Chem. Res. Chin. Univ., 2015, 31(6), 987—991 doi: 10.1007/s40242-015-5263-3

Low-temperature Heat Capacity and Standard Thermodynamic Functions of *D*-Galactose and Galactitol

CHENG Ze[1,2], XUE Bin[1*], TAN Zhicheng[2] and SHI Quan[2*]

1. School of Petrochemical Engineering, Shenyang University of Technology, Liaoyang 111003, P. R. China;
2. Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Liaoning Province Key Laboratory of Thermochemistry for Energy and Materials, Dalian National Laboratory for Clean Energy, Dalian 116023, P. R. China

Abstract The heat capacities of *D*-galactose and galactitol were measured on a quantum design physical property measurement system(PPMS) over a temperature range of 1.9—300 K, and the experimental data were fitted to a function of *T* using a series of theoretical and empirical models in appropriate temperature ranges. The fit results were used to calculate thermodynamic function values, $C_{p,m}^{\theta}$, $\Delta_0^T S_m^{\theta}$, and $\Delta_0^T H_m^{\theta}$ from 0 K to 300 K. The standard molar heat capacity, entropy and enthalpy values of *D*-galactose and galactitol at 298.15 K and 0.1 MPa were determined to be $C_{p,m}^{\theta}$ =(227.96±2.28) and (239.50±2.40) J·K^{-1}·mol^{-1}, S_m^{θ} = (211.22±2.11) and (230.82±2.30) J·K^{-1}·mol^{-1} and H_m^{θ} = (33.95±0.34) and (36.57± 0.37) kJ/mol, respectively.

Keywords *D*-Galactose; Galactitol; Low-temperature heat capacity; Physical property measurement system(PPMS); Standard thermodynamic function

1 Introduction

Galactose is one kind of monosaccharide constituted from six carbons and an aldehyde, and it is generally regarded as a functional component in plants and animals. Galactose exists in two forms of isomers, *D* and *L*, and *D*-galactose is a major element of gelatin, which is an important part of the majority of plants. For example, *D*-galactose exists in red algae and milk. In animals(snails, frog-spawn, bovine-lungs), polysaccharide composed of *D*-galactose can also be found. Moreover, *D*-galactose is a composition of the milk of mammals, and it is often used as nutritious sweetener because of its calories. Not only in the aspects mentioned above but also in the fields of organic synthesis, biological growth, biochemical research and liver function test, *D*-galactose has been widely used[1—6]. Galactitol is usually obtained from the hydrogenation process of Galactose. It is also called the sweet alcohol which is present in the plant of Melampyrum nemorosam L. As a chemical intermediate, galactitol can be widely used in medicine, microbiology and biochemical researches[7,8]. Although *D*-galactose and galactitol have been used and studied in many practical applications, their physicochemical properties have not been studied systematically, especially the thermodynamic properties. Accurate thermodynamic parameters are essential to understanding the nature and the corresponding energy balance calculations of *D*-galactose and galactitol, and therefore the comprehensive study of thermodynamic properties of these two compounds would favour the optimization of the chemical processing of these substances and promote further understanding of their practical applications.

A number of thermodynamic properties of *D*-galactose and galactitol have been reported in literature. For example, Banipal *et al.*[9,10] determined partial molar heat capacity of *D*-galactose in water at 298.15, 308.15 and 318.15 K and in NaCl(aq) at 298.15 K, respectively. Tewari and Goldberg reported the thermodynamic properties of the hydrolysis reactions of *D*-galactose using a high-pressure liquid chromatography and microcalorimetry method[11]. Daranas *et al.*[12] reported the thermodynamic properties of the binding reaction of *D*-galactose and deoxy derivatives. Wang and Zhuo determined the thermodynamic parameters of the interaction of HCl with *D*-galactose in water[13]. No calorimetric study has been performed on galactitol as far as we know, except the report from Williams using thermogravimetry(TG) and differential thermal analysis(DTA) in 2006[14]. Although some of the above work involved heat capacity calorimetric investigations, there have been no studies reported on low temperature heat capacity measurement of these two compounds over a wide temperature range.

