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A thermodynamic investigation of the cellulose allomorphs: Cellulose(am), cellulose Iβ(cr), cellulose II(cr), and cellulose III(cr) ☆

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ABSTRACT

The thermochemistry of samples of amorphous cellulose, cellulose I, cellulose II, and cellulose III was studied by using oxygen bomb calorimetry, solution calorimetry in which the solvent was cadoxen (a cadmium ethylenediamine solvent), and with a Physical Property Measurement System (PPMS) in zero magnetic field to measure standard massic heat capacities $C^{\circ}_{p,w}$ over the temperature range $T = (2$ to $302)$ K. The samples used in this study were prepared so as to have different values of crystallinity indexes *CI* and were characterized by X-ray diffraction, by Karl Fischer moisture determination, and by using gel permeation chromatography to determine the weight average degree of polymerization DP_w. NMR measurements on solutions containing the samples dissolved in cadoxen were also performed in an attempt to resolve the issue of the equivalency or non-equivalency of the nuclei in the different forms of cellulose that were dissolved in cadoxen. While large differences in the NMR spectra for the various cellulose samples in cadoxen were not observed, one cannot be absolutely certain that these cellulose samples are chemically equivalent in cadoxen. Equations were derived which allow one to adjust measured property values of cellulose samples having a mass fraction of water w_{H_2O} to a reference value of the mass fraction of water w_{ref}. The measured thermodynamic properties (standard massic enthalpy of combustion $\Delta_c H^{\circ}_w$, standard massic enthalpy of solution $\Delta_{sol} H^{\circ}_w$, and $C^{\circ}_{p,w}$) were used in conjunction with the measured *CI* values to calculate values of the changes in the standard massic enthalpies of reaction$\Delta_r H^{\circ *}_w$, the standard massic entropies of reaction $\Delta_r S^{\circ *}_w$, the standard massic Gibbs free energies of reaction $\Delta_r G^{\circ *}_w$, and the standard massic heat capacity $\Delta_r C^{\circ}_{p,w}$, for the interconversion reactions of the pure $(CI = 100)$ cellulose allomorphs, *i.e.*, cellulose(am), cellulose I(cr), cellulose II(cr), and cellulose II(cr), at the temperature $T = 298.15$ K, the pressure $p^{\circ} = 0.1$ MPa, and $w_{H_2O} = 0.073$. The "*" denotes that the thermodynamic property pertains to pure cellulose allomorphs. Values of standard massic enthalpy differences $\Delta^T_0 H^{\circ}_w$, standard massic entropy differences $\Delta^T_0 S^{\circ}_w$, and the standard massic thermal function $\Phi^{\circ}_w = \Delta^T_0 S^{\circ}_w - \Delta^T_0 H^{\circ}_w / T$ were calculated from the measured heat capacities for the cellulose samples and for the pure cellulose allomorphs. The extensive literature pertinent to the thermodynamic properties of cellulose has been summarized and, in many cases, property values have been calculated or recalculated from previously reported data. The thermodynamic property data show that cellulose(am) is the least stable of the cellulose allomorphs considered in this study. However, due to the uncertainties in the measured property values, it is not possible to use these values to order the relative stabilities of the cellulose (I, II, and III) crystalline allomorphs with a reasonable degree of certainty. Nevertheless,

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based on chemical reactivity information, the qualitative order of stability for these three allomorphs is cellulose III(cr) > cellulose II(cr) > cellulose Iβ(cr) at $T = 298.15$ K. However, as evidenced by the fact that cellulose I(cr) can be reformed by the application of heat and water to a sample of cellulose III(cr), the differences in the stabilities of these three allomorphs appear to be small and may be temperature dependent. Standard thermodynamic formation properties as well as property values for the conversion reactions of the cellulose allomorphs to α-D-glucose(cr) have been calculated on the assumption that $S^{\circ}_{w} \rightarrow 0$ as $T \rightarrow 0$. The values for the standard massic Gibbs free energy of reaction $\Delta_r G^{\circ}_{w}$ for the conversion of the cellulose allomorphs to α-D-glucose(cr), with the exception of anhydrous cellulose(am), all have positive values and thus are thermodynamically not favored for mass fractions of water $w_{H_2O} < 0.073$.

1. Introduction

Cellulose, as the most abundant biological substance on Earth, has been the subject of much study [1]. Four distinct crystalline forms of cellulose are known to exist [2]. Cellulose I exists as an α or a β form [3,4]. These two forms have essentially the same backbone but differ in their hydrogen bonding patterns and in the conformations of the anhydroglucose residues and the β-1,4 linkages [5]. Cellulose II can be prepared from cellulose I either by treatment with NaOH or by solubilization followed by recrystallization. Cellulose III is obtained by treatment of either cellulose I or cellulose II with liquid ammonia. Samples of cellulose III prepared from cellulose I are often referred to as cellulose III_I in order to distinguish them from the allomorph cellulose III_{II} prepared from cellulose II. The detailed structural differences between cellulose III_I and cellulose III_{II} have not been established. Cellulose IV is obtained by heating cellulose III. In recent years, X-ray and neutron diffraction studies [5–9] have much improved our understanding of the unit cell structure and hydrogen bonding arrangements in the cellulose allomorphs. Additional information on the cellulose allomorphs can be found in the literature [2,10–12]. Actual samples of cellulose (I, II, and III) share two common features. Specifically, each contains some amorphous cellulose, often at a high mass fraction, and, unless dried thoroughly and handled with extreme care, water is present.

The aim of this study is an improved knowledge of the thermodynamic properties of the following cellulose allomorphs: cellulose(am), cellulose Iβ(cr), cellulose II(cr), and cellulose III(cr). To accomplish this, we prepared samples of the aforementioned allomorphs having various values of crystallinity indexes. We then measured values of these crystallinity indexes *CI*, of the weight average degree of polymerization DP_w, and of the mass fraction of water w_{H_2O} in each of these samples. An early decision was made to work with cellulose samples that contained water. The principal reason for this decision was the fact that naturally occurring celluloses, in fact, contain water. Also, when one is working with anhydrous cellulose, the establishment that all water has been removed without changing the character of the cellulose sample [13] is a matter of concern. Additionally, the handling of anhydrous samples of cellulose requires extreme care.

The terminology, symbols, and conventions used in this study are basic to the thermodynamic discussion and treatment of results. The reader is referred to the "Glossary and conventions" (see section 4).

NMR measurements on solutions containing the samples dissolved in cadoxen, a cadmium ethylenediamine solvent, were also performed. This was followed by measurements of standard massic enthalpies of combustion $\Delta_c H^{\circ}_{w}$ of the samples in an oxygen bomb calorimeter, of standard massic heat capacities $C^{\circ}_{p,w}$ over the temperature range $T = (2$ to $302)$ K, and of standard massic enthalpies of solution $\Delta_{sol} H^{\circ}_{w}$ of the cellulose samples in cadoxen. Equations were derived which allow one to adjust measured property values of cellulose samples having a mass fraction of water w_{H_2O} to a reference value of the mass fraction of water w_{ref}. Thus, the aforementioned measurements led to values of the standard massic enthalpies of reaction $\Delta_r H^{\circ *}_{w}$, the standard massic entropies of reaction $\Delta_r S^{\circ *}_{w}$, and the standard massic Gibbs free energies of reaction $\Delta_r G^{\circ *}_{w}$ for the interconversion reactions of the pure ($CI = 100$) cellulose allomorphs at the temperature $T = 298.15$ K, the pressure $p^{\circ} = 0.1$ MPa, and $w_{H_2O} = 0.073$. The "*" denotes that the thermodynamic property pertains to pure cellulose allomorphs. Values of standard massic enthalpy differences $\Delta^{T}_{0} H^{\circ}_{w}$, standard massic entropy differences $\Delta^{T}_{0} S^{\circ}_{w}$, and the standard massic thermal function $\Phi^{\circ}_{w} = \Delta^{T}_{0} S^{\circ}_{w} - \Delta^{T}_{0} H^{\circ}_{w}/T$ were calculated from the measured heat capacities for the cellulose samples and for the pure allomorphs. The extensive literature pertinent to the thermodynamic properties of cellulose has been summarized and, in many cases, property values have been calculated or recalculated from previously reported data. The comparison of results at different values of w_{H_2O} required values of the standard massic enthalpies of hydration $\Delta_{hyd} H^{\circ *}_{w}$ of the cellulose allomorphs. These values were calculated from results reported in the studies of Nelson [14] and Rees [15]. In addition to having these thermodynamic property values available for practical engineering calculations, a quantitative understanding of the energy relationships amongst the aforementioned allomorphs is important in understanding the biomass recalcitrance problem [16], *i.e.*, the extreme difficulty of converting cellulose to glucose. Standard thermodynamic formation properties as well as property values for the conversion reactions of the cellulose allomorphs to α-D-glucose(cr) have been calculated on the assumption that $S^{\circ}_{w} \rightarrow 0$ as $T \rightarrow 0$.

2. Experimental

2.1. Preparation of cellulose samples

A sample of cellulose Iβ (cotton linters, CAS Number 9004-34-6; catalog number 22183, lot number BCBB5964V) was obtained from Sigma-Aldrich. Amorphous cellulose samples were prepared from the cellulose Iβ sample by using a planetary ball mill (Retsh model PM100, Haan, Germany). In order to evaluate the effect of ball milling on the de-crystallization of cellulose, a sample of the cellulose Iβ was subjected to ball milling for three different time periods, *i.e.* 24 h, 30 h, and 36 h at 25 °C and at 600 rpm using ZrO_2 bowls (volume = 50 mL) and nine ZrO_2 balls. In order to avoid excessive heating of the cellulose sample during ball milling, a 5 min on and 55 min off cycle was employed. Therefore, for 24 h, 30 h, and 36 h periods the effective milling times were 120, 150, and 180 min, respectively. From X-ray diffraction, it was found that each ball milling period (24 to 36) h produced essentially amorphous cellulose with no differences in the crystallinity of the three samples. The ball milled samples are designated respectively as amorphous cellulose (24 h), amorphous cellulose (30 h), and amorphous cellulose (36 h).

Cellulose II samples at different degrees of crystallinity were prepared by the aqueous NaOH treatment of cellulose Iβ (cotton linters – see above) carried out according to the method described by Atalla [17]. To obtain the least crystalline cellulose II sample, a sample of the cotton linters was soaked and stirred in an aqueous NaOH solution (mass fraction = 0.23) at a concentration of 5 g of cotton linters per 100 g of NaOH solution at 25 °C for 50 min under a nitrogen atmosphere. This mix is designated as "mix A". The NaOH solution was removed from this mix by filtration and then the filter cake was extensively washed with distilled water until the wash had a pH of ≈7. This sample is designated as cellulose II (25 °C). For obtaining a moderately crystalline cellulose II sample, a portion of mix A was diluted with deionized water to 17.5 mass per cent NaOH and heated at 70 °C for 50 min. This solution was then further heated at 70 °C under a nitrogen cover at successive NaOH mass fractions of 0.15, 0.12, 0.10, 0.08, 0.04, and 0.01. The lower concentrations of NaOH were obtained by dilution with warm deionized water. A 50 min heating time was used for each NaOH concentration. The mix obtained after the 50 min heating at 0.01 mass fraction NaOH is designated as "mix B." After the final washing with the 0.01 mass fraction NaOH, the cellulose was extensively washed with deionized water at 70 °C to obtain a pH of ≈7. The filtered sample is designated as cellulose II (70 °C). In order to obtain a highly crystalline cellulose II sample, a portion of mix B was dewatered by filtration and immersed in glycerol at 100 °C in a stainless steel reaction vessel (Parr Instrument Co., Model 4520, Moline, IL). After heating the sample at 145 °C for 7 days, the sample was cooled to ≈100 °C and washed with boiling deionized water. This sample is designated as cellulose II (145 °C). All samples were freeze dried after washing.

Cellulose III samples were prepared according to the method described earlier [2]. Briefly, a sample of cellulose Iβ (Fluka cotton linters – see above) having an oven dry equivalent weight (*i.e.*, the mass that would be present if water were to be removed by oven drying) of ≈4 g was placed in a stainless steel reaction vessel (Parr Instrument Company, Model 4714, Moline, IL). The reaction vessel was clamped shut, weighed, and then chilled in a (dry ice + acetone) bath at −75 °C to facilitate transfer of liquid ammonia into the reactor at atmospheric pressure. Anhydrous liquid ammonia was added slowly to the reaction vessel in the ratio ≈2.5 g ammonia per gram of cellulose by using a stainless steel transfer tube from a liquid ammonia cylinder equipped with an eductor tube. After adding ammonia, the vessel was immediately weighed and then cooled in the (dry ice + acetone) bath at −75 °C for 15 min. The vessel was then immersed in a water bath maintained at ≈25 °C until the temperature of the vessel was −33 °C, after which it was removed from the water bath and allowed to vent into a hood until all the ammonia had evaporated. The cellulose sample obtained was observed to be clumped together and retained the shape of the vessel. This clumping may be because the ammonia evaporates very slowly due to the fact that the sample is at ambient pressure. Thus, the sample was gently ground to a powder using a mortar and pestle. The sample obtained is designated as cellulose III (−33 °C). In order to obtain a cellulose III sample of intermediate crystallinity, cotton linters were treated at −75 °C for 15 min as described above, and then the vessel was immersed in a water bath maintained at 25 °C for 5 min. After completion of this reaction period and prior to its removal from the water bath, the treatment was terminated by immediately depressurizing the vessel in a ventilated hood. The ammonia treated cellulose was removed from the vessel and left in the hood overnight until all ammonia had evaporated. This sample is designated as cellulose III (25 °C). In order to obtain a cellulose III sample of high crystallinity, cotton linters were treated at −75 °C for 15 min as described above and then the vessel was immersed in a water bath maintained at 25 °C for 30 min. The vessel was then placed in a preheated fluidized sand bath (Techne Inc., Burlington, NJ) maintained at 130 °C for 1 h. After concluding this final heat treatment and prior to its removal from the sand bath, the reaction vessel was depressurized by allowing the ammonia to leak out in a ventilated hood. After releasing the ammonia, the vessel was cooled in a water bath maintained at 25 °C. The cellulose sample was removed from the vessel and left in the hood overnight until all the ammonia had evaporated. This sample is designated as cellulose III (130 °C). Unlike the cellulose III (−33 °C) sample, there was no clumping observed in the cellulose III (25 °C) and cellulose III (130 °C) samples. Chemical composition analyses of all the cellulose allomorphs were performed by using a previously described procedure [18]. This analysis showed (99 to 100)% glucan content for all the samples suggesting that no degradation of cellulose occurred during the various chemical treatments.

2.2. Preparation and handling of cadoxen

Cadoxen was prepared according to the method of Ladisch [19]. A mass (280 g) of redistilled ethylenediamine (Sigma Aldrich, St. Louis, MO) was mixed with 720 g nanopure water and saturated with CdO (Sigma Aldrich, St. Louis MO). Saturation was carried out in a stirred glass reaction bottle at −5 °C. Approximately 10 g of CdO was added to the bottle every 20 min until 90 g had been added. The solution was stirred for 3 h and then left to settle overnight. The clear solution was decanted into a new bottle, and the saturation process was repeated. After settling overnight, the solution was centrifuged in polypropylene centrifuge bottles at 8000 × G for 30 min. The stock solution of cadoxen was stored at 4 °C in glass bottles wrapped in aluminum foil and kept out of the light except for a few minutes during its transfer to the solution calorimeter. It was observed that a white precipitate formed in the bottom of a bottle holding cadoxen when a sample of cadoxen stock solution was brought from 4 °C to ambient temperature {typically (22.0 to 22.5) °C} and allowed to equilibrate at this temperature. While a chemical analysis of the precipitate was not done, it is highly likely that the precipitate is cadmium oxide (CdO). Thus, the cadoxen was preconditioned by allowing for the aforementioned precipitation to take place. Only the clear supernatant from this equilibrated solution was used for the dissolution of the cellulose samples in the solution calorimetry and NMR experiments. The provenance and purities of the materials used in this study is given in table 1.

2.3. X-ray diffraction measurements

The crystallinity indexes (*CI*) of cellulose samples were measured by X-ray diffraction (XRD) by using a Rigaku (Tokyo, Japan) Ultima IV diffractometer with CuK_α radiation having a wavelength $\lambda(K_\alpha 1) = 0.15406$ nm generated at 40 kV and 44 mA. The diffraction intensities of freeze dried samples placed on a quartz substrate were measured in the range of 8° to 42° 2θ using a step size of 0.02° at a rate of $2^\circ \cdot min^{-1}$. The crystallinity indexes of the cellulose samples were measured according to the amorphous subtraction method described by Park *et al.* [20,21]. Briefly, a diffractogram of the 36 h ball-milled cotton linter cellulose prepared according to the method mentioned in section 2.1 was subtracted from the diffractograms of the other cellulose samples so as to remove the influence of the amorphous component in the diffractograms. The ratio of the integrated area of each subtracted diffractogram to the area of the original diffractogram was then calculated and multiplied by 100 to give the *CI* value of the sample. The X-ray diffractograms for the cellulose samples are shown in figure 1.

2.4. Measurement of weight average degree of polymerization

Values of the weight average degree of polymerization (DP_w) of the various forms of cellulose were measured by using gel permeation chromatography (GPC). The procedure was modified from prior methods [22–24]. Cellulose samples were first carbanilated so that they would dissolve in the SEC eluant tetrahydrofuran (THF). Thus, a 10 mg mass of a vacuum dried cellulose sample was placed in a 5 mL reaction vial and 2 mL of dry pyridine and 0.4 mL of phenyl isocyanate were added. The reaction vial was kept at 70 °C for 24 h to complete the reaction. Methanol (Baker HPLC grade, 0.4 mL) was added to the reaction mixture to react with the excess phenyl isocyanate at the end of the reaction. The carbanilated cellulose was then precipitated in 26 mL of methanol:water (7:3, v/v) and the precipitate was washed twice with methanol/water (26 mL). The washed cellulose carbanilates were dissolved in THF (Baker HPLC grade, 20 mL) and the solutions filtered (0.45 μm nylon membrane syringe filters) before analysis.

Gel permeation chromatography (GPC) analysis was performed using a high-performance liquid chromatograph (model HP1050, Agilent Technologies Inc.) and five columns (Polymer Laboratories Ltd, 300 mm·7.5 mm) containing polystyrene-divinyl benzene copolymer gel beads (10 μm diameter) having nominal pore diameters of (10^3, 10^4, 10^5, 10^6 and 10^7)·10^{-10} m, connected in series in order of decreasing pore diameter. A calibration curve based on polystyrene standards of known molar mass (relative molecular mass) was obtained that allowed conversion of retention times into weight average molar masses (M_w). Consequently, all weight average molar masses determined in this work are not absolute but are relative to the calibration curve. The conditions for the chromatography were as follows: flow rate 1.0 mL·min^{-1}; UV detector wavelength 235 nm (with a bandwidth of 10 nm), injection volume 50 μL; and column temperature t = 25 °C. Values of the weight average molar mass were calculated using Cirrus GPC software (Polymer Laboratories Ltd). The DP_w values were then calculated by dividing the apparent molar mass by 519 (the molar mass of a repeating unit of carbanilated cellulose with a degree of substitution of 3.0).

2.5. Karl Fischer measurements

The mass fractions of water in the cellulose samples were measured by using Karl Fischer analyses with a Metrohm 795 KFT Titrino automatic titrator and a Metrohm 831 KF coulometer (Metrohm USA, Tampa, FL). The entire apparatus is enclosed in a transparent plastic tent that is kept under a positive pressure with dry nitrogen gas. The temperature was ambient (≈22.0 °C) with daily variations generally being less than ±0.3 K. Approximately 70 cm^3 of (methanol + formamide) in the volumetric ratio methanol:formamide = 2.5 were placed in the Karl Fischer apparatus and then titrated with Hydranal Composite 2 (Sigma-Aldrich, St. Louis, MO). This titration was continued overnight in order to obtain stable minimal drifts which were typically <2 · 10^{-5} cm^3·s^{-1}. The apparatus was calibrated by using ≈0.073 g of water-saturated octanol solution which was injected into the Karl Fischer apparatus through a septum. The mass fraction solubility of water in octanol w = (0.04874 ± 0.00013) at 22.0 °C was taken from the study of Lang [25]. Approximately 0.020 g of each cellulose sample was weighed into a platinum cup. A cup and its contents were then dropped into the Karl Fischer apparatus. The time allowed for the (octanol + water) calibrations was 30 min. A time of 60 min was allowed for the titration of the cellulose samples. The drifts observed during the last 10 min of each titration were consistent with the minimal drifts that were obtained following the overnight titration with no sample in the apparatus. The masses of all samples were determined gravimetrically by using a calibrated balance that had a readability of ±0.01 mg.

TABLE 1
The provenance and estimated mass fraction purities w of the materials used in this study.

Substance	Mass fraction	Source
Amorphous cellulose (24 h)	>0.99	[a]
Amorphous cellulose (30 h)	>0.99	[a]
Amorphous cellulose (36 h)	>0.99	[a]
Cadoxen[b]	>0.98[c]	[a]
Cellulose Iβ[d]	>0.995[e]	Sigma–Aldrich
Cellulose II (25 °C)	>0.99[e]	[a]
Cellulose II (70 °C)	>0.99[e]	[a]
Cellulose II (145 °C)	>0.99[e]	[a]
Cellulose III (−33 °C)	>0.99[e]	[a]
Cellulose III (25 °C)	>0.99[e]	[a]
Cellulose III (130 °C)	>0.99[e]	[a]
Copper	>0.99999[f]	Alfa Aesar
Water	[g]	NIST

[a] Prepared for this study (see section 2.1).
[b] Cadoxen has the empirical formula $C_6H_{24}CdN_6{\cdot}2H_2O$. Its Chemical Abstracts Service (CAS) registry number is 14874-24-9.
[c] This purity is estimated.
[d] The CAS registry number of cellulose is 9004-34-6. There do not appear to be separate registry numbers for the several cellulose allomorphs.
[e] This purity is estimated and is based, in part, on the information on purity provided by the supplier of the cellulose Iβ sample. This sample also contained a substantial amount of amorphous cellulose (see table 2).
[f] Based on information provided by the supplier.
[g] The mass fraction of organic substances in the NIST supplied distilled water was less than 2 · 10^{-9}. The conductivity of this water was ≈12.6 MΩ.

2.6. NMR measurements

NMR spectra (^{1}H, ^{13}C, and ^{113}Cd) were obtained for the cellulose samples dissolved in cadoxen. Masses of cellulose were dissolved in cadoxen by lateral shaking (≈100 shakes per minute) in a thermostat set at 25.0 °C. It was observed that the cellulose samples dissolved completely in the cadoxen within three hours lateral shaking. The solutions prepared from amorphous (ball-milled) cellulose, cellulose Iβ, and cellulose III were crystal clear. However, the solutions prepared from cellulose II had a murky appearance. For this reason, the samples of cellulose II were prepared at approximately one-half the mass fraction of the amorphous and cellulose Iβ and II samples. As a control, one sample of amorphous cellulose (36 h) was run at the same concentration as that used for the cellulose II samples. The collection of the NMR spectra was started within six hours following the preparation of the cellulose samples in cadoxen.

Each NMR sample was prepared by transferring ≈0.55 cm^3 of solution by glass pipette into a 5 mm thin-walled precision 600 MHz NMR tube (Wilmad 535-pp-7). A coaxial insert (Wilmad WGS-5BL) was then inserted into the tube containing approximately 0.070 cm^3 of a solution (28 mg·cm^{-3} of trimethyl-silylpropionate (TMSP-2,2,3,3-D4, Cambridge Isotope Laboratories DLM-48-1, DSO #12E-319, Lot no. L1-12486) in D_2O (99.9%, Cambridge Isotope Laboratories DLM-4-25, Lot no. 12E-521) that provided the lock signal and ^{1}H and ^{13}C chemical shift references. The same coaxial insert was used for all samples after appropriate cleaning. All samples were run in a Bruker Avance II 600 MHz NMR spectrometer system operating at a ^{1}H frequency of 600.13 MHz and equipped with a 5 mm broadband inverse probe. The temperature of the sample, based on a 99.8% methanol-d4 temperature calibration, was 20.0 °C. All pulse sequences used were standard Bruker pulse programs provided in the Topspin software (version 3.1, Bruker). The ^{1}H spectra were recorded using a 30° pulse angle (zg30 pulse program), 12.0 KHz spectral width, 64K complex data points

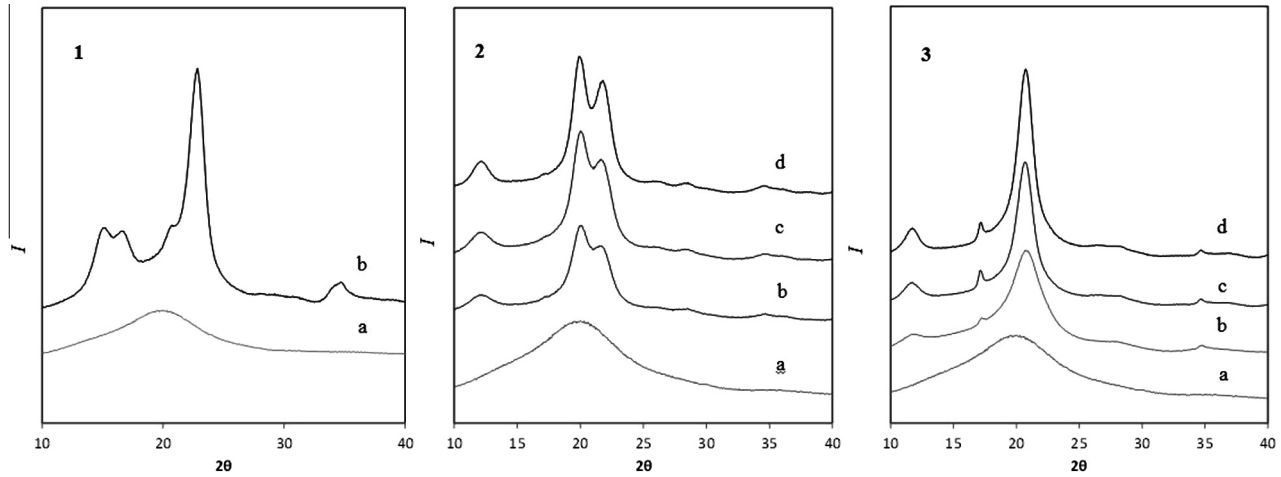

FIGURE 1. X-ray diffractograms (signal intensity *I vs.* the scattering angle 2θ): (1) XRDs for the amorphous cellulose (36 h) sample (1a) and for the cellulose Iβ sample (1b); (2) XRDs for the amorphous cellulose (36 h) sample (2a) and for the cellulose II samples prepared at different degrees of crystallinity {2b, cellulose II (25 °C); 2c, cellulose II (70 °C); and 2d, cellulose II (145 °C)}; and (3) XRDs for the amorphous cellulose (36 h) sample (3a) and for the cellulose III samples prepared at different degrees of crystallinity {3b, cellulose II (−33 °C); 3c, cellulose II (25 °C); and 3d, cellulose II (130 °C)}.

(2.73 s acquisition time), 8 s relaxation delay, and either 16 or 64 scans. The ^{1}H 90° pulse angles were determined for each sample and used in the acquisition of both ^{1}H and ^{13}C spectra. The ^{13}C spectra were recorded with ^{1}H power-gated decoupling (zgpg pulse program), a 36.0 KHz spectral width, 32k complex data points (0.45 s acquisition time), 1 s relaxation delay, 8192 scans, and 128 dummy scans. The ^{113}Cd spectra were recorded using a 90° pulse angle (zg pulse program), 53.5 KHz spectral width, 128K complex data points (1.22 s acquisition time), 10 s relaxation delay and 64 scans. The external chemical shift reference was 0.1 M $Cd(ClO_4)_2$ in D_2O. Spectra were processed by zero filling to twice the acquired time domain points, apodized using exponential functions, Fourier transformed, and phase and baseline corrected using Topspin 3.1.

2.7. Combustion calorimetry measurements

The standard massic energies of combustion of several cellulose samples were measured in two different isoperibol static bomb calorimetric systems. The combustion measurements of amorphous cellulose (24 h), cellulose Iβ, cellulose II (25 °C), cellulose II (70 °C), and cellulose II (145 °C) were carried out with an isoperibol combustion calorimeter previously described in the literature [26,27] and equipped with a twin valve static bomb made of stainless steel and with an internal volume of 0.342 dm^3. This system was calibrated with NIST Thermochemical Standard 39j benzoic acid with a certified standard massic energy of combustion, under bomb conditions, of $-(26434 \pm 3)\ J\cdot g^{-1}$ [28]. The value of the energy equivalent of the calorimeter was found to be $\varepsilon(\text{calor}) = (15995.3 \pm 2.0)\ J\cdot K^{-1}$ (the uncertainty is the standard deviation of the mean) for an average mass of water of 3119.6 g added to the calorimeter. The combustion measurements on the amorphous cellulose (30 h), amorphous cellulose (36 h), cellulose III (−33 °C), cellulose III (25 °C), and cellulose III (130 °C) used another static bomb calorimeter equipped with a twin valve bomb with an internal volume of 0.290 dm^3. This calorimeter and the detailed procedure have been described previously [29–31]. The calibration of this bomb calorimeter was performed with the same benzoic acid NIST Thermochemical Standard 39j [28]. From six calibration experiments the value of the energy equivalent of the calorimeter was $\varepsilon(\text{calor}) = (15551.2 \pm 1.6)\ J\cdot K^{-1}$ (the uncertainty is one standard deviation of the mean) for an average mass of water added to the calorimeter of 2900.0 g.

For both calorimeters, the calibration experiments were carried out in oxygen at a pressure of 3.04 MPa, with 1.00 cm^3 of deionized water added to the bomb, according to the method described by Coops *et al.* [32]. The LABTERMO program [33] was used to acquire data, control the calorimeter temperatures and to compute the adiabatic temperature changes.

The cellulose samples were burned in pellet form at T = 298.15 K, and with 1.00 cm^3 of deionised water introduced into the bomb, which was purged twice to remove air, before being charged with oxygen to the pressure 3.04 MPa. Details about the calorimetric temperature measurements, electrical energy for ignition, cotton thread fuse and the energetic effect for the amount of nitric acid produced in the combustion have been given previously [31,34].

The mass of cellulose m(cell) used in each experiment and on which the standard massic energy of combustion was based, was determined from the mass of CO_2 produced, taking into account the mass of CO_2 formed from the combustion of the cotton thread fuse. The procedure given by Hubbard *et al.* [35] was followed to obtain the corrections to the standard state ΔU_Σ and the calculation of the standard massic energy of combustion $\Delta_c U^\circ_w$. The relative atomic masses used throughout this study are those recommended by IUPAC [36].

2.8. Solution calorimetry measurements

The solution calorimeter and the associated measurement procedures have been described previously [37]. Three modifications were made to the apparatus for this investigation. Firstly, while the original gold reaction vessel was used for some initial measurements, it was deemed useful to use a glass reaction vessel so that the contents of the solution calorimeter could be examined visually following the dissolution process. Thus, a glass reaction vessel, holding essentially the same amount of solution (100 cm^3) as the gold reaction vessel, was fabricated. This vessel contained a heater having a resistance of 85.4 Ω and the resistance of the heater leads was 0.045 Ω. As was done with the gold vessel, the heater leads were thermally well-tempered to the calorimeter vessel. The quartz thermometer probe was the same removable one as used in the gold reaction vessel. The temperature obtained from the quartz thermometer probe was checked periodically against a NIST calibrated platinum resistance thermometer. Secondly, in order to obtain improved stirring and more effective dissolution of the

cellulose samples into the cadoxen, a set of stainless steel paddles (width = 1.5 cm; height = 0.80 cm; thickness = 0.065 cm) was fabricated and attached to the stirrer shaft just above the sample holder. There were two paddles. Each paddle was attached to half of a stainless steel cylinder. The two half-cylinders were attached to each other by using two small stainless steel screws going from one half of the cylinder to the other half. The fit of the two halves was tight enough so that the paddle assembly was firmly held in place to the original removable (sample holder + stirrer) assembly. With the new paddles, a stirring rate of 450 rpm was found to be satisfactory in terms of providing effective stirring without causing deterioration in the quality of the drifts. Thirdly, a small stainless steel connector or coupler (length = 0.60 cm, diameter = 0.64 cm) was fabricated and used to hold firmly the removable (sample holder + stirrer) assembly to the stainless-steel rod that turns that assembly. Small stainless steel screws held the connector to the removable (sample holder + stirrer) assembly and to the stainless-steel rod that turns that assembly. Typically, ≈ 0.020 g of cellulose sample was weighed into a glass sample ampoule which was sealed with a silicone rubber plug, which was then covered with bees wax. Thus, the final mass concentrations of the cellulose allomorphs in the 100.0 cm^3 of cadoxen in the calorimeter were ≈0.20 $g \cdot dm^{-3}$. A small amount of bees wax was also placed along the glass sample ampoule where the ampoule was held in place by the gold sample holder. This served to provide additional assurance that the ampoule would be firmly held in place during an experiment. Additionally, after being affixed to the gold sample holder, the bulbs and their contents were submersed in distilled water in order to see if any leaks were present. Following this, the water was removed by using a Kimwipe. Control experiments were also performed by allowing the silicone rubber plugs, the bees wax, the stainless steel, and the gold to sit in cadoxen for ≈24 h. There was no visible evidence for reaction of cadoxen with any of these materials. A calibrated 100 cm^3 pipette was used to deliver the cadoxen into the solution calorimeter. Two hours was allowed for a typical solution calorimetry measurement of the heat of solution of a sample of cellulose into cadoxen. The two hour period included a fore period of approximately 15 min. Following the two hour experiment, the calorimeter can was opened and the contents of the glass vessel were viewed. It was found that all of the cellulose samples, with the exception of the cellulose II (25 °C) sample, dissolved well in cadoxen. The cellulose II (25 °C) sample was observed to form a large clump in two separate experiments and, consequently, measurements of the enthalpy of solution of this sample was not possible. After reaction, the (cadoxen + cellulose) was removed from the solution calorimeter. This was followed by washing of the solution calorimeter with HCl(aq) {concentration $c \approx 1.0$ M), with water, and finally with acetone and air-drying. In the absence of information on the enthalpy of vaporization of cadoxen, the combined correction for (bulb-breaking + vaporization) was taken to be zero.

2.9. Heat-capacity measurements

Heat capacities were measured with logarithmic spacing from T = (2 to 100) K and in 10 K intervals from T = (110 to 300) K and at a pressure p = 1.2 mPa using a Quantum Design Physical Property Measurement System (PPMS), which uses a thermal relaxation technique. A mass (5 to 13) mg of each cellulose sample was mixed with about 5 mg of copper strips (Alfa Aesar, 0.99999 mass fraction purity), put into copper cups (mass ≈15 mg), and pressed into a disk approximately 3 mm in diameter and 1 mm in height following the method of Shi *et al.* [38]. The disks were successively mounted onto the PPMS puck with Apiezon N grease and then loaded into the PPMS calorimeter where the heat capacities were measured. The possible inaccuracies for the PPMS measurements of the standard massic heat capacities $C^{\circ}_{p,w}$ following this method are estimated to be $\pm 0.02 \cdot C^{\circ}_{p,w}$ for $2 < T/K < 10$ and $\pm 0.01 \cdot C^{\circ}_{p,w}$ for $10 < T/K < 302$ [39].

3. Results and discussion

3.1. X-ray diffraction, weight average degrees of polymerization, and Karl Fischer measurements

X-ray diffractograms (XRDs) for the cellulose samples are shown in figure 1. Evidence for the change from cellulose Iβ to cellulose II is seen in the appearance of a doublet in the XRDs for the $10\bar{1}$ and 002 peaks at 2θ values of about 20 and 22 (see figure 1.2). The change from cellulose Iβ to cellulose III is seen in the position of the 002 peak which shifts from a 2θ value of 23 to 21 as cellulose Iβ is converted to cellulose III (see figure 1.3). The values of the crystallinity indexes, the weight average degrees of polymerization, and the Karl Fischer measurements are given in tables 2–4, respectively. These results are needed for the characterization of the cellulose samples and for subsequent calculations.

3.2. NMR

NMR provides a convenient tool that can be used to probe the local environment of the nuclei under investigation. As such, it is a natural tool to look to in order to resolve the issue of the equivalency or non-equivalency of the nuclei in the different forms of cellulose that have been dissolved in cadoxen. Since one of the calorimetric approaches being used to measure the enthalpy differences between the crystalline forms of cellulose utilizes cadoxen as a solvent, this matter is of particular interest to this study. The mass fractions and mass concentrations of the cellulose samples used in the NMR measurements are given in table 5. The NMR spectra are shown in figures 2–6. In these figures, the spectra were normalized to have approximately the sample peak height for comparison purposes. For the samples having the lower mass fractions of cellulose in cadoxen, the signal to noise ratio was approximately half that of the higher mass fraction samples, as expected. However, for the cellulose II (145 °C) sample, the signal to noise ratio was much less. This is most likely due to incomplete dissolution of the sample which was obscured by its murky appearance. For ^{1}H–H2 to H6 (see figure 2), it is observed that the chemical shifts and peak shapes are in reasonable agreement except for the first (top-most) of the cellulose III (−33 °C) samples and for H2 and H3 for the cellulose III (25 °C) and cellulose III (130 °C) samples. Since two replicate measurements made on the cellulose III (−33 °C) sample yielded chemical shifts in agreement with the other cellulose samples, the first measurement involving cellulose III (−33 °C) is judged to be an outlier. It should be noted that, for all of the cellulose II samples and for the last sample of amorphous cellulose (36 h), the mass fraction of cellulose was approximately half of the mass fractions used for the other samples.

For ^{13}C–C1 (see figure 3), the chemical shifts and peak shapes are in good agreement – except that a close examination shows very small downfield shifts {amorphous cellulose (24 h) and cellulose III (−33 °C), w = 0.009330} and up field shifts {cellulose III (−33 °C), w = 0.009457 and cellulose III (130 °C)} from the other samples. Based upon the NMR spectra obtained for the cellulose III samples at essentially the same mass fraction of cellulose, these small differences are judged to be within the experimental uncertainties. For ^{13}C–C6 (see figure 4), the chemical shifts and peak shapes are in very good agreement for all samples. For ^{13}C–C2 to C5 (see figure 5), the sample of amorphous cellulose (36 h) with the lowest mass fraction of cellulose in cadoxen shows downfield shifts for C2, C3, and C5. Similar downfield shifts are seen in all

of the cellulose II samples. Thus, these downfield shifts may be attributable to the fact that the mass fractions of cellulose in cadoxen are lower than in the other samples. The chemical shifts and peak shapes for the cellulose Iβ sample are in accord with those seen for the amorphous samples run at the higher concentrations ($w \approx 0.10$). Note that the first (top-most) of the cellulose III (−33 °C) samples shows chemical shifts that deviate significantly from those of the other cellulose samples with the exception of C4, C6 and, perhaps, C5. Also, when compared to each other, differences in chemical shifts for C2 and C3 were seen in the two other samples of cellulose III (−33 °C). The remaining samples of cellulose III also show differences in chemical shifts C2 and C3, with cellulose III (25 °C) also showing a difference in the C5 chemical shift. A single peak was observed in the ^{113}Cd spectrum (see figure 6) which exhibited a trend of up field shifts and significant line broadening with increasing cellulose mass fraction. This trend is attributed to the dynamics of cellulose solvation in cadoxen with the observed resonance representing an average of chemical shifts for the Cd(II) species in solution. This may be due to a gradual increase in shielding as the coordination environment changes with increasing cellulose concentration. The ^{113}Cd spectra (see figure 6) are particularly interesting in that the samples having the lowest mass fractions have chemical shifts that are distinctly downfield from the samples having the highest mass fractions of cellulose in cadoxen. It should be noted, however, that the chemical shifts show a modest amount of scatter between the various samples and even for replicate preparations – see the cellulose III (−33 °C) spectra in figure 6. In summary, while large differences in the NMR spectra for the various cellulose samples in cadoxen were not observed, one cannot be absolutely certain that these samples are chemically equivalent. This matter is of particular importance in regards to the use of the results of the solution calorimetry measurements. Specifically the calculation of values of standard massic enthalpy differences between the various crystalline forms of cellulose from the measured standard massic enthalpies of solution assumes that the dissolved forms of the various cellulose samples are chemically equivalent (see section 3.4). If this is not the case, the calculated standard massic enthalpy differences would contain a systematic error of unknown magnitude.

3.3. Treatment of enthalpy of combustion data

3.3.1. Stoichiometry of the combustion reaction

The combustion reaction of a sample of cellulose, written on a molar basis, is

$$(C_6H_{10}O_5)_u\cdot(H_2O)_1\cdot(H_2O)_v(s) + 6u\ O_2(g) = 6u\ CO_2(g) + (5u + v + 1)\ H_2O(l). \quad (1)$$

TABLE 2
Values of the crystallinity indexes *CI* for the cellulose samples used in this study.[a]

Cellulose sample	*CI*
Amorphous cellulose (24 h)	0
Amorphous cellulose (30 h)	0
Amorphous cellulose (36 h)	0
Cellulose Iβ	62
Cellulose II (25 °C)	40
Cellulose II (70 °C)	49.2 ± 1.3
Cellulose II (145 °C)	57
Cellulose III (−33 °C)	32
Cellulose III (25 °C)	49
Cellulose III (130 °C)	59.3 ± 1.0

[a] The uncertainties given above for the cellulose II (70 °C) and cellulose III (130 °C) samples are equal to two estimated standard deviations of the mean based on three measurements made on each of these samples. The expanded uncertainties at approximately 95% confidence limits in the values of *CI* {type B evaluation [49] of $u_r(CI)$} are equal to $0.06\cdot CI$.

