^{-1}]	$-(G_{(T)} - G_{(298.15\ \mathrm{K})})$ [kJ·mol^{-1}]
100	68.759	−25.985	163.738	13.238
110	73.689	−25.269	170.615	12.004
120	75.785	−24.520	176.928	10.807
130	76.857	−23.757	182.868	9.673
140	78.228	−22.982	188.580	8.615
150	80.802	−22.188	194.156	7.631
160	85.123	−21.360	199.653	6.712
170	91.433	−20.479	205.121	5.845
180	99.725	−19.525	210.617	5.019
190	109.797	−18.479	216.213	4.230
200	121.296	−17.324	221.990	3.481
210	133.770	−16.050	228.027	2.782
220	146.701	−14.647	234.386	2.147
230	159.550	−13.116	241.095	1.590
240	171.791	−11.458	248.140	1.123
250	182.941	−9.684	255.464	0.748
260	192.590	−7.805	262.971	0.463
270	200.428	−5.838	270.540	0.258
280	206.266	−3.803	278.050	0.119
290	210.055	−1.719	285.394	0.034
300	211.906	0.392	292.501	0.003
310	212.096	2.513	299.346	0.010
320	211.084	4.630	305.945	0.087
330	209.516	6.733	312.344	0.243
340	208.224	8.821	318.590	0.490
350	208.233	10.902	324.713	0.826
360	210.755	12.994	330.709	1.227
370	217.178	15.130	336.577	1.658
380	229.066	17.356	342.435	2.111
390	248.139	19.735	348.768	2.714

temperature ranges. The phase transition took place between 270 K and 275 K.

The values of the molar heat capacities of the aqueous $K_2Cr_2O_7$ solution were fitted with the following polynomial expressions with a least squares method. For solid region (80–270 K),

$$C_{p,m} = 0.137T + 2.5068 \quad [\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}] \tag{3}$$

Fitting correlation $R^2 = 0.9993$.

For liquid region (275–370 K),

$$C_{p,m} = 76.75 \pm 1.12 \quad [\mathrm{J{\cdot}K^{-1}mol^{-1}}] \tag{4}$$

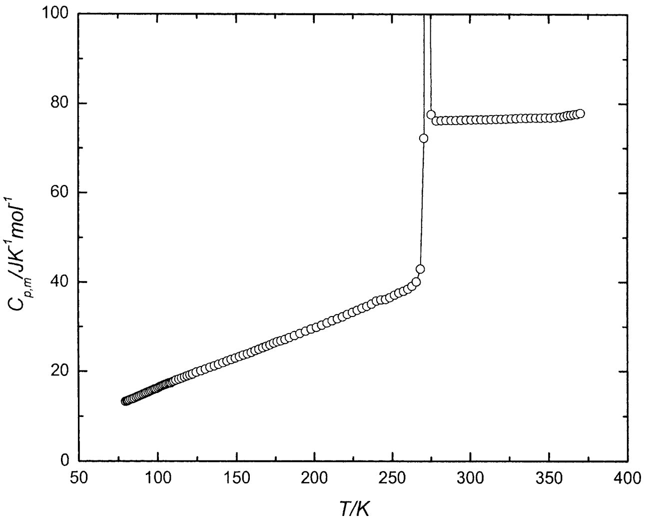

Fig. 3. Molar heat capacities of the aqueous $K_2Cr_2O_7$ solution as a function of temperature.

3.4. *The thermodynamic data of phase transition of aqueous $K_2Cr_2O_7$ (0.1699 mol·kg^{-1}) solution*

The fusion temperature (T_{fus}) was determined based on the value of the molar heat capacities of the aqueous $K_2Cr_2O_7$ solution, which is corresponding with the maximum of the value of the molar heat capacity of the solution. That is $T_{\mathrm{fus}} = 272.19$ K.

The melting enthalpy $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ and entropy $\Delta_{\mathrm{fus}}S_{\mathrm{m}}$ were calculated according to the relationship as follows [15]:

$$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = \frac{Q - n\int_{T_1}^{T_{\mathrm{m}}} C_{p(S)}\,\mathrm{d}T - n\int_{T_{\mathrm{m}}}^{T_2} C_{p(L)}\,\mathrm{d}T - \int_{T_1}^{T_2} C_0\,\mathrm{d}T}{n} \tag{5}$$

$$\Delta_{\mathrm{fus}}S_{\mathrm{m}} = \frac{\Delta_{\mathrm{fus}}H_{\mathrm{m}}}{T_{\mathrm{m}}} \tag{6}$$

