Heat capacity and thermodynamic functions of nano-TiO₂ rutile in relation to bulk-TiO₂ rutile

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Abstract

Several conflicting reports have suggested that the thermodynamic properties of materials change with respect to particle size. To investigate this, we have measured the constant pressure heat capacities of three 7 nm TiO₂ rutile 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 $T = (0.5 \text{ to } 320) \text{ K}$, and data were fitted to a sum of theoretical functions in the low temperature ($T < 15 \text{ K}$) range, orthogonal polynomials in the mid temperature range ($10 > T / \text{K} > 75$), and a combination of Debye and Einstein functions in the high temperature range ($T > 35 \text{ K}$). These fits were used to generate $C_{p,m}^\circ$, $\Delta_0^\text{T} S_m^\circ$, $\Delta_0^\text{T} H_m^\circ$, and ϕ_m° values at selected temperatures between (0.5 and 300) K for all samples. Standard molar entropies at $T = 298.15 \text{ K}$ were calculated to be (62.066, 59.422, and 58.035) $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ all with a standard uncertainty of $0.002 \cdot \Delta_0^\text{T} S_m^\circ$ for samples TiO₂·0.361H₂O, TiO₂·0.296H₂O, and TiO₂·0.244H₂O, respectively. These and other thermodynamic values were then corrected for water content to yield bare nano-TiO₂ thermodynamic properties at $T = 298.15 \text{ K}$, and we show that the resultant thermodynamic properties of anhydrous TiO₂ rutile nanoparticles equal those of bulk TiO₂ rutile 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

TiO₂ occurs naturally in three phases: rutile, anatase, and brookite [1-7]. Nanoparticles of TiO₂ anatase have received substantial attention for technological applications such as photocatalysis, while rutile is generally used for paints and cosmetics because of its high UV absorption but also has many technological uses [8-12]. Rutile is considered to be stable with respect to anatase and brookite both at high temperature and pressure [13-18]; however, phase stability has been reported to have a strong dependence on particle size wherein anatase becomes metastable with respect to rutile for 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 their bulk parent materials.

Several studies have suggested that the thermodynamic properties of nanoparticles differ from their bulk counterparts because the ratio of surface to bulk atoms is much larger in nanoparticles [24, 25]; however, other investigations have suggested the thermodynamic properties do not differ between bulk and nanophase materials [26, 27]. Contributions from the surface to the overall free energy certainly must be larger than contributions from the bulk for nanoparticles. Also, several studies have shown that surface energies are generally higher than those of the bulk which could explain the crossover in phase stability at lower sizes, but the larger surface energies reported could be attributed to adsorbates, which can greatly affect the surface energetics and therefore phase stability [22, 28-32].

The most common adsorbate on nanoparticles is water, and we have previously shown that, after accounting for the effects of adsorbed water, nanocrystalline TiO₂ has a similar heat capacity to that of bulk TiO₂ [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 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 rutile were done graphically and not quantitatively. We present heat capacity data measured for these well-characterized TiO_2 rutile 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 rutile are equal to those of bulk TiO_2 rutile 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

Rutile nanoparticles were prepared using a hydrothermal method with TiCl_4 (mass fraction purity 0.990, Alfa Aesar) as the starting material, the details of which can be found elsewhere [36]. The product was separated into three batches. Each batch was dehydrated in air at 100 °C for (2, 4, or 6) h 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 minute. The samples are designated herein as RI, RII, and RIII with stoichiometries of $\text{TiO}_2 \cdot 0.361\text{H}_2\text{O}$, $\text{TiO}_2 \cdot 0.296\text{H}_2\text{O}$, and $\text{TiO}_2 \cdot 0.244\text{H}_2\text{O}$ respectively. After drying, samples were stored in a glove box under argon atmosphere to prevent re-adsorption 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 with concentrations of 0.04 wt% and 840×10^{-6} , 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 (110) using the Scherrer formula [36-38], and particle sizes were determined to be 7 nm with an estimated standard uncertainty of 2 nm. Particles were also found to be phase pure to better than ± 0.05 mol%.

The morphology and particle size were further investigated using transmission electron microscopy (TEM) on a JEOL JEM 2000-FX under an acceleration voltage of 200 keV (see figure 2). Chemical composition was also determined with a scanning electron microscope (Phillips) equipped with an EDX analyzer. The TEM images show that the rutile particles formed as rods with 7 nm diameters and 35 nm lengths. This gives a rough surface area of $67 \text{ m}^2 \cdot \text{g}^{-1}$ which agrees relatively well with the BET measurements that gave a surface area of $104 \text{ m}^2 \cdot \text{g}^{-1}$ for all particles. This confirms the morphology of the particles, and shows that particle structure remains unchanged throughout the characterization measurements. The TGA and XRD measurements were also performed on each sample 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

Molar constant pressure heat capacities were determined with two techniques. From $T = (15 \text{ to } 320) \text{ K}$, measurements were made with an adiabatic calorimeter, the details of which have been published elsewhere [39, 40]. The calorimeter was gold plated with a volume of 10.5 cm^3 . Each of the three samples was pressed into pellets and then 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 within the range of $(0.5 \text{ to } 40) \text{ K}$ 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 (mass fraction purity 0.99999 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 values 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 $T = 15 \text{ K}$; however, the error increases to about $0.005 \cdot C_{p,m}$ in the region of $(15 \text{ to } 30) \text{ K}$ and becomes even worse above that due to radiation heat loss [41]. The adiabatic calorimeter produces values of heat capacity 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 $0.0005 \cdot C_{p,m}$ uncertainty 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 at constant pressure for the three nanocrystalline rutile samples RI, RII, and RIII are given separately in tables 3, 4, and 5. The data from the adiabatic and semi-adiabatic techniques have been combined and can be seen graphically in figure 3 where the inset shows results below $T = 15$ K. From the graph, the heat capacity is seen to increase as water content increases from sample to sample. It can also be seen that below about $T = 3$ K there is a slight Schottky anomaly in the heat capacity data.

4. Discussion

4.1 Nature of fitting equations

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 [42]

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

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, 43], and magnetic contributions take on various forms depending on the nature of the magnetism [24, 44-46]. 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 refer to the degeneracy for the ground and first excited states, respectively. Figure 4 shows the heat capacity results for all rutile 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, but the anomaly appears to arise from tunneling between hydroxyls shared between neighboring Ti atoms on the curved surface of the nanoparticle [47]. The low T region of the heat capacity was fitted with lattice, electronic and Schottky terms, and these fitting coefficients, the ranges of validity, and the %RMS for all samples are given in table 5 (the degeneracy terms in the Schottky anomalies, g_i , are set to unity for all fits).