TABLE 3
Values of the weight average degree of polymerization DP_w of the various forms of cellulose as measured by using gel permeation chromatography.[a,b]

Cellulose sample	$10^{-2}\ DP_w$
Amorphous cellulose (24 h)	1.9 ± 0.2
Amorphous cellulose (30 h)	1.8 ± 0.3
Amorphous cellulose (36 h)	1.8 ± 0.2
Cellulose Iβ	4.3 ± 0.5
Cellulose II (25 °C)	7.4 ± 1.0
Cellulose II (70 °C)	4.7 ± 0.5
Cellulose II (145 °C)	0.9 ± 0.2
Cellulose III (−33 °C)	2.8 ± 0.3
Cellulose III (25 °C)	2.9 ± 0.4
Cellulose III (130 °C)	2.8 ± 0.6

[a] The uncertainties given above are expanded uncertainties at approximately 95% confidence limits which have been estimated by combining in quadrature the estimated standard deviations of the mean for each respective measurement result with an estimate of possible systematic error of $0.05\cdot DP_w$. The coverage factor $k = 2$ for all of the samples except for the cellulose III (130 °C) sample, the value of which is based on a single measurement, an estimated statistical uncertainty of $0.1\cdot DP_w$, and a coverage factor $k = 3$.
[b] An approximate value of the weight average molar mass M_w can be obtained by multiplying DP_w by 162.141, the relative molecular mass (molar mass) of an anhydro glucose unit.

TABLE 4
The mass fraction of water w_{H_2O} in the cellulose samples as measured by using Karl Fischer analysis.[a]

Cellulose sample	w_{H_2O}
Amorphous cellulose (24 h)	0.0765 ± 0.0029
Amorphous cellulose (30 h)	0.0756 ± 0.0027
Amorphous cellulose (36 h)	0.0773 ± 0.0007
Cellulose Iβ	0.0485 ± 0.0007
Cellulose II (25 °C)	0.0900 ± 0.0026
Cellulose II (70 °C)	0.0806 ± 0.0030
Cellulose II (145 °C)	0.0710 ± 0.0024
Cellulose III (−33 °C)	0.0811 ± 0.0016
Cellulose III (25 °C)	0.0873 ± 0.0014
Cellulose III (130 °C)	0.0931 ± 0.0007

[a] The uncertainties in w_{H_2O} given above are expanded uncertainties with approximately 95% confidence limits. These uncertainties include the statistical uncertainties in the mass fraction of water in the calibrant (octanol + water) solution, in the calibrations [25], and in the measurements on the cellulose samples. Three to four measurements were performed on each sample.

Here, u is the average number of $C_6H_{10}O_5$ units in the cellulose and v is the average number of waters of hydration in the sample. Note the inclusion of $(H_2O)_1$ in the cellulose sample – this represents the unglycosylated ends of the chain which has an H on one end and an OH on the other end. Thus, the relative molecular mass of the anhydrous part of the cellulose sample is

$$M_r(\text{anhyd cell}) = u\cdot M_r(C_6H_{10}O_5) + M_r(H_2O). \quad (2)$$

Here, $M_r(C_6H_{10}O_5)$ is the relative molecular mass of $C_6H_{10}O_5$ and $M_r(H_2O)$ is the relative molecular mass of H_2O. Thus, if u is known, *i.e.*, from a measurement of the degree of polymerization, one can calculate M_r(anhyd cell). The relative molecular mass of the hydrated cellulose sample, is

$$M_r(\text{cell}) = u\cdot M_r(C_6H_{10}O_5) + (v+1)\cdot M_r(H_2O) = M_r(\text{anhyd cell}) + v\cdot M_r(H_2O). \quad (3)$$

The mass fractions of the $(H_2O)_1$, i.e. the intrinsic water, and $(H_2O)_v$ parts of the cellulose sample are given respectively by

$$w_{int} = M_r(H_2O)/M_r(\text{cell}), \quad (4)$$

$$w_{hyd} = v\cdot M_r(H_2O)/M_r(\text{cell}). \quad (5)$$

The total mass fraction of water in the cellulose sample is

TABLE 5
Mass fractions w and mass concentrations γ of the cellulose samples in cadoxen used in the NMR experiments.

Cellulose sample	w	$\gamma/(\mathrm{g\cdot cm^{-3}})$[a]
Amorphous (24 h)	0.009516	0.01021
Amorphous (30 h)	0.009530	0.01023
Amorphous (36 h)	0.009433	0.01012
Amorphous (36 h)	0.004676	0.005018
Iβ	0.009400	0.01009
II (25 °C)	0.004724	0.005070
II (70 °C)	0.004741	0.005088
II (145 °C)	0.004639	0.004979
III (−33 °C)	0.009330	0.01001
III (−33 °C)	0.009457	0.01015
III (−33 °C)	0.009455	0.01015
III (25 °C)	0.009515	0.01021
III (130 °C)	0.009412	0.01010

[a] The mass concentrations of the cellulose samples in cadoxen were calculated from the mass fractions by using a measured density of $(1.0732 \pm 0.0004)\ \mathrm{g\cdot cm^{-3}}$ for cadoxen. The estimated relative standard uncertainties (type B evaluation) are $u_r(w) = u_r(\gamma) = 0.001$.

$$w_{H_2O} = w_{int} + w_{hyd} = \{M_r(H_2O) + v\cdot M_r(H_2O)\}/M_r(\text{cell}) = (v+1)\cdot M_r(H_2O)/M_r(\text{cell}). \quad (6)$$

We now consider the combustion reaction of a hypothetical sample of $C_6H_{10}O_5(s)$:

$$C_6H_{10}O_5(s) + 6\ O_2(g) = 6\ CO_2(g) + 5\ H_2O(l). \quad (7)$$

On a standard massic basis, reaction (7) can be written as

$$1\ \mathrm{g}\ C_6H_{10}O_5(s) + 6\cdot\alpha_1\ \mathrm{g}\ O_2(g) = 6\cdot\alpha_2\mathrm{g}\ CO_2(g) + 5\cdot\alpha_3\ \mathrm{g}\ H_2O(l), \quad (8)$$

where $\alpha_1 = M_r(O_2)/M_r(C_6H_{10}O_5)$, $\alpha_2 = M_r(CO_2)/M_r(C_6H_{10}O_5)$, and $\alpha_3 = M_r(H_2O)/M_r(C_6H_{10}O_5)$. The quantities $M_r(O_2)$ and $M_r(CO_2)$, are, respectively, the relative molecular masses of O_2 and CO_2.

One can also represent cellulose as $(C_6H_{10}O_5)_u\cdot w_{H_2O}(s)$, for which the combustion reaction (1) can be written on a standard massic basis:

$$1\ \mathrm{g}\ (C_6H_{10}O_5)_u\cdot w_{H_2O}(s) + 6(1-w_{H_2O})\cdot\alpha_1\ \mathrm{g}\ O_2(g) = 6(1-w_{H_2O})\cdot\alpha_2\ \mathrm{g}\ CO_2(g) + 5(1-w_{H_2O})\cdot\alpha_3\ \mathrm{g}\ H_2O(l). \quad (9)$$

Note that, written on a massic basis, the amounts of $O_2(g)$, $CO_2(g)$, and $H_2O(l)$ in the combustion reaction (9) are independent of the number of $C_6H_{10}O_5$ units in the cellulose sample. Thus, for the combustion of a cellulose sample having a mass m(cell), the mass of $CO_2(g)$ produced is

$$m(CO_2) = 6\alpha_2(1-w_{H_2O})\cdot m(\text{cell}). \quad (10)$$

Thus, if $m(CO_2)$ is known, one can calculate w_{H_2O}. Then, since M_r(anhyd cell) is known {see equation (2)}, the combination of equations (3) and (6) allows for the calculation of v:

$$v = \{w_{H_2O}M_r(\text{anhyd cell}) - M_r(H_2O)\}/\{M_r(H_2O)\cdot(1-w_{H_2O})\}. \quad (11)$$

The relative molecular mass of the (hydrated) cellulose sample M_r(cell) can then be calculated by using equation (3). In summary, the above treatment allows one to use the mass of $CO_2(g)$ produced, the measured value of the degree of polymerization, and, of course, the total mass of the cellulose sample itself to calculate w_{int}, w_{hyd}, w_{H_2O}, the quantity v, and the relative molecular mass of the cellulose sample.

3.3.2. Adjustment of results to a reference value of the mass fraction of water

We now derive a relationship that will allow one to use the measured value of the standard massic enthalpy of combustion $\Delta_cH^\circ_w\{\text{cell}\cdot w_{H_2O}(s)\}$ of a cellulose sample containing a total mass fraction of water w_{H_2O} in order to obtain a value of $\Delta_cH^\circ_w\{\text{cell}\cdot w_{ref}(s)\}$ for that cellulose sample at a reference value of the mass fraction of water w_{ref}. To derive this relationship, we first consider the combustion reaction of a sample of carbon which

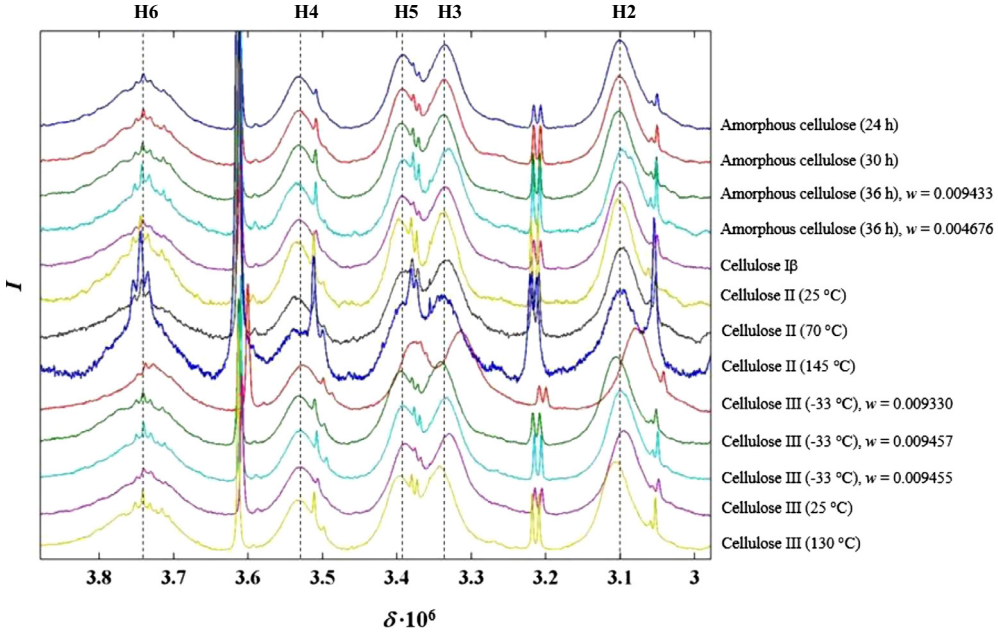

FIGURE 2. ^{1}H NMR spectra (signal intensity I *vs.* chemical shift δ) of cellulose samples (H2 to H6). The signal intensities obtained from the cellulose II samples and from one of the amorphous (36 h) samples have been increased so as to make them comparable to the signal intensities obtained from the other cellulose samples. Note that H1, $\delta = 4.44$, is not observable due to proximity with water. The external chemical shift reference is TMS. The mass fractions w and mass concentrations γ of the cellulose samples in cadoxen are given in table 5.

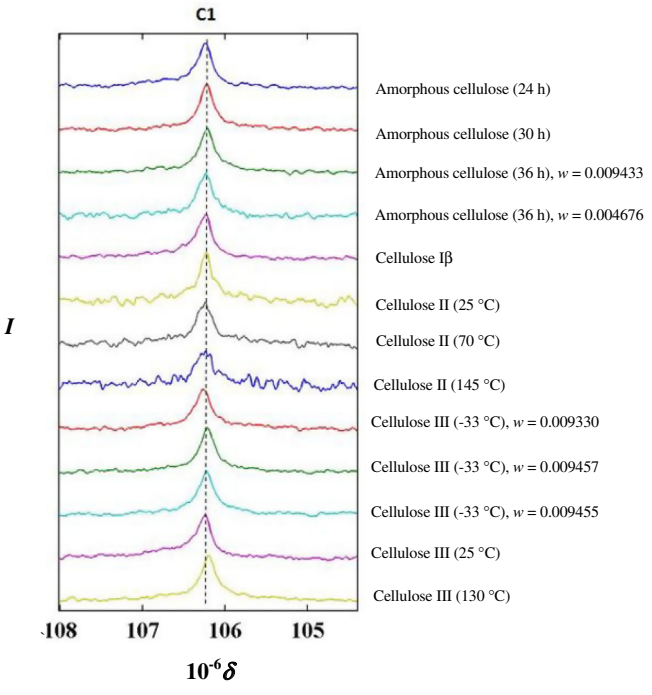

FIGURE 3. ^{13}C NMR spectra of cellulose samples (C1).

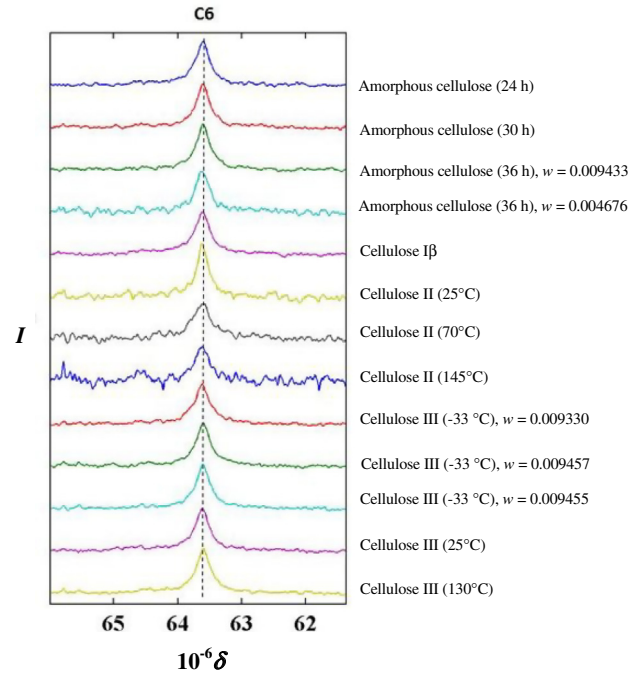

FIGURE 4. ^{13}C NMR spectra of cellulose samples (C6).

has some water in it. All of the following reactions are on a standard massic (per gram) basis. The following notation is used: C(s) is solid anhydrous carbon; w_{H_2O} is the mass fraction of water in the carbon sample; C·w_{H_2O}(s) is a sample of solid carbon having a mass fraction of water w_{H_2O}; and a subscript w denotes that an enthalpy change is on a standard massic basis. The combustion reaction of 1.0 g of C·w_{H_2O}(s) is:

$$1.0\ \text{g C}\cdot w_{H_2O}(\text{s}) + \beta_1(1 - w_{H_2O})\ \text{g O}_2(\text{g}) = \beta_2(1 - w_{H_2O})\ \text{g CO}_2(\text{g}) + w_{H_2O}\ \text{g H}_2\text{O(l)}. \quad (12)$$

Here, $\beta_1 = M_r(O_2)/A_r(C)$, $\beta_2 = M_r(CO_2)/A_r(C)$, and $A_r(C)$ is the relative atomic mass of C(s). The dehydration reaction of 1.0 g of C·w_{H_2O}(s) to form $(1 - w_{H_2O})$ g of C(s) and w_{H_2O} g of H_2O(l) is

$$1.0\ \text{g C}\cdot w_{H_2O}(\text{s}) = (1 - w_{H_2O})\ \text{g C(s)} + w_{H_2O}\ \text{g H}_2\text{O(l)}. \quad (13)$$

Division of reaction (13) by $-(1 - w_{H_2O})$ gives the hydration (wetting) reaction of 1.0 g of C(s) to form $\{1/(1 - w_{H_2O})\}$ g of C·w_{H_2O}(s)

$$1.0\text{g C(s)} + \{w_{H_2O}/(1 - w_{H_2O})\}\text{g H}_2\text{O(l)} = \{1/(1 - w_{H_2O})\}\text{g C}\cdot w_{H_2O}(\text{s}). \quad (14)$$

Reaction (15) is equal to {reaction (12) + $(1 - w_{H_2O})$·reaction (14)}:

$$(1 - w_{H_2O})\text{g C(s)} + \beta_1(1 - w_{H_2O})\text{g O}_2(\text{g}) = \beta_2(1 - w_{H_2O})\ \text{g CO}_2(\text{g}). \quad (15)$$

Division of reaction (15) by $(1 - w_{H_2O})$ gives the reaction for the combustion of 1 g of anhydrous C(s):

$$1\ \text{g C(s)} + \beta_1\text{g O}_2(\text{g}) = \beta_2\ \text{g CO}_2(\text{g}). \quad (16)$$

According to the above reaction scheme, we have the following standard massic enthalpy changes:

$$\Delta_r H^\circ_w(\text{reaction (12)}) = \Delta_c H^\circ_w\{\text{C}\cdot w_{H_2O}(\text{s})\}, \quad (17)$$

$$\Delta_r H^\circ_w(\text{reaction (14)}) = \Delta_{hyd} H^\circ_w\{\text{C}\cdot w_{H_2O}(\text{s})\}, \quad (18)$$

$$\Delta_r H^\circ_w(\text{reaction (15)}) = \Delta_r H^\circ_w(\text{reaction (12)}) + (1 - w_{H_2O})\cdot\Delta_r H^\circ_w(\text{reaction (14)}) = \Delta_c H^\circ_w\{\text{C}\cdot w_{H_2O}(\text{s})\} + (1 - w_{H_2O})\cdot\Delta_{hyd} H^\circ_w\{\text{C}\cdot w_{H_2O}(\text{s})\}, \quad (19)$$

$$\Delta_r H^\circ_w(\text{reaction (16)}) = \{\Delta_r H^\circ_w(\text{reaction (15)})/(1 - w_{H_2O})\} = \{1/(1 - w_{H_2O})\}\cdot\Delta_c H^\circ_w\{\text{C}\cdot w_{H_2O}(\text{s})\} + \Delta_{hyd} H^\circ_w\{\text{C}\cdot w_{H_2O}(\text{s})\}. \quad (20)$$

But $\Delta_r H^\circ_w$ (reaction (16)) is the standard massic enthalpy of combustion of 1 g of anhydrous C(s):

$$\Delta_c H^\circ_w\{\text{C(s)}\} = \{1/(1 - w_{H_2O})\}\cdot\Delta_c H^\circ_w\{\text{C}\cdot w_{H_2O}(\text{s})\} + \Delta_{hyd} H^\circ_w\{\text{C}\cdot w_{H_2O}(\text{s})\}. \quad (21)$$

Clearly, one could have derived equation (21) by using a different mass fraction of water, which we now choose as some reference value w_{ref} instead of w_{H_2O}, which could be any value. Thus,

$$\Delta_c H^\circ_w\{\text{C(s)}\} = \{1/(1 - w_{ref})\}\cdot\Delta_c H^\circ_w\{\text{C}\cdot w_{ref}(\text{s})\} + \Delta_{hyd} H^\circ_w\{\text{C}\cdot w_{ref}(\text{s})\}. \quad (22)$$

Equation (23) is obtained by equating equations (21) and (22) and then multiplying by $(1 - w_{ref})$:

$$\Delta_c H^\circ_w\{\text{C}\cdot w_{ref}(\text{s})\} = \{(1 - w_{ref})/(1 - w_{H_2O})\}\cdot\Delta_c H^\circ_w\{\text{C}\cdot w_{H_2O}(\text{s})\} + (1 - w_{ref})\cdot[\Delta_{hyd} H^\circ_w\{\text{C}\cdot w_{H_2O}(\text{s})\} - \Delta_{hyd} H^\circ_w\{\text{C}\cdot w_{ref}(\text{s})\}]. \quad (23)$$

In equation (23) the quantities w_{H_2O} and $\Delta_c H^\circ_w\{\text{C}\cdot w_{H_2O}(\text{s})\}$ are measured quantities and w_{ref} has an assigned value. Thus, they are known quantities. The quantity $\{\Delta_{hyd} H^\circ_w\{\text{C}\cdot w_{H_2O}(\text{s})\} - \Delta_{hyd} H^\circ_w\{\text{C}\cdot w_{ref}(\text{s})\}\}$ is estimated from the enthalpy of wetting data of Rees [15] (see below). Note that $\Delta_{hyd} H^\circ_w\{\text{C}\cdot w_{H_2O}(\text{s})\}$ is a standard massic quantity that is based on the mass of anhydrous C(s) and not C·w_{H_2O}(s). Finally, it should be noted that when one seeks an accurate value of $\Delta_c H^\circ_w\{\text{C(s)}\}$ for an anhydrous substance, equation (21) is, in fact, the simple and obvious correction that is generally made to $\Delta_c H^\circ_w\{\text{C}\cdot w_{H_2O}(\text{s})\}$ for the mass fraction of water in a sample. In

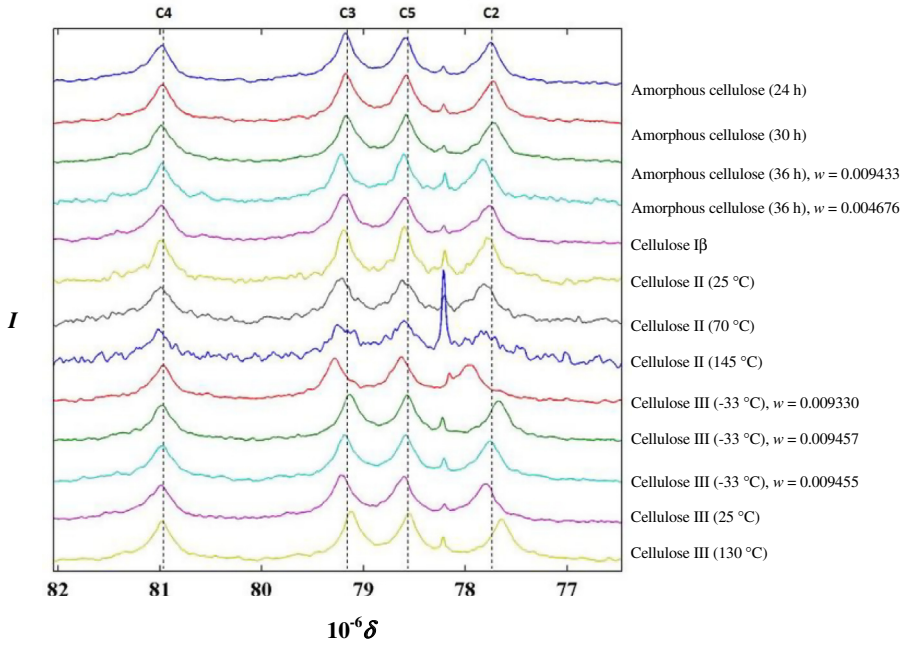

FIGURE 5. ^{13}C NMR spectra of cellulose samples (C2 to C5).

many cases, this correction is made with the assumption that the term $\Delta_{hyd}H^{\circ}_{w}\{C{\cdot}w_{H_2O}(s)\}$is negligible.

As stated above, the notation $\Delta_{hyd}H^{\circ}_{w}\{C{\cdot}w_{H_2O}(s)\}$ denotes the standard massic enthalpy change for the hydration reaction of 1.0 g of C(s) to form $\{1/(1-w_{H_2O})\}$ g of $C{\cdot}w_{H_2O}(s)$ {see reaction (14)}. This notation is clear and will suffice for now. However, in section 4, a more explicit notation is helpful in clarifying the treatment of results from the literature. Specifically, $\Delta_{hyd}H^{\circ}_{w}\{C{\cdot}w_{H_2O}(s)\}$ is written as $\Delta_{hyd}H^{\circ}_{w}\{C,0 \rightarrow w_{H_2O}\}$. The arrow denotes the change from the initial to final mass fraction of water for the hydration reaction of a substance. Information on the cellulose samples is also included in the notation.

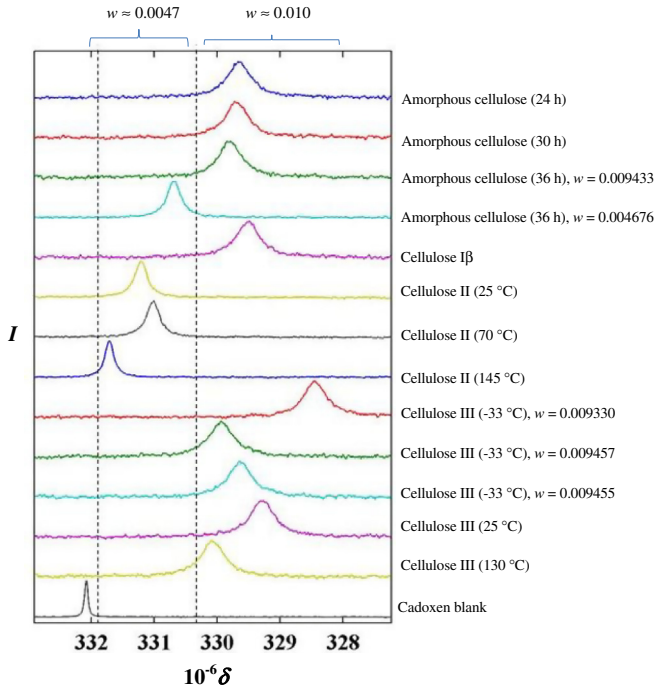

FIGURE 6. ^{113}Cd-NMR spectra of cellulose samples. The external chemical shift reference is 0.1 M $Cd(ClO_4)_2$ in D_2O.

Equation (23) was obtained by considering the combustion of 1.0 g of $C{\cdot}w_{H_2O}(s)$. However, it can be easily generalized to substances such as $C_{N1}H_{N2}O_{N3}{\cdot}w_{H_2O}(s)$, where $N1$, $N2$, and $N3$ are, respectively, the numbers of carbon, hydrogen, and oxygen atoms in the substance, by following the procedure used above to derive equation (23). Thus, equation (23) is valid for the combustion reaction of a substance such as cellulose. Accordingly, we use equation (23) and values of $\Delta_c H^{\circ}_{w}\{cell{\cdot}w_{H_2O}(s)\}$ obtained with samples that have different values of moisture content w_{H_2O} to calculate values of $\Delta_c H^{\circ}_{w}\{cell{\cdot}w_{ref}(s)\}$ at w_{ref}, the reference value of the mass fraction moisture content, which we take to be $w_{ref} = 0.073$, the mean value of w obtained from the cellulose samples obtained by using the Karl Fischer method. Equation (23) is the useful working equation that provides an adjustment or normalization to a common reference basis for the results of this study and allows for the calculation of the standard massic enthalpies of conversion of one crystalline form of cellulose to another crystalline form at a specified value of w_{ref}.

The data needed for the adjustment to a reference mass fraction of water $w_{ref} = 0.073$ by using equation (23) is estimated from the study of Rees [15] who gives a plot (see figure 4 in [15]) of "the heat of wetting (cal/gm of dry material) *vs.* moisture regain %" for five different cellulose samples. From the slopes of the five curves shown in this plot in the "moisture regain region" 4% to 10% (*i.e.*, $w_{H_2O} = 0.04$ to 0.10), we obtain the value $\eta = (3.4_6 \pm 0.7)$ J·(g dry material)$^{-1}$ that corresponds to a change of 0.01 in the value of w_{H_2O}. Since $\Delta_{hyd}H^{\circ}_{w}$ for cellulose is exothermic, a sample of cellulose having $w_{H_2O} < 0.073$ will require a positive adjustment to the measured value of $\Delta_c H^{\circ}_{w}$ in order to obtain $\Delta_c H^{\circ}_{w}(w_{ref} = 0.073)$. The adjustment is negative if $w_{H_2O} > 0.073$. Additionally, a factor of 100 is needed because the value of η pertains to a change in w_{H_2O} of 0.01. Thus, the last term in square brackets in equation (23) is estimated by use of the following equation:

$$\Delta_{hyd}H^{\circ}_{w}\{C{\cdot}w_{H_2O}(s)\} - \Delta_{hyd}H^{\circ}_{w}\{C{\cdot}w_{ref}(s)\} = \eta{\cdot}(0.073 - w_{H_2O}){\cdot}100. \quad (24)$$

In our treatment of uncertainties, we shall assume that the adjustment of values of $\Delta_{sol}H^{\circ}_{w}$ to w_{ref} = 0.073 is uncertain by 20%. Interestingly, the study of Rees [15], done in 1948, appears to be the most extensive and definitive study of the enthalpy of hydration of cellulose samples in the literature. A later, carefully done study by Morrison and Dzieciuch [40] on the enthalpy of hydration of cotton is in accord with the results of Rees [15].

3.3.3. Calculation of standard massic enthalpy differences between cellulose allomorphs

The treatment described above allows for the calculation of the state of hydration (w_{int}, w_{hyd}, w_{H_2O}, and the quantity v), the relative molecular masses, and values of the standard massic enthalpies of combustion $\Delta_cH^{\circ}_{w}\{\text{cell}\cdot w_{ref}(s)\}$ that have been normalized to a reference value of the mass fraction moisture content w_{ref}. Having done the normalization, one has values of $\Delta_cH^{\circ}_{w}\{\text{cell}\cdot w_{ref}(s)\}$ for each of the ten cellulose samples studied in this investigation at a reference mass fraction of water w_{ref} = 0.073. However, excepting the amorphous cellulose samples, the samples of cellulose Iβ, cellulose II, and cellulose III are each a mixture of that respective form of cellulose and amorphous cellulose. The mass fraction of crystalline cellulose w_{cr} in each of the samples of cellulose Iβ, II, and III is obtained by using the measured values of the crystallinity indexes CI (see table 2), *i.e.*, $w_{cr} = 0.01\cdot CI$. Thus, the measured standard massic enthalpy of combustion for a cellulose sample (cellulose I is used as the example) is taken to be:

$$\Delta_cH^{\circ}_{w}\{\text{cell I}\cdot w_{ref}(s)\} = w_{cr}\cdot\Delta_cH^{\circ *}_{w}\{\text{cell I}\cdot w_{ref}(cr)\} + (1-w_{cr})\cdot\Delta_cH^{\circ *}_{w}\{\text{cell}\cdot w_{ref}(am)\}, \quad (25)$$

where $\Delta_cH^{\circ *}_{w}\{\text{cell I}\cdot w_{ref}(cr)\}$ is the standard massic enthalpy of combustion of pure (CI = 100) cellulose I(cr) and $\Delta_cH^{\circ *}_{w}\{\text{cell}\cdot w_{ref}(am)\}$ is the standard massic enthalpy of combustion of pure amorphous cellulose. All of these enthalpies of combustion pertain to w_{ref}. Since, the quantity $\Delta_cH^{\circ *}_{w}\{\text{cell}\cdot w_{ref}(am)\}$ is known from direct measurements on the three amorphous cellulose samples, equation (25) can be used to calculate values of $\Delta_cH^{\circ *}_{w}\{\text{cell I}\cdot w_{ref}(cr)\}$. Clearly, this procedure can also be used for the cellulose II and III samples.

The values of $\Delta_cH^{\circ *}_{w}\{\text{cell am}\cdot w_{ref}(s)\}$, $\Delta_cH^{\circ *}_{w}\{\text{cell I}\cdot w_{ref}(s)\}$, $\Delta_cH^{\circ *}_{w}\{\text{cell II}\cdot w_{ref}(s)\}$, and $\Delta_cH^{\circ *}_{w}\{\text{cell III}\cdot w_{ref}(s)\}$ can then be used to calculate values of standard massic enthalpy changes for the following reactions:

$$\text{cellulose}\cdot w_{ref}(am) = \text{cellulose I}\cdot w_{ref}(cr), \quad (26)$$

$$\text{cellulose}\cdot w_{ref}(am) = \text{cellulose II}\cdot w_{ref}(cr), \quad (27)$$

$$\text{cellulose}\cdot w_{ref}(am) = \text{cellulose III}\cdot w_{ref}(cr), \quad (28)$$

$$\text{cellulose I}\cdot w_{ref}(cr) = \text{cellulose II}\cdot w_{ref}(cr), \quad (29)$$

$$\text{cellulose I}\cdot w_{ref}(cr) = \text{cellulose III}\cdot w_{ref}(cr), \quad (30)$$

$$\text{cellulose II}\cdot w_{ref}(cr) = \text{cellulose III}\cdot w_{ref}(cr). \quad (31)$$

Thus,

$$\Delta_rH^{\circ *}_{w}(\text{reaction (26)}) = \Delta_cH^{\circ *}_{w}\{\text{cell}\cdot w_{ref}(am)\} - \Delta_cH^{\circ *}_{w}\{\text{cell I}\cdot w_{ref}(cr)\}, \quad (32)$$

$$\Delta_rH^{\circ *}_{w}(\text{reaction (27)}) = \Delta_cH^{\circ *}_{w}\{\text{cell}\cdot w_{ref}(am)\} - \Delta_cH^{\circ *}_{w}\{\text{cell II}\cdot w_{ref}(cr)\}, \quad (33)$$

$$\Delta_rH^{\circ *}_{w}(\text{reaction (28)}) = \Delta_cH^{\circ *}_{w}\{\text{cell}\cdot w_{ref}(am)\} - \Delta_cH^{\circ *}_{w}\{\text{cell III}\cdot w_{ref}(cr)\}, \quad (34)$$

$$\Delta_rH^{\circ *}_{w}(\text{reaction (29)}) = \Delta_cH^{\circ *}_{w}\{\text{cell I}\cdot w_{ref}(cr)\} - \Delta_cH^{\circ *}_{w}\{\text{cell II}\cdot w_{ref}(cr)\}, \quad (35)$$

$$\Delta_rH^{\circ *}_{w}(\text{reaction (30)}) = \Delta_cH^{\circ *}_{w}\{\text{cell I}\cdot w_{ref}(cr)\} - \Delta_cH^{\circ *}_{w}\{\text{cell III}\cdot w_{ref}(cr)\}, \quad (36)$$

$$\Delta_rH^{\circ *}_{w}(\text{reaction (31)}) = \Delta_cH^{\circ *}_{w}\{\text{cell II}\cdot w_{ref}(cr)\} - \Delta_cH^{\circ *}_{w}\{\text{cell III}\cdot w_{ref}(cr)\}. \quad (37)$$

As mentioned above, it is important to recognize that when written on a standard massic basis, the amounts of O_2(g), CO_2(g), and H_2O(l) in the combustion reaction (9) are independent of the number of $C_6H_{10}O_5$ units in the cellulose sample. Also, note that, since all of the cellulose samples have been brought to a common value of w_{ref}, the terms involving O_2(g), CO_2(g), and H_2O(l) in reaction (9) will cancel when combining the combustion reactions for two different forms of cellulose. Implicit in this calculation is the assumption that the values of $\Delta_cH^{\circ *}_{w}$ do not depend on the degree of polymerization, *i.e.*, the quantity u.

3.4. Treatment of enthalpy of solution data

The solution reaction of a sample of cellulose into cadoxen written on a molar basis is

$$(C_6H_{10}O_5)_u\cdot(H_2O)_1\cdot(H_2O)_v(s) = (C_6H_{10}O_5)_u(\text{cad}) + (v+1)H_2O(\text{cad}). \quad (38)$$

As above (see section 3.3.1), we again have equations (2)–(6) and equation (11), which allows one to calculate M_r(anhyd cell), M_r(cell), w_{int}, w_{hyd}, and v if u and w_{H_2O} are known. The treatment of the enthalpy of solution data is similar to the treatment of the enthalpy of combustion data. Specifically, a relationship is derived that allows one to use the measured value of the standard massic enthalpy of solution $\Delta_{sol}H^{\circ}_{w}\{\text{cell}\cdot w_{H_2O}(s)\}$ of a cellulose sample having a mass fraction of water w_{H_2O} in order to obtain a value of $\Delta_{sol}H^{\circ}_{w}\{\text{cell}\cdot w_{ref}(s)\}$ of that cellulose sample at a reference value of the mass fraction of water w_{ref}. To do this, we consider reactions (39)–(45), which are all on a standard massic basis. Here, "(cad)" denotes that a substance is dissolved in cadoxen. The remaining notation is the same as that used in section 3.3 above. The dissolution reaction of 1.0 g of cell$\cdot w_{H_2O}(s)$ into cadoxen is:

$$1.0\text{ g cell}\cdot w_{H_2O}(s) = (1-w_{H_2O})\text{g cell(cad)} + w_{H_2O}\text{g}H_2O(\text{cad}). \quad (39)$$

The dehydration reaction of 1.0 g of cell$\cdot w_{H_2O}(s)$ to form $(1-w_{H_2O})$ g of cell(s) and w_{H_2O} g of H_2O(l) is:

$$1.0\text{ g cell}\cdot w_{H_2O}(s) = (1-w_{H_2O})\text{gcell(s)} + w_{H_2O}\text{g}H_2O(l). \quad (40)$$

Division of reaction (40) by $-(1-w_{H_2O})$ gives the hydration reaction of 1.0 g of cell(s):

$$1.0\text{ g cell(s)} + \{w_{H_2O}/(1-w_{H_2O})\}\text{g}H_2O(l) = \{1/(1-w_{H_2O})\}\text{g cell}\cdot w_{H_2O}(s). \quad (41)$$

Reaction (42) is {reaction (39) – reaction (40)}:

$$(1-w_{H_2O})\text{gcell(s)} + w_{H_2O}\text{g}H_2O(l) = (1-w_{H_2O})\text{g cell(cad)} + w_{H_2O}\text{g}H_2O(\text{cad}). \quad (42)$$

The solution reaction for w_{H_2O} g of H_2O(l) into cadoxen is:

$$w_{H_2O}\text{g}H_2O(l) = w_{H_2O}\text{g}H_2O(\text{cad}). \quad (43)$$

Reaction (44) is {reaction (42) – reaction (43)}:

$$(1-w_{H_2O})\text{gcell(s)} = (1-w_{H_2O})\text{g cell(cad)}. \quad (44)$$

Division of reaction (44) by $(1 - w_{H_2O})$ gives the solution reaction of 1.0 g of cell(s) into cadoxen:

$$1.0\ \text{g cell(s)} = 1.0\ \text{g cell(cad)}. \tag{45}$$

We now consider the enthalpy changes for the above reactions that pertain to a sample of cellulose having a mass fraction of water w_{H_2O}. The quantity $\Delta_r H^\circ_w$ (reaction (39)) is the standard massic enthalpy of solution of cell·w_{H_2O}(s) into cadoxen, *i.e.*,

$$\Delta_r H^\circ_w(\text{reaction (39)}) = \Delta_{sol} H^\circ_w\{\text{cell}\cdot w_{H_2O}(s)\}. \tag{46}$$

$\Delta_r H^\circ_w$(reaction (40)) is the negative of the standard massic enthalpy of hydration of (1 - w_{H_2O}) g of anhydrous cellulose, *i.e.*, cell(s), to form 1.0 g of cell·w_{H_2O}(s). And, $\Delta_r H^\circ_w$(reaction (41)) is the standard massic enthalpy of hydration of 1.0 g of cell(s) to form {1/(1 - w_{H_2O})} g of cell·w_{H_2O}(s). Thus,

$$\Delta_r H^\circ_w(\text{reaction (40)}) = -(1 - w_{H_2O})\cdot\Delta_{hyd} H^\circ_w\{\text{cell}\cdot w_{H_2O}(s)\}, \tag{47}$$

$$\Delta_r H^\circ_w(\text{reaction (41)}) = \Delta_{hyd} H^\circ_w\{\text{cell}\cdot w_{H_2O}(s)\}. \tag{48}$$

The quantity $\Delta_r H^\circ_w$(reaction (42)) is equal to {$\Delta_r H^\circ_w$(reaction (39)) – $\Delta_r H^\circ_w$(reaction (40))}. Then, by using equations (46) and (47)

$$\Delta_r H^\circ_w(\text{reaction (42)}) = \Delta_{sol} H^\circ_w\{\text{cell}\cdot w_{H_2O}(s)\} + (1 - w_{H_2O})\cdot\Delta_{hyd} H^\circ_w\{\text{cell}\cdot w_{H_2O}(s)\}. \tag{49}$$

$\Delta_r H^\circ_w$ (reaction (43)) is the enthalpy of solution of w_{H_2O} g of H_2O(l) into cadoxen, *i.e.*,

$$\Delta_r H^\circ_w(\text{reaction (43)}) = w_{H_2O}\cdot\Delta_{sol} H^\circ_w\{H_2O(l)\}. \tag{50}$$

Then,

$$\Delta_r H^\circ_w(\text{reaction (44)}) = \Delta_r H^\circ_w(\text{reaction (42)}) - \Delta_r H^\circ_w(\text{reaction (43)}),$$

$$\Delta_r H^\circ_w(\text{reaction (44)}) = \Delta_{sol} H^\circ_w\{\text{cell}\cdot w_{H_2O}(s)\} + (1 - w_{H_2O})\cdot\Delta_{hyd} H^\circ_w\{\text{cell}\cdot w_{H_2O}(s)\} - w_{H_2O}\cdot\Delta_{sol} H^\circ_w\{H_2O(l)\}. \tag{51}$$

The quantity $\Delta_r H^\circ_w$ (reaction (45)) is the standard massic enthalpy of solution of 1.0 g of anhydrous cellulose into cadoxen, *i.e.* $\Delta_{sol} H^\circ_w$ {cell(s)}. Thus,

$$\Delta_r H^\circ_w(\text{reaction (45)}) = \Delta_{sol} H^\circ_w\{\text{cell}(s)\} = \Delta_r H^\circ_w(\text{reaction (44)})/(1 - w_{H_2O}), \tag{52}$$

$$\Delta_{sol} H^\circ_w\{\text{cell}(s)\} = \{1/(1 - w_{H_2O})\}\cdot\Delta_{sol} H^\circ_w\{\text{cell}\cdot w_{H_2O}(s)\} + \Delta_{hyd} H^\circ_w\{\text{cell}\cdot w_{H_2O}(s)\} - \{w_{H_2O}/(1 - w_{H_2O})\}\ \Delta_{sol} H^\circ_w\{H_2O(l)\}. \tag{53}$$

Clearly, one could have derived equation (53) by using a different mass fraction of water, which we now choose as some reference value w_{ref} instead of w_{H_2O}. Thus,

$$\Delta_{sol} H^\circ_w\{\text{cell}(s)\} = \{1/(1 - w_{ref})\}\cdot\Delta_{sol} H^\circ_w\{\text{cell}\cdot w_{ref}(s)\} + \Delta_{hyd} H^\circ_w\{\text{cell}\cdot w_{ref}(s)\} - \{w_{ref}/(1 - w_{ref})\}\cdot\Delta_{sol} H^\circ_w\{H_2O(l)\}]. \tag{54}$$

By equating equations (53) and (54), one has

$$\{1/(1 - w_{ref})\}\cdot\Delta_{sol} H^\circ_w\{\text{cell}\cdot w_{ref}(s)\} + \Delta_{hyd} H^\circ_w\{\text{cell}\cdot w_{ref}(s)\} - \{w_{ref}/(1 - w_{ref})\}\cdot\Delta_{sol} H^\circ_w\{H_2O(l)\}] = \{1/(1 - w_{H_2O})\}\cdot\Delta_{sol} H^\circ_w\{\text{cell}\cdot w_{H_2O}(s)\} + \Delta_{hyd} H^\circ_w\{\text{cell}\cdot w_{H_2O}(s)\} - \{w_{H_2O}/(1 - w_{H_2O})\}\cdot\Delta_{sol} H^\circ_w\{H_2O(l)\}]. \tag{55}$$

Multiplication of equation (55) by $(1 - w_{ref})$ and rearrangement gives the useful working equation

$$\Delta_{sol} H^\circ_w\{\text{cell}\cdot w_{ref}(s)\} = \{(1 - w_{ref})/(1 - w_{H_2O})\}\cdot\Delta_{sol} H^\circ_w\{\text{cell}\cdot w_{H_2O}(s)\} + (1 - w_{ref})\cdot[\Delta_{hyd} H^\circ_w\{\text{cell}\cdot w_{H_2O}(s)\} - \Delta_{hyd} H^\circ_w\{\text{cell}\cdot w_{ref}(s)\}] + \{(w_{ref} - w_{H_2O})/(1 - w_{H_2O})\}\cdot\Delta_{sol} H^\circ_w\{H_2O(l)\}. \tag{56}$$

The quantities $w_{H_2O}, \Delta_{sol} H^\circ_w\{\text{cell}\cdot w_{H_2O}(s)\}$, and $\Delta_{sol} H^\circ_w\{H_2O(l)\}$ in equation (56) are measured quantities and w_{ref} has an assigned value. Thus, they are all known quantities. The quantity $[\Delta_{hyd} H^\circ_w\{\text{cell}\cdot w_{H_2O}(s)\} - \Delta_{hyd} H^\circ_w\{\text{cell}\cdot w_{ref}(s)\}]$ was discussed in section 3.3.2 and it is estimated from the "heat of wetting" data of Rees [15] {see equation (24)}. Thus, one can use equations (56) and (24) and values of $\Delta_{sol} H^\circ_w\{\text{cell}\cdot w_{H_2O}(s)\}$ obtained with samples that differ in their values of moisture content w_{H_2O} over a modest range to calculate values of $\Delta_{sol} H^\circ_w\{\text{cell}\cdot w_{ref}(s)\}$ at a reference value of the mass fraction moisture content w_{ref}. This adjustment or normalization, as described for the combustion data, serves to provide a common reference basis for the results of this study and allows, as described in section 3.3.3, for the calculation of the standard massic enthalpies of conversion of one crystalline form of cellulose to another crystalline form. Note that equation (56) contains an additional term $\{(w_{ref} - w_{H_2O})/(1 - w_{H_2O})\}\cdot\Delta_{sol} H^\circ_w\{H_2O(l)\}$ that is not present in equation (23). It turns out that this last term is negligible in comparison to the two other terms on the right-hand side of equation (56).

