2018-06-01

Application of the Entropy Concept to Thermodynamics and Life Sciences: Evolution Parallels Thermodynamics, Cellulose Hydrolysis Thermodynamics, and Ordered and Disordered Vacancies Thermodynamics

Marko Popovic

Brigham Young University

www.manaraa.com

Application of the Entropy Concept to Thermodynamics and Life Sciences: Evolution

Parallels Thermodynamics, Cellulose Hydrolysis Thermodynamics, and

Ordered and Disordered Vacancies Thermodynamics

Marko Popovic

A dissertation submitted to the faculty of
Brigham Young University
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

Brian F. Woodfield, Chair
Lee Duane Hansen
Harold Dennis Tolley
James E. Patterson
Jeremy Andrew Johnson

Department of Chemistry and Biochemistry

Brigham Young University

ABSTRACT

Application of the Entropy Concept to Thermodynamics and Life Sciences: Evolution
Parallels Thermodynamics, Cellulose Hydrolysis Thermodynamics, and
Ordered and Disordered Vacancies Thermodynamics

Marko Popovic
Department of Chemistry and Biochemistry, BYU
Doctor of Philosophy

Entropy, first introduced in thermodynamics, is used in a wide range of fields. Chapter 1 discusses some important theoretical and practical aspects of entropy: what is entropy, is it subjective or objective, and how to properly apply it to living organisms. Chapter 2 presents applications of entropy to evolution. Chapter 3 shows how cellulosic biofuel production can be improved. Chapter 4 shows how lattice vacancies influence the thermodynamic properties of materials.

To determine the nature of thermodynamic entropy, Chapters 1 and 2 describe the roots, the conceptual history of entropy, as well as its path of development and application. From the viewpoint of physics, thermal entropy is a measure of useless energy stored in a system resulting from thermal motion of particles. Thermal entropy is a non-negative objective property. The negentropy concept, while mathematically correct, is physically misleading. This dissertation hypothesizes that concepts from thermodynamics and statistical mechanics can be used to define statistical measurements, similar to thermodynamic entropy, to summarize the convergence of processes driven by random inputs subject to deterministic constraints. A primary example discussed here is evolution in biological systems. As discussed in this dissertation, the first and second laws of thermodynamics do not translate directly into parallel laws for the biome. But, the fundamental principles on which thermodynamic entropy is based are also true for information. Based on these principles, it is shown that adaptation and evolution are stochastically deterministic.

Chapter 3 discusses the hydrolysis of cellulose to glucose, which is a key reaction in renewable energy from biomass and in mineralization of soil organic matter to CO_2. Conditional thermodynamic parameters, $\Delta_{hyd}G'$, $\Delta_{hyd}H'$, and $\Delta_{hyd}S'$, and equilibrium glucose concentrations are reported for the reaction $C_6H_{10}O_5(\text{cellulose}) + H_2O(l) \rightleftarrows C_6H_{12}O_6(aq)$ as functions of temperature from 0 to 100ºC. Activity coefficients of aqueous glucose solution were determined as a function of temperature. The results suggest that producing cellulosic biofuels at higher temperatures will result in higher conversion.

Chapter 4 presents the data and a theory relating the linear term in the low temperature heat capacity to lattice vacancy concentration. The theory gives a quantitative result for disordered vacancies, but overestimates the contribution from ordered vacancies because ordering leads to a decreased influence of vacancies on heat capacity.

Keywords: negentropy, Shannon entropy, information, order, disorder, Gibbs free energy, cellulose hydrolysis, lattice vacancies, heat capacity, samarium and neodymium doped ceria

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF FIGURES

ix

1 ENTROPY WONDERLAND: A REVIEW OF THE ENTROPY CONCEPT

1.1 Abstract

The entropy concept was introduced in the mid-nineteenth century by Clausius and has been continually enriched, developed and interpreted by researchers in many scientific disciplines. The use of entropy in a wide range of fields has led to inconsistencies in its application and interpretation, as summarized by von Neuman "No one knows what entropy really is. (Tribus and McIrving, Scientific American, 1971, vol. 225, pp. 179-188)" To resolve this problem, thermodynamics and other scientific disciplines face several crucial questions concerning the entropy concept: (1) What is the physical meaning of entropy? (2) Is entropy a subjective or an objective property? (3) How to apply entropy to living organisms? To answer these questions, this chapter describes the roots, the conceptual history, as well the path of development and application in various scientific disciplines, including classical thermodynamics, statistical mechanics and life sciences. This and the next three chapters discuss applications of the entropy concept to evolution, cellulose hydrolysis, and thermodynamics of lattice defects.

Keywords: Thermal entropy; Residual entropy; Shannon entropy; Total entropy; Negentropy; Equilibrium thermodynamics; Nonequilibrium thermodynamics; Statistical mechanics; Life sciences.

"I intentionally chose the word Entropy as similar as possible to the word Energy."

Rudolf Clausius [1]

"The law that entropy always increases holds, I think, the supreme position among the laws of nature…" Sir Arthur Eddington [2]

"Classical thermodynamics is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts"

Albert Einstein [3]

1.2 Introduction – What is entropy?

The entropy concept is frequently used in many scientific disciplines, including equilibrium and non-equilibrium thermodynamics [4, 5], statistical mechanics [6-9], cosmology [10], life sciences [11-15], chemistry and biochemistry [4, 16], geosciences [17], linguistics [18], social sciences [19, 20] and information theory [21]. The use of entropy in a diverse range of disciplines has led to inconsistent application and interpretation of entropy [22-25], summarized in von Neumann's words: "*Whoever uses the term 'entropy' in a discussion always wins since no one knows what entropy really is, so in a debate one always has the advantage*" [24]. The situation has even been described as "*unbelievable confusion*" [22].

The confusion stems from a lack of consensus among scientists on key aspects of entropy, including its physical meaning, philosophical nature and application to living organisms. The physical meaning of entropy is debated and has been interpreted as information missing to completely specify motion of particles [23, 26], as a measure of dispersal of energy [27], and as energy that cannot be converted into work [1, 28, 29] (see section 1.3). An important philosophical question about entropy is whether it is subjective [23, 30, 31] or objective [32-35], i.e., does it depend on or exist independently of an observer (see section 1.4). Finally, application of entropy to living organisms is analyzed, including the concept of negentropy, low entropy of living structures, and change in entropy of living organisms during their lifespans [36, 37] (see section 1.5).

1.2.1 Entropy in Chemical Thermodynamics

A thermodynamic system is the material content of a macroscopic volume in space (the rest of the universe being the surroundings). Systems are categorized as isolated (constant mass, constant energy), closed (constant mass, exchanges energy with the surroundings), or open (exchanges both mass and energy with the surroundings) [4]. A thermodynamic system is in a state defined by state variables, such as the amount of matter, volume, temperature, entropy, enthalpy, energy and pressure. Of particular importance is the state of thermodynamic equilibrium of a system where there is no net flow of energy or matter between parts of the system.

The change in a thermodynamic state defines a thermodynamic process [4]. Thermodynamic processes are categorized into reversible and irreversible. In a reversible process, the system is infinitesimally out of (approximately in) equilibrium during the entire process [4]. The process can be reversed by an infinitesimal change in some property of the system or the surroundings. [4, 38]. In an irreversible process the system is not at equilibrium during the process.

Entropy was introduced in the nineteenth century in an attempt to explain the inefficiency of steam engines. In 1803, Lazarus Carnot wrote that any natural process has an inherent tendency to dissipate energy in unproductive ways [39]. In 1824, His son, Sadi Carnot, introduced the concept of producing work from heat flow, with a limiting maximum efficiency [40]. Definition of the thermodynamic system and a corresponding thermodynamic cycle was key to developing thermodynamics. The Carnot cycle was the first ever thermodynamic generalization of an engine (Figure 1-1) and led to great improvement in steam engine efficiency.

Thermodynamic cycles are indispensable in engineering because they allow analysis of the relationships among energy, heat, work and entropy. To help improve existing and invent new

www.manaraa.com

engines, other thermodynamic cycles analogous to the Carnot cycle were developed. An example is the Otto cycle, which describes the working of gasoline engines used in cars (Figure 1-2). An analysis of the Otto cycle from the system perspective is shown in Figure 1-3.
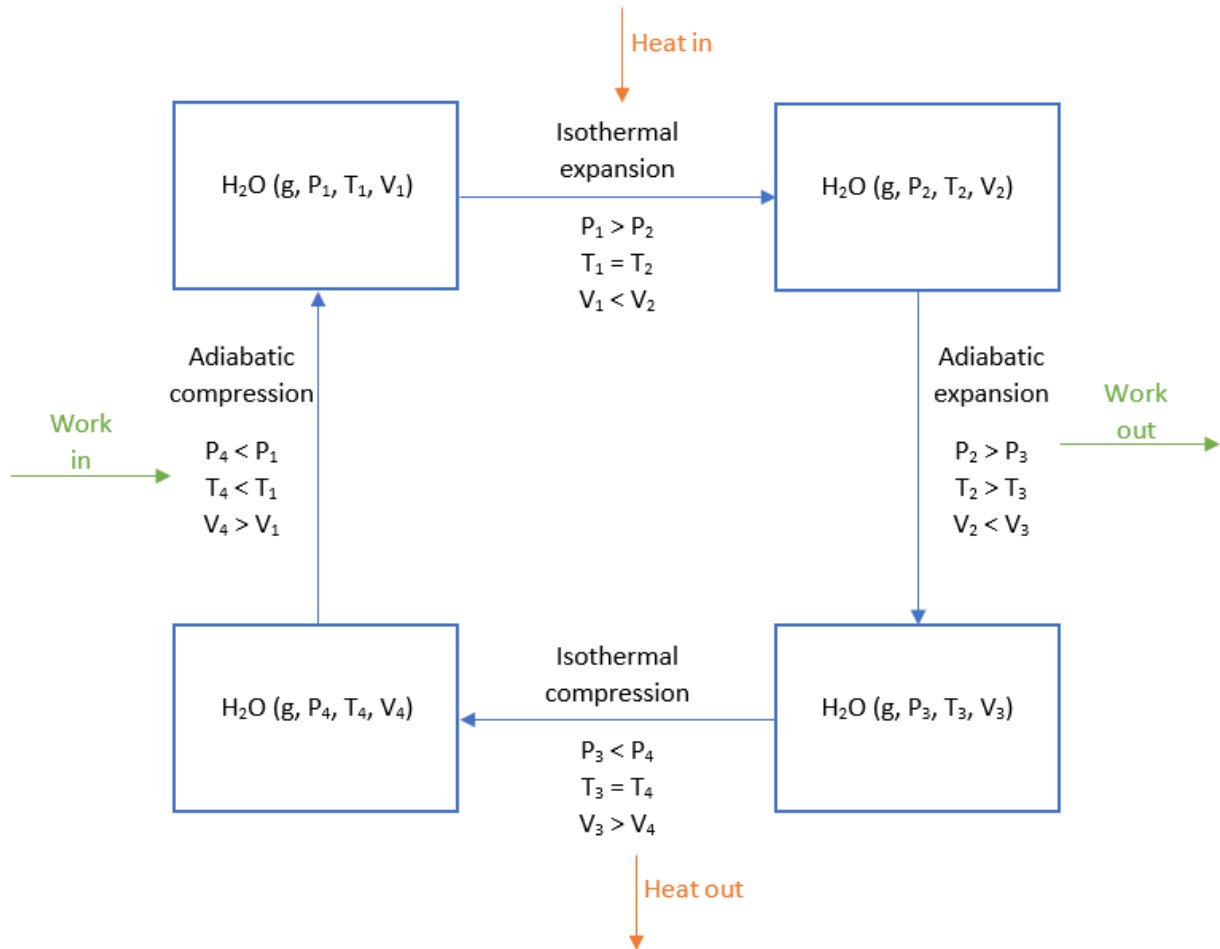
Figure 1-1:The Carnot cycle consist of four steps: isothermal expansion, adiabatic expansion, isothermal compression and adiabatic compression. The system undergoing the process is closed and contains only steam.

Clausius [1, 28, 29] realized that the Carnots had found an early statement of the Second Law of Thermodynamics, also known as the entropy law [20], and was the first to explicitly suggest the basic idea of entropy and the second law of thermodynamics [1]. Entropy was introduced with the following summary statements of the first and second laws of thermodynamics "*The energy of the*

universe is constant; the entropy of the universe tends to a maximum." [1]. Clausius defined change in thermodynamic entropy *dS* through heat exchanged in a reversible process Q_{rev} and temperature at which the process happened *T*.

$$dS = \frac{dQ_{rev}}{T} \tag{1}$$

Equation (1) holds for a closed thermodynamic system performing a reversible process. Thus, *TdS* is the minimum amount of energy lost to the surroundings as heat in a reversible process. Irreversible processes are less efficient, so they dissipate even more energy as heat.

(a) *T–s* diagram
(isentropic cycle)

(b) *p–V* diagram
(isentropic cycle)

(c) *p–V* indicator diagram
(actual cycle)

Combustion (4s to 1)
and power (1 to 2s)

Exhaust
(2s to 3 to 3′)

Intake
(3′ to 3)

Compression
(3 to 4s)

(d) The operation of a four-stroke Otto cycle engine
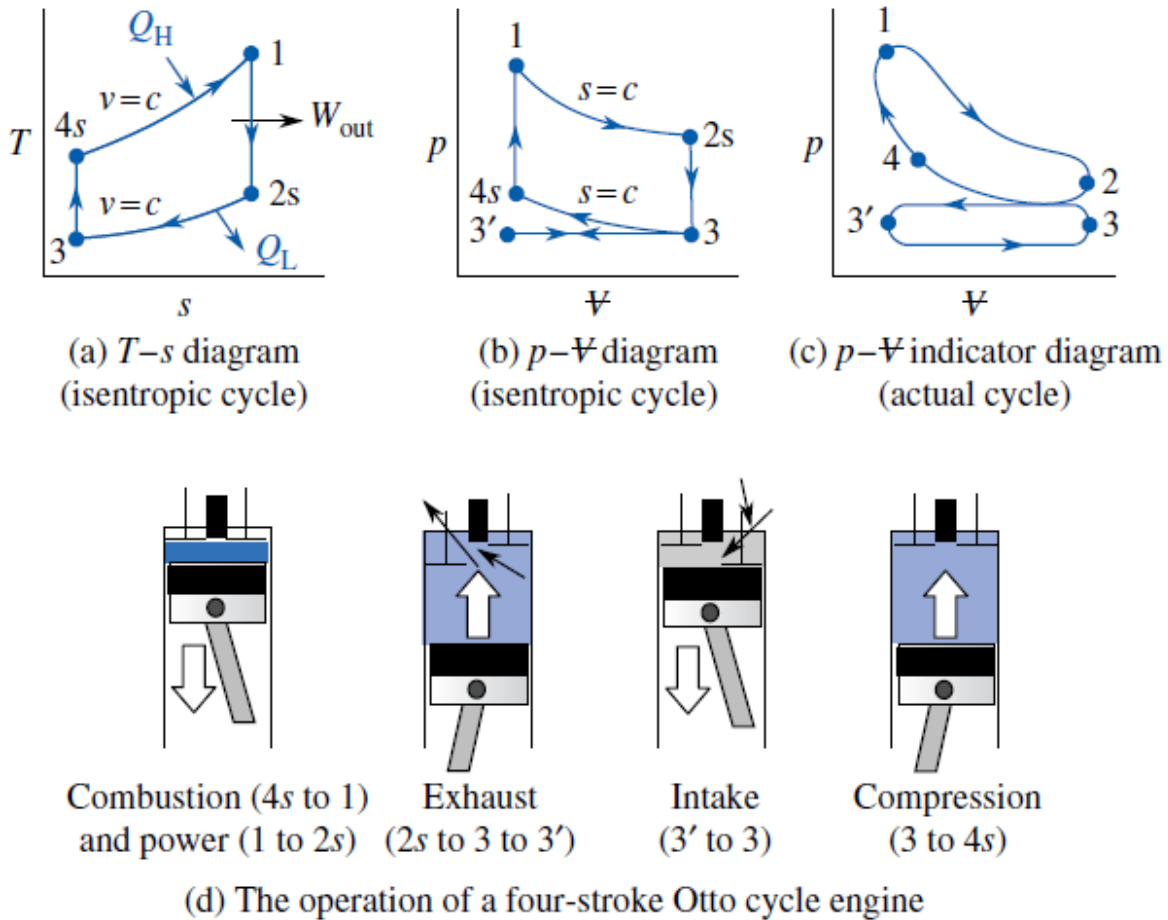
Figure 1-2: The Otto cycle describes a gasoline automobile engine. (a) A T-s diagram shows the minimum heat that must be lost in the process through the surface enclosed by the process. (b) A

www.manaraa.com

p-V diagram showing the maximum work that can be extracted by a reversible engine. (c) A p-V diagram showing the actual work extracted in a real engine. (d) A scheme showing the four stages in the Otto cycle: combustion and power, exhaust, intake and compression. (figure taken with permission from reference [37]).
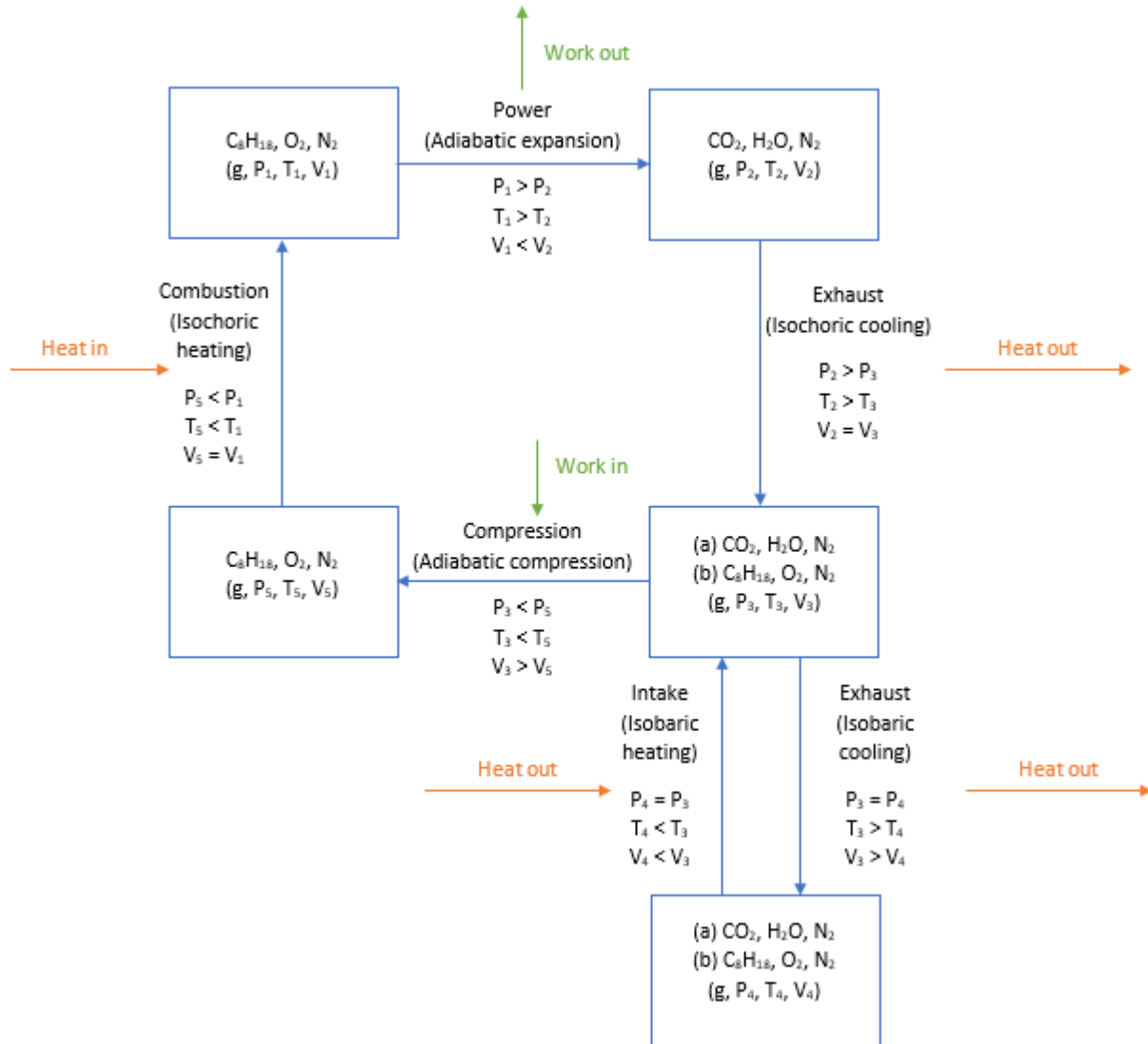
Figure 1-3: The Otto cycle describing a gasoline automobile engine. The system undergoing the Otto cycle is a mixture of hydrocarbons, oxygen and nitrogen, from intake to combustion, and CO_2, water and nitrogen, from combustion to exhaust.

In a reversible process, thermodynamic entropy of the universe is a conserved property (i.e., is constant) [4, 5, 37]. Entropy of the universe increases in an irreversible process [4, 5, 37]. Since

all spontaneous processes are irreversible, the entropy of the universe can only increase in time [8, 40].

From a macroscopic perspective, i.e. in classical thermodynamics, entropy is interpreted as a state function, that is, a property depending only on the current state of the system. The fact that entropy is generated in irreversible processes does not contradict entropy being a state function, because entropy can also be generated in the surroundings.

If the system consists of only a single material, adding heat in an isobaric process changes the entropy of the material. Entropy of a material is thus related to the heat capacity of the material at constant pressure. Thermodynamic entropy S at a temperature τ can be calculated as a function of heat capacity at constant pressure C_p.

$$S = S_0 + \int_{T=0}^{\tau} \frac{dQ_{rev}(T)}{T} = S_0 + \int_{T=0}^{\tau} \frac{C_p}{T} dT \qquad (2)$$

(T is temperature as the integrating variable). S_0 is the zero-point or residual entropy of the material at absolute zero. Note that the thermodynamic entropy equation contains two conceptually different types of entropy:

a) *Thermal entropy, $S_{Therm} = \int (C_p / T)\, dT$*, due to thermally induced motion of particles.

b) *Residual entropy, S_0* due to random arrangement of particles in a crystal lattice. S_0 is not a consequence of thermal motion. The *Third Law of Thermodynamics* defines a reference state for entropy as a perfect crystal at zero Kelvin with S_0 *(perfect crystal)* = 0, which allows determination of "absolute" entropy values, relative to the perfect crystal reference state. Since nothing can have a lower entropy than a perfect crystal, thermal entropy S_{Therm} and residual entropy S_0 are thus defined as non-negative properties ($S_{Therm} \geq 0$; $S_0 \geq 0$).

Collecting heat capacity data from near absolute zero to the temperature of interest is sometimes impossible, for example in materials that decompose during cooling. A typical example are entropies of solutes in solution. At low temperatures the solution freezes and separates. In such cases entropy cannot be determined directly by low temperature calorimetry using equation (1). Alternatively, entropy changes can be measured indirectly from measured Gibbs energy changes, ΔG, and enthalpy changes, ΔH, using the Gibbs equation:

$$\Delta G° = \Delta H° - T\Delta S° \tag{3}$$

The standard Gibbs energy change, $\Delta G°$, is a state function related to the equilibrium constant of a reaction at a constant temperature and pressure K_p [4], by

$$\Delta G° = -RT \ln K_p \tag{4}$$

Therefore, evaluation of K provides a value for $\Delta G°$. The standard reaction enthalpy change, $\Delta H°$, can be determined by reaction calorimetry or from the temperature dependence of K. Equation (3) can then be used to calculate the standard reaction entropy change, $\Delta S°$. If $S°$ for all of the reactants and products of the reaction except one can be determined from equation (2), then $S°$ for the remaining material can be calculated from

$$\Delta S° = S°_{products} - S°_{reactants} \tag{5}$$

Section 3.6 discusses a practical application of the Gibbs equation to find entropy using the Gibbs equation. $S°$ of aqueous glucose is determined from the solubility

$$glucose(cr) \rightleftarrows glucose(aq,sat) \qquad K' = (solubility\ of\ glucose) \tag{6}$$

$\Delta H°$ for this reaction was obtained from a van't Hoff plot of $\ln K$ versus $1/T$. Combining $\Delta G°$ and $\Delta H°$ (equation 3) results in $\Delta S°=57.6589$ J mol^{-1}K^{-1} at 25°C, and $S°$(glucose, aq, 25°C)=266.9 J mol^{-1}K^{-1}.

An analogous quantity to Gibbs energy, the Helmholtz energy, A, is a state function related to the equilibrium state at constant temperature and volume, K_V [4], by

$$\Delta A° = -RT \ln K_V \tag{7}$$

The standard Helmholtz energy change, $\Delta A°$, can be expressed as a function of internal energy, U, temperature, T, and entropy as

$$\Delta A° = \Delta U° - T\Delta S° \tag{8}$$

For example, $\Delta A°$ can be determined from the voltage of a sealed (i.e. constant volume) battery using the equation (7), by finding the equilibrium constant from the equation

$$\Delta A° = -\upsilon F E° \tag{9}$$

where υ is the number of electrons involved in the redox reaction, F is Faraday's constant and $E°$ is the standard electromotive force of the battery. $\Delta H°$ can be obtained from calorimetric measurements or from the temperature dependence of $E°$. Combining $\Delta A°$ and $\Delta H°$, equation (8), then gives $\Delta S°$ from which $S°$ can be calculated.