Heat capacity values from $T = (10 - 75)$ K were fitted 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:

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

The high temperature data ($T > 35$ K) were fitted 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 wider 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 5. A plot of the deviations for each fit from the measured values as a function of temperature is given in figure 5 showing that the fits are non-systematic and correctly represent the actual data. Above 10 K, the %RMS of the fits is less than 1 %, from about (1 to 10) 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 RI, RII, and RIII, respectively. The standard molar entropies of nanophase TiO_2 rutile were calculated to be (62.066, 59.422, and 58.035) $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, all with a standard uncertainty of $0.002 \cdot \Delta_0^T S_m^\circ$, for samples RI ($\text{TiO}_2 \cdot 0.361\text{H}_2\text{O}$), RII ($\text{TiO}_2 \cdot 0.296\text{H}_2\text{O}$), and RIII ($\text{TiO}_2 \cdot 0.244\text{H}_2\text{O}$), 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 thermodynamic contributions of the water from the thermodynamic properties of the TiO_2 rutile nanoparticles using two models. This correction allows for a direct comparison between nano and bulk TiO_2 rutile thermodynamic properties (values for bulk TiO_2 rutile 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 values of hexagonal ice were extrapolated from 273 K to 298.15 K using a theoretical fit of Debye and Einstein functions (see figure 6 taken from ref. [26]) and subsequently used to generate the thermodynamic properties of hexagonal ice at $T = 298.15$ K [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 $\text{TiO}_2 \cdot 0.005\text{H}_2\text{O}$ by 11.3 % at most. The calculated thermodynamic properties of nano $\text{TiO}_2 \cdot 0.005\text{H}_2\text{O}$ rutile at $T = 298.15$ K along with their per cent differences from the bulk values are given in table 10.

Results given in table 10 provide insight about the relationship between bulk TiO_2 thermodynamics and those of bare nanoparticles. The heat capacity deviations for all samples are quite consistent and small (less than 1.5 %) showing that the heat capacity at $T = 298.15$ K of bare TiO_2 nanoparticles is the same as bulk TiO_2 within experimental uncertainty; however, the calculated enthalpy and entropy deviate from the bulk enthalpy and entropy of TiO_2 by about 3 % and 6 %, respectively, for all three samples. 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 bare nanoparticle heat capacity from that of bulk TiO_2 below $T = 298.15$ K and

are included in table 10. The per cent deviations for the enthalpy and entropy are relatively large; therefore, the calculated heat capacity deviates from the bulk heat capacity at temperatures lower than $T = 298.15$ K even though they agree at $T = 298.15$ K. Treating water bound to a TiO_2 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 TiO_2 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 TiO_2 surface bound water in which it was presumed that the differences in the molar heat capacities between RII and RI represent the heat capacity contribution of the outermost layers of water, and the differences in the molar heat capacities between RIII to RII represent the heat capacity contribution of the innermost layers of water [26]. Water heat capacity data for inner and outer layers of water were calculated by taking these differences between heat capacity values and dividing by the differences in the number of moles of water on the samples. Figure 6 shows the heat capacity of these two types of TiO_2 surface-bound water taken from ref. [26]. This model assumes that for water coverage up to 0.244 moles, the water behaves as tightly bound “inner” water; above this coverage, the water behaves as loosely bound “outer” water. Because the heat capacity values below about 35 K for the tightly bound “inner” water abruptly decrease to negative values, the data were fitted 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 results. The thermodynamic properties for the loosely bound “outer” water were determined from a spline fit of those heat capacity values (shown in figure 6). Subtracting these water contributions from the thermodynamic properties of the samples RI, RII, and RIII results

in thermodynamic properties that agree with those of bulk $\text{TiO}_2 \cdot 0.005\text{H}_2\text{O}$ better than the hexagonal ice model having a maximum difference from bulk values of 7.40 % (see table 10).

These calculations for the RI and RII samples yield heat capacity and entropy values with deviations from the bulk values less than 2 % and enthalpy values with deviations less than 4.4 %. However, the calculations for the RIII sample deviate much more because it has about a monolayer of water, and the inner water data below 35 K were unreasonable introducing uncertainty in the calculation. Together these suggest that at lower temperatures and for lower water coverage 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 coverage are in part treated as hydroxyls bound to Ti atoms that incidentally cause the Schottky anomaly in the low temperature heat capacity [47]. Nevertheless, for higher coverage 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 results after accounting for the uncertainty of the heat capacity values ($0.0005 \cdot C_{p,m}$ 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 rutile 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. Conclusions

Heat capacities of several 7 nm TiO₂ rutile 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 rutile and those published for bulk TiO₂ are a result of different amounts and types of surface bound water.

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References

- [1] A. F. Wells and A. Wells, *Structural inorganic chemistry* (Clarendon Press Oxford, 1975), Vol. 707.
- [2] K. Raman and M. Jackson, *Am. Mineral* **50**, 1086 (1965).
- [3] G. D. Sherman, *Soil Science Society of America Journal* **16**, 15 (1952).
- [4] I. T. Rosenqvist, in *Clays and Clay Minerals. Proc. 11th Nat. Conf. on Clays and Clay Minerals, WF Bradley, Ed., Monograph* 1963), pp. 11.
- [5] G. Nagelschmidt, H. Donnelly, and A. Morcom, *Mineralogical Magazine* **28**, 492 (1949).

- [6] F. Ennos and A. Scott, Analyses and Physical Tests.'Special Reports on the Mineral Resources of Great Britain **28**, 471 (1924).
- [7] G. Brindley and K. Robinson, Mineralogical Magazine **28**, 244 (1947).
- [8] M. A. Fox and M. T. Dulay, Chemical reviews **93**, 341 (1993).
- [9] A. Fujishima and T. N. Rao, Pure and applied chemistry **70**, 2177 (1998).
- [10] M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann, Chemical reviews **95**, 69 (1995).
- [11] B. Ohtani, Y. Ueda, S. Nishimoto, T. Kagiya, and H. Hachisuka, J. Chem. Soc, 1955 (1990).
- [12] M. Anpo, N. Aikawa, and Y. Kubokawa, The Journal of Physical Chemistry **88**, 3998 (1984).
- [13] E. Heald and C. Weiss, American Mineralogist **57**, 10 (1972).
- [14] G. Nodop, Hamburger Beitr. angewandte Mineralogie, u. Kristallphysik **1**, 239 (1956).
- [15] T. Ghosh, S. Dhabal, and A. Datta, Journal of applied physics **94**, 4577 (2003).
- [16] A. A. Gribb and J. F. Banfield, American Mineralogist **82**, 717 (1997).
- [17] E. Osborn, Journal of the American Ceramic Society **36**, 147 (2006).
- [18] S. J. Smith, R. Stevens, S. Liu, G. Li, A. Navrotsky, J. Boerio-Goates, and B. F. Woodfield, American Mineralogist **94**, 236 (2009).
- [19] A. Navrotsky, Geochem. Trans **4**, 34 (2003).
- [20] H. Zhang and J. F. Banfield, J. Mater. Chem. **8**, 2073 (1998).
- [21] H. Zhang and J. F. Banfield, The Journal of Physical Chemistry B **104**, 3481 (2000).
- [22] A. A. Levchenko, G. Li, J. Boerio-Goates, B. F. Woodfield, and A. Navrotsky, Chemistry of materials **18**, 6324 (2006).