The treatment of the standard massic enthalpy of solution data then parallels the treatment of the standard massic enthalpy of combustion data. Thus, by analogy to equation (25), one has

$$\Delta_{sol} H^\circ_w\{\text{cellI}\cdot w_{ref}(s)\} = w_{cr}\cdot\Delta_{sol} H^{\circ *}_w\{\text{cellI}\cdot w_{ref}(cr)\} + (1 - w_{cr})\cdot\Delta_{sol} H^{\circ *}_w\{\text{cell}\cdot w_{ref}(am)\}. \tag{57}$$

As above (see section 3.3.3), $w_{cr} = 0.01\cdot CI$. The only change from equation (25) is that one is now dealing with standard massic enthalpies of solution rather than standard massic enthalpies of combustion. Also, by analogy to equations (32) to (37), one has

$$\Delta_r H^{\circ *}_w(\text{reaction (26)}) = \Delta_{sol} H^{\circ *}_w\{\text{cell}\cdot w_{ref}(am)\} - \Delta_{sol} H^{\circ *}_w\{\text{cell I}\cdot w_{ref}(cr)\}, \tag{58}$$

$$\Delta_r H^{\circ *}_w(\text{reaction (27)}) = \Delta_{sol} H^{\circ *}_w\{\text{cell}\cdot w_{ref}(am)\} - \Delta_{sol} H^{\circ *}_w\{\text{cell II}\cdot w_{ref}(cr)\}, \tag{59}$$

$$\Delta_r H^{\circ *}_w(\text{reaction (28)}) = \Delta_{sol} H^{\circ *}_w\{\text{cell}\cdot w_{ref}(am)\} - \Delta_{sol} H^{\circ *}_w\{\text{cell III}\cdot w_{ref}(cr)\}, \tag{60}$$

$$\Delta_r H^{\circ *}_w(\text{reaction (29)}) = \Delta_{sol} H^{\circ *}_w\{\text{cell I}\cdot w_{ref}(cr)\} - \Delta_{sol} H^{\circ *}_w\{\text{cell II}\cdot w_{ref}(cr)\}, \tag{61}$$

$$\Delta_r H^{\circ 8}_w(\text{reaction (30)}) = \Delta_{sol} H^{\circ *}_w\{\text{cell I}\cdot w_{ref}(cr)\} - \Delta_{sol} H^{\circ *}_w\{\text{cell III}\cdot w_{ref}(cr)\}, \tag{62}$$

$$\Delta_r H^{\circ *}_w(\text{reaction (31)}) = \Delta_{sol} H^{\circ *}_w\{\text{cell II}\cdot w_{ref}(cr)\} - \Delta_{sol} H^{\circ *}_w\{\text{cell III}\cdot w_{ref}(cr)\}. \tag{63}$$

Note that in combining the values of the standard massic enthalpies of solution to obtain equations (58)–(63), it is assumed that the various forms of cellulose in cadoxen are chemically equivalent. However, if this is not the case, this assumption could lead to systematic errors that would be extremely difficult, if not impossible, to obtain corrections for. This problem does not exist for the combustion experiments, where it is clear that the products of the combustion reactions {CO_2(g) and H_2O(l)}, are chemically equivalent.

3.5. Treatment of heat-capacity data

The treatment of the heat capacities and related thermal data is very similar to the treatments used for the standard massic enthalpies of combustion and solution (see sections 3.4 and 3.5). We first consider the treatment of values of the standard massic entropy differences $\Delta_0^T S_w^\circ = (S_{298.15}^\circ - S_0^\circ)_w$ for the cellulose samples. The values of $\Delta_0^T S_w^\circ$ can be adjusted to the reference mass fraction of water $w_{ref} = 0.073$ by assuming that

$$\Delta_0^T S_w^\circ\{\text{cell}\cdot w_{H_2O}(s)\} = (1 - w_{H_2O})\cdot\Delta_0^T S_w^\circ(\text{anhyd cell}) + w_{H_2O}\cdot S_{298.15,w}^\circ\{H_2O(cr, hex)\}, \quad (64)$$

$$\Delta_0^T S_w^\circ\{\text{cell}\cdot w_{ref}(s)\} = (1 - w_{ref})\cdot\Delta_0^T S_w^\circ(\text{anhyd cell}) + w_{ref}\cdot S_{298.15,w}^\circ\{H_2O(cr, hex)\}. \quad (65)$$

Here, $\Delta_0^T S_w^\circ\{\text{cell}\cdot w_{H_2O}(s)\}$ is the measured standard massic entropy difference for a cellulose sample having a mass fraction of water w_{H_2O}, $\Delta_0^T S_w^\circ\{\text{cell}\cdot w_{ref}(s)\}$ is the standard massic entropy difference for a cellulose sample having a mass fraction of water w_{ref}, $\Delta_0^T S_w^\circ$ (anhyd cell) is the standard massic entropy difference for anhydrous cellulose, and $S_{T,w}^\circ\{H_2O(cr, hex)\}$ is the standard massic entropy of crystalline hexagonal ice. The temperature T is arbitrary, but will be taken to be $T = 298.15$ K. Here, we have used the standard massic entropy of crystalline hexagonal ice to approximate the standard massic entropy of the water that is bound to cellulose [41,42]. By solving for $\Delta_0^T S_w^\circ$(anhyd cell) in equations (64) and (65) and then equating these two solutions, one obtains

$$\Delta_0^T S_w^\circ\{\text{cell}\cdot w_{ref}(s)\} = [\{(1 - w_{ref})/(1 - w_{H_2O})\}]\cdot[\Delta_0^T S_w^\circ\{\text{cell}\cdot w_{H_2O}(s)\} - w_{H_2O}\cdot S_{T,w}^\circ\{H_2O(cr, hex)\}] + w_{ref}\cdot S_{T,w}^\circ\{H_2O(cr, hex)\}. \quad (66)$$

This equation allows for the adjustment of the measured values of $\Delta_0^T S_w^\circ\{\text{cell}\cdot w_{H_2O}(s)\}$ to a reference value of the moisture content w_{ref}. Equations for related thermal functions have the same form as equation (66):

$$X\{\text{cell}\cdot w_{ref}(s)\} = [\{(1 - w_{ref})/(1 - w_{H_2O})\}]\cdot[X\{\text{cell}\cdot w_{H_2O}(s)\} - w_{H_2O}\cdot X\{H_2O(cr, hex)\}] + w_{ref}\cdot X\{H_2O(cr, hex)\}. \quad (67)$$

The quantity X in equation (67) can be the standard massic heat capacity $C_{p,w}^\circ$, the standard massic entropy difference $\Delta_0^T S_w^\circ$, the standard massic enthalpy difference $\Delta_0^T H_w^\circ$, or the function Φ_w° at the standard pressure p° and a specified temperature, *e.g.* $T = 298.15$ K. The function Φ_w° is defined as

$$\Phi_w^\circ = \Delta_0^T S_w^\circ - \Delta_0^T H_w^\circ/T. \quad (68)$$

The calculation of values of $\Delta_0^T S_w^{\circ*}$, $C_{p,w}^{\circ*}$, $\Delta_0^T H_w^{\circ*}$, and $\Phi_w^{\circ*}$ for the pure cellulose allomorphs uses the calculated values of X {cell·w_{ref}(s)} together with the *CI* values of the samples and follows the treatment given above for the standard massic enthalpies of combustion and solution {see equations (25) and (57)}. Then, if one *assumes* that the values of $S_w^{\circ*}$ at $T = 0$ are equal for the cellulose allomorphs, one can calculate values of $\Delta_r S_w^{\circ*}$ for reactions (26)–(31).

For the standard molar heat capacity $C_{p,m}^\circ$ of H_2O[(cr, hex)}, we use a fit done by Juliana Boerio-Goates [43] that used property values for H_2O[(cr, hex)}from several sources [44–48]. The fit is

$$C_{p,m}^\circ = 0.014C_D(T_D = 55\text{ K}) + 0.495C_D(T_D = 393\text{ K}) + 0.05C_E(T_E = 58\text{ K}) + 0.253C_E(T_E = 103\text{ K}) + 0.113C_E(T_E = 325\text{ K}) + 0.47C_E(T_E = 630\text{ K}) + 1.615C_E(T_E = 1280\text{ K}). \quad (69)$$

The Einstein and Debye heat-capacity functions, respectively, are

$$C_E = 3R\left(\frac{T_E}{T}\right)^2 \frac{e^{-T_E/T}}{(1 - e^{-T_E/T})^2}, \quad (70)$$

$$C_D = 9R\left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx. \quad (71)$$

In the above equations, T_D and T_E are, respectively, the Debye and Einstein temperatures and R is the gas constant (8.314 4621 J·K^{-1}·mol^{-1}). For H_2O[(cr, hex)} at $T = 298.15$ K : $C_{p,m}^\circ$ = 40.346 J·K^{-1}·mol^{-1}; $\Delta_0^T S_m^\circ$ = 41.546 J·K^{-1}·mol^{-1}; $\Delta_0^T H_m^\circ$ = 6.37782 10^{3}J·mol^{-1}; and Φ_m° = 20.1547J·K^{-1}·mol^{-1}.

3.6. Results of combustion experiments

The results of the combustion experiments are shown in table 6. The results in this table are used to calculate values of the standard massic enthalpy of combustion for each combustion experiment (see table 7) as follows:

$$\Delta_c H_w^\circ = \Delta_c U_w^\circ(CO_2)\cdot m(\text{cell}_{corr})/m(\text{cell}). \quad (72)$$

Here, $\Delta_c U_w^\circ(CO_2)$ is the standard massic energy of combustion based on the mass of CO_2 formed in each experiment, $m(\text{cell}_{corr})$ is the mass of cellulose corrected for the per cent CO_2 formed, and m(cell) is the mass of cellulose burned in each experiment. Table 7 also gives values of w_{H_2O}, the total mass fraction of water in the samples based on the mass of CO_2(g) produced {see equation (10)}, and $\Delta_c H_w^\circ(w_{ref} = 0.073)$, the standard massic enthalpy of combustion at the mass fraction of water w_{ref} = 0.073. This latter quantity was calculated by using equations (23) and (24).

The average values of $\Delta_c H_w^\circ(w_{ref} = 0.073)$ for each of the cellulose samples are given in the second column of table 8. As a first step, we use all of the values of $\Delta_c H_w^\circ(w_{ref} = 0.073)$ obtained for the three different samples of cellulose(am) (*i.e.*, twelve measurements) to obtain the average value $\Delta_c H_w^{\circ*}(w_{ref} = 0.073) = -(16062 \pm 14)$ J·g^{-1}. The "*", as above, denotes that the sample refers to a pure form of cellulose, which, in this case, is cellulose(am). This pooled value of $\Delta_c H_w^{\circ*}(w_{ref} = 0.073)$ is used together with the values of $\Delta_c H_w^\circ(w_{ref} = 0.073)$ obtained for the other cellulose samples (column 2 in table 8) and the values of the crystallinity indexes of the samples (see table 2) to calculate {see equation (25)} values of $\Delta_c H_w^{\circ*}$, the standard massic enthalpies of combustion of the pure crystalline forms of cellulose Iβ(cr), cellulose II(cr), and cellulose III(cr). These calculated values are given in the third column in table 8. For cellulose Iβ(cr), $\Delta_c H_w^{\circ*} = -(16048 \pm 40)$ J·g^{-1}. By taking the weighted averages of the respective cellulose II(cr) and cellulose III(cr) samples, the following values are obtained: $\Delta_c H_w^{\circ*} = -(15919 \pm 84)$ J·g^{-1} for cellulose II(cr) and $\Delta_c H_w^{\circ*} = -(16085 \pm 56)$ J·g^{-1}for cellulose III(cr). These values of $\Delta_c H_w^{\circ*}$ are then used to calculate {see equations (32) to (37)} values of $\Delta_r H_w^{\circ*}$ for reactions (26)–(31). These values are given in column 3 in table 9.

We now consider possible systematic errors in the combustion calorimetry measurements. Specifically, we estimate possible inaccuracies in these measurements to be as follows: mass m, 0.0002·m; energy equivalent of the calorimeter ε (calor), 0.0002·ε (calor); in the several corrections (fuse, HNO_3, carbon soot, ignition, and standard state) made to obtain the energy change for the isothermal combustion reaction under actual bomb conditions ΔU(IBP), 0.0002·ΔU(IBP); crystallinity index, 0.03·*CI*; mass fractions of water w_{H_2O} in the samples, 0.0003·w_{H_2O}; ΔH_{adj} for the adjustment of values of $\Delta_c H_w^\circ$ to $\Delta_c H_w^\circ(w_{H_2O} = 0.073)$, 0.20·$\Delta H_{adj}$; and, for each sample, a possible impurity at a mass fraction w = 0.005 having a standard massic energy of combustion 1.25 times that of the cellulose sample. By using propagation of error,

we find that the principal source of possible systematic error in the measurements is the possibility of impurities in the cellulose samples. The remaining sources of possible error are negligible in comparison to this possible error. The estimates of possible systematic error are combined in quadrature together with the statistical uncertainties in the previously obtained values of $\Delta_r H^\circ_w$ (see column 3 in table 9), expressed as one-half of the 95% confidence limits, to obtain values of the combined standard uncertainties [49]. These combined standard uncertainties are then multiplied by two to arrive at the expanded uncertainties [49] and final results given in column 4 in table 9.

3.7. Results of solution calorimetry experiments

The results of the solution calorimetry experiments are given in table 10. The treatment of results follows the procedure described in section 3.4 above. First, it is noted that the values of $\Delta_{sol}H^\circ_w(w_{H_2O} = 0.073)$ for the three different sample of amorphous (ball-milled cellulose) are in agreement within their uncertainties. The average of the results for the 24 h, 30 h, and 36 h cellulose(am) samples is $\Delta_{sol}H^{\circ*}_w(w_{H_2O} = 0.073) = -(156.1 \pm 2.3)\,J\cdot g^{-1}$. This value is used together with the values of $\Delta_{sol}H^\circ_w(w_{H_2O} = 0.073)$ for the other samples (see column 4 in table 10) and the values of the crystallinity indexes (see table 2) to calculate, using equations (24) and (56), the values of $\Delta_{sol}H^{\circ*}_w(w_{H_2O} = 0.073)$ given in column 5 in table 10. Thus, for cellulose Iβ(cr), the calculations yield $\Delta_{sol}H^{\circ*}_w(w_{H_2O} = 0.073) = -(49.6 \pm 13)\,J\cdot g^{-1}$. It is noted that the two values of $\Delta_{sol}H^{\circ*}_w(w_{H_2O} = 0.073)$ for cellulose II(cr) are not in agreement with each other. Interestingly, the imprecision in the value of $\Delta_{sol}H^{\circ*}_w(w_{H_2O} = 0.073)$ seen in the cellulose II (145 °C) sample data is much smaller than the imprecision in the value of $\Delta_{sol}H^{\circ*}_w(w_{H_2O} = 0.073)$ obtained from the cellulose II (70 °C) sample. Also, the value of $\Delta_{sol}H^{\circ*}_w(w_{H_2O} = 0.073)$ for the cellulose III (−33 °C) sample is not in agreement with the values of $\Delta_{sol}H^{\circ*}_w(w_{H_2O} = 0.073)$ obtained from the other two cellulose III samples, which have values of $\Delta_{sol}H^{\circ*}_w(w_{H_2O} = 0.073)$ that are in good agreement with each other. It is conceivable that these discrepancies might be explained by the large differences in the values of the weight average degree of polymerization DP_w of these cellulose samples. However, the DP_w values for all of the cellulose III samples are very close to each other (see table 3). It is also possible that the fundamental assumption regarding the chemical equivalency of the various forms of cellulose in cadoxen is incorrect. Indeed, based on the NMR spectra (see section 3.2), it is not possible to state with certainty that the various solutions containing cellulose in cadoxen are completely equivalent on a molecular level.

In any case, we proceed with the analysis of the results. The weighted averages of the results from the two cellulose II samples is $\Delta_{sol}H^{\circ*}_w(w_{H_2O} = 0.073) = -(43.0 \pm 7.4)\,J\cdot g^{-1}$ and the weighted average of the results from the three cellulose III samples is $\Delta_{sol}H^{\circ*}_w(w_{H_2O} = 0.073) = -(41.4 \pm 18)\,J\cdot g^{-1}$. Note that a weighted average gives little importance to a value that has a much larger uncertainty than the value(s) that have a much lower uncertainty. More importantly, the weighted averages for the cellulose II and cellulose III samples give the greatest weight to those samples having the highest *CI* values. These values of $\Delta_{sol}H^{\circ*}_w$ are then used to calculate, using equations analogous to equations (32) to (37), values of $\Delta_r H^{\circ*}_w$ for reactions (26)–(31). These values are given in column 3 in table 11.

We now consider possible systematic errors in the solution calorimetry measurements. Specifically, we estimate possible inaccuracies in these measurements to be as follows: mass m, $0.002\cdot m$; energy equivalent ε_f, $0.0005\cdot\varepsilon_f$; (ΔH for vaporization of cadoxen + ΔH of sample introduction), 0.10 J; crystallinity index, $0.03\cdot CI$; $\Delta_{sol}H^\circ_w$ of H_2O(l) into cadoxen, 0.24 $J\cdot g^{-1}$; mass fractions of water w_{H_2O} in the samples, $0.15\cdot w_{H_2O}$; ΔH_{adj} for the adjustment of values of $\Delta_{sol}H^\circ_w$ to $\Delta_{sol}H^\circ_w(w_{H_2O} = 0.073)$, $0.20\cdot\Delta H_{adj}$; and, for each sample, a possible impurity at a mass fraction $w = 0.005$ having a value $\Delta_{sol}H^\circ_w = 0$. By using propagation of error, we find that the principal source of possible systematic error in the measurements is our knowledge of the crystallinity indexes. This is followed closely by possible errors in the mass fractions of water in the samples and in the adjustment of values of $\Delta_{sol}H^\circ_w$ to $\Delta_{sol}H^\circ_w(w_{H_2O} = 0.073$ {see equation (24)}, and finally to possible impurities in the samples. The remaining sources of possible error are negligible in comparison with the just mentioned sources of possible error. Since the value of $\Delta_{sol}H^{\circ*}_w$ for cellulose Iβ(cr) is not too different from the values of $\Delta_{sol}H^{\circ*}_w$ for cellulose II(cr) and cellulose III(cr), the presence of a small amount of cellulose Iβ(cr) in either cellulose II(cr) or cellulose III(cr) will cause relatively small errors in the values of $\Delta_{sol}H^{\circ*}_w$ for these two substances. However, the much more serious concern is the mass fraction of cellulose(am) present in these samples. We note that there are significant differences between the values of w_{H_2O} obtained from the combustion results (table 7) and the Karl Fischer analyses (table 4). These differences are very likely attributable to the handling of the samples during the pelleting and in the preparations for the combustion experiments. A similar problem, and a possible source of both random and systematic error, arises in the loading of the glass bulbs used in the solution calorimetry measurements. This problem and the possible errors associated with it could be avoided, albeit with considerable difficulty, by the use of a constant humidity chamber for all sample handling. Alternatively, all of the samples could have been made anhydrous by drying the samples in a vacuum oven at a suitable temperature. However, the removal of the last traces of water, the establishment that one has a truly anhydrous cellulose that is otherwise unchanged, and keeping the samples in their anhydrous states are not trivial matters. Finally, in the absence of a basis for making an error estimate, we choose not to make one for the possible non-equivalence of the different forms of cellulose that have been dissolved in cadoxen. Thus, the estimates of possible systematic error are combined in quadrature together with the statistical uncertainties in the previously obtained values of $\Delta_r H^{\circ*}_w$ (see column 3 in table 11), expressed as one-half of the 95% confidence limits, to obtain values of the combined standard uncertainties [49]. These combined standard uncertainties are then multiplied by two to arrive at the final expanded uncertainties [49] and results given in column 4 in table 11.

Examination of the results given in tables 9 and 11 shows agreement between the values of $\Delta_r H^{\circ*}_w$ for reactions (27) and (30) based on results obtained from combustion calorimetry and from solution calorimetry. However, the values of $\Delta_r H^{\circ*}_w$ for reactions (26), (28), (29) and (31) are not in agreement. It is worth noting that in the only previous attempt made to use both combustion and solution calorimetry in this way is that of Nelson [14]. In that study [14], the results obtained from the combustion experiments differed by a factor of ten from the results obtained from solution calorimetry experiments. Clearly, the use of combustion calorimetry for this purpose suffers from two difficulties - looking for an accurate value that is a small difference between two large numbers and sensitivity to possible impurities. The principal difficulty with the solution calorimetry is the possible uncertainty due to the possibility of the chemical non-equivalence of the different forms of cellulose after dissolution in cadoxen. Note that the combustion of cellulose in O_2(g) results in the production of CO_2(g) and H_2O(l) and thus not suffer from this concern. However, two additional factors enter into this discussion. Firstly, there is the fact that earlier workers (see section 3.10.2 for a discussion of these literature results) used cupriethylenediamine and ferric sodium tartrate to dissolve cellulose samples and obtained results that are in

TABLE 6
Results of combustion experiments on cellulose samples at the temperature T = 298.15 K and the standard pressure p° = 0.1 MPa.[a]

	1	2	3	4
	Amorphous cellulose (24 h)			
$m(CO_2, total)$/g	2.26139	1.41717	0.92545	0.96833
m(cell)/g	1.54810	0.96909	0.63099	0.66024
$m(cell_{corr})$/g	1.38615	0.86709	0.56572	0.59161
m'(fuse)/g	0.00244	0.00328	0.00285	0.00320
ΔT_{ad}/K	1.50762	0.94582	0.61716	0.64604
$\varepsilon_f/(J\cdot K^{-1})$	18.35	16.83	15.93	16.01
$\Delta m(H_2O)$[b] /g	0	0	0	0
$-\Delta U$(IBP)/J[c]	24141.91	15143.91	9880.66	10342.90
ΔU(fuse)/J	39.63	53.27	46.28	51.97
$\Delta U(HNO_3)$/J	0	0	0	0
ΔU(ign)/J	0.59	0.68	0.83	1.05
ΔU_Σ/J	22.59	13.26	8.27	8.69
$-\Delta_c U^\circ_w(CO_2)/(J\cdot g^{-1})$	17371.63	17391.15	17376.79	17385.12
$w(CO_2)$	0.89539	0.89475	0.89656	0.89606
	$\langle\Delta_c U^\circ_w(CO_2)/(J\cdot g^{-1})\rangle = -(17381 \pm 14)J\cdot g^{-1}$; $\langle w(CO_2)\rangle = 0.89569 \pm 0.0013$			
	Amorphous cellulose (30 h)			
$m(CO_2, total)$/g	0.99711	1.05188	0.99508	1.11721
m(cell)/g	0.68346	0.72146	0.68173	0.76090
$m(cell_{corr})$/g	0.60980	0.64331	0.60882	0.68291
m'(fuse)/g	0.00281	0.00266	0.00241	0.00311
ΔT_{ad}/K	0.68310	0.72116	0.68219	0.76490
$\varepsilon_f/(J\cdot K^{-1})$	14.80	14.90	14.80	15.00
$\Delta m(H_2O)$[b'] /g	1.4	1.5	0.4	1.8
$-\Delta U$(IBP)/J[c]	10636.50	11229.55	10619.49	11911.77
ΔU(fuse)/J	45.63	43.20	39.14	50.51
$\Delta U(HNO_3)$/J	0.67	0.52	0.55	0.83
ΔU(carb)/J	4.95	0.99	2.97	0
ΔU(ign)/J	0.64	0.62	0.62	0.58
ΔU_Σ/J	9.10	9.65	9.07	10.24
$-\Delta_c U^\circ_w(CO_2)/(J\cdot g^{-1})$	17359.87	17374.47	17367.53	17352.49
$w(CO_2)$	0.89223	0.89168	0.89305	0.89751
	$\langle\Delta_c U^\circ_w(CO_2)/(J\cdot g^{-1})\rangle = -(17364 \pm 15)J\cdot g^{-1}$; $\langle w(CO_2)\rangle = 0.89362 \pm 0.0042$			
	Amorphous cellulose (36 h)			
$m(CO_2, total)$/g	1.11842	1.09899	1.43965	1.04107
m(cell)/g	0.75573	0.74391	0.97343	0.70275
$m(cell_{corr})$/g	0.68472	0.67265	0.88164	0.63649
m'(fuse)/g	0.00252	0.00248	0.00237	0.00287
ΔT_{ad}/K	0.76786	0.75530	0.98812	0.71522
$\varepsilon_f/(J\cdot K^{-1})$	14.95	14.96	15.56	14.81
$\Delta m(H_2O)$[b'] /g	1.0	−0.7	1.0	1.3
$-\Delta U$(IBP)/J[c]	11955.22	11754.25	15385.34	11136.41
ΔU(fuse)/J	40.92	40.28	38.49	46.61
$\Delta U(HNO_3)$/J	0.60	0.83	1.13	0.60
ΔU(carb)/J	6.93	4.29	0	1.32
ΔU(ign)/J	0.62	0.66	0.62	0.60
ΔU_Σ/J	10.15	9.98	13.46	9.38
$-\Delta_c U^\circ_w(CO_2)/(J\cdot g^{-1})/(J\cdot g^{-1})$	17394.67	17404.97	17390.61	17409.76
$w(CO_2)$	0.90604	0.90421	0.90570	0.90571
	$\langle\Delta_c U^\circ_w(CO_2)/(J\cdot g^{-1})\rangle = -(17400 \pm 14)J\cdot g^{-1}$; $\langle w(CO_2)\rangle = 0.90542 \pm 0.0013$			
	Cellulose Iβ			
$m(CO_2, total)$/g	1.36447	1.26024	1.07373	1.08583
m(cell)/g	0.89090	0.82347	0.69997	0.70842
$m(cell_{corr})$/g	0.83489	0.77163	0.65643	0.66387
m'(fuse)/g	0.00297	0.00260	0.00338	0.00314
ΔT_{ad}/K	0.91032	0.84122	0.71619	0.72482
$\varepsilon_f/(J\cdot K^{-1})$	16.62	16.44	16.12	16.14
$\Delta m(H_2O)$[b] /g	0	0	0	0
$-\Delta U$(IBP)/J [c]	14575.09	13468.40	11466.20	11604.76
ΔU(fuse)/J	48.23	42.22	54.89	50.99
$\Delta U(HNO_3)$/J	0	0	0	0
ΔU(carb)/J	0	5.61	6.93	3.63
ΔU(ign)/J	0.88	1.00	1.02	0.65
ΔU_Σ/J	12.07	11.06	9.26	9.38
$-\Delta_c U^\circ_w(CO_2)/(J\cdot g^{-1})$	17385.27	17392.70	17380.35	17395.00
$w(CO_2)$	0.93713	0.93705	0.93779	0.93711
	$\langle\Delta_c U^\circ_w(CO_2)/(J\cdot g^{-1})\rangle = -(17388 \pm 11)\,J\cdot g^{-1}$; $\langle w(CO_2)\rangle = 0.93727 \pm 0.00055$			
	Cellulose II (25 °C)			
$m(CO_2, total)$/g	0.88233	1.10336	1.11320	1.12203
m(cell)/g	0.58350	0.73054	0.73646	0.74298

TABLE 6 (*continued*)

	1	2	3	4
$m(\text{cell}_{\text{corr}})$/g	0.53895	0.67434	0.68108	0.68632
m'(fuse)/g	0.00319	0.00348	0.00248	0.00283
ΔT_{ad}/K	0.58716	0.73417	0.74019	0.74760
ε_f/(J·K^{-1})	15.81	16.20	16.21	16.23
$\Delta m(\text{H}_2\text{O})$[b] /g	0	−0.5	0	0
$-\Delta U$(IBP)/J[c]	9400.41	11753.00	11850.89	11969.61
ΔU(fuse)/J	51.81	56.52	40.28	45.96
$\Delta U(\text{HNO}_3)$/J	0	0	0	0
ΔU(carb)/J	4.95	4.29	0	2.31
ΔU(ign)/J	0.67	0.63	0.67	0.61
ΔU_Σ/J	7.60	9.71	9.78	9.88
$-\Delta_c U^\circ_w(\text{CO}_2)$/(J·g^{-1})	17341.03	17337.04	17326.64	17362.28
$w(\text{CO}_2)$	0.92365	0.92307	0.92480	0.92374
	$\langle\Delta_c U^\circ_w(\text{CO}_2)/(\text{J·g}^{-1})\rangle = -(17342 \pm 24)\ \text{J·g}^{-1}$; $\langle w(\text{CO}_2)\rangle = 0.92382 \pm 0.0012$			
	Cellulose II (70 °C)			
$m(\text{CO}_2, \text{total})$/g	1.17179	0.98275	1.07314	1.06070
m(cell)/g	0.78086	0.65405	0.71379	0.70470
$m(\text{cell}_{\text{corr}})$/g	0.71692	0.60052	0.65571	0.64786
m'(fuse)/g	0.00262	0.00295	0.00326	0.00347
ΔT_{ad}/K	0.77996	0.65382	0.71336	0.70515
ε_f/(J·K^{-1})	16.33	15.99	16.15	16.13
$\Delta m(\text{H}_2\text{O})$[b] /g	0	0	0	0
$-\Delta U$(IBP)/J[c]	12487.76	10467.68	11421.24	11289.75
ΔU(fuse)/J	42.55	47.91	52.94	56.35
$\Delta U(\text{HNO}_3)$/J	0	0	0	0
ΔU(ign)/J	0.67	0.82	0.69	0.71
ΔU_Σ/J	10.43	8.60	9.46	9.33
$-\Delta_c U^\circ_w(\text{CO}_2)$/(J·g^{-1})	17344.72	17336.92	17322.96	17324.84
$w(\text{CO}_2)$	0.91811	0.91814	0.91863	0.91934
	$\langle\Delta_c U^\circ_w(\text{CO}_2)/(\text{J·g}^{-1})\rangle = -(17332 \pm 16)\ \text{J·g}^{-1}$; $\langle w(\text{CO}_2)\rangle = 0.91856 \pm 0.00091$			
	Cellulose II (145 °C)			
$m(\text{CO}_2, \text{total})$/g	1.30703	1.04636	1.04798	1.06096
m(cell)/ g	0.85744	0.68214	0.68589	0.69324
$m(\text{cell}_{\text{corr}})$/g	0.79988	0.63932	0.64071	0.64825
m'(fuse)/g	0.00293	0.00321	0.00324	0.00346
ΔT_{ad}/K	0.86969	0.69546	0.69566	0.70471
ε_f/(J·K^{-1})	16.53	16.07	16.08	16.10
$\Delta m(\text{H}_2\text{O})$[b] /g	0	0	0	0
$-\Delta U$(IBP)/J [c]	13924.48	11134.78	11137.64	11282.77
ΔU(fuse)/J	47.58	52.13	52.62	56.19
$\Delta U(\text{HNO}_3)$/J	0	0	0	0
ΔU(carb)/J	3.30	0	6.27	3.30
ΔU(ign)/J	0.85	0.49	0.84	0.62
ΔU_Σ/J	11.57	9.00	9.06	9.17
$-\Delta_c U^\circ_w(\text{CO}_2)$/(J·g^{-1})	17338.39	17320.98	17296.80	17309.23
$w(\text{CO}_2)$	0.93287	0.93722	0.93412	0.93511
	$\langle\Delta_c U^\circ_w(\text{CO}_2)/(\text{J·g}^{-1})\rangle = -(17316 \pm 28)\ \text{J·g}^{-1}$; $\langle w(\text{CO}_2)\rangle = 0.93483 \pm 0.0029$			
	Cellulose III (−33 °C)			
$m(\text{CO}_2, \text{total})$/g	1.05605	1.11639	1.04874	1.16920
m(cell)/g	0.69668	0.73922	0.69614	0.75374
$m(\text{cell}_{\text{corr}})$/g	0.64659	0.68275	0.64150	0.71528
m'(fuse)/g	0.00250	0.00277	0.00282	0.00266
ΔT_{ad}/K	0.72561	0.76622	0.71914	0.80278
ε_f/(J·K^{-1})	14.83	14.94	14.83	14.94
$\Delta m(\text{H}_2\text{O})$[b'] /g	−1.6	−0.4	−0.8	−1.1
$-\Delta U$(IBP)/J[c]	11289.37	11925.17	11191.12	12491.86
ΔU(fuse)/J	40.60	44.98	45.80	43.20
$\Delta U(\text{HNO}_3)$/J	0.76	1.08	1.15	1.18
ΔU(carb)/J	9.24	0	4.95	0
ΔU(ign)/J	0.64	0.64	0.63	0.63
ΔU_Σ/J	9.29	9.92	9.29	10.13
$-\Delta_c U^\circ_w$ (CO_2)/(J·g^{-1})	17395.81	17384.39	17365.28	17388.09
$w(\text{CO}_2)$	0.92811	0.92360	0.92151	0.94897
	$\langle\Delta_c U^\circ_w(\text{CO}_2)/(\text{J·g}^{-1})\rangle = -(17383 \pm 21)\text{J·g}^{-1}$; $\langle w(\text{CO}_2)\rangle = 0.93055 \pm 0.0020$			
	Cellulose III (25 °C)			
$m(\text{CO}_2, \text{total})$/g	1.18489	1.11594	1.34973	1.30556
m(cell)/g	0.77945	0.73213	0.86112	0.83141
$m(\text{cell}_{\text{corr}})$/g	0.72715	0.68244	0.82600	0.79903
m'(fuse)/g	0.00223	0.00280	0.00279	0.00264
ΔT_{ad}/K	0.81106	0.76354	0.92411	0.89269
ε_f/(J·K^{-1})	15.05	14.93	15.22	15.18

(*continued on next page*)

TABLE 6 (*continued*)

	1	2	3	4
$\Delta m(H_2O)^{b'}$ /g	1.8	0.9	−0.5	0.6
$-\Delta U(IBP)/J$ [c]	12630.63	11887.60	14382.58	13897.57
ΔU(fuse)/J	36.22	45.47	45.31	42.87
$\Delta U(HNO_3)$/J	0.68	0.77	1.31	1.32
ΔU(carb)/J	26.40	0	0	0
ΔU(ign)/J	0.64	0.64	0.57	0.62
ΔU_Σ/J	10.51	9.81	11.74	11.29
$-\Delta_c U^\circ_w(CO_2)/(J\cdot g^{-1})$	17341.15	17337.13	17341.67	17323.62
$w(CO_2)$	0.93290	0.93213	0.95922	0.96105
	$\langle\Delta_c U^\circ_w(CO_2)/(J\cdot g^{-1})\rangle = -(17336 \pm 13) J\cdot g^{-1}$; $\langle w(CO_2)\rangle = 0.94633 \pm 0.0025$			
	Cellulose III (130 °C)			
$m(CO_2, total)/g$	1.18454	1.31089	1.23021	1.27488
m(cell)/g	0.78650	0.86272	0.81924	0.84617
$m(cell_{corr})$/g	0.72508	0.80234	0.75327	0.77991
m'(fuse)/g	0.00249	0.00279	0.00238	0.00315
ΔT_{ad}/K	0.81446	0.90027	0.84523	0.87718
$\varepsilon_f/(J\cdot K^{-1})$	15.05	15.20	15.13	15.16
$\Delta m(H_2O)^{b'}$ /g	−0.8	−0.2	0.4	−0.3
$-\Delta U(IBP)/J$ [c]	12674.72	14012.55	13157.90	13652.74
ΔU(fuse)/J	40.44	45.31	38.65	51.16
$\Delta U(HNO_3)$/J	3.22	3.43	3.25	3.24
ΔU(carb)/J	2.97	2.64	3.63	3.30
ΔU(ign)/J	0.64	0.66	0.64	0.66
ΔU_Σ/J	10.62	11.77	11.11	11.53
$-\Delta_c U^\circ_w(CO_2)/(J\cdot g^{-1})$	17409.68	17392.48	17402.15	17425.23
$w(CO_2)$	0.92190	0.93000	0.91948	0.92170
	$\langle\Delta_c U^\circ_w(CO_2)/(J\cdot g^{-1})\rangle = -(17407 \pm 22) J\cdot g^{-1}$; $\langle w(CO_2)\rangle = 0.92327 \pm 0.0073$			

[a] All uncertainties in this table are expanded uncertainties with approximately 95% confidence limits; $m(CO_2, total)$ is the mass of CO_2 recovered in each combustion; m(cell) is the mass of compound burned in each experiment; $m(cell_{corr})$ is the mass of compound corrected for the mass fraction of CO_2 formed; m'(fuse) is the mass of the fuse (cotton) used in each experiment; ΔT_{ad} is the corrected temperature rise; ε_f is the energy equivalent of the contents in the final state; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions and includes ΔU(ignition); ΔU(fuse) is the energy of combustion of the fuse (cotton); $\Delta U(HNO_3)$ is the energy correction for the nitric acid formation; ΔU(carb) is the energy correction for the carbon soot formation; ΔU(ign) is the electric energy for the ignition; ΔU_Σ is the standard state correction; $-\Delta_c U^\circ_w(CO_2)$ is the standard massic energy of combustion based on the mass of CO_2 formed in each experiment; and $w(CO_2)$ is the mass fraction of CO_2 formed. The estimated standard uncertainties in the temperature T and pressure p are $u(T) = 0.001$ K and $u(p) = 100$ Pa.

[b] $\Delta m(H_2O)$ is the deviation of mass of water added to the calorimeter from 3119.6 g.

[b'] $\Delta m(H_2O)$ is the deviation of mass of water added to the calorimeter from 2900.0 g.

[c] $\Delta U(IBP) = -\{\varepsilon(calor) + C_{p,w}(H_2O,l)\cdot\Delta m(H_2O) + \varepsilon_f\}\Delta T_{ad} + \Delta U(ign)$, where ε(calor) is the energy equivalent of the calorimeter and $C_{p,w}$ is the standard massic heat capacity of H_2O(l) at $T = 298.15$ K.

agreement with results in which cadoxen was used as the solvent. Thus, it is unlikely that three different solvents would each yield essentially the same values for standard massic reaction enthalpies if the dissolved celluloses were chemically non-equivalent. Also, one has a general agreement between the values of $\Delta_r H^{\circ *}_w$ for the mercerization reaction (29) obtained from the solution calorimetry measurements and from earlier measurements [50] that used an alternative approach. Thus, in addition to the facts that the uncertainties in the values of $\Delta_r H^{\circ *}_w$ for reactions (26)–(29) obtained by solution calorimetry are substantially less than those obtained by combustion calorimetry, there are additional facts that support preferring the solution calorimetry results. Nevertheless, the combustion calorimetry results stand on their own as important and useful property values for well characterized cellulose samples.

3.8. Results of heat-capacity experiments

The sample masses used for the heat-capacity measurements are given in table 12 and the standard massic heat capacities $C^\circ_{p,w}$ measured with the PPMS are given in table 13 and shown in figures 7 and 8. As can be seen in figure 7, all of the $C^\circ_{p,w}$ curves have inflection points at $T \approx (35,\ 140,\ \text{and}\ 215)$ K. Because of these inflection points, the high-temperature ($T > 30$ K) and mid-temperature ($10\ K < T < 45\ K$) values of $C^\circ_{p,w}$ were fit to orthogonal polynomials:

$$C^\circ_{p,w} = A_0 + A_1 T + A_2 T^2 + A_3 T^3 + A_4 T^4 + A_5 T^5. \quad (73)$$

The low-temperature values of $C^\circ_{p,w}$ were fit to a sum of theoretical functions that can potentially give information on the lattice, electronic, and magnetic properties of a material:

$$C^\circ_{p,w} = \gamma T + B_3 T^3 + B_5 T^5 + B_{gap} T^{3/2} e^{-\delta/T}. \quad (74)$$

In the above equation the T term represents lattice or oxygen vacancies, the T^3 and T^5 terms represent lattice vibrations, and the $T^{3/2}e^{-\delta/T}$ term possibly represents low frequency modes associated with amorphous materials [51–53]. The fitting parameters are given in table 14. Values of $C^\circ_{p,w}$, $\Delta^T_0 S^\circ_w$, $\Delta^T_0 H^\circ_w$, and Φ°_w have been calculated from the fits at selected temperatures from $T = (0$ to $300)$ K. These calculated values of thermodynamic properties for the cellulose samples are given in table 15. It is assumed that the difference $\{C^\circ_{p,w}(p = 0.1\ MPa) - C^\circ_{p,w}(p = 1.2\ mPa)\}$ is less than $0.001\cdot C^\circ_{p,w}$ ($p = 0.1$ MPa). Thus, no correction is made to the measured $C^\circ_{p,w}$ values for pressure.