In this work, the low temperature heat capacities of *D*-galactose and galactitol were measured on a commercial relaxation calorimeter over a temperature range of 1.9—300 K. Based on the curve fitting of the experimental heat capacities, the thermodynamic functions of these compounds were calculated. Moreover, the difference between the heat capacities of *D*-galactose and galactitol was discussed and explained in

*Corresponding authors. E-mail: shiquan@dicp.ac.cn; xue-b@163.com
Received July 8, 2015; accepted August 13, 2015.
Supported by the National Natural Science Foundation of China(No.21473198).

terms of their similar molecular structure.

2 Experimental

The sample information of *D*-galactose and galactitol used in this work is given in Table 1. The samples were purchased from J&K Corporation with a mass purity of higher than 0.99. The copper foil from Alfa Aesar Corporation used for the sample preparation in the heat capacity measurement is 0.025 mm in thickness with a mass fraction purity of 0.99999.

Table 1 Information of samples *D*-galactose and galactitol

Sample	CAS No.	Formula	M_r[a]	X[b](%)
D-Galactose	59-23-4	$C_6H_{12}O_6$	180.16	99
Galactitol	608-66-2	$C_6H_{14}O_6$	182.17	99

a. The value of M_r is based on the most recent set of relative atomic masses recommended by IUPAC; *b.* the mass fraction purity provided by the supplier.

The heat capacity measurement of *D*-galactose and galactitol was performed on a Quantum Design Physical Properties Measurement System(PPMS) over a temperature range of 1.9—300 K. The temperature intervals during the measurement were in logarithmic increase below 100 K and in a increase of 10 K above 100 K, respectively. The sample preparation for the heat capacity measurement was employed according to the technique developed by Shi *et al.*[15] for powdered sample measurement on a PPMS calorimeter, and the heat capacity measurement accuracy could achieve ±2% and ±1% below and above 10 K, respectively[16,17]. The detailed sample preparation process can be found in literature. In general, the powdered sample was mixed with a number of copper stripes in a copper cup, and then the sample, copper stripes and copper cup were pressed into a sample pellet together. The sample pellet was measured on the PPMS, and the heat capacity of the sample could be achieved by subtracting the known heat capacity of copper from the total heat capacity of the sample pellet. The sample mass used in the heat capacity measurement was 8.15 and 5.96 mg for *D*-galactose and galactitol, respectively.

3 Results and Discussion

The experimental heat capacities of *D*-galactose and galactitol measured on the PPMS are listed in Table 2, and plotted against the temperature in Fig.1. It can be seen from Fig.1 that the heat capacities of these two compounds increase with temperature increasing and no phase transitions or other anomalies can be found, suggesting that *D*-galactose and galactitol are thermodynamic stable in the entire experimental temperature range. Also, the heat capacity of galactitol is always lager than that of *D*-galactose due to its larger molecular weight.