- [23] M. Ranade *et al.*, Proceedings of the National Academy of Sciences of the United States of America **99**, 6476 (2002).
- [24] E. S. R. Gopal, *Specific heats at low temperatures* (Plenum Press New York, 1966), Vol. 227.
- [25] J. Rupp and R. Birringer, Physical Review B **36**, 7888 (1987).
- [26] J. Boerio-Goates, G. Li, L. Li, T. F. Walker, T. Parry, and B. F. Woodfield, Nano Letters **6**, 750 (2006).
- [27] N. X. Sun and K. Lu, Physical Review B **54**, 6058 (1996).
- [28] L. F. Liao, C. F. Lien, D. L. Shieh, M. T. Chen, and J. L. Lin, The Journal of Physical Chemistry B **106**, 11240 (2002).
- [29] C. L. Olson, J. Nelson, and M. S. Islam, The Journal of Physical Chemistry B **110**, 9995 (2006).
- [30] K. S. Finnie, D. J. Cassidy, J. R. Bartlett, and J. L. Woolfrey, Langmuir **17**, 816 (2001).
- [31] D. Yates, The Journal of Physical Chemistry **65**, 746 (1961).
- [32] A. Navrotsky, ChemPhysChem **12**, 2207 (2011).
- [33] J. B. Ott and J. Boerio-Goates, *Chemical Thermodynamics: Advanced Applications: Advanced Applications* (Academic Press, 2000), Vol. 2.
- [34] A. A. Levchenko, A. I. Kolesnikov, N. L. Ross, J. Boerio-Goates, B. F. Woodfield, G. Li, and A. Navrotsky, The Journal of Physical Chemistry A **111**, 12584 (2007).
- [35] N. L. Ross *et al.*, in *MRS Proceedings* (Cambridge Univ Press, 2011).
- [36] G. Li, L. Li, J. Boerio-Goates, and B. F. Woodfield, Journal of materials research **18**, 2664 (2003).

- [37] G. Li, J. Boerio-Goates, B. F. Woodfield, and L. Li, *Applied physics letters* **85**, 2059 (2004).
- [38] G. Li, L. Li, J. Boerio-Goates, and B. F. Woodfield, *Journal of the American Chemical Society* **127**, 8659 (2005).
- [39] J. Boerio-Goates and B. F. Woodfield, *Canadian journal of chemistry* **66**, 645 (1988).
- [40] B. Woodfield, J. Boerio-Goates, J. Shapiro, R. Putnam, and A. Navrotsky, *The Journal of Chemical Thermodynamics* **31**, 245 (1999).
- [41] J. C. Lashley, B. E. Lang, J. Boerio-Goates, B. F. Woodfield, T. W. Darling, F. Chu, A. Migliori, and D. Thoma, *The Journal of Chemical Thermodynamics* **34**, 251 (2002).
- [42] N. E. Phillips, *Critical Reviews in Solid State and Material Sciences* **2**, 467 (1971).
- [43] J. M. D. Coey, S. Von Molnar, and A. Torressen, *Journal of the Less Common Metals* **151**, 191 (1989).
- [44] R. Fisher, F. Bouquet, N. Phillips, J. Franck, G. Zhang, J. Gordon, and C. Marcenat, *Physical Review B* **64**, 134425 (2001).
- [45] K. Niira, *Physical Review* **117**, 129 (1960).
- [46] J. Majzlan, B. E. Lang, R. Stevens, A. Navrotsky, B. F. Woodfield, and J. Boerio-Goates, *American Mineralogist* **88**, 846 (2003).
- [47] J. Boerio-Goates, S. J. Smith, S. Liu, B. E. Lang, G. Li, B. F. Woodfield, and A. Navrotsky, *The Journal of Physical Chemistry C* **117**, 4544 (2013).
- [48] P. Flubacher, A. Leadbetter, and J. Morrison, *The Journal of Chemical Physics* **33**, 1751 (1960).
- [49] M. Sugisaki, H. Suga, and S. Seki, *Bulletin of the Chemical Society of Japan* **41**, 2591 (1968).

- [50] W. Giaque and J. Stout, *Journal of the American Chemical Society* **58**, 1144 (1936).
- [51] Y. Handa and D. Klug, *The Journal of Physical Chemistry* **92**, 3323 (1988).
- [52] O. Haida, T. Matsuo, H. Suga, and S. Seki, *The Journal of Chemical Thermodynamics* **6**, 815 (1974).

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

Sample	Provenance	Purification Method	Mass Fraction Purity	Method for Determining Purity	Particle Size Distribution
TiO ₂ ·0.361H ₂ O (RI)	Synthesized in-house	Calcination and Rinsing with Ethanol	> 0.999	ICP-OES	± 2 nm
TiO ₂ ·0.296H ₂ O (RII)	Synthesized in-house	Calcination and Rinsing with Ethanol	> 0.999	ICP-OES	± 2 nm
TiO ₂ ·0.244H ₂ O (RIII)	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 of TiO_2 rutile including pressures ($u(p) = 0.05 \cdot p$), molar mass, M , and sample mass, M_s ($u_r(M_s) = 0.001$).

	$\text{TiO}_2 \cdot 0.361\text{H}_2\text{O}$ (RI)	$\text{TiO}_2 \cdot 0.296\text{H}_2\text{O}$ (RII)	$\text{TiO}_2 \cdot 0.244\text{H}_2\text{O}$ (RIII)
$15 < (T / \text{K}) < 320$ Adiabatic measurements			
p (He gas) / kPa	2.27	2.27	2.40
M_s / g	9.286	7.834	6.4142
M / $\text{g} \cdot \text{mol}^{-1}$	86.369	85.198	84.262
$0.5 < (T / \text{K}) < 40$ Semi-adiabatic measurements			
p (He gas) / Pa	0.04	0.04	0.04
Apiezon-N / g	4.1×10^{-3}	5.6×10^{-3}	6.1×10^{-3}
M_s / g	0.2918	0.3149	0.3405

Table 3. Measured molar heat capacity values at constant pressure for rutile $\text{TiO}_2 \cdot 0.361\text{H}_2\text{O}$ (RI). $M = 86.369 \text{ g} \cdot \text{mol}^{-1}$. Values below $T = 25 \text{ K}$ 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 $(15 \text{ to } 25) \text{ K}$. Values above 25 K were collected using an adiabatic calorimeter at $p = 2.27 \text{ kPa}$ ($u(p) = 0.05 \cdot p$) and have a standard uncertainty of $0.004 \cdot C_{p,m}$ from $(25 \text{ to } 40) \text{ K}$, $0.002 \cdot C_{p,m}$ between $(40 \text{ and } 60) \text{ K}$, and $0.0005 \cdot C_{p,m}$ from $(60 \text{ to } 400) \text{ K}$.

