Heat Capacity and Thermodynamic Functions of nano-TiO₂ Anatase in Relation to bulk-TiO₂ Anatase

Jacob M. Schliesser, Stacey J. Smith, Guangshi Li, Liping Li, Trent F. Walker,
Thomas Perry, Juliana Boerio-Goates, and Brian F. Woodfield*

*Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602,
U.S.A.*

*Corresponding author. Tel.: +1 801 422 2093; fax: +1 801 422 0153.

E-mail address: Brian_Woodfield@byu.edu (B. F. Woodfield)

Abstract

Several conflicting reports have suggested that heat capacities and the thermodynamic properties of materials change as their particle size decreases into the nanoscale. To further investigate this, we have measured the constant pressure heat capacities of three 7 nm TiO₂ anatase samples containing varying amounts of surface-adsorbed water using a combination of adiabatic and semi-adiabatic calorimetric methods. These samples have a high degree of chemical, phase, and size purity determined by rigorous characterization. Molar heat capacities were measured from (0.5 to 320) K, and data were fit to a sum of theoretical functions in the low temperature ($T < 15$ K) range, orthogonal polynomials in the mid temperature range ($10 > T > 75$ K), and a combination of Debye and Einstein functions in the high temperature range ($T > 35$ K). These fits were used to generate $C_{p,m}^{\circ}$, $\Delta_0^T S_m^{\circ}$, $\Delta_0^T H_m^{\circ}$, and ϕ_m° values at smoothed temperatures between (0.5 and 300) K for all hydrated samples. Standard molar entropies at $T = 298.15$ K were calculated to be 73.868, 66.072, and 63.845 J·K⁻¹·mol⁻¹ all with a standard uncertainty of $0.002 \cdot \Delta_0^T S_m^{\circ}$ for samples TiO₂·0.677H₂O, TiO₂·0.532H₂O, and TiO₂·0.379H₂O, respectively. These and other thermodynamic values were then corrected for water content to yield bare nano-TiO₂ thermodynamic properties at $T = 298.15$ K, and we show that the resultant thermodynamic properties of anhydrous TiO₂ anatase nanoparticles equal those of bulk TiO₂ anatase within experimental uncertainty. Thus we show quantitatively that the difference in thermodynamic properties between bulk and nano-TiO₂ must be attributed to surface adsorbed water.

KEYWORDS: Titania, Heat Capacity, Thermodynamic properties, Nanoparticle

1. Introduction

Anatase TiO_2 nanoparticles find use in many technological areas from catalysts and catalyst supports, to solar cells, and even as household products [1-5]. TiO_2 occurs naturally in three phases: anatase, rutile, and brookite [6-12]. Rutile is considered to be stable with respect to anatase both at high temperature and pressure [13-18]; however, a strong dependence on phase stability with respect to particle size has been reported showing that anatase and brookite become more stable than rutile at particle sizes below about 15 nm [16, 19-23]. This crossover in phase stability has led many to assume that the energetics of nanoparticles differ from those of bulk materials.

Several arguments have been made suggesting that nanoparticles have substantially different thermodynamic properties from their bulk counterparts because the ratio of surface to bulk atoms is much larger in nanoparticles [24, 25], whereas other investigations suggest the thermodynamic properties do not differ between bulk and nanophase [26, 27]. Due to the large surface area inherent in nanoparticles, free energy contributions from the surface must be higher than contributions from the bulk. Several studies have shown that surface energies are generally higher than those of the bulk, but this could be attributed to adsorbates, which can greatly affect the surface energetics and therefore phase stability [22, 28-32].

Water is the most common adsorbate on nanoparticles, and we have previously shown that nanocrystalline TiO_2 has a similar heat capacity to that of bulk TiO_2 after accounting for the heat capacity of the adsorbed water [26]. The energetics of the water compensate for the surface energetics of the nanoparticle by inheriting a heat capacity much different from that of hexagonal ice or liquid water.

Heat capacity is a useful tool for understanding the bulk properties of a material. It provides information on all the energetic states available to a material, being a sum of lattice vibrations, electronic states, and magnetic properties [24]. Each of these contributing properties can be modeled with a mathematical function of physical significance, and by fitting the heat capacity data to a series of such functions, one can determine the underlying physical properties of the material that give rise to the fit. The measured heat capacity and the functions that represent it can then be used to generate third-law entropies and relative free energies, which are related to phase stability [33].

While several papers have been published previously providing important insight into the fundamental properties of several hydrated nanophase TiO_2 samples [26, 34, 35], the heat capacity data and thermodynamic functions of these samples have yet to be published, and all comparisons between bulk and nano TiO_2 anatase were only done graphically and not quantitatively. We present heat capacity data measured for these well-characterized TiO_2 anatase samples of varying water contents, account for water in the thermodynamic properties with physically meaningful models, and show quantitatively that the thermodynamic properties of nanophase TiO_2 anatase are equal to those of bulk TiO_2 anatase within experimental uncertainty. This investigation provides further support that surface-bound water plays a necessary role in phase stabilization of nanomaterials.

2. Experimental

2.1 Sample preparation and Characterization

Anatase nanoparticles were prepared using a modified sol-gel method with TiCl_4 (99.0% pure, Alfa Aesar) and ethanol (>97% Aldrich Co.) as the starting materials, the details of which can be found elsewhere [36, 37]. The product was separated into three batches. Each batch was

dehydrated in air at 100 °C for 2, 4, or 6 hrs resulting in three samples of different hydration. Water contents for each batch were measured by thermo gravimetric analysis (TGA) on a Netzsch TG/DTA under flowing Ar at 10 °C per min. The three samples of differing water content are designated herein as AI, AII, and AIII with stoichiometries of $\text{TiO}_2 \cdot 0.677\text{H}_2\text{O}$, $\text{TiO}_2 \cdot 0.532\text{H}_2\text{O}$, and $\text{TiO}_2 \cdot 0.379\text{H}_2\text{O}$, respectively. After drying, samples were stored in a glovebox under argon atmosphere to prevent readsorption of water from the air.

Particle composition and purity were analyzed using a Perkin-Elmer inductively coupled plasma optical emission spectrometer (ICP-OES) Optima 4300 DV. Besides water, C and Cl were the only contaminants detectable by ICP-OES with concentrations of 0.04 wt% and 840 ppm, respectively. Phase purity of the product was measured with powder X-ray diffraction (XRD) at room temperature on a Scintag diffractometer with a copper source at a scanning rate of 0.5 °/min and a power of 12 kW (see Figure 1). Average grain sizes were calculated from the most intense diffraction peak (101) using the Scherrer formula [36-38]. From line-broadening calculations, particle sizes were determined to be 7 nm with an estimated standard uncertainty of 2 nm. Particles were found to be phase pure to better than ± 0.05 mol%.

The XRD results were complemented by a study of the morphology and particle size using transmission electron microscopy (TEM) on a JEOL JEM 2000-FX under an acceleration voltage of 200 keV (see Figure 2). Chemical composition was examined with a scanning electron microscope (Phillips) equipped with an EDX analyzer. The TEM micrograph shows that the anatase particles formed as spheres with 7 nm diameters. This gives a rough surface area of $217 \text{ m}^2 \cdot \text{g}^{-1}$ which agrees relatively well with the BET measurements that gave a surface area of $250 \text{ m}^2 \cdot \text{g}^{-1}$ for all particles. This confirms the morphology of the particles, and shows that particle structure remains unchanged throughout the characterization measurements. Also, TGA and

XRD measurements were made on each sample before and after loading into the calorimeter vessel to ensure water content and particle size remained unchanged. Sample properties are given in Table 1.

2.2 Calorimetric Measurements

Constant pressure heat capacities were measured with two techniques. In the range of (15 to 320) K, measurements were made on an adiabatic calorimeter, the details of which have been published elsewhere [39, 40]. The calorimeter was gold plated with a volume of 10.5 cm³. Each of the three samples was pressed into pellets and loaded into the calorimeter under argon atmosphere. After loading, the argon was evacuated and displaced with helium to improve thermal conductivity, and the vessel was sealed using a gold gasket.