Table 3
Thermodynamic data of $K_2Cr_2O_7$ (cr) according to experimental Series 2

T [K]	$C_{p,m}$ [J·K^{-1}·mol^{-1}]	$(H_{(T)} - H_{(298.15\ K)})$ [kJ·mol^{-1}]	$(S_{(T)} - S_{0\ K})$ [J·K^{-1}·mol^{-1}]	$-(G_{(T)} - G_{(298.15\ K)})$ [kJ·mol^{-1}]
100	65.572	−25.897	163.897	13.166
110	74.109	−25.193	170.762	11.945
120	77.592	−24.432	177.139	10.744
130	78.647	−23.650	183.196	9.608
140	79.221	−22.861	189.026	8.555
150	80.679	−22.062	194.674	7.583
160	83.887	−21.241	200.179	6.677
170	89.292	−20.377	205.590	5.823
180	97.000	−19.448	210.982	5.007
190	106.847	−18.430	216.452	4.227
200	118.465	−17.305	222.104	3.484
210	131.343	−16.057	228.036	2.791
220	144.883	−14.676	234.318	2.161
230	158.454	−13.159	240.982	1.607
240	171.433	−11.509	248.009	1.141
250	183.252	−9.734	255.335	0.766
260	193.429	−7.849	262.857	0.478
270	201.604	−5.872	270.451	0.268
280	207.563	−3.824	277.989	0.124
290	211.259	−1.729	285.365	0.035
300	212.829	0.394	292.508	0.003
310	212.606	2.522	299.387	0.014
320	211.125	4.642	306.015	0.097
330	209.123	6.743	312.429	0.261
340	207.538	8.825	318.671	0.513
350	207.497	10.899	324.768	0.848
360	210.307	12.985	330. 728	1.243
370	217.431	15.119	336.577	1.668
380	230.471	17.353	342.481	2.131
390	251.132	19.754	348.988	2.781

Table 4
The experimental molar heat capacities ($C_{p,m}$ [J·K^{-1}·mol^{-1}])of $K_2Cr_2O_7$ solution (0.01699 mol·kg^{-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}]
79.786	13.270	159.615	24.169	272.195	18660.826
80.569	13.361	162.093	24.578	272.195	34752.966
81.344	13.440	164.535	24.902	272.198	25543.801
82.110	13.584	166.949	25.225	272.197	24783.362
83.076	13.750	169.340	25.546	272.196	32286.500
84.232	13.877	171.703	25.869	272.197	35012.075
85.369	14.050	174.049	26.246	272.197	19801.487
86.495	14.249	176.363	26.589	272.198	25104.733
87.607	14.435	178.649	26.791	272.199	28782.495
88.707	14.603	181.211	27.092	272.200	22765.560
89.794	14.759	184.050	27.500	272.200	24015.060
90.869	14.899	187.286	27.942	272.202	22776.868
91.930	15.060	190.909	28.468	272.208	19849.241
92.978	15.245	194.487	28.926	272.214	14511.602
94.015	15.407	198.012	29.422	272.219	12370.489
95.039	15.590	201.494	29.834	272.226	10923.376
96.054	15.743	204.925	30.327	272.246	6459.735
97.058	15.893	208.316	30.816	272.278	4181.102
98.053	16.049	211.665	31.267	273.105	174.288
99.040	16.138	214.971	31.746	275.251	77.572
100.017	16.296	218.237	32.189	278.449	76.157
100.987	16.514	221.460	32.699	281.628	76.205
101.950	16.660	224.650	33.140	284.807	76.220
102.905	16.766	227.799	33.617	287.994	76.232
103.851	16.938	230.914	34.062	291.177	76.252
104.794	17.060	233.993	34.530	294.367	76.293
105.726	17.138	237.039	35.031	297.580	76.325
106.652	17.292	240.042	35.710	300.788	76.353
107.573	17.414	243.005	35.954	303.988	76.387
108.486	17.446	245.954	36.023	307.184	76.404
109.392	17.615	248.877	36.500	310.371	76.432
110.293	17.829	251.768	37.004	313.554	76.470
111.650	17.996	254.626	37.506	316.729	76.492
113.446	18.229	257.452	37.906	319.899	76.526
115.220	18.486	260.248	38.421	323.061	76.551
116.972	18.716	263.012	39.045	326.216	76.630
118.706	18.950	265.734	40.031	329.365	76.663
120.420	19.155	268.365	42.937	332.505	76.718
122.116	19.396	270.317	72.278	335.637	76.748
124.448	19.746	271.393	464.109	338.762	76.768
127.396	20.125	272.058	1834.118	341.882	76.786
130.294	20.506	272.126	3714.552	344.996	76.806
133.147	20.851	272.149	4430.867	348.105	76.826
135.957	21.201	272.168	6445.519	351.202	76.858
138.725	21.540	272.179	9760.362	354.290	76.886
141.452	21.890	272.186	14478.068	357.362	76.999
144.145	22.260	272.192	14978.758	359.927	77.144
146.801	22.584	272.193	18003.255	361.985	77.406
149.423	22.930	272.194	52689.548	364.030	77.446
152.011	23.262	272.197	35569.640	366.062	77.629
154.570	23.575	272.195	38762.076	368.080	77.642
157.105	23.840	272.198	17791.020	370.081	77.874