Table 2 Experimental molar heat capacities of *D*-galactose and galactitol*

D-Galactose				Galactitol			
T/K	$C^{\theta}_{p,m}$/(J·K^{-1}·mol^{-1})	T/K	$C^{\theta}_{p,m}$/(J·K^{-1}·mol^{-1})	T/K	$C^{\theta}_{p,m}$/(J·K^{-1}·mol^{-1})	T/K	$C^{\theta}_{p,m}$/(J·K^{-1}·mol^{-1})
1.9252	0.0054294	43.688	29.668	1.9369	0.010282	43.795	32.912
2.1299	0.0074964	48.486	34.354	2.1485	0.013758	48.597	37.869
2.3571	0.0097805	53.816	39.528	2.3833	0.018695	53.943	43.377
2.6093	0.013278	59.732	45.206	2.6427	0.025429	59.857	49.682
2.8967	0.018066	66.314	51.286	2.9385	0.035804	66.425	56.434
3.2116	0.024697	73.629	57.699	3.2578	0.047470	73.736	63.535
3.5595	0.033676	81.741	65.133	3.6121	0.065461	81.839	71.959
3.9468	0.045835	90.722	72.495	4.0073	0.089305	90.808	79.931
4.3766	0.063443	100.67	80.105	4.4465	0.12396	100.78	88.552
4.8560	0.087985	110.85	88.194	4.9319	0.17099	110.92	97.796
5.3874	0.12081	120.87	96.188	5.4706	0.24001	120.99	106.34
5.9772	0.16693	130.97	103.82	6.0670	0.32937	131.08	114.31
6.6314	0.23050	141.07	110.96	6.7305	0.45172	141.15	121.57
7.3609	0.32114	151.21	118.38	7.4696	0.62509	151.28	129.35
8.1682	0.44597	161.29	125.59	8.2865	0.85492	161.38	136.62
9.0622	0.61828	171.39	132.71	9.1912	1.1588	171.47	143.92
10.127	0.87507	181.47	140.15	10.200	1.5576	181.57	151.45
11.229	1.2056	191.57	147.41	11.294	2.0650	191.65	158.82
12.462	1.6611	201.68	154.19	12.529	2.7433	201.76	165.56
13.832	2.2701	211.78	161.52	13.905	3.5916	211.87	173.48
15.370	3.0657	221.91	169.44	15.426	4.6469	221.95	181.77
17.048	4.1174	232.00	176.90	17.119	5.9377	232.00	189.02
18.932	5.4578	242.06	184.41	19.000	7.5218	242.09	196.43
21.020	7.0986	252.21	191.91	21.091	9.3935	252.24	203.93
23.333	9.1080	262.29	199.58	23.409	11.601	262.33	211.95
25.916	11.510	272.33	207.40	25.983	14.122	272.37	219.45
28.740	14.289	282.42	215.54	28.857	17.072	282.51	227.71
31.916	17.513	292.54	223.39	32.028	20.392	292.60	234.72
35.441	21.157	302.59	231.48	35.556	24.150	302.65	242.76
39.357	25.251			39.462	28.388		

*The experimental heat capacity uncertainties are determined to be ±2% below 10 K and ±1% above 10 K.

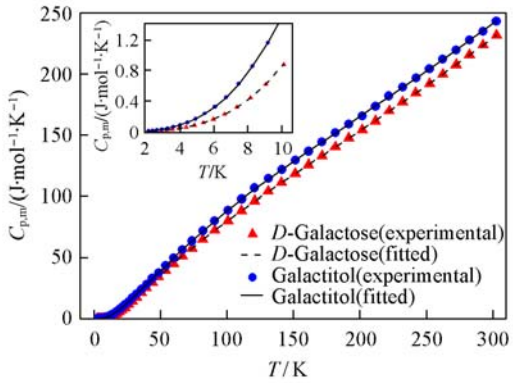


Fig.1 Plots of the experimental and fitted heat capacities *vs.* temperature of *D*-galactose and galactitol

In order to calculate the thermodynamic functions, the heat capacities of *D*-galactose and galactitol were fitted to a series of theoretical and empirical models in the appropriate temperature ranges. Heat capacity at low temperatures can be precisely modeled by the total influence of lattice, magnetons, electrons, nuclei and impurities[18,19]. Each heat capacity contribution can be described with an appropriate temperature dependent expression. In the low temperature range(T<10 K), the heat capacities of these two compounds are fitted to the following theoretical model:

$$C^{\theta}_{p,m}=\gamma T+B_3T^3+B_5T^5+B_7T^7 \quad (1)$$

where the linear term demonstrates the defect of the lattice and the oxygen vacancies, and the odd-power terms represent the vibration frequency. As can be seen from Fig.2, in this temperature range, the fitting deviations of the two samples are within ±2%, which indicates the model could accurately express the experimental data. In the middle temperature range(10 K<T<70 K), the heat capacities were fitted to an orthogonal polynomial function[20]:

$$C^{\theta}_{p,m}=A_0+A_1T+A_2T^2+A_3T^3+A_4T^4+A_5T^5+A_6T^6+A_7T^7+A_8T^8 \quad (2)$$