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	$C_{p,m} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
0.47164	1.9429×10^{-4}	20.661	0.70867	153.60	39.735
0.51854	3.0097×10^{-4}	21.651	0.82277	154.86	40.007
0.54473	3.5951×10^{-4}	22.733	0.95246	158.69	41.275
0.57037	3.8737×10^{-4}	23.390	0.97863	159.95	41.593
0.59855	4.5014×10^{-4}	23.817	1.0974	163.78	42.716
0.62752	5.0299×10^{-4}	24.775	1.2167	165.04	42.973
0.66010	5.0095×10^{-4}	25.000	1.2650	168.88	44.050
0.69168	6.3684×10^{-4}	25.507	1.3071	170.14	44.278
0.72709	7.1381×10^{-4}	26.193	1.4361	171.92	44.791
0.76285	8.1372×10^{-4}	26.952	1.5660	173.98	45.472
0.80085	9.2384×10^{-4}	27.488	1.6437	177.03	46.163
0.83898	1.0482×10^{-3}	28.801	1.8638	179.09	46.888
0.88115	1.1775×10^{-3}	29.205	1.9448	180.34	47.141
0.92267	1.3511×10^{-3}	30.228	2.1166	182.14	47.620
0.96933	1.4608×10^{-3}	31.677	2.3802	185.45	48.387
1.0655	1.7026×10^{-3}	31.818	2.4528	187.26	48.787
1.1307	1.8925×10^{-3}	34.141	2.9734	190.56	49.750
1.1733	2.1657×10^{-3}	34.911	3.1266	192.38	50.022
1.2291	2.2992×10^{-3}	37.902	3.8137	195.69	50.963
1.2897	2.5707×10^{-3}	41.135	4.5963	197.50	51.368
1.3508	2.6812×10^{-3}	44.305	5.3087	200.82	52.165
1.4169	2.9766×10^{-3}	44.778	5.5254	202.31	52.456
1.4832	2.9843×10^{-3}	49.086	6.7011	202.63	52.500
1.5581	3.3108×10^{-3}	51.959	7.5368	205.94	53.307
1.6326	3.3690×10^{-3}	53.710	8.0471	207.43	53.699
1.7149	3.6627×10^{-3}	54.332	8.2124	207.76	53.625
1.7963	3.7584×10^{-3}	54.964	8.3414	211.08	54.343
1.8154	3.8175×10^{-3}	57.198	9.0209	212.56	54.879
1.8867	3.9956×10^{-3}	57.424	9.0634	212.89	54.745
1.9014	4.0543×10^{-3}	58.484	9.3736	216.21	55.616
1.9755	4.2199×10^{-3}	60.305	9.9053	217.69	55.844
2.0756	4.3325×10^{-3}	60.518	10.026	219.54	56.191
2.0922	4.3665×10^{-3}	63.649	10.938	221.35	56.645
2.1730	4.4995×10^{-3}	64.747	11.320	222.83	57.036

2.1982	4.4582×10^{-3}	67.911	12.266	224.31	57.059
2.3019	4.6754×10^{-3}	69.429	12.710	227.97	58.063
2.4181	4.8186×10^{-3}	72.629	13.745	229.45	58.277
2.5326	5.1211×10^{-3}	74.148	14.210	232.27	58.938
2.6609	5.4052×10^{-3}	77.381	15.233	233.12	59.111
2.7863	5.6585×10^{-3}	78.914	15.776	234.59	59.291
2.9269	5.9642×10^{-3}	82.180	16.809	237.41	59.988
3.0664	6.2537×10^{-3}	83.675	17.343	238.26	60.107
3.2203	6.7609×10^{-3}	84.847	17.656	239.73	60.585
3.3754	7.1161×10^{-3}	88.306	18.837	242.56	60.803
3.5449	7.6624×10^{-3}	88.421	18.935	243.41	61.100
3.7113	8.3654×10^{-3}	89.688	19.304	244.88	61.272
3.8948	9.3457×10^{-3}	92.929	20.379	247.71	61.820
4.0832	9.8743×10^{-3}	93.311	20.452	248.56	61.785
4.2827	0.011142	94.579	20.924	250.03	62.434
4.4914	0.011955	97.850	22.004	252.86	62.757
4.7101	0.013488	98.224	22.160	253.71	62.959
4.9401	0.014798	99.498	22.599	255.19	63.098
5.1805	0.016575	100.41	22.868	256.17	63.340
5.4335	0.018483	102.79	23.665	258.01	63.761
5.6991	0.020625	103.16	23.793	260.34	64.027
5.9781	0.023006	104.44	24.243	261.32	64.339
6.2703	0.025355	104.90	24.386	263.17	64.586
6.5775	0.028503	107.74	25.311	265.45	64.934
6.8993	0.031396	108.12	25.457	266.48	65.169
7.2345	0.035680	109.88	26.027	268.32	65.390
7.5889	0.039533	112.72	26.988	270.60	65.831
7.9567	0.045198	113.10	27.126	271.63	65.929
8.3450	0.049985	114.87	27.699	273.48	66.255
8.7516	0.057145	117.72	28.631	275.76	66.471
9.1767	0.062528	118.10	28.749	276.79	66.783
9.6284	0.072166	119.87	29.357	278.64	67.051
10.104	0.079700	123.11	30.390	280.92	67.389
10.609	0.092822	124.89	30.989	281.95	67.648
11.120	0.10886	128.14	32.021	283.80	67.711
11.668	0.13111	129.85	32.409	286.09	67.983
12.225	0.13895	129.92	32.569	288.96	68.645
12.838	0.16721	133.18	33.604	291.25	68.902
13.443	0.18841	134.59	33.978	294.11	69.382
14.110	0.21749	134.97	34.146	296.41	69.604
14.774	0.24004	138.40	35.255	299.28	69.981
15.516	0.28036	139.65	35.522	301.58	70.335
16.269	0.33421	140.02	35.723	304.45	70.656
17.081	0.39179	143.46	36.804	306.75	70.974
17.888	0.45657	144.71	37.013	309.61	70.764

18.780	0.52743	148.53	38.252	314.79	70.867
19.674	0.61033	149.79	38.540	319.97	71.393

Table 4. Measured molar heat capacity values at constant pressure for rutile $\text{TiO}_2 \cdot 0.296\text{H}_2\text{O}$ (RII). $M = 85.198 \text{ g} \cdot \text{mol}^{-1}$. Values below $T = 25 \text{ K}$ 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 $(15 \text{ to } 25) \text{ K}$. Values above 25 K were collected using an adiabatic calorimeter at $p = 2.27 \text{ kPa}$ ($u(p) = 0.05 \cdot p$) and have a standard uncertainty of $0.004 \cdot C_{p,m}$ from $(25 \text{ to } 40) \text{ K}$, $0.002 \cdot C_{p,m}$ between $(40 \text{ and } 60) \text{ K}$, and $0.0005 \cdot C_{p,m}$ from $(60 \text{ to } 400) \text{ K}$.

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	$C_{p,m} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
0.51935	2.9877×10^{-4}	17.726	0.42154	164.57	41.232
0.54459	3.9317×10^{-4}	17.873	0.42685	165.84	41.934
0.57065	4.1815×10^{-4}	18.817	0.49053	167.48	42.004
0.59821	4.9281×10^{-4}	19.658	0.59784	169.68	42.531
0.62708	5.2800×10^{-4}	19.674	0.57110	172.58	43.273
0.65914	5.8448×10^{-4}	20.690	0.67291	174.79	43.885
0.69131	6.8334×10^{-4}	21.659	0.77959	177.69	44.554
0.72612	7.9212×10^{-4}	22.650	0.84838	179.90	45.136
0.76210	8.5043×10^{-4}	22.767	0.87814	181.17	44.958
0.79979	9.9051×10^{-4}	23.814	1.0580	182.80	45.816
0.83875	1.1029×10^{-3}	24.610	1.1192	183.85	46.089
0.88038	1.2522×10^{-3}	25.039	1.1941	185.02	46.350
0.92294	1.3858×10^{-3}	26.180	1.3555	187.92	47.049
0.96928	1.5020×10^{-3}	26.228	1.3087	188.97	47.198
1.0141	1.6952×10^{-3}	27.548	1.5549	190.14	47.544
1.0654	1.7498×10^{-3}	28.561	1.7338	193.05	48.200
1.1163	1.9777×10^{-3}	28.783	1.7998	194.10	48.419
1.1730	2.1730×10^{-3}	30.288	1.9966	195.26	48.691
1.2284	2.4309×10^{-3}	30.993	2.1651	198.11	49.234
1.2900	2.6914×10^{-3}	31.637	2.3082	199.22	49.507
1.3511	2.8913×10^{-3}	33.310	2.5713	200.39	49.779
1.4184	3.0959×10^{-3}	33.614	2.7434	203.40	50.505
1.4841	3.2513×10^{-3}	34.798	2.9081	204.36	50.510
1.5587	3.4285×10^{-3}	36.583	3.3561	205.52	50.882
1.6331	3.6475×10^{-3}	39.065	3.8972	208.53	51.393
1.7165	3.7209×10^{-3}	39.900	4.0371	209.49	51.745
1.7286	3.7869×10^{-3}	42.495	4.7103	210.66	51.892
1.8156	3.8679×10^{-3}	46.225	5.6439	213.66	52.539
1.8900	4.0632×10^{-3}	50.371	6.7395	214.63	52.531
1.9019	4.0849×10^{-3}	51.607	7.0974	215.80	52.970
1.9983	4.2292×10^{-3}	53.967	7.7500	218.80	53.558
2.0932	4.4832×10^{-3}	54.322	7.7937	219.77	53.754
2.1853	4.6058×10^{-3}	54.773	7.9664	220.94	54.009
2.1978	4.5470×10^{-3}	56.642	8.4714	223.95	54.430
2.3019	4.7383×10^{-3}	56.831	8.5531	224.91	54.725
2.4190	4.9062×10^{-3}	59.531	9.2738	226.06	54.851