where Q is the total mount of heat introduced into the sample; n the amount of substance of the sample; T_1 below T_{fus}; T_2 above T_{fus}; $C_{p(S)}, C_{p(L)}, C_0$ the heat capacity in solid and liquid state and heat capacity of empty cell, respectively. The fusion enthalpy $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ and entropy $\Delta_{\mathrm{fus}}S_{\mathrm{m}}$ were determined to be 6.115 kJ·mol^{-1} and 22.47 J·K^{-1}·mol^{-1}, respectively.

The thermodynamic function data of the aqueous $K_2Cr_2O_7$ solution based on standard state (298.15 K) in temperature range from 300 to 370 K were calculated according to the relationship of heat capacity with thermodynamic functions [16]. The results of thermodynamic functions $H_{(T)} - H_{(298.15\ \mathrm{K})}$, $S_{(T)} - S_{(298.15\ \mathrm{K})}$, $G_{(T)} - G_{(298.15\ \mathrm{K})}$, are listed in Table 5.

Table 5
Thermodynamic functions of aqueous $K_2Cr_2O_7$ solution (0.1699 $mol\cdot kg^{-1}$)

T [K]	$C_{p,m}$ [$J\cdot K^{-1}\cdot mol^{-1}$]	$(H_{(T)} - H_{(298.15\ K)})]$ [$kJ\cdot mol^{-1}$]	$(S_{(T)} - S_{(298.15\ K)})$ [$J\cdot K^{-1}\cdot mol^{-1}$]	$-(G_{(T)} - G_{(298.15\ K)})$ [$J\cdot mol^{-1}$]
298.15	76.75	0	0	0
300	76.75	0.142	0.475	0.440
305	76.75	0.526	1.743	5.994
310	76.75	0.9095	2.9914	17.839
315	76.75	1.293	4.219	35.874
320	76.75	1.677	5.428	60.001
325	76.75	2.061	6.618	90.124
330	76.75	2.444	7.790	126.151
335	76.75	2.828	8.944	167.993
340	76.75	3.212	10.081	215.562
345	76.75	3.596	11.202	268.775
350	76.75	3.980	12.306	327.551
355	76.75	4.363	13.394	391.807
360	76.75	4.747	14.468	461.470
365	76.75	5.1307	15.527	536.462
370	76.75	5.514	16.571	616.711

3.5. *Discussion*

From Fig. 2, it can be seen that no phase transition takes place in the temperature range from 100 to 390 K for $K_2Cr_2O_7$ (cr). However, the change of molar heat capacity of $K_2Cr_2O_7$ (cr) is different in the different temperature ranges. This may be the change of structure of $K_2Cr_2O_7$ (cr) at different temperatures. The value of the molar heat capacity of $K_2Cr_2O_7$ (cr) was measured to be about 207 $J\cdot K^{-1}\cdot mol^{-1}$ at 273.15 K, which is lower than 219.1 $J\cdot K^{-1}\cdot mol^{-1}$ reported in Ref. [17].

The fitting equations of Series 1 and Series 2 are different from each other. The coefficients of lower degree are in agreement between Eqs. (1) and (2), the coefficients of higher degree are not in agreement with each other. But the molar heat capacities and thermodynamic data derived from Eqs. (1) and (2) are in excellent agreement with each other. The reason may be that the values of X is $-1 \leqslant X \leqslant 1$, the effect of the coefficients of higher order is small.

The fusion temperature of aqueous $K_2Cr_2O_7$ solution (0.1699 $mol\cdot kg^{-1}$) is lower than that of water because of the electrolyte added. The molar heat capacities of aqueous $K_2Cr_2O_7$ solution (0.1699 $mol\cdot kg^{-1}$) are slight different to those of water because water is the main content in the solution.