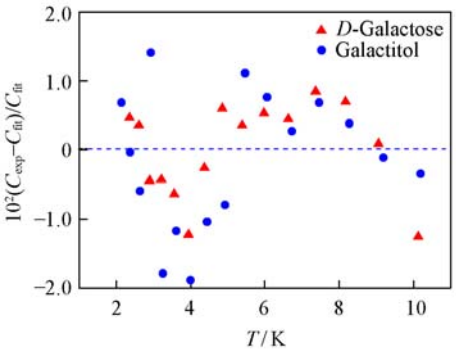


Fig.2 Plots of deviations of the experimental heat capacities from the fitted values against temperature for *D*-galactose and galactitol below 10 K

And in the high temperature range above 70 K, the heat capacities were fitted to a combination of Debye and Einstein functions[20—21]:

$$C^{\theta}_{p,m}=nD(\theta_D)+mE(\theta_E)+aT+bT^2 \quad (3)$$

where n_D and n_E are Debye and Einstein parameters; $D(\theta_D)$ and $E(\theta_E)$ are Debye and Einstein functions; θ_D and θ_E are Debye and Einstein temperatures. The term of ($aT+bT^2$) is related to a correction for the difference of (C_p–C_v), where C_p and C_v are heat capacity at constant pressure and volume, respectively. All the fitting parameters are listed in Table 3.

Table 3 Fitting parameters of heat capacities of *D*-galactose and galactitol

D-Galactose				Galactitol			
T/K	Parameter	Coefficient	RMS(%)	T/K	Parameter	Coefficient	RMS(%)
0—9.5	B_3	0.000737	0.66	0—8.56	B_3	0.001361	1.18
	B_5	1.13×10^{-6}			B_5	3.72×10^{-6}	
	B_7				B_7	-2.5×10^{-8}	
9.5—63.5	A_0	–0.13571	0.48	8.56—56.1	A_0	–0.00926	0.20
	A_1	0.092347			A_1	0.050477	
	A_2	–0.02287			A_2	–0.02423	
	A_3	0.003186			A_3	0.005639	
	A_4	-9.6×10^{-5}			A_4	–0.00029	
	A_5	1.19×10^{-6}			A_5	7.71×10^{-6}	
	A_6	-5.4×10^{-9}			A_6	-1.2×10^{-7}	
	A_7				A_7	9.34×10^{-10}	
	A_8				A_8	-3.1×10^{-12}	
63.5—310	n	1.76×10^{0}	0.16	56.1—310	n	4.36×10^{-1}	0.25
	θ_D	2.50×10^{2}			θ_D	1.10×10^{2}	
	m	7.89×10^{-1}			m	1.89×10^{0}	
	θ_E	4.48×10^{2}			θ_E	2.72×10^{2}	
	a	3.56×10^{-1}			a	4.68×10^{-1}	
	b	7.11×10^{-4}			b	5.09×10^{-4}	

The root-mean-square(RMS, %) deviations of the fitting results for *D*-galactose and galactitol are found to be 0.66%, 0.48% and 0.16%; and 1.18%, 0.20% and 0.25% in the low, middle and high temperature ranges, respectively. Using the fitting parameters in Table 3 and the corresponding thermodynamic relationship listed in Eqs. (4) and (5):

$$\Delta_0^T H^{\theta}_m=\int_0^T C_p\mathrm{d}T \quad (4)$$

$$\Delta_0^T S^{\theta}_m=\int_0^T \frac{C_p}{T}\mathrm{d}T \quad (5)$$

The molar thermodynamic functions of *D*-galactose and galactitol were calculated in a temperature range of 0—300 K, with the results shown in Table 4. The standard molar heat capacity, enthalpy and entropy values of *D*-galactose and galactitol at 298.15 K were determined to be (227.96±2.28) and (239.50±2.40) J·K^{-1}·mol^{-1}; (33.95±0.34) kJ/mol and