Measurements in the range of (0.5 to 40) K were taken using a semi-adiabatic calorimeter, a detailed description of which has been published previously [41]. The fine powders were put into separate cups of copper foil (99.999% Alfa Aesar) and pressed into pellets under argon atmosphere. A small amount of Apiezon-N grease was used to thermally attach each copper-covered pellet directly to the sample platform.

Resulting heat capacity data were obtained from experimental measurements by subtracting the contributions of the various components of the calorimeter and pellet. For the adiabatic calorimeter, contributions from the empty calorimeter, gold, grease, and helium were subtracted. For the semi-adiabatic calorimeter, contributions from the empty calorimeter, grease and copper foil were subtracted (experiment details can be found in Table 2).

Data taken with the semi-adiabatic pulse calorimeter have a standard uncertainty of $0.0025 \cdot C_{p,m}$ below about 15 K; however, the error increases to about $0.005 \cdot C_{p,m}$ in the region of (15 to 30) K and becomes even worse above that due to radiation heat loss [41]. The adiabatic

calorimeter produces data with standard uncertainties of $0.02 \cdot C_{p,m}$ below 13.8 K, $0.01 \cdot C_{p,m}$ between (13.8 and 25) K, $0.004 \cdot C_{p,m}$ from (25 to 40) K, $0.002 \cdot C_{p,m}$ between (40 and 60) K, and $0.0005 \cdot C_{p,m}$ from (60 to 400) K. The thermodynamic properties derived from these measurements have estimated standard uncertainties of about $0.002 \cdot X$ where X represents the thermodynamic property.

3. Results

Molar heat capacity measurements for the three nanocrystalline anatase samples AI, AII, and AIII are given separately in Tables 3, 4, and 5. The data is a combination of the adiabatic and semi-adiabatic techniques and can be seen graphically in Figure 3 where the inset shows the same data below $T = 15$ K. From the graph, one can see how the heat capacity increases as water content increases. It can also be seen that below about $T = 3$ K there is a slight anomaly in the heat capacity data, which is a Schottky anomaly whose origin is likely caused by tunneling between hydroxyls shared between neighboring Ti atoms on the curved surface of the nanoparticle [42].

4. Discussion

4.1 Nature of Fitting Equations

The total heat capacity is a measure of all the energetic states of a material. Modeling the heat capacity data with theoretical functions provides a means with which to extract valuable information about the magnetic, electronic, and vibrational properties of a sample. Because of the changing nature of each contribution, the heat capacity data is broken up into smaller temperature ranges which are then fit with theoretical functions.

In the low temperature regime ($T < 15$ K), lattice vibrations are modeled by a function containing odd powers in temperature [43]

$$C_{Lat} = \sum_{n=3,5,7,\dots} B_n T^n \quad (1)$$

A linear dependence on T (denoted as γT) is traditionally associated with electronic contributions to the heat capacity, but for insulating materials this linear dependence appears to arise from oxygen vacancies and defects [24, 44]. Magnetic contributions can take on various forms depending on the nature of the magnetism [24, 45-47], and for a system of interacting energy levels, a Schottky anomaly can occur seen by an anomaly in the heat capacity as in Figure 1. A simple two-level system has the form [24]:

$$C_{Sch} = R \left(\frac{\theta}{T} \right)^2 \frac{g_0}{g_1} \frac{e^{\theta/T}}{(1 + \frac{g_0}{g_1} e^{\theta/T})^2} \quad (2)$$

where R is the gas constant, θ is the energy separation of the two interacting energy levels in degK, and g_0 and g_1 are the degeneracies for the ground and first excited states, respectively. Figure 4 shows the heat capacity data for all anatase samples below $T = 8$ K where the inset shows the contribution to the heat capacity from the Schottky effect. The interpretation and significance of the Schottky anomaly have been published elsewhere [42]. The low T region of the heat capacity was fit with lattice, electronic and Schottky terms, and these fitting coefficients, the ranges of validity, and the %RMS for all samples are given in Table 6 (the degeneracy terms in the Schottky anomalies, g_i , are set to unity for all fits).

Data from 10 – 75 K were fit to a polynomial function to provide sufficient overlap with the low temperature and high temperature fits and to smoothly fit the inflection point around 50 K. Fits were of the form:

$$C_{mid T} = \sum_{n=0,1,2,\dots,6} A_n T^n \quad (3)$$

The high temperature data ($T > 35$ K) were fit to a sum of Debye and Einstein functions that provide information on the lattice specific heat

$$C_{high\ T} = m \cdot D(\Theta_D/T) + n_1 \cdot E(\Theta_{E,1}/T) + n_2 \cdot E(\Theta_{E,2}/T) \quad (4)$$

where $D(\Theta_D / T)$, $E(\Theta_{E,1} / T)$, and $E(\Theta_{E,2} / T)$ are Debye and Einstein functions; m , n_1 , n_2 , Θ_D , $\Theta_{E,1}$, and $\Theta_{E,2}$ are all adjustable parameters; and $(m + n_1 + n_2)$ should be approximately equal to the number of atoms in the formula unit. Generally one Debye and one Einstein function are sufficient to fit high temperature data, but for these samples such a fit was only valid above about 100 K. To fit a larger temperature range, an extra Einstein function was needed. The parameters for these mid and high T fits, their regions of validity, and the %RMS are also given in Table 6. A plot of the deviations for each fit from the measured data as a function of temperature is given in Figure 5 showing that the fits are non-systematic and represent the actual data well. Above 15 K the %RMS of the fits is less than 1%, from about (1 to 15) K it is around 5%, and below 1 K it increases to about 20%.

4.2 Thermodynamic Calculations

The standard molar thermodynamic functions $C_{p,m}^\circ$, $\Delta_0^T S_m^\circ$, $\Delta_0^T H_m^\circ$, and ϕ_m° were generated at smoothed temperatures from (0.5 to 300) K from the fits that represent the data. The resultant calculations are given in Tables 7, 8, and 9 for AI, AII, and AIII, respectively. The standard molar entropies of nanophase TiO_2 anatase were calculated to be 73.868, 66.072, and 63.845 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ all with a standard uncertainty of $0.002\cdot\Delta_0^T S_m^\circ$ for samples AI ($\text{TiO}_2\cdot 0.677\text{H}_2\text{O}$), AII ($\text{TiO}_2\cdot 0.532\text{H}_2\text{O}$), and AIII ($\text{TiO}_2\cdot 0.379\text{H}_2\text{O}$), respectively.

We attribute the differences in these thermodynamic properties to the different amounts of water bound to the surface of each species. By correcting the thermodynamic properties for the water's contribution, the thermodynamic properties of the anhydrous nanoparticles can be generated and directly compared with those of bulk materials. We have qualitatively shown elsewhere that the anhydrous TiO_2 nanoparticles have the same heat capacity as bulk TiO_2 within

experimental uncertainty [26], but we have failed to provide a quantitative comparison for heat capacities and other thermodynamic values.

In this study, we have subtracted the water's thermodynamic contributions from the thermodynamic properties of the TiO_2 anatase nanoparticles using two models. This correction allows for a direct comparison between nano and bulk TiO_2 anatase thermodynamic properties (values for bulk TiO_2 anatase are given in ref. [18]). The first model assumes that surface-bound water behaves as hexagonal ice. To obtain the thermodynamic properties of hexagonal ice at $T = 298.15$ K, heat capacity data of hexagonal ice were extrapolated from 273 to 298.15 K using a theoretical fit of Debye and Einstein functions and subsequently used to generate the thermodynamic properties of hexagonal ice at $T = 298.15$ K (see ref. [26] for more details and Figure 6 herein) [48-52]. Subtracting these values (accounting for moles of water) from those of the nanoparticles resulted in thermodynamic values that differ from those of bulk $\text{TiO}_2 \cdot 0.023\text{H}_2\text{O}$ by 14.8% at most. The calculated thermodynamic properties of nano $\text{TiO}_2 \cdot 0.023\text{H}_2\text{O}$ anatase along with their percent differences from the bulk values are given in Table 10.