1.2.2 Entropy in Statistical Mechanics

Statistical mechanics describes the behavior of thermodynamic systems starting from the behavior of their constituent particles [41]. To describe the motion of a particle, it is necessary to know six parameters – the position and velocity components along the x, y and z axes. The number

of independent parameters needed to completely describe a physical system is the *number of degrees of freedom* of that system. Thus, the number of degrees of freedom of a particle is 6. Since 6×10^{23} particles make one mole of a gas, the number of degrees of freedom for one mole of a monoatomic ideal gas is 36×10^{23}. Obviously, dealing with each particle individually is impossible in practice and statistical methods are used to simplify the problem through the concept of microstates.

The microstate of a system, in classical statistical mechanics, is the state of the system defined by the positions and velocities of the particles. Since the particles move and collide, the positions and velocities change in time. Thus, the microstates change in time, even though the gas is at macroscopic equilibrium, a state in which there is no flow of matter within the system or change in parameters such as temperature and pressure. Since microstates change in time without changing the macroscopic state of the system, many microstates constitute one macrostate, the state which can be described through a small number of thermodynamic parameters, e.g. internal energy and entropy.

The microstate of a system can, according to Boltzmann [41], be described by a single point in a hyperspace that has an axis to represent the velocity of each particle simultaneously along each of their axes. If we consider only non-polar particles, e.g. He atoms, the positions of particles are irrelevant here and are omitted for simplicity. Thus, only 3 degrees of freedom will be considered, corresponding to velocity. For example, a state consisting of the velocity of a single particle requires only 3 axes (v_x, v_y, v_z), while a system consisting of the velocities of a mole of particles of ideal gas requires a hyperspace with 18×10^{23} axes. Every point, considered by itself in such a hyperspace, defines the velocity of each particle, simultaneously. Each point in this hyperspace then represents a microstate. A microstate is a collection of particles with different

velocities. All microstates with the same total energy value in this hyperspace belong to the same macrostate. The number of such points (or microstates) with the same total energy is denoted W. W thus represents the number of accessible microstates at a fixed total energy level. Not all microstates may be occupied during a fixed time window, but all are possible. A system can be in only one microstate at a time.

Boltzmann [41] then postulated that there is a function η of only the number of accessible ways, W, of permuting the velocities of particles, without changing the total energy of the system. To satisfy extensivity properties, Boltzmann defined η as

$$\eta = \ln W \tag{10}$$

Equation (10) defines η in a very simple way. From the properties of an ideal gas, Boltzmann [41] found the η-function corresponds to entropy, S, i.e. $S = R \ln W$. Boltzmann originally used the universal gas constant R, but when the value of the Boltzmann constant k_B was determined as R/N_A, the equation took the modern form. Thus, entropy is now defined in statistical mechanics as

$$S = k_B \ln W \tag{11}$$

However, W, the number of accessible microstates for a fixed total energy, is difficult to determine. But, S can be estimated with Sterling's approximation, using a probability distribution, p_i, describing the probability of a particle being in a particular energy state ε_i. In this approximation

$$\eta \approx -N \sum_i p_i \ln p_i \tag{12}$$

where N is the number of particles, and in practice, S is approximated as

$$S \approx -k_B N \sum_i p_i \ln p_i \tag{13}$$

11

Realizing that it is impossible to actually track microstates in a system, Boltzmann [41] used statistics to find the probability distribution of the particle velocities. Boltzmann [41] proved there is only one distribution of velocities that maximizes entropy. The distribution, constrained by fixed total energy, is the Maxwell-Boltzmann distribution [41]. The continuous Maxwell-Boltzmann distribution has been modernized after the discovery of Heisenberg's uncertainty principle and turned into the quantum Boltzmann distribution

$$p_i = \frac{e^{-\varepsilon_i/k_B T}}{\sum_i e^{-\varepsilon_i/k_B T}} \tag{14}$$

where p_i is the probability of a specific particle having energy ε_i, T is temperature and k_B is the Boltzmann constant [4, 6-8, 41, 42]. It is important to note that the development of Boltzmann's theory based on microstates eventually boils down to calculating the probabilities of the *individual* particle energies. Gibbs [42] generalized Boltzmann's results. However, Gibbs' logic is more difficult to follow than Boltzmann's, while not introducing any further conclusions in this analysis.

The Boltzmann equation shows that entropy is proportional to the logarithm of the number of microstates available to a system at a fixed total energy. In particular, Boltzmann reduced the second law to a stochastic collision function, or a law of probability following from the random mechanical collisions of particles. Particles, for Boltzmann [41], were gas molecules colliding like billiard balls in a box. Such a system will almost always be found either moving towards or being in the macrostate with the greatest number of accessible microstates, such as a gas in a box at equilibrium. On the other hand, a state with molecules moving "*at the same speed and in the same direction*", Boltzmann concluded, is "*the most improbable case conceivable...an infinitely improbable configuration of energy*" [43]. Since coordinated motion is perceived as orderly, based on Boltzmann's work, entropy came to be viewed as a measure of disorder [36]. This point of view

12

has strict limitations, most importantly not being applicable to living systems, as will be discussed in detail in chapter 2.

1.2.3 Residual Entropy

Microstates of a gas in a box are defined as ways in which energies and positions of particles can be permuted with the total energy of the system remaining the same. In solids, particles can have multiple microstates available through particle arrangement. Residual entropy (S_0) was introduced in the first half of the 20th century by William Giauque and is a property of imperfect crystals, appearing as a consequence of arrangement of non-symmetric molecules or defects in a crystal lattice (Figure 1-4) [27, 44-48]. Residual entropy is the difference in entropy between an imperfect crystal and a perfect crystal, i.e. a crystal in the lowest energy state with no degeneracies. Residual entropy is a consequence of particle arrangement in a crystal lattice and does not result from any form of molecular motion, including the "zero-point energy" of vibration or rotation [8].

The presence of multiple microstates in a material at absolute zero leads to residual entropy, and the number of microstates is simply the number of possible arrangements. Residual entropy ($3–12$ J mol^{-1} K^{-1}) is present in imperfect crystals composed of non-symmetric particles, for example, CO, N_2O, $FClO_3$, and H_2O [44, 49].
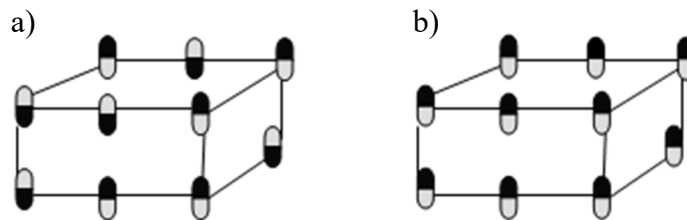
Figure 1-4: (a) An imperfect crystal of CO: each CO molecule in the crystal lattice can point either up or down. Therefore, there is randomness in molecular orientation leading to residual

13

entropy. (b) A perfect crystal of CO where all molecules in the lattice are oriented in the same direction. There is no randomness and residual entropy is zero.

Residual entropy is experimentally determined using calorimetry to measure the difference in heat capacity between an imperfect and a perfect crystal, converting it to entropy through equation (2). An example is the measurement of residual entropy of glycerol by Gibson and Giauque [50], who measured the heat capacity difference between perfect and imperfect crystals. In the case of CO only an imperfect crystal is available [46], so the entropy of the perfect crystal was calculated from a statistical mechanical calculation of entropy based on spectroscopic measurements on gaseous CO [46]. The entropy change from the available imperfect crystal was determined by calorimetric measurements of heat capacity and enthalpies of phase changes from absolute zero to the temperature of the gas [46]. The difference between the entropy calculated from the measured heat capacity, see equation 2, and the entropy of CO gas calculated from the spectroscopic measurements gives the residual entropy as 4.602 J mol^{-1} K^{-1} [46]. The residual entropy of imperfect crystalline CO calculated using equation (10) is 5.76 J mol^{-1} K^{-1}, slightly higher than the experimentally determined 4.602 J mol^{-1} K^{-1} [46].

Residual entropy can also be calculated from theory by determining the number of microstates available to a material at absolute zero. According to Kozliak [44], the simplest way to find residual entropy is by applying the Boltzmann–Planck equation:

$$S_0 = k_B \ln \frac{W_{2,random}}{W_{1,perfect}} \qquad (15)$$

W_2 and W_1 are the numbers of microstates of the imperfect and perfect crystal state, respectively [44]. The perfect crystal state has only one microstate, so $W_1 = 1$. The number of microstates in the imperfect crystal is related to the number of distinct orientations a molecule can have, m, and

the number of molecules that form the crystal, N, by the relation $W_2 = m^N$. This way to find W_2 is equivalent to tossing a coin or an m-sided die N times, thus the name "*coin tossing model*."

1.3 What is the physical meaning of entropy?

The physical meaning of thermodynamic entropy can be seen from the Helmholtz energy equation

$$A = U - TS \tag{16}$$

where A is Helmholtz energy, U is internal energy, T is temperature and S is thermodynamic entropy [4]. The Helmholtz equation (11) can be rearranged into the following form

$$1 = \frac{A}{U} + \frac{TS}{U} \tag{17}$$

As explained above, Helmholtz energy is equal to the maximum amount of expansion work that can be extracted from a system w_{max} [4]. Equation (17) can be rewritten as

$$1 = \frac{w_{max}}{U} + \frac{TS}{U} \tag{18}$$

The first term w_{max}/U (or A/U) represents the maximum fraction of the internal energy of a system that can be extracted as work. The second term TS/U represents the fraction of the internal energy of a system that is "trapped" as thermal energy and cannot be extracted as work. So, equation (18) becomes

$$x_w + x_Q = 1 \tag{19}$$

where $x_w = w_{max} / U$ and $x_Q = T \cdot S / U$, and S is in that case

$$S = \frac{U}{T} x_Q \tag{20}$$

15

Therefore, the term *TS/U* represents the minimum fraction of internal energy that cannot be converted into work. In that sense, entropy is a measure of the part of internal energy that cannot be converted into work, or in practical terms is useless energy. Thermodynamic entropy is a measure of the part of the total energy content in the form of chaotic motion (translation, rotation, vibration…) of the particles in a system. Since energy is dispersed among many forms of motion, the dispersion definition coincides with the useless energy definition.

1.4   Is entropy a subjective or an objective property

The philosophical nature of entropy is an open question, the problem being a lack of consensus whether entropy is a subjective or an objective property. Subjective is defined as "*characteristic of or belonging to reality as perceived rather than as independent of mind*" [51]. On the other hand, objective is defined as "*of, relating to, or being an object, phenomenon, or condition in the realm of sensible experience independent of individual thought and perceptible by all observers: having reality independent of the mind*" [52]. A significant part of the scientific community considers entropy as a subjective property [23, 30-32]. Others insist that entropy is an objective property [32-35]. So, von Neumann was right – no one knows what entropy really is (subjective or objective, energy or something else, arrangement of particles or realization of microstates, negentropy, many kinds of entropy…).

Entropy in general can be represented by the equation $S = c \ln W$, where c is a constant and W is the number of microstates available to a system, refer to chapter 2. In thermodynamics, W is the way in which velocities and positions of particles can be permuted without changing the energy of the system and c is the Boltzmann constant. However, entropy in general is a measure of the number of microstates available to a system. In this sense, entropy is a summary statistic of any

system of interest. However, the *kind* of entropy that is applicable to a certain problem depends on how the microstates are defined. Thus, there are many kinds of entropy applicable to many problems.

The following von Neumann-Shannon anecdote expresses the frustration over two different quantities being given the same name, i.e. Boltzmann entropy and Shannon information entropy. Shannon and his wife had a new baby. Von Neumann suggested they name their son after the son of Clausius, "entropy". Shannon decides to do so, to find out, in the years to follow, that people continually confuse his son with Clausius' son and also misuse and abuse the name [23].

The chemical thermodynamic definition of entropy states that: "*Qualitatively, entropy is simply a measure of how much the energy of atoms and molecules becomes more spread out in a process*" [27]. This definition is in line with Clausius' original intention to relate *Entropy* and *Energy*. From the work of Clausius, entropy is a measure of energy in a system that cannot be converted into work.

In 1948, Shannon introduced another member of the entropy manifold – Shannon entropy, $\check{S}$.

$$\check{S} = -K \sum_j p_j \ln p_j \tag{21}$$

where K is a constant and p_k is probability of message j. The similarity of equations (13) and (21) is the basis for one interpretation of entropy, i.e. entropy as information missing to completely specify the microstates of a system [23, 26, 53]. In section 1.2, it was noted that statistics has been used to decrease the number of variables that describe a system from the order of 10^{23} to a few key thermodynamic parameters, such as U and S. Entropy has been interpreted as information lost in this process. Therefore, Choe [54] applied entropy to finance and economics because "*The mathematical definition of Shannon entropy has the same form as entropy used in*

17

thermodynamics, and they share the same conceptual root in the sense that both measure the amount of randomness" [54]. This view of entropy as missing information is thus based on the similarity of the entropy equations in thermodynamics and information theory. Jaynes interpreted thermodynamic entropy as information missing to completely specify a thermodynamic system at the molecular level [26]. Since *we* are the ones who do not have the information, Jaynes' insight also suggests that entropy is subjective [26]. Denbigh [30] stated: "*there remains at the present time a strongly entrenched view to the effect that entropy is a **subjective** concept precisely because it is taken as a measure of missing information*".

Singh and Fiorentino [32] introduced four interpretations of the entropy concept. Their view is that there are several kinds of entropy applicable to different scientific disciplines. They clearly separated thermodynamic entropy as objective and information entropy as subjective. However, their philosophical view belongs to pragmatism, which holds that thought is an instrument for prediction and problem solving, rejecting the idea that thought needs to represent reality [55]. First, "*entropy as a measure of system property assumed to be an **objective** parameter*" [32]. Second, "*entropy assumed as a probability for measure of information probability*" [32]. Third, "*entropy assumed as a statistic of a probability distribution for measure of information or uncertainty*" [32]. Fourth, "*entropy as a Bayesian log-likelihood functions for measure of information*" [32]. The second, third and fourth are assumed to be **subjective** parameters [32]. However, Clausius [1], and after him Boltzmann [41] clearly stated: "*the entropy of the universe tends to a maximum*" [1]. This happens regardless of the observer. The tendency of the universe to maximize entropy was present long before intelligent life originated. Stars would explode in supernovae (and increase the entropy of the universe) independently of our ability to measure the phenomenon. Entropy change in chemical reactions occurs with or without observers. Thus, for Clausius and Boltzmann,

entropy is an objective parameter. Heat represents energy and is thus an objective parameter, and temperature represents a measure of molecular chaotic motion and thus is also an objective parameter. Energy is an objective property. Because these quantities define thermodynamic entropy, it is also an objective property.

Bunge was explicit: "*thermodynamic probability… is an objective property of the system… used to calculate another system property namely its entropy*" [34]. Further, Carnap wrote: "*Entropy in thermodynamics is asserted to have the same general character as temperature, pressure, heat, etc., all of which serve for the quantitative characterization of some objective property of a state of a physical system*" [35]. To claim that thermodynamic entropy is subjective is anthropocentric. Bohm and Peat wrote "*Entropy now has a clear meaning that is independent of subjective knowledge or judgement about details of the fluctuation*" [33], and explicitly "*entropy is an objective property*" [33].

Thus, the thermodynamic entropy should be considered as an objective parameter. At absolute zero temperature, molecules of CO or H_2O fail to align in a crystal lattice creating an imperfect crystal containing some residual entropy without an observer. Thus, the residual entropy should also be considered as an objective parameter. The experimental determination of glycerol entropy also shows that residual entropy (S_0) is an objective parameter, since two crystals take different amounts of heat for an equal change in their temperatures [50] and any observer will measure the same difference in heat.

On the other hand, information entropy depends on the reader. For example, a newspaper has a different amount of information to someone who speaks the language than someone who doesn't. An example is the verb "sacrer" in French, which can have two meanings: to bless or to curse. The

19

correct meaning is interpreted by the reader from context. Information entropy is thus reader dependent and is a subjective property.

1.5   How to apply entropy to living organisms?

The way entropy has been applied to living organisms is confused because the thermodynamics of the processes catalyzed by organisms has been confounded with the thermodynamics of the structure of organisms. Since entropy is a state function, the entropy of the structure of living organisms can be determined, just as for any other inanimate mixture, through the methods described in section 1.2.1. The entropy of the structure does not depend on the rates of processes that create the structure. Because some processes in living organisms are indirectly coupled, the thermodynamics of the processes are rate dependent and should be analyzed with nonequilibrium thermodynamics.

The application of thermodynamics and entropy to living organisms dates back to Boltzmann: "*The general struggle for existence of animate beings is not a struggle for raw materials, but a struggle for entropy, which becomes available through the transition of energy from the hot sun to the cold earth*" [43]. Boltzmann reasoning was extended by Schrödinger: "(An organism) *feeds upon negative entropy, attracting, as it were, a stream of negative entropy upon itself, to compensate the entropy increase it produces by living and thus to maintain itself on a stationary and fairly low entropy level*" [36].

Schrödinger introduced *negentropy* as entropy taken with a negative sign [36], a concept still in use today [56-59]. Schrodinger justified negentropy by equating the number of microstates with disorder in the Boltzmann equation. Disorder *D* and order *O* in living organisms were considered

by Schrödinger [36] to be reciprocals $D = 1/O$. Setting D equal to W, Schrödinger rearranged the Boltzmann equation into

$$-S = k_B \ln(1/D) = k_B \ln(O) \tag{22}$$

Schrödinger argued that, since $O=1/D$, negentropy $-S$ is a measure of order. Thus, Schrödinger [36] postulated a local decrease of entropy in living organisms, explained by the organization of biological structures. The equation for negentropy results from a mathematically correct manipulation of the Boltzmann equation, however negentropy is based on a false premise [60].

The root of the negentropy concept is the assumption that living organisms have a low entropy compared with inanimate matter of the same composition [36]. However, several recent studies question the validity of this assumption [11-15]. Hansen concluded that the entropy per unit mass of an organism "*doesn't have to decrease*" when biological molecules are synthesized from non-living matter [61, 62].

Thermodynamic entropy is just one component of the entropy manifold required to describe the biochemistry of living organisms. Thermodynamic entropy cannot explain information-related processes in organisms. Such processes require a different definition of microstates and are the subject of chapter 2. As late as 2006, Balmer [37] argued that: "*one characteristic that seems to make a living system unique is its peculiar affinity for self-organization*." However, the zebra's stripes, the parrot's color pattern, the shapes of leaves, the arrangement of macromolecules in cells, and the sequence of amino-acids in proteins are not results that can be explained by thermodynamics, but are consequences of the information coded in the organism's DNA that is controlled and expressed through the associated computational readout.

1.6 Conclusions

Entropy in physical sciences is a measure of the part of internal energy that cannot be converted into work, or in practical terms represents useless energy. Applications of entropy to other fields requires the appropriate definition of entropy.

Thermal entropy and residual entropy are objective parameters.

The negentropy concept represents a mathematically correct manipulation of the Boltzmann equation, but is based on false assumptions.

1.7 Nomenclature

A –   Helmholtz energy (J)

C_p –   Heat capacity at constant pressure (J K^{-1})

D –   Disorder

E –   Electromotive force (V)

F –   Faraday's constant (C mol^{-1})

G –   Gibbs energy (J)

H –   Enthalpy (J)

K –   Shannon equation constant

k_B –   Boltzmann constant (J K^{-1})

K_p –   Equilibrium constant at constant pressure

K_V –   Equilibrium constant at constant volume

K' –   Conditional equilibrium constant

m –   Number of distinct orientations a molecule can have in a crystal

N –   Number of particles

p_i –   the probability of a particle being in a particular energy state i

p_j –   probability of message j

22

Q_{rev} – Heat exchange in a reversible process (J)

R – Universal gas constant (J mol^{-1}K^{-1})

S – Thermodynamic entropy (J K^{-1})

S_0 – Residual entropy (J K^{-1})

$\check{S}$ – Shannon entropy (bits)

T – Temperature (K)

U – Internal energy (J)

W – Number of accessible ways of permuting the velocities of particles, without changing

the total energy of the system.

w_{max} – Maximum amount of expansion work that can be extracted from a system (J)

x_Q – Fraction of internal energy unavailable to do work

x_w – Fraction of internal energy available to do work

ε_i – Energy of energy state i (J)

η – Boltzmann's H-function

v – Number of electrons involved in a redox reaction (mol)

$\degree$ – Standard property

1.8   References

[1]   Clausius, R. On different forms of the fundamental equations of the mechanical theory of

heat and their convenience for application.In *The Second Law of Thermodynamics*;

Kestin, J., Ed.; Dowen, Hutchingson and Ross, Inc.: Stroudsburg, PA, 1976.

[2]   Eddington, A.S. *The nature of the Physical World*; Cambridge University Press:

Cambridge, UK, 1928.

[3]   Schlipp, P.A. *Albert Einstein: Philosopher-Scientist;* Open Court Publishing: La Salle, IL, 1973.

[4]   Atkins, P.; de Paula, J. *Physical Chemistry, 8th ed.*; W.H. Freeman and Company: New York, NY, 2006.

[5]   Demirel, Y. *Nonequilibrium Thermodynamics: Transport and Rate Processes in Physical, Chemical and Biological Systems, 3rd ed.*; Elsevier: Amsterdam, Netherlands, 2014.

[6]   Sandler, S. I. *An Introduction Applied to Statistical Thermodynamics*; John Wiley & Sons: New Jersey, NJ, 2011.

[7]   McQuarrie, D.A. *Statistical Mechanics*; University Science Books: Sausalito, CA, 2000.

[8]   Dugdale, J.S. *Entropy and its Physical Meaning*; Taylor & Francis, Ltd.: London, UK, 1996.

[9]   Goldstein, S.; Lebowitz, J.L. On the (Boltzmann) Entropy of Nonequilibrium Systems, *arXiv*, **2003**, arXiv:cond-mat/0304251 [cond-mat.stat-mech].

[10]   Liddle, A. *An Introduction to Modern Cosmology, 2nd ed.*; Wiley: Chichester, UK, 2003.

[11]   Gems, D.; Doonan, R. Antioxidant defense and aging in C. elegans, Is the oxidative damage theory of aging wrong?, *Cell Cycle*, **2009**, *8*(11), 1681-1687.

[12]   Hayflick, L. Entropy explains aging, genetic determinism explains longevity, and undefined terminology explains misunderstanding both. *PLoS Genet.*, **2007,** *3*(12), 2351-2354.

[13]   Hayflick, L. How and why we age, *Experimental Gerontology*, **1998**, *33*(7-8), 639-653.

[14]   Hayflick, L. Biological aging is no longer an unsolved problem. *Annals of the New York Academy of Sciences*, **2007**, 1100, 1–13 (DOI: 10.1196/annals.1395.001).

24

[15]   Silva, C.; Annamalai, K., Entropy generation and human ageing: Lifespan entropy and effect of physical activity level. *Entropy*, **2008**, *10*, 100-123.

[16]   Atkins, P.; De Paula, J. *Physical Chemistry for the Life Sciences;* W.H. Freeman and Company: New York, NY, 2006.

[17]   Rong, Q. Entropy-Based Set Pair Analysis Model on Geological Disaster Risk for Military Engineering, *Engineering*, **2012**, 4, 76-82.

[18]   Rosenfeld, R. Adaptive Statistical Language Modeling: A Maximum Entropy Approach, Ph.D. thesis, Carnegie Mellon University, Pittsburgh, PA, 1994, https://www.cs.cmu.edu/~roni/papers/me-thesis-TR-94-138.pdf.

[19]   Kovalev, A. Misuse of Thermodynamic Entropy in Economics, *Energy*, **2016**, *100,* 129-136, DOI: 10.1016/j.energy.2016.01.071.

[20]   Gabriel, A. Hotelling role for entropy-constrained economic growth, *Ecological economics*, **2017**, *133*(1), 35-41.

[21]   Shannon, C. A mathematical theory of communication, *The Bell System Technical Journal*, **1948**, *27*, 379-423.

[22]   Kostic, M.M. The Elusive Nature of Entropy and Its Physical Meaning, *Entropy*, **2014**, *16*, 953-967.

[23]   Ben-Naim, A. *Discover Entropy and the Second Law of Thermodynamics: a Playful Way of Discovering a Law of Nature*; World Scientific: Singapore, Singapore, 2012.

[24]   Tribus, M.; McIrving, E. C. Energy and Information, *Scientific American*, **1971**, *225*, 179-188.

[25]   Gillet, S. Entropy and its misuse, I. Energy, free and otherwise. *Ecological Economics*, **2006**, *56*(1), 58–70.

[26]   Jaynes, E.T. Information theory and statistical mechanics. *Phys. Rev.*, **1957**, *106*, 620-630.