Application of equation (67) to the values of $C^\circ_{p,w}$, $\Delta^T_0 S^\circ_w$, $\Delta^T_0 H^\circ_w$ and Φ°_w at $T = 298.15$ K yields values for these properties at $w_{H_2O} = 0.073$. These adjusted property values are given in the second part of table 16. Then, use of these adjusted property values and the crystallinity indexes in equations similar to equations (25) and (57) leads to the property values given in the third part of table 16. The weighted averages of these property values are given in the fourth part of table 16.

As can be seen in table 14, the root-mean-square (RMS) deviations of the fits are all substantially less than the estimated possible inaccuracies in the calorimetric measurements ($0.02\cdot C^\circ_{p,w}$ for

TABLE 7
Values of $\Delta_c H^\circ_w$, the standard massic enthalpy of combustion, w_{H_2O}, the total mass fraction of water in the sample, and $\Delta_c H^\circ_w(w_{ref} = 0.073)$, the standard massic enthalpy of combustion at the mass fraction of water $w_{ref} = 0.073$. The temperature $T = 298.15$ K and $p^\circ = 0.1$ MPa.

Sample no.	$\Delta_c H^\circ_w/(J\cdot g^{-1})$[a]	w_{H_2O}[b]	$\Delta_c H^\circ_w(w_{ref} = 0.073)/(J\cdot g^{-1})$[c,d]
	Amorphous cellulose (24 h)		
1	−15554.3	0.10305	−16085.8
2	−15560.7	0.10205	−16074.2
3	−15579.3	0.09942	−16045.4
4	−15578.0	0.09944	−16044.4
	$\langle w_{H_2O}\rangle = 0.1010 \pm 0.0029$		
	$\langle \Delta_c H^\circ_w(w_{ref} = 0.073)/(J\cdot g^{-1})\rangle = -(16062.4 \pm 33)$		
	Amorphous cellulose (30 h)		
1	−15488.9	0.10417	−16038.7
2	−15492.4	0.10474	−16052.7
3	−15510.1	0.10373	−16052.5
4	−15573.9	0.09843	−16021.9
	$\langle w_{H_2O}\rangle = 0.1028 \pm 0.0046$		
	$\langle \Delta_c H^\circ_w(w_{ref} = 0.073)/(J\cdot g^{-1})\rangle = -(16041.5 \pm 23)$		
	Amorphous cellulose (36 h)		
1	−15760.2	0.09128	−16083.5
2	−15737.7	0.09288	−16089.4
3	−15750.8	0.09187	−16084.7
4	−15768.3	0.09035	−16075.1
	$\langle w_{H_2O}\rangle = 0.0916 \pm 0.0017$		
	$\langle \Delta_c H^\circ_w(w_{ref} = 0.073)/(J\cdot g^{-1})\rangle = -(16083.2 \pm 9.4)$		
	Cellulose Iβ		
1	−16292.3	0.05957	−16054.9
2	−16297.8	0.06028	−16072.7
3	−16299.2	0.05809	−16036.1
4	−16301.1	0.05884	−16050.9
	$\langle w_{H_2O}\rangle = 0.05919 \pm 0.0015$		
	$\langle \Delta_c H^\circ_w(w_{ref} = 0.073)/(J\cdot g^{-1})\rangle = -(16053.7 \pm 24)$		
	Cellulose II (25 °C)		
1	−16017.0	0.07150	−15990.6
2	−16003.3	0.07260	−15996.3
3	−16023.7	0.07185	−16003.5
4	−16038.2	0.07270	−16032.9
	$\langle w_{H_2O}\rangle = 0.07216 \pm 0.00093$		
	$\langle \Delta_c H^\circ_w(w_{ref} = 0.073)/(J\cdot g^{-1})\rangle = -(16005.8 \pm 30)$		
	Cellulose II (70 °C)		
1	−15924.5	0.07855	−16022.4
2	−15918.0	0.07737	−15995.0
3	−15913.4	0.07683	−15980.8
4	−15927.4	0.07577	−15976.1
	$\langle w_{H_2O}\rangle = 0.0771 \pm 0.0019$		
	$\langle \Delta_c H^\circ_w(w_{ref} = 0.073)/(J\cdot g^{-1})\rangle = -(15993.6 \pm 33)$		
	Cellulose II (145 °C)		
1	−16174.5	0.06400	−16015.8
2	−16233.7	0.05811	−15971.9
3	−16157.4	0.06181	−15960.8
4	−16185.9	0.06026	−15962.0
	$\langle w_{H_2O}\rangle = 0.0610 \pm 0.0040$		
	$\langle \Delta_c H^\circ_w(w_{ref} = 0.073)/(J\cdot g^{-1})\rangle = -(15977.6 \pm 41)$		
	Cellulose III (−33 °C)		
1	−16145.1	0.06923	−16078.3
2	−16056.4	0.07267	−16050.5
3	−16002.3	0.07495	−16036.7
4	−16500.9	0.04751	−16050.4
	$\langle w_{H_2O}\rangle = 0.0661 \pm 0.020$		
	$\langle \Delta_c H^\circ_w(w_{ref} = 0.073)/(J\cdot g^{-1})\rangle = -(16054.0 \pm 28)$		
	Cellulose III (25 °C)		
1	−16177.6	0.06657	−16063.9
2	−16160.5	0.06406	−16003.1
3	−16634.4	0.03755	−16009.5
4	−16648.9	0.03578	−15993.3
	$\langle w_{H_2O}\rangle = 0.0510 \pm 0.026$		
	$\langle \Delta_c H^\circ_w(w_{ref} = 0.073)/(J\cdot g^{-1})\rangle = -(16017.5 \pm 50)$		
	Cellulose III (130 °C)		
1	−16050.1	0.07521	−16089.2
2	−16175.2	0.06698	−16068.8
3	−16000.8	0.07793	−16088.2
4	−16060.7	0.07486	−16093.8
	$\langle w_{H_2O}\rangle = 0.07375 \pm 0.0075$		
	$\langle \Delta_c H^\circ_w(w_{ref} = 0.073)/(J\cdot g^{-1})\rangle = -(16085.0 \pm 17)$		

[a] The standard massic enthalpy of combustion $\Delta_c H^\circ_w$ was calculated as follows (also see table 6): $\Delta_c H^\circ_w = \Delta_c U^\circ_w(CO_2)\cdot m(cell_{corr})/m(cell)$.
[b] The mass fraction of water w_{H_2O} is based on the mass of $CO_2(g)$ produced {see equation (10)}.
[c] The quantity $\Delta_c H^\circ_w(w_{ref} = 0.073)$ is the standard massic enthalpy of combustion at the mass fraction of water $w_{ref} = 0.073$. This quantity was calculated by using equations (23) and (24).
[d] All uncertainties correspond to expanded uncertainties with approximately 95% confidence limits.

TABLE 8
Standard massic enthalpies of combustion $\Delta_c H^\circ_w$ and $\Delta_c H^{\circ*}_w$ of cellulose samples at $T = 298.15$ K and $p^\circ = 0.1$ MPa.[a]

Sample	$\Delta_c H^\circ_w(w_{ref} = 0.073)/(J\cdot g^{-1})$	$\Delta_c H^{\circ*}_w/(J\cdot g^{-1})$
Amorphous cellulose (24 h)	−(16062.4 ± 33)	−(16062 ± 14)[b]
Amorphous cellulose (30 h)	−(16041.5 ± 23)	−(16062 ± 14)[b]
Amorphous cellulose (36 h)	−(16083.2 ± 9.4)	−(16062 ± 14)[b]
Cellulose Iβ	−(16053.7 ± 24)	−(16048 ± 40)
Cellulose II (25 °C)	−(16005.8 ± 30)	−(15921 ± 78)[c]
Cellulose II (70 °C)	−(15993.6 ± 33)	−(15923 ± 69)[c]
Cellulose II (145 °C)	−(15977.6 ± 41)	−(15914 ± 73)[c]
Cellulose III (−33 °C)	−(16054.0 ± 28)	−(16036 ± 92)[c]
Cellulose III (25 °C)	−(16017.5 ± 50)	−(15971 ± 103)[c]
Cellulose III (130 °C)	−(16085.0 ± 18)	−(16101 ± 31)[c]

[a] $\Delta_c H^\circ_w(w_{ref} = 0.073)$ is the standard massic enthalpy of combustion of the specified sample at the mass fraction of water $w_{ref} = 0.073$ (see table 7) and $\Delta_c H^{\circ*}_w$ is the standard massic enthalpy of combustion of the specified form of pure cellulose at the mass fraction of water $w_{ref} = 0.073$. $\Delta_c H^{\circ*}_w$ is calculated using equation (25) and the values of w_{cr} which are based on the measured values of the crystallinity indexes. All uncertainties correspond to expanded uncertainties with approximately 95% confidence limits.
[b] The average of the values of $\Delta_c H^{\circ*}_w(w_{ref} = 0.073)$ for the amorphous cellulose samples is $-(16062 \pm 14)\ J\cdot g^{-1}$. This is taken to be the value for $\Delta_c H^{\circ*}_w(w_{ref} = 0.073)$ for cellulose(am).
[c] By taking weighted averages the following values are obtained: $\Delta_c H^{\circ*}_w = -(15919 \pm 84)\ J\cdot g^{-1}$ for cellulose II(cr) and $\Delta_c H^{\circ*}_w = -(16085 \pm 56)\ J\cdot g^{-1}$ for cellulose III(cr).

TABLE 9
Values of $\Delta_r H^{\circ*}_w$, the standard massic enthalpy changes for reactions (26)–(31) obtained from combustion calorimetry. All reactions pertain to $T = 298.15$ K, $p^\circ = 0.1$ MPa, and $w_{H_2O} = 0.073$.

Reaction	$\Delta_r H^{\circ*}_w/(J\cdot g^{-1})$[a]	$\Delta_r H^{\circ*}_w/(J\cdot g^{-1})$[b]
Cellulose(am) = cellulose Iβ(cr) (26)	−(14 ± 20)	−(14 ± 68)
Cellulose(am) = cellulose II(cr) (27)	−(143 ± 85)	−(143 ± 119)
Cellulose(am) = cellulose III(cr) (28)	22 ± 58	22 ± 78
Cellulose Iβ(cr) = cellulose II(cr) (29)	−(129 ± 86)	−(129 ± 88)
Cellulose Iβ(cr) = cellulose III(cr) (30)	36 ± 58	36 ± 59
Cellulose II(cr) = cellulose III(cr) (31)	165 ± 101	165 ± 106

[a] The uncertainties in this column correspond to expanded uncertainties based on a type A evaluation [49] and with a coverage factor $k = 2$ [49].
[b] The uncertainties in this column correspond to expanded uncertainties with approximately 95% confidence limits based on both a type A and type B evaluation [49] and with a coverage factor $k = 2$ (see section 3.6).

$T < 10$ K and $0.01\cdot C^\circ_{p,w}$ for 10 K < T< 302 K). Thus, we assume that both the random errors and the possible systematic errors in the calorimetric measurements are accounted for by the aforementioned estimates of possible inaccuracies. However, there are additional possible systematic errors in the measurements that must be considered. Specifically, we estimate possible inaccuracies in these

TABLE 10
Standard massic enthalpies of solution of cellulose samples and of H_2O(l) in cadoxen at $T = 298.15$ K and $p = 0.1013$ MPa.[a,b]

Sample	N	$\Delta_{sol}H^{\circ}_{w}/(J\cdot g^{-1})$	$\Delta_{sol}H^{\circ}_{w}(w_{H_2O} = 0.073)/(J\cdot g^{-1})$	$\Delta_{sol}H^{\circ *}_{w}(w_{H_2O} = 0.073)/(J\cdot g^{-1})$
Amorphous cellulose (24 h)	6	−(152.5 ± 2.1)	−(154.2 ± 2.1)	−(154.2 ± 2.1)[d]
Amorphous cellulose (30 h)	5	−(154.9 ± 4.3)	−(156.2 ± 4.3)	−(156.2 ± 4.3)[d]
Amorphous cellulose (36 h)	5	−(155.9 ± 6.1)	−(158.0 ± 6.1)	−(158.0 ± 6.1)[d]
Cellulose Iβ	5	−(100.5 ± 8.1)	−(90.1 ± 8.1)	−(49.6 ± 13)
Cellulose II (25 °C)	[c]			
Cellulose II (70 °C)	6	−(71.6 ± 8.6)	−(74.6 ± 8.6)	9.6 ± 18
Cellulose II (145 °C)	5	−(93.9 ± 1.9)	−(93.0 ± 1.9)	−(45.5 ± 3.8)
Cellulose III (−33 °C)	8	−(98.5 ± 5.2)	−(102.0 ± 5.2)	13.1 ± 17
Cellulose III (25 °C)	8	−(104.4 ± 6.5)	−(110.6 ± 6.5)	−(63.2 ± 14)
Cellulose III (130 °C)	5	−(90.1 ± 9.3)	−(98.5 ± 9.3)	−(59.0 ± 16)
H_2O(l)	3	−(24.00 ± 0.21)		

[a] The quantities are defined as follows: $\Delta_{sol}H^{\circ}_{w}$ is the measured standard massic enthalpy of solution of the specified sample; N is the number of measurements; $\Delta_{sol}H^{\circ}_{w}(w_{ref} = 0.073)$ is the standard massic enthalpy of solution of the specified sample at the mass fraction of water $w_{ref} = 0.073$ and is calculated from $\Delta_{sol}H^{\circ}_{w}$ (column 3) by using equations (56) and (24); and $\Delta_{sol}H^{\circ *}_{w}$ is the standard massic enthalpy of solution of the specified cellulose allomorph at the mass fraction of water $w_{ref} = 0.073$ and is calculated by using equation (57). The estimated standard uncertainties in the temperature T and pressure p are $u(T) = 0.05$ K and $u(p) = 0.004$ MPa. The uncertainties given in columns 3 and 4 correspond to expanded uncertainties with approximately 95% confidence limits. The uncertainties given in column 5 were obtained by combining in quadrature the uncertainties in the respective values of $\Delta_{sol}H^{\circ}_{w}(w_{ref} = 0.073)$ with the uncertainty in the average value of $\Delta_{sol}H^{\circ *}_{w}(w_{ref} = 0.073)$ for the amorphous cellulose samples and thus also correspond to expanded uncertainties with approximately 95% confidence limits.

[b] The final mass concentrations of the cellulose allomorphs in the 100.0 cm^3 of cadoxen in the calorimeter were ≈0.20 $g\cdot dm^{-3}$. The final mass concentration of the water in the 100.0 cm^3 of cadoxen in the calorimeter was ≈0.91 $g\cdot dm^{-3}$.

[c] It was not possible to perform measurements with the cellulose II (25 °C) sample due to the formation of a large clump (moist, compacted mass) of the sample which did not dissolve in the cadoxen. This clumping was observed in two independent experiments. Interestingly, this sample of cellulose II dissolved in cadoxen with gentle shaking in a small bottle placed in a constant temperature bath at 25.0 °C. Clearly, the stirring action in the calorimeter is different than that which is obtained using a shaking device. This problem was not observed when using the other cellulose samples.

[d] The average of the values of $\Delta_{sol}H^{\circ}_{w}(w_{ref} = 0.073)$ for the amorphous cellulose samples is $-(156.1 \pm 2.3)$ $J\cdot g^{-1}$. This is taken to be the value for $\Delta_{sol}H^{\circ *}_{w}(w_{ref} = 0.073)$ for cellulose(am).

measurements to be as follows: mass m, $0.003\cdot m$; mass fraction of water w_{H_2O} in the samples, $0.15\cdot w_{H_2O}$; crystallinity index, $0.03\cdot CI$; and $C^{\circ}_{p,w}$(adj) for the adjustment of values of $C^{\circ}_{p,w}$ to $w_{H_2O} = 0.073$, $0.20\cdot C^{\circ}_{p,w}$(adj). We also estimate a possible mass fraction impurity in the cellulose samples as $w = 0.005$ and that the impurities have a standard massic heat capacity two times the standard massic heat capacities of the respective cellulose samples. These estimates of possible systematic error are used together with the measured values of the heat capacities to perform a propagation of error analysis. The possible errors in the calculated quantities x due to the propagation of each of these possible sources of error are combined in quadrature to calculate combined standard uncertainties $u(x)$. Finally, expanded uncertainties $U(x)$ are estimated by use of the coverage factor, $U(x) = 2u(x)$ [49]. These estimates of error will vary with each individual heat-capacity result and can be propagated to the other property values $\Delta^{T}_{0}S^{\circ}_{w}$, $\Delta^{T}_{0}H^{\circ}_{w}$, and Φ°_{w}. The expanded uncertainties given in table 16 are based on these estimates of possible systematic error. The averages given in the lower part of table 16 were calculated as weighted averages from the results obtained from the respective amorphous cellulose, cellulose II, and cellulose III samples. From the propagation of error analysis, it was found that the principal source of possible error in the measurements is our knowledge of the crystallinity indexes. This is followed closely by possible errors in the mass fractions of water in the samples and in the adjustment of property values to $w_{H_2O} = 0.073$, and finally to possible impurities in the samples and in the calorimetric measurements. The remaining sources of possible error are negligible in comparison with the just mentioned sources of possible error.

3.9. Property values for the conversion reactions of the cellulose allomorphs

Calculated property values for the conversion reactions of the cellulose allomorphs at $T = 298.15$ K and $p^{\circ} = 0.1$ MPa are given in table 17. The values of $\Delta_r H^{\circ *}_{0}$ in this table are based on the solution calorimetry measurements (see table 11). It is important to recognize that the calculations of the values of the standard massic entropy changes $\Delta_r S^{\circ *}_{w}$ and the standard massic Gibbs free energy changes $\Delta_r G^{\circ *}_{w}$ were made on the *assumption* that the values of $S^{\circ *}_{w}$ for all of the allomorphs approach the same value as $T \rightarrow 0$. Since the values of $\Delta_r S^{\circ *}_{w}$ and $\Delta_r C^{\circ *}_{p,w}$ were obtained as differences between values of $\Delta^{T}_{0}S^{\circ *}_{w}$ and $C^{\circ *}_{p,w}$, for the respective allomorphs and since these values are very close to each other, the uncertainties in $\Delta_r S^{\circ *}_{w}$ and $\Delta_r C^{\circ *}_{p,w}$ are large. Additionally, the propagation of errors leads to very large uncertainties in the $\Delta_r G^{\circ *}_{w}$ values.

There is also the question as to how the thermodynamic property values given in table 17 might vary with degree of polymerization. For reactions in aqueous solution, there is evidence [54] that the dependence of the enthalpy on the degree of polymerization is small for carbohydrates that contain α-1,4 and α-1,6 linkages. However, this matter has not been settled for the solid state. Indeed, to resolve this matter definitively, one would need enthalpy of solution measurements in which samples of a cellulose allomorph having the same respective values of CI and w_{H_2O}, but different values of $DP_{w,}$ were dissolved in a solvent such as cadoxen. An alternative approach would be to measure standard massic enthalpies of solution $\Delta_{sol}H^{\circ}_{w}$ of cellobiose(cr), cellotriose(cr), cellotetraose(cr), cellopentaose(cr), *etc.* to see if there is any departure from a constant value of $\Delta_{sol}H^{\circ}_{w}$. This approach is easier, but it is

TABLE 11
Values of $\Delta_r H^{\circ *}_{w}$, the standard massic enthalpy changes for reactions (26)–(31) obtained from measurements of standard massic enthalpies of solution of the cellulose samples into cadoxen. All reactions pertain to $T = 298.15$ K, $p^{\circ} = 0.1$ MPa, and $w_{H_2O} = 0.073$.[a]

Reaction	$\Delta_r H^{\circ *}_{w}/(J\cdot g^{-1})$[a]	$\Delta_r H^{\circ *}_{w}/(J\cdot g^{-1})$[b]
Cellulose(am) = cellulose Iβ(cr) (26)	−(106 ± 13)	−(106 ± 18)
Cellulose(am) = cellulose II(cr) (27)	−(113 ± 8)	−(113 ± 11)
Cellulose(am) = cellulose III(cr) (28)	−(115 ± 18)	−(115 ± 20)
Cellulose Iβ(cr) = cellulose II(cr) (29)	−(7 ± 15)	−(7 ± 16)
Cellulose Iβ(cr) = cellulose III(cr) (30)	−(8 ± 22)	−(8 ± 25)
Cellulose II(cr) = cellulose III(cr) (31)	−(2 ± 19)	−(2 ± 20)

[a] The uncertainties in this column correspond to expanded uncertainties based on a type A evaluation [49] and with a coverage factor $k = 2$ [49].

[b] The uncertainties in this column correspond to expanded uncertainties with approximately 95% confidence limits based on both a type A and type B evaluation [49] and with a coverage factor $k = 2$ (see section 3.7).

TABLE 12
Masses of samples used in the heat-capacity measurements: m(sample) is the mass of the cellulose sample; m(Cu) is the mass of the copper; and m(puck) is the mass of the PPMS puck.[a]

Sample	m(sample)/mg	m(Cu)/mg	m(puck)/mg
Amorphous cellulose (24 h)	9.30	20.83	30.13
Amorphous cellulose (30 h)	13.03	21.50	34.53
Amorphous cellulose (36 h)	12.30	21.75	34.05
Cellulose Iβ	9.31	20.55	29.86
Cellulose II (25 °C)	4.98	18.35	23.33
Cellulose II (70 °C)	7.53	21.51	29.04
Cellulose II (145 °C)	9.52	20.69	30.21
Cellulose III (−33 °C)	10.00	21.68	31.68
Cellulose III (25 °C)	8.93	20.94	29.87
Cellulose III (130 °C)	10.21	21.37	31.58

[a] The estimated standard uncertainties in the masses are u = 0.02 mg.

not as definitive as the aforementioned series of suggested measurements. Not considered in the above discussion is the issue of morphology, *i.e.*, the number of cellulose chains in a fibril of a given sample.

The amorphous cellulose samples were prepared by grinding cellulose Iβ. Since this grinding causes the breaking of hydrogen bonds and a disruption of the hydrophobic and other interactions [16], one expects the crystallization reactions (26)–(28) {*i.e.*, cellulose(am) → cellulose (Iβ, II, and III)(cr)} to be exothermic due to the bonded and non-bonded interactions reforming. And, as expected, the values of $\Delta_r H^\circ_w$ for reactions (26)–(28) are all negative. Also, for these same three reactions, the values of $\Delta_r G^\circ_w$ are all negative within their respective combined standard uncertainties. Thus, the aforementioned reactions can, in principle, be used to prepare cellulose (Iβ, II, and III)}(cr) from cellulose(am), which is clearly the least stable of the cellulose allomorphs. In this regard, Hess *et al.* [55] and Hermans and Weidinger [56,58] reported approximately 70 years ago that cellulose II(cr) could be produced by heating amorphous cellulose with water. More recently, Mittal *et al.* have conducted experiments in which cellulose(am) was converted to cellulose III(cr) [2]. This conversion is accomplished by using anhydrous ammonia [57].

Since the values of $\Delta_r G^{\circ *}_w$ for reactions (29)–(31) have large uncertainties, it is not possible to use these values to order quantitatively the relative stabilities of the cellulose (I, II, and III) crystalline allomorphs with a reasonable degree of certainty. However, it is known that cellulose II(cr) can be prepared from cellulose Iβ(cr) (treatment with NaOH at 25 °C) (see section 2.1). Thus, cellulose II(cr) is more stable than cellulose Iβ(cr) at T = 298.15 K. Also, cellulose III_I(cr) and cellulose III_{II}(cr) can be prepared from cellulose Iβ and II, respectively, by treatment with liquid ammonia at −75 °C (see section 2.1 and references 2 and 57). Note here that Hayashi *et al.* [59] state that "the crystalline structures of cellulose III derived from cellulose I and from cellulose II are different and should be differentiated from one another as cellulose III_I and cellulose III_{II}, in spite of the fact that they have nearly the same unit cell and equatorial diffractogram." Thus, if the stability of cellulose III(cr) relative to cellulose Iβ(cr) and cellulose II(cr) does not depend on temperature over the range (−75 to 25) °C, the qualitative order of stability for the allomorphs is cellulose III(cr) > cellulose II(cr) > cellulose Iβ(cr). However, Mittal *et al.* [2] report that cellulose I can be reformed by the application of heat and water to a sample of cellulose III_I. Thus, the difference in the stabilities of the allomorphs cellulose (I, II, and III) appear to be small and may be temperature dependent. The aforementioned order of stability of cellulose I(cr) in regards to cellulose II(cr) and cellulose III_I(cr) and, in particular, the smallness of the differences is consistent with the results of molecular dynamics simulations by Beckham *et al.* [16]. This discussion of relative stabilities assumes that kinetics do not dominate the molecular events. For example, if Ostwald's rule held for the cellulose allomorphs, nucleation events could run counter to thermodynamic equilibria.

3.10. Comparison with results in literature

3.10.1. Standard massic enthalpies of hydration of the cellulose allomorphs

In order to make comparisons of the property values from our study with those in the literature that pertain to w_{H_2O} = 0 it is helpful to use a shorthand notation in which the quantity $[\Delta_{hyd}H^\circ_w\{C{\cdot}w_{H_2Of}(s)\} - \Delta_{hyd}H^\circ_w\{C{\cdot}w_{H_2Oi}(s)\}]$ (see section 3.3.2) is abbreviated as $\Delta_{hyd}H^\circ_w(C, w_i \rightarrow w_f)$. The subscripts i and f denote, respectively, the initial and final mass fractions of water. The "C" specifies either the cellulose sample or the pure cellulose allomorph (CI = 100), in which case a "*" is also used. The change in the mass fraction of water that occurs due to the hydration (or dehydration) reaction that takes a substance from w_{H_2Oi} to w_{H_2Of} is written as "$w_i \rightarrow w_f$". And a completely wet sample is designated as "wet". Thus, the first step in obtaining the values of $\Delta_{hyd}H^{\circ *}_w$ (cellulose, 0 → 0.073) needed for the comparison of property values is to use the values of $\Delta_{hyd}H^\circ_w$(cellulose sample, 0 → wet) that were reported by Nelson [14]. Specifically, she [14] measured standard massic enthalpies of hydration for samples of celluloses (I, II, and III) and for nearly amorphous cellulose along with the CI values for these samples. These anhydrous samples were immersed in 100 cm^3 of H_2O(l) and were, presumably, hydrated completely during the course of the solution experiment. The sample of "amorphous" cellulose used by Nelson [14] was prepared by ball milling a sample of cellulose I. The CI value of this nearly amorphous sample was 0.11. Thus, for the hydration of the cellulose I sample, we have the following equation which is analogous to equation (25)

$$\Delta_{hyd}H^\circ_w(\text{cell I sample}, 0 \rightarrow \text{wet}) = w_{cr}{\cdot}\Delta_{hyd}H^{\circ *}_w\{\text{cell I(cr)}, 0 \rightarrow \text{wet}\} + (1 - w_{cr}){\cdot}\Delta_c H^{\circ *}_w\{\text{cell(am)}, 0 \rightarrow \text{wet}\}. \quad (75)$$

Equations similar to equation (75) can be written for the hydration of the cellulose II, cellulose III samples and the nearly amorphous cellulose sample used by Nelson [14] in her study. As done previously, w_{cr} is taken to be equal to 0.01· CI. Thus, by using Nelson's [14] values for $\Delta_{hyd}H^\circ_w$(cell samples, 0 → wet) and for CI, we now have a system of linear equations of the form of equation (75). We solve these equations for values of $\Delta_{hyd}H^{\circ *}_w(0 \rightarrow \text{wet})$ for the pure cellulose allomorphs. These values of $\Delta_{hyd}H^{\circ *}_w(0 \rightarrow \text{wet})$ are: $-123\ J{\cdot}g^{-1}$ for cellulose(am), $-28\ J{\cdot}g^{-1}$ for cellulose I(cr), $-22\ J{\cdot}g^{-1}$ for cellulose II(cr), and $-28\ J{\cdot}g^{-1}$ for cellulose III(cr). We note that there is a body of evidence in the literature [15,60–63] that the absorption of water occurs substantially in the amorphous regions of cellulose samples. Thus, it is of interest that the values of $\Delta_{hyd}H^{\circ *}_w(0 \rightarrow \text{wet})$ for cellulose I(cr) and cellulose II(cr) are less exothermic than $\Delta_{hyd}H^{\circ *}_w(0 \rightarrow \text{wet})$ for cellulose(am). However, these values are based entirely on Nelson's [14] very limited data set.

The next step in obtaining values of $\Delta_{hyd}H^{\circ *}_w$(cellulose, 0 → 0.073) was to read off values of $\Delta_{hyd}H^\circ_w(0 \rightarrow \text{wet})$ from Rees' [15] figure 4 for the five cellulose samples considered in his study. These samples are (1) cotton, (2) cotton mercerized with tension, (3) cotton mercerized without tension, (4) Fortisan, and (5) Tenasco. Sample 1 consists of {cellulose(am) + cellulose I(cr)} and samples 2, 3, 4, and 5 consist of {cellulose(am) + cellulose II(cr)}. Again, a system of simultaneous linear equations of the form of equation (75) can be established by using Rees' [15] values of $\Delta_{hyd}H^\circ_w(0 \rightarrow \text{wet})$ and the values of $\Delta_{hyd}H^{\circ *}_w(0 \rightarrow \text{wet})$ that were calculated above from Nelson's [14] study. Solution of these equations yields CI values of 81, 50, 46, 47, and 27 for Rees' [15] cellulose samples 1, 2, 3, 4, and 5, respectively. We then use values of

TABLE 13
Standard massic heat capacities $C^{\circ}_{p,w}$ for the cellulose samples at $p = 1.2$ mPa from $T = (1.937$ to $301.63)$ K.[a]

T/K	$C^{\circ}_{p,w}/(\mathrm{J\cdot K^{-1}\cdot g^{-1}})$	T/K	$C^{\circ}_{p,w}/(\mathrm{J\cdot K^{-1}\cdot g^{-1}})$
	Amorphous cellulose (24 h)		
1.9370	$5.8225\cdot10^{-5}$	43.929	0.17282
2.1382	$7.6523\cdot10^{-5}$	48.735	0.19622
2.3819	$1.0339\cdot10^{-4}$	54.074	0.22413
2.6457	$1.3821\cdot10^{-4}$	59.991	0.25280
2.9347	$1.9184\cdot10^{-4}$	66.566	0.28574
3.2581	$2.5929\cdot10^{-4}$	73.864	0.32142
3.6194	$3.8378\cdot10^{-4}$	81.963	0.36243
4.0172	$5.0555\cdot10^{-4}$	90.966	0.40831
4.4560	$7.1424\cdot10^{-4}$	100.96	0.45364
4.9455	$1.0026\cdot10^{-3}$	111.09	0.49833
5.4909	$1.4154\cdot10^{-3}$	121.13	0.54278
6.0946	$1.9735\cdot10^{-3}$	131.16	0.58766
6.7619	$2.7693\cdot10^{-3}$	141.28	0.63271
7.5014	$3.8161\cdot10^{-3}$	151.31	0.67922
8.3140	$5.2139\cdot10^{-3}$	161.43	0.72441
9.2325	$7.1118\cdot10^{-3}$	171.48	0.77463
10.245	$9.5514\cdot10^{-3}$	181.55	0.82378
11.369	0.012677	191.67	0.87538
12.617	0.016562	201.77	0.93001
14.006	0.021427	211.87	0.98029
15.534	0.027383	221.96	1.0347
17.264	0.034485	232.04	1.0876
19.135	0.042851	242.07	1.1407
21.260	0.052979	252.17	1.1992
23.583	0.064413	262.19	1.2539
26.153	0.077450	272.28	1.3034
29.007	0.092371	282.14	1.3527
32.177	0.10919	291.86	1.3873
35.695	0.12791	301.63	1.4122
39.592	0.14919		
	Amorphous cellulose (30 h)		
1.9136	$5.6140\cdot10^{-5}$	43.760	0.17213
2.1059	$7.4108\cdot10^{-5}$	48.574	0.19640
2.3260	$9.7460\cdot10^{-5}$	53.912	0.22421
2.5966	$1.3250\cdot10^{-4}$	59.843	0.25434
2.8811	$1.7984\cdot10^{-4}$	66.432	0.28669
3.1936	$2.5052\cdot10^{-4}$	73.741	0.32292
3.5447	$3.4735\cdot10^{-4}$	81.856	0.36370
3.9330	$4.7852\cdot10^{-4}$	90.866	0.40942
4.3826	$6.7978\cdot10^{-4}$	100.87	0.45534
4.8571	$9.4660\cdot10^{-4}$	111.00	0.50129
5.3960	$1.3301\cdot10^{-3}$	121.07	0.54525
5.9943	$1.8717\cdot10^{-3}$	131.17	0.59119
6.6643	$2.6400\cdot10^{-3}$	141.23	0.63545
7.3946	$3.6584\cdot10^{-3}$	151.36	0.68296
8.2109	$5.0363\cdot10^{-3}$	161.43	0.73047
9.1198	$6.8712\cdot10^{-3}$	171.55	0.77890
10.135	$9.2814\cdot10^{-3}$	181.70	0.82900
11.255	0.012347	191.78	0.87735
12.496	0.016231	201.86	0.92786
13.848	0.021154	211.92	0.97969
15.392	0.026738	221.97	1.0361
17.082	0.033977	231.93	1.0920
18.984	0.042270	241.97	1.1460
21.043	0.052197	251.98	1.2085
23.368	0.063560	262.00	1.2611
25.939	0.076667	272.05	1.3142
28.802	0.091676	281.91	1.3631
31.983	0.10871	291.51	1.3991
35.506	0.12775	301.18	1.4150
39.418	0.14891		
	Amorphous cellulose (36 h)		
1.9490	$5.7989\cdot10^{-5}$	43.928	0.16827
2.1749	$7.7117\cdot10^{-5}$	48.737	0.19174
2.4413	$1.1112\cdot10^{-4}$	54.074	0.21879
2.6831	$1.4042\cdot10^{-4}$	60.001	0.24805
2.9825	$1.9877\cdot10^{-4}$	66.574	0.28020
3.3120	$2.7175\cdot10^{-4}$	73.872	0.31556
3.6568	$3.7269\cdot10^{-4}$	81.981	0.35515
4.0582	$5.2364\cdot10^{-4}$	90.988	0.39994
4.5064	$7.2369\cdot10^{-4}$	100.99	0.44486
5.0043	$1.0231\cdot10^{-3}$	111.12	0.48907
5.5516	$1.4331\cdot10^{-3}$	121.16	0.53308
6.1519	$2.0065\cdot10^{-3}$	131.24	0.57643
6.8202	$2.7869\cdot10^{-3}$	141.29	0.61933
7.5467	$3.8253\cdot10^{-3}$	151.41	0.66668
8.3793	$5.2448\cdot10^{-3}$	161.44	0.71285
9.2932	$7.1058\cdot10^{-3}$	171.53	0.75653
10.307	$9.5054\cdot10^{-3}$	181.67	0.80642
11.429	0.012554	191.77	0.85457
12.665	0.016994	201.87	0.90497
14.032	0.022906	211.95	0.95222
15.601	0.026710	222.01	1.0057
17.248	0.033575	232.02	1.0591
19.139	0.041778	242.08	1.1095
21.253	0.051563	252.12	1.1619
23.566	0.062388	262.17	1.2124
26.140	0.075211	272.26	1.2670
29.002	0.089863	282.20	1.3163
32.176	0.10639	291.91	1.3606
35.694	0.12461	301.61	1.3884
39.592	0.14544		
	Cellulose Iβ		
1.9323	$6.1141\cdot10^{-5}$	43.792	0.16562
2.1236	$8.0362\cdot10^{-5}$	48.605	0.18861
2.3544	$1.0723\cdot10^{-4}$	53.954	0.21524
2.6118	$1.4459\cdot10^{-4}$	59.889	0.24436
2.8981	$1.9734\cdot10^{-4}$	66.480	0.27639
3.2130	$2.6957\cdot10^{-4}$	73.756	0.31286
3.5631	$3.6812\cdot10^{-4}$	81.901	0.35228
3.9559	$5.0527\cdot10^{-4}$	90.914	0.39670
4.3901	$6.9230\cdot10^{-4}$	100.92	0.43908
4.8749	$9.5480\cdot10^{-4}$	111.07	0.48259
5.4131	$1.3148\cdot10^{-3}$	121.09	0.52575
6.0097	$1.8207\cdot10^{-3}$	131.21	0.56800
6.6728	$2.5132\cdot10^{-3}$	141.27	0.61266
7.4090	$3.4447\cdot10^{-3}$	151.42	0.65616
8.2293	$4.7006\cdot10^{-3}$	161.48	0.69584
9.1357	$6.3575\cdot10^{-3}$	171.64	0.74299
10.141	$8.5171\cdot10^{-3}$	181.75	0.78894
11.260	0.011304	191.85	0.83355
12.502	0.014867	201.92	0.88005
13.878	0.019313	212.00	0.92881
15.448	0.024763	222.04	0.97840
17.082	0.031365	232.01	1.0249
18.994	0.039437	242.07	1.0733
21.057	0.048934	252.16	1.1247
23.378	0.059925	262.19	1.1711
25.955	0.072807	272.32	1.2202
28.828	0.087231	282.35	1.2690
32.005	0.10405	292.27	1.3123
35.530	0.12241	302.27	1.3547
39.446	0.14311		
	Cellulose II (25 °C)		
1.9435	$5.9193\cdot10^{-5}$	43.887	0.16459
2.1662	$8.1860\cdot10^{-5}$	48.698	0.18679
2.4262	$1.1045\cdot10^{-4}$	54.040	0.21310
2.6711	$1.4581\cdot10^{-4}$	59.966	0.24132
2.9686	$1.9258\cdot10^{-4}$	66.547	0.27260
3.2953	$2.7774\cdot10^{-4}$	73.851	0.30726
3.6482	$3.8171\cdot10^{-4}$	81.958	0.34694
4.0406	$5.2100\cdot10^{-4}$	90.967	0.39266
4.4865	$7.4297\cdot10^{-4}$	100.96	0.43625
4.9801	$1.0435\cdot10^{-3}$	111.10	0.48177
5.5262	$1.4572\cdot10^{-3}$	121.15	0.52251
6.1264	$2.0059\cdot10^{-3}$	131.24	0.56609
6.7892	$2.7854\cdot10^{-3}$	141.28	0.60412
7.5160	$3.8163\cdot10^{-3}$	151.41	0.65304
8.3423	$5.2144\cdot10^{-3}$	161.52	0.69347
9.2531	$7.0405\cdot10^{-3}$	171.57	0.74208
10.261	$9.4047\cdot10^{-3}$	181.72	0.78678
11.379	0.012422	191.80	0.83541
12.621	0.016199	201.87	0.88041
13.998	0.020901	211.95	0.93139
15.525	0.026371	222.00	0.98192

TABLE 13 (*continued*)

T/K	$C^{\circ}_{p,w}/(\mathrm{J\cdot K^{-1}\cdot g^{-1}})$	T/K	$C^{\circ}_{p,w}/(\mathrm{J\cdot K^{-1}\cdot g^{-1}})$
17.257	0.033221	232.03	1.0318
19.089	0.041081	242.03	1.0814
21.196	0.050467	252.13	1.1329
23.502	0.061367	262.20	1.1843
26.079	0.073707	272.33	1.2336
28.943	0.087798	282.37	1.2891
32.119	0.10415	292.31	1.3358
35.638	0.12205	302.37	1.3951
39.546	0.14235		
	Cellulose II (70 °C)		
1.9431	$5.8971\cdot10^{-5}$	43.897	0.16316
2.1525	$8.3937\cdot10^{-5}$	48.707	0.18535
2.4044	$1.1050\cdot10^{-4}$	54.046	0.21206
2.6603	$1.5092\cdot10^{-4}$	59.970	0.24015
2.9526	$1.9954\cdot10^{-4}$	66.548	0.27006
3.2766	$2.7422\cdot10^{-4}$	73.851	0.30413
3.6356	$3.9530\cdot10^{-4}$	81.954	0.34308
4.0331	$5.2930\cdot10^{-4}$	90.963	0.38721
4.4662	$7.4242\cdot10^{-4}$	100.95	0.42921
4.9614	$1.0459\cdot10^{-3}$	111.08	0.47272
5.5099	$1.4632\cdot10^{-3}$	121.12	0.51569
6.1134	$2.0298\cdot10^{-3}$	131.20	0.55716
6.7776	$2.8135\cdot10^{-3}$	141.24	0.59842
7.5163	$3.8572\cdot10^{-3}$	151.36	0.64225
8.3277	$5.2309\cdot10^{-3}$	161.44	0.68439
9.2389	$7.0860\cdot10^{-3}$	171.50	0.72664
10.251	$9.4645\cdot10^{-3}$	181.58	0.77529
11.372	0.012456	191.71	0.81980
12.620	0.016236	201.80	0.87063
14.000	0.020867	211.90	0.91601
15.530	0.025607	222.01	0.96344
17.241	0.033015	232.09	1.0086
19.107	0.041026	242.18	1.0628
21.217	0.050300	252.23	1.1110
23.537	0.060954	262.30	1.1596
26.104	0.073231	272.41	1.2028
28.964	0.087407	282.42	1.2521
32.137	0.10318	292.31	1.2968
35.654	0.12105	302.31	1.3420
39.559	0.14145		
	Cellulose II (145 °C)		
1.9307	$5.8737\cdot10^{-5}$	43.905	0.16327
2.1317	$7.6741\cdot10^{-5}$	48.719	0.18525
2.3660	$1.0302\cdot10^{-4}$	54.061	0.21215
2.6231	$1.3881\cdot10^{-4}$	59.983	0.23946
2.9169	$1.9181\cdot10^{-4}$	66.558	0.26997
3.2354	$2.6425\cdot10^{-4}$	73.862	0.30343
3.5897	$3.6226\cdot10^{-4}$	81.969	0.34269
3.9901	$5.1199\cdot10^{-4}$	90.981	0.38553
4.4310	$7.0689\cdot10^{-4}$	100.97	0.42789
4.9195	$9.9320\cdot10^{-4}$	111.10	0.47105
5.4662	$1.3798\cdot10^{-3}$	121.14	0.51313
6.0706	$1.9477\cdot10^{-3}$	131.21	0.55544
6.7302	$2.6851\cdot10^{-3}$	141.26	0.59676
7.4716	$3.7250\cdot10^{-3}$	151.37	0.63955
8.2970	$5.1051\cdot10^{-3}$	161.45	0.68070
9.2065	$6.9177\cdot10^{-3}$	171.49	0.72468
10.220	$9.2655\cdot10^{-3}$	181.62	0.77232
11.344	0.012237	191.70	0.81830
12.587	0.015998	201.79	0.86465
13.971	0.020576	211.89	0.91268
15.510	0.026291	221.98	0.96019
17.235	0.032928	232.06	1.0098
19.111	0.041238	242.15	1.0616
21.223	0.050352	252.19	1.1094
23.543	0.060987	262.26	1.1568
26.113	0.073269	272.37	1.2059
28.967	0.087335	282.36	1.2521
32.139	0.10311	292.21	1.2940
35.660	0.12078	302.08	1.3360
39.566	0.14106		