From Table 10 we can draw some conclusions about the relationship between bulk TiO_2 thermodynamics and those of bare nanoparticles. The heat capacity results deviate most for sample AI which has more layers of surface water than the other samples suggesting that this model poorly represents the outermost layers of water. This is a reasonable conclusion because the outer layers of water are far from the high energy TiO_2 surface that binds the inner layers of water as solid H_2O even above the normal melting point of water; therefore, the outermost layers of water will likely resemble liquid water more than hexagonal ice above $T = 273.15$ K [53]. Because enthalpy and entropy are related to the shape of the heat capacity curve as a function of temperature, these values approximate the deviation of the heat capacity data from that of bulk

TiO₂ below $T = 298.15$ K and are included in Table 10. For samples AI and AII the entropy and enthalpy values differ substantially from the bulk values suggesting that the hexagonal ice model results in an anhydrous nano TiO₂ heat capacity that differs from that of bulk TiO₂ at temperatures below $T = 298.15$ K. Sample AIII appears to be the only sample that produces heat capacity, entropy, and enthalpy values similar to those of bulk TiO₂ using this model, which is likely due to the fact that this sample only contains one or two layers of water. The innermost layers of water will be tightly bound to the surface and therefore behave more like hexagonal ice. Treating water bound to a TiO₂ surface as hexagonal ice is not a great model and has limited usefulness, but it does provide a fair estimate of the water bound to TiO₂ rutile nanoparticles and is much simpler than the second model used.

The second model uses heat capacity data and subsequent thermodynamic properties from our previous paper on nanophase TiO₂ surface bound water [26]. Figure 6 shows the heat capacity data of two layers of TiO₂ surface-bound water taken from ref. [26]. As outlined in ref. [26], this model assumes that for water coverages up to 0.379 moles, the water behaves as tightly bound “inner” water; above this coverage, the water behaves as loosely bound “outer” water. Because the heat capacity data below about 75 K for the tightly bound “inner” water become sporadic and eventually negative, the data were fit to a sum of Debye and Einstein functions to produce a quality extrapolation to low temperatures (see the inset of Figure 6). The thermodynamic properties of the “inner” water were then determined from this extrapolated data. The thermodynamic properties for the loosely bound “outer” water were determined from a spline fit of those heat capacity data (shown in Figure 6). Subtracting these water contributions from the thermodynamic properties of the samples AI, AII, and AIII results in thermodynamic

properties that agree with those of bulk $\text{TiO}_2 \cdot 0.023\text{H}_2\text{O}$ better than the hexagonal ice model (see Table 10).

These calculations for the AI and AII samples yield heat capacity, entropy, and enthalpy values with percent deviations from the bulk values less than 5%; however, the calculations for the AIII sample deviate much more because it has about a monolayer of water according to this model, and the inner water data below 75 K were unreasonable introducing uncertainty in the calculation. Together these suggest that at lower temperatures and for lower water coverages the thermodynamics of these nanoparticles cannot be modeled as a TiO_2 core and an H_2O shell separately because of their strong interaction with each other. This property has been discussed elsewhere in which the low water coverages are in part treated as hydroxyls bound to Ti atoms that incidentally cause the Schottky anomaly in the low temperature heat capacity [42]. Nevertheless, for higher coverages in which there are fewer hydroxyls and more water molecules this model results in thermodynamic values of bare TiO_2 whose difference from bulk TiO_2 lie within the standard uncertainty of the calculated data after accounting for the uncertainty of the data ($0.0005 \cdot C_{p,m}$ to $0.005 \cdot C_{p,m}$ depending on the temperature), the fits ($0.01 \cdot C_{p,m}$ to $0.2 \cdot C_{p,m}$ depending on temperature), the thermodynamic calculations ($0.002 \cdot X$), and the water modeling (estimated to be $0.05 \cdot C_{p,m}$). These uncertainties result in an estimated standard uncertainty for the values in Table 10 of $0.07 \cdot X$ where X represents the thermodynamic property.

These calculations quantitatively augment the results from our previous study showing that the difference in thermodynamic properties between nanophase and bulk TiO_2 anatase must be attributed to the difference in water content and not an intrinsic property of nanoparticles [26]. This also supports the proposition that each layer of surface-bound water has different properties

depending on its position and morphology and that water compensates for the large surface energetics of nanoparticles by forming stronger bonds than the hydrogen bonds in hexagonal ice.

5. Conclusion

Heat capacities of several 7 nm TiO₂ anatase nanoparticles of varying amounts of surface-adsorbed water were measured from (0.5 to 320) K. Fits of each data set were used to generate $C_{p,m}^{\circ}$, $\Delta_0^T S_m^{\circ}$, $\Delta_0^T H_m^{\circ}$, and φ_m° values at smoothed temperatures between (0.5 and 300) K, and the thermodynamic values at $T = 298.15$ K have been corrected for water contributions using two models. These results show quantitatively that the differences between the thermodynamic properties values of nanophase TiO₂ anatase and those published for bulk TiO₂ are a result of different amounts and types of surface bound water.

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Table 1. Description of all samples including provenance, purification methods, purities, how purities were determined, and distribution of particle sizes.

Sample	Provenance	Purification Method	Mass Fraction Purity	Method for Determining Purity	Particle Size Distribution
TiO ₂ ·0.677H ₂ O (AI)	Synthesized in-house	Calcination and Rinsing with Ethanol	> 0.999	ICP-OES	± 2 nm
TiO ₂ ·0.532H ₂ O (AII)	Synthesized in-house	Calcination and Rinsing with Ethanol	> 0.999	ICP-OES	± 2 nm
TiO ₂ ·0.379H ₂ O (AIII)	Synthesized in-house	Calcination and Rinsing with Ethanol	> 0.999	ICP-OES	± 2 nm

Table 2. Details of the calorimetric experiments for the adiabatic and semi-adiabatic measurements including pressures ($u(p) = 0.05 \cdot p$), molar mass, M , and sample mass, M_s ($u_r(M_s) = 0.001$).

	TiO ₂ ·0.677H ₂ O (AI)	TiO ₂ ·0.532H ₂ O (AII)	TiO ₂ ·0.379H ₂ O (AIII)
15 < (T / K) < 320 Adiabatic measurements			
p (He gas) / kPa	2.80	2.40	2.40
M_s / g	8.548	7.508	6.012
M / g·mol ⁻¹	92.062	89.450	86.694
0.5 < (T / K) < 40 Semi-adiabatic measurements			
p (He gas) / Pa	0.04	0.04	0.04
Apiezon-N / g	4.8×10^{-3}	4.4×10^{-3}	6.9×10^{-3}
M_s / g	0.2953	0.2478	0.2590

Table 3. Measured molar heat capacity data at constant pressure for $\text{TiO}_2 \cdot 0.677\text{H}_2\text{O}$ (AI). $M = 92.062 \text{ g} \cdot \text{mol}^{-1}$. Data below 25 K were collected with a semi-adiabatic calorimeter at $p = 0.04 \text{ Pa}$ ($u(p) = 0.05 \cdot p$) and have a standard uncertainty of $0.0025 \cdot C_{p,m}$ below about 15 K and $0.005 \cdot C_{p,m}$ from (15 to 25) K. Data above 25 K were collected with an adiabatic calorimeter at $p = 2.80 \text{ kPa}$ ($u(p) = 0.05 \cdot p$) and have a standard uncertainty of $0.004 \cdot C_{p,m}$ from (25 to 40) K, $0.002 \cdot C_{p,m}$ between (40 and 60) K, and $0.0005 \cdot C_{p,m}$ from (60 to 400) K.