[27]   Kozliak, E.; Lambert, F.; Residual entropy, the third law and latent heat. *Entropy*, **2008**, *10,* 274-284.

[28]   Clausius, R. *The Mechanical Theory of Heat – with its Applications to the Steam Engine and to Physical Properties of Bodies*; John van Voorst: London, UK, 1867.

[29]   Clausius, R. On a Mechanical Theorem Applicable to Heat. *Philosophical Magazine Series 4*, **1870**, *40*(265), 122–127.

[30]   Denbigh, K.G.; Denbigh, J.S. *Entropy in Relation to Incomplete Knowledge;* Cambridge university press: Cambridge, UK, 1985.

[31]   Jaynes, E.T. Information theory and statistical mechanics. *Phys. Rev.*, **1957**, *106,* 620-630.

[32]   Singh, V.; Fiorentino, M. *Entropy and Energy Dissipation in Water Resources*; Springer-Science: Berlin, Germany, 1992.

[33]   Bohm, D.; Peat, D. *Science, Order, and Creativity*; Routledge: London, 2000 (page 139).

[34]   Bunge, M. *Epistemology & Methodology III: Philosophy of Science and Technology Part I*; Springer: Berlin, Germany, 1985.

[35]   Hintikka, J. *Rudolf Carnap, Logical Empiricist: Materials and Perspectives*; Springer: Berlin, Germany, 1975.

[36]   Schrödinger, E. *What is life? The physical aspect of the living cell, 10th printing*; Cambridge university press: Cambridge, UK, 2003.

[37]   Balmer, R.T. *Modern Engineering Thermodynamics*; Academic Press: Cambridge, MA, 2011.

26

[38]   Sears, W.; Salinger, L. *Thermodynamics, Kinetic Theory, and Statistical Thermodynamics, 3rd ed.*; Addison-Wesley: Boston, MA, 1986.

[39]   Müller, I. *A History of Thermodynamics: The Doctrine of Energy and Entropy*; Springer: Berlin, Germany, 2007.

[40]   Lucia, U. Probability, ergodicity, irreversibility and dynamical systems. *Proceedings of the Royal Society A*, **2008**, *464*, 1089–1104.

[41]   Boltzmann, L. *Lectures on Gas Theory*; Dover Publications: Mineola, NY, 1995. (English translation of: Boltzmann, L. *Vorlesungen über gastheorie*; J.A. Bath: Leipzig, Germany, 1896).

[42]   Gibbs, J.W. *Elementary Principles in Statistical Mechanics*; Yale University Press: New Haven, CT, 1902.

[43]   Boltzmann, L. The second law of thermodynamics. In *Theoretical physics and philosophical problems*; McGuinness, B.F., Ed.; Springer-Verlag: New York, NY, 1974.

[44]   Kozliak, E. Consistent Application of the Boltzmann Distribution to Residual Entropy in Crystals, *J Chem. Educ.*, **2007**, *84*, 493-498.

[45]   Popovic, M. Are Shannon entropy and Residual entropy synonyms?, *Proceedings, 2nd Int. Electron. Conf. Entropy Appl.*, Sciforum Electronic Conference Series, 2015, Vol. 2, pp. A004.

[46]   Clayton, J.; Giauque, W. The Heat Capacity and Entropy of Carbon Monoxide, *J. Am. Chem. Soc.*, **1932**, *54*, 2610-2626.

[47]   Johari, G. Configurational and residual entropies of nonergodic crystals and the entropy's behavior on glass formation, *The Journal of Chemical Physics*, **2010**, *132*, 124509, DOI:10.1063/1.3364999.

[48] Sestak, J.; Mares, J.; Hubik, P. *Glassy, Amorphous and Nano-Crystalline Materials: Thermal Physics, Analysis, Structure and Properties;* Springer: Berlin, Germany, 2011.

[49] Pauling, L. The structure and entropy of ice and of other crystals with some randomness of atomic arrangement, *J.Am.Chem.Soc.*, **1935**, 57(12), 2680-2684.

[50] Gibson, G.E.; Giauque, W.F. The third law of thermodynamics. Evidence from the specific heats of glycerol that the entropy of a glass exceeds that of a crystal at the absolute zero, *J.Am.Chem.Soc.*, **1923**, *45*(1), 93-104.

[51] Merriam-Webster Dictionary, *Subjetcive*, [Online], Available at: https://www.merriam-webster.com/dictionary/subjective (Accessed on July 2, 2018).

[52] Merriam-Webster Dictionary, *Objective*, [Online], Available at: https://www.merriam-webster.com/dictionary/objective (Accessed on July 2, 2018).

[53] Ben-Naim, A.; Casadei, D. *Modern thermodynamics*; World Scientific: Singapore, Singapore, 2016.

[54] Choe, G.H. *Stochastic Analysis for Finance with Simulations*; Springer: Berlin, Germany, 2016 (page 583).

[55] Russell, B. *A History of Western Philosophy*; Simon and Schuster: New York, NY, 1945.

[56] Mahulikar, S.P.; Herwig, H. Exact thermodynamic principles for dynamic order existence and evolution in chaos. *Chaos, Solitons & Fractals*, **2009**, *41*(4), 1939-1948.

[57] Davis, P.; Rieper, E. Self-organization and entropy reduction in a living cell, *BioSystems*, **2013**, *111*, 1–10.

[58] Ho, M.W. What is (Schrödinger's) Negentropy?, *Modern Trends in BioThermoKinetics*, **1994**, *3*, 50-61.

[59]   Ho, M.W. *The Rainbow and the Worm: The Physics of Organisms*; World Scientific: Singapore, Singapore, 1998.

[60]   Hansen, L.D.; Popovic, M.; Tolley, H.D.; Woodfield, B.F. Laws of evolution parallel the laws of thermodynamics. *J. Chem. Thermo.*, **2018**, *124*, 141-148.

[61]   Hansen, L.; Criddle, R.S.; Battley, E.H. Biological calorimetry and the thermodynamics of the origination and evolution of life, *Pure Appl. Chem.*, **2009**, *81*(10), 1843–1855.

[62]   Hansen, L.; Criddle, R.S.; Battley, E.H. Equilibrium thermodynamics and metabolic Calorimetry of living systems, *Proceedings*, 20th ICCT, Warsaw, Poland, 2008, Vol 1.

2 LAWS OF EVOLUTION PARALLEL THE LAWS OF THERMODYNAMICS

2.1 Abstract

We hypothesize that concepts from thermodynamics and statistical mechanics can be used to define summary statistics, similar to thermodynamic entropy, to summarize the convergence of processes driven by random inputs subject to deterministic constraints. A primary example used here is evolution in biological systems. Evolution is initiated by random events that change the local environment, but acceptance and survival of an organism is dependent on the limits imposed by physical laws. This results in convergent evolution of forms of organisms because only those changes are retained that meet the universal physical requirements. The remarkable success of thermodynamic entropy in chemical systems has elevated entropy to a foundational principle of science, exceeding its initial empirical roots in thermodynamic modeling. However, heat, the currency of thermodynamics, does not translate directly into information, the currency of life. Consequently, the first and second laws of thermodynamics do not translate directly into parallel laws for the biome. But, as discussed herein, the fundamental principles on which thermodynamic entropy is based are also true for information. Based on these principles, we show that adaptation and evolution are stochastically deterministic, i.e. having a specific deterministic direction arising from many random events. Over time, natural selection, resulting from random events governed by deterministic constraints, minimizes the difference in the information describing the local environment and the biological system. An ability to collect information about the environment and respond appropriately is an inherent property of animate matter. Therefore, an information theory that includes both information processing and storage and is formulated on the same foundation as the immensely powerful concepts used in statistical mechanics provides statistics, similar to thermodynamic entropy, that summarize distribution functions for environmental

properties and organism performance. This work thus establishes the foundational principles of a quantitative theory that encompasses both behavioral and biological evolution and may be extended to other fields such as economics, market dynamics and health systems.

Key words: information, disorder, order, entropy, statistical mechanics

2.2 Introduction

Since the early 20th century, biologists have accepted that living organisms are constrained by the same laws of Newtonian mechanics and thermodynamics as non-living systems. [1] However, quantitative application of the second law of thermodynamics and entropy to biological organisms and systems have proven to be particularly problematic because "… *no one knows what entropy really is …*" [2]. Indeed, in a recent article, Ben Naim [3] indicates that neither entropy nor the second law can be effectively applied to living systems. To examine Ben Naim's conclusions, and to lay a conceptual framework for developing an information based theory for biological systems, this review begins with the historical foundations of entropy and the second law of thermodynamics. The conclusions reached in this development indicate there is a viable concept of information entropy and an equivalent to the "first and second laws" of thermodynamics for bio-systems.

This work concludes there are two laws governing evolution that parallel the first and second laws of thermodynamics. First law: Given appropriate conditions, life will originate and evolve. [4] Second law: Natural selection always drives organism performance or fitness toward an optimum state dependent on the local environment. Although random mutations, statistical aberrations and empirical adaptations driving biological evolution are stochastic in nature, the probabilities generating these "random events" are deterministic and completely specified by the

31

constraints of the system in which evolution is occurring. These proposed laws are based on concepts similar to those of statistical mechanics, but the perceived or observed "order" in biostructures and DNA sequences consists of distinguishable objects and requires a different definition of the microstates (see note 1) than the definition used as the basis of the Boltzmann equation that forms the foundation of chemical thermodynamics.

2.3   The Macroscopic Definition of Entropy

Thermodynamic entropy and the second law are rooted in efforts to explain the inefficiency of steam engines used by industry and transportation in the early 19th century. The work of Lazarus Carnot [5] and his son, Sadi Carnot [6], showed that any natural process has an inherent tendency to dissipate energy in unproductive ways. Rudolf Clausius [7] coined the term "*entropy*" to represent the portion of heat energy that cannot be converted into work. Thermodynamic entropy was thus first defined operationally in terms of heat exchanged between a system and the surroundings, relative to the amount of work done by or on the system. This strange property called entropy unified observations of work, heat, and energy and led Clausius [7] to propose the first and second laws of thermodynamics; "The energy of the universe is constant; the entropy of the universe tends to a maximum". In accord with Clausius' statement of the second law, the entropy of a system may decrease so long as the entropy increase of the surroundings is greater. The work of the Carnots, Clausius and Kelvin, together with earlier work on the properties of gases, also led to the realization of an absolute temperature scale, i.e. a scale with a defined zero that cannot be negatively exceeded.

Based on the reversible Carnot cycle, Clausius defined entropy, *S*, as

$$dS_{Macro} = \delta Q_{reversible}/T \tag{1}$$

32

δQ is the quantity of heat added to the system and T is the absolute temperature. Extension of this definition to irreversible processes requires writing equation 1 with the more familiar greater-than-or-equal sign which describes a characteristic of entropy for irreversible processes rather than being a definition of entropy. (See supplement 1.) Equation 1 shows that entropy has the same units as heat capacity, and the thermodynamic entropy of a material is defined by the temperature rise associated with a finite and known heat input including any thermally-induced phase transitions in the material (See note 2). Entropy is thus also described by equation 2. (See supplement 2 for a derivation of equation 2 from equation 1, and see note 2 concerning notation.)

$$S_{Macro}(T) = S_{Macro}(0) + \int_0^T \frac{C_p}{T} dT \qquad \text{or} \qquad S_{Macro}(T) - S_{Macro}(0) = \int_0^T \frac{C_p}{T} dT \qquad (2)$$

C_p is heat capacity at constant pressure, T is absolute temperature, and $S_{Macro}(T)$ is the entropy at temperature T. $S_{Macro}(T) - S_{Macro}(0)$ is the change in entropy resulting from changing the temperature from 0 to T.

Initially it was proposed that $S_{Macro}(0) = 0$, i.e. the third law of thermodynamics. The statistical mechanical development of entropy (presented below) shows that $S_{Macro}(0) = 0$ for an ideal or "perfectly ordered" material. However, recognizing that most materials cannot be obtained in a perfect state, Giauque [8] introduced $S_{Macro}(0)$ into equation 2 about a century after Clausius. $S_{Macro}(0)$ can be measured by calorimetric methods only in special cases where both perfect and imperfect phases of the material exist near absolute zero temperature. [9] Otherwise, $S_{Macro}(0)$ must be calculated by the methods of statistical mechanics.

2.4   The Microscopic Definition of Entropy

While the concept of entropy in Clausius' thermodynamics does not require a particulate composition of matter, statistical mechanics defines entropy in terms of the statistical properties of the energies of the particles constituting the system. The system is assumed to consist of N particles, e.g., atoms or molecules, each in one of a set of discrete (quantized) energy states. The total energy is equal to the sum of the energies of each of the N particles. The analysis assumes that this total energy is a known value related to the absolute temperature.

As in the macroscopic model, entropy represents how the system stores energy in a manner that cannot be used to produce work. By conceptualizing the system of N particles as a gas in a container with particles behaving like rigid balls moving in three dimensions, a paradigm for entropy at the microscopic level was constructed, originally by Ludwig Boltzmann. [10] Heuristically, if all the balls were moving in the same direction, their collective momentum could be completely converted into work, but if the direction is totally random, the momentum cannot be converted into work. Thus, the balls absorb energy by moving faster, but the random nature of this movement prevents harnessing all of this energy for work. Hence an increased velocity of the N particles in random directions would be accompanied by an increase in entropy.

Boltzmann developed a distribution function for the number of indistinguishable particles in each quantized energy state. (Boltzmann represented the energy for each particle as momentum. However, the argument can be extended to any quantized energy state as long as the independence assumptions implicit in Boltzmann's development hold. In this paper we use quantized energy states rather than the momentum.) Boltzmann defined entropy with the distribution of the N particles among the quantized energy states. Explicitly, as energy is added, the number of particles

34

in higher energy states increases. The change in entropy is represented by the change in the distribution of energy packets among the N particles. For example, heat added to the system adds energy packets to the particles, expanding the number of accessible energy states.

The results are summarized in equations 3 and 4, where the symbol p_i is used to represent the probability that a single particle (randomly selected from the N particles) will be in quantized energy state i. The energy level of quantized energy state i is denoted as ε_i. The expected number of particles in quantized energy state i is $N \cdot p_i$. Using this notation, the expected value of the total internal energy, U, of a system is given as

$$U = \sum_i p_i \varepsilon_i \tag{3}$$

where the summation in equation 3 is over all energy states. [11-13] (See note 4.)

The entropy of the system is thus defined by the simultaneous energy states of all of the indistinguishable particles at each instant in time. To represent this concept, Boltzmann [14] defined a "microstate" as the individual quantized energy state of all of the N particles collectively at a point in time. This concept of microstates is the foundation for development of the microscopic model of entropy [14]. Boltzmann used the word "complexion" rather than "microstate", and his definition of a complexion and explanation of the use of these in his development are extremely vague, so we offer a modern definition here. If the quantized energy level of each of the N particles is represented as a vector, with the energy level of the "first" particle as the first entry in the vector, the energy level of the "second" particle as the second entry in the vector, and so forth, the resulting vector represents the microstate of the system. Boltzmann defines entropy in the microscopic model as being a function of the number of distinguishable microstates, denoted W, at a specific

temperature, volume and pressure. Assuming the microscopic entropy is a function of W only and that entropy is an extensive property, it can be shown that $S_{micro}(T)$ is of the form (see [15]):

$$S_{micro}(T) = k_B \ln(W) \tag{4}$$

(Boltzmann originally used the ideal gas constant, R, in equation 4, but this was replaced with k_B when it was realized that $k_B = R$/Avogadro's number. The value of k_B is thus determined experimentally.) An outline of the further development of statistical mechanics is contained in supplement 3, and more extensive details are in the referenced literature (e.g. see [10, 11-13, 16].

The assumption that entropy is proportional to $\ln(W)$ is the basis for the third law of thermodynamics, often stated as "the entropy of a perfect crystal at absolute zero is exactly equal to zero" based on reasoning that a perfect crystal at absolute zero only has one microstate, and therefore $W = 1$, and $\ln(W) = 0$ [8, 17]. The Boltzmann-Planck equation

$$\Delta S_{micro}(T) = k_B \ln\left(\frac{W}{W_{ref}}\right) \tag{5}$$

includes a term, W_{ref}, to allow for reference states other than a "perfect crystal". W_{ref} is the number of accessible, distinguishable microstates in the reference system.

Equating equations (2) and (4), i.e. equating $S_{Macro}(T) + S_{Macro}(0)$ to $S_{micro}(T)$, indicates a potential equality between entropy in Clausius thermodynamics and entropy in statistical mechanics, namely

$$S_{micro}(T) = k_B \ln(W_T) = S_{Macro}(0) + \int_0^T \frac{C_p}{T} dT \tag{6}$$

36

Abundant experimental evidence [18] validates this equality and it is currently universally accepted. Thus, in answer to von Neumann's claim that "no one knows what entropy really is" [2], thermodynamic entropy is a measure of the number of accessible microstates in a system.

The number of accessible microstates at a given temperature, $W(T)$, increases with temperature because the total internal energy of the system increases and more microstates become accessible, and thus $S(T)$ increases with temperature. C_p/T increases with temperature because, as indicated by equation 6, heat capacity divided by temperature is directly proportional to the logarithm of the number of accessible microstates. ΔS_{Macro} of any phase transitions is always positive because the number of accessible microstates increases during thermally induced phase transitions, e.g., W of the solid is less than W of the liquid, which is less than W of the gas. At absolute zero temperature, $\int C_p/T \mathrm{d}T = 0$, and therefore

$$S_{micro}(0) = k_B \ln(W_0) = S_{Macro}(0) \qquad (7)$$

One issue that is easy to overlook is how the number of microstates, W, is determined. In the case of indistinguishable particles, the microstates can be grouped into subsets with equivalent numbers of particles in each quantized energy state. To clarify this, we define a "configuration" as a vector characterizing a microstate by tabulating the number of entries in the microstate vector in each energy state. The first entry in the configuration vector is the number of particles in the lowest energy state. The second entry is the number of particles in the next lowest energy state, and so forth. Many microstates will have different particles in different energy states, but the same number of particles in each energy state and thus the same configuration. Therefore, every microstate within a configuration has the same number of particles in each energy state and hence the same total energy. For any value of total energy, only a subset of the configurations have that

37

particular total energy, and only a subset of the possible microstates can be accessed. Each of the accessible microstates has the same total energy and is assumed to be equally likely.

As the number of particles, N, becomes large, only one configuration dominates. [11, 12, 16] In other words, for any fixed total energy, almost all of the distinguishable microstates belong to the same configuration. Consequently, for a large number of atoms, one need consider only one configuration [11], referred to here as the "dominant configuration." For any set of quantized energy states, this dominant configuration is determined uniquely by the total energy of the system. The number of accessible microstates in this predominant configuration is commonly used as an approximate expression for entropy, i.e. as the value of W in equation 4 [11]. In this approximation, the number of distinguishable microstates in the predominant configuration is given by

$$W = \frac{N!}{\prod_i(n_i!)} \tag{8}$$

where n_i is the number of particles in the ith quantized energy state for the predominant configuration. Using Stirling's approximation, $\ln N! = N \ln N - N$, and assuming indistinguishable particles, then, for W given in equation 8, $\ln(W)$ is approximated by $-\sum p_i \ln p_i$. Thus, entropy, $S_{micro}(T)$ in equation 4, is approximated by (See supplement 2)

$$S_{micro}(T) \approx -k_B \sum_i p_i \ln(p_i) \tag{9}$$

Entropy, as defined by Boltzmann's equation 4, is approximated by equation 9 under the assumption that only the number of microstates in the predominant configuration need to be counted. In other words, equation 9 is not the definition of entropy but rather a computational approximation when all the microstates are equally likely and there are a large number of microstates. Equation 9 is often quoted as Gibbs' definition of entropy [12], though it is only a

good approximation to equation 4 under an assumption of a dominant configuration arising from the microstates formed by the collection of indistinguishable particles. In a variety of other applications, in biology for example, the assumption of indistinguishable molecules and the assumption that sequential order is immaterial, as implied by equation (8) do not hold. Consequently, the predominant configuration, yielding equation (9) as a good approximation of entropy, may not exist.

This "definition" of entropy given in equation (9) provides the derivation of the Boltzmann distribution for probabilities, p_i, of each quantized energy state, equation 10 [11-13, 15]. Explicitly,

$$p_i = \frac{e^{-\varepsilon_i/k_B T}}{\sum_i e^{-\varepsilon_i/k_B T}} \tag{10}$$

Regardless of the microstate that the system is in, it will tend to one of the microstates in the dominant configuration. Adding or removing energy from the system changes the dominant configuration to which the system will go. Thus, a change in entropy caused by a change in total energy is simply a description of the characteristic differences in the two dominant configurations: the initial one and the final one. This is the essence of the second law of thermodynamics, namely, that the change in entropy is measuring the change in the dominant configuration specified by the change in total energy.

2.5   Shannon's Information Entropy

Information theory was initially developed for the purpose of maximizing transmission of messages over phone lines. Claude Shannon [19] formulated a definition of information entropy, $\check{S}$, by specifying a finite set of M possible messages with message i having a probability $p_{S,i}$ of occurring. In defining $\check{S}$, Shannon used three assumptions: (See note 5 for nomenclature used here.)

39

1. $\check{S}$ is a continuous function of $p_{S,i}$.

2. All messages are equally likely ($p_{S,i} = 1/M$) and $\check{S}$ is a monotonic increasing function of M.

3. $\check{S}$ is a weighted sum of the individual values of $\check{S}$.

These conditions are satisfied only by [19]

$$\check{S} = -K_S \sum_i p_{S,i} \ln(p_{S,i}) \tag{11}$$

where the sum is over all messages, i=1 to M. Shannon subsequently used equation 11 as a definition of information entropy. The fact that equation 11 is for any type of message and based only on the probability of each of the messages makes application of this definition very flexible. For example, if each message is equally likely, then $p_{S,i} = 1/M$ for all i. In this case, $\check{S}$ reduces to

$$\check{S} = K_S \ln(M) \tag{12}$$

and $K_S = 1$.

This is where most applications of Shannon's entropy stop, but we extend this further to highlight the important similarities **and** differences between Boltzmann's thermodynamic entropy and Shannon's information entropy. Suppose a message is made of n characters in a sequence and each character can be one of m distinguishable symbols. Then, if we assume the order of the symbols is important, the number of distinguishable messages that can be represented is $M = m^n$. If each permutation of the m symbols is equally likely and the likelihood of an outcome of any symbol in any character location in the sequence is independent of any other outcome, then the probability, $p_{S,i}$, of the ith message is

$$p_{S,i} = \frac{1}{M} = m^{-n} \tag{13}$$

40

www.manaraa.com

Substituting equation (13) into equation (11) gives

$$\check{S} = K_S \ln(m^n) = K_S n \ln(m) \qquad (14)$$

The messages represented as a sequence of symbols are similar to the thermodynamic microstates with the exception that the *order of the symbols is important here*, contrary to the case in thermodynamics. Recognizing a message as a microstate, equation 14 expresses Shannon's definition of entropy as the logarithm of the number of microstates. Although the formulation of Shannon entropy is completely different than the statistical mechanics definition of thermodynamic entropy, the end result is the same except for the multiplicative scale given by the constant. The underlying foundation that entropy is the logarithm of the number of distinguishable microstates is exactly the same; in consequence, the two formulas for entropy are similar, but unrelated in meaning. This supports Ben Naim's statement [3] that there is no "second law" in biology stemming from thermodynamics that applies to the life sciences beyond the thermodynamics of the chemistry, even though the formulas are similar. On the other hand, both definitions are based on the number of accessible microstates that a system (viewing a message as a specific microstate) can be in. In this sense, equation 12 is identical in form to Boltzmann's equation 4. If the *n*-tuple, *x,* is considered to be a microstate, equation 12 is exactly the same, in principle, as the definition of thermodynamic entropy given in equation 4. That is, both equations are based on the number of microstates, suggesting a close connection between the concepts used in their derivation.

However, the similarity of equations 12 and 4 requires further examination. Many different kinds of systems allow the above three assumptions, including equivalent assumptions made by Boltzmann, but these equations were arrived at for very different purposes. The parameter *W* is the

number of distinguishable microstates accessible for *N indistinguishable* particles considered collectively. And for a message of *n* positions where all symbols are equally likely to appear in any position, then m^n is the number of microstates for a message. Hence equation 4 and equation 12 define entropy in exactly the same manner; as the number of distinguishable microstates possible before any realization of the process. In applying equation 12 to the problem of transmission capacity, Shannon was only interested in the number of distinguishable messages, not their content, and therefore equation 11, where p_i is the probability of a message, could be used to evaluate *M* in equation 12. However, note the definitions of a microstate and K_S are entirely different from the definitions of a microstate and k_B in evaluating *W* in Boltzmann's equation.

Equation 12 resembles Boltzmann's equation 4, but the reasons for choosing the function in equation 11 to represent information, i.e., a logarithmic function is mathematically tractable and linearizes variables that increase exponentially [19], are completely different from the postulates about microstates made in using equation 9 to evaluate *W* in the Boltzmann equation. The probabilities, $p_{S,i}$, in equation 11 are *not* described by the Boltzmann distribution. Further, the K_S in equations 11 and 12 is not equivalent to the Boltzmann constant, k_B, relating energy to temperature. The meaning of equation 12 is therefore entirely different from the meaning of equation 4 defining thermodynamic entropy in statistical mechanics. As a consequence, Boltzmann and Shannon entropies represent completely different quantities that are not additive in any sense.

