



Thermochemistry of α -D-xylose(cr) [☆]

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ARTICLE INFO

Article history:

Received 6 September 2012

Received in revised form 21 September 2012

Accepted 22 September 2012

Available online 8 November 2012

Keywords:

Calorimetry

Combustion

Enthalpy

Entropy

Heat capacity

Thermochemistry

α -D-xylose

ABSTRACT

The thermochemistry of α -D-xylose(cr) was studied by means of oxygen bomb calorimetry and a Physical Property Measurement System (PPMS) in zero magnetic field. The sample of α -D-xylose(cr) used in this study was one well-characterized by HPLC, Karl Fischer analysis, NMR, and by carbon dioxide analysis. The standard molar enthalpy of combustion was found to be $\Delta_c H_m^\circ = -(2342.2 \pm 0.8)$ kJ·mol⁻¹ at $T = 298.15$ K and at the standard pressure $p^\circ = 0.1$ MPa. The standard molar heat capacity for α -D-xylose(cr) was measured with the PPMS over the temperature range $1.9001 \leq T/K \leq 303.66$. At $T = 298.15$ K, $C_{p,m}^\circ = (178.1 \pm 1.8)$ J·K⁻¹·mol⁻¹. The values of $C_{p,m}^\circ$ were fit as a function of T by using theoretical and empirical models for appropriate temperature ranges. The results of these fits were used to calculate values of $C_{p,m}^\circ$, the entropy increment $\Delta_0^T S_m^\circ$, $\Delta_0^T H_m^\circ$, and $\Phi_m^\circ = (\Delta_0^T S_m^\circ - \Delta_0^T H_m^\circ/T)$ from $T = 0.5$ K to $T = 300$ K. Derived quantities for α -D-xylose(cr) are the standard molar enthalpy of formation $\Delta_f H_m^\circ = -(1054.5 \pm 1.1)$ kJ·mol⁻¹, the third law standard molar entropy $S_m^\circ = (175.3 \pm 1.9)$ J·K⁻¹·mol⁻¹, and the standard molar Gibbs energy of formation $\Delta_f G_m^\circ = -(750.5 \pm 1.0)$ kJ·mol⁻¹. A comparison of values of $\Delta_c H_m^\circ$ and S_m° for the five-carbon aldoses demonstrated a striking similarity in the values of these respective properties for α -D-xylose(cr), D-ribose(cr), and D-arabinose(cr). Thermochemical network calculations were performed that led to values of the standard formation properties at $T = 298.15$ K for a variety of biochemical substances: D-xylose(aq), D-xylose⁻(aq), D-xylose²⁻(aq), D-lyxose(cr and aq), D-lyxose⁻(aq), D-xylulose(aq), xylitol(aq), 1,4- β -D-xylobiose(am and aq), and 1,4- β -D-xylotriose(am and aq).

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1. Introduction

The substance α -D-xylose is the fundamental building block of the five-carbon fraction of biomass and thus is the precursor to hemicellulose, which comprises about 30 per cent of plant matter. D-xylose participates in several enzyme-catalyzed reactions which, in turn, are involved in four metabolic pathways: a reduction pathway, an isomerase pathway, and two oxidative pathways. Xylose is also used in tanning, dyeing, and as a diabetic food. Clearly, accurate thermodynamic property values are essential to a basic understanding of α -D-xylose as well as enabling equilibrium and energy balance calculations. In a recent study [1], it was pointed out that there was a need for modern values of the standard molar entropy

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S_m° and of the standard molar enthalpy of formation $\Delta_f H_m^\circ$ of α -D-xylose(cr). Indeed the most recent values of these properties for this substance were reported, respectively, in 1935 and 1957. In the 1935 study leading to a value of S_m° the lowest temperature at which heat-capacity measurements were made was 100 K. In this study, we report measured values of the standard molar enthalpy of combustion $\Delta_c H_m^\circ$ and standard molar heat capacities $C_{p,m}^\circ$ for α -D-xylose from the temperature $T = 1.9$ K to 303.66 K. Derived quantities include the standard molar entropy, the standard molar enthalpy of formation, and the Gibbs energy of formation $\Delta_f G_m^\circ$. By using the aforementioned property values with property values from the literature, we performed thermochemical network calculations that lead to values of standard formation properties for a number of biochemical species and substances.

2. Experimental

2.1. Materials

Information on the sample of α -D-xylose(cr) used in this study is given in table 1. This sample is the same as used in a previous

TABLE 1

Information on the sample of α -D-xylose(cr) used in this study: Chemical Abstracts Service (CAS) registry number, empirical formula, relative molecular mass M_r , mass fraction moisture content w as determined by Karl Fischer analysis, supplier, estimated mole fraction purity x as determined by HPLC, and mole fraction anomer purity x_a .

CAS No.	Formula	M_r^a	w	x^b	x_a^c
58-86-6	C ₅ H ₁₀ O ₅	150.1298	0.00060	0.998	>0.99

^a The value of M_r is based on the most recent set of relative atomic masses recommended by IUPAC [2].

^b The most likely impurity in the sample is D-glucose [1].

^c The NMR analysis led to the following mole fractions impurities obtained by signal averaging during the first 94 min after dissolution of the α -D-xylose(cr) sample: β -D-xylopyranose, 0.00641; unknown impurity, 0.00015; α -D-glucopyranose, 0.00032; D-xylofuranose A, 0.00094; and D-xylofuranose B, 0.00032 [1].

study [1]. It was characterized by HPLC, by Karl Fischer analysis, and by NMR. A density $\rho = 1.51 \text{ g}\cdot\text{cm}^{-3}$ (see table 2 in reference 3) was used for α -D-xylose(cr) when making buoyancy corrections.

2.2. Combustion calorimetry measurements

The massic energy of combustion of the α -D-xylose sample was measured by using an isoperibol static bomb calorimeter, equipped with a twin-valve combustion bomb Type 1105, Parr Instrument Company,¹ with an internal volume of 0.340 dm^3 [4,5]. The energy equivalent of the calorimeter $\varepsilon(\text{calor})$ was determined by following the procedure described by Coops *et al.* [6], from the combustion of benzoic acid (National Institute of Standards and Technology Standard Reference Material 39j), which has a certified massic energy of combustion under standard bomb conditions of $\Delta_c u^\circ = -(26434 \pm 3) \text{ J}\cdot\text{g}^{-1}$ [7]. The value of the energy equivalent of the calorimeter was found to be $\varepsilon(\text{calor}) = (15905.0 \pm 0.8) \text{ J}\cdot\text{g}^{-1}$, as a mean of eight calibration experiments for an average mass of water added to the calorimeter of 3119.6 g. The uncertainty refers to the standard deviation of the mean.

For all combustion experiments, samples in pellet form were ignited at $T = (298.150 \pm 0.001) \text{ K}$ in oxygen, at a pressure $p = 3.04 \text{ MPa}$, with a volume $V = 1.00 \text{ cm}^3$ of deionised water added to the bomb. The calorimeter temperatures were measured to $\pm(1 \cdot 10^{-4}) \text{ K}$, at time intervals of 10 s, with a quartz crystal thermometer (Hewlett-Packard HP 2804A) that is interfaced to a PC programmed to acquire data, control the calorimeter temperatures and to compute the corrected temperature rise, by using the program LABTERMO [8]. At least 100 temperature readings were taken for the main period and for both the fore and after periods. The energy of ignition $\Delta U(\text{ign})$ was measured from the change in potential difference across a capacitor when discharged through a platinum ignition wire (diameter $d = 0.05 \text{ mm}$, mass fraction $w = 0.9999$). All the necessary weighings for the combustion experiments were made with an imprecision of $\pm(1 \cdot 10^{-5}) \text{ g}$ and corrections from apparent mass to true mass were made. The gases of combustion were analyzed to recover the carbon dioxide resulting from the combustion experiments. The mass of sample used in each experiment and on which the energy of combustion was based, was determined from the total mass of $\text{CO}_2(\text{g})$ produced, as determined from the $\text{CO}_2(\text{g})$ recoveries and taking into account the amount of $\text{CO}_2(\text{g})$ formed from the combustion of the cotton thread fuse. The ratio of the average mass of carbon dioxide recovered in the combustion experiments of α -D-xylose to the value calculated from the mass of the sample, together with the standard

¹ Certain commercial equipment, instruments, or materials are identified in this paper to specify the experimental procedures adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology (NIST), nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

deviation of the mean, was (0.9997 ± 0.0002) . The calculation of this ratio included the known amount of moisture (see Section 2.1) in the sample. Also, no soot residue was found in any experiment. For the cotton thread fuse, empirical formula $\text{CH}_{1.686}\text{O}_{0.843}$, the massic energy change $\Delta_c u^\circ = -16240 \text{ J}\cdot\text{g}^{-1}$ [6], a value that has been previously confirmed in our laboratory. Corrections for the nitric acid formed were based on the standard molar energy change $\Delta_r U_m^\circ \{ \text{HNO}_3(\text{aq}), \text{ concentration } c = 0.1 \text{ mol}\cdot\text{dm}^{-3} \} = -59.7 \text{ kJ}\cdot\text{mol}^{-1}$ [9] for the reaction $\{ 1/2 \text{ N}_2(\text{g}) + 5/4 \text{ O}_2(\text{g}) + 1/2 \text{ H}_2\text{O}(\text{l}) = \text{HNO}_3(\text{aq}) \}$. The value of the pressure coefficient of massic energy $(\partial u/\partial p)_T$ was taken to be $-0.2 \text{ J}\cdot\text{g}^{-1}\cdot\text{MPa}^{-1}$ [10] at $T = 298.15 \text{ K}$, a typical value for most organic compounds. The corrections to the standard state ΔU_Σ and calculation of $\Delta_c u^\circ$ of α -D-xylose were made following the procedure given by Hubbard *et al.* [11].