TABLE 13 (*continued*)

T/K	$C^{\circ}_{p,w}/(\mathrm{J\cdot K^{-1}\cdot g^{-1}})$	T/K	$C^{\circ}_{p,w}/(\mathrm{J\cdot K^{-1}\cdot g^{-1}})$
	Cellulose III (−33 °C)		
1.9400	$6.1571\cdot10^{-5}$	43.899	0.16272
2.1548	$8.0878\cdot10^{-5}$	48.710	0.18491
2.4045	$1.1663\cdot10^{-4}$	54.052	0.21166
2.6557	$1.5418\cdot10^{-4}$	59.974	0.23873
2.9514	$2.0785\cdot10^{-4}$	66.554	0.26906
3.2757	$2.8891\cdot10^{-4}$	73.856	0.30337
3.6354	$4.0121\cdot10^{-4}$	81.961	0.34214
4.0256	$5.4529\cdot10^{-4}$	90.970	0.38520
4.4668	$7.5671\cdot10^{-4}$	100.96	0.42806
4.9600	$1.0410\cdot10^{-3}$	111.10	0.47097
5.5110	$1.4633\cdot10^{-3}$	121.12	0.51368
6.1118	$2.0385\cdot10^{-3}$	131.19	0.55548
6.7780	$2.7620\cdot10^{-3}$	141.24	0.59930
7.5119	$3.8061\cdot10^{-3}$	151.35	0.64200
8.3293	$5.1804\cdot10^{-3}$	161.43	0.68419
9.2409	$6.9837\cdot10^{-3}$	171.48	0.72574
10.257	$9.2982\cdot10^{-3}$	181.55	0.77372
11.380	0.012260	191.68	0.81876
12.621	0.015908	201.77	0.86491
14.005	0.020503	211.87	0.91099
15.553	0.026015	221.95	0.96074
17.250	0.032702	232.03	1.0061
19.111	0.040720	242.11	1.0559
21.221	0.049798	252.14	1.1094
23.539	0.060491	262.21	1.1556
26.112	0.072789	272.29	1.2005
28.967	0.086971	282.27	1.2476
32.141	0.10285	292.12	1.2879
35.657	0.12046	302.02	1.3312
39.564	0.14073		
	Cellulose III (25 °C)		
1.9360	$6.0643\cdot10^{-5}$	43.873	0.16301
2.1615	$8.5663\cdot10^{-5}$	48.686	0.18556
2.4158	$1.2118\cdot10^{-4}$	54.027	0.21171
2.6625	$1.5299\cdot10^{-4}$	59.954	0.23991
2.9615	$2.1179\cdot10^{-4}$	66.533	0.27124
3.2712	$2.7925\cdot10^{-4}$	73.836	0.30583
3.6605	$4.0684\cdot10^{-4}$	81.948	0.34491
4.0318	$5.3932\cdot10^{-4}$	90.959	0.38920
4.4756	$7.4836\cdot10^{-4}$	100.96	0.43309
4.9670	$1.0476\cdot10^{-3}$	111.09	0.47612
5.5126	$1.4598\cdot10^{-3}$	121.14	0.51966
6.1054	$2.0082\cdot10^{-3}$	131.23	0.56261
6.7767	$2.7669\cdot10^{-3}$	141.28	0.60258
7.5057	$3.7861\cdot10^{-3}$	151.41	0.65011
8.3310	$5.1675\cdot10^{-3}$	161.45	0.69074
9.2393	$6.9411\cdot10^{-3}$	171.55	0.73271
10.248	$9.2629\cdot10^{-3}$	181.70	0.78002
11.370	0.012221	191.79	0.82531
12.607	0.015925	201.88	0.87195
13.987	0.020494	211.95	0.91982
15.520	0.025889	222.02	0.97302
17.229	0.032777	232.03	1.0186
19.079	0.040496	242.10	1.0672
21.184	0.049712	252.15	1.1158
23.493	0.060518	262.21	1.1636
26.068	0.072953	272.33	1.2152
28.932	0.086959	282.35	1.2671
32.106	0.10304	292.24	1.3090
35.628	0.12072	302.23	1.3647
39.536	0.14090		
	Cellulose III (130 °C)		
1.9358	$6.2961\cdot10^{-5}$	43.899	0.16398
2.1424	$8.2582\cdot10^{-5}$	48.713	0.18592
2.3867	$1.1333\cdot10^{-4}$	54.056	0.21286
2.6373	$1.5134\cdot10^{-4}$	59.978	0.24071
2.9321	$2.0248\cdot10^{-4}$	66.560	0.27192
3.2521	$2.8065\cdot10^{-4}$	73.866	0.30648
3.6100	$3.9167\cdot10^{-4}$	81.974	0.34552
4.0092	$5.3964\cdot10^{-4}$	90.987	0.38847
4.4515	$7.4023\cdot10^{-4}$	100.99	0.43095
4.9414	$1.0233\cdot10^{-3}$	111.12	0.47475

(*continued on next page*)

TABLE 13 (*continued*)

T/K	$C^{\circ}_{p,w}/(\mathrm{J\cdot K^{-1}\cdot g^{-1}})$	T/K	$C^{\circ}_{p,w}/(\mathrm{J\cdot K^{-1}\cdot g^{-1}})$
5.4881	$1.4246\cdot10^{-3}$	121.17	0.51943
6.0847	$1.9737\cdot10^{-3}$	131.25	0.56160
6.7545	$2.7399\cdot10^{-3}$	141.30	0.60769
7.4968	$3.7686\cdot10^{-3}$	151.43	0.64751
8.3247	$5.1367\cdot10^{-3}$	161.51	0.69226
9.2365	$6.9259\cdot10^{-3}$	171.56	0.73537
10.249	$9.2690\cdot10^{-3}$	181.70	0.78198
11.371	0.012239	191.78	0.82934
12.620	0.015946	201.89	0.87829
13.997	0.020540	212.00	0.92467
15.568	0.026208	222.09	0.97557
17.231	0.032895	232.18	1.0314
19.107	0.040757	242.26	1.0720
21.215	0.050184	252.33	1.1256
23.536	0.060863	262.40	1.1751
26.108	0.073315	272.50	1.2270
28.964	0.087546	282.51	1.2778
32.139	0.10344	292.36	1.3160
35.658	0.12123	302.20	1.3530
39.561	0.14140		

[a] The estimated standard uncertainties in the temperature T and pressure p are $u(T) = 0.001$ K and $u(p) = 0.10$ mPa. The expanded uncertainties at approximately 95% confidence limits in the values of $C^{\circ}_{p,w}$ are $U(C^{\circ}_{p,w}) = 0.02\cdot C^{\circ}_{p,w}(2 < T/\mathrm{K} < 20)$ and $U(C^{\circ}_{p,w}) = 0.01\cdot C^{\circ}_{p,w}(10 < T/\mathrm{K302})$.

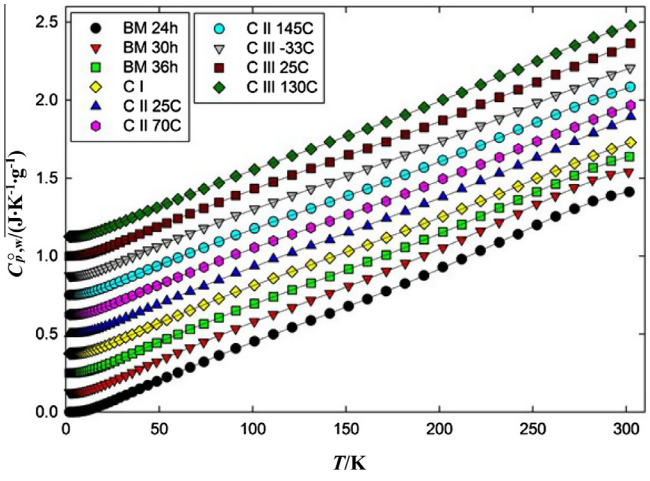

FIGURE 7. Heat-capacity data with fits for the ten cellulose samples measured using a PPMS from $T = (2$ to $300)$ K. The data are successively offset by $0.125\ \mathrm{J\cdot K^{-1}\cdot g^{-1}}$. The samples include the three amorphous cellulose samples, one cellulose Iβ sample (C I), the three cellulose II (C II) samples, and the three cellulose III (C III) samples.

$\Delta_{\mathrm{hyd}}H^{\circ}_{\mathrm{w}}(0 \rightarrow 0.073)$ for these five cellulose samples that are again obtained from Rees' [15] figure 4 together with the calculated *CI* values to set up one more system of linear equations analogous to equation (75). The solution of these equations gives $\Delta_{\mathrm{hyd}}H^{\circ*}_{\mathrm{w}}(0 \rightarrow 0.073) = -55\ \mathrm{J\cdot g^{-1}}$ for cellulose(am), $\Delta_{\mathrm{hyd}}H^{\circ*}_{\mathrm{w}}(0 \rightarrow 0.073) = -32\ \mathrm{J\cdot g^{-1}}$ for cellulose I(cr), and $\Delta_{\mathrm{hyd}}H^{\circ*}_{\mathrm{w}}(0 \rightarrow 0.073) = -44\ \mathrm{J\cdot g^{-1}}$ for cellulose II(cr). For cellulose III(cr) we estimate $\Delta_{\mathrm{hyd}}H^{\circ*}_{\mathrm{w}}(0 \rightarrow 0.073) = -38\ \mathrm{J\cdot g^{-1}}$ as the average of the $\Delta_{\mathrm{hyd}}H^{\circ*}_{\mathrm{w}}(w = 0 \rightarrow 0.073)$ values for cellulose I(cr) and cellulose II(cr). These values of $\Delta_{\mathrm{hyd}}H^{\circ*}_{\mathrm{w}}(0 \rightarrow 0.073)$ are estimated to be uncertain by $0.25\cdot\Delta_{\mathrm{hyd}}H^{\circ*}_{\mathrm{w}}(0 \rightarrow 0.073)$. We use these values of $\Delta_{\mathrm{hyd}}H^{\circ*}_{\mathrm{w}}(0 \rightarrow 0.073)$ in the comparison of property values that follows.

3.10.2. Literature results that lead to values of $\Delta_{\mathrm{r}}H^{\circ}_{w}$ for reactions (26)–(31)

The results of previous studies by Calvet and Hermans [65], Nelson [14], and Dale and Tsao [66] for reactions (26)–(28), all of which refer to $w_{\mathrm{H_2O}} = 0$, are shown in table 18. Comparisons of these results with those obtained in this study that pertain to $w_{\mathrm{H_2O}} = 0.073$ can be made by using the values of $\Delta_{\mathrm{hyd}}H^{\circ*}_{\mathrm{w}}(0 \rightarrow 0.073)$ given in section 3.10.1 and a thermochemical cycle calculation. Thus, for reaction (26)

$$\begin{aligned}\Delta_{\mathrm{r}}H^{\circ*}_{\mathrm{w}}(w_{\mathrm{H_2O}} = 0) = {} & \Delta_{\mathrm{r}}H^{\circ*}_{w}(w_{\mathrm{H_2O}} = 0.073) \\ & + \Delta_{\mathrm{hyd}}H^{\circ*}_{\mathrm{w}}\{\mathrm{cell(am)}, 0 \rightarrow 0.073\} \\ & - \Delta_{\mathrm{hyd}}H^{\circ*}_{\mathrm{w}}\{\mathrm{cell}\ I(cr), 0 \rightarrow 0.073\}. \end{aligned} \quad (76)$$

Analogous equations hold for reactions (27)–(31). The values of $\Delta_{\mathrm{r}}H^{\circ*}_{\mathrm{w}}(w_{\mathrm{H_2O}} = 0)$ calculated from our values of $\Delta_{\mathrm{r}}H^{\circ*}_{\mathrm{w}}(w_{\mathrm{H_2O}} = 0.073)$ are also shown in table 18. These values are seen to be more exothermic for reactions (26) and (28) than the earlier studies. However, all values for reactions (26)–(28) are in agreement within their uncertainties. Values of $\Delta_{\mathrm{r}}H^{\circ*}_{\mathrm{w}}$ for the mercerization reaction (29) are also summarized in table 18. Our result is in agreement with the values of $\Delta_{\mathrm{r}}H^{\circ*}_{\mathrm{w}}$ obtained from the studies of Calvet [64], Ranby [50], Nelson [14], and Dale and Tsao [66]. The value of $\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{w}}$ for reaction (29) calculated from the study of Ioelovich [78] appears to be an outlier.

Nelson [14] also measured (see pages 44 and 45 in her thesis) the standard massic enthalpies of combustion $\Delta_{\mathrm{c}}H^{\circ}_{\mathrm{w}}$ of samples of cellulose I, cellulose II, and cellulose III. She [14] used two different samples of cellulose I having respective *CI* values of 87.8 and 93.4, which were measured by using acid hydrolysis. The values of $\Delta_{\mathrm{c}}H^{\circ}_{\mathrm{w}}$ and *CI* for these two samples were then used to calculate values of $\Delta_{\mathrm{c}}H^{\circ*}_{\mathrm{w}}$ for cellulose(am) and for cellulose I(cr). By using her [14] measured values of *CI* for the cellulose II and cellulose III samples, she [14] then calculated values of $\Delta_{\mathrm{c}}H^{\circ*}_{\mathrm{w}}$ for cellulose II(cr) and cellulose III(cr). Her [14] results (see pages 77 and 78 in her thesis) were: $\Delta_{\mathrm{c}}H^{\circ*}_{\mathrm{w}} = -18376\ \mathrm{J\cdot g^{-1}}$ for cellulose(am); $\Delta_{\mathrm{c}}H^{\circ*}_{\mathrm{w}} = -17330\ \mathrm{J\cdot g^{-1}}$ for cellulose I(cr); $\Delta_{\mathrm{c}}H^{\circ*}_{\mathrm{w}} = -17125\ \mathrm{J\cdot g^{-1}}$ for cellulose II(cr); and $\Delta_{\mathrm{c}}H^{\circ*}_{\mathrm{w}} = -17205\ \mathrm{J\cdot g^{-1}}$ for cellulose III(cr). These results were then used to calculate the following values: $\Delta_{\mathrm{r}}H^{\circ*}_{\mathrm{w}} = -1046\ \mathrm{J\cdot g^{-1}}$ for reaction (26); $\Delta_{\mathrm{r}}H^{\circ*}_{\mathrm{w}} = -1251\ \mathrm{J\cdot g^{-1}}$ for reaction (27); and $\Delta_{\mathrm{r}}H^{\circ*}_{\mathrm{w}} = -1172\ \mathrm{J\cdot g^{-1}}$ for reaction (28). It is seen that the results obtained by use of Nelson's [14] combustion experiments differ by a factor of ten from the results obtained by her [14] from her solution calorimetry experiments (see table 18). This very large discrepancy may be due to the fact that the two samples of cellulose I that she used had *CI* values that were too close together,

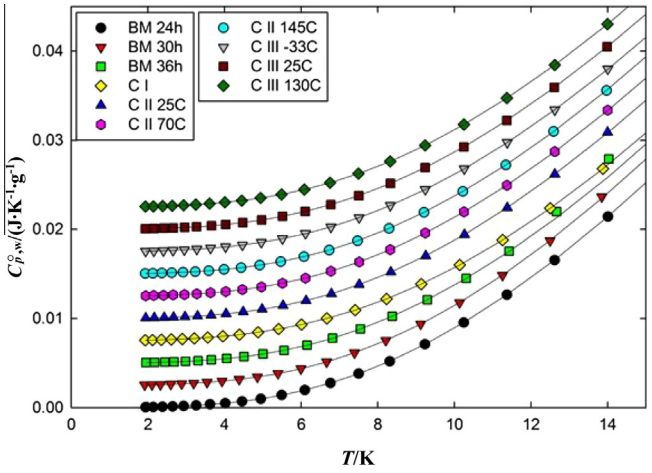

FIGURE 8. Low temperature ($T < 15$ K) heat-capacity data with fits for the ten cellulose samples measured using a PPMS. The data are successively offset by $2.5\cdot10^{-3}\ \mathrm{J\cdot K^{-1}\cdot g^{-1}}$. The samples include the three amorphous cellulose samples, one cellulose Iβ sample (C I), the three cellulose II (C II) samples, and the three cellulose III (C III) samples.

TABLE 14

The fitting parameters {see equations (73) and (74)} of the heat-capacity data for the cellulose samples at p° = 1.2 mPa covering the range T = (1.9 to 305) K. The fits are divided into three overlapping ranges: T = 13 K (low T), 10 K < T < 37 K (mid T), and T > 33 K (high T). The root-mean-square (RMS) deviations of the fits over the specified temperature ranges are also given.

Parameters	Cellulose(am) (24 h)	Cellulose(am) (30 h)	Cellulose(am) (36 h)	Cellulose Iβ	Cellulose II (25 °C)	Cellulose II (70 °C)	Cellulose II (145 °C)	Cellulose III (−33 °C)	Cellulose III (25 °C)	Cellulose III (130 °C)
					Low T fits					
$\gamma/(J\cdot K^{-2}\cdot g^{-1})$	$5.6173\cdot10^{-6}$	$3.5834\cdot10^{-6}$	$3.8027\cdot10^{-6}$	$2.3324\cdot10^{-6}$	$3.4099\cdot10^{-6}$	$3.7503\cdot10^{-6}$	$2.5306\cdot10^{-6}$	$1.0816\cdot10^{-6}$	$2.8385\cdot10^{-6}$	$3.5148\cdot10^{-6}$
$B_3/(J\cdot K^{-4}\cdot g^{-1})$	$6.5479\cdot10^{-6}$	$7.0974\cdot10^{-6}$	$6.8456\cdot10^{-6}$	$7.8957\cdot10^{-6}$	$7.0883\cdot10^{-6}$	$7.1081\cdot10^{-6}$	$7.3982\cdot10^{-6}$	$8.2021\cdot10^{-6}$	$7.6772\cdot10^{-6}$	$7.7617\cdot10^{-6}$
$B_5/(J\cdot K^{-6}\cdot g^{-1})$	$-1.0802\cdot10^{-8}$	$-1.4559\cdot10^{-8}$	$-1.4100\cdot10^{-8}$	$-1.4177\cdot10^{-8}$	$-1.2910\cdot10^{-8}$	$-1.1949\cdot10^{-8}$	$-1.6163\cdot10^{-8}$	$-1.9661\cdot10^{-8}$	$-1.4640\cdot10^{-8}$	$-1.4899\cdot10^{-8}$
$B_{gap}/(J\cdot K^{-5/2}\cdot g^{-1})$	$5.7094\cdot10^{-4}$	$6.5559\cdot10^{-4}$	$6.2151\cdot10^{-4}$	$4.0723\cdot10^{-4}$	$5.0924\cdot10^{-4}$	$4.6913\cdot10^{-4}$	$6.1626\cdot10^{-4}$	$6.2929\cdot10^{-4}$	$4.6276\cdot10^{-4}$	$4.8924\cdot10^{-4}$
δ/K	16.689	18.499	17.944	20.291	17.045	16.355	18.980	20.990	17.990	18.828
RMS%	0.476	0.561	0.920	0.322	0.544	0.968	0.540	0.725	0.945	0.520
Temperature range/K	1.9 to 12.81	1.9 to 10.24	1.9 to 10.82	1.9 to 10.14	1.9 to 10.30	1.9 to 10.04	1.9 to 10.37	1.9 to 10.24	1.9 to 10.29	1.9 to 10.38
					Mid T fits					
$A_0/(J\cdot K^{-1}\cdot g^{-1})$	$8.5954\cdot10^{-3}$	$8.4463\cdot10^{-3}$	$9.9376\cdot10^{-3}$	$9.1701\cdot10^{-3}$	$5.6980\cdot10^{-3}$	$7.8578\cdot10^{-3}$	$1.1167\cdot10^{-2}$	$6.7463\cdot10^{-3}$	$7.0367\cdot10^{-3}$	$8.2392\cdot10^{-3}$
$A_1/(J\cdot K^{-2}\cdot g^{-1})$	$-3.1881\cdot10^{-3}$	$-3.2624\cdot10^{-3}$	$-3.4618\cdot10^{-3}$	$-3.1158\cdot10^{-3}$	$-2.5195\cdot10^{-3}$	$-3.0636\cdot10^{-3}$	$-3.8797\cdot10^{-3}$	$-2.6534\cdot10^{-3}$	$-2.7917\cdot10^{-3}$	$-3.0399\cdot10^{-3}$
$A_2/(J\cdot K^{-3}\cdot g^{-1})$	$4.0933\cdot10^{-4}$	$4.2760\cdot10^{-4}$	$4.3115\cdot10^{-4}$	$3.7720\cdot10^{-4}$	$3.5906\cdot10^{-4}$	$4.1429\cdot10^{-4}$	$4.8339\cdot10^{-4}$	$3.6059\cdot10^{-4}$	$3.7815\cdot10^{-4}$	$3.9446\cdot10^{-4}$
$A_3/(J\cdot K^{-4}\cdot g^{-1})$	$-9.8320\cdot10^{-6}$	$-1.1096\cdot10^{-5}$	$-1.1060\cdot10^{-5}$	$-8.4416\cdot10^{-6}$	$-8.7035\cdot10^{-6}$	$-1.1397\cdot10^{-5}$	$-1.3957\cdot10^{-5}$	$-8.5883\cdot10^{-6}$	$-9.4517\cdot10^{-6}$	$-9.7870\cdot10^{-6}$
$A_4/(J\cdot K^{-5}\cdot g^{-1})$	$1.1699\cdot10^{-7}$	$1.5327\cdot10^{-7}$	$1.4679\cdot10^{-7}$	$9.4949\cdot10^{-8}$	$1.1008\cdot10^{-7}$	$1.6951\cdot10^{-7}$	$2.1128\cdot10^{-7}$	$1.0500\cdot10^{-7}$	$1.2404\cdot10^{-7}$	$1.2329\cdot10^{-7}$
$A_5/(J\cdot K^{-6}\cdot g^{-1})$	$-5.3657\cdot10^{-10}$	$-9.0129\cdot10^{-10}$	$-7.9858\cdot10^{-10}$	$-4.3902\cdot10^{-10}$	$-5.8194\cdot10^{-10}$	$-1.0666\cdot10^{-9}$	$-1.3067\cdot10^{-9}$	$-5.2618\cdot10^{-10}$	$-6.8170\cdot10^{-10}$	$-6.1886\cdot10^{-10}$
RMS%	0.097	0.291	0.186	0.099	0.149	0.136	0.215	0.089	0.085	0.098
Temperature range/K	12.81 to 36.00	10.24 to 33.23	10.82 to 36.60	10.14 to 33.47	10.30 to 34.05	10.04 to 35.55	10.37 to 36.88	10.24 to 36.00	10.29 to 35.26	10.38 to 36.56
					High T fits					
$A_0/(J\cdot K^{-1}\cdot g^{-1})$	−0.059030	−0.056427	−0.058802	−0.060648	−0.057258	−0.058645	−0.057547	−0.059065	−0.056438	−0.057220
$A_1/(J\cdot K^{-2}\cdot g^{-1})$	$5.0094\cdot10^{-3}$	$4.8300\cdot10^{-3}$	$4.9459\cdot10^{-3}$	$5.0020\cdot10^{-3}$	$4.9054\cdot10^{-3}$	$4.9760\cdot10^{-3}$	$4.8955\cdot10^{-3}$	$4.9863\cdot10^{-3}$	$4.8224\cdot10^{-3}$	$4.8630\cdot10^{-3}$
$A_2/(J\cdot K^{-3}\cdot g^{-1})$	$1.2681\cdot10^{-5}$	$1.7388\cdot10^{-5}$	$1.0894\cdot10^{-5}$	$8.7792\cdot10^{-6}$	$7.3043\cdot10^{-6}$	$5.5046\cdot10^{-6}$	$7.4489\cdot10^{-6}$	$4.9667\cdot10^{-6}$	$8.3730\cdot10^{-6}$	$8.5468\cdot10^{-6}$
$A_3/(J\cdot K^{-4}\cdot g^{-1})$	$-2.0845\cdot10^{-7}$	$-2.5133\cdot10^{-7}$	$-1.7861\cdot10^{-7}$	$-1.5542\cdot10^{-7}$	$-1.2794\cdot10^{-7}$	$-1.2122\cdot10^{-7}$	$-1.4358\cdot10^{-7}$	$-1.1593\cdot10^{-7}$	$-1.3532\cdot10^{-7}$	$-1.4878\cdot10^{-7}$
$A_4/(J\cdot K^{-5}\cdot g^{-1})$	$1.0278\cdot10^{-9}$	$1.1893\cdot10^{-9}$	$8.5414\cdot10^{-10}$	$7.2632\cdot10^{-10}$	$5.9256\cdot10^{-10}$	$5.9834\cdot10^{-10}$	$7.0007\cdot10^{-10}$	$5.7863\cdot10^{-10}$	$6.1201\cdot10^{-10}$	$7.1322\cdot10^{-10}$
$A_5/(J\cdot K^{-6}\cdot g^{-1})$	$-1.5926\cdot10^{-12}$	$-1.8037\cdot10^{-12}$	$-1.2818\cdot10^{-12}$	$-1.0588\cdot10^{-12}$	$-8.3924\cdot10^{-13}$	$-8.9459\cdot10^{-13}$	$-1.0492\cdot10^{-12}$	$-8.7188\cdot10^{-13}$	$-8.6337\cdot10^{-13}$	$-1.0636\cdot10^{-12}$
RMS%	0.318	0.313	0.253	0.304	0.426	0.335	0.292	0.283	0.322	0.287
Temperature range/K	36.00 to 305	33.23 to 305	36.60 to 305	33.47 to 305	34.05 to 305	35.55 to 305	36.88 to 305	36.00 to 305	35.26 to 305	36.56 to 305

TABLE 15
Standard thermodynamic functions for the cellulose samples as a function of temperature at p° = 0.1 MPa: $C^\circ_{p,w}$ is the standard massic heat capacity; $\Delta^T_0 S^\circ_w$ is the standard massic entropy difference $\{S^\circ_w < (T) - S^\circ_w(T=0)\}$, $\Delta^T_0 H^\circ_w$ is the standard massic enthalpy difference $\{H^\circ_w(T) - H^\circ_w(T=0)\}$, and the function $\Phi^\circ_w = \Delta^T_0 S^\circ_w - \Delta^T_0 H^\circ_w/T$. Uncertainties are discussed in section 3.8.

T/K	$C^\circ_{p,w}$/(J·K^{-1}·g^{-1})	$\Delta^T_0 S^\circ_w$/(J·K^{-1}·g^{-1})	$\Delta^T_0 H^\circ_w$/(kJ·g^{-1})	Φ°_w/(J·K^{-1}·g^{-1})
		Amorphous cellulose (24 h)		
0	0	0	0	0
1	$1.215\cdot10^{-5}$	$7.798\cdot10^{-6}$	$4.414\cdot10^{-9}$	$3.384\cdot10^{-6}$
2	$6.366\cdot10^{-5}$	$2.920\cdot10^{-5}$	$3.373\cdot10^{-8}$	$1.234\cdot10^{-5}$
3	$2.024\cdot10^{-4}$	$8.678\cdot10^{-5}$	$9.327\cdot10^{-8}$	$5.569\cdot10^{-5}$
4	$5.009\cdot10^{-4}$	$2.167\cdot10^{-4}$	$1.905\cdot10^{-7}$	$1.691\cdot10^{-4}$
5	$1.040\cdot10^{-3}$	$4.509\cdot10^{-4}$	$4.720\cdot10^{-7}$	$3.565\cdot10^{-4}$
6	$1.884\cdot10^{-3}$	$8.113\cdot10^{-4}$	$1.230\cdot10^{-6}$	$6.062\cdot10^{-4}$
7	$3.078\cdot10^{-3}$	$1.312\cdot10^{-3}$	$2.842\cdot10^{-6}$	$9.065\cdot10^{-4}$
8	$4.648\cdot10^{-3}$	$1.965\cdot10^{-3}$	$5.718\cdot10^{-6}$	$1.250\cdot10^{-3}$
9	$6.599\cdot10^{-3}$	$2.775\cdot10^{-3}$	$1.028\cdot10^{-5}$	$1.632\cdot10^{-3}$
10	$8.926\cdot10^{-3}$	$3.748\cdot10^{-3}$	$1.694\cdot10^{-5}$	$2.053\cdot10^{-3}$
11	0.01161	$4.885\cdot10^{-3}$	$2.609\cdot10^{-5}$	$2.513\cdot10^{-3}$
12	0.01460	$6.184\cdot10^{-3}$	$3.808\cdot10^{-5}$	$3.011\cdot10^{-3}$
13	0.01787	$7.612\cdot10^{-3}$	$5.342\cdot10^{-5}$	$3.503\cdot10^{-3}$
14	0.02142	$9.064\cdot10^{-3}$	$7.304\cdot10^{-5}$	$3.847\cdot10^{-3}$
15	0.02521	0.01067	$9.633\cdot10^{-5}$	$4.248\cdot10^{-3}$
16	0.02921	0.01242	$1.235\cdot10^{-4}$	$4.703\cdot10^{-3}$
17	0.03340	0.01432	$1.548\cdot10^{-4}$	$5.212\cdot10^{-3}$
18	0.03776	0.01635	$1.904\cdot10^{-4}$	$5.774\cdot10^{-3}$
19	0.04227	0.01851	$2.304\cdot10^{-4}$	$6.387\cdot10^{-3}$
20	0.04691	0.02080	$2.750\cdot10^{-4}$	$7.050\cdot10^{-3}$
25	0.07156	0.03388	$5.703\cdot10^{-4}$	0.01106
30	0.09761	0.04921	$9.929\cdot10^{-4}$	0.01612
35	0.12427	0.06626	$1.547\cdot10^{-3}$	0.02205
40	0.15076	0.08459	$2.235\cdot10^{-3}$	0.02871
45	0.17700	0.10386	$3.055\cdot10^{-3}$	0.03598
50	0.20301	0.12386	$4.005\cdot10^{-3}$	0.04376
55	0.22877	0.14442	$5.084\cdot10^{-3}$	0.05197
60	0.25424	0.16542	$6.292\cdot10^{-3}$	0.06055
65	0.27941	0.18676	$7.626\cdot10^{-3}$	0.06943
70	0.30427	0.20838	$9.086\cdot10^{-3}$	0.07859
75	0.32881	0.23021	0.01067	0.08797
80	0.35304	0.25221	0.01237	0.09754
85	0.37696	0.27433	0.01420	0.10729
90	0.40060	0.29655	0.01614	0.11719
95	0.42398	0.31883	0.01820	0.12721
100	0.44712	0.34117	0.02038	0.13735
110	0.49283	0.38594	0.02508	0.15792
120	0.53799	0.43076	0.03024	0.17879
130	0.58295	0.47559	0.03584	0.19989
140	0.62802	0.52044	0.04190	0.22119
150	0.67356	0.56532	0.04840	0.24263
160	0.71986	0.61026	0.05537	0.26420
170	0.76721	0.65532	0.06280	0.28589
180	0.81582	0.70054	0.07072	0.30767
190	0.86584	0.74599	0.07913	0.32954
200	0.91729	0.79170	0.08804	0.35150
210	0.97010	0.83773	0.09748	0.37356
220	1.0241	0.88410	0.10745	0.39571
230	1.0788	0.93082	0.11796	0.41796
240	1.1338	0.97790	0.12902	0.44031
250	1.1883	1.0253	0.14063	0.46276
260	1.2413	1.0729	0.15278	0.48531
270	1.2918	1.1207	0.16545	0.50796
273.15	1.3069	1.1358	0.16954	0.51511
280	1.3382	1.1686	0.17861	0.53070
290	1.3789	1.2163	0.19220	0.55352
298.15	1.4064	1.2548	0.20355	0.57216
300	1.4118	1.2636	0.20616	0.57640
		Amorphous cellulose (30 h)		
0	0	0	0	0
1	$1.067\cdot10^{-5}$	$5.946\cdot10^{-6}$	$3.545\cdot10^{-9}$	$2.401\cdot10^{-6}$
2	$6.366\cdot10^{-5}$	$2.631\cdot10^{-5}$	$3.326\cdot10^{-8}$	$9.677\cdot10^{-6}$
3	$2.060\cdot10^{-4}$	$8.184\cdot10^{-5}$	$1.080\cdot10^{-7}$	$4.583\cdot10^{-5}$
4	$5.051\cdot10^{-4}$	$2.076\cdot10^{-4}$	$2.238\cdot10^{-7}$	$1.516\cdot10^{-4}$
5	$1.041\cdot10^{-3}$	$4.387\cdot10^{-4}$	$4.859\cdot10^{-7}$	$3.415\cdot10^{-4}$
6	$1.883\cdot10^{-3}$	$8.006\cdot10^{-4}$	$1.159\cdot10^{-6}$	$6.075\cdot10^{-4}$
7	$3.079\cdot10^{-3}$	$1.310\cdot10^{-3}$	$2.615\cdot10^{-6}$	$9.366\cdot10^{-4}$
8	$4.654\cdot10^{-3}$	$1.978\cdot10^{-3}$	$5.277\cdot10^{-6}$	$1.319\cdot10^{-3}$
9	$6.613\cdot10^{-3}$	$2.812\cdot10^{-3}$	$9.581\cdot10^{-6}$	$1.747\cdot10^{-3}$

TABLE 15 (*continued*)

T/K	$C^{\circ}_{p,w}$/(J·K^{-1}·g^{-1})	$\Delta_0^T S^{\circ}_w$/(J·K^{-1}·g^{-1})	$\Delta_0^T H^{\circ}_w$/(kJ·g^{-1})	Φ°_w/(J·K^{-1}·g^{-1})
10	$8.938\cdot10^{-3}$	$3.812\cdot10^{-3}$	$1.594\cdot10^{-5}$	$2.218\cdot10^{-3}$
11	0.01163	$4.834\cdot10^{-3}$	$2.586\cdot10^{-5}$	$2.483\cdot10^{-3}$
12	0.01465	$5.973\cdot10^{-3}$	$3.897\cdot10^{-5}$	$2.725\cdot10^{-3}$
13	0.01796	$7.275\cdot10^{-3}$	$5.526\cdot10^{-5}$	$3.024\cdot10^{-3}$
14	0.02154	$8.735\cdot10^{-3}$	$7.499\cdot10^{-5}$	$3.379\cdot10^{-3}$
15	0.02535	0.01035	$9.841\cdot10^{-5}$	$3.789\cdot10^{-3}$
16	0.02936	0.01211	$1.258\cdot10^{-4}$	$4.253\cdot10^{-3}$
17	0.03357	0.01402	$1.572\cdot10^{-4}$	$4.771\cdot10^{-3}$
18	0.03794	0.01606	$1.929\cdot10^{-4}$	$5.341\cdot10^{-3}$
19	0.04246	0.01823	$2.331\cdot10^{-4}$	$5.962\cdot10^{-3}$
20	0.04711	0.02053	$2.779\cdot10^{-4}$	$6.632\cdot10^{-3}$
25	0.07183	0.03366	$5.744\cdot10^{-4}$	0.01068
30	0.09807	0.04906	$9.987\cdot10^{-4}$	0.01577
35	0.12484	0.06619	$1.556\cdot10^{-3}$	0.02173
40	0.15137	0.08459	$2.247\cdot10^{-3}$	0.02842
45	0.17777	0.10395	$3.070\cdot10^{-3}$	0.03573
50	0.20399	0.12404	$4.024\cdot10^{-3}$	0.04355
55	0.22998	0.14470	$5.109\cdot10^{-3}$	0.05181
60	0.25569	0.16581	$6.323\cdot10^{-3}$	0.06042
65	0.28110	0.18729	$7.666\cdot10^{-3}$	0.06935
70	0.30619	0.20904	$9.134\cdot10^{-3}$	0.07855
75	0.33095	0.23101	0.01073	0.08798
80	0.35538	0.25315	0.01244	0.09761
85	0.37948	0.27542	0.01428	0.10742
90	0.40327	0.29778	0.01624	0.11737
95	0.42677	0.32022	0.01831	0.12746
100	0.45001	0.34270	0.02050	0.13766
110	0.49582	0.38775	0.02523	0.15834
120	0.54098	0.43283	0.03042	0.17934
130	0.58585	0.47790	0.03605	0.20057
140	0.63078	0.52296	0.04214	0.22199
150	0.67615	0.56802	0.04867	0.24356
160	0.72231	0.61313	0.05566	0.26525
170	0.76957	0.65833	0.06312	0.28704
180	0.81819	0.70369	0.07106	0.30893
190	0.86834	0.74926	0.07949	0.33090
200	0.92007	0.79511	0.08843	0.35296
210	0.97333	0.84128	0.09790	0.37512
220	1.0279	0.88782	0.10790	0.39736
230	1.0835	0.93473	0.11846	0.41970
240	1.1394	0.98203	0.12957	0.44215
250	1.1949	1.0297	0.14124	0.46469
260	1.2490	1.0776	0.15346	0.48735
270	1.3004	1.1257	0.16621	0.51010
273.15	1.3158	1.1409	0.17033	0.51728
280	1.3476	1.1739	0.17946	0.53294
290	1.3887	1.2219	0.19314	0.55587
298.15	1.4162	1.2607	0.20458	0.57461
300	1.4215	1.2695	0.20720	0.57887
		Amorphous cellulose (36 h)		
0	0	0	0	0
1	$1.063\cdot10^{-5}$	$6.082\cdot10^{-6}$	$3.591\cdot10^{-9}$	$2.491\cdot10^{-6}$
2	$6.214\cdot10^{-5}$	$2.614\cdot10^{-5}$	$3.236\cdot10^{-8}$	$9.961\cdot10^{-6}$
3	$2.010\cdot10^{-4}$	$8.113\cdot10^{-5}$	$1.007\cdot10^{-7}$	$4.757\cdot10^{-5}$
4	$4.949\cdot10^{-4}$	$2.060\cdot10^{-4}$	$2.065\cdot10^{-7}$	$1.544\cdot10^{-4}$
5	$1.023\cdot10^{-3}$	$4.346\cdot10^{-4}$	$4.654\cdot10^{-7}$	$3.416\cdot10^{-4}$
6	$1.851\cdot10^{-3}$	$7.908\cdot10^{-4}$	$1.147\cdot10^{-6}$	$5.996\cdot10^{-4}$
7	$3.025\cdot10^{-3}$	$1.290\cdot10^{-3}$	$2.618\cdot10^{-6}$	$9.161\cdot10^{-4}$
8	$4.566\cdot10^{-3}$	$1.943\cdot10^{-3}$	$5.290\cdot10^{-6}$	$1.281\cdot10^{-3}$
9	$6.477\cdot10^{-3}$	$2.754\cdot10^{-3}$	$9.582\cdot10^{-6}$	$1.690\cdot10^{-3}$
10	$8.741\cdot10^{-3}$	$3.728\cdot10^{-3}$	$1.589\cdot10^{-5}$	$2.138\cdot10^{-3}$
11	0.01133	$4.829\cdot10^{-3}$	$2.483\cdot10^{-5}$	$2.571\cdot10^{-3}$
12	0.01421	$5.936\cdot10^{-3}$	$3.758\cdot10^{-5}$	$2.805\cdot10^{-3}$
13	0.01740	$7.197\cdot10^{-3}$	$5.336\cdot10^{-5}$	$3.093\cdot10^{-3}$
14	0.02084	$8.611\cdot10^{-3}$	$7.245\cdot10^{-5}$	$3.436\cdot10^{-3}$
15	0.02452	0.01017	$9.511\cdot10^{-5}$	$3.832\cdot10^{-3}$
16	0.02840	0.01188	$1.216\cdot10^{-4}$	$4.281\cdot10^{-3}$
17	0.03248	0.01372	$1.520\cdot10^{-4}$	$4.781\cdot10^{-3}$
18	0.03672	0.01570	$1.866\cdot10^{-4}$	$5.332\cdot10^{-3}$
19	0.04110	0.01780	$2.255\cdot10^{-4}$	$5.933\cdot10^{-3}$
20	0.04561	0.02002	$2.688\cdot10^{-4}$	$6.581\cdot10^{-3}$
25	0.06959	0.03274	$5.560\cdot10^{-4}$	0.01050
30	0.09500	0.04766	$9.671\cdot10^{-4}$	0.01542
35	0.12108	0.06425	$1.507\cdot10^{-3}$	0.02120

(*continued on next page*)

TABLE 15 (*continued*)