In summary, the sequence of individual particles in a message string has no effect on heat capacity or other thermodynamic functions summarizing the objective properties of particles. In thermodynamics and statistical mechanics, the particles are indistinguishable, their order is immaterial, and the energy states defining a microstate are irrelevant to information. A non-zero $S_{micro}(0)$ or $S_{Macro}(0)$ is caused by random disarray in the molecules in a material, and thus can be

chosen to define the reference state of the material. But, because these are a consequence of random events, they are not equivalent to information. Shannon or information entropy, $\check{S}$, is a subjective quantity dependent on the sequence of events, letters, or molecules and does not contribute to the thermodynamic entropy at absolute zero temperature. However, both definitions of entropy are based on the logarithm of the number of accessible microstates, suggesting a tight relationship between the concepts being modeled.

2.6 Order, disorder and entropy

The assumption that biological structures are distinguished from inanimate matter by having an extraordinarily low thermodynamic entropy was powerfully promoted by Erwin Schrödinger's [20] book *What is Life*. This assumption was universally accepted and unquestioned until Hansen et al. [4] invalidated it by showing that a large body of data indicates the entropies of a random collection of molecules and biological structures are the same. This conjecture is also supported by direct experimental measurements showing that $S_{\text{Macro}}(T) - S_{\text{Macro}}(0)$ has the same value for biological structures as for inanimate material of the same composition [4]. The work of Battley [21] showing the thermodynamic entropies of organic materials, living or dead, are directly proportional to the weighted sum of the entropies of the elements again shows thermodynamic entropy depends on composition and not on the structural "order" of an organism. The assumption that living structures have a low thermodynamic entropy is further invalidated by an experimental finding that *M. thermoautotrophicum* grows despite producing a positive entropy in the system. [22] Thus, in contradiction to the claims of several authors, e.g., Schrödinger, [20]; Morowitz, [23]; Brillouin, [24]; Balmer, [25], the organized molecular arrangement in cells and organisms does not decrease the thermodynamic entropy of the organism. The presence of a very large

number of rotational and vibrational microstates overwhelms any possible entropy decrease from the perceived or observed "order" of molecules in cells.

Schrödinger's mistake was in equating "order or organization" with low entropy. Schrödinger's derivation of negentropy begins by incorrectly assuming thermodynamic entropy, S, is related to disorder, D, by the Boltzmann equation

$$S = k_B \ln(D) \tag{15}$$

Schrödinger then reasoned that disorder, D, is reciprocal to order, O, and therefore, $D=1/O$. Substituting into the Boltzmann equation,

$$-S = -k_B \ln\left(\frac{1}{D}\right) = k_B \ln(O) \tag{16}$$

and therefore negentropy, $-S$, is a measure of order. Equations 15 and 16 are a misuse of the Boltzmann equation based on falsely assuming that "order" and "disorder" are reciprocals and that "order" equates with number of microstates. As explained earlier in this paper, these assumptions are inconsistent with the definitions of microstates in both information and thermodynamics.

In statistical mechanics, a "perfectly ordered" system is a system that has only one accessible microstate, and a system that is "highly ordered" has only a small number of accessible, distinguishable microstates. However, "ordered" and "disordered" terminology is an inaccurate description of microstates when applied in other contexts. In general, the "order" or "disorder" of an arrangement is not related to the number of thermodynamic microstates, i.e., perceived "order" is not related to thermodynamic entropy and "organized" would better describe matter in biological structures. Since there are a large number of rotational and vibrational microstates of equal energy in a DNA molecule or in a cell that are independent of sequence or organization, thermodynamic

44

entropy does not distinguish between animate and inanimate matter. However, because sequence matters in information entropy, $\check{S}$, does distinguish between potentially animate matter and inanimate matter and $\check{S}$ is thus a distinguishing characteristic of animate matter. If we assume only one sequence of DNA codes for a viable organism and only one organization of cellular components allows a living organism, $\check{S} = 0$ is a requirement for animate matter under these assumptions.

Because of the similarity of equation 12 to Boltzmann's equation 4, Brillouin [24, 26] incorrectly equated information defined by equation 12 to Schrödinger's [20] negentropy, i.e., Brillouin assumed information decreases the thermodynamic entropy of a system. Following Brillouin, Morowitz [23, 27] extended the same logic to living cells and concluded the information content of a living cell is

$$I = \log_2(N) \tag{17}$$

where N is the number of possible configurations of the atoms forming a viable cell [23]. Further, Morowitz concluded there is only one configuration of atoms out of a large number, N, of possible configurations that allows the cell to be alive, then correctly concluded the Shannon or information entropy is zero, but incorrectly equated this entropy with $S_{Macro}(0)$.

Because of the work of Brillouin and Morowitz, the false concept that the information content of living cells decreases their thermodynamic entropy became generally accepted, especially since it offered an explanation for Schrödinger's incorrect assumption of a low entropy of biological structures. This confusion was further increased by Jaynes [28] use of Shannon's approach to derive statistical mechanics in an alternative way. However, equivalence of equations 4 and 12 requires that all postulates and assumptions be the same for both applications, i.e. statistical

45

mechanics and information. Shannon's three postulates are fulfilled in both systems, however, application of equation 12 to DNA information requires different assumptions. In DNA, sequence matters, messages are not equally likely, and sequence randomness would destroy the information, but not change the thermodynamic entropy. Therefore, although equations 4 and 12 are both appropriate for calculating the "entropy" of DNA, the specification and enumeration of microstates depends on the question being asked. Furthermore, neither of the definitions of microstates used by Shannon or Boltzmann may be appropriate for answering a particular question.

Both Brillouin [26] and Morowitz [27] incorrectly viewed thermodynamic entropy as a measure of the lack of information about the microstates of a system, a view that appeared to be supported by Landauer's principle [29]. From an analogy between erasure of data and thermalization of a set of spins, Landauer calculated that erasing N bits of information must generate $kN\ ln(2)$ of thermodynamic entropy which represents the smallest amount of energy that must be used to erase a bit from an information storage medium. But, since it does not depend on the sequence of bits being erased, the thermodynamic entropy is unrelated to the information content, i.e. erasing a random sequence costs the same energy as erasing an ordered sequence of the same length.

2.7   Evolution and Adaptation of Living Organisms

A new model for living organisms that includes sequence-coded information is necessary. [30] The "organism as a machine" model from the last century is incomplete. Organisms collect information about their immediate environment and use that information to determine their response. [31] An organism is thus analogous to a robot with sensors and an onboard computer that processes data from sensors and guides the response of the robot, e.g. an adaptive, self-driving

car. This capability obviously increases in proceeding from simple single cell organisms to higher organisms with nervous systems and brains. DNA is analogous to the read only memory (ROM) in a computer, providing the template to boot up and use the inputs to survive. As with ROM, to provide system stability, rewriting information for survival is more complex than altering random access files. However, DNA code can be altered by methylation and restructuring chromatin. [32] "Genomes are in constant flux: They are prone to deletions, duplications, and insertions; recombination and rearrangement; and invasion and disruption by selfish genetic elements such as transposable elements. These many changes are subject to the vagaries of natural selection, resulting in a genome organization not based on principles of efficiency or economy of space, but instead contingent on the evolutionary history of the organism." [33].

Information processing is thus central to the origin and evolution of life and to adaptation to the environment. A model for evolution and adaptation must allow for natural selection to process information as well as operate in response to thermodynamic, environmental and natural constraints. Convolution of the performance curve of an organism as a function of all environmental constraints (see note 6) with the probability function describing the environmental constraints, both abiotic and biotic, thus gives direction to adaptive evolution. As a consequence, we propose the apparently random events that constitute natural selection behave in a deterministic way. This determinism in the temporal and spatial parameters and constraints of the probability distribution of selective events is the consequence of the physical constraints imposed by the environment.

Although relatively simple in concept, defining distribution functions of the constraints and organism performance in a given environment is too complex to be realistic. However, the concepts used in statistical mechanics and information theory suggest the existence of a governing

statistic that summarizes the activities of biological systems in the same manner that thermodynamic entropy summarizes chemical processes. Thus, we hypothesize that $k\ln W$ is a generic expression summarizing the probability constraints of any system in which the microstates can be defined and enumerated. Comparison of $k\ln W$ for the environment with $k\ln W$ for organism performance by enumerating the accessible microstates in each system measures fitness in the same way thermodynamic entropy predicts the position of equilibrium for a physical system, and thus expresses a second law of evolution. New terminology is needed to simply express these concepts and laws. Therefore, we propose to call the summary statistic for the environment the *envotropy* and the summary statistic of a population of a species, the *demotropy*. These terms clearly distinguish these summary statistics from the thermodynamic *entropy* which has frequently been misused and confused with other statistics. In these terms, the second law of evolution becomes, "the demotropy evolves toward the envotropy".

This concept of deterministic stochasticity has been stated as "The manifestations of life, its expressions, its forms, are so diverse that they must contain a large element of the accidental. And yet the nature of life is so uniform that it must be constrained by many necessities." [34] An evolutionary event that initiates a new capability and leads to macroevolution, such as light sensing, must be stochastic, i.e. by chance, but once such an event occurs, the ultimate outcome is deterministic, e.g. fully functioning eyes will eventually come to exist but the structure of the eye is contingent on the evolutionary history. In the same sense, the biological outcome from a geological or climatic event that creates a new environmental niche is deterministically stochastic. The deterministic nature of evolution is delightfully clear from the figure on page 20 of Losos' article [35] (Figure 2-1) showing convergent evolution of Australian marsupials and placental counterparts. Although random mutations, statistical aberrations and empirical adaptations driving

48

biological evolution are stochastic in nature, the probabilities generating these "random events" are deterministic, completely specified by the constraints of the system in which evolution is occurring. In other words, the evolutionary path of organisms within a system is deterministic, not stochastic, with the determinism being consistent within the constraints of the system. Therefore, if the constraints existent on earth exist elsewhere in the universe, random evolutionary processes will result in ecosystems, organisms and system dynamics that are similar to those on earth.

Figure 2-1: Convergent evolution of Australian marsupials and placental counterparts. (Reproduced by permission from [35])

A "second law" presupposes and requires the existence of a first law which we propose as: "Given appropriate conditions, life will originate and evolve." If the right conditions persist for a sufficient length of time, life will originate and eventually evolve into complex organisms. For now, "the appropriate conditions" means carbon based life that requires liquid water, a source of energy, etc.; the same as current life on earth. Under these conditions, the origin and evolution of living organisms has been shown to be thermodynamically spontaneous [4], and what is thermodynamically possible is inevitable, even for events with a very small probability.

The laws of evolution parallel the laws of thermodynamics, but are very different in application. The first law of thermodynamics is a conservation law while the first law of life in essence establishes that life based on compounds of C, H, O and N can exist only under a limiting set of thermodynamic conditions. The second law of thermodynamics establishes a direction and a fixed destination, i.e. maximum thermodynamic entropy, for physical systems as defined by pressure, volume and temperature. The second law of life similarly establishes a direction and destination, i.e. the envotropy, but the destination is a range of values, is variable, not fixed and likely has many demotropic values that satisfy a viable condition. The envotropy is subject to gradual change and also to sudden stochastic events that lead to extinction of species whose demontropic value falls entirely outside the range of the envotropy.

2.8   Summary

In 1867, Clausius [7] introduced entropy, S, as a thermodynamic property defined operationally by $\delta Q_{rev}/T$ to describe heat energy that cannot be converted into work. In 1875, Boltzmann [10, 14] introduced the concept of entropy as a measure of the number of accessible microstates described by the formula $S = k_B \ln(W)$. This *tour de force* explained Clausius' laws of

50

thermodynamics in terms of the statistical properties of the energies of atoms and molecules. However, Boltzmann further recognized that for a large system of indistinguishable particles, the system can be approximated by a single, most-probable configuration which can be used to simplify the entropy equation to $S = -k_B\Sigma p_i\ln p_i$. It is important to recognize that the equation, $S = -k_B\Sigma p_i\ln p_i$, is an approximation to the more general Boltzmann equation, $S = k_B\ln(W)$, and is only valid under the assumptions of (a) a single most-probable configuration, (b) a large number of particles, and (c) indistinguishable particles.

In 1948, Shannon [19] introduced information entropy ($\check{S}$) as a statistical model for communication. The form of Shannon's equation is identical to the Boltzmann equation, but the meaning is completely different. Information systems cannot have a single most-probable configuration because the symbols must be distinguishable and the sequence of symbols is the message.

Schrödinger's [20] incorrect assumption that the structures of living organisms have an unusually low entropy led some to incorrectly assume that S and $\check{S}$ are equivalent. However, the information in DNA is contained in the sequence of the bases, A, T, G and C, and does not have any effect on the value of $S(0)$ determined by statistical mechanics or the value of $S(T)$ determined from heat capacity measurements. Determination of $S(0)$ does not involve any decoding of sequence. Therefore, we conclude that $\check{S}$ is a subjective quantity fundamentally different from the objective thermodynamic entropy, $S(0)$. Application of information theory to DNA to evaluate $\check{S}$ requires definition of a reference state, but what would the reference state be for calculation of the information entropy of a DNA sequence? A perfect DNA sequence is the sequence that codes for an optimally functioning organism, but that sequence varies greatly both within and among species.

51

Thermodynamic entropy, S, and information entropy, $\check{S}$, are different quantities that cannot be combined. However, it appears that a second law can be constructed for information entropies by use of the same principles used for thermodynamic entropy. For example, in the case of thermodynamic entropy the second law predicts the direction of change in a dominant configuration of a large number of indistinguishable particles when the constraints on the system are changed, e.g., by addition of energy. In the case of information entropy, there is not necessarily a dominant configuration, however, microstates can be defined taking into account that the symbols are distinguishable and sequence matters. Thus, we posit that a second law for information can be constructed in a manner similar to thermodynamic entropy as a change in the distribution of microstates required to change the message in response to a change in the constraints. $S = K\ln(W)$ is thus the fundamental equation governing the calculation of entropy for many systems beyond the well-established application in chemistry and physics. The calculation of entropy for any system can therefore be generalized to counting the number of accessible microstates. In terms of DNA and organisms, adaptation and evolution can be viewed as a change in the distribution of the information microstates that optimizes fitness in response to constraints imposed by environmental changes.

Based on the general principle of enumerating microstates, we posit a paradigm wherein adaptation and evolution are stochastically deterministic, i.e. having a specific direction arising from many random events. Natural selection over time, resulting from random events governed by deterministic constraints, minimizes the difference in the information describing the local environment and the biological system. Therefore, this paradigm lays the foundation for an information theory formulated on the immensely powerful statistical concept of enumerating microstates that provides summary statistics similar to thermodynamic entropy. To avoid

confusion of thermodynamic entropy with various other "entropies", we propose the summary statistics for the environment and for the population demographics be called the "envotropy" and the "demotropy", respectively, and that a similar nomenclature be developed for the summary statistics of other systems. This work thus proposes a foundation for a quantitative theory for summary statistics of information systems including biological systems, economics, markets, and health systems.

2.9   Notes

1. In statistical mechanics, a microstate is a specific microscopic configuration of a thermodynamic system that the system may occupy with a certain probability in the course of its thermal fluctuations. (https://en.wikipedia.org/wiki/Microstate_(statistical_mechanics) accessed 5 Nov. 2017)

2. Since for most first order phase changes the temperature is constant and the transition occurs at constant pressure, the entropy change for the transition, $\Delta S_{\text{phase transitions}}$, is calculated as $Q_{\text{phase transition}}/T$ for each phase transition where Q is the heat absorbed in the phase transition and T is the fixed temperature of the phase transition. In this paper, the $\Delta S_{\text{phase transitions}}$ term is omitted for simplicity and included with second order and other ill-defined transitions that are included in the integral of C_p/T.

3. The integration in equation 2 goes from 0 K to a temperature τ at which the entropy S is determined, while T is the integration variable. However, in most texts T is used to denote both the integration variable and the limit of integration, the convention used here. Although entropy is always measured as the difference from a defined reference state, in the context of equation 2 the symbol S is traditionally written omitting the Δ used with

53

other thermodynamic quantities, e.g. ΔH and ΔG. The subscripts, Macro and micro, are used to distinguish between thermodynamic entropy that is measured by calorimetry and entropy that is calculated by statistical mechanics. Note that values of $S_{Macro}(T)$ do not include $S_{Macro}(0)$, but values of $S_{micro}(T)$ include the entropy at absolute zero temperature.

4. U should technically be indicated by [U], but is here denoted simply as U since, by the law of large numbers, the difference between U and [U] is insignificant for the systems of interest here.

5. The symbol, $\check{S}$, is used in this paper instead of the H used in Shannon's original work.

6. A performance curve is a plot of the rate of any activity of an organism, such as reproductive rate, versus one or more parameters describing the environment, such as temperature. The performance curve of an organism is defined here as the rate of successful reproduction plotted as a function of all environmental constraints.

2.10 Supplement 1: The Second Law of Classical Thermodynamics

This supplement gives a short overview of the second law in classical thermodynamics, explaining fundamental properties (e.g. heat, work…) and deriving the fundamental equations of thermodynamics. Much of this is taken from the text by Ott and Boerio-Goates [9].

2.10.1 Clausius Inequality Derivation

The Carnot engine is a hypothetical heat engine that is of fundamental significance in formulating the second law of thermodynamics and entropy. The Carnot engine operates using a

reversible cycle that consists of alternating reversible isothermal and adiabatic expansions and compressions (Figure 2-2). The cycle has four steps that return the system to its initial condition:

1. An isothermal expansion

2. An adiabatic expansion

3. An isothermal compression

4. An adiabatic compression
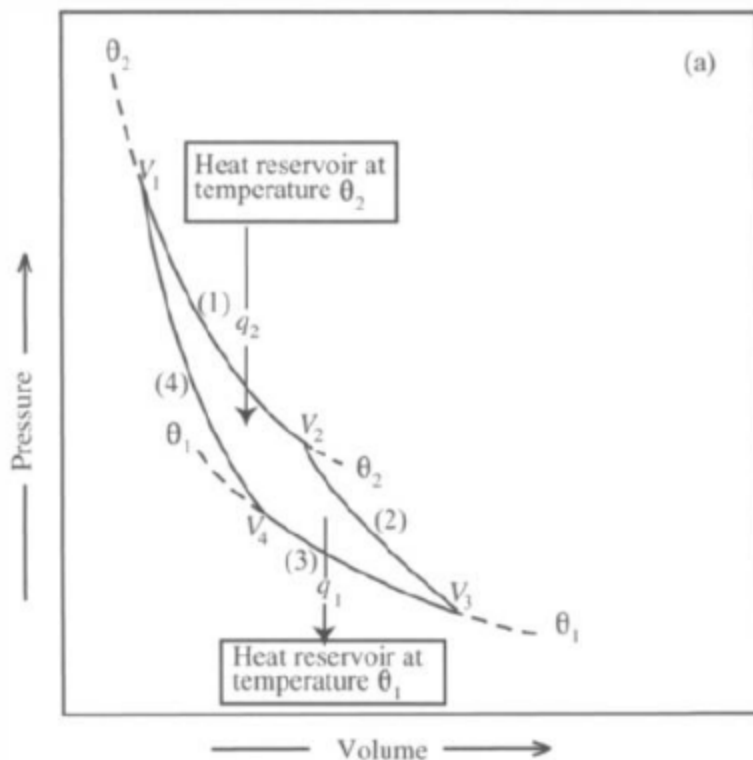
Figure 2-2: The Carnot cycle.

A thermodynamic temperature of the reservoirs is defined to be proportional to heat exchanged by the reservoirs with the system

$$T_2 = k \cdot q_2 \qquad \qquad (S.1.1)$$

And

$$T_1 = -k \cdot q_1 \qquad \text{(S.1.2)}$$

where k is a proportionality constant, T_1 and T_2 are the thermodynamic temperatures of the first and second reservoirs, respectively; while q_1 and q_2 are amount of heat exchanged with the first and second reservoirs, respectively. The minus sign in equation (S.1.2) must be included because thermodynamic temperature is always positive, while $q_1<0$. Equations (S.1.1) and (S.1.2) can be manipulated into

$$\frac{1}{k} = \frac{q_2}{T_2} \qquad \text{(S.1.3)}$$

$$\frac{1}{k} = -\frac{q_1}{T_1} \qquad \text{(S.1.4)}$$

By subtracting equation (S.1.4) from (S.1.3)

$$\frac{1}{k} - \frac{1}{k} = \frac{q_2}{T_2} - \left(-\frac{q_1}{T_1}\right) \qquad \text{(S.1.5)}$$

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = \sum \frac{q_{rev}}{T} = 0 \qquad \text{(S.1.6)}$$

where q_{rev} is heat exchanged in a reversible process. Equation (S.1.6) shows that q_1 and q_2 are not state functions, but q_{rev}/T is a state function, since the sum of q_{rev}/T terms in the cycle add to zero. This important observation led to the formulation of the entropy function.

If we have any kind of cycle in general, we can approximate it as a sum of many Carnot cycles (Figure 2-3).
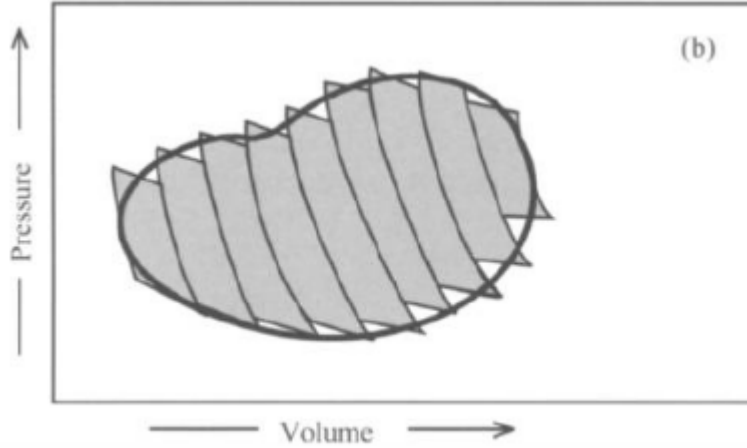
Figure 2-3: Approximation of a real cyclic process with Carnot cycles.

In that case, since equation (S.1.6) holds for each of the Carnot cycles, for the overall cycle we have

$$\sum \frac{q_{rev}}{T} = 0 \tag{S.1.7}$$

The more Carnot cycles included, the better the approximation to the overall cycle. To precisely approximate the overall cycle, an infinite number of infinitesimal Carnot cycles are used by replacing the sum in equation (S.1.7) with a circular integral

$$\oint \frac{q_{rev}}{T} = 0 \tag{S.1.8}$$

Equation (S.1.8) shows the integral around a closed path of q_{rev}/T is zero, thus showing that q_{rev}/T is a state function. This state function is named entropy, and given the symbol, S. Therefore,

$$dS = \frac{\delta q_{rev}}{T} \tag{S.1.9}$$

where d is used before S to denote an exact differential – a state function, while δ is used before q_{rev} to denote that it is an inexact differential – it is not a state function. While q_{rev} is not a state function, division by T it gives the state function, S.

The consideration above was for reversible processes only (i.e. q_{rev}). Generalizing equation (S.1.9) for all processes, including irreversible processes, begins with the first law of thermodynamics. In a reversible process, the work is always minimal. If the system does work, we will be able to extract the largest work from it. Since w is negative for a system doing work, its most negative value will be reached when the process is reversible. If a work is done on the system, the smallest amount of work will need to be done if the process is reversible. So, since by convention, work done on the system is positive, it will have the lowest possible positive value. Thus, in a reversible process work is always minimal: $w_{rev}=w_{min}$.

Since U is a state function it doesn't matter whether a process that changes it is reversible or irreversible, as long as the system goes between two defined states, the change in U will be the same, regardless of the path taken. Therefore, in a reversible process if U is constant and w is minimal, and since q and w are reciprocal, q will be maximal: $q_{rev}=q_{max}$. If q is maximal in a reversible process, in an irreversible process it will be lower, thus: $q_{irrev} < q_{rev}$, where q_{irrev} is the heat received by a system in an irreversible process. This combined with equation (S.1.9) implies that

$$dS > \frac{\delta q_{irrev}}{T} \qquad (S.1.10)$$

By combining equations (S.1.9) and (S.1.10) we obtain the general case

$$dS \geq \frac{\delta q}{T} \qquad (S.1.11)$$

58

which is the Clausius inequality. There are also other derivations, such as the Caratheodory Principle, that arrive at the same conclusion.

2.11 Supplement 2: Clausius' Entropy

In this supplement equation (2) from the main body of the paper is derived from equation (1). The entire derivation is based on macroscopic classical thermodynamics. Good sources of further information on the subject are textbooks, such as Atkins and de Paula [36, 37], Dugdale [13], Ott and Boerio-Goates [9], or Chang [38].