Table 4 Standard thermodynamic functions of *D*-galactose and galactitol

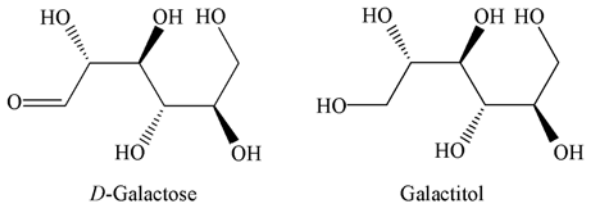
T/K	*D*-Galactose			Galactitol		
	$C_{p,m}^{\theta}$/(J·K^{-1}·mol^{-1})	$\Delta_0^T H_m^{\theta}$/(J·mol^{-1})	$\Delta_0^T S_m^{\theta}$/(J·K^{-1}·mol^{-1})	$C_{p,m}^{\theta}$/(J·K^{-1}·mol^{-1})	$\Delta_0^T H_m^{\theta}$/(J·mol^{-1})	$\Delta_0^T S_m^{\theta}$/(J·K^{-1}·mol^{-1})
0.5	0.000092173	0.000011520	0.000030719	0.00017027	0.000021279	0.000056740
1.0	0.00073823	0.00018446	0.00024593	0.0013649	0.00034092	0.00045448
1.5	0.0024963	0.00093504	0.00083095	0.0046219	0.0017298	0.0015370
2.0	0.0059330	0.0029605	0.0019728	0.011006	0.0054838	0.0036533
2.5	0.011628	0.0072443	0.0038612	0.021617	0.013440	0.0071602
3.0	0.020177	0.015064	0.0066889	0.037602	0.027996	0.012424
3.5	0.032198	0.028000	0.010653	0.060153	0.052136	0.019822
4.0	0.048333	0.047947	0.015957	0.090513	0.089450	0.029742
4.5	0.069257	0.077131	0.022807	0.12996	0.14416	0.042585
5.0	0.095675	0.11812	0.031420	0.17980	0.22114	0.058760
5.5	0.12833	0.17384	0.042018	0.24133	0.32591	0.078684
6.0	0.16802	0.24762	0.054831	0.31584	0.46464	0.10278
6.5	0.21556	0.34317	0.070102	0.40454	0.64412	0.13146
7.0	0.27185	0.46464	0.088080	0.50850	0.87172	0.16515
7.5	0.33782	0.61663	0.10903	0.62863	1.1553	0.20424
8.0	0.41449	0.80424	0.13322	0.76556	1.5032	0.24909
8.5	0.50289	1.0331	0.16093	0.91955	1.9237	0.30003
9.0	0.60418	1.3093	0.19248	1.0887	2.4251	0.35731
9.5	0.71952	1.6396	0.22817	1.2741	3.0152	0.42106
10	0.84544	2.0303	0.26823	1.4760	3.7020	0.49148
11	1.1373	3.0172	0.36206	1.9282	5.3987	0.65285
12	1.4842	4.3233	0.47549	2.4435	7.5794	0.84227
13	1.8874	6.0044	0.60984	3.0187	10.306	1.0602
14	2.3473	8.1170	0.76619	3.6505	13.636	1.3067
15	2.8633	10.718	0.94541	4.3348	17.624	1.5816
16	3.4344	13.862	1.1481	5.0673	22.321	1.8845
17	4.0590	17.604	1.3748	5.8439	27.773	2.2148
18	4.7349	21.997	1.6257	6.6601	34.022	2.5717
19	5.4594	27.090	1.9009	7.5118	41.105	2.9545
20	6.2295	32.931	2.2004	8.3951	49.056	3.3621
25	10.644	74.768	4.0492	13.163	102.75	5.7384
30	15.662	140.38	6.4277	18.281	181.26	8.5872
35	20.860	231.68	9.2322	23.552	285.80	11.800
40	25.955	348.80	12.352	28.874	416.86	15.292
45	30.846	490.88	15.694	34.174	574.51	19.000
50	35.606	657.03	19.191	39.395	758.47	22.871
55	40.412	847.02	22.808	44.536	968.32	26.867
60	45.407	1061.5	26.537	49.699	1203.8	30.963
65	50.074	1300.6	30.363	54.893	1465.3	35.146
70	54.610	1562.4	34.241	60.021	1752.6	39.402
75	59.044	1846.6	38.160	65.049	2065.4	43.715
80	63.382	2152.7	42.110	69.959	2402.9	48.071
85	67.631	2480.2	46.080	74.742	2764.7	52.456
90	71.796	2828.8	50.064	79.398	3150.1	56.861
95	75.885	3198.1	54.056	83.932	3558.5	61.276
100	79.903	3587.6	58.051	88.350	3989.3	65.694
110	87.752	4426.0	66.036	96.879	4915.7	74.517
120	95.389	5341.9	74.000	105.06	5925.7	83.300
130	102.86	6333.3	81.932	112.98	7016.1	92.024
140	110.20	7398.7	89.824	120.69	8184.6	100.68
150	117.46	8537.0	97.675	128.25	9429.3	109.26
160	124.65	9747.6	105.49	135.70	10749	117.78
170	131.81	11030	113.26	143.08	12143	126.23
180	138.97	12384	120.99	150.43	13611	134.61
190	146.13	13809	128.70	157.76	15152	142.94
200	153.33	15307	136.38	165.09	16766	151.22
210	160.58	16876	144.03	172.44	18453	159.46
220	167.88	18518	151.67	179.82	20215	167.65