2.3. Heat capacity measurements

Heat capacity measurements on the α -D-xylose(cr) sample were performed using a Quantum Design Physical Property Measurement System (PPMS) in zero magnetic field with logarithmic spacing in the temperature range from (2 to 100) K and 10 K temperature intervals from $T = (100 \text{ to } 300) \text{ K}$. The inaccuracy of heat-capacity measurements on a high-purity copper pellet was found to be $\pm 2\%$ and $\pm 0.6\%$ in the temperature ranges from (2 to 20) K and from (20 to 300) K, respectively [12]. Heat capacities of the powdered α -D-xylose(cr) sample were measured by using a new technique developed in our recent work of powdered sample measurement with a PPMS calorimeter, which can achieve an inaccuracy of $\pm 2\%$ and $\pm 1\%$ in the temperature ranges below 10 K and from (10 to 300) K, respectively, for both conducting and non-conducting powdered samples [13]. The details of sample preparation and heat-capacity experimental procedure can be found in our recent publications [12,13]. In general, the powdered samples were prepared for the PPMS measurements by mixing them with about 50 pieces of copper strips in a copper cup which was then compressed into a pellet using a stainless steel die. The copper strips and cup were formed from a foil of 0.025 mm thickness and 0.99999 mass fraction purity purchased from Alfa Aesar. The detailed measurement steps are: (1) the addenda measurement of the PPMS platform with Apiezon N (used to thermally attach the pellet to the platform) and (2) the heat capacity measurement of the pellet consisting of the sample, the copper strips, and the copper cup. Step (2) gives the total heat capacity of the sample, the copper strips and the copper cup, and therefore the sample heat capacity can be calculated by subtracting the known heat capacity of copper from the total heat capacity [13].

3. Results and discussion

3.1. Results of combustion calorimetry measurements

Detailed results for each combustion experiment performed for α -D-xylose are given in table 2, in which $\Delta m(\text{H}_2\text{O})$ is the deviation of the mass of water added to the calorimeter from 3119.6 g, the mass assigned to $\varepsilon(\text{calor})$, ΔU_Σ is the energy correction to the standard state and the remaining terms are as previously defined [10,11]. The internal energy change associated with the isothermal bomb process, $\Delta U(\text{IBP})$, was calculated by using

$$\Delta U(\text{IBP}) = -[\varepsilon(\text{calor}) + c_p \{ \text{H}_2\text{O}(\text{l}) \} \Delta m \{ \text{H}_2\text{O}(\text{l}) \} + \varepsilon_f] \Delta T_{\text{ad}} + \Delta U(\text{ign}). \quad (1)$$

The terms in equation (1) are: $\varepsilon(\text{calor})$ is the energy equivalent of the calorimeter; the massic heat capacity of $\text{H}_2\text{O}(\text{l})$, $c_p \{ \text{H}_2\text{O}(\text{l}) \} = 4.1793 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$ [9]; $\Delta m(\text{H}_2\text{O})$ is the deviation of the

TABLE 2
Standard massic energy of combustion of α -D-xylose at $T = 298.15$ K and at the pressure $p^\circ = 0.1$ MPa.^a

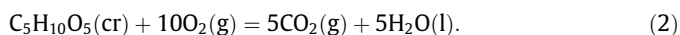
Experiment	1	2	3	4	5	6
$m(\text{CO}_2, \text{total})/\text{g}$	1.53580	^b	1.55045	1.43711	^b	1.53173
$m(\text{sample})/\text{g}$	0.89247	0.90479	0.70931	0.85845	0.81356	0.79945
$m(\text{fuse})/\text{g}$	0.00293	0.00333	0.00341	0.00641	0.00681	0.00679
T_i/K	298.1499	298.1506	298.1505	298.1499	298.1497	298.1517
T_f/K	299.1481	299.1612	298.9758	299.1197	299.0800	299.0677
$\Delta T_{\text{ad}}/\text{K}$	0.87769	0.89063	0.69931	0.84867	0.80520	0.79087
$\varepsilon_i/(\text{J}\cdot\text{K}^{-1})$	15.78	15.80	15.46	15.68	15.78	15.65
$\varepsilon_f/(\text{J}\cdot\text{K}^{-1})$	16.99	17.02	16.42	16.85	16.89	16.74
$\varepsilon(\text{calor})_{\text{corr}}/(\text{J}\cdot\text{K}^{-1})$	15905.0	15905.0	15905.0	15905.0	15905.0	15905.0
$\Delta m(\text{H}_2\text{O})/\text{g}$	0.0	0.0	0.0	0.0	0.0	0.0
$-\Delta U(\text{IBP})/\text{J}^c$	13973.42	14179.46	11132.87	13511.23	12819.16	12590.88
$\Delta U(\text{fuse})/\text{J}$	47.58	54.08	55.38	104.10	110.59	110.27
$\Delta U(\text{HNO}_3)/\text{J}$	0.36	0.36	0.37	0.28	0.31	0.20
$\Delta U(\text{ign})/\text{J}$	1.15	1.17	1.14	1.17	1.15	1.15
$\Delta U_{\Sigma}/\text{J}$	10.87	11.05	8.45	10.47	9.87	9.69
$-\Delta_c u^\circ/(\text{J}\cdot\text{g}^{-1})$	15591.12	15599.17	15604.84	15605.31	15608.42	15599.12
$\langle \Delta_c u^\circ \rangle = -(15601.3 \pm 2.5) \text{J}\cdot\text{g}^{-1}$						

^a $m(\text{CO}_2, \text{total})$ is the mass of CO_2 recovered in each combustion; $m(\text{cpd})$ and $m(\text{fuse})$ are, respectively, the mass of compound and the mass of fuse (cotton) used in each experiment; T_i is the initial temperature; T_f is the final temperature; ΔT_{ad} is the corrected temperature rise; ε_i is the energy equivalent of the contents in the initial state; ε_f is the energy equivalent of the contents in the final state; $\varepsilon(\text{calor})_{\text{corr}}$ is the energy equivalent of the calorimeter corrected for the amount of water used; $\Delta m(\text{H}_2\text{O})$ is the deviation of the mass of water added to the calorimeter from 3119.6 g; $\Delta U(\text{IBP})$ is the energy change for the isothermal combustion reaction under actual bomb conditions; $\Delta U(\text{fuse})$ is the energy of combustion of the fuse (cotton); $\Delta U(\text{HNO}_3)$ is the energy correction for nitric acid formation; $\Delta U(\text{ign})$ is the energy of ignition; ΔU_{Σ} is the standard state correction; and $\Delta_c u^\circ$ is the standard massic energy of combustion. The uncertainty in $\langle \Delta_c u^\circ \rangle$ is equal to one estimated standard deviation of the mean.

^b The quantity $m(\text{CO}_2, \text{total})$ was not measured in these experiments. Values of $m(\text{CO}_2, \text{total})$, based on the results of the other four experiments, were used in the calculations.