The Clausius equation (equation 1) is

$$dS_{Macro} = \delta Q_{reversible}/T \qquad (S.2.1)$$

Heat capacity at constant pressure, C_p, is defined as

$$C_p = \delta Q_p/dT \qquad (S.2.2)$$

Q_p is heat exchanged at constant pressure between a system and its surroundings [9, 36-38]. Assuming the process is reversible, δQ_p can be set equal to $\delta Q_{reversible}$ and equation (S.2.2) rearranged into

$$\delta Q_{reversible} = C_p dT \qquad (S.2.3)$$

Substituting (S.2.3) into (S.2.1),

$$dS = \frac{C_p}{T} dT \qquad (S.2.4)$$

Integrating equation (S.2.4) from absolute zero to a temperature T evaluates the entropy

59

$$\int_0^T dS = \int_0^T \frac{C_p}{T} dT \tag{S.2.5}$$

Note that the integration in equation (S.2.5) goes from 0 K to a temperature τ at which the entropy S is determined, while T is the integration variable. However, in most texts T is used to denote both the integration variable and the limit of integration, the convention used here. After the integration of the left-hand side, equation (S.2.5) gives

$$S\big|_0^T = \int_0^T \frac{C_p}{T} dT \tag{S.2.6}$$

$$S_T - S_0 = \int_0^T \frac{C_p}{T} dT \tag{S.2.7}$$

S_T is the entropy at temperature T and S_0 is the entropy at zero kelvin. Rearranging equation (S.2.7),

$$S_T = S_0 + \int_0^T \frac{C_p}{T} dT \tag{S.2.8}$$

Equation (S.2.8a) allows calculation of the entropy of a substance at any temperature, T, using S_0 and determination of C_p as a function of temperature [9, 36-38]. Equation (S.2.8) is equation (3) from the main body of the paper.

Note that, if the substance exhibits phase transitions, heat is added, but does not change the temperature [9, 36-38]. Therefore, a phase transition entropy term, $\Delta S_{phase\ transitions}$, must be included in equation (S.2.8a),

$$S_T = S_0 + \Delta S_{phase\ transitions} + \int_0^T \frac{C_p}{T} dT \tag{S.2.9}$$

The value of $\Delta S_{phase\ transitions}$ is evaluated by noting that, at the phase transition temperature, any heat exchanged between the system and surroundings is reversible because the two phases in the system are in equilibrium [9, 36-38]. The change in entropy during a phase transition, $\Delta_{trs}S$, is

$$\Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}} \tag{S.2.10}$$

$\Delta_{trs}H$ is the enthalpy change of the phase transition, T_{trs} is the temperature at which the phase transition occurs [9, 36-38]. If the substance exhibits multiple phase transitions, the total phase transition entropy $\Delta S_{phase\ transitions}$ is just the sum of the entropy changes of the individual phase transitions,

$$\Delta S_{phase\ transitions} = \sum \Delta_{trs}S \tag{S.2.11}$$

Second order and other ill-defined transitions are included in the integral of C_p/T. However, in this paper, the $\Delta S_{phase\ transitions}$ term is omitted for simplicity and included with second order and other ill-defined transitions that are included in the integral of C_p/T. Therefore, equation (S.2.8) will be used in all following discussions.

2.12 Supplement 3: Statistical Entropy Equations

In this supplement, equation (9) from the main body of the paper is derived from equation (4). The discussion is based on the framework of statistical mechanics. Good sources of further information of the subject are Dugdale [13], Nash [15], and Sandler [12].

Relating equations (4) and (9) really means showing that:

$$\ln W = -N \sum_{i=1}^{q} p_i \ln p_i \tag{S.3.1}$$

61

Where p_i is the probability an atom is in quantized energy state i and q is the number of quantized energy states. For a specific configuration, denoted C, we know that the number of atoms in quantized state i is fixed for all i. Denote these counts as n_i, i = 1, 2,…,q. Then for this configuration, the number of microstates, W_C, is given by

$$W_C = \frac{N!}{\prod_i(n_i!)} \tag{S.3.2}$$

Recall Stirling's approximation

$$\ln(N!) = N\ln(N) - N \tag{S.3.3}$$

Taking logarithms of both sides of equation S.3.2 we get

$$\ln W_C = N\ln(N) - N - \sum_{i=1}^{q}[n_i\ln(n_i) - n_i] \tag{S.3.4}$$

Recall, $\Sigma n_i = N$. Consequently S.3.4 can be simplified to

$$\begin{aligned}
\ln W_C &= N\ln(N) - N - \sum_{i=1}^{q}[n_i\ln(n_i) - n_i] \\
&= -\sum_{i=1}^{q} n_i[\ln(n_i) - \ln(N)] \\
&= -\sum_{i=1}^{q} n_i\ln\frac{n_i}{N} \\
&= -N\sum_{i=1}^{q} \frac{n_i}{N}\ln\frac{n_i}{N} \\
&= -N\sum_{i=1}^{q} p_i\ln p_i
\end{aligned} \tag{S.3.5}$$

Where $p_i = n_i / N$ is the proportion of molecules in quantized energy state i in configuration C.

The above derivation gives the number of microstates in the specific configuration, C. However, as is well known, for indistinguishable particles, for large N, there is only one configuration that dominates (see Nash [15]) for large n. Therefore, $\ln W$ can be approximated by

62

$$\ln W \approx \ln W_{C_0}$$

$$= -N \sum_{i=1}^{q} p_{0,i} \ln p_{0,i} \qquad \text{(S.3.6)}$$

where C_0 is the dominant configuration and $p_{0,i} = n_i / N$ is the proportion in quantized energy state i, for that configuration.

For any set of atoms and total energy, there is a dominant configuration. Changing the energy or the number of atoms changes the dominant configuration. The system moving to the dominant configuration is the second law. Note that Gibbs arrived at the same expression for entropy without relying on energy levels and the existence particles. The common assumption in each approach is the necessity of a large number of indistinguishable particles that result in a single dominant configuration.

2.13 References:

[1]   Allen, G.E. Mechanism, vitalism and organicism in late nineteenth and twentieth-century biology: the importance of historical context. *Stud. Hist. Phil. Biol. & Biomed. Sci.*, **2005**, *36*, 261–283.

[2]   Tribus, M.; McIrving, E. C. Energy and Information, *Scientific American*, **1971**, *225*, 179-188.

[3]   Ben-Naim, A. Can entropy be defined for, and the second law applied to living systems? *arXiv*, **2017**, arXiv:1705.02461 [physics.pop-ph].

[4]   Hansen, L.; Criddle, R.S.; Battley, E.H. Biological calorimetry and the thermodynamics of the origination and evolution of life, *Pure Appl. Chem.*, **2009**, *81* (10), 1843–1855.

[5]   Müller, I. *A History of Thermodynamics: The Doctrine of Energy and Entropy;* Springer: Berlin, Germany, 2007.

[6]   Carnot, S. *Reflections on the Motive Power of Fire, and on Machines Fitted to Develop That Power;* in *The Second Law of Thermodynamics,* Kestin, J., ed.; Dowen, Hutchingson & Ross, Inc.: Stroudsburg, PA, 1976. (page 16)

[7]   Clausius, R. *On Different forms of the Fundamental Equations of the Mechanical Theory of Heat and Their Convenience for Application;* in *The Second Law of Thermodynamics,* Kestin, J., ed.; Dowen, Hutchingson & Ross, Inc.: Stroudsburg, PA, 1976. (page 162)

[8]   Clayton, J. O.; Giauque, W. F. The Heat Capacity and Entropy of Carbon Monoxide. *J. Am. Chem. Soc.*, **1932**, *54*, 2610-2626.

[9]   Ott, J. B.; Boerio-Goates, J. *Chemical Thermodynamics: Principles and Applications, 1st ed.;* Academic Press: Cambridge, MA, USA, 2000.

[10]   Boltzmann, L. *Lectures on gas theory;* Dover publications: Mineola, NY, 1995.

(translation of *Vortesungen uber gastheorie*; J.A. Bath: Leipzig, Germany: part 1 was

published in 1896, part 2 was published in 1898).

[11]   McQuarrie, D. A. *Statistical Mechanics*; University Science Books: Sausalito, CA, 2000.

[12]   Sandler, S.I. *An introduction to applied statistical thermodynamics;* Wiley: Hoboken, NJ,

USA, 2011.

[13]   Dugdale, J.S. *Entropy and its Physical Meaning;* Taylor & Francis Ltd: London, UK,

1996.

[14]   Sharp, K.; Matschinsky, F. Translation of Ludwig Boltzmann's Paper "On the

Relationship between the Second Fundamental Theorem of the Mechanical Theory of

Heat and Probability Calculations Regarding the Conditions for Thermal Equilibrium"

Sitzungberichte der Kaiserlichen Akademie der Wissenschaften. Mathematisch-

Naturwissen Classe. Abt. II, LXXVI 1877, pp 373-435 (Wien. Ber. 1877, 76:373-435).

Reprinted in Wiss. Abhandlungen, Vol. II, reprint 42, p. 164-223, Barth, Leipzig, 1909.

Entropy, **2015**, *17* (4), 1971-2009.

[15]   Nash, L.K. *Elements of statistical thermodynamics;* Adison-Wesley: Boston, MA, 1968.

[16]   Gibbs, J.W. *Elementrary principles in statistical mechanics;* Dover publications:

Mineola, NY, 2014. (reprint of Gibbs, J.W. *Elementrary principles in statistical

mechanics;* Yale University Press: New Haven, CT, 1902.)

[17]   Kozliak, E. Consistent Application of the Boltzmann Distribution to Residual Entropy in

Crystals. *J. Chem. Edu.*, **2007**, *84*, 493-498.

[18]   Lewis, G.N.; Randall, M.; Pitzer, K.S.; Brewer, L. *Thermodynamics;* McGraw-Hill: New

York, NY, USA, 1961.

[19] Shannon, C. A mathematical theory of communication. *The Bell System Technical Journal*, **1948**, *27*, 379-423.

[20] Schrödinger, E. *What is life? The physical aspect of the living cell, 10th printing*; Cambridge university press: Cambridge, UK, 2003.

[21] Battley, E.H. An empirical method for estimating the entropy of formation and the absolute entropy of dried microbial biomass for use in studies on the thermodynamics of microbial growth. *Thermochimica Acta*, **1999**, *326* (1), 7-15.

[22] von Stockar, U.; Liu, J. Does microbial life always feed on negative entropy? Thermodynamic analysis of microbial growth. *Biochim Biophys Acta*, **1999**, *1412* (3),191-211.

[23] Morowitz, H.J. Some order-disorder considerations in living systems. *Bulletin of mathematical biophysics*, **1955**, *17* (2), 81-86.

[24] Brillouin, L. Maxwell's Demon Cannot Operate: Information and Entropy I. *J. Appl. Phys.*, **1951**, *22*, 334-337.

[25] Balmer, R. T. *Modern Engineering Thermodynamics*; Academic Press: Boston, MA, USA, 2011.

[26] Brillouin, L. *Science and information theory*; Academic press: New York, NY, 1962.

[27] Morowitz, H.J. *Energy flow in biology*; Academic press: New York, NY, 1968.

[28] Jaynes, E.T. Information theory and statistical mechanics I. *Phys.Rev.* **1957**, *106*, 620-630.

[29] Landauer, R. Irreversibility and heat generation in the computing process. *IBM Journal of Research and Development*, **2000**, *44*, 261-269. (Reprint from *IBM Journal of Research and Development*, **1961**, *5*(3))

[30] Rosen, R. Life Itself: A Comprehensive Inquiry into the Nature, Origin, and Fabrication of Life. Columbia University Press, NY, 1991.

[31] Lan, G.; Tu, Y. Information processing in bacteria: memory, computation, and statistical physics: a key issues review. *Rep. Prog. Phys.*, **2016**, *79*, 052601.

[32] Shapiro, J.A. Evolution: A View from the 21st Century. FT Press Science, 2011, ISBN 978-0-13-278093-3.

[33] Zahn, L.M.; Riddihough, G. Building on nature's design. *Science*, **2017**, *355*(6329), 1038-1039.

[34] Bronowski, J. *The Ascent of Man*; Little, Brown and Company: Boston, MA, 1973, p. 291.

[35] Losos, J.B., Improbable replications, Replaying evolution, often but not inevitably, yields similar outcomes. *Natural History,* **2017**, *July/August*, 16-21.

[36] Atkins, P.; de Paula, J. *Physical Chemistry, 8th ed*.; W.H. Freeman and Company, New York, NY, 2006.

[37] Atkins, P.; de Paula, J. *Physical chemistry for the life sciences;* W.H. Freeman and Company: New York, NY, 2011.

[38] Chang, R. *Physical chemistry for the Chemical and Biological Sciences, 3rd ed.;* University Science Books: Sausalito, CA, 2000.

3   THERMODYNAMICS OF HYDROLYSIS OF CELLULOSE TO GLUCOSE FROM 0 TO 100ºC: CELLULOSIC BIOFUEL APPLICATIONS AND CLIMATE CHANGE IMPLICATIONS

3.1   Abstract

Hydrolysis of cellulose to glucose is a key reaction in renewable energy from biomass and in mineralization of soil organic matter to CO_2. Conditional thermodynamic parameters, $\Delta_{hyd}G'$, $\Delta_{hyd}H'$, and $\Delta_{hyd}S'$, and equilibrium glucose concentrations are reported for the reaction $C_6H_{10}O_5(cellulose) + H_2O(l) \rightleftarrows C_6H_{12}O_6(aq)$ as functions of temperature from 0 to 100ºC. Activity coefficients of aqueous glucose solution were determined as a function of temperature. The reaction free energy $\Delta_{hyd}G'$ becomes more negative as temperature increases, suggesting that producing cellulosic biofuels at higher temperatures will result in higher conversion. Also, cellulose is a major source of carbon in soil and is degraded by soil microorganisms into CO_2 and H_2O. Therefore, global warming will make this reaction more rapid, leading to more CO_2 and accelerated global warming by a positive feedback.

Key Words: Renewable energy; Biomass; Soil organic matter; Lignocellulose; Global warming; Glucose activity coefficient.

3.2   Introduction

Most of the carbon fixed by terrestrial plants is used to synthesize lignocellulose. As one of the largest reservoirs of organic compounds on the planet, lignocellulose has the potential to replace a significant amount of petroleum as a feedstock for production of chemicals and liquid fuels. Because lignocellulose is a major part of soil organic matter, oxidation of lignocellulose to

68

CO_2 is a major contributor of atmospheric CO_2, but the temperature dependence of the rate of this reaction is very uncertain.

Lignocellulose consists of approximately equal parts lignin, cellulose and hemicellulose. Lignin is a two-dimensional polyphenol, cellulose is a largely crystalline polymer of glucose with a coiled structure, and hemicellulose consists of relatively short polysaccharides of various sugars with no long range structural order. Hemicellulose is relatively easily separated and solubilized by hydrolysis with acid or base catalysis under mild conditions and is readily metabolized to CO_2 by soil organisms. The difficulty of depolymerizing and solubilizing the lignin and cellulose in lignocellulose is a major roadblock to use of biomass as a chemical feedstock and may limit the rate of oxidation to CO_2 in soil. The hydrolysis reactions of lignin and cellulose may be significant in turnover of soil organic matter with potential positive feedback exacerbating global warming, but it is unknown whether these reactions occur to a significant extent at normal soil temperatures. The potential use of lignocellulose as a feedstock for chemical and fuel production also depends on the thermodynamics of the depolymerizing hydrolysis reactions.

Several exozymes that catalyze hydrolysis of lignocellulose are known [1], but whether or not these could be used in an economically viable process depends on the extent of reaction that can be obtained. Therefore, it is important to quantify the thermodynamics of hydrolysis of lignocellulose. This study quantifies the thermodynamics of the cellulose component of lignocellulose to aqueous glucose as a function of temperature from 0 to 100ºC.

3.3 Thermodynamic data

Goldberg et al. [2] reports $\Delta_{cr}H°$, $\Delta_{cr}S°$, $\Delta_{cr}G°$, and $\Delta_{cr}C_p°$ for the hydrolysis of four cellulose allomorphs (amorphous cellulose, cellulose I, cellulose II and cellulose III) to crystalline

anhydrous α-D-glucose at 25°C (Table 3-1) and heat capacities for the allomorphs from 2 to 300 K. The calculation assumes the molar entropy of cellulose per monomer unit is equal to the entropy change of heating cellulose from absolute zero to room temperature, residual entropy was neglected, since it could not be determined. Boerio-Goates [3] reports heat capacity data for crystalline anhydrous α-D-glucose from 10 to 340 K. Osborne *et al.* [4] reports heat capacity data on liquid water from 273 to 373 K.

Table 3-1: Heat capacity coefficients for equation (9), and $\Delta_{cr}H°_{ref}$, $\Delta_{cr}S°_{ref}$ and $\Delta_{cr}C_p°$ values for equations 5 and 6. (From reference 2.)

	Amorphous cellulose	Cellulose I	Cellulose II	Cellulose III
$\Delta_{cr}H_{ref}°$ (kJ/mol)	-(6.4 ± 2.7)	8.2 ± 3.7	13.6 ± 3.3	9.9 ± 4.1
$\Delta_{cr}S_{ref}°$ (J/mol K)	-(28.6 ± 3.3)	-(24 ± 11)	-(5 ± 16)	-(0.6 ± 19)
$\Delta_{cr}C_p°$ (J/mol K)	-(47.3 ± 3.0)	-(37 ± 11)	-(22 ± 15)	-(18 ± 17)
q_0 (J mol^{-1} K^{-1})	93.3460	-76.5740	-117.0000	-126.7400
q_1 (J mol^{-1} K^{-2})	-1.0488	0.4127	0.8477	0.9178
q_2 (J mol^{-1} K^{-3})	0.0026	-0.0009	-0.0018	-0.0018
q_3 (J mol^{-1} K^{-4})	$-2\cdot10^{-6}$	0	0	0

Many references report glucose solubility in water [5-9], but due to difficulties of making measurements on saturated glucose solutions, the results differ significantly. Some reports [7, 8]

give solubility as mass of glucose per liter of solution, but reliable solution density data to convert these to temperature independent, and thus thermodynamically useful molal units, are not available. Because reliable density data over the range of temperatures analyzed in this study are not available, only references that give solubility in mass fractions were used. Examination of experimental procedures indicates the data published by Young [6] are the most reliable and cover sufficient temperature range for this study, Table 3-3.

Vapor pressure measurements of aqueous glucose solutions was reported by Taylor and Rowlinson [10]. These data were used to calculate activity coefficients of aqueous glucose.

3.4   Reactions

The reaction of interest is cellulose hydrolysis in water to produce an aqueous solution of glucose,

$$(C_6H_{10}O_5)_u \cdot (H_2O)_1 \cdot (H_2O)_{v\,(s)} + (u\text{-}v\text{-}1)H_2O_{(l)} \rightleftarrows uC_6H_{12}O_{6\,(aq,\,hyd)} \tag{1}$$

$(C_6H_{10}O_5)_u \cdot (H_2O)_1 \cdot (H_2O)_{v\,(s)}$ is cellulose, u is the average number of monosaccharide units in the polymer, v is the average number of waters of hydration [2], $C_6H_{12}O_{6(aq,\,hyd)}$ is glucose in the cellulose hydrolysis equilibrium solution. No direct thermodynamic measurements have been made on this reaction, and therefore, the reaction was divided into two reactions for which thermodynamic data are available. One reaction is hydrolysis of cellulose to crystalline glucose,

$$(C_6H_{10}O_5)_u \cdot (H_2O)_1 \cdot (H_2O)_{v\,(s)} + (u\text{-}v\text{-}1)H_2O_{(l)} \rightleftarrows uC_6H_{12}O_{6\,(cr)} \tag{2}$$

where $C_6H_{12}O_{6(cr)}$ is anhydrous α-D-glucose. Even though α-D-glucose monohydrate $C_6H_{12}O_6 \cdot H_2O$ is the most thermodynamically stable form up to 50°C, reaction (2) was used in the entire temperature region where thermodynamic values were estimated. The product of reaction

(1) is anhydrous α-D-glucose and the reactant in reaction (3) is anhydrous α-D-glucose. Therefore, even though it is not the most thermodynamically stable form below 50°C, anhydrous α-D-glucose is used to complete the Hess' law cycle in Scheme 1. The other reaction is dissolution of crystalline glucose to make the final aqueous solution.

$$C_6H_{12}O_{6\,(cr)} \rightleftarrows C_6H_{12}O_{6\,(aq,\,sat)} \tag{3}$$

where $C_6H_{12}O_{6\,(aq,\,sat)}$ is glucose in a saturated aqueous solution.   Completing the cycle also requires correction for the thermodynamics of dilution of glucose since the equilibrium concentrations differ, i.e. saturated and in equilibrium with cellulose.

$$C_6H_{12}O_{6\,(aq,\,sat)} \rightleftarrows C_6H_{12}O_{6\,(aq,\,hyd)} \tag{4}$$

Scheme 1 shows how the thermodynamic data for reactions 2, 3 and 4 are combined to determine the thermodynamics of reaction 1.

Scheme 1. Separating the cellulose hydrolysis to aqueous glucose reaction into components.

$(C_6H_{10}O_5)_u \cdot (H_2O)_1 \cdot (H_2O)_{v\,(s)} + (u-v-1)H_2O_{(l)} \rightleftarrows uC_6H_{12}O_{6\,(cr)}$ $\qquad\qquad\Delta_{cr}X^0$

$C_6H_{12}O_{6\,(cr)} \rightleftarrows C_6H_{12}O_{6\,(aq,\,sat)}$ $\qquad\qquad\qquad\qquad\qquad\qquad\quad\Delta_{sol}X'$

$C_6H_{12}O_{6\,(aq,\,sat)} \rightleftarrows C_6H_{12}O_{6\,(aq,\,hyd)}$ $\qquad\qquad\qquad\qquad\qquad\quad\Delta_{dil}X^0$

$(C_6H_{10}O_5)_u \cdot (H_2O)_1 \cdot (H_2O)_{v(s)} + (u-v-1)H_2O_{(l)} \rightleftarrows uC_6H_{12}O_{6(aq,\,hyd)}$ $\Delta_{hyd}X' = \Delta_{cr}X^0 + \Delta_{sol}X' + \Delta_{dil}X^0$
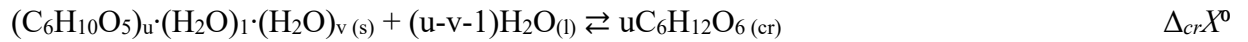
3.5   Cellulose hydrolysis to solid glucose

The thermodynamics of reaction (2) can be extrapolated from 25 to 100⁰C by assuming $\Delta_{cr}C_p°$ does not change with temperature and using the value of $\Delta_{cr}C_p°$ (Table 3-1) from Goldberg *et al.* [2] as a constant in integrating $dH=\int C_p dT$ and $dS=\int (C_p/T)dT$, i.e.,

72

$$\Delta_{cr}H° = \Delta_{cr}H°_{ref} + \Delta_{cr}C_p°(T - T_{ref}) \qquad (5)$$

$$\Delta_{cr}S° = \Delta_{cr}S°_{ref} + \Delta_{cr}C_p° \ln(T/T_{ref}) \qquad (6)$$

$\Delta_{cr}H°_{ref}$ and $\Delta_{cr}S°_{ref}$ are the standard reaction enthalpy and entropy at the reference temperature 25°C, taken from Goldberg *et al.* [2] (Table 3-1).

The standard Gibbs energy change of reaction (2), $\Delta_{cr}G°$, was then calculated with the equation

$$\Delta_{cr}G° = \Delta_{cr}H° + T\Delta_{cr}S° \qquad (7)$$

To test whether assuming constant $\Delta_{cr}C_p°$ leads to a significant error in the final results, the heat capacity data for cellulose [2] and anhydrous α-D-glucose [3] were fit to

$$C_p(T) = p_1 D(\Theta_D) + p_2 D(\Theta_E) + p_3 T + p_4 T^2 \qquad (8)$$

and extrapolated to 100°C. $C_p(T)$ is the heat capacity as a function of temperature, $D(\Theta_D)$ is the Debye function, Θ_D is the Debye temperature, $E(\Theta_E)$ is the Einstein function, Θ_E is the Einstein temperature, T is Kelvin temperature, and p_1, p_2, p_3 and p_4 are coefficients that satisfy $p_1 + p_2 + p_3 + p_4 = 1$. The fitted parameters are given in Table 3-2. The data were then corrected for cellulose water content and crystallinity and averaged as described by Goldberg *et al.* [2] The extrapolated C_p data were then used to find $\Delta_{cr}C_p°$, which was then used to extrapolate the $\Delta_{cr}G°$, $\Delta_{cr}H°$, and $\Delta_{cr}S°$ of reaction (2) up to 100°C. Because the results did not differ significantly from the approximation of constant $\Delta_{cr}C_p°$, equations (5) and (6) are used in all subsequent calculations.