T / K	$C_{p,m} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	T / K	$C_{p,m} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	T / K	$C_{p,m} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
0.47190	2.8353×10^{-4}	10.492	0.17368	166.24	50.142
0.51840	4.8636×10^{-4}	11.006	0.19232	169.08	51.254
0.54421	5.9251×10^{-4}	11.533	0.21783	171.16	51.778
0.56956	7.2400×10^{-4}	12.101	0.24274	174.18	52.951
0.59756	9.2324×10^{-4}	12.684	0.27134	176.27	53.424
0.62641	1.0095×10^{-3}	13.292	0.30405	179.29	54.574
0.65874	1.1821×10^{-3}	13.926	0.34231	181.38	55.090
0.69064	1.3643×10^{-3}	14.587	0.38266	183.93	56.137
0.72472	1.6960×10^{-3}	15.296	0.43070	186.49	56.735
0.76057	1.9273×10^{-3}	16.026	0.48458	189.01	57.763
0.79771	2.3917×10^{-3}	16.802	0.54702	191.60	58.310
0.83627	2.7475×10^{-3}	17.596	0.61451	194.14	59.375
0.87669	3.1785×10^{-3}	18.453	0.69360	196.72	59.899
0.91904	3.6555×10^{-3}	19.322	0.78338	199.26	60.842
0.96400	4.0554×10^{-3}	20.267	0.88061	201.84	61.512
1.0096	4.6637×10^{-3}	21.223	0.99860	203.72	62.083
1.0586	5.0879×10^{-3}	22.258	1.1268	204.38	62.384
1.1098	5.7651×10^{-3}	23.305	1.2731	206.96	63.145
1.1643	6.2814×10^{-3}	23.739	1.3106	208.56	63.559
1.2207	6.8981×10^{-3}	24.440	1.4383	208.70	63.503
1.2819	7.5176×10^{-3}	25.586	1.6239	212.09	64.593
1.3444	8.1355×10^{-3}	25.711	1.6379	213.69	65.042
1.4106	8.6488×10^{-3}	26.828	1.8316	213.83	65.092
1.4787	9.3178×10^{-3}	27.036	1.8530	218.81	66.588
1.5503	9.6567×10^{-3}	27.884	2.0367	218.95	66.961
1.6280	0.010318	28.085	2.0546	219.76	66.996
1.7075	0.010576	29.459	2.3085	223.94	68.127
1.7913	0.010957	29.891	2.3643	224.07	68.436
1.8799	0.011263	30.852	2.5938	224.90	68.624

1.9395	0.011227	32.305	2.9410	229.07	69.611
1.9714	0.011535	35.031	3.7059	229.22	69.564
2.0693	0.011830	38.021	4.5258	230.04	69.733
2.1354	0.011866	41.335	5.4932	232.14	70.326
2.1705	0.012082	44.993	6.6677	234.21	71.062
2.3505	0.012404	45.889	6.9488	234.37	71.015
2.4081	0.012441	49.861	8.3387	235.18	71.154
2.5885	0.013001	51.602	8.9025	239.35	72.561
2.6510	0.013074	53.581	9.6847	239.51	72.486
2.8495	0.013602	55.963	10.414	242.42	73.456
2.9189	0.013800	58.674	11.600	244.48	73.876
3.1372	0.014580	58.838	11.465	244.65	73.859
3.2132	0.014892	62.169	12.684	247.56	74.845
3.4557	0.016030	64.230	13.422	249.63	75.130
3.5375	0.016384	65.966	14.081	249.79	75.184
3.8015	0.018082	66.050	14.113	252.70	75.995
3.8903	0.018635	68.524	15.070	254.78	76.488
4.1815	0.021018	70.232	15.679	254.94	76.576
4.2784	0.021777	71.475	16.092	257.85	77.358
4.5990	0.024846	74.894	17.451	259.92	77.897
4.7055	0.025926	79.258	19.091	260.08	77.929
5.0561	0.030200	84.092	20.968	263.00	78.724
5.1737	0.031787	88.949	22.767	265.23	79.183
5.5571	0.037173	93.839	24.605	266.60	79.514
5.6851	0.039109	98.759	26.454	266.72	79.440
6.1062	0.045851	100.68	27.176	270.38	80.531
6.2479	0.048169	105.61	29.030	271.71	80.718
6.7109	0.056814	110.59	30.816	275.53	81.530
6.8697	0.060170	115.58	32.626	276.86	81.832
7.3790	0.071353	120.59	34.440	276.96	81.993
7.5540	0.075605	125.61	36.250	280.70	82.786
8.1100	0.089738	130.65	38.052	282.02	82.996
8.3012	0.094965	135.70	39.899	282.12	83.145
8.9123	0.11217	140.75	41.685	285.86	83.909
9.1236	0.11878	143.64	42.739	287.18	84.096
9.1358	0.12049	145.82	43.476	287.28	84.227
9.5961	0.14290	148.73	44.421	292.35	85.278
9.7933	0.14053	153.81	46.267	297.51	86.331

10.019	0.15290	158.89	47.876	302.68	87.384
10.028	0.14874	163.98	49.682		

Table 4. Measured molar heat capacity data at constant pressure for $\text{TiO}_2 \cdot 0.532\text{H}_2\text{O}$ (AII). $M = 89.450 \text{ g}\cdot\text{mol}^{-1}$. Data below 25 K were collected with a semi-adiabatic calorimeter at $p = 0.04 \text{ Pa}$ ($u(p) = 0.05 \cdot p$) and have a standard uncertainty of $0.0025 \cdot C_{p,m}$ below about 15 K and $0.005 \cdot C_{p,m}$ from (15 to 25) K. Data above 25 K were collected with an adiabatic calorimeter at $p = 2.40 \text{ kPa}$ ($u(p) = 0.05 \cdot p$) and have a standard uncertainty of $0.004 \cdot C_{p,m}$ from (25 to 40) K, $0.002 \cdot C_{p,m}$ between (40 and 60) K, and $0.0005 \cdot C_{p,m}$ from (60 to 400) K.

T / K	$C_{p,m} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T / K	$C_{p,m} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T / K	$C_{p,m} / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
0.51531	4.2305×10^{-4}	14.738	0.30672	168.28	46.617
0.54520	3.7353×10^{-4}	15.464	0.34774	170.33	47.021
0.56849	4.9268×10^{-4}	16.196	0.38936	171.41	47.426
0.59902	5.1534×10^{-4}	17.001	0.44475	173.39	47.978
0.62643	6.0797×10^{-4}	17.804	0.49771	175.44	48.538
0.65973	6.2494×10^{-4}	18.685	0.56718	176.52	48.762
0.69121	7.6636×10^{-4}	19.562	0.63987	178.50	49.356
0.72708	8.3581×10^{-4}	20.529	0.72753	180.55	49.853
0.76193	9.8045×10^{-4}	21.497	0.82098	181.64	50.177
0.80062	1.1067×10^{-3}	22.271	0.89052	183.62	50.810
0.83839	1.2686×10^{-3}	22.556	0.93381	185.64	51.163
0.88037	1.4511×10^{-3}	23.613	1.0590	186.76	51.496
0.92235	1.6463×10^{-3}	24.175	1.0778	188.74	51.956
0.96848	1.7919×10^{-3}	24.766	1.2046	190.77	52.476
1.0130	2.0465×10^{-3}	25.920	1.3594	191.88	52.632
1.0639	2.3474×10^{-3}	26.261	1.3853	193.87	53.279
1.0894	2.4012×10^{-3}	27.181	1.5380	194.30	53.349
1.1150	2.4992×10^{-3}	28.452	1.7425	194.53	53.397
1.1713	2.7862×10^{-3}	28.541	1.7388	196.04	53.623
1.1975	2.7694×10^{-3}	29.565	1.9399	197.01	54.002
1.2272	3.0348×10^{-3}	29.849	1.9608	198.96	54.512
1.3188	3.3815×10^{-3}	31.055	2.2326	199.39	54.525
1.3495	3.6009×10^{-3}	32.464	2.5340	199.66	54.678
1.4161	3.8294×10^{-3}	35.409	3.2342	204.08	55.745
1.4491	3.9324×10^{-3}	38.739	4.0598	204.53	55.834
1.4825	4.1278×10^{-3}	40.363	4.5098	204.79	55.891
1.5575	4.2654×10^{-3}	43.951	5.5343	209.21	57.019
1.5950	4.4351×10^{-3}	47.804	6.6760	209.63	56.891
1.6320	4.6050×10^{-3}	53.966	8.6191	209.92	57.117
1.7150	4.7874×10^{-3}	55.182	9.1597	214.35	58.163
1.7277	4.7666×10^{-3}	55.319	9.1776	214.75	58.134
1.7548	4.8993×10^{-3}	55.791	9.2685	215.06	58.283
1.7961	5.0114×10^{-3}	55.814	9.3718	219.49	59.226
1.8126	5.1808×10^{-3}	56.465	9.5809	219.89	59.321
1.8866	5.2167×10^{-3}	58.000	9.9141	220.20	59.313