^c $\Delta U(\text{IBP})$ includes $\Delta U(\text{ign})$.

mass of water added to the calorimeter from 3119.6 g; ε_f is the energy equivalent of the contents in the final state; ΔT_{ad} is the calorimeter temperature change corrected for heat exchange with the surrounding constant-temperature bath and for the energy of stirring; and $\Delta U(\text{ign})$ is the electrical energy for ignition. The mean value of the massic energy of combustion $\Delta_c u^\circ$ at the standard pressure $p^\circ = 0.1$ MPa is given in the last row of table 2. The uncertainty in this value is the standard deviation of the mean. This value of $\Delta_c u^\circ$ refers to the combustion reaction



The sample of α -D-xylose(cr) used has been well-characterized by HPLC, Karl Fischer analysis, NMR [1], and by CO_2 analysis (see Sections 2.1 and 2.2). The most likely impurity in this sample was found (see table 1 in reference 1) to be D-glucose(cr) with a possible mass fraction impurity $w = 0.002$ [1]. For D-glucose(cr), $\Delta_c u^\circ = -15558.4 \text{J}\cdot\text{g}^{-1}$ [14], a value which is very close to the value $\Delta_c u^\circ = -(15601.3 \pm 2.5) \text{J}\cdot\text{g}^{-1}$ measured for the sample of α -D-xylose(cr) used in this study. On this basis, the aforementioned mass fraction impurity of D-glucose(cr) in the sample of α -D-xylose(cr) would cause an error of $0.09 \text{J}\cdot\text{g}^{-1}$ in $\Delta_c u^\circ$. A similar type of uncertainty analysis is now done for the anomeric purities in the sample of α -D-xylose(cr) (see Section 2.1) using some estimated property values. Specifically, $\Delta_r H^\circ = 15.2 \text{kJ}\cdot\text{mol}^{-1}$ for the reaction $\{\beta\text{-fructopyranose}(\text{aq}) = \beta\text{-fructofuranose}(\text{aq})\}$ and $\Delta_r H^\circ\{\alpha\text{-D-glucose}(\text{cr})\} - \Delta_r H^\circ\{\beta\text{-D-glucose}(\text{cr})\} = -6.2 \text{kJ}\cdot\text{mol}^{-1}$ from tables 10 and 15, respectively, in Ref. [3]. These respective values, together with the results of the anomeric purities obtained by NMR, give estimated errors of $-0.22 \text{J}\cdot\text{g}^{-1}$ and $-0.11 \text{J}\cdot\text{g}^{-1}$ in $\Delta_c u^\circ$. These possible systematic errors due to impurities in the sample are substantially less than the estimated standard deviation of the mean ($\pm 2.5 \text{J}\cdot\text{g}^{-1}$) in the value of $\Delta_c u^\circ$. Thus the component of uncertainty due to impurities in the sample of α -D-xylose(cr) is judged to be very small. The derived standard molar energy $\Delta_c U_m^\circ$ and standard molar enthalpy $\Delta_c H_m^\circ$ of combustion, and the standard molar enthalpy of formation $\Delta_f H_m^\circ$ of D-xylose(cr) at $T = 298.15$ K are given in table 3. In accordance with Rossini [15] and Olofsson and Sunner [16], the uncertainties assigned to $\Delta_c U_m^\circ$, $\Delta_c H_m^\circ$, and $\Delta_f H_m^\circ$ are, in each

TABLE 3

Standard molar energy of combustion $\Delta_c U_m^\circ$, standard molar enthalpy of combustion $\Delta_c H_m^\circ$, and standard molar enthalpy of formation $\Delta_f H_m^\circ$, for α -D-xylose(cr) at $T = 298.15$ K and at the pressure $p^\circ = 0.1$ MPa. The uncertainties are discussed in Section 3.1.

Compound	$-\Delta_c U_m^\circ/(\text{kJ}\cdot\text{mol}^{-1})$	$-\Delta_c H_m^\circ/(\text{kJ}\cdot\text{mol}^{-1})$	$-\Delta_f H_m^\circ/(\text{kJ}\cdot\text{mol}^{-1})$
α -D-xylose(cr)	2342.2 ± 0.8	2342.2 ± 0.8	1054.5 ± 1.1

case, twice the overall standard deviation of the mean and include the estimated uncertainties in the calibration and in the values of auxiliary quantities used, in conformity with standard thermochemical practice. The value of $\Delta_f H_m^\circ$ was derived from $\Delta_c H_m^\circ$ by using the CODATA [17] values $\Delta_f H_m^\circ = -(285.830 \pm 0.040) \text{kJ}\cdot\text{mol}^{-1}$ for $\text{H}_2\text{O}(\text{l})$ and $\Delta_f H_m^\circ = -(393.51 \pm 0.13) \text{kJ}\cdot\text{mol}^{-1}$ for $\text{CO}_2(\text{g})$.

3.2. Results of heat capacity measurements

The results of measurements of the standard molar heat capacity $C_{p,m}^\circ$ of α -D-xylose are shown in figure 1 and listed in table 4. It can be seen from the heat capacity curves that there are no phase transitions or other thermal anomalies over the experimental temperature range from 1.9 K to 305 K.

To calculate the thermodynamic functions, we performed curve fitting on the measured values of $C_{p,m}^\circ$ using different fitting methods in different temperature regions. Both series 1 and series 2 (see table 4) were used in the fitting. In the low temperature region ($T < 10$ K), the heat capacities were fitted by using the theoretical model

$$C_{p,m}^\circ = \gamma T + B_3 T^3 + B_5 T^5 + B_7 T^7 + B_9 T^9, \quad (3)$$

where the linear term represents defects and oxygen vacancies, and the odd-powers in temperature represent the lattice. In the high temperature region ($T > 50$ K), the heat capacities were fitted by using a combination of Debye and Einstein specific-heat functions [18–20]:

$$C_{p,m}^\circ = n_D D(\theta_D) + n_E E(\theta_E) + aT + bT^2, \quad (4)$$

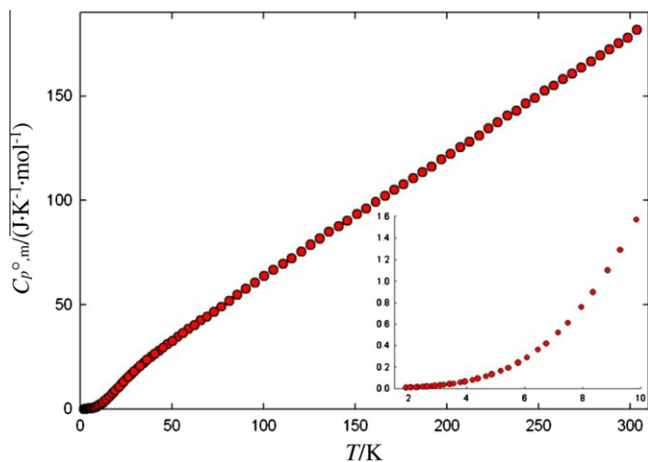


FIGURE 1. The standard molar heat capacity $C_{p,m}^{\circ}$ of α -D-xylose(cr) as a function of temperature in the range $T = (2$ to $300)$ K.

where $D(\theta_D)$ and $E(\theta_E)$ are Debye and Einstein functions, respectively, and the terms involving T and T^2 constitute an approximation to $(C_{p,m}^{\circ} - C_{v,m}^{\circ})$, where $C_{v,m}^{\circ}$ is the standard molar heat capacity at constant volume. Since this combined Debye and Einstein function is unlikely to yield an accurate representation of the heat capacity at low temperatures [19], the heat capacities in the middle temperature region ($10 \text{ K} < T < 50 \text{ K}$) were fitted using an orthogonal polynomial function [21]:

$$C_{p,m}^{\circ} = A_0 + A_1T + A_2T^2 + A_3T^3 + A_4T^4 + A_5T^5 + A_6T^6. \quad (5)$$

The parameters for these fits as well as their temperature ranges are given in table 5. As can be seen in this table, the root-mean-square (RMS) deviations of the fits (RMS = 0.71% for $T \leq 11 \text{ K}$; RMS = 0.42% for $11 \leq T/\text{K} \leq 52.55$; and RMS = 0.25% for $52.55 \leq T/\text{K} \leq 305$) are substantially less than the estimated inaccuracies in the calorimetric measurements (2% for $T < 10 \text{ K}$ and 1% for $10 < T/\text{K} < 305$). The amount of water in the sample of D-xylose(cr) is very small (mass fraction $w = 0.00060$) [1] and no evidence of water is seen in the calorimetric results. As stated above (see Section 3.1), the sample is of a very high purity. On this basis, we judge that a reasonable estimate of the total or combined standard uncertainties [22] in the values of the heat capacities are $0.021 \cdot C_{p,m}^{\circ}$ for $T < 10 \text{ K}$, $0.011 \cdot C_{p,m}^{\circ}$ for $10 < T/\text{K} < 52.55$, and $0.010 \cdot C_{p,m}^{\circ}$ for $52.55 < T/\text{K} < 305$.