T/K	$C^{\circ}_{p,w}$/(J·K^{-1}·g^{-1})	$\Delta^{T}_{0}S^{\circ}_{w}$/(J·K^{-1}·g^{-1})	$\Delta^{T}_{0}H^{\circ}_{w}$/(kJ·g^{-1})	Φ°_{w}/(J·K^{-1}·g^{-1})
40	0.14709	0.08213	$2.178\cdot10^{-3}$	0.02768
45	0.17282	0.10094	$2.978\cdot10^{-3}$	0.03477
50	0.19834	0.12047	$3.906\cdot10^{-3}$	0.04236
55	0.22363	0.14056	$4.961\cdot10^{-3}$	0.05037
60	0.24867	0.16110	$6.141\cdot10^{-3}$	0.05874
65	0.27342	0.18198	$7.447\cdot10^{-3}$	0.06741
70	0.29789	0.20314	$8.875\cdot10^{-3}$	0.07635
75	0.32206	0.22452	0.01043	0.08551
80	0.34593	0.24607	0.01210	0.09487
85	0.36952	0.26775	0.01388	0.10441
90	0.39284	0.28953	0.01579	0.11408
95	0.41590	0.31139	0.01781	0.12389
100	0.43872	0.33330	0.01995	0.13382
110	0.48376	0.37723	0.02456	0.15395
120	0.52817	0.42123	0.02962	0.17439
130	0.57224	0.46525	0.03512	0.19507
140	0.61625	0.50927	0.04107	0.21594
150	0.66048	0.55329	0.04745	0.23696
160	0.70523	0.59734	0.05428	0.25811
170	0.75074	0.64146	0.06156	0.27936
180	0.79724	0.68568	0.06930	0.30071
190	0.84488	0.73006	0.07751	0.32213
200	0.89374	0.77463	0.08620	0.34364
210	0.94384	0.81944	0.09538	0.36523
220	0.99506	0.86453	0.10508	0.38690
230	1.0472	0.90991	0.11529	0.40865
240	1.0998	0.95559	0.12602	0.43049
250	1.1526	1.0016	0.13729	0.45241
260	1.2046	1.0478	0.14907	0.47442
270	1.2553	1.0942	0.16137	0.49652
273.15	1.2707	1.1088	0.16535	0.50349
280	1.3034	1.1407	0.17417	0.51869
290	1.3477	1.1873	0.18743	0.54095
298.15	1.3800	1.2250	0.19855	0.55913
300	1.3868	1.2336	0.20111	0.56326
		Cellulose Iβ		
0	0	0	0	0
1	$1.021\cdot10^{-5}$	$4.962\cdot10^{-6}$	$3.126\cdot10^{-9}$	$1.836\cdot10^{-6}$
2	$6.742\cdot10^{-5}$	$2.572\cdot10^{-5}$	$3.540\cdot10^{-8}$	$8.020\cdot10^{-6}$
3	$2.192\cdot10^{-4}$	$8.032\cdot10^{-5}$	$1.476\cdot10^{-7}$	$3.111\cdot10^{-5}$
4	$5.205\cdot10^{-4}$	$1.940\cdot10^{-4}$	$3.917\cdot10^{-7}$	$9.608\cdot10^{-5}$
5	$1.033\cdot10^{-3}$	$3.939\cdot10^{-4}$	$8.790\cdot10^{-7}$	$2.181\cdot10^{-4}$
6	$1.813\cdot10^{-3}$	$7.023\cdot10^{-4}$	$1.827\cdot10^{-6}$	$3.978\cdot10^{-4}$
7	$2.902\cdot10^{-3}$	$1.136\cdot10^{-3}$	$3.539\cdot10^{-6}$	$6.300\cdot10^{-4}$
8	$4.326\cdot10^{-3}$	$1.705\cdot10^{-3}$	$6.367\cdot10^{-6}$	$9.095\cdot10^{-4}$
9	$6.093\cdot10^{-3}$	$2.420\cdot10^{-3}$	$1.069\cdot10^{-5}$	$1.233\cdot10^{-3}$
10	$8.194\cdot10^{-3}$	$3.283\cdot10^{-3}$	$1.686\cdot10^{-5}$	$1.597\cdot10^{-3}$
11	0.01062	$4.192\cdot10^{-3}$	$2.611\cdot10^{-5}$	$1.819\cdot10^{-3}$
12	0.01337	$5.232\cdot10^{-3}$	$3.808\cdot10^{-5}$	$2.059\cdot10^{-3}$
13	0.01641	$6.421\cdot10^{-3}$	$5.295\cdot10^{-5}$	$2.348\cdot10^{-3}$
14	0.01973	$7.757\cdot10^{-3}$	$7.100\cdot10^{-5}$	$2.686\cdot10^{-3}$
15	0.02329	$9.248\cdot10^{-3}$	$9.248\cdot10^{-5}$	$3.072\cdot10^{-3}$
16	0.02707	0.01086	$1.176\cdot10^{-4}$	$3.508\cdot10^{-3}$
17	0.03105	0.01262	$1.467\cdot10^{-4}$	$3.991\cdot10^{-3}$
18	0.03521	0.01451	$1.798\cdot10^{-4}$	$4.523\cdot10^{-3}$
19	0.03953	0.01653	$2.171\cdot10^{-4}$	$5.101\cdot10^{-3}$
20	0.04399	0.01867	$2.589\cdot10^{-4}$	$5.725\cdot10^{-3}$
25	0.06793	0.03101	$5.377\cdot10^{-4}$	$9.506\cdot10^{-3}$
30	0.09350	0.04564	$9.409\cdot10^{-4}$	0.01428
35	0.11955	0.06202	$1.474\cdot10^{-3}$	0.01991
40	0.14528	0.07966	$2.136\cdot10^{-3}$	0.02627
45	0.17084	0.09825	$2.926\cdot10^{-3}$	0.03323
50	0.19618	0.11756	$3.844\cdot10^{-3}$	0.04069
55	0.22128	0.13744	$4.888\cdot10^{-3}$	0.04858
60	0.24610	0.15776	$6.056\cdot10^{-3}$	0.05683
65	0.27063	0.17843	$7.348\cdot10^{-3}$	0.06538
70	0.29486	0.19937	$8.762\cdot10^{-3}$	0.07420
75	0.31879	0.22054	0.01030	0.08325
80	0.34241	0.24187	0.01195	0.09250
85	0.36572	0.26332	0.01372	0.10192
90	0.38875	0.28488	0.01561	0.11148
95	0.41149	0.30651	0.01761	0.12118
100	0.43397	0.32819	0.01972	0.13099
110	0.47823	0.37163	0.02428	0.15089

TABLE 15 (*continued*)

T/K	$C^{\circ}_{p,w}$/(J·K^{-1}·g^{-1})	$\Delta^{T}_{0}S^{\circ}_{w}$/(J·K^{-1}·g^{-1})	$\Delta^{T}_{0}H^{\circ}_{w}$/(kJ·g^{-1})	Φ°_{w}/(J·K^{-1}·g^{-1})
120	0.52171	0.41511	0.02928	0.17109
130	0.56466	0.45857	0.03471	0.19154
140	0.60731	0.50198	0.04057	0.21216
150	0.64994	0.54533	0.04686	0.23293
160	0.69280	0.58865	0.05357	0.25381
170	0.73613	0.63194	0.06072	0.27478
180	0.78014	0.67526	0.06830	0.29582
190	0.82501	0.71864	0.07632	0.31693
200	0.87085	0.76212	0.08480	0.33811
210	0.91771	0.80574	0.09374	0.35933
220	0.96556	0.84953	0.10316	0.38062
230	1.0143	0.89352	0.11306	0.40196
240	1.0636	0.93773	0.12345	0.42337
250	1.1133	0.98216	0.13433	0.44483
260	1.1628	1.0268	0.14571	0.46635
270	1.2114	1.0716	0.15758	0.48794
273.15	1.2265	1.0857	0.16142	0.49475
280	1.2585	1.1165	0.16994	0.50958
290	1.3031	1.1614	0.18275	0.53129
298.15	1.3368	1.1980	0.19351	0.54901
300	1.3440	1.2063	0.19599	0.55304
		Cellulose II (25 °C)		
0	0	0	0	0
1	$1.049\cdot10^{-5}$	$5.770\cdot10^{-6}$	$3.457\cdot10^{-9}$	$2.314\cdot10^{-6}$
2	$6.340\cdot10^{-5}$	$2.608\cdot10^{-5}$	$3.223\cdot10^{-8}$	$9.969\cdot10^{-6}$
3	$2.075\cdot10^{-4}$	$8.269\cdot10^{-5}$	$1.048\cdot10^{-7}$	$4.777\cdot10^{-5}$
4	$5.115\cdot10^{-4}$	$2.092\cdot10^{-4}$	$2.434\cdot10^{-7}$	$1.484\cdot10^{-4}$
5	$1.051\cdot10^{-3}$	$4.363\cdot10^{-4}$	$5.933\cdot10^{-7}$	$3.177\cdot10^{-4}$
6	$1.888\cdot10^{-3}$	$7.853\cdot10^{-4}$	$1.434\cdot10^{-6}$	$5.463\cdot10^{-4}$
7	$3.064\cdot10^{-3}$	$1.271\cdot10^{-3}$	$3.126\cdot10^{-6}$	$8.244\cdot10^{-4}$
8	$4.602\cdot10^{-3}$	$1.903\cdot10^{-3}$	$6.063\cdot10^{-6}$	$1.145\cdot10^{-3}$
9	$6.505\cdot10^{-3}$	$2.689\cdot10^{-3}$	$1.065\cdot10^{-5}$	$1.506\cdot10^{-3}$
10	$8.760\cdot10^{-3}$	$3.632\cdot10^{-3}$	$1.727\cdot10^{-5}$	$1.904\cdot10^{-3}$
11	0.01136	$4.630\cdot10^{-3}$	$2.701\cdot10^{-5}$	$2.174\cdot10^{-3}$
12	0.01427	$5.741\cdot10^{-3}$	$3.980\cdot10^{-5}$	$2.424\cdot10^{-3}$
13	0.01743	$7.006\cdot10^{-3}$	$5.563\cdot10^{-5}$	$2.727\cdot10^{-3}$
14	0.02083	$8.421\cdot10^{-3}$	$7.474\cdot10^{-5}$	$3.082\cdot10^{-3}$
15	0.02445	$9.981\cdot10^{-3}$	$9.737\cdot10^{-5}$	$3.489\cdot10^{-3}$
16	0.02826	0.01168	$1.237\cdot10^{-4}$	$3.948\cdot10^{-3}$
17	0.03224	0.01351	$1.539\cdot10^{-4}$	$4.456\cdot10^{-3}$
18	0.03638	0.01547	$1.882\cdot10^{-4}$	$5.013\cdot10^{-3}$
19	0.04066	0.01755	$2.268\cdot10^{-4}$	$5.617\cdot10^{-3}$
20	0.04505	0.01975	$2.696\cdot10^{-4}$	$6.268\cdot10^{-3}$
25	0.06845	0.03228	$5.525\cdot10^{-4}$	0.01018
30	0.09330	0.04694	$9.565\cdot10^{-4}$	0.01506
35	0.11874	0.06323	$1.487\cdot10^{-3}$	0.02076
40	0.14389	0.08073	$2.143\cdot10^{-3}$	0.02715
45	0.16889	0.09912	$2.925\cdot10^{-3}$	0.03412
50	0.19372	0.11820	$3.832\cdot10^{-3}$	0.04157
55	0.21835	0.13782	$4.862\cdot10^{-3}$	0.04942
60	0.24276	0.15787	$6.015\cdot10^{-3}$	0.05762
65	0.26692	0.17826	$7.289\cdot10^{-3}$	0.06612
70	0.29085	0.19892	$8.684\cdot10^{-3}$	0.07486
75	0.31452	0.21979	0.01020	0.08383
80	0.33794	0.24084	0.01183	0.09298
85	0.36111	0.26202	0.01358	0.10230
90	0.38405	0.28331	0.01544	0.11177
95	0.40676	0.30469	0.01742	0.12136
100	0.42925	0.32612	0.01951	0.13106
110	0.47367	0.36913	0.02402	0.15075
120	0.51748	0.41222	0.02898	0.17074
130	0.56088	0.45536	0.03437	0.19097
140	0.60410	0.49851	0.04019	0.21140
150	0.64735	0.54166	0.04645	0.23198
160	0.69089	0.58483	0.05314	0.25268
170	0.73493	0.62803	0.06027	0.27349
180	0.77968	0.67130	0.06784	0.29439
190	0.82533	0.71467	0.07587	0.31537
200	0.87200	0.75819	0.08435	0.33642
210	0.91979	0.80189	0.09331	0.35754
220	0.96872	0.84580	0.10275	0.37874
230	1.0188	0.88996	0.11269	0.40000
240	1.0698	0.93440	0.12313	0.42134
250	1.1216	0.97912	0.13409	0.44276

(*continued on next page*)

TABLE 15 (*continued*)

T/K	$C^{\circ}_{p,w}$/(J·K^{-1}·g^{-1})	$\Delta^{T}_{0}S^{\circ}_{w}$/(J·K^{-1}·g^{-1})	$\Delta^{T}_{0}H^{\circ}_{w}$/(kJ·g^{-1})	Φ°_{w}/(J·K^{-1}·g^{-1})
260	1.1739	1.0241	0.14557	0.46425
270	1.2263	1.0694	0.15757	0.48583
273.15	1.2427	1.0837	0.16146	0.49264
280	1.2782	1.1149	0.17009	0.50748
290	1.3289	1.1607	0.18313	0.52922
298.15	1.3688	1.1980	0.19412	0.54699
300	1.3777	1.2065	0.19666	0.55103
		Cellulose II (70 °C)		
0	0	0	0	0
1	$1.085\cdot10^{-5}$	$6.118\cdot10^{-6}$	$3.630\cdot10^{-9}$	$2.488\cdot10^{-6}$
2	$6.436\cdot10^{-5}$	$2.693\cdot10^{-5}$	$3.250\cdot10^{-8}$	$1.068\cdot10^{-5}$
3	$2.107\cdot10^{-4}$	$8.505\cdot10^{-5}$	$1.038\cdot10^{-7}$	$5.043\cdot10^{-5}$
4	$5.206\cdot10^{-4}$	$2.141\cdot10^{-4}$	$2.507\cdot10^{-7}$	$1.515\cdot10^{-4}$
5	$1.069\cdot10^{-3}$	$4.434\cdot10^{-4}$	$6.351\cdot10^{-7}$	$3.164\cdot10^{-4}$
6	$1.916\cdot10^{-3}$	$7.932\cdot10^{-4}$	$1.546\cdot10^{-6}$	$5.356\cdot10^{-4}$
7	$3.103\cdot10^{-3}$	$1.278\cdot10^{-3}$	$3.343\cdot10^{-6}$	$8.001\cdot10^{-4}$
8	$4.652\cdot10^{-3}$	$1.907\cdot10^{-3}$	$6.418\cdot10^{-6}$	$1.105\cdot10^{-3}$
9	$6.568\cdot10^{-3}$	$2.688\cdot10^{-3}$	$1.117\cdot10^{-5}$	$1.447\cdot10^{-3}$
10	$8.841\cdot10^{-3}$	$3.626\cdot10^{-3}$	$1.799\cdot10^{-5}$	$1.827\cdot10^{-3}$
11	0.01143	$4.593\cdot10^{-3}$	$2.806\cdot10^{-5}$	$2.042\cdot10^{-3}$
12	0.01431	$5.709\cdot10^{-3}$	$4.091\cdot10^{-5}$	$2.300\cdot10^{-3}$
13	0.01745	$6.976\cdot10^{-3}$	$5.677\cdot10^{-5}$	$2.610\cdot10^{-3}$
14	0.02083	$8.392\cdot10^{-3}$	$7.589\cdot10^{-5}$	$2.971\cdot10^{-3}$
15	0.02443	$9.951\cdot10^{-3}$	$9.850\cdot10^{-5}$	$3.384\cdot10^{-3}$
16	0.02821	0.01165	$1.248\cdot10^{-4}$	$3.847\cdot10^{-3}$
17	0.03216	0.01347	$1.550\cdot10^{-4}$	$4.358\cdot10^{-3}$
18	0.03625	0.01543	$1.892\cdot10^{-4}$	$4.919\cdot10^{-3}$
19	0.04049	0.01750	$2.275\cdot10^{-4}$	$5.526\cdot10^{-3}$
20	0.04483	0.01969	$2.702\cdot10^{-4}$	$6.179\cdot10^{-3}$
25	0.06792	0.03214	$5.513\cdot10^{-4}$	0.01009
30	0.09248	0.04667	$9.518\cdot10^{-4}$	0.01495
35	0.11785	0.06283	$1.477\cdot10^{-3}$	0.02062
40	0.14288	0.08020	$2.129\cdot10^{-3}$	0.02697
45	0.16766	0.09847	$2.906\cdot10^{-3}$	0.03389
50	0.19222	0.11741	$3.806\cdot10^{-3}$	0.04129
55	0.21654	0.13687	$4.828\cdot10^{-3}$	0.04909
60	0.24061	0.15674	$5.971\cdot10^{-3}$	0.05723
65	0.26440	0.17694	$7.233\cdot10^{-3}$	0.06566
70	0.28793	0.19740	$8.614\cdot10^{-3}$	0.07434
75	0.31119	0.21806	0.01011	0.08323
80	0.33418	0.23888	0.01173	0.09231
85	0.35691	0.25982	0.01345	0.10155
90	0.37939	0.28086	0.01529	0.11092
95	0.40164	0.30197	0.01725	0.12042
100	0.42367	0.32313	0.01931	0.13003
110	0.46717	0.36556	0.02377	0.14951
120	0.51008	0.40805	0.02865	0.16928
130	0.55262	0.45056	0.03397	0.18929
140	0.59500	0.49306	0.03970	0.20947
150	0.63746	0.53556	0.04587	0.22979
160	0.68023	0.57807	0.05245	0.25023
170	0.72352	0.62060	0.05947	0.27076
180	0.76750	0.66320	0.06693	0.29138
190	0.81231	0.70589	0.07482	0.31207
200	0.85804	0.74871	0.08318	0.33284
210	0.90474	0.79170	0.09199	0.35366
220	0.95234	0.83489	0.10127	0.37455
230	1.0007	0.87829	0.11104	0.39551
240	1.0497	0.92191	0.12129	0.41653
250	1.0990	0.96576	0.13203	0.43763
260	1.1480	1.0098	0.14327	0.45879
270	1.1963	1.0541	0.15499	0.48001
273.15	1.2113	1.0680	0.15878	0.48671
280	1.2433	1.0984	0.16719	0.50131
290	1.2879	1.1428	0.17985	0.52266
298.15	1.3219	1.1790	0.19049	0.54011
300	1.3293	1.1872	0.19294	0.54407
		Cellulose II (145 °C)		
0	0	0	0	0
1	$9.913\cdot10^{-6}$	$4.993\cdot10^{-6}$	$3.099\cdot10^{-9}$	$1.894\cdot10^{-6}$
2	$6.386\cdot10^{-5}$	$2.492\cdot10^{-5}$	$3.279\cdot10^{-8}$	$8.525\cdot10^{-6}$
3	$2.091\cdot10^{-4}$	$7.988\cdot10^{-5}$	$1.168\cdot10^{-7}$	$4.095\cdot10^{-5}$
4	$5.099\cdot10^{-4}$	$2.027\cdot10^{-4}$	$2.621\cdot10^{-7}$	$1.372\cdot10^{-4}$
5	$1.042\cdot10^{-3}$	$4.274\cdot10^{-4}$	$5.701\cdot10^{-7}$	$3.133\cdot10^{-4}$

TABLE 15 (*continued*)

T/K	$C^{\circ}_{p,w}$/(J·K^{-1}·g^{-1})	$\Delta_0^T S^{\circ}_w$/(J·K^{-1}·g^{-1})	$\Delta_0^T H^{\circ}_w$/(kJ·g^{-1})	Φ°_w/(J·K^{-1}·g^{-1})
6	$1.871\cdot10^{-3}$	$7.789\cdot10^{-4}$	$1.291\cdot10^{-6}$	$5.637\cdot10^{-4}$
7	$3.042\cdot10^{-3}$	$1.274\cdot10^{-3}$	$2.781\cdot10^{-6}$	$8.768\cdot10^{-4}$
8	$4.579\cdot10^{-3}$	$1.923\cdot10^{-3}$	$5.444\cdot10^{-6}$	$1.243\cdot10^{-3}$
9	$6.481\cdot10^{-3}$	$2.733\cdot10^{-3}$	$9.698\cdot10^{-6}$	$1.656\cdot10^{-3}$
10	$8.728\cdot10^{-3}$	$3.705\cdot10^{-3}$	$1.594\cdot10^{-5}$	$2.111\cdot10^{-3}$
11	0.01129	$4.722\cdot10^{-3}$	$2.541\cdot10^{-5}$	$2.412\cdot10^{-3}$
12	0.01416	$5.825\cdot10^{-3}$	$3.811\cdot10^{-5}$	$2.649\cdot10^{-3}$
13	0.01731	$7.081\cdot10^{-3}$	$5.382\cdot10^{-5}$	$2.941\cdot10^{-3}$
14	0.02071	$8.486\cdot10^{-3}$	$7.281\cdot10^{-5}$	$3.286\cdot10^{-3}$
15	0.02433	0.01004	$9.531\cdot10^{-5}$	$3.683\cdot10^{-3}$
16	0.02815	0.01173	$1.215\cdot10^{-4}$	$4.133\cdot10^{-3}$
17	0.03213	0.01355	$1.517\cdot10^{-4}$	$4.632\cdot10^{-3}$
18	0.03626	0.01551	$1.858\cdot10^{-4}$	$5.182\cdot10^{-3}$
19	0.04052	0.01758	$2.242\cdot10^{-4}$	$5.779\cdot10^{-3}$
20	0.04489	0.01977	$2.669\cdot10^{-4}$	$6.424\cdot10^{-3}$
25	0.06798	0.03224	$5.484\cdot10^{-4}$	0.01030
30	0.09237	0.04677	$9.489\cdot10^{-4}$	0.01514
35	0.11754	0.06289	$1.473\cdot10^{-3}$	0.02080
40	0.14269	0.08024	$2.124\cdot10^{-3}$	0.02713
45	0.16743	0.09847	$2.900\cdot10^{-3}$	0.03404
50	0.19195	0.11739	$3.798\cdot10^{-3}$	0.04142
55	0.21623	0.13682	$4.819\cdot10^{-3}$	0.04921
60	0.24024	0.15667	$5.960\cdot10^{-3}$	0.05733
65	0.26398	0.17684	$7.221\cdot10^{-3}$	0.06575
70	0.28743	0.19726	$8.599\cdot10^{-3}$	0.07441
75	0.31060	0.21788	0.01009	0.08329
80	0.33349	0.23866	0.01170	0.09235
85	0.35610	0.25956	0.01343	0.10157
90	0.37845	0.28055	0.01527	0.11093
95	0.40055	0.30160	0.01721	0.12041
100	0.42243	0.32270	0.01927	0.13000
110	0.46558	0.36499	0.02371	0.14944
120	0.50813	0.40733	0.02858	0.16916
130	0.55030	0.44967	0.03387	0.18911
140	0.59234	0.49199	0.03959	0.20924
150	0.63453	0.53430	0.04572	0.22950
160	0.67710	0.57660	0.05228	0.24987
170	0.72028	0.61895	0.05926	0.27033
180	0.76427	0.66136	0.06669	0.29088
190	0.80923	0.70388	0.07455	0.31150
200	0.85523	0.74655	0.08287	0.33218
210	0.90230	0.78941	0.09166	0.35293
220	0.95037	0.83249	0.10092	0.37375
230	0.99929	0.87582	0.11067	0.39464
240	1.0488	0.91939	0.12091	0.41559
250	1.0985	0.96321	0.13165	0.43662
260	1.1478	1.0073	0.14288	0.45772
270	1.1961	1.0515	0.15460	0.47889
273.15	1.2110	1.0654	0.15839	0.48558
280	1.2426	1.0958	0.16680	0.50013
290	1.2862	1.1402	0.17944	0.52144
298.15	1.3189	1.1763	0.19006	0.53885
300	1.3258	1.1845	0.19251	0.54280
		Cellulose III (−33 °C)		
0	0	0	0	0
1	$9.264\cdot10^{-6}$	$3.812\cdot10^{-6}$	$2.582\cdot10^{-9}$	$1.229\cdot10^{-6}$
2	$6.720\cdot10^{-5}$	$2.401\cdot10^{-5}$	$3.393\cdot10^{-8}$	$7.046\cdot10^{-6}$
3	$2.229\cdot10^{-4}$	$7.984\cdot10^{-5}$	$1.408\cdot10^{-7}$	$3.290\cdot10^{-5}$
4	$5.356\cdot10^{-4}$	$2.008\cdot10^{-4}$	$3.482\cdot10^{-7}$	$1.137\cdot10^{-4}$
5	$1.075\cdot10^{-3}$	$4.204\cdot10^{-4}$	$7.369\cdot10^{-7}$	$2.730\cdot10^{-4}$
6	$1.905\cdot10^{-3}$	$7.659\cdot10^{-4}$	$1.521\cdot10^{-6}$	$5.123\cdot10^{-4}$
7	$3.071\cdot10^{-3}$	$1.256\cdot10^{-3}$	$3.030\cdot10^{-6}$	$8.229\cdot10^{-4}$
8	$4.597\cdot10^{-3}$	$1.902\cdot10^{-3}$	$5.654\cdot10^{-6}$	$1.195\cdot10^{-3}$
9	$6.477\cdot10^{-3}$	$2.710\cdot10^{-3}$	$9.804\cdot10^{-6}$	$1.621\cdot10^{-3}$
10	$8.686\cdot10^{-3}$	$3.682\cdot10^{-3}$	$1.587\cdot10^{-5}$	$2.095\cdot10^{-3}$
11	0.01121	$4.670\cdot10^{-3}$	$2.542\cdot10^{-5}$	$2.360\cdot10^{-3}$
12	0.01404	$5.765\cdot10^{-3}$	$3.802\cdot10^{-5}$	$2.597\cdot10^{-3}$
13	0.01713	$7.009\cdot10^{-3}$	$5.358\cdot10^{-5}$	$2.887\cdot10^{-3}$
14	0.02046	$8.398\cdot10^{-3}$	$7.235\cdot10^{-5}$	$3.231\cdot10^{-3}$
15	0.02401	$9.930\cdot10^{-3}$	$9.456\cdot10^{-5}$	$3.625\cdot10^{-3}$
16	0.02775	0.01160	$1.204\cdot10^{-4}$	$4.071\cdot10^{-3}$
17	0.03168	0.01340	$1.501\cdot10^{-4}$	$4.566\cdot10^{-3}$
18	0.03576	0.01532	$1.838\cdot10^{-4}$	$5.109\cdot10^{-3}$
19	0.03998	0.01737	$2.217\cdot10^{-4}$	$5.700\cdot10^{-3}$

(*continued on next page*)

TABLE 15 (*continued*)

T/K	$C^{\circ}_{p,w}$/(J·K^{-1}·g^{-1})	$\Delta^{T}_{0}S^{\circ}_{w}$/(J·K^{-1}·g^{-1})	$\Delta^{T}_{0}H^{\circ}_{w}$/(kJ·g^{-1})	Φ°_{w}/(J·K^{-1}·g^{-1})
20	0.04432	0.01953	$2.638\cdot10^{-4}$	$6.337\cdot10^{-3}$
25	0.06746	0.03187	$5.424\cdot10^{-4}$	0.01017
30	0.09205	0.04633	$9.408\cdot10^{-4}$	0.01496
35	0.11730	0.06241	$1.464\cdot10^{-3}$	0.02058
40	0.14230	0.07971	$2.113\cdot10^{-3}$	0.02688
45	0.16702	0.09790	$2.887\cdot10^{-3}$	0.03375
50	0.19152	0.11677	$3.783\cdot10^{-3}$	0.04110
55	0.21577	0.13616	$4.801\cdot10^{-3}$	0.04886
60	0.23977	0.15596	$5.940\cdot10^{-3}$	0.05696
65	0.26351	0.17610	$7.199\cdot10^{-3}$	0.06535
70	0.28697	0.19648	$8.575\cdot10^{-3}$	0.07398
75	0.31017	0.21708	0.01007	0.08284
80	0.33311	0.23783	0.01168	0.09187
85	0.35579	0.25870	0.01340	0.10107
90	0.37823	0.27968	0.01523	0.11041
95	0.40044	0.30072	0.01718	0.11987
100	0.42244	0.32182	0.01924	0.12944
110	0.46589	0.36413	0.02368	0.14885
120	0.50877	0.40651	0.02855	0.16856
130	0.55128	0.44891	0.03385	0.18849
140	0.59364	0.49132	0.03958	0.20861
150	0.63608	0.53372	0.04573	0.22887
160	0.67882	0.57613	0.05230	0.24925
170	0.72205	0.61858	0.05931	0.26973
180	0.76595	0.66109	0.06674	0.29029
190	0.81064	0.70370	0.07463	0.31092
200	0.85621	0.74643	0.08296	0.33163
210	0.90268	0.78933	0.09175	0.35240
220	0.95000	0.83241	0.10102	0.37324
230	0.99805	0.87570	0.11076	0.39415
240	1.0466	0.91920	0.12098	0.41512
250	1.0953	0.96291	0.13169	0.43615
260	1.1438	1.0068	0.14289	0.45726
270	1.1914	1.0509	0.15456	0.47843
273.15	1.2062	1.0648	0.15834	0.48511
280	1.2376	1.0950	0.16671	0.49966
290	1.2814	1.1392	0.17931	0.52095
298.15	1.3147	1.1752	0.18989	0.53835
300	1.3219	1.1834	0.19233	0.54230
		Cellulose III (25 °C)		
0	0	0	0	0
1	$1.050\cdot10^{-5}$	$5.395\cdot10^{-6}$	$3.321\cdot10^{-9}$	$2.073\cdot10^{-6}$
2	$6.679\cdot10^{-5}$	$2.632\cdot10^{-5}$	$3.441\cdot10^{-8}$	$9.119\cdot10^{-6}$
3	$2.182\cdot10^{-4}$	$8.336\cdot10^{-5}$	$1.271\cdot10^{-7}$	$4.099\cdot10^{-5}$
4	$5.289\cdot10^{-4}$	$2.073\cdot10^{-4}$	$3.171\cdot10^{-7}$	$1.280\cdot10^{-4}$
5	$1.070\cdot10^{-3}$	$4.278\cdot10^{-4}$	$7.400\cdot10^{-7}$	$2.798\cdot10^{-4}$
6	$1.901\cdot10^{-3}$	$7.668\cdot10^{-4}$	$1.657\cdot10^{-6}$	$4.906\cdot10^{-4}$
7	$3.063\cdot10^{-3}$	$1.240\cdot10^{-3}$	$3.413\cdot10^{-6}$	$7.521\cdot10^{-4}$
8	$4.579\cdot10^{-3}$	$1.857\cdot10^{-3}$	$6.389\cdot10^{-6}$	$1.058\cdot10^{-3}$
9	$6.451\cdot10^{-3}$	$2.625\cdot10^{-3}$	$1.098\cdot10^{-5}$	$1.405\cdot10^{-3}$
10	$8.663\cdot10^{-3}$	$3.548\cdot10^{-3}$	$1.756\cdot10^{-5}$	$1.792\cdot10^{-3}$
11	0.01121	$4.529\cdot10^{-3}$	$2.719\cdot10^{-5}$	$2.058\cdot10^{-3}$
12	0.01406	$5.625\cdot10^{-3}$	$3.980\cdot10^{-5}$	$2.308\cdot10^{-3}$
13	0.01718	$6.872\cdot10^{-3}$	$5.540\cdot10^{-5}$	$2.610\cdot10^{-3}$
14	0.02053	$8.266\cdot10^{-3}$	$7.423\cdot10^{-5}$	$2.964\cdot10^{-3}$
15	0.02411	$9.803\cdot10^{-3}$	$9.653\cdot10^{-5}$	$3.368\cdot10^{-3}$
16	0.02788	0.01148	$1.225\cdot10^{-4}$	$3.822\cdot10^{-3}$
17	0.03182	0.01329	$1.523\cdot10^{-4}$	$4.325\cdot10^{-3}$
18	0.03592	0.01522	$1.862\cdot10^{-4}$	$4.876\cdot10^{-3}$
19	0.04015	0.01727	$2.242\cdot10^{-4}$	$5.474\cdot10^{-3}$
20	0.04451	0.01944	$2.665\cdot10^{-4}$	$6.117\cdot10^{-3}$
25	0.06770	0.03183	$5.463\cdot10^{-4}$	$9.981\cdot10^{-3}$
30	0.09233	0.04634	$9.459\cdot10^{-4}$	0.01481
35	0.11765	0.06247	$1.471\cdot10^{-3}$	0.02045
40	0.14267	0.07981	$2.122\cdot10^{-3}$	0.02677
45	0.16754	0.09805	$2.897\cdot10^{-3}$	0.03367
50	0.19225	0.11699	$3.797\cdot10^{-3}$	0.04105
55	0.21677	0.13646	$4.819\cdot10^{-3}$	0.04884
60	0.24108	0.15637	$5.964\cdot10^{-3}$	0.05696
65	0.26515	0.17662	$7.230\cdot10^{-3}$	0.06539
70	0.28898	0.19714	$8.615\cdot10^{-3}$	0.07406
75	0.31256	0.21788	0.01012	0.08296
80	0.33589	0.23880	0.01174	0.09204
85	0.35897	0.25986	0.01348	0.10130

TABLE 15 (*continued*)

T/K	$C^{\circ}_{p,w}$/(J·K^{-1}·g^{-1})	$\Delta_0^T S^{\circ}_w$/(J·K^{-1}·g^{-1})	$\Delta_0^T H^{\circ}_w$/(kJ·g^{-1})	Φ°_w/(J·K^{-1}·g^{-1})
90	0.38180	0.28102	0.01533	0.11069
95	0.40440	0.30227	0.01730	0.12022
100	0.42677	0.32359	0.01937	0.12985
110	0.47092	0.36634	0.02386	0.14941
120	0.51440	0.40918	0.02879	0.16927
130	0.55741	0.45206	0.03415	0.18937
140	0.60015	0.49493	0.03994	0.20967
150	0.64286	0.53779	0.04615	0.23011
160	0.68576	0.58065	0.05279	0.25068
170	0.72907	0.62352	0.05987	0.27135
180	0.77299	0.66643	0.06738	0.29211
190	0.81769	0.70942	0.07533	0.31294
200	0.86330	0.75252	0.08373	0.33384
210	0.90990	0.79576	0.09260	0.35481
220	0.95752	0.83918	0.10194	0.37584
230	1.0061	0.88282	0.11175	0.39693
240	1.0555	0.92668	0.12206	0.41809
250	1.1056	0.97078	0.13287	0.43931
260	1.1559	1.0151	0.14417	0.46061
270	1.2060	1.0597	0.15598	0.48197
273.15	1.2217	1.0738	0.15981	0.48871
280	1.2555	1.1044	0.16829	0.50340
290	1.3035	1.1493	0.18109	0.52490
298.15	1.3411	1.1860	0.19187	0.54247
300	1.3494	1.1943	0.19436	0.54646
		Cellulose III (130 °C)		
0	0	0	0	0
1	$1.126\cdot10^{-5}$	$6.099\cdot10^{-6}$	$3.677\cdot10^{-9}$	$2.422\cdot10^{-6}$
2	$6.876\cdot10^{-5}$	$2.783\cdot10^{-5}$	$3.649\cdot10^{-8}$	$9.584\cdot10^{-6}$
3	$2.213\cdot10^{-4}$	$8.506\cdot10^{-5}$	$1.364\cdot10^{-7}$	$3.960\cdot10^{-5}$
4	$5.309\cdot10^{-4}$	$2.078\cdot10^{-4}$	$3.362\cdot10^{-7}$	$1.238\cdot10^{-4}$
5	$1.068\cdot10^{-3}$	$4.265\cdot10^{-4}$	$7.568\cdot10^{-7}$	$2.752\cdot10^{-4}$
6	$1.894\cdot10^{-3}$	$7.643\cdot10^{-4}$	$1.647\cdot10^{-6}$	$4.898\cdot10^{-4}$
7	$3.052\cdot10^{-3}$	$1.237\cdot10^{-3}$	$3.348\cdot10^{-6}$	$7.592\cdot10^{-4}$
8	$4.566\cdot10^{-3}$	$1.857\cdot10^{-3}$	$6.244\cdot10^{-6}$	$1.077\cdot10^{-3}$
9	$6.441\cdot10^{-3}$	$2.630\cdot10^{-3}$	$1.073\cdot10^{-5}$	$1.437\cdot10^{-3}$
10	$8.661\cdot10^{-3}$	$3.560\cdot10^{-3}$	$1.721\cdot10^{-5}$	$1.840\cdot10^{-3}$
11	0.01121	$4.557\cdot10^{-3}$	$2.670\cdot10^{-5}$	$2.130\cdot10^{-3}$
12	0.01405	$5.652\cdot10^{-3}$	$3.931\cdot10^{-5}$	$2.377\cdot10^{-3}$
13	0.01717	$6.899\cdot10^{-3}$	$5.490\cdot10^{-5}$	$2.676\cdot10^{-3}$
14	0.02054	$8.293\cdot10^{-3}$	$7.374\cdot10^{-5}$	$3.026\cdot10^{-3}$
15	0.02413	$9.832\cdot10^{-3}$	$9.606\cdot10^{-5}$	$3.428\cdot10^{-3}$
16	0.02792	0.01151	$1.221\cdot10^{-4}$	$3.880\cdot10^{-3}$
17	0.03189	0.01332	$1.520\cdot10^{-4}$	$4.381\cdot10^{-3}$
18	0.03602	0.01526	$1.859\cdot10^{-4}$	$4.931\cdot10^{-3}$
19	0.04029	0.01732	$2.241\cdot10^{-4}$	$5.528\cdot10^{-3}$
20	0.04467	0.01950	$2.665\cdot10^{-4}$	$6.172\cdot10^{-3}$
25	0.06797	0.03193	$5.473\cdot10^{-4}$	0.01004
30	0.09263	0.04649	$9.485\cdot10^{-4}$	0.01488
35	0.11794	0.06267	$1.475\cdot10^{-3}$	0.02053
40	0.14317	0.08007	$2.128\cdot10^{-3}$	0.02688
45	0.16809	0.09837	$2.906\cdot10^{-3}$	0.03380
50	0.19282	0.11737	$3.808\cdot10^{-3}$	0.04120
55	0.21734	0.13690	$4.834\cdot10^{-3}$	0.04901
60	0.24161	0.15685	$5.981\cdot10^{-3}$	0.05716
65	0.26562	0.17714	$7.250\cdot10^{-3}$	0.06561
70	0.28937	0.19769	$8.637\cdot10^{-3}$	0.07431
75	0.31286	0.21846	0.01014	0.08322
80	0.33607	0.23940	0.01177	0.09233
85	0.35903	0.26046	0.01350	0.10160
90	0.38173	0.28163	0.01536	0.11101
95	0.40420	0.30287	0.01732	0.12055
100	0.42646	0.32417	0.01940	0.13020
110	0.47040	0.36688	0.02388	0.14977
120	0.51375	0.40967	0.02880	0.16965
130	0.55676	0.45249	0.03416	0.18976
140	0.59966	0.49532	0.03994	0.21005
150	0.64271	0.53816	0.04615	0.23050
160	0.68615	0.58102	0.05279	0.25107
170	0.73022	0.62394	0.05987	0.27174
180	0.77510	0.66695	0.06740	0.29250
190	0.82094	0.71008	0.07538	0.31334
200	0.86783	0.75337	0.08382	0.33426
210	0.91579	0.79687	0.09274	0.35525

(*continued on next page*)

TABLE 15 (*continued*)

T/K	$C^{\circ}_{p,w}$/(J·K^{-1}·g^{-1})	$\Delta^{T}_{0}S^{\circ}_{w}$/(J·K^{-1}·g^{-1})	$\Delta^{T}_{0}H^{\circ}_{w}$/(kJ·g^{-1})	Φ°_{w}/(J·K^{-1}·g^{-1})
220	0.96474	0.84060	0.10214	0.37632
230	1.0145	0.88458	0.11204	0.39746
240	1.0649	0.92882	0.12243	0.41868
250	1.1154	0.97332	0.13334	0.43997
260	1.1656	1.0180	0.14474	0.46135
270	1.2147	1.0630	0.15664	0.48280
273.15	1.2298	1.0771	0.16049	0.48957
280	1.2619	1.1080	0.16903	0.50432
290	1.3062	1.1531	0.18187	0.52591
298.15	1.3394	1.1897	0.19265	0.54356
300	1.3464	1.1980	0.19514	0.54757

[a] The standard uncertainties in the temperatures T are $u(T) = 0.001$ K. The expanded uncertainties in the property values $C^{\circ}_{p,w}$, $\Delta^{T}_{0}S^{\circ}_{w}$, and $\Delta^{T}_{0}H^{\circ}_{w}$ at approximately 95% confidence limits are: $U(C^{\circ}_{p,w}) = 0.02{\cdot}C^{\circ}_{p,w}$ $(2 < T/K < 20)$ and $U(C^{\circ}_{p,w}) = 0.01{\cdot}C^{\circ}_{p,w}$ $(10 < T/K < 302)$; $U(\Delta^{T}_{0}S^{\circ}_{w}) = 0.02{\cdot}\Delta^{T}_{0}S^{\circ}_{w}$ $(2 < T/K < 20)$ and $U(\Delta^{T}_{0}S^{\circ}_{w}) = 0.01{\cdot}\ \Delta^{T}_{0}S^{\circ}_{w}$ $(10 < T/K < 302)$; and $U(\Delta^{T}_{0}H^{\circ}_{w}) = 0.02{\cdot}\Delta^{T}_{0}H^{\circ}_{w}$ $(2 < T/K < 20)$ and $U(\Delta^{T}_{0}H^{\circ}_{w} <) = 0.01{\cdot}\Delta^{T}_{0}H^{\circ}_{w}$ $(10 < T/K < 302)$. The expanded uncertainties in $U(\Phi^{\circ}_{w})$ are temperature dependent and can be calculated by combining in quadrature the values of $U(\Delta^{T}_{0}S^{\circ}_{w})$ and $U(\Delta^{T}_{0}H^{\circ}_{w})/T$.

TABLE 16
Standard thermodynamic functions for the cellulose samples and for the pure allomorphs at $T = 298.15$ K and $p^{\circ} = 0.1$ MPa: $C^{\circ}_{p,w}$ is the standard massic heat capacity; $\Delta^{T}_{0}S^{\circ}_{w}$ is the standard massic entropy difference $\{S^{\circ}_{w}(T) - S^{\circ}_{w}(T\ =\ 0)\}$, $\Delta^{T}_{0}H^{\circ}_{w}$ is the standard massic enthalpy difference $\{H^{\circ}_{w}(T) - H^{\circ}_{w}(T = 0)\}$, and the function $\Phi^{\circ}_{w} = \Delta^{T}_{0}S^{\circ}_{w} - \Delta^{T}_{0}H^{\circ}_{w}/T$. All values except the "Measured" ones are corrected to a water mass fraction $w_{ref} = 0.073$ using equation (67). The basis for the expanded uncertainties (approximately 95% confidence limits) in these property values is discussed in section 3.8.