1.9011	5.2102×10^{-3}	58.218	10.104	225.03	60.395
1.9303	5.3631×10^{-3}	60.146	10.829	225.34	60.474
1.9765	5.4637×10^{-3}	60.276	10.823	229.77	61.449
2.0753	5.7114×10^{-3}	60.305	10.859	234.92	62.524
2.0922	5.7086×10^{-3}	60.983	11.114	235.63	62.653
2.1746	5.9363×10^{-3}	61.523	11.190	237.56	63.056
2.3010	6.2118×10^{-3}	61.538	11.192	240.78	63.649
2.4209	6.2533×10^{-3}	64.465	12.290	241.93	63.928
2.5325	6.7175×10^{-3}	64.704	12.311	242.72	64.206
2.6632	7.1004×10^{-3}	64.834	12.361	245.93	64.768
2.7876	7.4364×10^{-3}	65.288	12.494	246.02	64.808
2.9284	7.8361×10^{-3}	65.750	12.721	247.86	65.316
3.0687	8.4116×10^{-3}	69.365	13.935	248.31	65.080
3.2240	8.9777×10^{-3}	69.494	13.978	250.07	65.682
3.3783	9.6012×10^{-3}	69.550	13.983	251.08	65.824
3.5482	0.010238	70.441	14.308	253.02	66.344
3.7156	0.011125	74.211	15.641	253.47	66.101
3.9017	0.012214	74.290	15.661	254.09	66.460
4.0877	0.013482	75.171	15.964	258.09	67.110
4.2912	0.014768	77.519	16.812	258.17	67.085
4.4957	0.016355	78.982	17.338	258.62	67.321
4.7202	0.018171	79.061	17.360	262.06	67.932
4.9448	0.020267	82.419	18.555	263.33	68.164
5.1917	0.022732	87.262	20.249	263.77	68.070
5.4391	0.025445	92.143	22.007	266.00	68.541
5.7101	0.028478	97.056	23.698	268.93	69.028
5.9811	0.031735	101.99	25.460	269.93	69.135
6.2811	0.035615	106.96	27.190	272.72	69.764
6.5792	0.039743	109.43	28.060	273.65	70.015
6.9081	0.044737	111.94	28.893	273.83	69.872
7.2372	0.050171	114.42	29.789	274.09	70.032
7.5963	0.056660	119.43	31.445	276.84	70.122
7.9557	0.063672	124.45	33.157	277.70	70.609
8.3517	0.071846	129.49	34.789	277.88	70.686
8.7459	0.080368	134.54	36.452	279.26	70.829
9.1831	0.090055	137.79	37.484	283.03	71.684
9.1862	0.088006	139.60	38.047	287.16	72.421
9.6179	0.10116	142.84	39.161	288.20	72.618
9.6496	0.10556	147.91	40.676	292.33	72.791
10.098	0.11392	152.99	42.182	293.37	73.238
10.135	0.11358	154.45	42.499	298.53	74.030
10.578	0.12806	157.02	43.203	302.66	74.831
10.625	0.14095	158.08	43.681	303.70	75.229
11.160	0.15965	160.62	44.270	307.83	75.606
11.666	0.18831	161.08	44.464	308.87	75.572

12.215	0.19462	163.18	45.167	313.00	76.297
12.804	0.22455	165.22	45.612	314.04	76.557
13.415	0.24274	166.31	46.042	318.16	77.238
14.064	0.27702				

Table 5. Measured molar heat capacity data at constant pressure for $\text{TiO}_2 \cdot 0.379\text{H}_2\text{O}$ (AIII). $M = 86.694 \text{ g} \cdot \text{mol}^{-1}$. Data below 25 K were collected with a semi-adiabatic calorimeter at $p = 0.04 \text{ Pa}$ ($u(p) = 0.05 \cdot p$) and have a standard uncertainty of $0.0025 \cdot C_{p,m}$ below about 15 K and $0.005 \cdot C_{p,m}$ from (15 to 25) K. Data above 25 K were collected with an adiabatic calorimeter at $p = 2.40 \text{ kPa}$ ($u(p) = 0.05 \cdot p$) and have a standard uncertainty of $0.004 \cdot C_{p,m}$ from (25 to 40) K, $0.002 \cdot C_{p,m}$ between (40 and 60) K, and $0.0005 \cdot C_{p,m}$ from (60 to 400) K.

T / K	$C_{p,m} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	T / K	$C_{p,m} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	T / K	$C_{p,m} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
0.47162	3.3409×10^{-4}	35.352	3.1254	228.23	58.636
0.49433	4.7908×10^{-4}	38.117	3.8592	228.28	58.804
0.51836	5.4342×10^{-4}	41.475	4.7225	232.30	59.776
0.54333	6.3586×10^{-4}	43.864	5.3380	232.35	59.953
0.56924	7.5353×10^{-4}	45.191	5.7388	232.61	59.642
0.59773	8.6574×10^{-4}	47.732	6.5393	233.01	59.713
0.62535	1.0367×10^{-3}	51.940	7.8031	234.98	60.339
0.65800	1.1488×10^{-3}	52.435	8.0628	236.32	60.340
0.68870	1.3832×10^{-3}	52.920	7.7423	236.41	60.431
0.72404	1.6837×10^{-3}	54.532	8.6166	237.76	60.581
0.75834	1.8982×10^{-3}	55.265	8.7457	238.16	60.844
0.79686	2.2611×10^{-3}	56.379	9.2360	239.08	60.914
0.83400	2.6464×10^{-3}	57.874	9.6781	240.13	61.153
0.87638	3.0396×10^{-3}	58.112	9.6999	240.13	61.153
0.91671	3.4337×10^{-3}	61.431	10.846	240.35	61.424
0.96431	3.9367×10^{-3}	65.665	12.302	240.51	61.311
1.0065	4.3257×10^{-3}	70.357	13.887	243.31	61.905
1.0594	5.0618×10^{-3}	70.606	13.946	244.22	61.828
1.1066	5.4943×10^{-3}	72.989	14.727	244.38	62.026
1.1644	6.0740×10^{-3}	75.134	15.499	244.64	62.205
1.2171	6.6194×10^{-3}	77.634	16.292	245.28	62.227
1.2807	7.0963×10^{-3}	79.927	17.155	245.28	62.227
1.3404	7.9125×10^{-3}	82.449	17.819	248.40	62.956
1.4086	8.2983×10^{-3}	84.754	18.723	248.46	62.819
1.4730	8.9252×10^{-3}	87.300	19.589	248.77	62.757
1.5488	9.4644×10^{-3}	89.622	20.483	249.38	62.964
1.6213	9.8240×10^{-3}	92.183	21.244	250.44	63.126
1.7049	0.010218	94.524	22.059	250.44	63.126
1.7848	0.010598	97.098	22.934	251.89	63.454
1.8067	0.010556	99.458	23.788	252.43	63.539
1.8772	0.010869	99.803	23.857	252.90	63.736
1.8929	0.010719	104.41	25.523	254.53	64.129
1.9640	0.011141	104.81	25.571	255.05	63.911
1.9820	0.011151	109.38	27.308	255.60	64.120
2.0660	0.011291	109.78	27.242	255.60	64.120
2.0819	0.011430	114.38	28.773	255.95	64.185