2.5330	5.1080×10^{-3}	60.146	9.5424	229.09	55.409
2.6609	5.4330×10^{-3}	62.869	10.279	230.05	55.907
2.7885	5.5680×10^{-3}	64.369	10.782	231.19	55.929
2.9275	5.8007×10^{-3}	67.123	11.519	234.24	56.351
3.0689	6.1227×10^{-3}	69.045	12.156	235.20	56.444
3.2238	6.2357×10^{-3}	71.834	12.974	236.34	56.826
3.3770	6.7781×10^{-3}	73.759	13.605	239.38	57.427
3.5483	7.2490×10^{-3}	76.579	14.444	240.35	57.459
3.7141	7.7268×10^{-3}	78.525	15.082	241.49	57.701
3.9020	8.2299×10^{-3}	81.374	15.945	242.39	57.617
4.0863	9.1952×10^{-3}	83.336	16.612	244.53	58.222
4.2911	9.9428×10^{-3}	85.356	17.159	245.50	58.517
4.4951	0.010851	87.449	17.917	246.64	58.439
4.7211	0.011712	89.272	18.522	247.54	58.663
4.9459	0.013271	92.443	19.543	250.65	59.440
5.1932	0.014621	94.191	20.082	251.80	59.407
5.4416	0.016383	97.349	21.088	252.69	59.580
5.7122	0.018199	99.11	21.681	255.81	59.914
5.9875	0.020360	102.29	22.686	256.95	60.304
6.2265	0.022140	104.06	23.269	257.85	60.433
6.2848	0.022295	107.25	24.330	260.97	60.780
6.5853	0.025077	109.03	24.878	262.11	60.996
6.8497	0.027342	112.23	25.948	263.00	61.420
6.9127	0.027427	114.02	26.505	266.13	61.771
7.2800	0.034587	117.23	27.510	267.27	62.038
7.5402	0.035405	119.02	28.156	268.16	62.038
7.6018	0.034365	122.25	29.106	271.28	62.697
7.9848	0.041081	124.03	29.604	272.43	62.501
8.2824	0.044242	127.28	30.683	273.32	62.601
8.3608	0.043884	129.06	31.195	276.45	63.079
8.7493	0.051017	130.20	31.479	277.59	63.551
9.1053	0.055492	132.32	32.194	278.49	63.531
9.1922	0.055124	134.10	32.725	281.62	63.797
9.6238	0.063734	135.36	33.038	282.75	64.129
9.6610	0.067110	136.59	33.333	283.64	64.333
10.024	0.069755	139.16	34.187	286.78	64.772
10.121	0.070250	140.42	34.565	287.91	64.937
10.231	0.081019	141.66	34.823	288.81	64.977
10.605	0.082810	144.23	35.661	291.94	65.496
11.197	0.096602	145.49	35.967	293.07	65.245
11.658	0.12592	146.73	36.310	293.98	65.538
12.184	0.13355	149.30	37.059	297.11	66.178
12.263	0.12852	150.57	37.441	298.24	66.033
12.759	0.14539	151.81	37.744	299.16	65.939
13.384	0.15882	154.39	38.520	302.28	66.496
14.099	0.19751	155.65	38.882	303.41	66.728
14.829	0.25417	156.89	39.133	307.45	67.160

15.506	0.26582	159.48	39.864	308.57	67.475
16.243	0.31200	160.74	40.139	313.75	68.067
17.118	0.35817	162.41	40.752	318.92	68.670

Table 5. Measured molar heat capacity values at constant pressure for rutile $\text{TiO}_2 \cdot 0.244\text{H}_2\text{O}$ (RIII). $M = 84.262 \text{ g} \cdot \text{mol}^{-1}$. Values below $T = 25 \text{ K}$ 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 $(15 \text{ to } 25) \text{ K}$. Data above 25 K were collected using 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 $(25 \text{ to } 40) \text{ K}$, $0.002 \cdot C_{p,m}$ between $(40 \text{ and } 60) \text{ K}$, and $0.0005 \cdot C_{p,m}$ from $(60 \text{ to } 400) \text{ K}$.

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	$C_{p,m} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
0.47164	2.0197×10^{-4}	10.607	0.096169	123.55	28.651
0.51874	2.9531×10^{-4}	10.662	0.098224	126.77	29.764
0.54497	3.4747×10^{-4}	11.160	0.10978	127.63	30.074
0.57045	3.8979×10^{-4}	11.711	0.12707	131.81	31.311
0.59875	4.6066×10^{-4}	12.263	0.14217	132.67	31.581
0.62730	5.1439×10^{-4}	12.810	0.16122	137.01	32.803
0.65959	5.6156×10^{-4}	12.865	0.16219	137.73	33.067
0.69137	6.7398×10^{-4}	13.460	0.18408	142.08	34.287
0.72661	7.6248×10^{-4}	14.147	0.21247	142.80	34.447
0.76191	8.6522×10^{-4}	14.810	0.24255	147.15	35.668
0.80034	9.9463×10^{-4}	15.558	0.28423	147.88	35.902
0.83847	1.1438×10^{-3}	16.289	0.32441	152.24	37.076
0.88069	1.3030×10^{-3}	17.098	0.38005	152.96	37.281
0.92225	1.4691×10^{-3}	17.903	0.43517	157.33	38.457
0.96888	1.6274×10^{-3}	18.796	0.51213	158.01	38.596
1.0134	1.8330×10^{-3}	19.680	0.58691	162.43	39.741
1.0649	2.0205×10^{-3}	20.666	0.68537	163.05	39.913
1.1149	2.2482×10^{-3}	21.639	0.78475	167.53	41.056
1.1713	2.5162×10^{-3}	22.717	0.91248	168.15	41.219
1.2263	2.6305×10^{-3}	23.453	0.93927	172.64	42.324
1.2884	2.8705×10^{-3}	23.783	1.0400	173.26	42.514
1.3514	3.1291×10^{-3}	24.961	1.1953	177.76	43.531
1.4181	3.3529×10^{-3}	25.523	1.2018	178.38	43.725
1.4849	3.5270×10^{-3}	26.124	1.3536	182.87	44.806
1.5581	3.7586×10^{-3}	27.421	1.5296	183.50	44.919
1.6338	3.9406×10^{-3}	27.824	1.5196	188.00	46.005
1.7147	4.1277×10^{-3}	28.702	1.7221	188.62	46.092
1.7286	4.1612×10^{-3}	29.193	1.7747	193.09	47.060
1.7969	4.3085×10^{-3}	30.131	1.9481	193.75	47.160
1.8154	4.3278×10^{-3}	31.547	2.2010	198.22	48.224
1.8869	4.4635×10^{-3}	31.632	2.2186	198.88	48.332
1.9021	4.4954×10^{-3}	33.118	2.5087	203.35	49.219
1.9765	4.6348×10^{-3}	34.369	2.7814	204.02	49.333
1.9985	4.5779×10^{-3}	34.672	2.8180	208.49	50.298
2.0757	4.7718×10^{-3}	36.086	3.0442	209.16	50.372
2.0929	4.8232×10^{-3}	37.393	3.4199	213.63	51.058
2.1746	4.9911×10^{-3}	39.912	4.0152	214.29	51.405