Table 3-2: Adjustible parameters for cellulose and α-D-glucose heat capacity equation (8).

p_1	Θ_D (K)	p_2	Θ_E (K)	p_3	p_4	%RMS

Cel. Am. 24h	0.0241	285.10	0.0505	921.95	$2.716 \cdot 10^{-6}$	0	1.577999
Cel. Am. 30h	0.0245	287.40	0.0520	938.33	$2.709 \cdot 10^{-6}$	0	1.732902
Cel. Am. 36h	0.0213	272.21	0.0310	854.85	$5.297 \cdot 10^{-6}$	0	1.183929
Cel. Iβ	0.0202	265.84	0.0224	797.81	$6.082 \cdot 10^{-6}$	0	0.924771
Cel. II 25ºC	0.0186	258.12	0.0154	735.23	$7.757 \cdot 10^{-6}$	0	0.90598
Cel. II 70ºC	0.0194	263.13	0.0222	788.12	$6.099 \cdot 10^{-6}$	0	1.036268
Cel. II 145ºC	0.0198	266.77	0.0251	821.86	$5.667 \cdot 10^{-6}$	0	1.138173
Cel. III -33ºC	0.0194	263.64	0.0225	785.44	$5.955 \cdot 10^{-6}$	0	1.068027
Cel. III 25ºC	0.0185	256.85	0.0160	720.36	$7.321 \cdot 10^{-6}$	0	0.839996
Cel. III 130ºC	0.0200	267.58	0.0255	817.55	$5.782 \cdot 10^{-6}$	0	1.122759
α-D-glucose	0.8582	328.92	2.5036	1795.93	0	0.6486	0.158449

Using the extrapolated heat capacities of cellulose and anhydrous α-D-glucose and the water heat capacity determined by Osborne *et al.* [4], the heat capacity change, $\Delta_{cr}C_p°$, for reaction (2) was determined for each of the cellulose allomorphs and fit to a third order polynomial in *T* where *T* is temperature in Kelvins.

$$\Delta_{cr}C_p(T) = q_0 + q_1 T + q_2 T^2 + q_3 T^3 \tag{9}$$

The values of $q_0, q_1, q_2,$ and q_3 are given in Table 3-1.

$\Delta_{cr}C_p$ *(T)* for reaction (2) was extrapolated to 100°C and substituted into the equations $dH=\int C_p dT$ and $dS=\int (C_p/T)dT$, which were then integrated from 25°C to 100°C.

$$\Delta_{cr}H° = \Delta_{cr}H°_{ref} + \frac{1}{4}q_3\left(T^4 - T^4_{ref}\right) + \frac{1}{3}q_2\left(T^3 - T^3_{ref}\right) + \frac{1}{2}q_1\left(T^2 - T^2_{ref}\right) + q_0\left(T - T_{ref}\right) \tag{10}$$

$$\Delta_{cr}S° = \Delta_{cr}S°_{ref} + \frac{1}{3}q_3\left(T^3 - T^3_{ref}\right) + \frac{1}{2}q_2\left(T^2 - T^2_{ref}\right) + q_1\left(T - T_{ref}\right) + q_0 \ln\left(\frac{T}{T_{ref}}\right) \tag{11}$$

Substituting equations (10) and (11) into (7), and comparing $\Delta_{cr}G°$ values found from $\Delta_{cr}C_p°$ described by equation (8) and found from constant $\Delta_{cr}C_p°$, indicates the approximation in the latter method causes an average error of 0.16% and a maximum error of 1.12% compared with equation (8), thus justifying the use of equations (5) and (6) in subsequent derivations.

3.6 Glucose solubility

The thermodynamic parameters for reaction (3), solution of crystalline glucose into water, are based on the solubility of anhydrous α-D-glucose in water, Table 3-3. For practical purposes, concentrations are more convenient than activities, so conditional thermodynamic parameters of

dissolution of glucose in water based on molality were determined. The conditional equilibrium constant for reaction (3) is

$$K'_{sol} = b^{eq}_{sol} \tag{12}$$

where b^{eq}_{sol} is the equilibrium solubility of glucose expressed in molal units. The conditional equilibrium constants of reaction (3) are given in Table 3-4. (Note that a prime symbol refers to a saturated glucose solution as a specified condition.)

Table 3-3: Solubility of α-D-glucose in water. Molality is denoted b and mass fraction is denoted w. Conversion between b and w is done with the equation b = w / [180.16 (1-w)], where 180.16 is the molar mass of glucose.

θ (°C)	w (wt%)	T (K)	b (mol/kg H$_2$O)
-12.06	49.81	261.09	5.509
-10.00	50.49	263.15	5.660
0.00	53.80	273.15	6.464
10.00	57.19	283.15	7.414
20.00	60.65	293.15	8.554
30.00	64.18	303.15	9.945
40.00	67.78	313.15	11.679
50.00	71.46	323.15	13.900
54.71	73.22	327.86	15.177

The conditional enthalpy of dissolution of glucose in water, $\Delta_{sol}H'$, is determined with the van't Hoff relation

$$-\frac{\Delta_{sol}H'}{R} = \frac{d \ln K'_{sol}}{d(1/T)} \tag{13}$$

The van't Hoff plot is shown in Figure 3-1 with data from Table 3-4 fitted to a second order polynomial in T^{-1}.

$$\ln K'_{sol} = mT^{-2} + nT^{-1} + k \tag{14}$$

m, n and k are constants given in Table 3-5. The first derivative of the polynomial gives the enthalpy change for dissolution as

$$\Delta_{sol}H' = -R(2mT^{-1} + n) \tag{15}$$

Values of $\Delta_{sol}H'$ are given in Table 3-6.
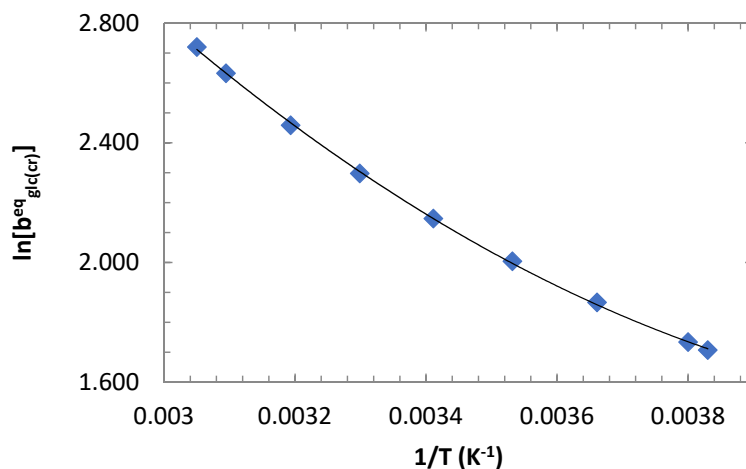
Figure 3-1: Van't Hoff plot for dissolution of crystalline α-D-glucose in water, $C_6H_{12}O_6(cr) \rightleftarrows C_6H_{12}O_6(aq)$. The line going through the points is a second order polynomial fit.

77

Table 3-4: Conditional equilibrium constants (K'_{sol}) and conditional Gibbs energy changes ($\Delta_{sol}G'$), calculated from solubilities, for dissolution of anhydrous α-D-glucose in water.

T (K)	K'_{sol}	$\Delta_{sol}G'$ (kJ/mol)
261.09	5.5094	-3.7042
263.15	5.6598	-3.7924
273.15	6.4639	-4.2381
283.15	7.4142	-4.7162
293.15	8.5539	-5.2313
303.15	9.9448	-5.7895
313.15	11.6790	-6.3989
323.15	13.9000	-7.0710
327.86	15.1767	-7.4136

The conditional Gibbs energy change for dissolution of glucose in water, $\Delta_{sol}G'$, is related to the conditional equilibrium constant by

$$\Delta_{sol}G' = -RT \ln K'_{sol} \tag{16}$$

The values of $\Delta_{sol}G'$ given in Table 3-4 were then fitted to the function,

$$\Delta_{sol}G' = \Delta H_I - \Delta a\, T \ln(T) - \frac{1}{2}\Delta b\, T^2 - \frac{1}{2}\Delta c\, T^{-1} + I\, T \tag{17}$$

78

$\Delta_{sol}G'$ is in J/mol, T is in K, and ΔH_I, Δa, Δb, Δc and I are constants given in Table 3-5. Function (17) was chosen because it is the most physically meaningful function for fitting free energy changes as a function of temperature [11]. Equation 17 was used to extrapolate $\Delta_{sol}G'$ up to 100°C. The results are given in Table 3-6.

Table 3-5: Fitting parameters of equations (14), (17) and the Margules equation (23).

m (J/mol K^2)	675212
n (J/mol K)	-5927.9
k (J/mol)	14.511
ΔH_I (J/mol)	1.121324
Δa (J/mol K)	0
Δb (J/mol K^2)	0.251533
Δc (J K/mol)	0.99969
I (J/mol K)	18.83267
$\alpha_{2,0}$	-6.4626
$\alpha_{2,1}$	4.4641
$\alpha_{3,0}$	9.9271
$\alpha_{3,1}$	-9.9685

79

The conditional entropy of dissolution of glucose in water, $\Delta_{sol}S'$, was calculated in two ways; from the Gibbs equation,

$$\Delta_{sol}S' = (\Delta_{sol}H' - \Delta_{sol}G')/T \qquad (18)$$

and by the first derivative of the Gibbs equation with respect to T

$$\Delta_{sol}S' = -\frac{d\Delta_{sol}G'}{dT} \qquad (19)$$

The values of $\Delta_{sol}S'$ calculated by the two methods are shown in Figure 3-2. The results of the two methods differ on average by 5.66%. The cause of the deviation is probably the loss of significant figures during differentiation in the second method (eq. 19). Therefore, since equation (18) does not include differentiation, entropy changes calculated from equation 18 were selected and presented in Table 3-6.
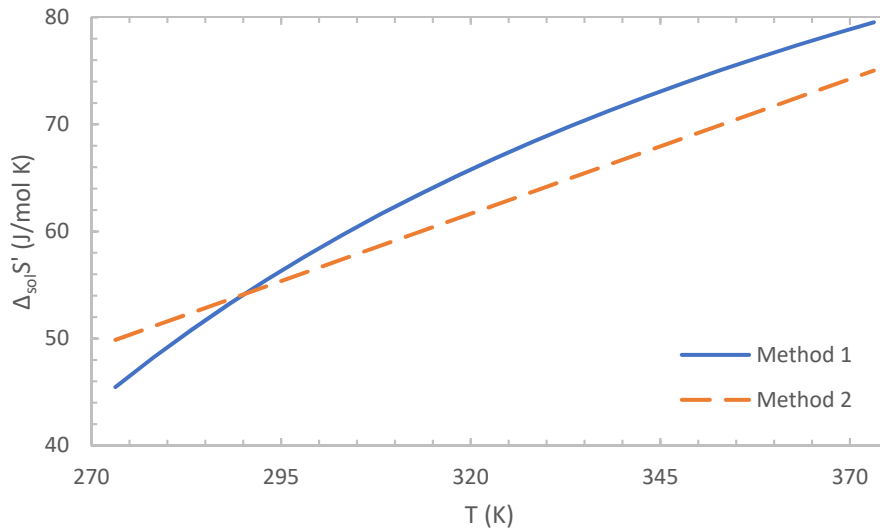
Figure 3-2: Comparison of $\Delta_{sol}S'$ found by method 1 -the Gibbs equation (equation 18), and 2 - first derivative of the Gibbs energy (equation 19).

Table 3-6: Enthalpy, entropy and Gibbs energy changes for dissolution of anhydrous α-D-glucose in water extrapolated from 54.71 to 100°C. The value of $\Delta_{sol}H'$ at 298.15 found in this research,

80

11.63 kJ/mol, agrees with the value in a review by Goldberg and Tewari [16], 10.85 kJ/mol. The small difference is probably due to the fact that values reported here are conditional and concentration dependent, while Ref. 16 reports the value at infinite dilution.

T (K)	$\Delta_{sol}H'$ (kJ/mol)	$\Delta_{sol}S'$ (J/mol K)	$\Delta_{sol}G'$ (kJ/mol)
273.15	8.1803	45.4652	-4.2383
278.15	8.9192	48.2123	-4.4908
283.15	9.6320	50.7924	-4.7496
288.15	10.3201	53.2189	-5.0147
293.15	10.9847	55.5040	-5.2861
298.15	11.6270	57.6589	-5.5637
303.15	12.2481	59.6934	-5.8477
308.15	12.8490	61.6170	-6.1379
313.15	13.4308	63.4379	-6.4345
318.15	13.9943	65.1639	-6.7373
323.15	14.5403	66.8020	-7.0464
328.15	15.0697	68.3586	-7.3618
333.15	15.5832	69.8396	-7.6835
338.15	16.0816	71.2505	-8.0114

343.15	16.5654	72.5964	-8.3457
348.15	17.0353	73.8817	-8.6863
353.15	17.4919	75.1107	-9.0331
358.15	17.9357	76.2874	-9.3862
363.15	18.3674	77.4153	-9.7456
368.15	18.7873	78.4979	-10.1113
373.15	19.1959	79.5381	-10.4833

3.7 Glucose dilution

The free energy change of reaction (4) $\Delta_{dil}G$, the dilution of aqueous glucose solution from saturated to the concentration in the cellulose hydrolysis mixture, is given as the change in free energy of mixing between the cellulose equilibrium $\Delta_{mix}G_{eq}$ and saturated $\Delta_{mix}G_{sat}$ mixtures

$$\Delta_{dil}G = \Delta_{mix}G_{eq} - \Delta_{mix}G_{sat} \tag{20}$$

The free energy of mixing is a function of composition and temperature and is given by the equation

$$\Delta_{mix}G_{eq} = nRT(x_w \ln x_w + x_{Glc} \ln x_{Glc} + x_w \ln \gamma_w + x_{Glc} \ln \gamma_{Glc}) \tag{21}$$

82

x_w and x_{Glc} are the mole fractions of water and glucose, respectively; n is the total number of moles in the solution, while γ_w and γ_{Glc} are the activity coefficients of water and glucose, respectively [12].

The activity coefficients were found from vapor pressure measurements done by Taylor and Rowlinson [10], using Raoult's law

$$\gamma_w = \frac{p}{(1-x_{Glc})p^*} \tag{22}$$

where p is the vapor pressure of the glucose solution of concentration x_{Glc}, and p^* is the vapor pressure of pure water at the same temperature [12, 13].

Since the experimental data did not cover the entire range of concentrations and temperatures, it was fitted to the Margules equation and then extrapolated. The Margules equation gives the activity coefficient of the solvent as a function of the solute concentration and temperature [12, 13, 15]. It was found that the best fit of the data, with the least number of parameters is given by a two-suffix Margules equation

$$\ln \gamma_w = \alpha_2 x_{Glc}^2 + \alpha_3 x_{Glc}^3 \tag{23a}$$

α_2 and α_3 are temperature-dependent coefficients

$$\alpha_2 = \frac{\alpha_{2,0}}{\theta} + \alpha_{2,1} \tag{23b}$$

$$\alpha_3 = \frac{\alpha_{3,0}}{\theta} + \alpha_{3,1} \tag{23c}$$

where $\theta = T / 298.15$ K, while $\alpha_{2,0}$; $\alpha_{2,1}$; $\alpha_{3,0}$; and $\alpha_{3,1}$ are the fitting parameters, given in Table 3-5. The fitting was done using least-squares regression. The sum of the squares of the residuals was

83

minimized using the GRG-Nonlinear method in Excel Solver, as described by Chapra and Canale [14]. The absolute average deviation of the fit was 11.7%.

The activity coefficient of glucose can be found using the Gibbs-Duhem equation [12, 13] and is a function of temperature and the mole fraction of water.

$$\ln \gamma_{Glc} = \beta_2 x_w^2 + \beta_3 x_w^3 \tag{24a}$$

β_2 and β_3 are temperature-dependent coefficients, that are related to α_2 and α_3:

$$\beta_2 = \alpha_2 + \frac{3}{2}\alpha_3 \tag{24b}$$

$$\beta_3 = -\alpha_3 \tag{24c}$$

A review of the theory behind the Margules equation is given by Sandler [15], while Starzak and Mathlouthi [13] give a detailed explanation of how it is applied in practice.

Using equations (20), (21), (23) and (24), $\Delta_{dil}G$ can be determined, knowing the initial and final concentration of the solution $x_{Glc,sat}$ and $x_{Glc,hyd}$, respectively. The initial concentration $x_{Glc,sat}$ is the solubility of glucose in water, which was found using an equation given by Young [6].

$$w_{Glc,sat} = 53.8 + 0.335\, t + 3.65 \cdot 10^{-4}\, t^2 \tag{25}$$

where $w_{Glc,sat}$ is the solubility of glucose in water in mass fraction percents and t is temperature in degrees Celsius. The mole fraction of glucose was calculated using the equation $x_{Glc,sat} = (w_{Glc} / M_{Glc}) / \{(w_{Glc} / M_{Glc}) + [(1 - w_{Glc}) / M_w]\}$, where M_{Glc} and M_w are molar masses of glucose and water, respectively. However, there is a problem with the final concentration $x_{Glc,hyd}$: according to equations (20) and (21), $\Delta_{dil}G$ depends on the composition of the hydrolysis mixture, that is it depends on the equilibrium glucose mole fraction $x_{Glc,hyd}$, related to b^{eq}_{hyd} by the equation

84

$x_{Glc,hyd} = 1 / \{1 + [1 / (M_w \, b^{eq}_{hyd})]\}$. On the other hand, according to equations (35) and (36), b^{eq}_{hyd} depends on $\Delta_{dil}G$. So, we have a circular problem, finding b^{eq}_{hyd} requires $\Delta_{dil}G$, while to find $\Delta_{dil}G$ we need b^{eq}_{hyd}. The problem was solved iteratively. Starting from a guess value of $\Delta_{dil}G$, $\Delta_{dil}G$ and b^{eq}_{hyd} were iteratively calculated until convergence was reached. The calculation was done by giving an initial $\Delta_{dil}G$, then calculating b^{eq}_{hyd} and from it a new $\Delta_{dil}G$, until the old and the new values of $\Delta_{dil}G$ became nearly identical, using GRG-Nonlinear method in Excel Solver. The $\Delta_{dil}G$ values determined in this way are given in Table 3-7.

Enthalpy $\Delta_{dil}H$ and entropy $\Delta_{dil}S$ change of reaction (4) were calculated by fitting a polynomial to $\Delta_{dil}G$ as a function of temperature. The first derivative was used to determine the entropy change: $\Delta_{dil}S = - \, d(\Delta_{dil}G) / dT$. While the enthalpy change was calculated from the Gibbs equation: $\Delta_{dil}H = \Delta_{dil}G + T \, \Delta_{dil}S$. The values of $\Delta_{dil}H$ and $\Delta_{dil}S$ are given in Table 3-7. Like with $\Delta_{dil}G$, each cellulose allomorph has its own value, because the equilibrium glucose concentrations differ and thus the dilution thermodynamic parameters are different as well.

3.8 Cellulose hydrolysis to aqueous glucose

The conditional Gibbs energy change for hydrolysis of cellulose to aqueous glucose (reaction 1), $\Delta_{hyd}G'$, is found by adding the Gibbs energy changes for reactions (2), (3) and (4):

$$\Delta_{hyd}G' = \Delta_{cr}G° + \Delta_{sol}G' + \Delta_{dil}G \qquad (26)$$

The values of $\Delta_{hyd}H'$, $\Delta_{hyd}S'$ and $\Delta_{hyd}G'$ are given in Table 3-8. After substituting equation (17) for $\Delta_{sol}G'$ and equations (5), (6), and (7) for $\Delta_{cr}G°$ and grouping the terms by the power of T, the final result for $\Delta_{hyd}G'$ is

$$\Delta_{hyd}G' = -\frac{1}{2}\Delta bT^2 + \left\{\Delta_{cr}C_p^\circ\left[1 + \ln(T_{ref})\right] + I - \Delta_{cr}S^\circ_{ref}\right\}T - \frac{1}{2}\Delta cT^{-1} - \left(\Delta_{cr}C_p^\circ +\right.$$

$$\left.\Delta a\right)T\ln(T) + \left(\Delta_{cr}H^\circ_{ref} + \Delta H_I - \Delta_{cr}C_p^\circ T_{ref}\right) + \Delta_{dil}G \qquad (27)$$

Note that in equations (27), (30) and (31) $\Delta_{cr}H^o_{ref}$ is in J/mol. Similarly, the conditional enthalpy, $\Delta_{hyd}H'$, and conditional entropy for hydrolysis of cellulose into aqueous glucose, $\Delta_{hyd}S'$, are defined as

$$\Delta_{hyd}H' = \Delta_{cr}H^\circ + \Delta_{sol}H' + \Delta_{dil}H \qquad (28)$$

$$\Delta_{hyd}S' = \Delta_{cr}S^\circ + \Delta_{sol}S' + \Delta_{dil}S \qquad (29)$$

The dependence of $\Delta_{hyd}H'$ on T is found by substituting equations (5) and (15) into (28). Similarly, the dependence of $\Delta_{hyd}S'$ on T is found by substituting equations (6), (15), (17) and (19) into (29).

Table 3-7: Thermodynamic parameters of reaction (4), $C_6H_{12}O_6$ $_{(aq,sat)}$ $\rightleftarrows$ $C_6H_{12}O_6$ $_{(aq,hyd)}$.

T (K)	Amorphous Cellulose			Celluose 1			Celluose 2			Celluose 3		
	$\Delta_{dil}H$ (kJ/mol)	$\Delta_{dil}S$ (J/mol K)	$\Delta_{dil}G$ (kJ/mol)	$\Delta_{dil}H$ (kJ/mol)	$\Delta_{dil}S$ (J/mol K)	$\Delta_{dil}G$ (kJ/mol)	$\Delta_{dil}H$ (kJ/mol)	$\Delta_{dil}S$ (J/mol K)	$\Delta_{dil}G$ (kJ/mol)	$\Delta_{dil}H$ (kJ/mol)	$\Delta_{dil}S$ (J/mol K)	$\Delta_{dil}G$ (kJ/mol)
273.15	-5.3523	-16.7881	-0.7948	-11.7590	-15.1964	-7.6332	-9.4208	-6.2956	-7.7307	-6.3187	-3.9854	-5.2564
278.15	-5.1303	-15.3996	-0.8516	-11.4586	-13.5853	-7.68043	-8.9911	-4.5407	-7.7331	-5.8602	-2.2101	-5.2474
283.15	-5.0015	-14.4102	-0.9118	-11.2516	-12.3857	-7.73035	-8.6533	-3.2000	-7.7376	-5.4934	-0.8494	-5.2403
288.15	-4.9739	-13.8198	-0.9757	-11.1462	-11.5974	-7.78317	-8.4159	-2.2735	-7.7443	-5.2268	0.0966	-5.2352
293.15	-5.0553	-13.6284	-1.0436	-11.1505	-11.2205	-7.83935	-8.2870	-1.7613	-7.7536	-5.0685	0.6280	-5.2325
298.15	-5.2539	-13.8360	-1.1159	-11.2729	-11.255	-7.89918	-8.2750	-1.6633	-7.7660	-5.0269	0.7449	-5.2328
303.15	-5.5775	-14.4427	-1.1931	-11.5216	-11.7009	-7.96315	-8.3881	-1.9795	-7.7817	-5.1103	0.4471	-5.2364
308.15	-6.0342	-15.4484	-1.2756	-11.9048	-12.5581	-8.03182	-8.6346	-2.7100	-7.8016	-5.3270	-0.2654	-5.2440
313.15	-6.6319	-16.8531	-1.3643	-12.4306	-13.8268	-8.10581	-9.0229	-3.8547	-7.8262	-5.6852	-1.3924	-5.2561

87

318.15	-7.3786	-18.6569	-1.4597	-13.1074	-15.5068	-8.18598	-9.5612	-5.4137	-7.8563	-6.1933	-2.9340	-5.2738
323.15	-8.2824	-20.8597	-1.5629	-13.9434	-17.5983	-8.27322	-10.2577	-7.3869	-7.8929	-6.8595	-4.8903	-5.2978
328.15	-9.3511	-23.4615	-1.6751	-14.9468	-20.1011	-8.36877	-11.1208	-9.7744	-7.9372	-7.6922	-7.2612	-5.3295
333.15	-10.5928	-26.4624	-1.7976	-16.1258	-23.0153	-8.4741	-12.1588	-12.5761	-7.9907	-8.6996	-10.0467	-5.3704
338.15	-12.0154	-29.8623	-1.9324	-17.4886	-26.3409	-8.59109	-13.3799	-15.7920	-8.0554	-9.8900	-13.2468	-5.4223
343.15	-13.6270	-33.6612	-2.0818	-19.0436	-30.0779	-8.72215	-14.7924	-19.4222	-8.1335	-11.2717	-16.8615	-5.4877
348.15	-15.4354	-37.8591	-2.2488	-20.7988	-34.2263	-8.87049	-16.4046	-23.4666	-8.2284	-12.8531	-20.8908	-5.5698
353.15	-17.4488	-42.4561	-2.4376	-22.7626	-38.7861	-9.0403	-18.2248	-27.9252	-8.3443	-14.6423	-25.3348	-5.6730
358.15	-19.6750	-47.4521	-2.6538	-24.9431	-43.7573	-9.23749	-20.2613	-32.7981	-8.4871	-16.6477	-30.1933	-5.8028
363.15	-22.1220	-52.8471	-2.9054	-27.3487	-49.1398	-9.47036	-22.5224	-38.0853	-8.6650	-18.8776	-35.4665	-5.9678
368.15	-24.7979	-58.6412	-3.2040	-29.9874	-54.9338	-9.75108	-25.0162	-43.7866	-8.8904	-21.3403	-41.1543	-6.1797
373.15	-27.7106	-64.8343	-3.5674	-32.8676	-61.1391	-10.0985	-27.7513	-49.9022	-9.1819	-24.0440	-47.2567	-6.4571

88

Table 3-8: Conditional thermodynamic parameters for hydrolysis of cellulose into aqueous glucose – reaction (1), $(C_6H_{10}O_5)_u \cdot (H_2O)_1 \cdot (H_2O)_{v\,(s)} + (u-v-1)H_2O_{(l)} \rightleftarrows uC_6H_{12}O_{6\,(aq,\,hyd)}$.