2.1619	0.011539	114.78	28.895	256.93	64.365
2.1829	0.011586	119.40	30.373	259.68	64.638
2.2908	0.011875	119.80	30.480	259.98	64.837
2.4038	0.012059	122.56	31.395	260.21	65.178
2.5223	0.012275	124.43	32.051	260.65	64.936
2.6459	0.012442	124.83	32.082	260.76	65.117
2.7765	0.012948	127.59	32.980	260.76	65.117
2.9123	0.012925	129.47	33.623	260.96	65.052
3.0546	0.013296	132.64	34.563	263.99	65.640
3.2063	0.013675	134.52	35.192	264.66	66.314
3.3659	0.014349	137.70	36.128	264.85	65.827
3.5316	0.014939	139.58	36.757	264.99	65.817
3.7030	0.015940	140.20	36.827	265.37	65.726
3.8826	0.016842	142.77	37.640	265.91	65.910
4.0744	0.018157	144.68	38.337	265.91	65.910
4.2706	0.019475	145.27	38.361	267.98	66.238
4.4830	0.021256	148.15	39.248	268.69	66.379
4.6978	0.022801	149.78	39.648	269.02	66.790
4.9300	0.025556	150.35	39.923	270.02	66.348
5.1684	0.027905	153.36	40.620	270.53	66.820
5.4217	0.031326	154.87	41.230	271.07	66.888
5.6843	0.034228	155.44	41.333	271.07	66.888
5.9636	0.038616	158.45	41.975	271.94	66.945
6.2520	0.042179	159.96	42.717	272.73	66.710
6.5586	0.047810	160.54	42.795	273.06	67.024
6.8740	0.052392	163.55	43.514	275.18	67.163
7.2089	0.059674	165.07	44.138	275.69	68.155
7.5568	0.065855	165.64	44.269	275.87	67.449
7.9242	0.074965	168.66	44.843	276.24	67.470
8.3037	0.082345	170.17	45.478	276.24	67.470
8.7073	0.093699	170.75	45.541	276.77	67.589
9.1275	0.10330	173.77	46.225	277.10	67.618
9.5705	0.11704	175.29	46.840	278.37	67.916
10.039	0.12879	175.86	46.922	279.79	68.005
10.529	0.14674	178.88	47.572	280.34	68.297
10.968	0.16030	180.41	48.022	280.80	68.243
11.508	0.19328	180.98	48.241	281.13	68.329
12.091	0.21296	184.00	48.852	281.40	68.384
12.670	0.23708	186.10	49.520	281.40	68.384
13.208	0.26599	189.12	50.121	283.53	68.797
13.904	0.29358	191.23	50.804	283.69	68.703
14.532	0.32840	194.25	51.511	284.83	69.435
15.285	0.37312	195.85	51.792	285.07	69.009
15.991	0.41202	197.03	52.152	285.17	68.848
16.782	0.46897	199.38	52.647	285.50	69.168
17.578	0.52416	199.69	52.804	288.70	69.753

18.446	0.59799	201.77	52.974	289.07	69.442
19.301	0.66811	202.16	53.141	289.20	69.483
20.265	0.76401	203.81	53.642	292.34	70.044
21.213	0.85257	206.90	54.114	293.10	70.579
21.632	0.86328	207.30	54.456	293.87	70.261
22.267	0.98327	207.93	54.619	297.14	70.840
23.296	1.0928	212.04	55.349	297.50	70.988
24.449	1.2552	212.05	55.488	299.04	71.277
25.579	1.4040	212.44	55.491	301.18	71.546
26.845	1.5950	216.15	56.444	302.67	71.849
28.098	1.7790	217.18	56.449	304.20	72.179
28.662	1.8705	217.58	56.749	305.21	72.412
29.483	2.0001	220.02	57.234	307.84	72.579
30.858	2.2351	220.22	57.274	309.25	72.772
31.080	2.2626	222.31	57.681	309.37	72.896
32.321	2.5039	222.72	57.722	313.01	73.333
32.401	2.5182	224.11	58.129	313.29	73.330
33.840	2.7206	224.25	58.058	314.54	73.372
33.916	2.8222	227.46	58.673	317.33	73.741
35.093	3.1345	227.87	58.952		

Table 6. Parameters for low T (< 15 K), mid T ($10 < T < 75$ K), and high T (> 35 K) fits of the heat capacity (in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) of all hydrated nano- TiO_2 anatase samples.

	Parameters	$\text{TiO}_2\cdot 0.677\text{H}_2\text{O}$ (AI)	$\text{TiO}_2\cdot 0.532\text{H}_2\text{O}$ (AII)	$\text{TiO}_2\cdot 0.379\text{H}_2\text{O}$ (AIII)
Low T Fits	$\gamma / \text{J}\cdot\text{K}^{-2}\cdot\text{mol}^{-1}$	5.9408×10^{-4}	6.5641×10^{-4}	6.8770×10^{-4}
	$B_3 / \text{J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1.9778×10^{-4}	1.3657×10^{-4}	1.6875×10^{-4}
	$B_5 / \text{J}\cdot\text{K}^{-6}\cdot\text{mol}^{-1}$	-7.9607×10^{-7}	-4.9298×10^{-7}	-7.3186×10^{-7}
	$B_7 / \text{J}\cdot\text{K}^{-8}\cdot\text{mol}^{-1}$	3.1125×10^{-9}	2.6463×10^{-9}	3.3557×10^{-9}
	$B_9 / \text{J}\cdot\text{K}^{-10}\cdot\text{mol}^{-1}$	-5.0429×10^{-12}	-5.8554×10^{-12}	-6.2926×10^{-12}
	n / mol	2.4244×10^{-3}	8.5993×10^{-4}	2.3080×10^{-3}
	Θ_{Sch} / K	4.8047	4.8047	4.8169
	%RMS	3.54	2.94	2.80
	Range / K	0.4719 – 13.94	0.5153 – 14.18	0.4716 – 12.98
Mid T Fits	$A_0 / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	-0.088426	-0.64302	-0.34975
	$A_1 / \text{J}\cdot\text{K}^{-2}\cdot\text{mol}^{-1}$	0.016444	0.14766	0.083509
	$A_2 / \text{J}\cdot\text{K}^{-3}\cdot\text{mol}^{-1}$	2.0508×10^{-4}	-0.011556	-6.6292×10^{-3}
	$A_3 / \text{J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	3.1573×10^{-5}	4.9962×10^{-4}	3.6042×10^{-4}
	$A_4 / \text{J}\cdot\text{K}^{-5}\cdot\text{mol}^{-1}$	2.9371×10^{-6}	-7.1462×10^{-6}	-6.0205×10^{-6}
	$A_5 / \text{J}\cdot\text{K}^{-6}\cdot\text{mol}^{-1}$	-6.8884×10^{-8}	4.0556×10^{-8}	4.7708×10^{-8}
	$A_6 / \text{J}\cdot\text{K}^{-7}\cdot\text{mol}^{-1}$	4.0713×10^{-10}	-5.8468×10^{-11}	-1.5728×10^{-10}
	%RMS	0.809	1.56	1.44
	Range / K	13.94 – 49.30	14.18 – 46.75	12.98 – 43.34
High T Fits	m / mol	1.1273	1.2812	1.2318
	Θ_D / K	286.59	321.82	320.44
	n_l / mol	1.6601	1.8821	1.7720
	$\Theta_{E,1} / \text{K}$	491.09	583.84	578.36
	n_2 / mol	2.7282	1.5136	1.3699
	$\Theta_{E,2} / \text{K}$	1048.8	1297.6	1244.1
	%RMS	0.260	0.344	0.607
	Range / K	49.30 – 305	46.75 – 320	43.34 – 320

Table 7. Standard thermodynamic functions of $\text{TiO}_2 \cdot 0.677\text{H}_2\text{O}$ (AI). $\varphi_m^\circ = \Delta_o^T S_m^\circ - \Delta_o^T H_m^\circ / T$. $M = 92.062 \text{ g} \cdot \text{mol}^{-1}$. All calculated thermodynamic values have an estimated standard uncertainty of about $0.002 \cdot X$ where X represents the thermodynamic property.