Sample	$C^{\circ}_{p,w}$/(J·K^{-1}·g^{-1})	$\Delta^{T}_{0}S^{\circ}_{w}$/(J·K^{-1}·g^{-1})	$\Delta^{T}_{0}H^{\circ}_{w}$ /(J·g^{-1})	Φ°_{w}/(J·K^{-1}·g^{-1})
		Measured		
Amorphous cellulose (24 h)	1.406 ± 0.022	1.255 ± 0.019	203.6 ± 3.1	0.5722 ± 0.022
Amorphous cellulose (30 h)	1.416 ± 0.022	1.261 ± 0.019	204.6 ± 3.1	0.5746 ± 0.022
Amorphous cellulose (36 h)	1.380 ± 0.021	1.225 ± 0.019	198.6 ± 3.1	0.5591 ± 0.021
Cellulose Iβ	1.337 ± 0.021	1.198 ± 0.018	193.5 ± 3.0	0.5490 ± 0.021
Cellulose II (25 °C)	1.369 ± 0.021	1.198 ± 0.018	194.1 ± 3.0	0.5470 ± 0.021
Cellulose II (70 °C)	1.322 ± 0.020	1.179 ± 0.018	190.5 ± 2.9	0.5401 ± 0.021
Cellulose II (145 °C)	1.319 ± 0.020	1.176 ± 0.018	190.1 ± 2.9	0.5389 ± 0.021
Cellulose III (−33 °C)	1.315 ± 0.020	1.175 ± 0.018	189.9 ± 2.9	0.5384 ± 0.021
Cellulose III (25 °C)	1.341 ± 0.021	1.186 ± 0.018	191.9 ± 2.9	0.5425 ± 0.021
Cellulose III (130 °C)	1.339 ± 0.021	1.190 ± 0.018	192.7 ± 3.0	0.5436 ± 0.021
		Water corrected		
Amorphous cellulose (24 h)	1.403 ± 0.030	1.251 ± 0.033	203.0 ± 4. 9	0.5701 ± 0.026
Amorphous cellulose (30 h)	1.414 ± 0.030	1.258 ± 0.032	204.2 ± 4.8	0.5731 ± 0.026
Amorphous cellulose (36 h)	1.376 ± 0.030	1.220 ± 0.033	197.8 ± 5.0	0.5565 ± 0.026
Cellulose Iβ	1.360 ± 0.033	1.227 ± 0.034	197.6 ± 5.2	0.5637 ± 0.025
Cellulose II (25 °C)	1.353 ± 0.038	1.177 ± 0.042	191.1 ± 6.2	0.5363 ± 0.029
Cellulose II (70 °C)	1.314 ± 0.032	1.170 ± 0.036	189.1 ± 5.3	0.5353 ± 0.026
Cellulose II (145 °C)	1.321 ± 0.029	1.179 ± 0.031	190.4 ± 4.7	0.5401 ± 0.024
Cellulose III (−33 °C)	1.307 ± 0.033	1.165 ± 0.036	188.4 ± 5.4	0.5332 ± 0.026
Cellulose III (25 °C)	1.327 ± 0.036	1.169 ± 0.040	189.3 ± 6.0	0.5334 ± 0.028
Cellulose III (130 °C)	1.320 ± 0.040	1.165 ± 0.044	189.1 ± 6.6	0.5308 ± 0.029
		Pure allomorphs		
Cellulose Iβ	1.337 ± 0.063	1.216 ± 0.063	195.1 ± 9.7	0.5619 ± 0.043
Cellulose II (25 °C)	1.284 ± 0.11	1.078 ± 0.11	175.2 ± 17	0.4910 ± 0.077
Cellulose II (70 °C)	1.228 ± 0.077	1.094 ± 0.081	176.1 ± 12	0.5031 ± 0.057
Cellulose II (145 °C)	1.263 ± 0.061	1.130 ± 0.063	181.9 ± 10	0.5202 ± 0.046
Cellulose III (−33 °C)	1.112 ± 0.12	0.999 ± 0.13	160.2 ± 19	0.4625 ± 0.089
Cellulose III (25 °C)	1.253 ± 0.084	1.091 ± 0.089	176.4 ± 13	0.4990 ± 0.060
Cellulose III (130 °C)	1.266 ± 0.074	1.111 ± 0.080	180.4 ± 12	0.5063 ± 0.074
		Weighted averages		
Cellulose(am)	1.398 ± 0.017	1.243 ± 0.019	201.7 ± 2.8	0.5665 ± 0.015
Cellulose Iβ(cr)	1.337 ± 0.063	1.216 ± 0.063	195.1 ± 9.7	0.5619 ± 0.043
Cellulose II(cr)	1.255 ± 0.087	1.110 ± 0.091	179.0 ± 14	0.5094 ± 0.065
Cellulose III(cr)	1.232 ± 0.10	1.083 ± 0.11	175.2 ± 16	0.4933 ± 0.083

making the extrapolation to a value of $\Delta_{c}H^{\circ *}_{w}$ for cellulose(am) very uncertain. This large discrepancy may have also caused Nelson to forego journal publication of her important work. The results of Nelson [14] are discussed further below in conjunction with other values of $\Delta_{c}H^{\circ}_{w}$ for cellulose from the literature.

A complication that arises in the comparison of property values is the fact that there are two forms of cellulose I, *i.e.*, cellulose Iα and cellulose Iβ. Cellulose Iα is produced by bacteria and algae, while cellulose Iβ is the predominant form found in plants [3]. Thus, while essentially all of the previous studies in which thermodynamic property values were reported did not state which form of cellulose I they used, most of these studies identified the source of the cellulose I that they used to be from plants and in no case was the cellulose identified as having been produced by bacteria or algae. Thus, it is highly likely that cellulose Iβ was the predominant form used in the studies with which comparisons of results are made. Nevertheless, it is likely that many of the samples of cellulose Iβ used in these studies contained some cellulose Iα [4,79].

TABLE 17
Calculated property values for the conversion reactions of the cellulose allomorphs at T = 298.15 K and p° = 0.1 MPa. Here, ΔH°_w is the change in the standard massic enthalpy, ΔG°_w is the change in the standard massic Gibbs free energy, ΔS°_w is the change in the standard massic entropy, and $\Delta C^\circ_{p,w}$ is the change in the standard massic heat capacity. All substances in these reactions are a mass fraction of water w_{H_2O} = 0.073. The uncertainties are expanded uncertainties at approximately 95% confidence limits.

Reaction	$\Delta_r H^{\circ *}_w$/(J·g^{-1})	$\Delta_r G^{\circ *}_w$/(J·g^{-1})	$\Delta_r S^{\circ *}_w$/(J·K^{-1}·g^{-1})[a]	$\Delta_r C^{\circ *}_{p,w}$/(J·K^{-1}·g^{-1})
Cellulose(am) = cellulose I(cr) (26)	−(106 ± 18)	−(98 ± 27)	−(0.027 ± 0.065)	−(0.061 ± 0.065)
Cellulose(am) = cellulose II(cr) (27)	−(113 ± 11)	−(73 ± 30)	−(0.133 ± 0.093)	−(0.143 ± 0.089)
Cellulose(am) = cellulose III(cr) (28)	−(115 ± 20)	−(67 ± 38)	−(0.160 ± 0.11)	−(0.166 ± 0.10)
Cellulose I(cr) = cellulose II(cr) (29)	−(7 ± 16)	25 ± 37	−(0.106 ± 0.11)	−(0.082 ± 0.11)
Cellulose I(cr) = cellulose III(cr) (30)	−(8 ± 25)	32 ± 45	−(0.133 ± 0.12)	−(0.104 ± 0.12)
Cellulose II(cr) = cellulose III(cr) (31)	−(2 ± 20)	6 ± 47	−(0.027 ± 0.14)	−(0.022 ± 0.13)

[a] The values of $\Delta_r S^{\circ *}_w$ and $\Delta_r G^{\circ *}_w$ are based on the assumption that the values of $S^{\circ *}_w$ for all of the allomorphs approach the same value as $T \to 0$. See section 3.9.

3.10.3. Literature results for the standard massic enthalpies of combustion

Results from the literature for the standard massic enthalpies of combustion $\Delta_c H^\circ_w$ of samples of cellulose in oxygen {reaction (9)} are shown in table 19. We first consider the measured values of $\Delta_c H^\circ_w$ for cellulose I samples. Ioelovich *et al.* [88], Ur'yash *et al.* [91], and Blokhin *et al.* [92] measured values of $\Delta_c H^\circ_w$ for cellulose I samples at various *CI* values. By fitting their respective values of $\Delta_c H^\circ_w$ vs *CI* and extrapolating to *CI* = 100, the results reported by Ioelovich *et al.* [88], by Ur'yash *et al.* [91], and by Blokhin *et al.* [92] lead, respectively, to $\Delta_c H^{\circ *}_w = -17337\ \mathrm{J\cdot g^{-1}}$, $\Delta_c H^{\circ *}_w = -17458\ \mathrm{J\cdot g^{-1}}$, and $\Delta_c H^{\circ *}_w = -17165\ \mathrm{J\cdot g^{-1}}$ for cellulose I(cr). The earlier, very carefully done measurements of Jessup and Prosen [83] and Colbert *et al.* [87] did not include a measurement of *CI* but the samples that they used probably had high *CI* values. We use the value $\Delta_r H^\circ_w = -113\ \mathrm{J\cdot g^{-1}}$ for reaction (26) {this is the average of the values of $\Delta_r H^\circ_w$ for reaction (26) at w = 0; see table 18} and assume that the cellulose samples used by Jessup and Prosen [83] and by Colbert *et al.* [87] had *CI* values of ≈75. This assumption gives an adjustment of $-(0.25 \cdot -113\ \mathrm{J\cdot g^{-1}}) = 28\ \mathrm{J\cdot g^{-1}}$ to be applied to the values of $\Delta_c H^\circ_w$ obtained by Jessup and Prosen [83] and by Colbert *et al.* [87]. Note that $\Delta_c H^{\circ *}_w$ for cellulose(am) is more exothermic than $\Delta_c H^{\circ *}_w$ for cellulose I (cr). Hence, the sign of the $28\ \mathrm{J\cdot g^{-1}}$ adjustment is positive. Applying these corrections, one obtains $\Delta_c H^{\circ *}_w = -17421\ \mathrm{J\cdot g^{-1}}$ and $\Delta_c H^{\circ *}_w = -17317\ \mathrm{J\cdot g^{-1}}$ for cellulose I(cr) from the respective studies of Jessup and Prosen [83] and Colbert *et al.* [87]. Applying a similar correction to Nelson's [14] results, one obtains $\Delta_c H^{\circ *}_w = -17414\ \mathrm{J\cdot g^{-1}}$ for cellulose I(cr). In making the adjustment to Nelson's [14] values of $\Delta_c H^\circ_w$ for the two samples of cellulose I(cr), we used the respective averages of her [14] reported *CI* values that are based on acid hydrolysis and XRD. All of these values pertain to T = 298.15 K and w_{H_2O} = 0. The average of the results obtained from five studies [14,83,87,88,91] is $\Delta_c H^{\circ *}_w = -(17390 \pm 54)\ \mathrm{J\cdot g^{-1}}$. Here, the uncertainty is equal to two estimated standard deviations of the mean. The value of $\Delta_c H^{\circ *}_w = -17165\ \mathrm{J\cdot g^{-}1}$ from Blokhin *et al.* [92] is an outlier and was not used in calculating the average. From our study, we have $\Delta_c H^{\circ *}_w = -(16048 \pm 40)\ \mathrm{J\cdot g^{-1}}$ for cellulose I(cr) (see table 8) that pertains to T = 298.15 K and w_{H_2O} = 0.073. We use equation (23) together with our measured value of $\Delta_c H^{\circ *}_w(w_{H_2O} = 0.073)$ for cellulose I(cr) and the value $\Delta_{hyd} H^{\circ *}_w\ (0 \to 0.073) = -32\ \mathrm{J\cdot g^{-1}}$ for cellulose I(cr) and calculate $\Delta_c H^{\circ *}_w = -(17344 \pm 41)\ \mathrm{J\cdot g^{-1}}$ for w_{H_2O} = 0. This value is in agreement with the value $\Delta_c H^{\circ *}_w = -(17390 \pm 54)\ \mathrm{J\cdot g^{-1}}$ for cellulose I(cr) obtained from what appear to be the best of the studies in the literature.

Nelson [14] and Ioelovich *et al.* [88] report values of $\Delta_c H^\circ_w$ and *CI* for cellulose II samples. We adjust their [14,88] reported values to *CI* = 100 using the same methods used for treating the $\Delta_c H^\circ_w$ values for the cellulose I samples and obtain $\Delta_c H^{\circ *}_w = -(17354 \pm 11)\ \mathrm{J\cdot g^{-1}}$ and $\Delta_c H^{\circ *}_w = -(17337 \pm 12)\ \mathrm{J\cdot g^{-1}}$ for cellulose II(cr) from these two respective studies. As above, we use our measured value for $\Delta_c H^{\circ *}_w(w_{H_2O} = 0.073)$ with equation (23) and with $\Delta_{hyd} H^{\circ *}_w\ (0 \to 0.073) = -44\ \mathrm{J\cdot g^{-1}}$ to calculate $\Delta_c H^{\circ *}_w = -(17217 \pm 85)\ \mathrm{J\cdot g^{-1}}$ for cellulose II(cr) at w_{H_2O} = 0. Both Nelson's [59] and Ioelovich's [88] uncertainties are very optimistic and do not include any possible systematic errors. Thus, it is likely that all three values of $\Delta_c H^{\circ *}_w$ for cellulose II(cr) are in agreement.

The only value of $\Delta_c H^\circ_w$ in the literature for a cellulose III sample comes from the study of Nelson [14]. As above, we adjust her [14] reported value of $\Delta_c H^\circ_w$ to *CI* = 100 and obtain $\Delta_c H^{\circ *}_w = -(17359 \pm 18)\ \mathrm{J\cdot g^{-1}}$ for cellulose III(cr). Adjustment of our measured value for $\Delta_c H^{\circ *}_w(w_{H_2O} = 0.073)$ to w = 0 {equation (23) with $\Delta_{hyd} H^{\circ *}_w(0 \to 0.073) = -38\ \mathrm{J\cdot g^{-1}}$} leads to $\Delta_c H^{\circ *}_w = -(17390 \pm 57)$. The two values of $\Delta_c H^{\circ *}_w$ for cellulose III(cr) are in good agreement.

There are two direct measurements of $\Delta_c H^{\circ *}_w$ for cellulose(am) in the literature: $\Delta_c H^{\circ *}_w = -(17548 \pm 27)\ \mathrm{J\cdot g^{-1}}$ from Ur'yash *et al.* [91] and $\Delta_c H^{\circ *}_w = -(16980 \pm 50)\ \mathrm{J\cdot g^{-1}}$ from Blokhin *et al.* [92]. Additionally, extrapolation of the $\Delta_c H^\circ_w$ values for the cellulose I and cellulose II samples from the study of Ioelovich *et al.* [88] to *CI* = 0 gives $\Delta_c H^{\circ *}_w = -17561\ \mathrm{J\cdot g^{-1}}$ for cellulose(am). All three values of $\Delta_c H^{\circ *}_w$ pertain to w_{H_2O} = 0. Again we adjust our measured value for $\Delta_c H^{\circ *}_w(w_{H_2O} = 0.073)$ to w_{H_2O} = 0 {equation (23) with $\Delta_{hyd} H^{\circ *}_w = -55\ \mathrm{J\cdot g^{-1}}$} and obtain $\Delta_c H^{\circ *}_w = -(17382 \pm 20)\ \mathrm{J\cdot g^{-1}}$, a value that is in the range of the aforementioned values from the literature. Nelson's [14] long extrapolation of her $\Delta_c H^\circ_w$ values for cellulose (I, II, and III) samples to *CI* = 0 led to $\Delta_c H^{\circ *}_w = -18376\ \mathrm{J\cdot g^{-1}}$ for cellulose(am). This value is an outlier. The values of $\Delta_c H^{\circ *}_w(w_{H_2O} = 0)$ for cellulose(am), cellulose I(cr), cellulose II(cr), and cellulose III(cr) are summarized in table 20.

3.10.4. Literature results for standard massic heat capacities and derived thermal functions

Results from the literature pertinent to the standard massic heat capacities $C^\circ_{p,w}$ and the thermodynamic properties derived from these measured values are shown in table 21. Note that for two studies (Kozolv *et al.* [99] and Ur'yash *et al.* [91]), we calculated the values of $\Delta^T_0 S^\circ_w$ and $\Delta^T_0 H^\circ_w$ from the reported results by using a Hermite polynomial fit (*Mathematica* function "Interpolation") of the $C^\circ_{p,w}$ values and an empirical extrapolation to T = 0 followed by the necessary integrations. One sees from table 21 that there are four previous studies {Kozolv *et al.* [99], Hatakema *et al.* [102], Mochalov *et al.* [104], and Blokhin *et al.* [92]} where standard massic heat capacities were measured on cellulose samples and where *CI* values are also known. In three of these studies [92,102,104], the results cover a sufficient range of *CI* values and have a precision sufficient to permit a reasonable extrapolation of measured property values with *CI* and calculation of thermodynamic property values for cellulose(am) and cellulose I(cr). The results of these calculations are also shown in table 21.

Values of $C^\circ_{p,w}$, $\Delta^T_0 S^{\circ *}_w$, $\Delta^T_0 H^{\circ *}_w$, and $\Phi^{\circ *}_w$ for the anhydrous (w_{H_2O} = 0) pure cellulose allomorphs can be calculated from our measured values of these quantities that pertain to w_{H_2O} = 0.073. This is done by setting w_{ref} equal to zero in equation (67) to give

TABLE 18
Summary of results from the literature for the standard massic enthalpy change $\Delta_r H^{\circ *}_w$ for reactions (26)–(29). The temperature $T = 298.15$ K except for the studies of Calvet [64] and Calvet and Hermans[a] [65] where $T = 290.15$ K. The pressure $p^\circ \approx 0.1$ MPa. The uncertainties are either those reported by the authors or calculated from their reported property values, in which case the uncertainties are based on two estimated standard deviations of the mean.

Worker(s)	$\Delta_r H^{\circ *}_w / (J \cdot g^{-1})$	w_{H_2O}
Cellulose(am) = cellulose I(cr), reaction (26)		
Nelson [14][b]	−(108 ± 23)	0
Dale and Tsao [66][c]	−(115 ± 9)	0
Dale and Tsao [66][d]	−(105 ± 10)	0
This study	−(106 ± 18)	0.073
This study[e]	−(129 ± 24)	0
Cellulose(am) = cellulose II(cr), reaction (27)		
Nelson [14][b]	−(131 ± 27)	0
Dale and Tsao [66][c]	−(140 ± 18)	0
Dale and Tsao [66][d]	−(131 ± 18)	0
This study	−(113 ± 11)	0.073
This study[e]	−(124 ± 21)	0
Cellulose(am) = cellulose III(cr), reaction(28)		
Nelson [14][b]	−(110 ± 25)	0
This study	−(115 ± 20)	0.073
This study[e]	−(132 ± 26)	0
Cellulose I(cr) = cellulose II(cr), reaction (29)		
Calvet [64][f]	17	Wet
Calvet [64][f]	12	0
Lauer [68][g]	≈29	Wet
Lauer [68][g]	≈24	0
Ranby [50][h]	−8	Wet
Ranby [50][h]	−13	0
Nelson [14][i]	−(23 ± 35)	0
Dale and Tsao [66][j]	−(26 ± 20)	0
Ioelovich [78][k]	−55	0
This study	−(7 ± 16)	0.073
This study[e]	5 ± 21	0

[a] Calvet and Hermans [65] (result not shown in table) dissolved samples of rayon and cotton linters in cupriethylenediamine solution at $T = 290.15$ K. The *CI* values of the samples they [65] used were based on X-ray diffraction data. Note that the reaction is clearly exothermic even though Calvet and Hermans [65] give a positive sign for $\Delta_r H^{\circ *}_w$. A relative molecular mass $M_r = 162.141$ was used to convert their [65] reported value of $\Delta_r H^{\circ *}_w$ to a standard massic basis. Must importantly, in the treatment of their results, Calvet and Hermans [65] made no recognition of the fact that rayon is cellulose II and that cotton linters are cellulose I. Thus, the value of $\Delta_r H^{\circ *}_w = -106\ J \cdot g^{-1}$ obtained from the study of Calvet and Hermans is, in fact, the average of the values of $\Delta_r H^{\circ *}_w$ for reactions (26) and (27). Calvet and Hermans also measured values of $\Delta_{hyd} H^{\circ}_w$ (0 → wet) for the rayon and cotton linter samples. However, since they did not measure a value $\Delta_{hyd} H^{\circ}_w$ (0 → wet) for cellulose(am), it is not possible to calculate values of $\Delta_{hyd} H^{\circ *}_w$(0 → wet) for pure cellulose I(cr) or pure cellulose II(cr). Nevertheless, the values of $\Delta_{hyd} H^{\circ}_w$(0 → wet) measured by Calvet and Hermans [65] are in accord with those obtained by Rees [15].

[b] Nelson [14] used cupriethylenediamine to dissolve cellulose samples and a thermochemical cycle to obtain values of $\Delta_{sol} H^{\circ *}_w$ ($w_{H_2O} = 0$). The values of $\Delta_r H^{\circ *}_w$ given here are based on the summary of results given on page 79 of Nelson's thesis. The uncertainty is an estimate based on the value assumed for the crystallinity index for the cellulose sample (N7) having the lowest crystallinity. The temperature is presumably 298.15 K.

[c] Dale and Tsao [66] dissolved samples of cellulose I, cellulose II, and amorphous cellulose in cadoxen and in ferric sodium tartrate. All of the samples were dry. The result given here is based on experiments that used cadoxen. The uncertainties are based on the high and low values given in their table V. The reaction temperature was 298.15 K [67].

[d] This result, obtained by Dale and Tsao [66], is based on experiments that used ferric sodium tartrate.

[e] Calculated from the values of $\Delta_r H^{\circ *}_w$ that pertain to $w_{H_2O} = 0.073$. The uncertainties are expanded uncertainties and include estimates for possible errors in the values of $\Delta_{hyd} H^{\circ *}_w$.

[f] Calvet [64] gives $\Delta_r H^{\circ *}_w = -4\ cal \cdot g^{-1}$ at $T = 290.15$ K but states that the reaction is endothermic for the mercerization reaction of wet cellulose. By using values of $\Delta_{hyd} H^{\circ *}_w$(0 → wet) for cellulose I(cr) and cellulose II(cr) calculated from Nelson's study [14] (see section 3.10.1), we calculated $\Delta_r H^{\circ *}_w = 12\ J \cdot g^{-1}$ for reaction (29) that pertains to $w_{H_2O} = 0$.

[g] Lauer [68] reports $\Delta_r H^{\circ}$ = "1108 cal/$C_6H_{10}O_5$" for the mercerization reaction of wet cellulose. This corresponds to $\Delta_r H^{\circ}_w \approx 2\ J \cdot g^{-1}$ for reaction (29). By using values of $\Delta_{hyd} H^{\circ *}_w$(0 → wet) for cellulose I(cr) and cellulose II(cr) calculated from Nelson's study [14] (see section 3.10.1), we calculate $\Delta_r H^{\circ *}_w \approx 24\ J \cdot g^{-1}$ for reaction (29) that pertains to $w_{H_2O} = 0$. The sign of the enthalpy change is uncertain.

[h] Ranby [50], in his study and review, calculated $\Delta_r H^{\circ *}_w \approx -8\ J \cdot g^{-1}$ for the mercerization reaction of wet cellulose from the enthalpy of solution measurements of Morrison *et al.* [69,70] in which NaOH was used. Ranby [50] also summarized the earlier studies [71–77] on the mercerization reaction. By using values of $\Delta_{hyd} H^{\circ *}_w$(0 → wet) for cellulose I(cr) and cellulose II(cr) calculated from Nelson's study [14] (see section 3.10.1), we calculate $\Delta_r H^{\circ *}_w = -13\ J \cdot g^{-1}$ for reaction (29) that pertains to $w_{H_2O} = 0$.

[i] Calculated from the results of Nelson [14] by using her results for reactions (26) and (27) given in this table.

[j] Calculated from the results of Dale and Tsao [66] by using their results for reactions (26) and (27) given in this table.

[k] Ioelovich [78] measured values of $\Delta_{sol} H^{\circ}_w$ for samples of cellulose I and cellulose II into cadoxen. He [78] used two samples for both cellulose I and cellulose II, each of which had different *CI* values. We extrapolated the respective values of $\Delta_{sol} H^{\circ}_w$ to *CI* = 100 and then subtracted the resultant values of $\Delta_{sol} H^{\circ *}_w$ for the two pure allomorphs to obtain $\Delta_r H^{\circ *}_w = -55\ J \cdot g^{-1}$ for reaction (29). This result pertains to $w_{H_2O} = 0$.

$$X\{\text{anhydrous cellulose}\} = (1 - w_{H_2O})^{-1} \cdot [X\{\text{cell} \cdot w_{H_2O}(s)\} - w_{H_2O} \cdot X\{H_2O(cr, hex)\}]. \quad (77)$$

We shall assume that this adjustment of the property values to $w_{H_2O} = 0$ is uncertain by 25%. The adjusted property values are shown in table 22. The comparison of our results with those obtained from the literature cannot be certain due to the fact that uncertainties were not assigned to the property values in the previous studies [92,102,104]. Nevertheless, one sees that the value of $C^{\circ *}_{p,w}$, for cellulose(am) and for cellulose Iβ(cr) from Hatakema *et al.* [102], who used DSC in their study, are outliers. Also, the values of $C^{\circ}_{p,w}*$ for cellulose Iβ(cr) are most likely in agreement. But our value of $C^{\circ *}_{p,w}$ for cellulose(am) most likely differs from the values

obtained from the studies of Mochalov *et al.* [104] and Blokhin *et al.* [92]. Most importantly, all of the values of $\Delta_0^T S_w^{\circ *}$, $\Delta_0^T H_w^{\circ *}$, and $\Phi_w^{\circ *}$ at $T = 298.15$ K and $w_{H_2O} = 0$ for both cellulose(am) and cellulose Iβ(cr) are in agreement or near agreement.

Then, by using these values, we calculate values of $\Delta_r S_w^{\circ *}$ and $\Delta_r C_{p,w}^{\circ *}$ for the reaction {cellulose(am) = cellulose I(cr)}, reaction (26), at $T = 298.15$ K. These calculated values are shown in table 23. One sees that our values for $\Delta_r S_w^{\circ *}$ and for $\Delta_r C_{p,w}^{\circ *}$ at $w_{H_2O} = 0$ are in agreement with the results obtained from Mochalov *et al.* [104] and from Blokhin *et al.* [92]. The value of $\Delta_r C_{p,w}^{\circ *}$, for cellulose(am) and for cellulose I(cr) calculated from the study of Hatakema *et al.* [102] is again an outlier. The results presented in this study appear to be the first thermal property measurements on samples of cellulose II and cellulose III. We are not aware of any measurements of thermodynamic property values for cellulose IV.

3.11. Calculation of standard formation properties

The calculation of the standard formation properties of the cellulose allomorphs relies to a large extent on the value of $\Delta_c H_w^\circ\{\text{cellulose}\cdot w_{ref}(\text{am})\} = -(16062 \pm 14)\ \text{J}\cdot\text{g}^{-1}$ (see table 8). This value is used in preference to the values of $\Delta_c H_w^\circ$ for the other allomorphs due to the fact that the uncertainty in this value is much less than the uncertainties in these other values of $\Delta_c H_w^\circ$. Auxiliary data used in these calculations are the standard molar enthalpies of formation $\Delta_f H_m^\circ\{H_2O(l)\} = -(285.830 \pm 0.040)\ \text{kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H_m^\circ\{CO_2(g)\} = -(393.51 \pm 0.13)\ \text{kJ}\cdot\text{mol}^{-1}$ from the CODATA tables [105]. These calculations are conveniently done by using molar properties. Thus, we use equations (3) and (6) together with an assumed value $u = 300$, which is close to the average value $\langle DP_w\rangle = 313$ (see table 3), and $w_{H_2O} = 0.073$ to solve the aforementioned equations and obtain $M_r = 5.24728\cdot10^4$ and $v = 211.629$. Thus, by using the combustion reaction (1) and the aforementioned values for $\Delta_f H_m^\circ\{H_2O(l)\}$ and for $\Delta_f H_m^\circ\{CO_2(g)\}$, we calculate $\Delta_f H_m^\circ\{\text{cellulose}\cdot w_{ref}(\text{am})\} = -(355.02 \pm 0.77)\ \text{MJ}\cdot\text{mol}^{-1}$, where $w_{ref} = w_{H_2O} = 0.073$. Then, the standard massic enthalpy of formation $\Delta_f H_w^\circ\{\text{cellulose}\cdot w_{ref}(\text{am})\}$ is calculated by dividing $\Delta_f H_m^\circ\{\text{cellulose}\cdot w_{ref}(\text{am})\}$ by M_r. Since the value of $\Delta_f H_m^\circ\{\text{cellulose}\cdot w_{ref}(\text{am})\}$ depends on the assumed value of u, it is convenient to have a value of $\Delta_f H_u^\circ$ (the subscript "u" denotes the monomer unit) that pertains to the hydrated cellulose monomer unit $C_6H_{10}O_5$. A value for $\Delta_f H_u^\circ\{\text{cellulose}\cdot w_{ref}(\text{am})\}$ is readily obtained either by dividing $\Delta_f H_m^\circ\{\text{cellulose}\cdot w_{ref}(\text{am})\}$ by u or by multiplying $\Delta_f H_w^\circ$ by the value of M_r for the monomer unit. This latter calculation is very accurate when a large value of u is used.

The calculation of values of $\Delta_f H_m^\circ$ for the cellulose allomorphs I, II, and III uses the value of $\Delta_c H_w^\circ\{\textit{cellulose}\cdot w_{ref}(\text{am})\}$ calculated above together with the values of $\Delta_r H_w^{\circ *}$ for reactions (26)–(28) (see table 11) to calculate values of $\Delta_c H_w^\circ\{\text{cellulose}\cdot w_{ref}\}$ for these three allomorphs. This provides one set of values of $\Delta_c H_w^\circ$ for these three allomorphs. However, we also have a set of directly measured values of $\Delta_c H_w^\circ\{\text{cellulose}\cdot w_{ref}\}$ (see table 8) for these three allomorphs. Thus, we calculate the respective weighted averages of these values to obtain a "best" set of values for $\Delta_c H_w^\circ$ for the cellulose allomorphs: $\Delta_c H_w^\circ\{\text{cellulose I(cr)}\cdot w_{ref}\} = -(15979 \pm 20)\ \text{J}\cdot\text{g}^{-1}$, $\Delta_c H_w^\circ\{\text{cellulose I(cr)}\cdot w_{ref}\} = -(15948 \pm 17)\ \text{J}\cdot\text{g}^{-1}$, and $\Delta_c H_w^\circ\{\text{cellulose I(cr)}\cdot w_{ref}\} = -(15969 \pm 22)\ \text{J}\cdot\text{g}^{-1}$. The calculation of values of $\Delta_f H_m^\circ\{\text{cellulose}\cdot w_{ref}\}$ for the cellulose allomorphs I, II, and III follows the procedure described above to calculate $\Delta_f H_m^\circ\{\text{cellulose}\cdot w_{ref}(\text{am})\}$. These calculated values are given in table 24.

In the calculations that follow, *it is assumed* that the value of S_w° for each of the cellulose allomorphs is equal to the respective measured value of $\Delta_0^T S_w^\circ$, *i.e.*, $S_w^\circ \to 0$ as $T \to 0$ for each allomorph. In principle, if one had detailed structural information on the cellulose allomorphs, one could calculate the thermodynamic probability W [106,107] for a mole of each of the allomorphs. In turn, this would allow for the calculation of the residual molar entropies $S_w^\circ(T \to 0)$ by use of the Boltzmann equation

$$S_w^\circ = R\ln W. \tag{78}$$

As an example, we use the value $W = 6\cdot10^{23}$ and calculate $S_w^\circ = 455\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. However for a substance having a relative molecular mass $M_r = 5\cdot10^4$, one obtains $S_w^\circ = 0.009\ \text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$, which is a very small uncertainty in the value of S_w°. In any case, we do not have the structural information and we do not know W. Also, the calculation of the values of W, even if the crystal structures of the cellulose allomorphs were completely determined, would not be a trivial matter.

In any case, we now consider the formation reaction for one mole of cellulose(am), namely

$$6uC(s) + (5u + v + 1)H_2(g) + (1/2)(5u + v + 1)O_2(g) = (C_6H_{10}O_5)_u\cdot(H_2O)_1\cdot(H_2O)_v(\text{am}). \tag{79}$$

First, a value of the standard molar entropy $S_m^\circ\{\text{cellulose}\cdot w_{ref}\}$ for all four cellulose allomorphs is obtained by multiplying the values of $S_w^\circ\{\text{cellulose}\cdot w_{ref}\}$ by the calculated value of M_r.Then, by using the CODATA [105] values $S_m^\circ\{C(s)\} = (5.74 \pm 0.10)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $S_m^\circ\{H_2(g)\} = (130.680 \pm 0.003)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and $S_m^\circ\{O_2(g)\} = (209.152 \pm 0.005)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, we calculate the standard molar entropies of formation $\Delta_f S_w^\circ\{\text{cellulose}\cdot w_{ref}\}$.These values of $\Delta_f S_w^\circ\{\text{cellulose}\cdot w_{ref}\}$ are then combined with the previously calculated values of $\Delta_f H_m^\circ\{\text{cellulose}\cdot w_{ref}\}$ to yield values for $\Delta_f G_m^\circ\{\text{cellulose}\cdot w_{ref}\}$.Then, as above, values of massic quantities are obtained by dividing the molar quantities by M_r and property values for the monomer unit are obtained by dividing the molar quantities by u.These calculated values are also given in table 24.Note that we used an assumed value $u = 300$ in performing these calculations.However, the use of $u = 1000$ in these calculations yields identical values of thermodynamic properties to within the number of digits shown in table24.

Values of the standard formation properties of the anhydrous cellulose allomorphs are obtained by first using the "best" set of values of $\Delta_c H_w^\circ\{\text{cellulose}\cdot w_{ref}\}$ (see above) together with the values of $\Delta_{hyd} H_w^\circ\{\text{cellulose}\cdot w_{ref},\ 0 \to w_{ref}\}$ obtained previously (see section 3.10.1) to calculate values of $\Delta_c H_w^\circ\{\text{cellulose}\cdot w = 0\}$. These values are, in turn, used to calculate values of $\Delta_f H_w^\circ\{\text{cellulose}\cdot w = 0\}$ by using the same procedure (see above) that was used to calculate values of $\Delta_f H_w^\circ\{\text{cellulose}\cdot w_{ref}\}$. The values of $\Delta_f H_u^\circ\{\text{cellulose}\cdot w = 0\}$ that pertain to the anhydrous monomer unit were calculated by multiplying the corresponding values of $\Delta_f H_w^\circ\{\text{cellulose}\cdot w = 0\}$ by the value of M_r for the anhydrous monomer unit $C_6H_{10}O_5$. The massic entropies for the anhydrous cellulose allomorphs (see table 22) were used to calculate values of $\Delta_f S_m^\circ$ as was done above for the hydrated samples. These values of $\Delta_f S_m^\circ\{\text{cellulose}\cdot w = 0\}$ were then combined with the corresponding values of $\Delta_f H_m^\circ\{\text{cellulose}\cdot w = 0\}$ to calculate values of $\Delta_f G_m^\circ\{\text{cellulose}\cdot w = 0\}$. The values of S_w° and $C_{p,w}^\circ$ given in table 24 were taken either from table 16 (allomorphs having $w_{H_2O} = 0.073$) or from table 22 (allomorphs having $w_{H_2O} = 0$) and which are all based on our results. *It is important to note the following items.* If our assumption regarding the equality of S_w° to $\Delta_0^T S_w^\circ$ is in error, the true values of $\Delta_r S_w^\circ$ and $\Delta_r S_u^\circ$ will be less than (more negative) than the values given in table 24. Also, the true values of $\Delta_r G_w^\circ$ and $\Delta_r G_u^\circ$ will be greater than (more positive) than the tabulated values. Similar considerations apply to the values of $\Delta_r S_w^{\circ *}$ and $\Delta_r G_w^{\circ *}$ given in tables 17 and 23. Clearly the values of the enthalpies and heat capacities are not affected by this assumption.

TABLE 19
Summary of results from the literature for the standard massic enthalpies of combustion $\Delta_c H^\circ_w$ of samples of cellulose in oxygen {reaction (9)}. The mass fractions of water w_{H_2O} and crystallinity indexes *CI*, if reported, are given in columns 3 and 4, respectively. The values of $\Delta_c H^\circ_w$ given in column 5 refer to $T = 298.15$ K and $p^\circ = 0.1$ MPa. The uncertainties are either those reported by the authors or calculated from their results, in which case the uncertainties are based on two estimated standard deviations of the mean.[a,b,c]

Reference	Sample	w_{H_2O}	*CI*	$\Delta_c H^\circ_w/(J \cdot g^{-1})$
Binder [80][d]	Cellulose I			−17527
Karrer and Fioroni [81][e]	Cellulose I			−17510
Heisenberg [82][f]	Cellulose I – ramie cellulose			−(17544 ± 21)
	Cellulose II – low-stretched rayon			−(17602 ± 13)
	Cellulose II – highly-stretched rayon			−(17707 ± 13)
Jessup and Prosen [83][g]	Cellulose I – crystalline cotton linters	0		−(17433 ± 3)
	Cellulose I – Wood pulp	0		−(17466 ± 19)
Nelson [14][h]	Cellulose I – cotton yarn kiln-dried and thoroughly alcohol extracted	0	88	−(17458 ± 3)
	Cellulose I – hydrocellulose prepared from the above cellulose I sample	0	93	−(17400 ± 7)
	Cellulose II – hydrocellulose prepared from mercerized cotton	0	80	−(17380 ± 2)
	Cellulose III – hydrocellulose prepared from amine-swollen cotton	0	85	–(17377 ± 6)
Tang and Neill [84][i]	Cellulose I			−16862
Susott *et al.* [85][j]	Cellulose I – filter paper	0.031		−16797
Murphey and Master [86][k]	Cellulose I from northern red oak			−17030
Colbert *et al.* [87][l]	Cellulose I – microcrystalline Avicel pH-10	0		−(17345 ± 11)
Ioelovich *et al.* [88][m]	Cellulose I – raw wood	0	66	−(17414 ± 7)
	Cellulose II – mercerized cellulose	0	53	−(17417 ± 7)
	Cellulose I – ground for 1 h	0	52	−(17445 ± 8)
	Cellulose I – ground for 3 h	0	28	−(17499 ± 8)
	Cellulose II – regenerated viscose fibers	0	40	−(17452 ± 7)
Chen and Frendi [89][n]	Cellulose I – pure and fire-retarded cellulose			−16700
Milosavljevic *et al.* [90][o]	Cellulose I – ashless filter paper pulp			−17100
Ur'yash *et al.* [91][p]	Cellulose(am) – ball-milled from wood cellulose I	0	0	−(17548 ± 27)
	Cellulose(am) – ball-milled reformed wood cellulose I	0	4	−(17508 ± 19)
	Cellulose I – reformed wood cellulose	0	65	−(17491 ± 15)
	Cellulose I – microcrystalline cellulose from cotton	0	≈86	−(17293 ± 5)
Blokhin *et al.* [92][q]	Cellulose I – "Ankir" cotton microcrystalline cellulose	0	90	−(17290 ± 40)
	Cellulose I – wood sulfite cellulose from the Koryazhama Branch of the Ilim Group	0	80	−(16610 ± 110)
	Cellulose I – straw cellulose obtained by nitric acid delignification of rape straw stems	0	74	−(17510 ± 40)
	Cellulose I(am) – prepared by regeneration of cellulose from {nitrogen (IV) oxide + ethyl acetate solution}	0	0	−(16980 ± 50)
This study	Cellulose(am)	0.073	0	−(16062 ± 14)
	Cellulose I(cr)	0.073	100	−(16048 ± 40)
	Cellulose II(cr)	0.073	100	−(15919 ± 84)
	Cellulose III(cr)	0.073	100	−(16085 ± 56)

[a] For the combustion of cellulose in oxygen {reaction (9)}, $\Delta_c H^\circ_w = \Delta_c U^\circ_w$. The uncertainties are those given by the investigators.
[b] Calories were converted to joules by using the relationship 1 $cal_{th} = 4.184$ J.
[c] In two cases [83,87] where the results were very precise, the values of $\Delta_c H^\circ_w$ were adjusted from the temperature at which the combustion took place to $T = 298.15$ K. This adjustment required a value of $\Delta_c C^\circ_{p,w}$ for reaction (9). This value was calculated by using the standard molar heat capacities tabulated by Wagman *et al.* [110] for O_2(g), CO_2(g), and H_2O(l). Thus, for cellulose I having $w_{H_2O} = 0$ and *CI* = 0.76, $C^\circ_{p,w} = 1.23\ J \cdot K^{-1} \cdot g^{-1}$ [92] and $\Delta_c C^\circ_{p,w} = 1.38\ J \cdot K^{-1} \cdot g^{-1}$.
[d] Binder [80] reports $\Delta_c H^\circ_w = 4189\ cal \cdot g^{-1}$. Few details are given. This is an approximate value.
[e] Karrer and Fioroni [81] report $\Delta_c H^\circ_w = 4185\ cal \cdot g^{-1}$. This is an approximate value.
[f] Heisenberg's [82] values are approximate.
[g] Jessup and Prosen [83] made a correction for $\Delta_{hyd} H^\circ_w$ for both samples studied. We applied small corrections (see note *c* above) to adjust their measured values from $T = 303.15$ K to $T = 298.15$ K. The ratios of CO_2 formed to CO_2 calculated are 0.99576 and 0.99590 for the two samples studied. The uncertainties given to the values of $\Delta_c H^\circ_w$ in column 5 were calculated from the results given in their [83] table 3.
[h] Nelson [14] used both acid hydrolysis to measure the *CI* values for all of the cellulose samples. These *CI* values are given in the above table. *CI* values were also measured for the two cellulose I samples by using XRD. These values are: *CI* = 80 for the "cotton yarn kiln-dried" sample and *CI* = 70 for the "hydrocellulose prepared" sample. We have rounded Nelson's *CI* values.
[i] Tang and Neill [84] gave few details in their study. This value is approximate.
[j] Susott *et al.* [85]. Susott *et al.* [85] reported $\Delta_c H^\circ_w = -4143\ cal \cdot g^{-1} = -17334\ J \cdot g^{-1}$ on a dry weight basis, *i.e.* $\Delta_c H^\circ_w$ (dry) = $\Delta_c H^\circ_w$ (wet)/$(1 - w_{H_2O})$. The value of $\Delta_c H^\circ_w$ given in column 5 refers to the wet or "as burned" basis.
[k] Murphey and Master [86] gave few details in their study. This value is approximate.
[l] Colbert *et al.* [87] dried the cellulose sample and added a small amount of water prior to combustion. The reason for this, they [87] noted, was that extremely dry cellulose does not produce a complete burn. They [87] made a correction to the measured enthalpy change for water using Rees' data [15]. The combustion produced a negligible amount of ash. The mass fraction purity by CO_2 analysis was 0.9981 ± 0.0010. Colbert *et al.* [87] report $\Delta_c U^\circ_w = -(17340.76 \pm 10.64)\ J \cdot g^{-1}$ at $T = 301.15$ K. We apply a small correction (see note c above) to adjust their measured value to $T = 298.15$ K.
[m] Ioelovich *et al.* [88] report values of $\Delta_c H^\circ_w$ in $kJ \cdot mol^{-1}$. These values were converted to a standard massic basis by using a relative molecular mass $M_r = 162.141$.
[n] Chen and Frendi [89] gave few details in their study. This value is approximate.
[o] Milosavljevic *et al.* [90] gave few details in their study. This value is approximate.
[p] Ur'yash *et al.* [91]. The *CI* value for the sample of microcrystalline cellulose was estimated based on comparisons with their [91] measured standard massic enthalpies of combustion having known *CI* values. They [91] also stated that they used reformed wood cellulose that was 98% α-cellulose. However, the fact that the cellulose was from wood implies that the sample was cellulose Iβ.
[q] Blokhin *et al.* [92] report the mass fraction impurities of ash and sulfur in their samples. The values of $\Delta_c H^\circ_w$ given here refer to the ash free samples.

