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Low-temperature heat capacity and standard thermodynamic functions of β-D-(-)-arabinose ($C_5H_{10}O_5$)

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ABSTRACT

The heat capacities of β-D-(-)-arabinose were measured using a Quantum Design Physical Property Measurement System (PPMS) over the temperature range from (1.9 to 300) K, and the experimental values were fitted as a function of temperature using a series of theoretical and empirical models in the appropriate temperature ranges, from which the corresponding thermodynamic functions were calculated. The standard molar heat capacity, entropy and enthalpy of β-D-(-)-arabinose at $T = 298.15$ K and $P = 0.1$ MPa were determined to be $C^{o}_{p,m} = (186.29 \pm 1.86)\ J \cdot K^{-1} \cdot mol^{-1}$, $S^{o}_{m} = (181.72 \pm 1.83)\ J \cdot K^{-1} \cdot mol^{-1}$ and $H^{o}_{m} = (28.52 \pm 0.29)\ kJ \cdot mol^{-1}$, respectively.

1. Introduction

Arabinose is a kind of monosaccharide containing five carbon atoms, which has been widely used as a fundamental biomass substance in the food and biochemical fields. When absorbed into human body with saccharose, arabinose is able to impede the digesting process of the latter to some extent and protect the cells from glucose-induced oxidative stress [1], thus making it as a promising medicine for diabetes. Arabinose is also an intermediate in the browning and crosslinking of protein by glucose, so as to be of vital biochemical importance [2]. Moreover, as one of the elementary saccharides, arabinose is often used for a testing sample or substrate in biological experiments [3]. As the preparation processes and applications of arabinose have made great progress, the thermodynamic properties of this compound have also been concerned for further understanding its nature from the viewpoint of thermodynamics.

Some thermodynamic properties of arabinose have already been reported previously in literature. For example, Zhuo *et al.* determined the thermodynamic parameters of interaction of arabinose with HCl (aq) in the temperature range from (278.15 to 318.15) K [4]. Banipal *et al.* reported the thermodynamic properties of the mixtures of arabinose with other organic or inorganic compounds, such as the partial molar heat capacities of arabinose in water, salt solutions and urea solutions [5–7]. Desai and Wilhoit measured the combustion energy and enthalpy of formation of arabinose in 1970 [8]. Recently, Goldberg *et al.* performed a calorimetric study on α-D-xylose (an important isomer of β-D-(-)-arabinose), in which the low temperature heat capacity and combustion energy of this compound were measured [9]. However, the heat capacity measurements and the standard thermodynamic functions on arabinose have not been reported till now.

In the present study, the heat capacities of β-D-(-)-arabinose have been measured using a Quantum Design Physical Property Measurement System (PPMS) over a temperature range from $T =$ (1.9 to 300) K, and the standard thermodynamic functions have been calculated based on the data fitting of the experimental heat capacities. A heat capacity crossover between β-D-(-)-arabinose and D-xylose studied by Goldberg *et al.* [9] has been observed at around $T = 46$ K, and a reasonable explanation has been provided for this interesting phenomenon.

2. Experimental

2.1. Materials

The information on the sample of β-D-(-)-arabinose used in this study is given in table 1. The sample was purchased from Alfa Aesar Corporation with mass fraction purity of 0.99. The mass fraction purity and the water content of the sample were further determined by HPLC and Karl Fisher analysis titration in our

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TABLE 1
Information on the sample of β-D-(-)-arabinose.

CAS No.	Formula	M_r [a]	X [b]	x_e [c]	w [d]
6748-95-4	$C_5H_{10}O_5$	150.1295	0.99	0.998	0.00065

[a] The value of M_r is based on the most recent set of relative atomic masses recommended by IUPAC [10]. According to the new recommendation of atomic weights, each atom has a range of weight; hence, each molecule has a range of weight, the minimum weight of arabinose molecule is 150.1210, and the maximum weight is 150.1380. So we choose the mean value of the min and the max, and the mean value is 150.1295.
[b] The mass fraction purity is provided by the supplier.
[c] The mass fraction purity is measured by HPLC in our laboratory.
[d] The water content (mass fraction purity) is determined by Karl Fisher analysis in our laboratory.

laboratory before the calorimetric measurement. The water contents in the sample are found to be about 0.065% weight percent, which is far below the heat capacity measurement errors and therefore the corresponding effect could be neglected. The HPLC result shows that the mass fraction purity of the sample is better than 0.998. The standard reference materials used in the measurement are α-Al_2O_3 (SRM720) and benzoic acid (SRM39j) provided by National Institute of Standards and Technology, and a piece of copper pellet with a mass fraction purity of 0.999999 (metals basis) from Alfa Aesar Corporation. The copper foil with 0.025 mm thickness and a mass fraction purity of 0.99999 used in the PPMS measurement was purchased from Alfa Aesar Corporation (see table 2).