Using the fitting parameters given in table 5, we calculated the standard molar thermodynamic functions for α -D-xylose at selected temperatures from $T = 0.5 \text{ K}$ to $T = 300 \text{ K}$. These calculated results are given in table 6. At $T = 298.15 \text{ K}$, $C_{p,m}^{\circ} = (178.1 \pm 1.8) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ and the standard molar entropy $S_m^{\circ} = (175.3 \pm 1.9) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. The solid form of α -D-xylose(cr) used in this study is assumed to be the ordered crystalline state (orthorhombic, $P2_12_12_1$) as reported by Hordvik [23]. Accordingly, the value $S_m^{\circ} = 0$ at $T \rightarrow 0$ has been taken in accordance with the third law of thermodynamics and in the apparent absence of any frozen disorder in the crystalline state. The error in S_m° due to errors in the $C_{p,m}^{\circ}$ values was estimated by using a propagation of error analysis in which each value of $C_{p,m}^{\circ}$ was assumed to be in error by $0.0011 \cdot C_{p,m}^{\circ}$. Similarly, at $T = 298.15 \text{ K}$, $\Delta_0^{\circ} H_m^{\circ} = (2.751 \pm 0.030) \cdot 10^4 \text{ J} \cdot \text{mol}^{-1}$ and $\Phi_m^{\circ} = (84.6 \pm 2.2) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. In table 6, we report additional digits for the property values beyond what would be considered significant on the basis of the uncertainties in order to avoid rounding errors. By using the measured values of $\Delta_f H_m^{\circ}$ and S_m° of α -D-xylose(cr), the standard Gibbs energy of formation of this substance is calculated to be $\Delta_f G_m^{\circ} = -(750.5 \pm 1.0) \text{ kJ} \cdot \text{mol}^{-1}$. In this calculation we used the following values from

TABLE 4

Standard molar heat capacities $C_{p,m}^{\circ}$ at constant pressure for α -D-xylose from $T = (2$ to $300)$ K.^a

T/K	$C_{p,m}^{\circ}/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	T/K	$C_{p,m}^{\circ}/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
Series 1		Series 2	
1.9001	0.0066450	2.0404	0.0082424
2.0829	0.0087877	2.2425	0.010966
2.2997	0.011872	2.4717	0.014708
2.5385	0.015960	2.6324	0.017828
2.7871	0.021242	2.9014	0.024009
3.0782	0.029069	3.2037	0.032882
3.4135	0.040371	3.5443	0.045253
3.7729	0.055612	3.9390	0.063740
4.2031	0.079312	4.3835	0.090965
4.6605	0.11237	4.8696	0.13054
5.1791	0.16193	5.4361	0.19159
5.7752	0.23856	6.0817	0.28662
6.4662	0.35907	6.7445	0.41814
7.1587	0.51889	7.4966	0.61191
7.9594	0.75843	8.3533	0.89694
8.8628	1.1009	9.2999	1.2924
9.8635	1.5685	10.354	1.8302
10.970	2.2125	11.523	2.5459
12.188	2.7359	12.718	3.4082
13.562	4.0281	14.253	4.5512
15.067	5.2376	15.841	5.8725
16.591	6.4705	17.611	7.4369
18.418	8.1942	18.989	8.7940
20.269	9.9692	21.170	10.744
22.576	12.061	23.637	13.081
25.132	14.387	26.286	15.413
27.981	16.854	29.319	17.967
31.146	19.422	32.679	20.558
34.685	22.144	36.332	23.551
38.593	25.087	40.526	26.514
42.932	27.975	45.127	29.461
47.756	31.183	50.198	32.512
53.125	34.565	55.822	36.429
59.085	38.301	62.207	40.201
65.768	42.388	69.146	44.367
73.117	46.673	76.877	49.051
81.258	51.824	85.507	54.655
90.302	57.699	95.148	60.594
100.35	63.676	105.25	66.606
110.61	69.547	115.43	72.274
120.64	75.357	125.54	78.608
130.77	81.561	135.74	84.749
140.87	87.466	145.76	90.112
151.03	93.154	155.98	95.918
161.11	99.114	166.15	102.13
171.25	104.92	176.34	107.50
181.48	110.56	186.59	113.51
191.69	116.09	196.81	119.53
201.94	122.16	207.17	125.24
212.26	128.07	217.50	130.91
222.61	134.51	227.74	137.35
232.87	140.48	237.95	142.93
243.02	146.31	248.07	148.90
253.18	152.43	258.24	154.94
263.22	158.02	268.36	160.56
273.41	163.59	278.46	166.47
283.51	169.47	288.47	172.37
293.61	175.31	298.67	177.87
303.66	181.61		

^a The combined standard uncertainties [22] in the values of the heat capacities are judged to be $\pm 0.02 \cdot C_{p,m}^{\circ}$ for $2 < T/\text{K} < 20$ and $\pm 0.006 \cdot C_{p,m}^{\circ}$ for $20 < T/\text{K} < 300$.

the CODATA tables [17]: $S_m^{\circ} = 5.74 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for C(cr); $S_m^{\circ} = 130.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for $\text{H}_2(\text{g})$; and $S_m^{\circ} = 205.152 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for $\text{O}_2(\text{g})$.

3.3. Comparison with earlier results

Berthelot and Matignon [24] and Karrer and Fioroni [25] report, respectively, $\Delta_c u = -3739.9 \text{ cal} \cdot \text{g}^{-1} = -15648 \text{ J} \cdot \text{g}^{-1}$ and

TABLE 5

Parameters in equations (3)–(5) for fits of the standard molar heat capacity (in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) for α -**D**-xylose(cr). The root-mean-square (RMS) deviations of the fits are also given.

Parameter	Temperature range	Coefficients
	$0 \leq T/\text{K} \leq 11.00$	
γ		$4.90240\cdot 10^{-4}$
B_3		$7.93539\cdot 10^{-4}$
B_5		$1.58664\cdot 10^{-5}$
B_7		$-8.85557\cdot 10^{-8}$
B_9		$1.44290\cdot 10^{-10}$
	RMS% = 0.71	
	$11.00 \leq T/\text{K} \leq 52.55$	
A_0		3.88311
A_1		-1.33818
A_2		$1.54554\cdot 10^{-1}$
A_3		$-5.09034\cdot 10^{-3}$
A_4		$8.46160\cdot 10^{-5}$
A_5		$-7.02342\cdot 10^{-7}$
A_6		$2.31316\cdot 10^{-9}$
	RMS% = 0.41	
	$52.55 \leq T/\text{K} \leq 305.00$	
n_D		$3.70811\cdot 10^{-1}$
θ_D		134.8
n_E		$3.17794\cdot 10^{-1}$
θ_E		351.4
a		$5.04997\cdot 10^{-1}$
b		$1.26966\cdot 10^{-4}$
	RMS% = 0.25	

$\Delta_c u = -3735 \text{ cal}\cdot\text{g}^{-1} = -15627 \text{ J}\cdot\text{g}^{-1}$ for α -**D**-xylose(cr). These investigators [24,25] did not assign any uncertainties. Neglecting any corrections to the standard state or to $T = 298.15 \text{ K}$, these early studies, which were performed, respectively, in 1890 and in 1923, compare well with the result of this study $\langle \Delta_c u \rangle = -(15601.3 \pm 2.5) \text{ J}\cdot\text{g}^{-1}$ at $T = 298.15$ and $p^\circ = 0.1 \text{ MPa}$. In the most recent previous study of the enthalpy of combustion, Skuratov *et al.* [26] report $\Delta_c H_m^\circ = -(559.2 \pm 0.2) \text{ kcal}\cdot\text{mol}^{-1} = -(2339.7 \pm 0.9) \text{ kJ}\cdot\text{mol}^{-1}$ for α -**D**-xylose(cr) at $T = 293.15 \text{ K}$. We calculate $\Delta_c C_{p,m}^\circ = 90.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for the change in heat capacity for the combustion reaction (2) by using the value of $C_{p,m}^\circ$ for α -**D**-xylose(cr) determined in this study together with the values of $C_{p,m}^\circ$ for $\text{O}_2(\text{g})$, $\text{CO}_2(\text{g})$, and $\text{H}_2\text{O}(\text{l})$ from the NBS tables [9]. By using this value of $\Delta_c C_{p,m}^\circ$, one obtains $\Delta_c H_m^\circ = -(2340.1 \pm 0.9) \text{ kJ}\cdot\text{mol}^{-1}$ at $T = 298.15 \text{ K}$. This value is in near agreement with the result of this study, $\Delta_c H_m^\circ = -(2342.2 \pm 0.8) \text{ kJ}\cdot\text{mol}^{-1}$.

Miller [27] reports $S_m^\circ = 34.30 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 143.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for α -**D**-xylose(cr) based on heat capacities measured from $T = 100 \text{ K}$ to $T = 298.15 \text{ K}$. Unfortunately, Miller did not report his measured $C_{p,m}^\circ$ values. To obtain his value of S_m° , Miller [27] had to make a large extrapolation to $T \rightarrow 0$. The result of our study is $S_m^\circ = (175.3 \pm 1.9) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. We judge the value of S_m° obtained by Miller [27] to be inaccurate.