The values of $S_{(T)} - S_{(0\ K)}$ and $S_{(T)} - S_{(298.15\ K)}$ are increasing with increasing temperature for $K_2Cr_2O_7$ (cr) and aqueous $K_2Cr_2O_7$ solution (0.1699 $mol\cdot kg^{-1}$), respectively. These show that the molecules of crystal and liquid are becoming more active at higher temperature.

The heat capacities and thermodynamic data of $K_2Cr_2O_7$ (cr) and the aqueous $K_2Cr_2O_7$ solution (0.1699 $mol\cdot kg^{-1}$) obtained in the present investigation are useful for investigation of the mechanism of heat transfer of the working fluid.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China under the NSFC No. 20073047 and K.C. Wong Education Foundation, Hong Kong.

References

[1] A.S Salem, A.A. Bilad, Experimental performance of a heat pipe, Internat. Comm. Heat Mass Transfer 26 (5) (1999) 679–684.

[2] S.T. Tu, H. Zhang, W.W. Zhou, Corrosionfailures of high temperature heat pipes, Engrg. Failure Anal. 6 (1999) 363–370.

[3] T.C. Jen, G. Gutierrez, S. Eapen, G. Barber, H. Zhao, P.S. Szuba, J. Labataille, J. Manjunathaiah, Investigation of heat pipe cooling in drilling applications, Part I: Preliminary numerical analysis and verification, Internat. J. Machine Tools Manufacture 42 (2002) 643–652.

[4] L. Lin, A. Faghri, Heat transfer in micro region of a rotating miniature heat pipe, Internat. J. Heat Mass Transfer 42 (1999) 1363–1369.

[5] S. Valérie, C.Z. Mohamed, L. Monique, Effect of interfacial phenomena on evaporative heat transfer in micro heat pipes, Internat. J. Therm. Sci. 39 (2000) 498–504.

[6] M. Akyurt, O.M. Al-Rabghi, Curtailing noncondensables in steel heat pipe using a NaCl solution, Energy Conversion Management 40 (1999) 281–286.

[7] L. Ke, Y.G. Chen, H.D. Xie, Study on low temperature character of water heat pipe, J. Chongqing University (Natural Science Edition) (Chinese) 18 (3) (1995) 36–41.

[8] H.D. Huang, Y.M. Chen, S.M. Zhang, Internal thermosyphon reboiler, J. Chemical Industry and Engineering (Chinese) 3 (1987) 293–299.

[9] F. Xue, S.Z. Zhao, Patent CN 1253162A, 2000.

[10] S. Z. Zhao, Patent CN 1102200, 1995.

[11] I. Dellien, F.M. Hall, I.G. Hepler, Chromium, Molybdenum, and Tungsten: Thermodynamic properties, chemical equilibria and standard potentials, Chem. Rev. 76 (3) (1976) 283–310.

[12] J.K. Hovey, I.G. Hepler, Apparent and partial molar heat capacities and volumes of CrO_4^{2-} (aq), $HcrO_4^-$ (aq), and $Cr_2O_7^{2-}$ (aq) at 25 °C: Chemical relation and calculation of equilibrium constants for high temperature, J. Phys. Chem. 94 (1990) 7821–7830.

[13] Z.C. Tan, G.Y. Sun, Y. Sun, A.X. Yin, W.B. Wang, J.C. Ye, L.X. Zhou, An adiabatic low-temperature calorimeter for heat capacity measurement of small sample, J. Therm. Anal. 45 (1995) 59–67.

[14] D.A. Ditmars, S. Ishihara, S.S. Chang, G. Bernstein, E.D. West, Enthalpy and heat capacity standard reference material: Synthetic sapphire (α-Al_2O_3) from 10 to 2250 K, J. Res. Natl. Bur. Stands. 87 (1982) 159.

[15] R.L. David, CRC Handbook of Chemistry and Physics 80th, CRC Press, Boca Raton, 1999, Chapter 6-6.

[16] Z.C. Tan, B. Xue, S.W. Lu, S.H. Meng, X.H. Yuan, Y.J. Song, Heat capacities and thermodynamic properties of Fenpropathrin ($C_{22}H_{23}O_3N$), J. Therm. Anal. Cal. 63 (2001) 297–308.

[17] Y.B. Yao, T. Xie, Y.M. Gao, Handbook of Physical Chemistry, Shanghai Science Technology Press, Shanghai, 1985, p. 1100 (in Chinese).