2.2. Heat capacity measurements

The heat capacity measurements were performed using a Quantum Design Physical Property Measurement System (PPMS), which was recently set up at Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. In order to verify the PPMS calorimeter's performance, we have measured the heat capacities of a copper pellet and a α-Al_2O_3 crystal cylinder in the temperature range from T = (1.9 to 400) K and a powdered benzoic acid in the range from (1.9 to 300) K. Consequently, the powdered β-D-(-)-arabinose sample has been measured in the temperature range from T = (1.9 to 300) K. The temperature intervals used in the measurements are logarithmic spacing below T = 100 K and 10 K above T = 100 K. The powdered benzoic acid and β-D-(-)-arabinose samples have been prepared for the heat capacity measurement according to the technique developed by Shi *et al.* [11,12], in which the powdered sample was pressed into a pellet with a number of copper stripes in a copper cup and subsequently was loaded into the PPMS calorimeter. The detailed sample preparation process can be found in the corresponding literature [12]. The heat capacity measurement is generally performed in two steps: (1) the addenda measurement with Apiezon grease for the sample background, and (2) the heat capacity measurement of the pellet including the sample, the copper stripes and the cup. The heat capacity of sample can be consequently obtained by subtracting the known heat capacity of copper from the total heat capacity of the pellet. The sample masses of the copper pellet and the α-Al_2O_3 cylinder used in the heat capacity measurement are (67.81 and 48.94) mg, respectively. The masses of copper foil and powdered sample are (14.81 and 11.10) mg for the benzoic acid measurement, and (16.75 and 10.78) mg for the β-D-(-)-arabinose measurement, respectively. The heat capacity contributions of the copper and sample to the total heat capacity in the benzoic acid and β-D-(-)-arabinose measurements are shown in figure 1. Also, the fitting deviations, time constant τ_1 and τ_2 used in the PPMS relaxation measurements for all samples are presented in the Supplemental Materials.

TABLE 2
Provenance and purity of the materials used in heat capacity measurements for calibration of the PPMS calorimeter.

Materials	Provenances	Mass fraction purity
α-Al_2O_3 (SRM720)	National Institute of Standards and Technology	>0.9995
Benzoic acid (SRM39j)	National Institute of Standards and Technology	0.999996 (mol fraction)
Copper pellet	Alfa Aesar Corporation	0.999999
Copper foil	Alfa Aesar Corporation	0.99999

3. Results and discussion

3.1. Heat capacities of copper pellet, α-Al_2O_3 cylinder and powdered benzoic acid

The heat capacities of the copper pellet and the α-Al_2O_3 cylinder have been measured using the PPMS calorimeter within the temperature range from T = (1.9 to 400) K, and for the powdered benzoic acid the measurement has been performed from T = (1.9 to 300) K due to easy sublimation of this sample at high temperature and high vacuum. All the experimental values for the three samples are listed in Supplemental Materials. The experimental heat capacity of copper has been compared with the reported heat capacity data from Martin [13] below T = 30 K, while at temperatures above 30 K compared with the data from Stevens measured using an adiabatic calorimeter [14]. The deviations of the present values from those reported are shown in figure 2. It can be seen from the figure that the deviations of the PPMS measured copper data below T = 20 K are within ±2% except for three outliers, and from T = (20 to 400) K the deviations are within ±1% (except for the last data at T = 400 K). The heat capacity of α-Al_2O_3 has been compared with the values measured by a vacuum adiabatic calorimeter from T = (10 to 380) K and by a drop method using a Bunsen ice calorimeter from T = (273 to 1173) K. These reference data were recommended in the National Bureau of Standards Certificate for Standard Reference Material 720 [15]. It can be seen from the results that the deviation of the measured α-Al_2O_3 data from the references is within ±2% below T = 20 K and within ±1% from T = (20 to 400) K. The measured heat capacity of the powdered benzoic acid has been compared with the results by Clay *et al.* [16] and Hemmingway *et al.* [17], and the results shown in

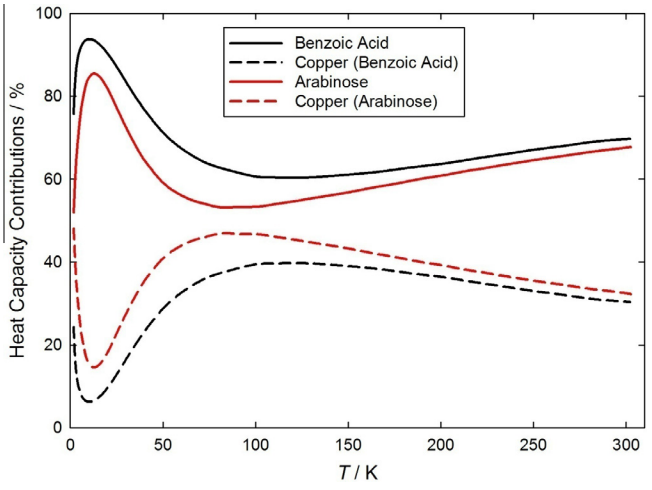

FIGURE 1. Plot of the individual heat capacity contributions of the copper and sample to the total heat capacity in the benzoic acid and β-D-(-)-arabinose measurements.