2.2004	4.9252×10^{-3}	40.742	4.1098	218.77	52.298
2.3030	5.1603×10^{-3}	43.551	4.8585	219.39	52.447
2.4200	5.2837×10^{-3}	47.341	5.8194	223.91	53.303
2.5346	5.4940×10^{-3}	51.568	6.9144	224.52	53.404
2.6619	5.6931×10^{-3}	53.039	7.2110	229.06	54.075
2.7896	5.9519×10^{-3}	54.923	7.7318	229.66	54.216
2.9302	6.2164×10^{-3}	56.259	8.1857	234.21	55.041
3.0707	6.6099×10^{-3}	57.346	8.4366	234.81	54.991
3.2250	6.9538×10^{-3}	60.683	9.4003	239.36	55.882
3.3795	7.4622×10^{-3}	64.910	10.659	239.97	56.107
3.5499	7.9064×10^{-3}	69.594	12.055	244.48	56.740
3.7168	8.6658×10^{-3}	70.031	12.152	245.12	56.790
3.9043	9.3135×10^{-3}	74.315	13.494	249.63	57.556
4.0881	0.010301	74.716	13.560	250.27	57.595
4.2932	0.011133	79.126	14.922	254.78	58.395
4.4972	0.012380	79.497	15.032	255.43	58.548
4.7227	0.013448	83.918	16.393	259.94	59.116
4.9470	0.015208	84.321	16.536	260.59	59.185
5.1948	0.016718	88.777	17.875	265.10	59.970
5.4422	0.019035	89.184	18.066	265.75	60.166
5.7141	0.020957	91.955	18.922	270.27	60.766
5.9872	0.024043	93.672	19.557	270.91	60.722
6.2864	0.026611	94.081	19.603	275.43	61.342
6.5853	0.030457	96.824	20.448	276.08	61.370
6.9149	0.033623	101.76	22.001	280.58	62.024
7.2431	0.038183	106.73	23.568	281.22	62.282
7.6046	0.041622	107.42	23.813	285.75	62.652
7.9656	0.047324	111.71	25.127	286.38	62.991
8.3610	0.052128	112.50	25.440	290.91	63.432
8.7589	0.059543	113.52	25.825	296.08	64.042
9.1939	0.066104	116.72	26.692	301.25	64.758
9.1945	0.065368	117.51	26.942	306.42	65.274
9.6304	0.074959	118.52	27.212	311.60	65.873
9.6621	0.075756	121.74	28.225	316.77	66.512
10.120	0.082969	122.63	28.541	322.59	67.328
10.139	0.084313				

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 rutile samples.

	Parameters	$\text{TiO}_2 \cdot 0.361\text{H}_2\text{O}$ (RI)	$\text{TiO}_2 \cdot 0.296\text{H}_2\text{O}$ (RII)	$\text{TiO}_2 \cdot 0.244\text{H}_2\text{O}$ (RIII)
Low T Fits	$\gamma / \text{J} \cdot \text{K}^{-2} \cdot \text{mol}^{-1}$	5.0799×10^{-4}	5.6401×10^{-4}	5.0175×10^{-4}
	$B_3 / \text{J} \cdot \text{K}^{-4} \cdot \text{mol}^{-1}$	1.0591×10^{-4}	8.5540×10^{-5}	1.0222×10^{-4}
	$B_5 / \text{J} \cdot \text{K}^{-6} \cdot \text{mol}^{-1}$	-6.3275×10^{-7}	-4.0714×10^{-7}	-3.9957×10^{-7}
	$B_7 / \text{J} \cdot \text{K}^{-8} \cdot \text{mol}^{-1}$	4.0695×10^{-9}	2.5985×10^{-9}	1.7538×10^{-9}
	$B_9 / \text{J} \cdot \text{K}^{-10} \cdot \text{mol}^{-1}$	-8.4230×10^{-12}	-4.8464×10^{-12}	-2.4774×10^{-12}
	n / mol	6.3687×10^{-4}	6.7230×10^{-4}	8.0415×10^{-4}
	Θ_{Sch} / K	4.8818	4.8753	4.8902
	%RMS	4.50	2.94	3.43
	Range / K	0.4716 – 14.19	0.5194 – 13.59	0.4716 – 11.98
Mid T Fits	$A_0 / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	-0.50602	-0.30390	-0.11532
	$A_1 / \text{J} \cdot \text{K}^{-2} \cdot \text{mol}^{-1}$	0.14552	0.090967	0.044133
	$A_2 / \text{J} \cdot \text{K}^{-3} \cdot \text{mol}^{-1}$	-0.015701	-0.010253	-5.6796×10^{-3}
	$A_3 / \text{J} \cdot \text{K}^{-4} \cdot \text{mol}^{-1}$	8.6669×10^{-4}	6.0228×10^{-4}	3.9631×10^{-4}
	$A_4 / \text{J} \cdot \text{K}^{-5} \cdot \text{mol}^{-1}$	-1.8653×10^{-5}	-1.2406×10^{-5}	-7.9599×10^{-6}
	$A_5 / \text{J} \cdot \text{K}^{-6} \cdot \text{mol}^{-1}$	1.9052×10^{-7}	1.1921×10^{-7}	7.3140×10^{-8}
	$A_6 / \text{J} \cdot \text{K}^{-7} \cdot \text{mol}^{-1}$	-7.5993×10^{-10}	-4.4583×10^{-10}	-2.6116×10^{-10}
	%RMS	1.45	2.86	1.40
	Range / K	14.19 – 55.61	13.59 – 35.06	11.98 – 44.78
High T Fits	m / mol	0.79845	0.83570	0.96799
	Θ_D / K	265.59	276.98	300.02
	n_1 / mol	1.4661	1.5639	1.7910
	$\Theta_{E,1} / \text{K}$	459.23	488.15	554.44
	n_2 / mol	1.6243	1.2864	0.93744
	$\Theta_{E,2} / \text{K}$	885.45	948.38	1153.2
	%RMS	0.312	1.34	0.515
	Range / K	55.61 – 320	35.06 – 320	44.78 – 320