TABLE 20
Summary of results from the literature for standard massic enthalpies of combustion $\Delta_c H^{\circ *}_w$ at $T = 298.15$ K, $p^\circ = 0.1$ MPa, and $w_{H_2O} = 0$ for cellulose(am), cellulose I(cr), cellulose II(cr), and cellulose III(cr). The basis for these values is given in section 3.10.3. The uncertainties are either those reported by the authors or calculated from their results, in which case the uncertainties are based on two estimated standard deviations of the mean.

Reference	Cellulose(am) $\Delta_c H^{\circ *}_w/(J \cdot g^{-1})$	Cellulose I(cr) $\Delta_c H^{\circ *}_w/(J \cdot g^{-1})$	Cellulose II(cr) $\Delta_c H^{\circ *}_w/(J \cdot g^{-1})$	Cellulose III(cr) $\Delta_c H^{\circ *}_w/(J \cdot g^{-1})$
Jessup and Prosen [83]		−(17421 ± 38)		
Nelson [14]		−(17414 ± 7)	−(17354 ± 11)	−(17359 ± 18)
Colbert *et al.* [87]		−(17317 ± 11)		
Ioelovich *et al.* [88]	−(17561 ± 8)	−(17337 ± 7)	−(17337 ± 12)	
Ur'yash *et al.* [91]	−(17548 ± 27)	−(17458 ± 20)		
Blokhin *et al.* [92]	−(16980 ± 50)	−(17165 ± 50)		
This study	−(17382 ± 20)	−(17344 ± 41)	−(17217 ± 85)	−(17390 ± 57)

3.12. Thermodynamic property values for the conversion of the cellulose allomorphs to α-D-glucose(cr)

Considering the practical importance of converting cellulose to glucose, it is of interest to calculate the thermodynamic properties for the conversion reaction

$$(C_6H_{10}O_5)_u\cdot(H_2O)_1\cdot(H_2O)_v(s) + (u - v - 1)H_2O(l) = uC_6H_{12}O_6(cr). \quad (80)$$

Here, $(C_6H_{10}O_5)_u\cdot(H_2O)_1\cdot(H_2O)_v(s)$ represents either cellulose(am), cellulose I(cr), cellulose II(cr), or cellulose III(cr), and $C_6H_{12}O_6(cr)$ is α-D-glucose(cr).The standard formation properties for the cellulose allomorphs were calculated above and are given in table 24.From the literature we have the following property values for α-D-glucose(cr):$\Delta_f H^\circ_m = -(1273.04 \pm 0.87)\ kJ{\cdot}mol^{-1}$ [108], $S^\circ_w = (209.2 \pm 0.4)\ J{\cdot}K^{-1}\ mol^{-1}$ [109], and $C^\circ_{p,m} = (219.2 \pm 0.4)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ [109].Using these property values and the standard molar entropies of C(cr), $H_2(g)$, and $O_2(g)$ [105], we calculate $\Delta_f G^\circ_m = -(907.87 \pm 0.88)\ kJ{\cdot}mol^{-1}$ for α-D-glucose(cr).The only additional auxiliary data required to calculate the thermodynamic properties for the conversion reactions (80), and not given above, are:$C^\circ_{p,w}\{H_2O(l)\} = 75.291\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ [110], $S^\circ_m\{H_2O(l)\} = (69.95 \pm 0.03)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ [105], and $\Delta_f G^\circ_m\{H_2O(l)\} = -(237.140 \pm 0.041)\ kJ{\cdot}mol^{-1}$ [105]. The calculations of the reaction quantities are, as was done for the standard formation properties, most conveniently carried out on a molar basis. Here, we again use an assumed value of *u*, *i.e.*, $u = 300$, to calculate M_r which is then used to multiply the standard massic formation properties given in table 24 to give the desired standard molar formation properties for the cellulose allomorphs. Then, with a knowledge of the state of hydration, *i.e.*the value of v (see section 3.11), one calculates the reaction quantities on a molar basis.These molar values are then easily converted to a massic basis (division of the molar quantity by M_r) and a monomer unit basis (division of the molar quantity by u).We note that the calculated property values given in table 25 do not depend on the value of u. *It is important to note the following items.* If our assumption regarding the equality of S°_w to $\Delta^T_0 S^\circ_w$ is in error, the true values of $\Delta_r S^\circ_w$ and $\Delta_r S^\circ_u$ will be less than (more negative) than the values given in table 24. Also, the true values of $\Delta_r G^\circ_w$ and $\Delta_r G^\circ_u$ will be greater than (more positive) than the tabulated values. The property values given in tables 24 and 25 pertain to $w_{H_2O} = 0$ and$w_{H_2O} = 0.073$.

For comparison with the above property values for reaction (80), we consider the reaction

$$\text{cellobiose(cr)} + H_2O(l) = 2\ \text{α-D-glucose(cr)}, \quad (81)$$

which, in fact, is reaction (80) for $u = 2$ and $v = 0$. By using the standard formation properties for cellobiose(cr) given by Tewari *et al.* [111] we calculate $\Delta_r H^\circ_m = -17.2\ kJ{\cdot}mol^{-1}$, $\Delta_r G^\circ_m = -0.1\ kJ{\cdot}mol^{-1}$, and $\Delta_r S^\circ_m = -57.4\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ for reaction (81) at $T = 298.15$ K. As a comparison, the reaction of cellobiose(aq) to α-D-glucose(aq) is

$$\text{cellobiose(aq)} + H_2O(l) = 2\ \text{α-D-glucose(aq)} \quad (82)$$

for which the standard reaction quantities are $\Delta_r H^\circ_m = -2.4\ kJ{\cdot}mol^{-1}$, $\Delta_r G^\circ_m = -16.1\ kJ{\cdot}mol^{-1}$, and $\Delta_r S^\circ_m = 46.0\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ at $T = 298.15$ K [111]. It is seen that reaction (82) is driven largely by a positive value of $\Delta_r S^\circ_m$. Also, there is very good evidence [54,111] that the values of $\Delta_r H^\circ_m$, $\Delta_r G^\circ_m$, and $\Delta_r S^\circ_m$ for reaction (82) will also hold for the similar hydrolysis reactions of larger cello-oligomers, *e.g.*

$$\text{cellotriose(aq)} + H_2O(l) = \text{cellobiose(aq)} + \text{α-D-glucose(aq)}, \quad (83)$$

$$\text{cellotetraose(aq)} + H_2O(l) = \text{cellotriose(aq)} + \text{α-D-glucose(aq)}, \quad (84)$$

$$\text{cellopentaose(aq)} + H_2O(l) = \text{cellotetraose(aq)} + \text{α-D-glucose(aq)}, \text{etc.} \quad (85)$$

On a massic basis, the property values for reaction (81) are $\Delta_r H^\circ_w = -50.3\ J{\cdot}g^{-1}$, $\Delta_r G^\circ_w = -0.3\ J{\cdot}g^{-1}$, and $\Delta_r S^\circ_w = -0.13\ J{\cdot}K^{-1}{\cdot}g^{-1}$. These values can be compared with the values for anhydrous cellulose(am) given in table 25.Note that the value $\Delta_r H^\circ_w = -50.3\ J{\cdot}g^{-1}$ for reaction (81) is less exothermic than the value $\Delta_r H^\circ_w = -101\ J{\cdot}g^{-1}$ for cellulose(am), but more exothermic than the values of $\Delta_r H^\circ_w$ for the other cellulose allomorphs (see table 25).Indeed, all of the values of $\Delta_r H^\circ_w$ are endothermic for all of the cellulose allomorphs with the exception of cellulose(am).This is consistent with the view that the hydrogen bonding along with the hydrophobic and other interactions have been destroyed by ball-milling during the preparation of cellulose(am) and that there is additional bonded and non-bonded interactions in the other cellulose allomorphs.Of particular interest is the fact that the conversion reactions for the cellulose allomorphs, with the exception of anhydrous cellulose(am), all have positive values of $\Delta_r G^\circ_w$ and thus are thermodynamically not favored.This conclusion is not invalidated by our assumption regarding the equality of S°_w to$\Delta^T_0 S^\circ_w$.

In terms of "energy cost", cellulose(am) is the least expensive and the cellulose (I, II, and III) crystalline allomorphs are the most expensive to convert to α-D-glucose(cr). This conclusion is valid for cellulose allomorphs having mass fractions of water less than or equal to $w_{H_2O} = 0.073$. However, the enzyme-catalyzed conversions of the allomorphs to shorter chains and to α-D-glucose occur after an allomorph has essentially been fully wetted, in which case the allomorph is best described either as (cr, wet) or (am, wet). Unfortunately, we do not have values of the massic Gibbs free energies of hydration $\Delta_{hyd} G^{\circ *}_w$ which are needed to adjust the standard massic Gibbs free energies of formation $\Delta_f G^\circ_w$ given in table 24 to the (cr, wet) or (am, wet) states. Also, when these allomorphs are wet, an enzyme (*e.g.* a cellulase), which requires an aqueous environment, can proceed to break down the inter-chain linkages and eventually the glycosidic linkages. Indeed, there may be differences in the

TABLE 21
Summary of results from the literature for the standard massic heat capacities $C^{\circ}_{p,w}$, the standard massic entropy differences $\Delta^{T}_{0}S^{\circ}_{w} = \{S^{\circ}_{w}(T) - S^{\circ}_{w}(T=0)\}$, and the standard massic enthalpy differences $\Delta^{T}_{0}H^{\circ}_{w} = \{H^{\circ}_{w}(T) - H^{\circ}_{w}(T=0)\}$ for samples of cellulose at T = 298.15 and p° = 0.1 MPa. The mass fractions of water w_{H_2O} and crystallinity indexes *CI*, if reported, are given in columns 3 and 4, respectively. Where necessary, thermochemical calories were converted to joules by using the relationship 1 cal_{th} = 4.184 J. The uncertainties in the property values from our study are expanded uncertainties at approximately 95% confidence limits.

Reference	Sample	w_{H_2O}	*CI*	$C^{\circ}_{p,w}/(J\cdot K^{-1}\cdot g^{-1})$	$\Delta^{T}_{0}S^{\circ}_{w}/(J\cdot K^{-1}\cdot g^{-1})$	$\Delta^{T}_{0}H^{\circ}_{w}/(J\cdot g^{-1})$
Fleury [93][a]	Cellulose I			1.53		
Padoa [94][b]	Cellulose I			1.45		
Shipley *et al.* [95][c]	Cellulose I – purified from absorbent cotton by treatment with sodium hydroxide and acetic acid	0		1.47		
Mikhailov and Fainberg [96][d]	Cellulose I – ramie fiber	0		1.36		
	Cellulose I – high strength chatillion thread	0		1.59		
	Cellulose I – high strength meryl thread	0		1.45		
	Cellulose I – directional hydrated cellulose	0		1.40		
	Cellulose I – cotton thread	0		1.77		
Fainberg and Mikhailov [97][e]	Cellulose I – natural ramie fiber			1.38		
	Cellulose I – super-strong, highly hydrated cellulose fiber from acetyl cellulose			1.23		
	Cellulose I – super-strong, highly hydrated cellulose fiber			1.16		
	Cellulose I – high-strength viscose fibers produced by the cord method			1.26		
	Cellulose I – high-strength viscose fibers produced by the cord method. The method of production of this sample differs from the one above			1.28		
	Cellulose I – unstretched viscose fiber produced by the cord method			1.26		
McMillin [98][f]	Cellulose I	0		1.17		
Kozlov *et al.* [13][g]	Cellulose I					
Kozlov *et al.* [99][h]	Cellulose I from cotton (domestic source) – solvent dried	0	72	1.67	1.337	226.4
	Cellulose I from cotton (domestic source) – oven dried at 135 °C	0	72	1.53	1.062	196.6
	Cellulose I from cotton (foreign source) – solvent dried	0	80	1.20	1.070	176.2
	Cellulose I from cotton (foreign source) – oven dried at 135 °C		80	1.25	0.961	163.5
Karachevtsev and Kozlov [100][i]	Cellulose I					
Kaimins [101][j]	Amorphous cellulose prepared from sulfate pulp by grinding					
Hatakema *et al.* [102][k]	Amorphous cellulose	0	0	0.995		
	Cellulose I from wood	0	38	1.102		
	Cellulose I from jute	0	46	1.098		
	Cellulose I from American cotton	0	52	1.097		
Mochalov *et al.* [104][l]	Amorphous cellulose prepared from wood by an 8 h ball milling of the sample having *CI* = 0.65	0	0	1.255	1.178	183.7
	Cellulose I was prepared by a 3 h ball milling of the sample having *CI* = 0.65	0	40	1.231	1.161	181.0
	Cellulose I from wood	0	65	1.217	1.144	178.8
Ur'yash *et al.* [91][m]	Cellulose I – microcrystalline cellulose from cotton	0	≈86	1.230	1.12	179.8
Blokhin *et al.* [92][n]	Cellulose I – "Ankir" cotton microcrystalline cellulose	0	90	1.201	1.117	178.2
	Cellulose I – wood sulfite cellulose from the Koryazhama Branch of the Ilim Group	0	80	1.218	1.125	179.5
	Cellulose I – straw cellulose obtained by nitric acid delignification of rape straw stems	0	74	1.232	1.130	180.9
	Cellulose I – wood amorphous cellulose prepared by regeneration of cellulose from {nitrogen (IV) oxide + ethyl acetate solution}	0	0	1.266	1.148	184.4
This study	Cellulose(am)	0.073	0	1.398 ± 0.017	1.243 ± 0.019	201.7 ± 2.8
	Cellulose Iβ(cr)	0.073	100	1.337 ± 0.063	1.216 ± 0.063	195.1 ± 9.7
	Cellulose II(cr)	0.073	100	1.255 ± 0.087	1.102 ± 0.091	179.0 ± 14
	Cellulose III(cr)	0.073	100	1.232 ± 0.10	1.083 ± 0.11	175.2 ± 16

[a] Few details are given in this early study by Fleury [93].
[b] Few details are given in this early study by Padoa [94].
[c] Shipley *et al.* [95] used an adiabatic calorimeter for their measurements and tabulate values of $C^{\circ}_{p,w}$ at T = (213.15, 233.15, 253.15, 273.15, and 293.15) K. The value given in column 5 was extrapolated from these values.
[d] Mikhailov and Fainberg [96] did not report the temperature at which they measured $C^{\circ}_{p,w}$. We assume that T = 298.15 K.
[e] Fainberg and Mikhailov [97] measured heat capacities from T = (333 to 473) K. The values of $C^{\circ}_{p,w}$ given in column 5 were extrapolated to T = 298.15 K by using the functions given by Fainberg and Mikhailov [97] (see their table 2).
[f] McMillin [98] measured values of $C^{\circ}_{p,w}$ at T = (333, 373, and 413) K using a DSC. The value of $C^{\circ}_{p,w}$ given in column 5 is extrapolated from these values and pertains to T = 298.15 K.
[g] Kozlov *et al.* [13] used samples of cellulose I that were dried at (80, 110, and 150) °C for six hours. Standard massic heat capacities of these samples were measured in an adiabatic calorimeter from T = (80 to 320) K. The results are presented only in graphical form. Very substantial differences in property values are seen in the $C^{\circ}_{p,w}$ values with the three samples dried at different temperatures.
[h] Kozlov *et al.* [99] measured values of $C^{\circ}_{p,w}$ from T = (80 to 300) K for four samples of cellulose I from cotton. The samples were either solvent (methanol, ether, and hexane) dried or oven dried at 135 °C. *CI* values were determined by using XRD. The values of $C^{\circ}_{p,w}$ given in column 5 were obtained by interpolation from the tabulated $C^{\circ}_{p,w}$ values. The values of $\Delta^{T}_{0}S^{\circ}_{w}$ and $\Delta^{T}_{0}H^{\circ}_{w}$ were calculated from the values tabulated by Kozlov *et al.* [99] by using a Hermite polynomial fit to the $C^{\circ}_{p,w}$ values and an empirical extrapolation to T = 0 followed by the necessary integrations.
[i] Karachevtsev and Kozlov [100] measured the heat capacities of 13 cellulose samples that were dried at various temperatures. Water was removed by placing samples under high vacuum for 30 to 40 h until there was no flow in the system. They [100] used an adiabatic calorimeter to measure heat capacities from T = (80 to 300) K on these 13 samples. They [100] give values of $C^{\circ}_{p,m}$ only in graphical form. However, they [100] reported values of $\Delta^{T}_{0}S^{\circ}_{w}$. Considerable differences were found in the values of $C^{\circ}_{p,w}$ and $\Delta^{T}_{0}S^{\circ}_{w}$ for samples that had been oven dried at various temperatures even though their XRD patterns were the same. Indeed, the values of $\Delta^{T}_{0}S^{\circ}_{w}$ (T = 300 K) varied from (0.68 to

1.44) $J \cdot K^{-1} \cdot g^{-1}$. Here, we used a molar mass of 162.141 $g \cdot mol^{-1}$ to calculate values of $\Delta_0^T S_w^\circ$. In view of the large scatter in their [100] results, no values of $C_{p,w}^\circ$ and $\Delta_0^T S_w^\circ$ are given in this table.

[j] Kaimins [101] measured heat capacities from $T = (160$ K to 350) K. The results are given only in graphical form.

[k] Hatakema *et al.* [102] measured values of $C_{p,w}^\circ$ from $T = (350$ to 435) K with a DSC. The *CI* values were obtained by using XRD. The values of $C_{p,w}^\circ$ given in column 5 were obtained by extrapolation to $T = 298.15$ K and the use of the coefficients given in their [102] table 1. Extrapolation of the $C_{p,w}^\circ$ values having the highest *CI* values to *CI* = 100, gives $C_{p,w}^{\circ *} = 1.079\ J \cdot K^{-1} \cdot g^{-1}$ for cellulose I(cr) with *CI* = 100. The same results were published in a conference proceedings [103].

[l] Mochalov *et al.* [104] measured values of $C_{p,w}^\circ$ from $T = (80$ to 400) K by using an adiabatic calorimeter. Samples were vacuum dried at $T = 370$ K. *CI* values were determined by using XRD. They [104] tabulated property values ($C_{p,w}^\circ$, $\Delta_0^T H^\circ$, and $\Delta_0^T S^\circ$) from 10 K to 400 K. The property values given in this table were obtained by interpolation of the values reported by Mochalov *et al.* [104].

[m] Ur'yash *et al.* [91] used an adiabatic calorimeter to measure values of $C_{p,w}^\circ$ from $T = (80.05$ to 329.3) K. The *CI* value for the sample of microcrystalline cellulose was estimated based on comparisons with their measured standard massic enthalpies of combustion having known *CI* values. The values of $C_{p,m}^\circ$ were converted to a standard massic basis by using the relative molecular mass $M_r = 162.14$ used by Ur'yash *et al.* [91]. Integration of their results [91] gives the values of $\Delta_0^T S_w^\circ$ and $\Delta_0^T H_w^\circ$ given in columns 6 and 7, respectively. The values of $\Delta_0^T S_w^\circ$ and $\Delta_0^T H_w^\circ$ were calculated from the values tabulated by Ur'yash *et al.* [91] by using a Hermite polynomial fit to the $C_{p,w}^\circ$ values and an empirical extrapolation to $T = 0$ followed by the necessary integrations.

[n] Blokhin *et al.* [92] used an adiabatic calorimeter to measure values of $C_{p,m}^\circ$ from $T = (5$ to 368) K. They also report the mass fraction impurities of ash and sulfur in their samples. The reported property values ($C_{p,m}^\circ$, $\Delta_0^T H_m^\circ$ and $\Delta_0^T S_w^\circ$ were converted from a molar basis to a standard massic basis by using a relative molecular mass $M_r = 162.141$. Uryash *et al.* [91] also report thermal anomalies ("relaxation transitions") in the range $T = (284$ to 343) K. These anomalies are not seen in our results nor in the results of Blokhin *et al.* [92].

TABLE 22

Summary of results from the literature for the standard massic heat capacities $C_{p,w}^{\circ *}$, the standard massic entropy differences $\Delta_0^T S_w^{\circ *} = \{S_w^\circ(T) - S_w^\circ(T = 0)\}$, the standard massic enthalpy differences $\Delta_0^T H_w^{\circ *} = \{H_w^{\circ *}(T) - H_w^{\circ *}(T = 0)\}$, and the function $\Phi_w^{\circ *} = (\Delta_0^T S_w^{\circ *} - \Delta_0^T H_w^{\circ *}/T)$ for cellulose(am) and for cellulose I(cr) at $T = 298.15$ and $p^\circ = 0.1$ MPa. The results obtained by Hatakema *et al.* [102], Mochalov *et al.* [104], and Blokhin *et al.* (2011) pertain to a mass fraction of water $w_{H_2O} = 0$. The results of this study were obtained at $w_{H_2O} = 0.073$. Equation (77) was used to calculate the values from our study that pertain to $w_{H_2O} = 0$. The uncertainties in the values from our study are expanded uncertainties at approximately 95% confidence limits.

Reference	$C_{p,w}^{\circ *}/(J \cdot K^{-1} \cdot g^{-1})$	$\Delta_0^T S_w^{\circ *}/(J \cdot K^{-1} \cdot g^{-1})$	$\Delta_0^T H_w^{\circ *}/(J \cdot g^{-1})$	$\Phi_w^{\circ *}/(J \cdot K^{-1} \cdot g^{-1})$
		Cellulose(am)		
Hatakema *et al.* [102]	0.995			
Mochalov *et al.* [104]	1.255	1.178	183.7	0.5621
Blokhin *et al.* [92]	1.266	1.148	184.43	0.5294
This study ($w_{H_2O} = 0.073$)	1.398 ± 0.017	1.243 ± 0.019	201.7 ± 2.8	0.5665 ± 0.015
This study ($w_{H_2O} = 0$)	1.332 ± 0.024	1.160 ± 0.028	189.7 ± 4.1	0.5231 ± 0.019
		Cellulose Iβ(cr)		
Hatakema *et al.* [102]	1.079			
Mochalov *et al.* [104]	1.196	1.127	176.3	0.5358
Blokhin *et al.* [92]	1.182	1.108	176.4	
This study ($w_{H_2O} = 0.073$)	1.337 ± 0.063	1.216 ± 0.063	195.1 ± 9.7	0.562 ± 0.043
This study ($w_{H_2O} = 0$)	1.266 ± 0.065	1.130 ± 0.067	182.6 ± 10	0.518 ± 0.044
		Cellulose II(cr)		
This study ($w_{H_2O} = 0.073$)	1.26 ± 0.09	1.10 ± 0.09	179 ± 14	0.509 ± 0.065
This study ($w_{H_2O} = 0$)	1.18 ± 0.09	1.02 ± 0.09	165 ± 14	0.462 ± 0.066
		Cellulose III(cr)		
This study ($w_{H_2O} = 0.073$)	1.23 ± 0.10	1.10 ± 0.09	179 ± 14	0.51 ± 0.07
This study ($w_{H_2O} = 0$)	1.15 ± 0.10	0.99 ± 0.11	161 ± 16	0.44 ± 0.08

rates at which the allomorphs break down. For example, Ciolacu *et al.* [112] demonstrated that cellulose II is more effectively hydrolyzed by several cellulase enzymes than either cellulose I or cellulose III. One must also consider the equilibrium constants or, equivalently the values of $\Delta_r G_w^\circ$, between the polymeric cellulose chains and eventually cellobiose(aq) and α-D-glucose(aq). Indeed, since the final reaction(s) in the conversion of cellulose to α-D-glucose have negative values of $\Delta_r G_m^\circ$ {see the discussion regarding reactions (82)–(85) above} the overall conversion reaction is aided. Additionally, if the α-D-glucose can be removed from the reaction media as it is formed, the entire reaction system will be pulled to the right and to completion by means of Le Chatelier's principle.

We believe that a significant improvement in the accuracy of the thermodynamic properties of the cellulose allomorphs requires the preparation of highly pure samples, *i.e.*, samples that have both high and well-known *CI* values, low amounts of chemical impurities, and a consistent morphology. The availability of high purity samples would also aid in structural investigations of the celluloses as well as other property measurements. Additionally, due to the paucity and age of the data in the literature, there is a need for modern investigations that will lead to accurate values of $\Delta_{hyd} H_w^{\circ *}$ and $\Delta_{hyd} G_w^{\circ *}$ for the pure cellulose allomorphs and to an improved understanding of the nature of water in the celluloses. While values of $\Delta_{hyd} H_w^{\circ *}$ are best done calorimetrically, the determination

TABLE 23

Summary of results from the literature for the changes in the standard massic entropy $\Delta_r S_w^{\circ *}$ and in the standard massic heat capacity $\Delta_r C_{p,w}^\circ$ for the reaction {cellulose(am) = cellulose I(cr)}, reaction (26), at $T = 298.15$ K and $p^\circ = 0.1$ MPa calculated from results in the literature. The results obtained by Hatakema *et al.* [102], Mochalov *et al.* [104], and Blokhin *et al.* [92] pertain to a mass fraction of water $w_{H_2O} = 0$. The results of this study were obtained at $w_{H_2O} = 0.073$. Equation (77) was used to calculate the values from our study that pertains to $w_{H_2O} = 0$. The values of $\Delta_r S_w^{\circ *}$ are based on the assumption that the values of $S_w^{\circ *}$ for cellulose(am) and cellulose I(cr) approach the same value as $T \to 0$. The uncertainties in the values from our study are expanded uncertainties at approximately 95% confidence limits.

Reference	$\Delta_r S_w^{\circ *}/(J \cdot K^{-1} \cdot g^{-1})$	$\Delta_r C_{p,w}^\circ/(J \cdot K^{-1} \cdot g^{-1})$
Hatakema *et al.* [102]		+0.084
Mochalov *et al.* [104]	−0.051	−0.059
Blokhin *et al.* [92]	−0.040	−0.084
This study ($w_{H_2O} = 0.073$)	−(0.027 ± 0.065)	−(0.061 ± 0.065)
This study ($w_{H_2O} = 0$)	−(0.029 ± 0.072)	−(0.066 ± 0.070)

TABLE 24

Standard formation properties of cellulose(am), cellulose I(cr), cellulose II(cr), and cellulose III(cr) at $T = 298.15$ K and $p^\circ = 0.1$ MPa. The quantity $\Delta_f H^\circ_w$ is the standard massic enthalpy of formation, $\Delta_f G^\circ_w$ is the standard massic Gibbs free energy of formation, S°_w is the standard massic entropy, and $C^\circ_{p,w}$ is the standard massic heat capacity. The corresponding quantities for the monomer unit $C_6H_{10}O_5$ are $\Delta_f H^\circ_u$, $\Delta_f G^\circ_u$, S°_u, and $C^\circ_{p,u}$. For cellulose having a mass fraction of water $w_{H_2O} = 0.073$, the relative molecular mass of the monomer unit is $M_r = 174.909$. For anhydrous cellulose, the relative molecular mass of the monomer unit is $M_r = 162.141$.[a,b,c]

Substance	$\Delta_f H^\circ_w/(kJ\cdot g^{-1})$	$\Delta_f G^\circ_w/(kJ\cdot g^{-1})$	$S^\circ_w/(J\cdot K^{-1}\cdot g^{-1})$	$C^\circ_{p,w}/(J\cdot K^{-1}\cdot g^{-1})$	$\Delta_f H^\circ_u/(kJ\cdot mol^{-1})$	$\Delta_f G^\circ_u/(kJ\cdot mol^{-1})$	$S^\circ_u/(J\cdot K^{-1}\cdot mol^{-1})$	$C^\circ_{p,u}/(J\cdot K^{-1}\cdot mol^{-1})$
Cellulose(am)·$w_{H_2O} = 0.073$	−(6.766 ± 0.015)	−(4.808 ± 0.016)	1.243 ± 0.019	1.398 ± 0.017	−(1183.4 ± 2.6)	−(840.9 ± 2.8)	217.4 ± 3.3	244.5 ± 3.0
Cellulose Iβ(cr)·$w_{H_2O} = 0.073$	−(6.849 ± 0.020)	−(4.883 ± 0.028)	1.216 ± 0.063	1.337 ± 0.063	−(1198.0 ± 3.6)	−(854.1 ± 4.8)	212.7 ± 11	233.9 ± 11
Cellulose II(cr)·$w_{H_2O} = 0.073$	−(6.880 ± 0.018)	−(4.882 ± 0.033)	1.110 ± 0.091	1.255 ± 0.087	−(1203.4 ± 3.2)	−(854.0 ± 5.7)	194.1 ± 16	219.5 ± 15
Cellulose III(cr)·$w_{H_2O} = 0.073$	−(6.859 ± 0.023)	−(4.853 ± 0.040)	1.083 ± 0.11	1.232 ± 0.10	−(1199.7 ± 4.0)	−(848.9 ± 7.0)	189.4 ± 19	215.5 ± 17
Cellulose(am)·$w_{H_2O} = 0$	−(5.991 ± 0.021)	−(4.129 ± 0.022)	1.160 ± 0.028	1.332 ± 0.024	−(971.8 ± 3.3)	−(669.7 ± 3.6)	188.1 ± 4.5	216.0 ± 3.9
Cellulose Iβ(cr)·$w_{H_2O} = 0$	−(6.104 ± 0.022)	−(4.233 ± 0.030)	1.130 ± 0.067	1.266 ± 0.065	−(990.1 ± 3.6)	−(686.6 ± 4.8)	183.2 ± 11	205.3 ± 11
Cellulose II(cr)·$w_{H_2O} = 0$	−(6.126 ± 0.021)	−(4.221 ± 0.034)	1.02 ± 0.09	1.18 ± 0.09	−(993.6 ± 3.4)	−(684.7 ± 5.5)	165 ± 15	191 ± 15
Cellulose III(cr)·$w_{H_2O} = 0$	−(6.109 ± 0.025)	−(4.196 ± 0.041)	0.99 ± 0.11	1.15 ± 0.10	−(990.8 ± 4.0)	−(680.5 ± 6.7)	161 ± 18	186 ± 16

[a] The values of S°_w, S°_u, $\Delta_f G^\circ_w$ and $\Delta_f G^\circ_u$ are based on the assumption (see section 3.11) that the measured values of $\Delta^T_0 S^\circ_w$ (see table 16) are equal to S°_w.

[b] Since it is clear that all substances in this table are the pure allomorphs, a "*" is not placed next to the symbol for a thermodynamic property.

[c] The uncertainties given above are expanded uncertainties at approximately 95% confidence limits. They were calculated by using propagation of error together with the uncertainties given previously (see tables 8, 16, 17) and the uncertainties in the property values of C(s), $H_2(g)$, $O_2(g)$, $H_2O(l)$, and $CO_2(g)$ given in the CODATA tables [105]. No component of uncertainty due to the assumption given in footnote "*a*" is included in the uncertainties.

TABLE 25

Standard thermodynamic quantities for the conversion reactions $\{(C_6H_{10}O_5)_u\cdot(H_2O)_1\cdot(H_2O)_v(s) + (u - v - 1)H_2O(l) = u\,C_6H_{12}O_6(cr)\}$ of the cellulose allomorphs to α-D-glucose(cr) at $T = 298.15$ K and $p^\circ = 0.1$ MPa. The quantity $\Delta_r H^\circ_w$ is the standard massic enthalpy change, $\Delta_r G^\circ_w$ is the standard massic Gibbs free energy change, $\Delta_r S^\circ_w$ is the standard massic entropy change, and $\Delta_r C^\circ_{p,w}$ is the standard massic heat capacity change. The corresponding quantities based on the monomer unit $C_6H_{10}O_5$ are $\Delta_r H^\circ_u$, $\Delta_r G^\circ_u$, $\Delta_r S^\circ_u$, and $\Delta_r C^\circ_{p,u}$. For cellulose having a mass fraction of water $w_{H_2O} = 0.073$, the relative molecular mass of the monomer unit is $M_r = 174.909$. For anhydrous cellulose, the relative molecular mass of the monomer unit is $M_r = 162.141$.[a,b,c]

Reacting substance	$\Delta_r H^\circ_w/(J\cdot g^{-1})$	$\Delta_r G^\circ_w/(J\cdot g^{-1})$	$\Delta_r S^\circ_w/(J\cdot K^{-1}\cdot g^{-1})$	$\Delta_r C^\circ_{p,w}/(J\cdot K^{-1}\cdot g^{-1})$	$\Delta_r H^\circ_u/(kJ\cdot mol^{-1})$	$\Delta_r G^\circ_u/(kJ\cdot mol^{-1})$	$\Delta_r S^\circ_u/(J\cdot K^{-1}\cdot mol^{-1})$	$\Delta_r C^\circ_{p,u}/(J\cdot K^{-1}\cdot mol^{-1})$
Cellulose(am)·$w_{H_2O} = 0.073$	−(37 ± 16)	12 ± 17	−(0.163 ± 0.019)	−(0.270 ± 0.017)	−(6.4 ± 2.7)	2.1 ± 2.9	−(28.6 ± 3.3)	−(47.3 ± 3.0)
Cellulose Iβ(cr)·$w_{H_2O} = 0.073$	47 ± 21	88 ± 28	−(0.136 ± 0.063)	−(0.209 ± 0.063)	8.2 ± 3.7	15.3 ± 4.9	−(24 ± 11)	−(37 ± 11)
Cellulose II(cr)·$w_{H_2O} = 0.073$	78 ± 19	87 ± 33	−(0.030 ± 0.091)	−(0.127 ± 0.087)	13.6 ± 3.3	15.2 ± 5.8	−(5 ± 16)	−(22 ± 15)
Cellulose III(cr)·$w_{H_2O} = 0.073$	56 ± 23	57 ± 40	−(0.00 ± 0.11)	−(0.10 ± 0.10)	9.9 ± 4.1	10.0 ± 7.0	−(0.6 ± 19)	−(18 ± 17)
Cellulose(am)·$w_{H_2O} = 0$	−(101 ± 21)	−(11 ± 23)	−(0.300 ± 0.028)	−(0.443 ± 0.024)	−(16.4 ± 3.4)	−(1.8 ± 3.7)	−(48.7 ± 4.6)	−(71.9 ± 3.9)
Cellulose Iβ(cr)·$w_{H_2O} = 0$	12 ± 23	93 ± 30	−(0.270 ± 0.067)	−(0.377 ± 0.065)	2.0 ± 3.7	15.0 ± 4.9	−(44 ± 11)	−(61 ± 11)
Cellulose II(cr)·$w_{H_2O} = 0$	33 ± 22	81 ± 35	−(0.160 ± 0.090)	−(0.291 ± 0.090)	5.4 ± 3.5	13.2 ± 5.6	−(26 ± 15)	−(47 ± 15)
Cellulose III(cr)·$w_{H_2O} = 0$	16 ± 25	55 ± 41	−(0.13 ± 0.11)	−(0.26 ± 0.10)	2.7 ± 4.1	9.0 ± 6.7	−(21 ± 18)	−(42 ± 16)

[a] The values of ΔS°_w, ΔS°_u, $\Delta_f G^\circ_w$, and $\Delta_f G^\circ_u$ are based on the assumption (see section 3.11) that the measured values of $\Delta^T_0 S^\circ_w$ (see table 16) are equal to S°_w.

[b] Since it is clear that all substances in this table are the pure allomorphs, a "*" is not placed next to the symbol for a thermodynamic property.

[c] The uncertainties given above are expanded uncertainties at approximately 95% confidence limits. They were calculated by using propagation of error together with the uncertainties given in table 24 and the uncertainties in the property values of $H_2O(l)$ and α-D-glucose(cr) (see section 3.12). No component of uncertainty due to the assumption given in footnote "*a*" is included in the uncertainties.

of values of $\Delta_{hyd}G^{\circ *}_{w}$ require careful vapor pressure measurements together with accurate measurements of the mass fraction of water in the celluloses.

4. Glossary and conventions

Symbol	Name (SI unit)
(am)	denotes an amorphous substance
$A_0, \ldots, A_5$	parameters used to fit heat capacities ($J{\cdot}K^{-1}{\cdot}g^{-1}$, $\ldots, J \cdot K^{-6}{\cdot}g^{-1}$)
A_r	relative atomic mass (1)
B_3, B_5, B_{gap}	parameters used to fit heat capacities ($J{\cdot}K^{-4}{\cdot}g^{-1}$, $J{\cdot}K^{-6}{\cdot}g^{-1}$, $J{\cdot}K^{-5/2}{\cdot}g^{-1}$)
C_p	heat capacity at constant pressure ($J{\cdot}K^{-1}$)
c	concentration ($mol{\cdot}dm^{-3}$)
(cad)	denotes a cadoxen solution
cell	denotes cellulose
CI	crystallinity index (1)
(cr)	denotes a crystalline substance
DP_w	weight average degree of polymerization (1)
ε_f	energy equivalent ($J{\cdot}K^{-1}$)
G	Gibbs free energy ($J{\cdot}mol^{-1}$)
(g)	denotes a gaseous substance
H	enthalpy (J)
(l)	denotes a liquid substance
m	mass (kg)
M_r	relative molecular mass (molar mass) (1)
M_w	weight average molar mass ($kg{\cdot}mol^{-1}$)
N	number of entities (1)
p	pressure (Pa)
R	gas constant ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)
(s)	denotes a solid substance
S	entropy ($J{\cdot}K^{-1}$)
t	Celsius temperature (°C)
T	thermodynamic temperature (K)
u	average number of $C_6H_{10}O_5$ units in a cellulose sample (1)
$u(x)$	standard uncertainty of a quantity x
$u_r(x)$	relative standard uncertainty of a quantity x, $u_r(x) = u(x)/\lvert x \rvert$
U	internal energy (J)
$U(x)$	expanded uncertainty in a quantity x
v	average number of waters of hydration in a cellulose sample (1)
w	mass fraction (1)
wet	denotes a completely hydrated sample
$\alpha_1, \alpha_2, \alpha_3$	ratio of relative molecular masses (1)
β_1, β_2	ratio of a relative molecular mass to a relative atomic mass (1)
γ	mass concentration ($g{\cdot}dm^{-3}$)
γ	parameter used to fit heat capacities ($J{\cdot}K^{-2}{\cdot}g^{-1}$)
δ	parameter used to fit heat capacities (K)
Δ	denotes a change
η	empirical constant {see equation (24)} $\{J{\cdot}(g\ dry\ material)^{-1}\}$
Φ	$\Phi = \Delta_0^T S - \Delta_0^T H/T$ ($J{\cdot}K^{-1}{\cdot}g^{-1}$)

Subscripts

c	denotes a combustion reaction
cell	denotes cellulose
corr	denotes a corrected value
cr	denotes a crystalline form
D	denotes a Debye heat capacity
E	denotes an Einstein heat capacity
f	denotes a formation reaction
hyd	denotes hydration {see equation (5)}
H_2O	denotes water
int	denotes intrinsic {see equation (4)}
m	denotes a molar quantity
r	denotes a reaction
ref	denotes a reference value
sol	denotes a solution reaction
u	denotes a property value based on a monomer
w	denotes a standard massic quantity

Superscripts

°	denotes a standard quantity
*	denotes a pure substance or a reaction involving pure substances

Conventions

The cellulose I, II, and III samples used in this study and in the literature are mixtures of their respective forms with cellulose(am) and are designated as solids, *i.e.* by using an "(s)". Pure (*i.e.*, $CI = 100$) cellulose I, II, and III are denoted, respectively, as cellulose I(cr), cellulose II(cr), and cellulose III(cr). Pure amorphous cellulose is denoted as cellulose(am). Samples that contain water are denoted by the addition of "w_{H_2O}", *e.g.*, cellulose(am)·w_{H_2O}. While a given cellulose I sample, as an example, could be designated precisely as {cellulose I(cr) + cellulose(am)}, the more compact notation "cellulose I sample" will be used. Clearly, the mass fractions of the two components in a given sample should be specified if known. A superscript "*" is used to denote that a quantity pertains to a pure allomorph ($CI = 100$) or a reaction involving pure allomorphs and not a mixture of allomorphs. However, if it is clear that one is dealing with a pure allomorph, a "*" is not placed next to the symbol for a thermodynamic property. The standard state of a solid (or liquid) is the solid (or liquid) at the pressure $p^{\circ} = 0.1$ MPa. Its activity is set to be unity.

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