To be continued on the next page.

T/K	*D*-Galactose			Galactitol		
	$C_{p,m}^{\theta}$ /(J·K^{-1}·mol^{-1})	$\Delta_0^T H_m^{\theta}$ /(J·mol^{-1})	$\Delta_0^T S_m^{\theta}$ /(J·K^{-1}·mol^{-1})	$C_{p,m}^{\theta}$ /(J·K^{-1}·mol^{-1})	$\Delta_0^T H_m^{\theta}$ /(J·mol^{-1})	$\Delta_0^T S_m^{\theta}$ /(J·K^{-1}·mol^{-1})
230	175.26	20234	159.30	187.25	22050	175.80
240	182.71	22024	166.91	194.72	23960	183.93
250	190.25	23888	174.52	202.26	25945	192.03
260	197.88	25829	182.13	209.85	28005	200.11
270	205.61	27846	189.75	217.52	30142	208.18
273.15	208.07	28498	192.15	219.95	30831	210.71
280	213.45	29942	197.37	225.26	32356	216.23
290	221.40	32116	205.00	233.07	34648	224.27
298.15	227.96	33947	211.22	239.50	36573	230.82
300	229.46	34370	212.64	240.97	37018	232.30

(36.57±0.37) kJ/mol; and (211.22±2.11) and (230.82±2.30) J·K^{-1}·mol^{-1}, respectively.

As for the difference between the heat capacities of *D*-galactose and galactitol, it can be further understood from their molecular structures, which are shown in Fig.3. It can be seen from Fig.3 that these two compounds have similar structures, and the main difference is that one of the six hydroxyl groups in galactitol has been replaced by a carbonyl group in *D*-galactose. This difference makes galactitol have a larger molecular weight than *D*-galactose, which is the main reason why the heat capacity of galactitol is larger than that of *D*-galactose. On the other hand, it is well known that *D*-galactose tends to form a hexatomic ring structure in solution due to the carbonyl group involved in this compound. Although the hexatomic ring hardly exists in solid, the carbonyl group in *D*-galactose is likely to bond with its neighbor hydroxyl group to form a hydrogen bond. The neighbored hydroxyl groups in galactitol may also form hydrogen bonds. However, the relatively larger electronegativtiy of the oxygen in the carbonyl group would generate a more stable hydrogen bond in *D*-galactose than that in galactitol, which may result in a more stable structure and reduce the vibration frequencies of the relative carbonyl and hydroxyl groups in the molecule of *D*-galactose. These reduced vibration frequencies in *D*-galactose may make its heat capacity smaller than that of galactitol. Nevertheless, this explanation is mainly based on the experimental heat capacities, and a further investigation should be performed with other analytical techniques or theoretical calculations.