It is important to recognize that in this study, all measurements were performed on the same well-characterized sample of α -**D**-xylose(cr). This same sample was also used in a recent study [1] in which both the saturation molality $m(\text{sat})$ and the standard molar entropy of solution $\Delta_{\text{sol}} H_m^\circ$ were measured. We believe that this is a useful approach to obtain accurate values of the standard formation properties of important materials.

It is of interest to compare the property values determined in this study with those for the other five-carbon aldoses, namely ribose, arabinose, and lyxose. The following values of $\Delta_c H_m^\circ$ have been reported in the literature for **D**-ribose(cr): $-2334.3 \text{ kJ}\cdot\text{mol}^{-1}$ from Stroh and Finke [28]; $-(2345.8 \pm 0.7) \text{ kJ}\cdot\text{mol}^{-1}$ from Desai and Wilhoit [29]; $-(2349.47 \pm 0.95) \text{ kJ}\cdot\text{mol}^{-1}$ from Colbert *et al.* [30]; and $-(2347.59 \pm 0.91) \text{ kJ}\cdot\text{mol}^{-1}$ from Gubareva *et al.* [31].

For **D**-arabinose(cr), we have: $\Delta_c H_m^\circ = -(2338.8 \pm 1.6) \text{ kJ}\cdot\text{mol}^{-1}$ from Desai and Wilhoit [29]; $\Delta_c H_m^\circ = -2335.9 \text{ kJ}\cdot\text{mol}^{-1}$ from Stroh and Finke [28]; and $\Delta_c H_m^\circ = -2343.6 \text{ kJ}\cdot\text{mol}^{-1}$ from Karrer and Fioroni [25]. Stroh and Finke [28] and Karrer and Fioroni [25] did not report uncertainties with their values. The only value of S_m° for the other five-carbon aldoses is the unpublished result of Boerio-Goates *et al.* [32], $S_m^\circ = (175.7 \pm 0.6) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for **D**-ribose(cr). There do not appear to be any values of $\Delta_c H_m^\circ$ or S_m° in the literature for lyxose(cr). All of the aforementioned values pertain to $T = 298.15 \text{ K}$. The results obtained in this study for α -**D**-xylose(cr), namely $\Delta_c H_m^\circ = -(2342.2 \pm 0.8) \text{ kJ}\cdot\text{mol}^{-1}$ and $S_m^\circ = (175.3 \pm 1.9) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, are seen to be remarkably similar to the corresponding property values of the other five-carbon aldoses. It should be noted that the anomeric composition of the sample is known only in the current study (see Section 2.1) and in the study of Colbert *et al.* [30], who reported that the NMR results were consistent with the anomeric composition {mole fraction $x(\beta\text{-pyranose}) = 0.65$ and $x(\alpha\text{-pyranose}) = 0.35$ }. Since there may be differences in the values of $\Delta_c H_m^\circ$ and S_m° for the different anomers, the agreement in property values seen here may be fortuitous.

3.4. Thermochemical network calculations and standard formation properties

The results obtained in this study for S_m° , $C_{p,m}^\circ$, and $\Delta_f H_m^\circ$ for α -**D**-xylose(cr) can be used together with results from the literature to construct a thermochemical network, which, in turn can be used to calculate the standard molar formation properties for a number of substances. The network of substances and reactions which have thermodynamic properties connected to those of α -**D**-xylose(cr) is shown in table 7. In this table, the substance or reaction, the type of property, and the property value are given in columns 1, 2, and 3, respectively. Additionally, one has the following constraint for each substance:

$$\Delta_f G_m^\circ = \Delta_f H_m^\circ - T \Delta_f S_m^\circ \quad (6)$$

Here, $\Delta_f G_m^\circ$ and $\Delta_f S_m^\circ$ are, respectively, the standard molar Gibbs energy and entropy change for the formation reaction for the substance of interest. The property values of several key substances (see above) were taken from the CODATA tables [17]. This thermochemical network constitutes a system of linear equations that, when solved, yields values of $\Delta_f H_m^\circ$, $\Delta_f G_m^\circ$, S_m° , and $C_{p,m}^\circ$ for the substances in the network. It is clear that where replicate measurements have been made, one must either select one of the several values in the table or provide fractional weights for the data. In all cases, we have given a high weight to those studies where there has been some discussion of errors in the measurements. Additionally, we have given a higher weight to values of standard molar enthalpies of reaction obtained from direct calorimetric measurements than those values obtained from equilibrium constants measured at several temperatures. It is important to appreciate that the weighting and selection of data is subjective. However, by having such a reaction catalogue in hand, the reader can weight the property values as she or he deems "best" and obtain a new set of selected values for the standard formation properties, entropies, and heat capacities. The calculated values of $\Delta_f H_m^\circ$, $\Delta_f G_m^\circ$, S_m° , and $C_{p,m}^\circ$ are given in table 8.

A striking similarity in the respective values of S_m° and $\Delta_c H_m^\circ$ for the five-carbon aldoses was noted in Section 3.3. We use this similarity to estimate $S_m^\circ = 175.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for **D**-lyxose(cr). Then, by using the CODATA [17] values of S_m° for $\text{C}(\text{cr})$, $\text{H}_2(\text{g})$, and $\text{O}_2(\text{g})$, we calculate the standard molar entropy of formation $\Delta_f S_m^\circ = -1019.48 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for **D**-lyxose(cr). This value is used with the value $\Delta_f G_m^\circ = -747.47 \text{ kJ}\cdot\text{mol}^{-1}$ for **D**-lyxose(cr) given in table 8 to calculate $\Delta_f H_m^\circ = -1051.4 \text{ kJ}\cdot\text{mol}^{-1}$ for **D**-lyxose(cr). By

TABLE 6

Standard thermodynamic functions of α -D-xylose(cr) as a function of temperature T and at the standard pressure $p^\circ = 0.1$ MPa; $C_{p,m}^\circ$ is the standard molar heat capacity; $\Delta_0^\circ S_m^\circ$, where S_m° is the standard molar entropy; $\Delta_0^\circ H_m^\circ$, where H_m° is the standard molar enthalpy; and the function $\Phi_m^\circ = \Delta_0^\circ S_m^\circ - \Delta_0^\circ H_m^\circ/T$. Uncertainties are discussed in Section 3.2.

T/K	$C_{p,m}^\circ/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$	$\Delta_0^\circ S_m^\circ/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$	$\Delta_0^\circ H_m^\circ/(\text{J}\cdot\text{mol}^{-1})$	$\Phi_m^\circ/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$
0.5	0.00034481	0.00027828	0.000073720	0.00013084
1.0	0.0012996	0.00075791	0.00044614	0.00031178
1.5	0.0035325	0.0016520	0.0015857	0.00059485
2.0	0.0078253	0.0031965	0.0043211	0.0010360
2.5	0.015121	0.0056608	0.0099103	0.0016967
3.0	0.026561	0.0093563	0.020131	0.0026459
3.5	0.043514	0.014643	0.037389	0.0039609
4.0	0.067582	0.021936	0.064830	0.0057288
4.5	0.10060	0.031705	0.10646	0.0080470
5.0	0.14459	0.044475	0.16725	0.011024
5.5	0.20176	0.060823	0.25324	0.014779
6.0	0.27439	0.081372	0.37159	0.019440
6.5	0.36478	0.10678	0.53059	0.025148
7.0	0.47517	0.13772	0.73971	0.032049
7.5	0.60759	0.17489	1.0094	0.040296
8.0	0.76377	0.21896	1.3513	0.050048
8.5	0.94503	0.27057	1.7774	0.061463
9.0	1.1521	0.33032	2.3006	0.074701
9.5	1.3852	0.39875	2.9339	0.089916
10	1.6438	0.47627	3.6901	0.10726
11	2.2187	0.65979	5.6203	0.14885
12	2.8713	0.88030	8.1593	0.20036
13	3.5900	1.1381	11.385	0.26234
14	4.3635	1.4322	15.358	0.33519
15	5.1818	1.7609	20.127	0.41909
16	6.0357	2.1224	25.733	0.51408
17	6.9170	2.5146	32.207	0.62008
18	7.8186	2.9354	39.574	0.73689
19	8.7339	3.3826	47.849	0.86426
20	9.6573	3.8541	57.044	1.0019
25	14.247	6.5048	116.87	1.8302
30	18.555	9.4889	199.03	2.8546
35	22.467	12.648	301.75	4.0266
40	26.032	15.884	423.12	5.3061
45	29.364	19.144	561.68	6.6625
50	32.577	22.405	716.56	8.0737
55	35.677	25.656	887.22	9.5245
60	38.818	28.895	1073.5	11.004
65	41.940	32.125	1275.4	12.504
70	45.047	35.347	1492.8	14.021
75	48.137	38.561	1725.8	15.550
80	51.210	41.765	1974.2	17.088
85	54.266	44.962	2237.9	18.634
90	57.304	48.150	2516.8	20.185
95	60.324	51.329	2810.9	21.741
100	63.326	54.500	3120.0	23.299
110	69.281	60.815	3783.1	26.423
120	75.177	67.096	4505.5	29.551
130	81.024	73.345	5286.5	32.680
140	86.831	79.562	6125.8	35.807
150	92.608	85.750	7023.0	38.930
160	98.362	91.911	7977.9	42.049
170	104.10	98.046	8990.2	45.163
180	109.83	104.16	10060	48.270
190	115.56	110.25	11187	51.372
200	121.29	116.32	12371	54.468
210	127.02	122.38	13613	57.558
220	132.76	128.42	14912	60.642
230	138.51	134.45	16268	63.720
240	144.27	140.47	17682	66.792
250	150.04	146.47	19153	69.859
260	155.83	152.47	20683	72.921
270	161.64	158.46	22270	75.978
273.15	163.47	160.35	22782	76.941
280	167.46	164.44	23915	79.031
290	173.30	170.42	25619	82.079
298.15	178.08	175.29	27051	84.561
300	179.16	176.40	27382	85.124