T / K	$C_{m,p}^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Delta_o^T S_m^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Delta_o^T H_m^\circ / \text{kJ} \cdot \text{mol}^{-1}$	$\varphi_m^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
0.5	4.1641×10^{-4}	0	0	0
1	4.5247×10^{-3}	1.3017×10^{-3}	1.0573×10^{-6}	2.4447×10^{-4}
1.5	9.3018×10^{-3}	4.1090×10^{-3}	4.6007×10^{-6}	1.0419×10^{-3}
2	0.011688	7.1638×10^{-3}	9.9386×10^{-6}	2.1945×10^{-3}
2.5	0.012735	9.8935×10^{-3}	1.6065×10^{-5}	3.4677×10^{-3}
3	0.013957	0.012312	2.2707×10^{-5}	4.7433×10^{-3}
3.5	0.016165	0.014615	3.0189×10^{-5}	5.9892×10^{-3}
4	0.019545	0.016981	3.9069×10^{-5}	7.2139×10^{-3}
4.5	0.024029	0.019532	4.9918×10^{-5}	8.4388×10^{-3}
5	0.029555	0.022340	6.3271×10^{-5}	9.6861×10^{-3}
6	0.043894	0.028927	9.9613×10^{-5}	0.012324
7	0.062971	0.037064	1.5265×10^{-4}	0.015257
8	0.086768	0.046973	2.2712×10^{-4}	0.018583
9	0.11586	0.058814	3.2793×10^{-4}	0.022377
10	0.15158	0.072808	4.6107×10^{-4}	0.026701
12.5	0.26174	0.11777	9.6985×10^{-4}	0.040178
15	0.41235	0.17817	1.8038×10^{-3}	0.057916
20	0.85112	0.35202	4.8774×10^{-3}	0.10814
25	1.5058	0.60804	0.010674	0.18107
30	2.4482	0.96147	0.020438	0.28019
35	3.6556	1.4265	0.035598	0.40937
40	5.0776	2.0053	0.057352	0.57151
45	6.6650	2.6936	0.086650	0.76808
50	8.3687	3.4825	0.12416	0.99928
55	10.147	4.3635	0.17045	1.2644
60	11.930	5.3228	0.22564	1.5622
65	13.734	6.3487	0.28978	1.8905
70	15.580	7.4338	0.36305	2.2473
75	17.467	8.5728	0.44565	2.6308
80	19.377	9.7610	0.53776	3.0391
85	21.290	10.993	0.63943	3.4705
90	23.189	12.264	0.75063	3.9236
95	25.066	13.568	0.87128	4.3967
100	26.922	14.901	1.0013	4.8885
110	30.589	17.639	1.2888	5.9225
120	34.234	20.457	1.6130	7.0158
130	37.857	23.341	1.9735	8.1603
140	41.423	26.277	2.3699	9.3492
150	44.892	29.254	2.8016	10.577
160	48.254	32.259	3.2674	11.838

170	51.527	35.283	3.7664	13.128
180	54.737	38.320	4.2977	14.443
190	57.896	41.364	4.8609	15.780
200	61.002	44.413	5.4555	17.135
210	64.041	47.463	6.0808	18.507
220	66.998	50.511	6.7360	19.892
230	69.866	53.552	7.4204	21.290
240	72.640	56.585	8.1330	22.697
250	75.317	59.605	8.8729	24.113
260	77.887	62.609	9.6390	25.536
270	80.327	65.595	10.430	26.965
273.15	81.064	66.531	10.684	27.415
280	82.612	68.558	11.245	28.397
290	84.763	71.495	12.082	29.833
298.15	86.477	73.868	12.780	31.004
300	86.856	74.404	12.940	31.270

Table 8. Standard thermodynamic functions of $\text{TiO}_2 \cdot 0.532\text{H}_2\text{O}$ (AII). $\phi_m^\circ = \Delta_o^T S_m^\circ - \Delta_0^T H_m^\circ / T$. $M = 89.450 \text{ g} \cdot \text{mol}^{-1}$. All calculated thermodynamic values have an estimated standard uncertainty of about $0.002 \cdot X$ where X represents the thermodynamic property.

T / K	$C_{m,p}^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Delta_o^T S_m^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Delta_0^T H_m^\circ / \text{kJ} \cdot \text{mol}^{-1}$	$\phi_m^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
0.5	4.2419×10^{-4}	0	0	0
1	1.9721×10^{-3}	6.4273×10^{-4}	5.0952×10^{-7}	1.3321×10^{-4}
1.5	4.1266×10^{-3}	1.8670×10^{-3}	2.0561×10^{-6}	4.9630×10^{-4}
2	5.5127×10^{-3}	3.2613×10^{-3}	4.4960×10^{-6}	1.0133×10^{-3}
2.5	6.6000×10^{-3}	4.6060×10^{-3}	7.5189×10^{-6}	1.5984×10^{-3}
3	8.0795×10^{-3}	5.9313×10^{-3}	1.1165×10^{-5}	2.2097×10^{-3}
3.5	0.010170	7.3258×10^{-3}	1.5701×10^{-5}	2.8397×10^{-3}
4	0.012885	8.8538×10^{-3}	2.1438×10^{-5}	3.4943×10^{-3}
4.5	0.016333	0.010562	2.8708×10^{-5}	4.1829×10^{-3}
5	0.020688	0.012500	3.7923×10^{-5}	4.9156×10^{-3}
6	0.032110	0.017233	6.4053×10^{-5}	6.5571×10^{-3}
7	0.046258	0.023211	1.0302×10^{-4}	8.4943×10^{-3}
8	0.064560	0.030519	1.5795×10^{-4}	0.010775
9	0.087666	0.039413	2.3369×10^{-4}	0.013448
10	0.11532	0.050040	3.3480×10^{-4}	0.016561
12.5	0.20506	0.084860	7.2906×10^{-4}	0.026535
15	0.32566	0.13242	1.3858×10^{-3}	0.040035
20	0.67505	0.27013	3.8207×10^{-3}	0.079093
25	1.2164	0.47499	8.4612×10^{-3}	0.13654
30	2.0191	0.76301	0.016421	0.21565
35	3.1160	1.1533	0.029150	0.32043
40	4.4144	1.6525	0.047915	0.45462
45	5.8331	2.2533	0.073489	0.62021
50	7.3906	2.9467	0.10646	0.81743
55	9.0409	3.7283	0.14753	1.0459
60	10.720	4.5867	0.19692	1.3047
65	12.428	5.5121	0.25478	1.5924
70	14.162	6.4964	0.32125	1.9072
75	15.915	7.5331	0.39643	2.2474
80	17.681	8.6166	0.48042	2.6114
85	19.455	9.7417	0.57326	2.9975
90	21.230	10.904	0.67497	3.4043
95	23.001	12.099	0.78555	3.8304
100	24.764	13.324	0.90497	4.2743
110	28.249	15.848	1.1701	5.2111
120	31.658	18.453	1.4697	6.2055
130	34.972	21.119	1.8029	7.2498
140	38.174	23.828	2.1688	8.3370
150	41.253	26.568	2.5660	9.4609
160	44.203	29.325	2.9934	10.616

170	47.020	32.090	3.4496	11.798
180	49.710	34.854	3.9334	13.002
190	52.278	37.611	4.4434	14.225
200	54.734	40.356	4.9785	15.463
210	57.087	43.083	5.5377	16.713
220	59.345	45.792	6.1200	17.974
230	61.511	48.478	6.7243	19.241
240	63.586	51.140	7.3499	20.515
250	65.571	53.776	7.9957	21.793
260	67.466	56.385	8.6610	23.073
270	69.278	58.965	9.3448	24.355
273.15	69.834	59.772	9.5639	24.759
280	71.019	61.516	10.046	25.637
290	72.703	64.038	10.765	26.918
298.15	74.041	66.072	11.363	27.960
300	74.341	66.531	11.500	28.196

Table 9. Standard thermodynamic functions of $\text{TiO}_2 \cdot 0.379\text{H}_2\text{O}$ (AIII). $\varphi_m^\circ = \Delta_o^T S_m^\circ - \Delta_0^T H_m^\circ / T$. $M = 86.694 \text{ g} \cdot \text{mol}^{-1}$. All calculated thermodynamic values have an estimated standard uncertainty of about $0.002 \cdot X$ where X represents the thermodynamic property.