Table 7. Standard thermodynamic functions of rutile $\text{TiO}_2 \cdot 0.361\text{H}_2\text{O}$ (RI). $\varphi_m^\circ = \Delta_o^T S_m^\circ - \Delta_o^T H_m^\circ / T$. $M = 86.369 \text{ g} \cdot \text{mol}^{-1}$. 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	2.8629×10^{-4}	0	0	0
1	1.5731×10^{-3}	5.2506×10^{-4}	4.1565×10^{-7}	1.0941×10^{-4}
1.5	3.0872×10^{-3}	1.4581×10^{-3}	1.5919×10^{-6}	3.9687×10^{-4}
2	4.2166×10^{-3}	2.5120×10^{-3}	3.4372×10^{-6}	7.9345×10^{-4}
2.5	5.0384×10^{-3}	3.5427×10^{-3}	5.7540×10^{-6}	1.2410×10^{-3}
3	6.0604×10^{-3}	4.5449×10^{-3}	8.5104×10^{-6}	1.7081×10^{-3}
3.5	7.6101×10^{-3}	5.5883×10^{-3}	1.1905×10^{-5}	2.1870×10^{-3}
4	9.6779×10^{-3}	6.7343×10^{-3}	1.6207×10^{-5}	2.6825×10^{-3}
4.5	0.012200	8.0152×10^{-3}	2.1657×10^{-5}	3.2025×10^{-3}
5	0.015234	9.4526×10^{-3}	2.8492×10^{-5}	3.7543×10^{-3}
6	0.022851	0.012880	4.7406×10^{-5}	4.9790×10^{-3}
7	0.032502	0.017096	7.4877×10^{-5}	6.3989×10^{-3}
8	0.044887	0.022211	1.1332×10^{-4}	8.0456×10^{-3}
9	0.060593	0.028369	1.6576×10^{-4}	9.9512×10^{-3}
10	0.080253	0.035733	2.3582×10^{-4}	0.012150
12.5	0.15110	0.060617	5.1789×10^{-4}	0.019186
15	0.26136	0.097236	1.0242×10^{-3}	0.028958
20	0.63679	0.21843	3.1752×10^{-3}	0.059673
25	1.2514	0.42205	7.7947×10^{-3}	0.11027
30	2.0944	0.72135	0.016066	0.18580
35	3.1258	1.1196	0.029051	0.28959
40	4.2985	1.6122	0.047560	0.42318
45	5.5818	2.1916	0.072220	0.58672
50	6.9491	2.8499	0.10352	0.77950
55	8.3774	3.5787	0.14181	1.0003
60	9.8507	4.3706	0.18737	1.2478
65	11.361	5.2184	0.24038	1.5203
70	12.906	6.1167	0.30103	1.8162
75	14.489	7.0609	0.36951	2.1341
80	16.107	8.0475	0.44598	2.4727
85	17.749	9.0732	0.53062	2.8306
90	19.399	10.134	0.62348	3.2067
95	21.064	11.228	0.72463	3.6000
100	22.740	12.351	0.83414	4.0093
110	26.086	14.675	1.0783	4.8725
120	29.376	17.087	1.3557	5.7894
130	32.576	19.565	1.6655	6.7533
140	35.676	22.093	2.0068	7.7585
150	38.675	24.657	2.3787	8.7994

160	41.569	27.246	2.7800	9.8714
170	44.351	29.851	3.2097	10.970
180	47.010	32.461	3.6666	12.091
190	49.536	35.071	4.1495	13.232
200	51.930	37.674	4.6569	14.389
210	54.200	40.263	5.1876	15.560
220	56.360	42.834	5.7405	16.741
230	58.425	45.386	6.3145	17.931
240	60.399	47.914	6.9087	19.128
250	62.277	50.418	7.5222	20.329
260	64.043	52.896	8.1539	21.534
270	65.688	55.344	8.8026	22.741
273.15	66.183	56.109	9.0103	23.122
280	67.224	57.761	9.4673	23.949
290	68.694	60.146	10.147	25.156
298.15	69.878	62.066	10.712	26.139
300	70.146	62.499	10.841	26.362

Table 8. Standard thermodynamic functions of rutile $\text{TiO}_2 \cdot 0.296\text{H}_2\text{O}$ (RII). $\varphi_m^\circ = \Delta_o^T S_m^\circ - \Delta_o^T H_m^\circ / T$. $M = 85.198 \text{ g} \cdot \text{mol}^{-1}$. 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	2.8451×10^{-4}	0	0	0
1	1.6176×10^{-3}	5.5508×10^{-4}	4.3792×10^{-7}	1.1716×10^{-4}
1.5	3.2644×10^{-3}	1.5386×10^{-3}	1.6789×10^{-6}	4.1929×10^{-4}
2	4.2757×10^{-3}	2.6290×10^{-3}	3.5862×10^{-6}	8.3592×10^{-4}
2.5	5.0468×10^{-3}	3.6657×10^{-3}	5.9162×10^{-6}	1.2992×10^{-3}
3	5.9488×10^{-3}	4.6624×10^{-3}	8.6564×10^{-6}	1.7769×10^{-3}
3.5	7.1084×10^{-3}	5.6624×10^{-3}	1.1908×10^{-5}	2.2603×10^{-3}
4	8.6746×10^{-3}	6.7083×10^{-3}	1.5832×10^{-5}	2.7502×10^{-3}
4.5	0.010816	7.8475×10^{-3}	2.0679×10^{-5}	3.2522×10^{-3}
5	0.013552	9.1239×10^{-3}	2.6748×10^{-5}	3.7743×10^{-3}
6	0.020124	0.012160	4.3498×10^{-5}	4.9100×10^{-3}
7	0.028533	0.015863	6.7630×10^{-5}	6.2016×10^{-3}
8	0.039602	0.020363	1.0145×10^{-4}	7.6814×10^{-3}
9	0.053953	0.025820	1.4793×10^{-4}	9.3839×10^{-3}
10	0.072238	0.032414	2.1067×10^{-4}	0.011347
12.5	0.13946	0.055129	4.6826×10^{-4}	0.017668
15	0.24515	0.089246	9.4008×10^{-4}	0.026574
20	0.60239	0.20369	2.9715×10^{-3}	0.055110
25	1.1793	0.39592	7.3324×10^{-3}	0.10262
30	1.9836	0.67855	0.015144	0.17374
35	2.9748	1.0568	0.027476	0.27175
40	4.1011	1.5262	0.045117	0.39830
45	5.3313	2.0794	0.068659	0.55362
50	6.6436	2.7084	0.098566	0.73704
55	8.0220	3.4057	0.13521	0.94746
60	9.4532	4.1648	0.17887	1.1835
65	10.926	4.9793	0.22981	1.4439
70	12.432	5.8440	0.28819	1.7270
75	13.965	6.7538	0.35417	2.0315
80	15.526	7.7047	0.42788	2.3562
85	17.113	8.6935	0.50947	2.6997
90	18.715	9.7169	0.59903	3.0610
95	20.336	10.772	0.69665	3.4389
100	21.968	11.857	0.80241	3.8326
110	25.220	14.103	1.0384	4.6634
120	28.399	16.435	1.3066	5.5467
130	31.464	18.830	1.6060	6.4760
140	34.407	21.270	1.9354	7.4454
150	37.238	23.741	2.2937	8.4492