using this value of $\Delta_f H_m^\circ$ with the CODATA [17] values of $\Delta_f H_m^\circ$ for $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$, we obtain $\Delta_c H_m^\circ = -2345.3 \text{ kJ}\cdot\text{mol}^{-1}$. This value of $\Delta_c H_m^\circ$ is remarkably close to the measured values of $\Delta_c H_m^\circ$ for

D-arabinose(cr), **D**-ribose(cr), and α -**D**-xylose(cr). The estimated values of S_m° and $\Delta_f H_m^\circ$ for **D**-lyxose(cr) have been included in table 8.

TABLE 7
Catalogue of thermochemical measurements at $T = 298.15 \text{ K}$.^a

Reaction or substance	Property	Value	Reference	Note	Weight
$\alpha\text{-D-xylose}(\text{cr}) + 7.5 \text{ O}_2(\text{g}) = 5 \text{ CO}_2(\text{g}) + 5 \text{ H}_2\text{O}(\text{l})$	$\Delta_r H_m^0$	$-(2340.1 \pm 0.9) \text{ kJ}\cdot\text{mol}^{-1}$	[26]	<i>b</i>	0
$\alpha\text{-D-xylose}(\text{cr}) + 7.5 \text{ O}_2(\text{g}) = 5 \text{ CO}_2(\text{g}) + 5 \text{ H}_2\text{O}(\text{l})$	$\Delta_r H_m^0$	$-(2342.2 \pm 0.8) \text{ kJ}\cdot\text{mol}^{-1}$	This study		1
$\alpha\text{-D-xylose}(\text{cr})$	S_m^0	$143.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	[27]	<i>c</i>	0
$\alpha\text{-D-xylose}(\text{cr})$	S_m^0	$(175.3 \pm 1.9) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	This study		1
$\alpha\text{-D-xylose}(\text{cr}) = \alpha\text{-D-xylose}(\text{aq})$	$\Delta_r H_m^0$	$(12.1 \pm 0.17) \text{ kJ}\cdot\text{mol}^{-1}$	[33]	<i>d</i>	0
$\alpha\text{-D-xylose}(\text{cr}) = \text{D-xylose}(\text{aq})$	$\Delta_r H_m^0$	$(12.10 \pm 0.12) \text{ kJ}\cdot\text{mol}^{-1}$	[1]		1
$\alpha\text{-D-xylose}(\text{cr}) = \text{D-xylose}(\text{aq})$	$\Delta_r C_{p,m}^0$	$-(6.7 \pm 0.9) \text{ kJ}\cdot\text{mol}^{-1}$	[1]	<i>e</i>	1
$\alpha\text{-D-lyxose}(\text{cr}) = \alpha\text{-D-lyxose}(\text{aq})$	$\Delta_r H_m^0$	$(10.10 \pm 0.01) \text{ kJ}\cdot\text{mol}^{-1}$	[33]		0
$\alpha\text{-D-lyxose}(\text{cr}) = \alpha\text{-D-lyxose}(\text{aq})$	$\Delta_r C_{p,m}^0$	$-(8.3 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$	[34]	<i>f</i>	1
$1,4\text{-}\beta\text{-D-xylobiose}(\text{am}) = 1,4\text{-}\beta\text{-D-xylobiose}(\text{aq})$	$\Delta_r H_m^0$	$-(8.1 \pm 2.7) \text{ kJ}\cdot\text{mol}^{-1}$	[1]		1
$1,4\text{-}\beta\text{-D-xylotriose}(\text{am}) = 1,4\text{-}\beta\text{-D-xylotriose}(\text{aq})$	$\Delta_r H_m^0$	$-(24.1 \pm 6.4) \text{ kJ}\cdot\text{mol}^{-1}$	[1]		1
$1,4\text{-}\beta\text{-D-xylobiose}(\text{aq}) + \text{H}_2\text{O}(\text{l}) = 2 \text{ D-xylose}(\text{aq})$	$\Delta_r H_m^0$	$(0.12 \pm 0.26) \text{ kJ}\cdot\text{mol}^{-1}$	[35]		1
$1,4\text{-}\beta\text{-D-xylobiose}(\text{aq}) + \text{H}_2\text{O}(\text{l}) = 2 \text{ D-xylose}(\text{aq})$	$\Delta_r C_{p,m}^0$	$-(18.05 \pm 0.25) \text{ kJ}\cdot\text{mol}^{-1}$	[35]		1
$1,4\text{-}\beta\text{-D-xylotriose}(\text{aq}) + \text{H}_2\text{O}(\text{l}) = 1,4\text{-}\beta\text{-D-xylobiose}(\text{aq}) + \text{D-xylose}(\text{aq})$	$\Delta_r C_{p,m}^0$	$-18.05 \text{ kJ}\cdot\text{mol}^{-1}$	[35]	<i>g</i>	1
$\text{D-xylose}(\text{aq}) = \text{D-xylulose}(\text{aq})$	$\Delta_r H_m^0$	$22.3 \text{ kJ}\cdot\text{mol}^{-1}$	[36]	<i>h</i>	0
$\text{D-xylose}(\text{aq}) = \text{D-xylulose}(\text{aq})$	$\Delta_r H_m^0$	$(16.09 \pm 0.67) \text{ kJ}\cdot\text{mol}^{-1}$	[37]		1
$\text{D-xylose}(\text{aq}) = \text{D-xylulose}(\text{aq})$	$\Delta_r H_m^0$	$18.8 \text{ kJ}\cdot\text{mol}^{-1}$	[38]	<i>i</i>	0
$\text{D-xylose}(\text{aq}) = \text{D-xylulose}(\text{aq})$	$\Delta_r C_{p,m}^0$	$4.22 \text{ kJ}\cdot\text{mol}^{-1}$	[39]	<i>j</i>	0
$\text{D-xylose}(\text{aq}) = \text{D-xylulose}(\text{aq})$	$\Delta_r C_{p,m}^0$	$4.38 \text{ kJ}\cdot\text{mol}^{-1}$	[40]	<i>k</i>	0
$\text{D-xylose}(\text{aq}) = \text{D-xylulose}(\text{aq})$	$\Delta_r C_{p,m}^0$	$5.37 \text{ kJ}\cdot\text{mol}^{-1}$	[36]		0
$\text{D-xylose}(\text{aq}) = \text{D-xylulose}(\text{aq})$	$\Delta_r C_{p,m}^0$	$(4.39 \pm 0.03) \text{ kJ}\cdot\text{mol}^{-1}$	[37]		1
$\text{D-xylose}(\text{aq}) = \text{D-xylulose}(\text{aq})$	$\Delta_r C_{p,m}^0$	$4.99 \text{ kJ}\cdot\text{mol}^{-1}$	[38]		0
$\text{D-xylulose}(\text{aq}) = \text{D-lyxose}(\text{aq})$	$\Delta_r C_{p,m}^0$	$-2.33 \text{ kJ}\cdot\text{mol}^{-1}$	[41]	<i>l</i>	1
$\text{D-xylulose}(\text{aq}) = \text{D-lyxose}(\text{aq})$	$\Delta_r C_{p,m}^0$	$-3.64 \text{ kJ}\cdot\text{mol}^{-1}$	[42]		1
$\text{D-xylose}(\text{aq}) = \text{H}^+(\text{aq}) + \text{D-xylose}^-(\text{aq})$	$\Delta_r H_m^0$	$(34.31 \pm 0.84) \text{ kJ}\cdot\text{mol}^{-1}$	[43]		0
$\text{D-xylose}(\text{aq}) = \text{H}^+(\text{aq}) + \text{D-xylose}^-(\text{aq})$	$\Delta_r H_m^0$	$(37.66 \pm 0.84) \text{ kJ}\cdot\text{mol}^{-1}$	[44]		1
$\text{D-xylose}(\text{aq}) = \text{H}^+(\text{aq}) + \text{D-xylose}^-(\text{aq})$	$\Delta_r C_{p,m}^0$	$69.3 \text{ kJ}\cdot\text{mol}^{-1}$	[45]	<i>m</i>	1
$\text{D-xylose}(\text{aq}) = \text{H}^+(\text{aq}) + \text{D-xylose}^-(\text{aq})$	$\Delta_r C_{p,m}^0$	$69.2 \text{ kJ}\cdot\text{mol}^{-1}$	[46]	<i>n</i>	1
$\text{D-xylose}(\text{aq}) = \text{H}^+(\text{aq}) + \text{D-xylose}^-(\text{aq})$	$\Delta_r C_{p,m}^0$	$67.8 \text{ kJ}\cdot\text{mol}^{-1}$	[47]	<i>o</i>	0
$\text{D-xylose}(\text{aq}) = \text{H}^+(\text{aq}) + \text{D-xylose}^-(\text{aq})$	$\Delta_r C_{p,m}^0$	$(70.16 \pm 0.17) \text{ kJ}\cdot\text{mol}^{-1}$	[43]		0
$\text{D-xylose}(\text{aq}) = \text{H}^+(\text{aq}) + \text{D-xylose}^-(\text{aq})$	$\Delta_r C_{p,m}^0$	$(69.36 \pm 0.12) \text{ kJ}\cdot\text{mol}^{-1}$	[44]		1
$\text{D-lyxose}(\text{aq}) = \text{H}^+(\text{aq}) + \text{D-lyxose}^-(\text{aq})$	$\Delta_r H_m^0$	$(33.47 \pm 0.84) \text{ kJ}\cdot\text{mol}^{-1}$	[43]		1
$\text{D-xylose}^-(\text{aq}) = \text{H}^+(\text{aq}) + \text{D-xylose}^{2-}(\text{aq})$	$\Delta_r C_{p,m}^0$	$81.6 \text{ kJ}\cdot\text{mol}^{-1}$	[47]	<i>o</i>	0
$\text{D-lyxose}(\text{aq}) = \text{H}^+(\text{aq}) + \text{D-lyxose}^-(\text{aq})$	$\Delta_r C_{p,m}^0$	$(69.12 \pm 0.17) \text{ kJ}\cdot\text{mol}^{-1}$	[43]		1
$\text{D-lyxose}(\text{aq}) = \text{H}^+(\text{aq}) + \text{D-lyxose}^-(\text{aq})$	$\Delta_r C_{p,m}^0$	$(69.12 \pm 0.17) \text{ kJ}\cdot\text{mol}^{-1}$	[44]		1
$\text{xylitol}(\text{aq}) = \text{D-xylulose}(\text{aq}) + \text{H}_2(\text{g})$	$\Delta_r H_m^0$	$71.34 \text{ kJ}\cdot\text{mol}^{-1}$	[48]	<i>p</i>	1
$\text{xylitol}(\text{aq}) = \text{D-xylulose}(\text{aq}) + \text{H}_2(\text{g})$	$\Delta_r C_{p,m}^0$	$39.08 \text{ kJ}\cdot\text{mol}^{-1}$	[48]	<i>p</i>	1
$\alpha\text{-D-xylose}(\text{cr})$	$C_{p,m}^0$	$184 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	[49]	<i>q</i>	1
$\alpha\text{-D-xylose}(\text{cr})$	$C_{p,m}^0$	$184 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	[33]	<i>r</i>	1
$\alpha\text{-D-xylose}(\text{cr})$	$C_{p,m}^0$	$(178.1 \pm 1.8) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	This study		1
$\alpha\text{-D-xylose}(\text{aq})$	$C_{p,m}^0$	$(281 \pm 2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	[49]	<i>q</i>	1
$\alpha\text{-D-lyxose}(\text{cr})$	$C_{p,m}^0$	$184 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	[33]	<i>s</i>	1
$\alpha\text{-D-xylose}(\text{cr}) = \text{D-xylose}(\text{aq})$	$C_{p,m}^0$	$(102 \pm 17) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	[33]	<i>s</i>	0
$\text{D-lyxose}(\text{cr}) = \text{D-lyxose}(\text{aq})$	$\Delta_r C_{p,m}^0$	$(101 \pm 12) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	[33]		1
$\text{D-xylose}(\text{aq}) = \text{D-xylulose}(\text{aq})$	$\Delta_r C_{p,m}^0$	$(40 \pm 23) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	[37]	<i>t</i>	1
$\text{D-xylose}(\text{aq}) = \text{H}^+(\text{aq}) + \text{D-xylose}^-(\text{aq})$	$\Delta_r C_{p,m}^0$	$-103 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	[44]	<i>u</i>	1
$\text{D-lyxose}(\text{aq}) = \text{H}^+(\text{aq}) + \text{D-lyxose}^-(\text{aq})$	$\Delta_r C_{p,m}^0$	$-117 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	[44]	<i>u</i>	1