T / K	$C_{m,p}^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Delta_o^T S_m^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Delta_0^T H_m^\circ / \text{kJ} \cdot \text{mol}^{-1}$	$\varphi_m^\circ / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
0.5	4.6797×10^{-4}	0	0	0
1	4.2808×10^{-3}	1.2663×10^{-3}	1.0220×10^{-6}	2.4424×10^{-4}
1.5	9.1020×10^{-3}	3.9847×10^{-3}	4.4575×10^{-6}	1.0130×10^{-3}
2	0.011170	6.9407×10^{-3}	9.6196×10^{-6}	2.1309×10^{-3}
2.5	0.012165	9.5426×10^{-3}	1.5459×10^{-5}	3.3591×10^{-3}
3	0.013329	0.011858	2.1818×10^{-5}	4.5856×10^{-3}
3.5	0.014953	0.014027	2.8863×10^{-5}	5.7805×10^{-3}
4	0.017423	0.016173	3.6911×10^{-5}	6.9450×10^{-3}
4.5	0.021159	0.018427	4.6500×10^{-5}	8.0939×10^{-3}
5	0.026215	0.020908	5.8293×10^{-5}	9.2490×10^{-3}
6	0.039002	0.026776	9.0675×10^{-5}	0.011664
7	0.054859	0.033926	1.3726×10^{-4}	0.014317
8	0.075914	0.042571	2.0223×10^{-4}	0.017291
9	0.10147	0.052943	2.9054×10^{-4}	0.020660
10	0.13160	0.065153	4.0670×10^{-4}	0.024483
12.5	0.22748	0.10426	8.4931×10^{-4}	0.036318
15	0.35526	0.15651	1.5706×10^{-3}	0.051806
20	0.73500	0.30600	4.2136×10^{-3}	0.095319
25	1.3156	0.52935	9.2720×10^{-3}	0.15847
30	2.0780	0.83344	0.017669	0.24447
35	3.0711	1.2252	0.030440	0.35549
40	4.2956	1.7129	0.048770	0.49366
45	5.6891	2.2981	0.073678	0.66076
50	7.1736	2.9738	0.10581	0.85756
55	8.7218	3.7292	0.14550	1.0837
60	10.363	4.5582	0.19320	1.3382
65	12.030	5.4534	0.24917	1.6200
70	13.717	6.4066	0.31354	1.9275
75	15.418	7.4109	0.38637	2.2593
80	17.128	8.4605	0.46774	2.6139
85	18.842	9.5504	0.55766	2.9896
90	20.554	10.676	0.65615	3.3852
95	22.261	11.833	0.76319	3.7993
100	23.958	13.018	0.87874	4.2305
110	27.310	15.459	1.1351	5.1396
120	30.584	17.976	1.4247	6.1040
130	33.764	20.551	1.7465	7.1160
140	36.834	23.166	2.0996	8.1688

150	39.788	25.809	2.4828	9.2566
160	42.621	28.468	2.8949	10.374
170	45.331	31.133	3.3348	11.517
180	47.922	33.798	3.8012	12.681
190	50.397	36.456	4.2929	13.862
200	52.760	39.102	4.8087	15.058
210	55.018	41.731	5.3477	16.266
220	57.175	44.341	5.9088	17.483
230	59.236	46.928	6.4909	18.707
240	61.205	49.491	7.0932	19.936
250	63.087	52.028	7.7147	21.169
260	64.884	54.537	8.3546	22.404
270	66.600	57.019	9.0121	23.640
273.15	67.126	57.794	9.2227	24.030
280	68.243	59.471	9.6864	24.876
290	69.821	61.893	10.377	26.111
298.15	71.069	63.845	10.951	27.116
300	71.349	64.286	11.083	27.344

Table 10. All thermodynamic values at $T = 298.15$ K and percent deviation from bulk thermodynamic properties derived from two water correction models: first assumes water is similar to hexagonal ice $\text{H}_2\text{O}_{(s)}$ (thermodynamic properties extrapolated to $T = 298.15$ K), and second follows the calculation of ref. [26] assuming some loosely and some tightly bound water $\text{H}_2\text{O}_{(in/out)}$. Units are in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. These calculated thermodynamic values have an estimated standard uncertainty of at most $0.07\cdot X$ and are discussed in section 4.2.

		$\Delta_o^T C_m^\circ$	% error	$\Delta_o^T S_m^\circ$	% error	$\Delta_o^T H_m^\circ$	% error	ϕ_m°	% error
$\text{H}_2\text{O}_{(s)}$	AI	60.09	8.96	46.70	6.21	8.609	0.45	17.82	14.2
	AII	53.50	2.98	44.93	9.77	8.117	6.14	17.70	14.8
	AIII	56.71	2.82	49.05	1.48	8.680	0.38	19.94	4.06
$\text{H}_2\text{O}_{(in/out)}$	AI	52.90	4.07	51.95	4.33	8.804	1.81	22.42	7.86
	AII	52.90	4.08	51.95	4.33	8.804	1.80	22.42	7.86
	AIII	63.05	14.3	57.95	16.4	9.887	14.3	24.79	19.2

Figure Captions

Figure 1. XRD patterns of 7.7 nm $\text{TiO}_2 \cdot 0.677\text{H}_2\text{O}$ anatase particles (AI). XRD patterns for AII and AII samples are equivalent.

Figure 2. TEM micrograph of 7.7 nm $\text{TiO}_2 \cdot 0.677\text{H}_2\text{O}$ anatase particles (AI) on a holey carbon support. TEM images for AII and AIII are equivalent.

Figure 3. Plot of the molar heat capacity data at constant pressure as a function of temperature for the nanophase TiO_2 anatase samples $\text{TiO}_2 \cdot 0.677\text{H}_2\text{O}$ (AI- red circles), $\text{TiO}_2 \cdot 0.532\text{H}_2\text{O}$ (AII- blue squares), and $\text{TiO}_2 \cdot 0.379\text{H}_2\text{O}$ (AIII- green triangles) measured using semi-adiabatic (data below 30 K) and adiabatic (data above 30 K) calorimeters. The inset shows the same data for $T < 15$ K.

Figure 4. Plot of molar heat capacity data at constant pressure for samples AI (red circles), AII (blue squares), and AIII (green triangles) below $T < 8$ K. The inset shows the heat capacity of the Schottky anomaly for each of the samples.

Figure 5. Plot of the percent deviations of the fit functions for samples AI (red circles), AII (blue squares), and AIII (green triangles) from the heat capacity data against temperature on a logarithmic scale. Inset shows deviations below 1 K.

Figure 6. Plot of the calculated molar heat capacity data of nano- TiO_2 surface-bound water and hexagonal ice taken from ref. [26]. Inset shows data below data below 75 K.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Graphical Abstract