T (K)	Amorphous Cellulose			Celluose 1			Celluose 2			Celluose 3		
	$\Delta_{hyd}H'$ (kJ/mol)	$\Delta_{hyd}S'$ (J/mol)	$\Delta_{hyd}G'$ (kJ/mol)	$\Delta_{hyd}H'$ (kJ/mol)	$\Delta_{hyd}S'$ (J/mol)	$\Delta_{hyd}G'$ (kJ/mol)	$\Delta_{hyd}H'$ (kJ/mol)	$\Delta_{hyd}S'$ (J/mol)	$\Delta_{hyd}G'$ (kJ/mol)	$\Delta_{hyd}H'$ (kJ/mol)	$\Delta_{hyd}S'$ (J/mol)	$\Delta_{hyd}G'$ (kJ/mol)
273.15	-2.3888	4.2304	-3.5725	5.5471	9.5201	2.9215	12.9102	36.1073	3.0180	12.2123	42.4672	0.5861
278.15	-1.6644	7.5080	-3.7574	6.4013	13.2071	2.7272	13.9689	40.2102	2.7793	13.3197	46.6630	0.3384
283.15	-1.0593	10.2348	-3.9478	7.1361	16.3277	2.5272	14.9094	43.7391	2.5343	14.3093	50.2831	0.0843
288.15	-0.5801	12.4238	-4.1440	7.7446	18.8948	2.3212	15.7249	46.7070	2.2827	15.1740	53.3406	-0.1767
293.15	-0.2335	14.0867	-4.3464	8.2198	20.9204	2.1089	16.4083	49.1259	2.0241	15.9068	55.8476	-0.4448
298.15	-0.0263	15.2339	-4.5555	8.5546	22.4150	1.8897	16.9526	51.0067	1.7581	16.5006	57.8148	-0.7206
303.15	0.0347	15.8752	-4.7718	8.7421	23.3884	1.6632	17.3506	52.3592	1.4842	16.9483	59.2523	-1.0045
308.15	-0.0575	16.0194	-4.9958	8.7749	23.8494	1.4288	17.5950	53.1924	1.2017	17.2426	60.1690	-1.2972

313.15	-0.3100	15.6743	-5.2283	8.6458	23.8062	1.1858	17.6785	53.5146	0.9100	17.3761	60.5733	-1.5993
318.15	-0.7298	14.8473	-5.4702	8.3474	23.2661	0.9332	17.5937	53.3331	0.6082	17.3415	60.4725	-1.9117
323.15	-1.3240	13.5451	-5.7225	7.8725	22.2359	0.6702	17.3332	52.6550	0.2954	17.1313	59.8737	-2.2354
328.15	-2.0998	11.7737	-5.9863	7.2135	20.7216	0.3955	16.8894	51.4864	-0.0297	16.7380	58.7832	-2.5717
333.15	-3.0645	9.5387	-6.2631	6.3630	18.7290	0.1075	16.2550	49.8332	-0.3686	16.1542	57.2066	-2.9220
338.15	-4.2254	6.8452	-6.5550	5.3134	16.2632	-0.1956	15.4222	47.7006	-0.7233	15.3721	55.1494	-3.2884
343.15	-5.5896	3.6979	-6.8642	4.0573	13.3291	-0.5164	14.3835	45.0934	-1.0962	14.3841	52.6164	-3.6732
348.15	-7.1647	0.1012	-7.1939	2.5869	9.9309	-0.8581	13.1311	42.0162	-1.4905	13.1827	49.6121	-4.0797
353.15	-8.9579	-3.9411	-7.5483	0.8948	6.0726	-1.2248	11.6575	38.4730	-1.9105	11.7600	46.1406	-4.5122
358.15	-10.9768	-8.4253	-7.9331	-1.0269	1.7581	-1.6226	9.9549	34.4676	-2.3621	10.1085	42.2058	-4.9764
363.15	-13.2287	-13.3481	-8.3562	-3.1859	-3.0094	-2.0598	8.0154	30.0035	-2.8537	8.2202	37.8111	-5.4807
368.15	-15.7212	-18.7063	-8.8293	-5.5897	-8.2266	-2.5486	5.8314	25.0839	-3.3974	6.0874	32.9598	-6.0371

90

| 373.15 | -18.4617 | -24.4971 | -9.3704 | -8.2463 | -13.8908 | -3.1079 | 3.3951 | 19.7119 | -4.0121 | 3.7023 | 27.6549 | -6.6641 |

$$\Delta_{hyd}H' = \Delta_{cr}C_p{}^{\circ}\,T - 2RmT^{-1} + \left(\Delta_{cr}H{}^{\circ}{}_{ref} - Rn - \Delta_{cr}C_p{}^{\circ}\,T_{ref} + \Delta_{dil}H\right) \qquad (30)$$

$$\Delta_{hyd}S' = \frac{1}{2}\Delta bT - (Rn + \Delta H_I)T^{-1} + \left(\frac{1}{2}\Delta c - 2Rm\right)T^{-2} + \left(\Delta_{cr}C_p{}^{\circ} + \Delta a\right)\ln(T) +$$

$$\left[\Delta_{cr}S{}^{\circ}{}_{ref} - I - \Delta_{cr}C_p{}^{\circ}\ln\left(T_{ref}\right) + \Delta_{dil}S\right] \qquad (31)$$

Inserting the values of the constants into equations (26), (30), and (31) gives expressions for the dependence of $\Delta_{hyd}G'$, $\Delta_{hyd}H'$ in J/mol and $\Delta_{hyd}S'$ in J/mol K as functions of T in Kelvins,

The equilibrium concentration of glucose in reaction (1), $b^{eq}{}_{hyd}$ is calculated from $\Delta_{hyd}G'$ by

$$\Delta_{hyd}G' = -RT\ln K'_{hyd} \qquad (35)$$

$$K'_{hyd} = b^{eq}_{hyd} \qquad (36)$$

The values of $b^{eq}{}_{hyd}$ for the four cellulose allomorphs are given in Table 3-9. A comparison of b_{hyd} values found with the constant $\Delta_{cr}C_p{}^{\circ}$ approximation and with $\Delta_{cr}C_p{}^{\circ}$ as a function of temperature, shows the approximation leads to an average error less than $\approx$0.15 %, the highest error observed was less than 2.65%.

Table 3-9: Equilibrium glucose concentrations from hydrolysis of cellulose to aqueous glucose. Estimated uncertainties are given in the footnotes*.

T (K)	b^{eq}_{hyd} (mol/kg)			
	Amorphous Cellulose	Celluose 1	Celluose 2	Celluose 3
273.15	4.8216	0.2762	0.2648	0.7725
278.15	5.0774	0.3075	0.3006	0.8639

92

283.15	5.3494	0.3418	0.3408	0.9648
288.15	5.6395	0.3795	0.3856	1.0765
293.15	5.9497	0.4209	0.4358	1.2002
298.15	6.2825	0.4666	0.4920	1.3374
303.15	6.6410	0.5169	0.5550	1.4897
308.15	7.0286	0.5725	0.6256	1.6592
313.15	7.4497	0.6342	0.7050	1.8483
318.15	7.9095	0.7027	0.7946	2.0601
323.15	8.4144	0.7792	0.8959	2.2980
328.15	8.9727	0.8650	1.0109	2.5667
333.15	9.5948	0.9619	1.1424	2.8719
338.15	10.2944	1.0721	1.2934	3.2209
343.15	11.0896	1.1984	1.4685	3.6238
348.15	12.0055	1.3451	1.6735	4.0937
353.15	13.0773	1.5177	1.9169	4.6497
358.15	14.3564	1.7245	2.2106	5.3188
363.15	15.9212	1.9783	2.5732	6.1428

| 368.15 | 17.8973 | 2.2994 | 3.0343 | 7.1879 |
| 373.15 | 20.4998 | 2.7231 | 3.6445 | 8.5683 |

*The uncertainties δb are in the form $b^{eq}_{hyd} \pm \delta b$ and are given as a function of temperature by the following equations.

Amorphous cellulose: $\delta b = 1.279 \cdot 10^{-5}\, T^3 - 1.146 \cdot 10^{-2}\, T^2 + 3.454\, T - 345.8$.

Cellulose I: $\delta b = 4.697 \cdot 10^{-6}\, T^3 - 4.197 \cdot 10^{-3}\, T^2 + 1.261\, T - 126.6$.

Cellulose II: $\delta b = 8.456 \cdot 10^{-6}\, T^3 - 7.553 \cdot 10^{-3}\, T^2 + 2.265\, T - 227.0$.

Cellulose III: $\delta b = 2.302 \cdot 10^{-5}\, T^3 - 2.056 \cdot 10^{-2}\, T^2 + 6.170\, T - 618.7$

Mass fraction conversions of cellulose into glucose were calculated from the b^{eq}_{hyd} values. For the hydrolysis reaction per monomer,

$$C_6H_{10}O_5 \cdot xH_2O_{(s)} + (1-x)\, H_2O_{(l)} \rightleftarrows C_6H_{12}O_{6(aq)} \tag{37}$$
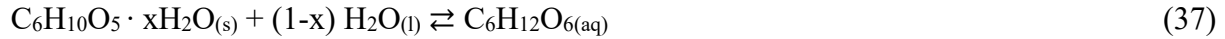
$C_6H_{10}O_5$ is the monomer in cellulose, $C_6H_{12}O_{6(aq)}$ is glucose in aqueous solution, and x is the number of hydration water molecules per glucose monomer. From Goldberg $et\ al.$ [2], x = 0.7. The mass fraction conversion, η, is expressed as the fraction of cellulose carbon converted into glucose: $\eta = n_{glc}\, /\, n_{cel,0}$, where n_{glc} is the number of moles of glucose obtained from hydrolysis and $n_{cel,0}$ is number of moles of glucose monomers initially present in the reactor in the form of cellulose. Equation 38 was used to calculate η.

$$\eta = M_{r,cel}\, \frac{b^{eq}_{hyd}\, \rho_w}{1+(1-x)b^{eq}_{hyd}M_{r,w}}\, \frac{V_{w,0}}{m_{c,0}} \tag{38}$$

$M_{r,cel}$ is the molar mass of a cellulose monomer including the water of hydration, 174.909 from Goldberg $et\ al.$ [2], ρ_w is the density of pure water, $M_{r,w}$ is the molar mass of water, $V_{w,0}$ is the

94

initial volume of pure water into which the cellulose was inserted and $m_{c,0}$ is the initial mass of cellulose inserted into the reactor. The denominator accounts for the water of hydration used in the reaction, and $b^{eq}_{hyd} \rho_w V_{w.0}$ is the number of moles of glucose in the solution after hydrolysis. Equation (38) shows that η depends on the $V_{w.0}$, since if the final glucose solution is diluted below b^{eq}_{hyd} all cellulose will dissolve. Mass fraction conversion values are given in Figure 3-3.

3.9 Discussion

Because the energy cost of obtaining glucose from all forms of cellulose decreases with increasing temperature, global warming may lead to faster mineralization of soil lignocellulose, thus providing a positive feedback increasing the rate of global warming.

Figure 3-3 shows that surprisingly large concentrations of glucose can be obtained from hydrolysis of amorphous cellulose and cellulose III. Enzymatic equilibration of amorphous cellulose in water would produce approximately 4.8 molal glucose at room temperature and 20.5 molal glucose in boiling water. Cellulose III equilibrates to approximately 0.7 molal glucose at room temperature and 8.5 molal in boiling water. These two forms of cellulose are thus amenable to use in commercial processes for production of bioethanol or other fuels and chemicals that can be derived from glucose. Although lower concentrations of glucose are produced at equilibrium, cellulose I and II may also be viable feedstocks for commercial use after treatment, such as ball-milling to reduce the number of hydrogen bonds. The stability of celluloses I, II, and III is due to a high degree of hydrogen bonding. Ball-milling of these forms of cellulose results in amorphous cellulose which is more easily converted into glucose.

95
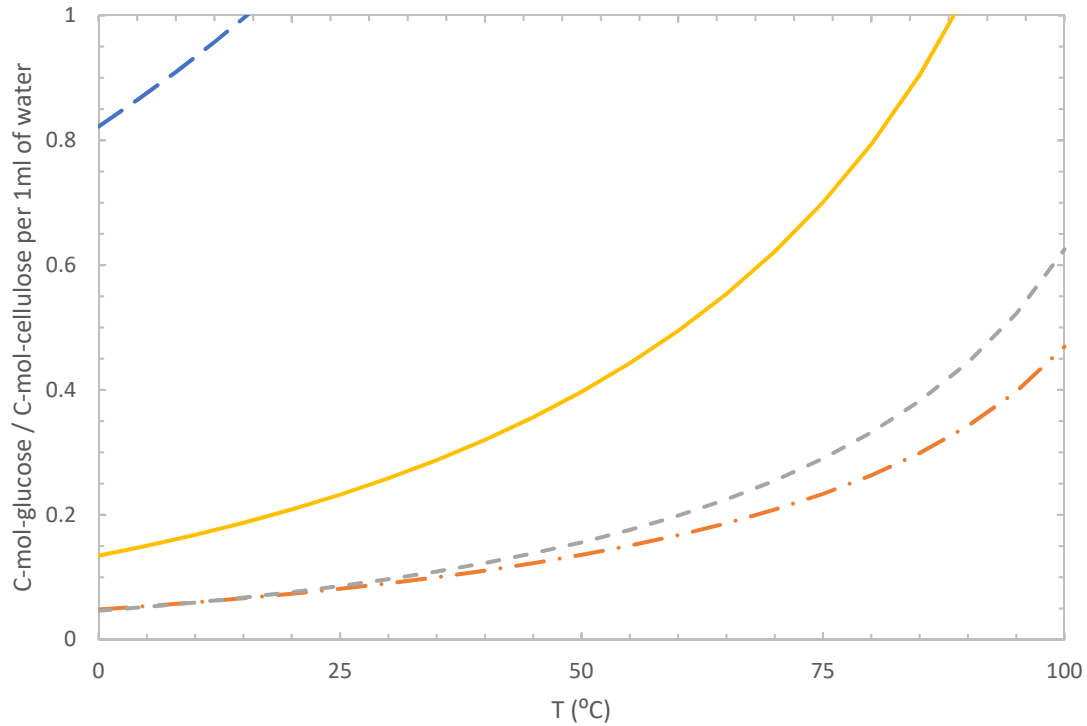
Figure 3-3: Mass fraction conversion of cellulose into glucose calculated from equation 38, if 1 g of cellulose is mixed with 1 ml of water as the initial reaction mixture. The long-dashed line represents amorphous cellulose (– – –), the dot-line is cellulose I (– · – · –), the short-dashed line is cellulose II (- - -) and the full line is cellulose III.

3.10 References

[1]   Himmel, M. E.; Ding, S. Y.; Johnson, P. K.; Adney, W. S.; Nimlos, M. R.; Brady, J. W.; Foust, T. D. Biomass recalcitrance: engineering plants and enzymes for biofuels production, *Science*, **2007**, *315*(9), 804-807.

[2]   Goldberg, R. N.; Schliesser, J.; Mittal, A.; Decker, S.; Santos, A. F. L. O. M.; Freitas, V. L. S.; Urbas, A.; Lang, B. E.; Heiss, C.; Ribeiro de Silva, M. D. M. C.; Woodfield, B. F.; Katahira, R.; Wang, W.; Johnson, D. K. Thermodynamic investigation of the cellulose

allomorphs: Cellulose(am), cellulose Iβ(cr), cellulose II(cr), and cellulose III(cr), *J.Chem.Thermodynamics*, **2015**, *81*, 184-226.

[3]   Boerio-Goates, J.; Heat-capacity measurements and thermodynamic functions of crystalline α-D-glucose at temperatures from 10 K to 340 K, *J. Chem. Thermodynamics*, **1991**, *23* (5), 403-409.

[4]   Osborne, N. S.; Stimson, H. F.; Ginnings, D. C. Measurements of heat capacity and heat of vaporization of water in the range 0° to 100°C, *Journal of research of the national bureau of standards*, **1939**, *2*, 197-260.

[5]   Alves, L. A.; Almeida e Silva, J. B.; Giulietti, M. Solubility of D-Glucose in Water and Ethanol/Water Mixtures, *J. Chem. Eng. Data*, **2007**, *52*, 2166-2170.

[6]   Young, F. E. D-Glucose-water phase diagram, *J. Phys. Chem.*, **1957**, *61*(5), 616–619.

[7]   Yalkowsky, S. H.; He, Y.; Jain, P. *Handbook of aqueous solubility data, 2nd ed.,* Taylor & Francis group, New York, 2010.

[8]   Zhang, D.; Montanes, F.; Srinivas, K.; Fornari, T.; Ibanez, E.; King, J. W. Measurement and correlation of the solubility of carbohydrates in subcritical water. *Ind. Eng. Res.*, **2010**, *49*, 6691-6698.

[9]   Gray, M. C.; Converse, A. O.; Wyman, C. E. Sugar monomer and olygomer solubility: data and predictions for application to biomass hydrolysis, *Appl. Biochem. Biotechnol.*, **2003**, *105-108*, 179-193.

[10]   Taylor, J. B.; Rowlinson, J. S. The thermodynamic properties of aqueous solutions of glucose, *Transactions of the Faraday Society*, **1955**, *51*, 1183-1192.

[11]   G. N. Lewis, M. Randall, K. S. Pitzer, L. Brewer, *Thermodynamics*, McGraw-Hill, New York, 1961.

97

[12]   P. Atkins, J. de Paula, *Physical chemistry, 8th ed.*, W. H. Freeman and Company, New York, 2006.

[13]   M. Starzak, M. Mathlouthi, Temperature dependence of water activity in aqueous solutions of sucrose, *Food Chemistry*, 2006, **96**, 346-370.

[14]   S. C. Chapra, R. P. Canale, *Numerical methods for engineers, 6th ed.,* McGraw-Hill, New York, 2010.

[15]   S. I. Sandler, *Chemical, Biochemical and Engineering Thermodynamics, 4th ed.,* John Wiley & Sons: Hoboken, 2006.

[16]   R. N. Goldberg, Y. B. Tewari, Thermodynamic and Transport Properties of Carbohydrates and their Monophosphates: The Pentoses and Hexoses, *Journal of Physical and Chemical Reference Data*, 1989, **18,** 809-880

4 EFFECTS OF VACANCIES IN HEAT CAPACITIES OF $Ce_{1-x}Nd_{x/2}Sm_{x/2}O_{2-x/2}$ WITH x = 0.026 AND 0.077 FROM 2 TO 300 K

Marko Popovic[1], Jacob Schliesser[1], Lee D. Hansen[1], Alexandra Navrotsky[2], and Brian F. Woodfield[1]*

[1]Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602, U.S.A.

[2]Peter A. Rock Thermochemistry Laboratory and NEAT ORU, University of California, Davis, CA 95616, U.S.A.

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

Email address: brian_woodfield@byu.edu (B. F. Woodfield)

4.1 Abstract:

Vacancy concentration in an insulating material, n_{vac}, has been theoretically related to a linear term in the low temperature heat capacity, $\gamma = c \cdot n_{vac}$, however this relation has never been tested in the context of large concentrations of ordered or partially ordered vacancies, such as in oxides showing ionic conductivity. To find the influence of vacancy ordering on heat capacity, a Quantum Design PPMS calorimeter was used to determine the heat capacity from 1.8 to 300 K of two samples of samarium-neodymium co-doped ceria ($Ce_{1-x}Nd_{x/2}Sm_{x/2}O_{2-x/2}$ with x = 0.026 and 0.077), where vacancy concentration and ordering are controlled by sample stoichiometry. The low temperature heat capacities were fitted to a series of theoretical functions, which were then used to calculate the vacancy concentrations from the measured heat capacities. Comparison of calculated vacancy

concentrations with sample stoichiometries showed the linear term is quantitative for nearly randomly distributed vacancies at low dopant concentration ($x = 0.026$), but the prediction is low by an order of magnitude when vacancies are clustered and partially ordered. ($x = 0.077$). Vacancy ordering was thus found to decrease the vacancy contribution from that calculated with the linear term in heat capacity. The studied compounds also exhibit a heat capacity upturn from 2 to 4 K, due to an energy splitting of nuclear magnetic states. In the sample with $x = 0.077$, there is a sharp heat capacity drop-off below 2 K, arising from ineffective heat transfer between the nuclei and lattice. The absolute entropy of the materials was calculated from 0 to 300 K. The standard entropy (including residual entropy) at 298.15 K is 66.220 J mol^{-1} K^{-1} for $x = 0.026$ and 70.109 J mol^{-1} K^{-1} for $x = 0.077$. The residual entropy of the samples was calculated to be 3.073 J mol^{-1} K^{-1} for $x = 0.026$ and 5.054 J·K^{-1}·mol^{-1} for $x = 0.077$. The Gibbs free energies of formation at 298.15 K are -1097.38 kJ mol^{-1} for $x = 0.026$ and -1082.82 kJ mol^{-1} for $x = 0.077$ (residual entropy included into the calculation).

Keywords: Solid electrolytes; Oxygen vacancies Calorimetry; Linear heat capacity term; Schottky anomaly.

4.2 Introduction

Hardness, diffusion and ionic conductivity are some of the properties of materials influenced by vacancies, defects where there is a missing atom in a crystal structure.[1] Vacancies are present in every crystalline material at room temperature to some degree but not present in ideal materials cooled to equilibrium at absolute zero.[1] Lattice vacancies can be formed during crystallization by vibration of atoms, local rearrangement of atoms, plastic deformation and ionic bombardments.

Vacancies form spontaneously because their presence increases the entropy of a material or can be formed by kinetic effects such as rapid crystallization.[1] Lattice vacancies can also be caused by impurities, e.g., replacement of a monovalent ion by a divalent ion, which requires a monovalent ion vacancy for the crystal to remain electrically neutral.[1] Vacancies can be ordered or disordered in a lattice, but in the vast majority of crystals vacancies are disordered.

Lattice vacancies in solid oxide ion conductors play a vital role in fuel cell technology. In solid oxide fuel cells, a fuel such as hydrogen is oxidized into protons and electrons at the anode, whilst at the cathode, an oxidizing agent such as oxygen is reduced to oxide, and the protons and oxides combine to form water.[2] Depending on the electrolyte, either protons or oxide ions are transported through an ion conducting but electronically insulating electrolyte, while electrons travel around an external circuit delivering electric power.[2] Compared with conventional power generation methods, solid oxide fuel cells offer advantages of high efficiency and low emissions.[2]

Because solid oxide fuel cells require ionically conductive materials, they typically operate at high temperatures.[3,4] Solid electrolytes in which ionic charges are conducted by oxygen vacancies are suitable for this role.[4] Yttria-stabilized zirconia is currently considered to be the most reliable candidate electrolyte for solid oxide fuel cells,[4] but yttria-stabilized zirconia requires operating temperatures near 1000 °C to achieve the necessary conductivity.[4] At these high temperatures, interface reactions decrease the efficiency of the fuel cell, thus finding alternative materials is desirable.[4] Ceria-based materials are a widely investigated group of candidates as an alternate electrolyte for solid oxide fuel cells.[3]

Lanthanide dopants added to a CeO_2 lattice create oxygen vacancies by the reaction

$$Ln_2O_3 \xrightarrow{CeO_2} 2\,Ln'_{Ce} + 3O_O^x + V_O^{\bullet\bullet} \tag{1}.$$
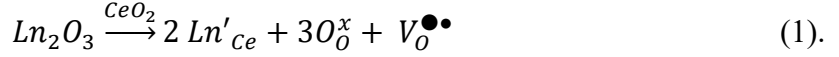
where *Ln* represents a lanthanide series dopant and $V^{\bullet\bullet}{}_O$ is an oxygen vacancy (Kroger-Vink notation).[5] One mole of vacancies forms for each mole of Ln_2O_3 added to a mole of CeO_2. Neodymia-samaria co-doped ceria (SNDC) with the formula $Ce_{1-x}Nd_{x/2}Sm_{x/2}O_{2-x/2}$ where $0 < x < 0.3$, are unique because vacancy ordering is controlled by the dopant concentration where an increasing dopant concentration causes vacancies to become increasingly ordered.[5] Vacancy ordering has no sharp onset with increasing dopant concentration but gradually becomes more dominant as the vacancy concentration increases.[5] Enthalpies of formation of SNDC from the binary oxides at room temperature, $\Delta H_{f,ox}(25\ °C)$, have been determined by Byukkilic *et al.*, using high temperature oxide melt solution calorimetry.[5] This paper extends that work, including entropy, heat capacity, and the effect of oxygen vacancies on the linear term in the low temperature heat capacity.