^a The quantities $\Delta_r H_m^0$, $\Delta_r C_{p,m}^0$, and $\Delta_r C_{p,m}^0$ are, respectively, the standard molar enthalpy, standard molar Gibbs energy, and standard molar heat-capacity changes for the specified reaction. The quantities $C_{p,m}^0$ and S_m^0 are, respectively, the standard molar heat capacity and the standard molar entropy for the specified substance. The standard state for the solute is the hypothetical ideal solution of unit molality ($m^\circ = 1 \text{ mol}\cdot\text{kg}^{-1}$) and the standard state for the solvent is the pure solvent. The standard pressure $p^\circ = 0.1 \text{ MPa}$. The empirical formulas of the substances are given in table 8. The uncertainties in the values are those reported by the authors of the respective publications.

^b The value of $\Delta_r H_m^0$ reported by Skuratov *et al.* [26] at $T = 293.15 \text{ K}$ was adjusted to $T = 298.15 \text{ K}$. This calculation and the early results of Berthelot [24] and of Karrer and Fioroni [25] are discussed in Section 3.3.

^c Miller's [27] result is based on measured standard molar heat capacities for $T > 100 \text{ K}$.

^d Jasra and Ahluwalia [33] measured values of the standard molar enthalpy of solution of both **D-xylose**(cr) and **L-xylose**(cr) into $\text{H}_2\text{O}(\text{l})$. The value given here is the average of these two values. The uncertainty covers both of the reported values.

^e Goldberg *et al.* [1] summarized the results of six studies [34,50–54] where the solubility of for $\alpha\text{-D-xylose}(\text{cr})$ was measured. From the temperature dependence of the solubilities, they [1] also calculated the following values of the standard molar enthalpy of solution $\Delta_{\text{sol}} H_m^0$: $16.4 \text{ kJ}\cdot\text{mol}^{-1}$ from Jacobsen [51]; $16.5 \text{ kJ}\cdot\text{mol}^{-1}$ from Jónsdóttir *et al.* [52]; and $15.9 \text{ kJ}\cdot\text{mol}^{-1}$ from Zhang *et al.* [54].

^f This is an unpublished result of Tewari cited in reference 3. The value of the standard molar Gibbs energy of solution $\Delta_{\text{sol}} G_m^0$ is based on a reported saturation molality $m(\text{sat}) = 17.84 \text{ mol}\cdot\text{kg}^{-1}$ and an estimated activity coefficient $\gamma = 1.6$.

^g Based on the assumption that the value of the equilibrium constant for this reaction is the same as for the reaction $\{1,4\text{-}\beta\text{-D-xylobiose}(\text{aq}) + \text{H}_2\text{O}(\text{l}) = 2 \text{ D-xylose}(\text{aq})\}$.

^h The value of $\Delta_r H_m^0$ is based on the values of the equilibrium constant obtained at five different temperatures.

ⁱ The value of $\Delta_r H_m^0$ is based on the values of the equilibrium constant at six different temperatures.

^j The value of the equilibrium constant K reported by Hochster and Watson [39] at $T = 300.15 \text{ K}$ was adjusted to $T = 298.15 \text{ K}$ by using a value of $\Delta_r H_m^0 = 16.09 \text{ kJ}\cdot\text{mol}^{-1}$ for the reaction.

^k The value of the equilibrium constant K reported by Slein [40] at $T = 303.15 \text{ K}$ was adjusted to $T = 298.15 \text{ K}$ by using a value of $\Delta_r H_m^0 = 16.09 \text{ kJ}\cdot\text{mol}^{-1}$ for the reaction.

^l The value of the equilibrium constant at $T = 298.15 \text{ K}$ is assumed to have the same value as that measured at $T = 303.15 \text{ K}$.