D-Galactose Galactitol

Fig.3 Molecular structures of *D*-galactose and galactitol

4 Conclusions

In this work, the heat capacities of *D*-galactose and galactitol have been measured in a temperature range of 1.9—300 K on the PPMS, and the experimental heat capacities have been fitted to a series of theoretical and empirical models. The thermodynamic functions of these two compounds have been calculated based on the heat capacity curve fitting. The standard heat capacity, enthalpy and entropy values of *D*-galactose and galactitol at 298.15 K and 0.1 MPa have been determined to be (227.96±2.28) and (239.50±2.40) J·K^{-1}·mol^{-1}; (33.95±0.34) and (36.57±0.37) kJ/mol; (211.22±2.11) and (230.82±2.30) J·K^{-1}·mol^{-1}, respectively. The difference between the heat capacities of these two compounds has been reasonably explained based on their molecular structures.

References

[1] Walker-Nasir E., Kaleem A., Hoessli D. C., *Curr. Org. Chem.*, **2008**, *12*, 940
[2] Fery P. A., *Biochemistry*, **1996**, *35*, 89
[3] Topic E., Arambasin S., Zadro R., *Annales De Biologie Clinique*, **1998**, *46*, 546
[4] Yeung H. W., NG T. B., Wong D. M., *Int. J. Pept. Protein Res.*, **1986**, *27*, 208
[5] Feng Y., Rainyeau D., Chachaty C., Yu Z. W., Wolf C., Quinn P. J., *Biophys. J.*, **2004**, *86*(4), 2008
[6] Wang S. R., Ru B., Lin H Z., Sun W X., Yu C. J., Luo Z. Y., *Chem. Res. Chinese Universities*, **2014**, *30*(5), 848
[7] Ficicioglu C., Hussa C., Gallagher P. R., *Clin. Chem.*, **2010**, *56*, 1177
[8] Yager C. T., Chen J., Reynolds R., *Molecular Genetics and Metabolism*., **2003**, *80*, 283
[9] Banipal P. K., Banipal T. S., Ahluwalia J. C., *J. Chem. Thermodyn*., **2002**, *34*, 1825
[10] Banipal P. K., Banipal T. S., Lark B. S., *J. Chem. Soc. Faraday Trans.*, **1997**, *93*, 81
[11] Tewari Y. B., Goldberg R. N., *Biophys. Chem.*, **1991**, *40*, 59
[12] Daranas A. H., Shimizu H., Homans S. W., *J. Am. Chem. Soc.*, **2004**, *126*, 11870
[13] Wang J. J., Zhuo K. L., *J. Chem. Soc. Faraday Trans.*, **1998**, *94*, 3359
[14] Williams P. A. M., Etcheverry S. B., Barrio D. A., *Carbohydr. Res.*, **2006**, *341*, 717
[15] Shi Q., Snow C. L., Boerio-Goates J., Woodfield B. F., *J. Chem. Thermodyn*., **2010**, *42*, 1107
[16] Shi Q., Boerio-Goates J., Woodfield B. F., *J. Chem. Thermodyn*., **2011**, *43*, 1263
[17] Shi Q., Zhang L. Y., Schlesinger M. E., Boerio-Goates J., Woodfield B. F., *J. Chem. Thermodyn*., **2013**, *61*, 51
[18] Gopal E. S. R., *Specific Heats at Low Temperatures*, Plenum Press, New York, **1966**, 20
[19] Phillips N. E., Rev C., *Solid State Sci.*, **1971**, *2*, 467
[20] Snow C. L. Shi Q., Boerio-Goates J., Woodfield B. F., *J. Chem. Thermodyn*., **2010**, *42*, 1136
[21] Woodfield B. F., Boerio-Goates J., Shapiro L., Putnam R. L., Navrotsky A., *J. Chem. Thermodyn*., **1999**, *31*, 245