160	39.962	26.232	2.6798	9.4827
170	42.580	28.733	3.0926	10.541
180	45.080	31.239	3.5310	11.622
190	47.452	33.740	3.9938	12.720
200	49.687	36.232	4.4796	13.833
210	51.785	38.707	4.9871	14.959
220	53.759	41.162	5.5149	16.094
230	55.629	43.593	6.0619	17.237
240	57.415	45.999	6.6272	18.386
250	59.129	48.378	7.2100	19.538
260	60.767	50.729	7.8095	20.692
270	62.313	53.052	8.4250	21.848
273.15	62.778	53.777	8.6220	22.212
280	63.748	55.344	9.0554	23.003
290	65.068	57.604	9.6996	24.158
298.15	66.079	59.422	10.234	25.097
300	66.304	59.831	10.356	25.310

Table 9. Standard thermodynamic functions of rutile $\text{TiO}_2 \cdot 0.244\text{H}_2\text{O}$ (RIII). $\varphi_m^\circ = \Delta_o^T S_m^\circ - \Delta_o^T H_m^\circ / T$. $M = 84.262 \text{ g} \cdot \text{mol}^{-1}$. 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	2.4642×10^{-4}	0	0	0
1	1.7657×10^{-3}	5.6438×10^{-4}	4.4952×10^{-7}	1.1486×10^{-4}
1.5	3.5884×10^{-3}	1.6482×10^{-3}	1.8171×10^{-6}	4.3676×10^{-4}
2	4.6651×10^{-3}	2.8425×10^{-3}	3.9057×10^{-6}	8.8963×10^{-4}
2.5	5.4283×10^{-3}	3.9661×10^{-3}	6.4305×10^{-6}	1.3939×10^{-3}
3	6.3644×10^{-3}	5.0333×10^{-3}	9.3640×10^{-6}	1.9119×10^{-3}
3.5	7.7627×10^{-3}	6.1123×10^{-3}	1.2873×10^{-5}	2.4343×10^{-3}
4	9.7578×10^{-3}	7.2721×10^{-3}	1.7227×10^{-5}	2.9654×10^{-3}
4.5	0.012390	8.5671×10^{-3}	2.2737×10^{-5}	3.5144×10^{-3}
5	0.015649	0.010036	2.9721×10^{-5}	4.0915×10^{-3}
6	0.023934	0.013587	4.9323×10^{-5}	5.3662×10^{-3}
7	0.034456	0.018037	7.8331×10^{-5}	6.8473×10^{-3}
8	0.047339	0.023451	1.1902×10^{-4}	8.5741×10^{-3}
9	0.063036	0.029903	1.7394×10^{-4}	0.010575
10	0.082219	0.037503	2.4625×10^{-4}	0.012878
12.5	0.14996	0.062550	5.2999×10^{-4}	0.020151
15	0.25637	0.098632	1.0288×10^{-3}	0.030047
20	0.61095	0.21617	3.1138×10^{-3}	0.060480
25	1.1721	0.40890	7.4842×10^{-3}	0.10953
30	1.9358	0.68715	0.015173	0.18138
35	2.8795	1.0543	0.027143	0.27880
40	3.9711	1.5086	0.044214	0.40325
45	5.1770	2.0450	0.067044	0.55514
50	6.4674	2.6566	0.096125	0.73411
55	7.8195	3.3360	0.13182	0.93928
60	9.2191	4.0761	0.17440	1.1694
65	10.660	4.8706	0.22408	1.4233
70	12.139	5.7145	0.28106	1.6994
75	13.657	6.6036	0.34554	1.9964
80	15.196	7.5341	0.41767	2.3133
85	16.746	8.5018	0.49752	2.6486
90	18.311	9.5032	0.58515	3.0015
95	19.886	10.535	0.68064	3.3707
100	21.466	11.596	0.78402	3.7553
110	24.616	13.789	1.0144	4.5671
120	27.720	16.065	1.2762	5.4300
130	30.744	18.404	1.5686	6.3376
140	33.665	20.790	1.8907	7.2845
150	36.467	23.209	2.2415	8.2653

160	39.143	25.648	2.6197	9.2754
170	41.689	28.098	3.0239	10.311
180	44.103	30.550	3.4530	11.367
190	46.385	32.996	3.9055	12.441
200	48.539	35.431	4.3803	13.530
210	50.569	37.849	4.8759	14.630
220	52.483	40.246	5.3913	15.740
230	54.289	42.619	5.9252	16.857
240	56.000	44.966	6.4767	17.980
250	57.624	47.285	7.0449	19.106
260	59.169	49.576	7.6290	20.234
270	60.636	51.837	8.2280	21.362
273.15	61.082	52.542	8.4198	21.718
280	62.021	54.067	8.8414	22.491
290	63.318	56.266	9.4682	23.617
298.15	64.313	58.035	9.9883	24.534
300	64.533	58.434	10.107	24.742

Table 10. All thermodynamic values of TiO₂ rutile at $T = 298.15$ K and per cent deviation from bulk thermodynamic properties derived from two water correction models: the first model assumes water is similar to hexagonal ice H₂O_(s) (thermodynamic properties extrapolated to $T = 298.15$ K), and the second follows the calculation of ref. [26] assuming some loosely and some tightly bound water H₂O_(in/out). These calculated thermodynamic values have an estimated standard uncertainty of at most $0.07 \cdot X$ and are discussed in section 4.2.

		$\Delta_o^T C_m^\circ /$ J·K ⁻¹ ·mol ⁻¹	Error / %	$\Delta_o^T S_m^\circ /$ J·K ⁻¹ ·mol ⁻¹	Error / %	$\Delta_o^T H_m^\circ /$ J·K ⁻¹ ·mol ⁻¹	Error / %	$\phi_m^\circ /$ J·K ⁻¹ ·mol ⁻¹	error / %
H ₂ O _(s)	RI	55.51	0.680	47.28	6.17	8.441	2.24	18.96	11.3
	RII	54.34	1.45	47.33	6.06	8.378	2.98	19.23	10.1
	RIII	54.67	0.852	48.11	4.51	8.464	1.98	19.72	7.82
H ₂ O _(in/out)	RI	54.46	1.23	50.77	0.851	8.854	2.54	22.12	3.41
	RII	56.24	1.99	51.32	1.94	9.012	4.36	22.44	4.92
	RIII	58.93	6.87	52.48	4.28	9.274	7.40	22.97	7.39

Figure Captions

Figure 1. XRD patterns of 7 nm $\text{TiO}_2 \cdot 0.361\text{H}_2\text{O}$ rutile particles (RI). XRD patterns for RII and RII samples are equivalent.

Figure 2. TEM micrograph of 7 nm $\text{TiO}_2 \cdot 0.361\text{H}_2\text{O}$ rutile particles (RI) on a holey carbon support. TEM images for RII and RIII are equivalent.

Figure 3. Plot of the molar heat capacity data at constant pressure as a function of temperature for the nanophase TiO_2 rutile samples $\text{TiO}_2 \cdot 0.361\text{H}_2\text{O}$ (RI- red circles), $\text{TiO}_2 \cdot 0.296\text{H}_2\text{O}$ (RII- blue squares), and $\text{TiO}_2 \cdot 0.244\text{H}_2\text{O}$ (RIII- 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. Low temperature ($T < 8$ K) plot of the molar heat capacity data of TiO_2 rutile at constant pressure for samples RI (red circles), RII (blue squares), and RIII (green triangles). The inset shows the heat capacity of the Schottky anomaly for each of the samples.

Figure 5. Plot of the per cent deviations of the fit functions for samples RI (red circles), RII (blue squares), and RIII (green triangles) from the heat capacity data against temperature on a logarithmic scale. Inset shows deviations below $T = 1$ K.

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

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Graphical Abstract