^m The value of the equilibrium constant reported by Osaka [45] at $T = 293.15 \text{ K}$ was adjusted to $T = 298.15 \text{ K}$ by using a value of $\Delta_r H_m^0 = 37.7 \text{ kJ}\cdot\text{mol}^{-1}$.

ⁿ The value of the equilibrium constant reported by Michaelis [46] at $T = 291 \text{ K}$ was adjusted to $T = 298.15 \text{ K}$ by using a value of $\Delta_r H_m^0 = 37.7 \text{ kJ}\cdot\text{mol}^{-1}$.

^o The temperature and ionic strength were not specified by Schaal [47].

^p Tewari and Goldberg [48] measured the apparent equilibrium constant K and the calorimetric molar enthalpy change $\Delta_r H_m(\text{cal})$ for the overall biochemical reaction {xylitol(aq) + NAD_{ox}(aq) = **D**-xylulose(aq) + NAD_{red}(aq)}. With these measured values, they [48] calculated equilibrium constants and values of $\Delta_r H_m^o$ and $\Delta_r G_m^o$ for the reference reaction {xylitol(aq) + NAD_{ox}(aq) = **D**-xylulose(aq) + NAD_{red}²⁻ + H⁺(aq)}. Then, they [48] adjusted the values of $\Delta_r H_m^o$ and $\Delta_r G_m^o$ recommended by Miller and Smith-Magowan [55] for the reaction {NAD_{ox}(aq) + H₂(g) = NAD_{red}²⁻ + H⁺(aq)} to ionic strength $I = 0$. Combination of the two aforementioned reactions gives the reaction {xylitol(aq) = **D**-xylulose(aq) + H₂(g)}. The values of $\Delta_r H_m^o$ and $\Delta_r G_m^o$ for this last reaction are given in this table.

^q The value of $C_{p,m}^o$ reported by Kawaizumi et al. [49] was measured at $T = 303.15$ K.

^r Jasra and Ahluwalia [33] reported values for the standard molar heat capacities $C_{p,m}^o$ of **D**-lyxose(cr) and **D**-xylose(cr). However, it is not clear how these values were derived from their measurements.

^s Jasra and Ahluwalia [33] reported values for $\Delta C_{p,m}^o$ obtained from the measurement of $\Delta_{\text{rot}} H_m^o$ of **D**-xylose(cr) and **L**-xylose(cr) at two temperatures. The value given in the table is the average of these two values of $\Delta C_{p,m}^o$. The uncertainty covers both of the reported values.

^t Based on values of $\Delta_r H_m^o$ at five different temperatures.

^u Based on values of $\Delta_r H_m^o$ at two different temperatures.

TABLE 8

Selected values of the standard molar enthalpy of formation $\Delta_f H_m^o$, standard molar Gibbs energy of formation $\Delta_f G_m^o$, standard molar entropy S_m^o , standard molar heat capacity $C_{p,m}^o$, and the relative molecular masses M_r for the substances of interest to this study at $T = 298.15$ K and $p^o = 0.1$ MPa.^a

Substance and state	Formula	M_r	$\Delta_f H_m^o / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_f G_m^o / (\text{kJ} \cdot \text{mol}^{-1})$	$S_m^o / (\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	$C_{p,m}^o / (\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
α - D -xylose(cr)	C ₅ H ₁₀ O ₅	150.13	-1054.50	-750.48	175.29	178.1
D -xylose(aq)	C ₅ H ₁₀ O ₅	150.13	-1042.40	-757.18	238.35	281
D -xylose ⁻ (aq)	C ₅ H ₉ O ₅	149.12	-1004.74	-687.82	132.02	384
D -xylose ²⁻ (aq)	C ₅ H ₈ O ₅ ²⁻	148.12		-606.22		
D -lyxose(cr)	C ₅ H ₁₀ O ₅	150.13	-1051.5 ^b	-747.47	175.5 ^b	184
D -lyxose(aq)	C ₅ H ₁₀ O ₅	150.13		-755.77		285
D -lyxose ⁻ (aq)	C ₅ H ₉ O ₅	149.12		-686.65		168
D -xylulose(aq)	C ₅ H ₁₀ O ₅	150.13	-1026.31	-752.79	277.59	321
xylitol(aq)	C ₅ H ₁₂ O ₅	152.15	-1097.65	-791.87	300.07	
1,4- D -xylobiose(am)	C ₁₀ H ₁₈ O ₉	282.24	-1790.99			
1,4- D -xylobiose(aq)	C ₁₀ H ₁₈ O ₉	282.24	-1799.09	-1259.17	345.80	
1,4- β - D -xylotriose(am)	C ₁₅ H ₂₆ O ₁₃	414.36	-2531.38			
1,4- D -xylotriose(aq)	C ₁₅ H ₂₆ O ₁₃	414.36	-2555.48	-1761.16	454.26	

^a The standard state for the solute is the hypothetical ideal solution of unit molality ($m^o = 1$ mol·kg⁻¹) and the standard state for the solvent is the pure solvent. Additional numbers of significant figures are included in the values of the formation properties in order to preserve the integrity of the values of calculated properties.

^b This is an estimated value (see Section 3.4).

Note that in table 8, only the thermodynamic properties of the **D** forms of the substances are shown. However, the values of the thermodynamic properties of the pure **D** and **L** forms are predicted by theory to be the same. For a system that exhibits ideal behaviour, the molar entropy of a mixture of **D** and **L** forms is given by:

$$S(\mathbf{DL}) = S(\mathbf{D}) - R(x_{\mathbf{D}} \ln x_{\mathbf{D}} + x_{\mathbf{L}} \ln x_{\mathbf{L}}). \quad (7)$$

Here, $x_{\mathbf{D}}$ and $x_{\mathbf{L}}$ are, respectively, the mole fractions of the **D** and **L** forms in the mixture, $S(\mathbf{D})$ is the molar entropy of the pure **D** form, and R is the molar gas constant. Thus, the Gibbs energy of an ideal **DL** mixture is given by

$$G(\mathbf{DL}) = H(\mathbf{DL}) - TS(\mathbf{DL}). \quad (8)$$

Since the enthalpy of the **DL** mixture will be same as the enthalpy of the pure **D** or **L** form, one obtains

$$\begin{aligned} G(\mathbf{DL}) &= H(\mathbf{D}) - TS(\mathbf{DL}) \\ &= H(\mathbf{D}) - T\{S(\mathbf{D}) - R(x_{\mathbf{D}} \ln x_{\mathbf{D}} + x_{\mathbf{L}} \ln x_{\mathbf{L}})\}. \end{aligned} \quad (9)$$

Rearrangement of equation (9) gives

$$G(\mathbf{DL}) = G(\mathbf{D}) + RT(x_{\mathbf{D}} \ln x_{\mathbf{D}} + x_{\mathbf{L}} \ln x_{\mathbf{L}}). \quad (10)$$

Application of equation (10) to the standard molar formation properties gives

$$\Delta_f G_m^o(\mathbf{DL}) = \Delta_f G_m^o(\mathbf{D}) + RT(x_{\mathbf{D}} \ln x_{\mathbf{D}} + x_{\mathbf{L}} \ln x_{\mathbf{L}}). \quad (11)$$

Thus, if one knows $\Delta_f G_m^o(\mathbf{D})$, and the mole fractions of a **DL** mixture, equation (11) allows for the calculation of $\Delta_f G_m^o$ for that **DL** mixture. Since the temperature and pressure derivatives of the entropy of mixing term in equation (7) are zero, all of the other thermodynamic properties (i.e., those derived as temperature or pressure derivatives of the Gibbs energy) of **DL** mixtures are

predicted to be identical to those of the pure **D** or **L** forms. This discussion is valid for systems that exhibit ideal behaviour, i.e., gases and dilute solutions. One cannot expect it to be valid for solids or for liquids that have significant structure, e.g., a crystal lattice.

The thermodynamic network calculations described above were enabled by the fact that the thermodynamic properties G , H , S , and C_p are state functions. The assembled set of reactions, substances, and property values given in table 7 is referred to as a reaction catalogue. However, such a table or catalogue can be *substantially* expanded to include a wide variety of biochemical reactions and substances. This, in turn, would allow for many more network calculations to be performed. For example, see the Thermodynamics of Enzyme-catalyzed Reactions Database [56] for a survey of property values for biochemical reactions. Having a very large catalogue of thermochemical property values available would allow for the calculation of properties for many reactions and substances which have not been the subject of direct measurement and would also reveal discrepancies in existing measurements. Most importantly, reliable thermodynamic property values would permit the estimation (e.g., the Benson approach) of many other property values and greatly enhance the utilization of thermodynamics for practical applications in bio-manufacturing, in medical research, and in quantitative biochemistry (i.e., metabolic control analysis).

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