In addition to lattice, electronic, and magnetic contributions, the low temperature heat capacity of solids can be affected by contributions from Schottky anomalies which can originate from nuclear and/or electronic energy levels. Systems with a limited number of accessible energy levels at low temperature exhibit a Schottky anomaly, which is manifested as a peak in the heat capacity instead of the gradually increasing heat capacity exhibited by systems with many closely spaced energy levels.[6,7,8] The contribution of a two-level system to the heat capacity $C_{V,Sch}$ is

$$C_{V,Sch} = R\left(\frac{\Delta\varepsilon}{T}\right)^2 \frac{g_0}{g_1} \frac{\exp(\Delta\varepsilon/kT)}{[1+(g_0/g_1)\exp(\Delta\varepsilon/kT)]^2} \tag{2}$$

where R is the universal gas constant and g_0 and g_1 are the degeneracies of the ground and upper energy levels, respectively.[7]

According to Schliesser and Woodfield,[8] localized Schottky effects can also be caused by lattice vacancies, leading to a linear term, γT, in the low temperature heat capacity. According to this model, many small Schottky anomalies are produced by deformation of the local structure around vacancies.[8] Since vacancies can appear in different positions in a crystal lattice, there is a distribution of Schottky anomalies of different energies, resulting in a pseudo-linear heat capacity contribution.[8] The coefficient of the linear term, γ, and the vacancy concentration, n_{eff}, are related by

$$\gamma = c \cdot n_{eff} \tag{3}$$

where c is a constant.[8] The value of c depends on the statistical model used to describe the distribution of the vacancies.[8]

In this study, the heat capacities of two SNDC samples were determined from 2 to 300 K with a Physical Properties Measurement System (PPMS), manufactured by Quantum Design. The two samples were 5-SNDC ($Ce_{0.948}Nd_{0.0260}Sm_{0.0260}O_{1.9740}$) and 15-SNDC ($Ce_{0.847}Nd_{0.077}Sm_{0.077}O_{1.924}$) with vacancy concentrations of 0.0260, and 0.077, respectively. The SNDC samples were chosen because stoichiometry can be used to control their vacancy concentrations. They also exhibit increasing vacancy ordering, as the vacancy concentration increases.

4.3 Experimental Methods

4.3.1 Sample Synthesis and Characterization

The samarium-neodymium co-doped ceria solid solutions were synthesized by a co-precipitation method.[5] The general equation of this class of compounds is $Ce_{1-x}Nd_{x/2}Sm_{x/2}O_{2-x/2}$.[5] Chemical analyses by wavelength dispersive spectroscopy (WDS) showed that for 5-SNDC, $x = 0.052 \pm 0.001$, and for 15-SNDC, $x = 0.153 \pm 0.004$.[5] According to equation (1), the stoichiometry shows that the vacancy concentration of 5-SNDC is 0.0260 ± 0.0005, while for 15-SNDC it is 0.077 ± 0.002. The molar mass of 5-SNDC is 172.07 g mol^{-1}, and for 15-SNDC, 171.99 g mol^{-1}, as calculated from the sample compositions. Powder X-ray diffraction data indicate that both samples have a cubic fluorite structure with space group Fm3m and no peaks from secondary phases were observed.[5] TGA measurements showed that Ce is only in the +4 oxidation state and the oxygen stoichiometry is governed by trivalent dopant content. The compositions of both samples can thus be described by the general equation $Ln_xCe_{1-x}O_{2-0.5x}$.[5] For more details on sample synthesis and characterization, see ref. 5.

4.3.2 Heat Capacity Measurements

Heat capacity measurements were performed with a Quantum Design Physical Property Measurement System (PPMS) in zero magnetic field with logarithmic spacing over the temperature range from 2 to 100 K with 10 K temperature intervals from 100 to 300 K. The accuracy of the heat capacity measurements on a high-purity copper pellet was $\pm$ 2% from 2 to 20 K and $\pm$ 0.6% from 20 to 300 K.[9] The powdered SNDC samples were measured with a new technique developed in our laboratory for both conducting and non-conducting powdered samples

104

that achieves an accuracy of ± 2% below 10 K and ± 1% from 10 to 300 K. The details of sample preparation and heat capacity experimental procedure is given in a publication by Shi *et al.*.[10] In general, sample mounting consists of mixing the sample with weighed copper strips in a weighed copper cup (0.025 mm thickness copper foil with a purity of 0.99999 mass fraction), which is then compressed with a stainless steel die into a 2.8 mm diameter by 3.5 mm high pellet. A typical heat capacity measurement involves two measurements, (1) measuring the heat capacity of the PPMS platform with ≈1 mg Apiezon N which is used to adhere the sample to the platform ($C_{P,1}$), and (2) measuring the heat capacity of the platform, Apiezon *N* and pellet consisting of the sample, copper strips, and the copper cup ($C_{P,2}$). The heat capacity of the sample, copper strips and copper cup is $C_{P,3} = (C_{P,2} - C_{P,1})$, and the heat capacity of the sample is obtained by subtracting the heat capacity of the copper strips and cup from $C_{P,3}$. The heat capacity of the copper was found from the mass (23.66 mg of copper for 5-SNDC and 26.58 mg for 15-SNDC) and specific heat capacity of copper.[11,12] The heat capacities of a 33.6 mg 5-SNDC sample and a 73.2 mg 15-SNDC sample were measured with this method from 2 to 300 K.

4.4   Results

The heat capacities of 5-SNDC and 15-SNDC are given in Figure 4-1 and in Table 4-1 and Table 4-2, respectively. Note that an upturn with decreasing temperature is present in the heat capacity in the vicinity of 2 to 4 K in both samples but is less noticeable in 5-SNDC. This upturn is likely caused by a nuclear Schottky anomaly due to the paramagnetic moment of Nd nuclei.
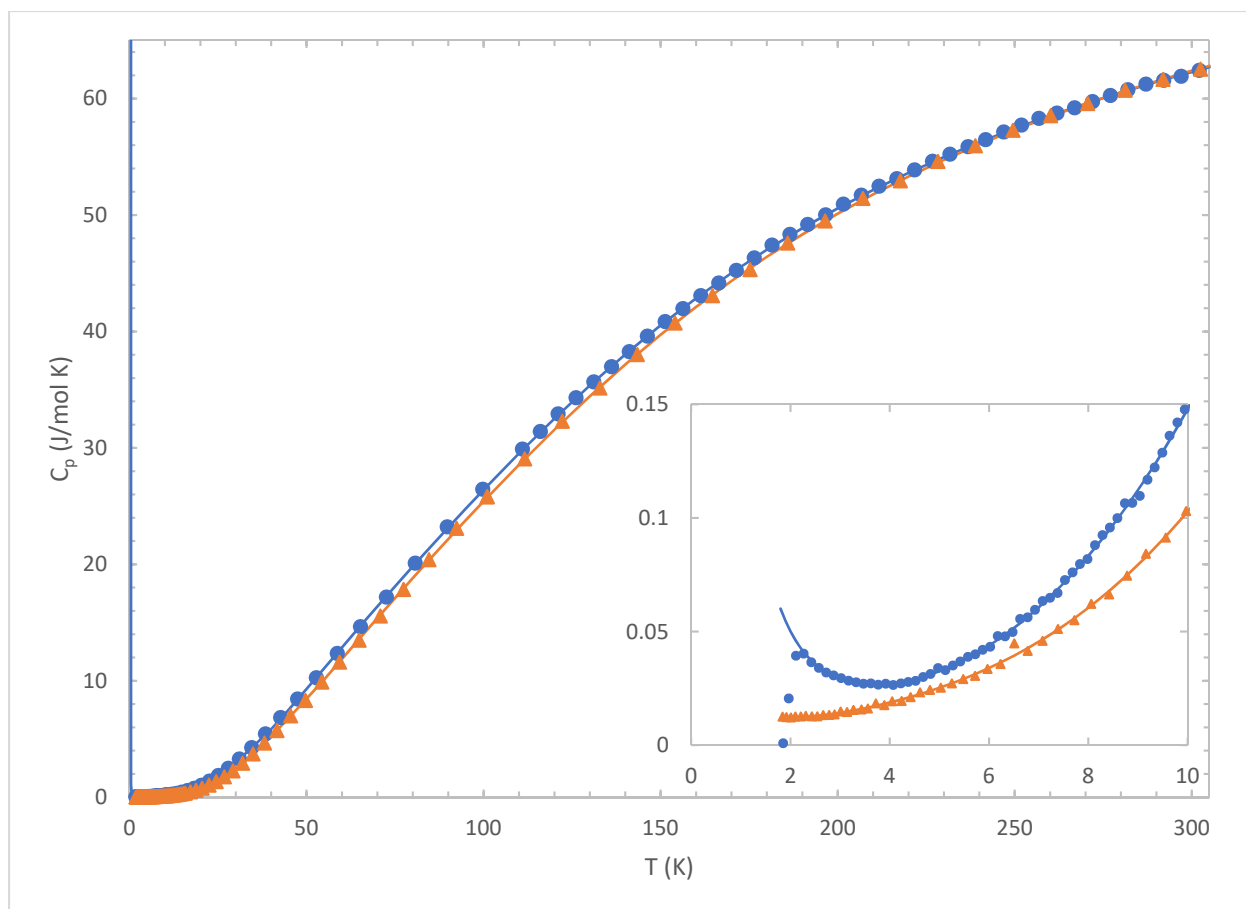
Figure 4-1: Heat capacity of neodymia-samaria co-doped ceria (5-SNDC (▲), $Ce_{0.948}Nd_{0.0260}Sm_{0.0260}O_{1.9740}$, and 15-SNDC (●), $Ce_{0.847}Nd_{0.077}Sm_{0.077}O_{1.924}$) as functions of temperature. The points represent experimental data, and the lines are the fits with functions as described in the text.

Table 4-1: 5-SNDC ($Ce_{0.948}Nd_{0.0260}Sm_{0.0260}O_{1.9740}$) experimental heat capacity.

T (K)	Cp (J mol⁻¹ K⁻¹)	T (K)	Cp (J mol⁻¹ K⁻¹)	T (K)	Cp (J mol⁻¹ K⁻¹)	T (K)	Cp (J mol⁻¹ K⁻¹)
1.84	0.0125	5.03	0.0253	13.38	0.2174	84.56	20.3964
1.92	0.0123	5.25	0.0272	13.97	0.2454	92.41	23.0807
2.01	0.0122	5.48	0.0291	14.57	0.2761	100.97	25.7906
2.10	0.0126	5.72	0.0305	15.24	0.3136	101.01	25.8112
2.21	0.0126	5.97	0.0335	15.73	0.3422	111.59	29.0483
2.31	0.0129	6.23	0.0357	17.18	0.4450	122.20	32.2787

106

2.43	0.0127	6.51	0.0448	18.78	0.5847	132.82	35.1303
2.54	0.0127	6.78	0.0415	20.51	0.7667	143.40	38.0077
2.66	0.0132	7.08	0.0459	22.44	1.0283	154.05	40.7112
2.78	0.0133	7.39	0.0511	24.49	1.3277	164.62	43.0594
2.89	0.0135	7.72	0.0550	26.76	1.7489	175.28	45.3087
3.01	0.0148	8.06	0.0622	29.24	2.2489	185.89	47.5891
3.14	0.0146	8.42	0.0663	31.94	2.9042	196.47	49.4882
3.27	0.0155	8.78	0.0746	34.88	3.7123	207.10	51.4166
3.43	0.0157	9.16	0.0842	38.10	4.6359	217.70	52.9363
3.56	0.0161	9.56	0.0913	41.63	5.7156	228.31	54.5974
3.72	0.0184	9.97	0.1030	45.49	6.9740	238.89	55.9400
3.89	0.0176	10.40	0.1128	49.70	8.3002	249.50	57.2703
4.05	0.0193	10.80	0.1243	54.30	9.8813	260.10	58.5237
4.24	0.0194	11.26	0.1368	59.33	11.5886	270.62	59.5752
4.42	0.0211	11.75	0.1524	64.83	13.4741	281.20	60.7151
4.61	0.0232	12.27	0.1715	70.82	15.5483	291.87	61.6385
4.81	0.0243	12.81	0.1930	77.39	17.8403	302.48	62.5215

Table 4-2: 15-SNDC ($Ce_{0.847}Nd_{0.077}Sm_{0.077}O_{1.924}$) experimental heat capacity.

T (K)	Cp (J mol^{-1} K^{-1})	T (K)	Cp (J mol^{-1} K^{-1})	T (K)	Cp (J mol^{-1} K^{-1})	T (K)	Cp (J mol^{-1} K^{-1})
1.86	0.0008	6.33	0.0478	11.98	0.2383	156.31	41.9476
1.97	0.0205	6.48	0.0498	13.32	0.3154	161.39	43.0593
2.11	0.0394	6.63	0.0555	14.81	0.4202	166.43	44.1565
2.27	0.0402	6.78	0.0563	16.47	0.5618	171.42	45.2312
2.42	0.0365	6.93	0.0596	18.31	0.7566	176.50	46.3102

107

2.57	0.0340	7.08	0.0634	20.35	1.0196	181.48	47.4018
2.72	0.0320	7.23	0.0648	22.63	1.3779	186.56	48.3246
2.87	0.0307	7.38	0.0670	25.16	1.8547	191.59	49.1814
3.02	0.0295	7.53	0.0727	27.97	2.4729	196.62	50.0096
3.17	0.0283	7.68	0.0760	31.09	3.2645	201.66	50.9235
3.32	0.0277	7.83	0.0797	34.57	4.2459	206.69	51.7008
3.47	0.0271	7.98	0.0819	38.43	5.4287	211.72	52.4714
3.62	0.0272	8.14	0.0880	42.73	6.8264	216.74	53.1074
3.77	0.0266	8.29	0.0924	47.51	8.4163	221.78	53.8712
3.92	0.0270	8.44	0.0958	52.82	10.2540	226.80	54.6024
4.07	0.0265	8.59	0.0999	58.73	12.3374	231.76	55.2125
4.22	0.0272	8.74	0.1064	65.29	14.6330	236.85	55.8540
4.38	0.0278	8.89	0.1066	72.58	17.1743	241.81	56.4623
4.52	0.0283	9.04	0.1097	80.73	20.0834	246.91	57.1263
4.68	0.0300	9.19	0.1169	89.76	23.2118	251.93	57.7211
4.82	0.0313	9.34	0.1223	99.80	26.4408	256.88	58.2898
4.97	0.0339	9.49	0.1287	111.01	29.8805	261.98	58.7472
5.12	0.0330	9.64	0.1362	116.05	31.3992	266.93	59.1996
5.27	0.0350	9.80	0.1420	121.08	32.9039	272.03	59.7352
5.42	0.0368	9.94	0.1478	126.13	34.2980	277.05	60.2545
5.58	0.0388	10.10	0.1519	131.16	35.6546	281.99	60.7549
5.73	0.0400	10.25	0.1590	136.16	36.9670	287.08	61.2342
5.87	0.0420	10.41	0.1654	141.20	38.2541	292.11	61.5595
6.02	0.0433	10.57	0.1719	146.28	39.5879	297.04	61.9033
6.18	0.0480	10.78	0.1801	151.32	40.8429	302.15	62.4187

108

Fitting the heat capacity data was accomplished by separating the data into low (1.8-15 K), medium (15-70 K) and high temperature regions (70-302 K). Below 15 K the heat capacity was represented by

$$C_{p,m} = AT^{-2} + \gamma T + B_3 T^3 + B_5 T^5 + B_7 T^7 \tag{4}$$

where B_3, B_5, B_7, A, and γ are constants obtained from fitting the data. The fitted values of A, γ, B_3, B_5 and B_7 are given in Table 4-3. The $B_3 T^3$, $B_5 T^5$ and $B_7 T^7$ terms represent vibrations of the crystal lattice,[6,7,13,14] the AT^{-2} term represents the upturn in the low temperature heat capacity arising from spin ordering of Nd nuclei,[7] and the linear term γT is due to oxygen vacancies in these insulating materials.[15] The medium temperature region was fit to 10th order polynomials, equation 5, which do not have a theoretical basis but are used to provide a smooth overlap between the low and high temperature functions.[16]

$$C_{p,m} = \sum_{i=0}^{10} a_i T^i \tag{5}$$

Table 4-3: Fitting parameters. The low temperature region (1.8 - 15 K) was fitted to equation 4, the medium temperature region (15 - 70 K) to equation 5, and the high temperature region (70 - 302 K) to equation 6.

Low temperature region			Medium temperature region		
Parameters	15-SNDC	5-SNDC	Parameters	15-SNDC	5-SNDC
A (J K mol^{-1})	1.81E-01	1.92E-02	a_0 (J K^{-1} mol^{-1})	-6.49E-02	9.37E-02
γ (J K^{-2} mol^{-1})	1.86E-03	3.61E-03	a_1 (J K^{-2} mol^{-1})	6.31E-02	-4.24E-02
B_3 (J K^{-4} mol^{-1})	1.27E-04	4.35E-05	a_2 (J K^{-3} mol^{-1})	-1.97E-02	8.79E-03

109

Parameter		
B_5 (J K^{-6} mol^{-1})	3.66E-08	3.55E-07
B_7 (J K^{-8} mol^{-1})	-3.16E-10	-1.26E-09
%RMS	1.62	2.91
T_{range} (K)	0 to 12.82	0 to 10.40

Parameter		
a_3 (J K^{-4} mol^{-1})	3.30E-03	-7.86E-04
a_4 (J K^{-5} mol^{-1})	-2.89E-04	4.38E-05
a_5 (J K^{-6} mol^{-1})	1.57E-05	-1.11E-06
a_6 (J K^{-7} mol^{-1})	-5.25E-07	1.32E-08
a_7 (J K^{-8} mol^{-1})	1.08E-08	-4.58E-11
a_8 (J K^{-9} mol^{-1})	-1.34E-10	-5.10E-13
a_9 (J K^{-10} mol^{-1})	9.21E-13	5.47E-15
a_{10} (J K^{-11} mol^{-1})	-2.67E-15	-1.52E-17
%RMS	1.27	2.13
T_{range} (K)	12.82 to 37.65	10.4 to 51.95

High temperature region

Parameters	15-SNDC	5-SNDC
m	1.2400	1.3233
θ_D (K)	302.4986	327.5724
n	1.3968	1.3957
Θ_E (K)	574.5200	608.6273
p	0.0232	0.0210
%RMS	0.3929	0.7455

The polynomial coefficient values, a_i, are also given in Table 4-3. Heat capacities in the high temperature region were fit to a combination of Debye and Einstein functions, which represent the contribution of lattice vibrations at higher temperatures.

110

$$C_{p,m} = m \cdot D(\Theta_D/T) + n \cdot E(\Theta_E/T) + p \cdot T \qquad (6)$$

where $D(\Theta_D/T)$ is the Debye function and $E(\Theta_{E,1}/T)$ is the Einstein function and the adjustable

parameters are m, n, p, Θ_D and Θ_E. The linear pT term is the correction to convert the Debye and

Einstein functions, which describe heat capacity at constant volume C_V to heat capacity at constant

pressure.[17] The fitted values of the parameters in equation 6 are also given in Table 4-3. The fits

are shown and compared to experimental data in Figure 4-1, and the deviations of the fits from

experimental data are shown in Figure 4-2. The fits were used to determine standard

thermodynamics functions of 5-SNDC and 15-SNDC, which are given in Table 4-4 and Table 4-5,
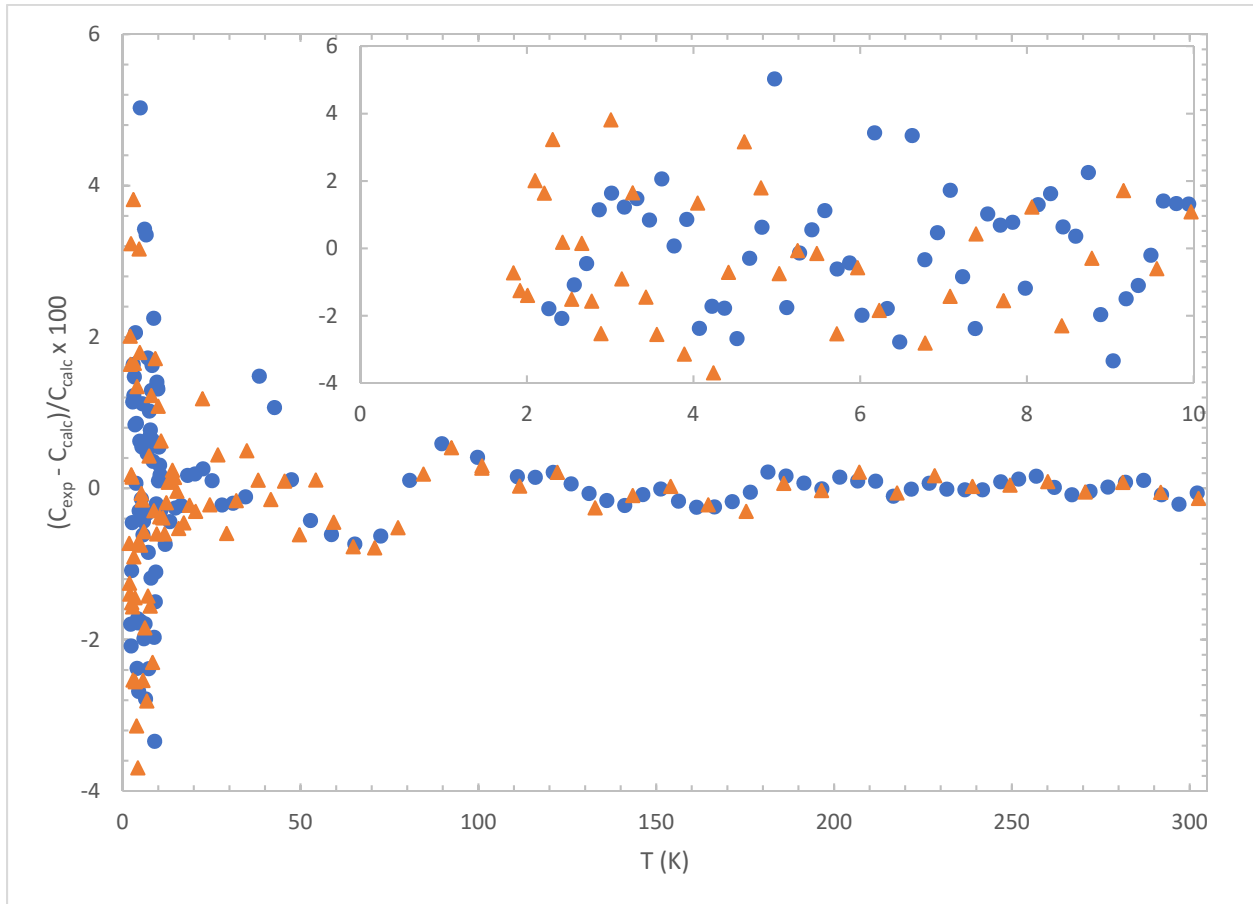
respectively.

Figure 4-2: Deviations of measured heat capacities from fitted functions. The circles (●) represent 15-SNDC and the triangles (▲) represent 5-SNDC experimental data. C_{exp} is the experimental heat capacity, while C_{calc} is heat capacity calculated from fitting the data to functions as described in the text.

Table 4-4: Standard thermodynamics functions of 5-SNDC. $\Delta_0{}^T S_m°$ is the standard molar entropy at temperature T assuming $S_0 = 0$. $\Delta_0{}^T H_m°$ is the standard molar enthalpy change on heating from absolute zero to T, $\Phi_m° = \Delta_0{}^T S - \Delta_0{}^T H/T$.

T (K)	$C_{p,m}$ (J mol^{-1} K^{-1})	$\Delta_0{}^T S_m°$ (J mol^{-1} K^{-1})	$\Delta_0{}^T H_m°$ (kJ mol^{-1})	$\Phi_m°$ (J mol^{-1} K^{-1})
2.00	0.0124	0.0070	7.08E-06	0.0035
5.00	0.0255	0.0196	5.20E-05	0.0092
10.00	0.1009	0.0553	3.31E-04	0.0222
20.00	0.7114	0.2649	3.68E-03	0.0806
30.00	2.4364	0.8375	0.0184	0.2247
40.00	5.2125	1.9000	0.0560	0.5004
50.00	8.4506	3.4074	0.1241	0.9246
60.00	11.8771	5.2450	0.2254	1.4875
70.00	15.3866	7.3401	0.3618	2.1713
80.00	18.8217	9.6199	0.5329	2.9583
90.00	22.1656	12.0307	0.7379	3.8314
100.00	25.4128	14.5351	0.9759	4.7759
110.00	28.5519	17.1053	1.2458	5.7795
120.00	31.5660	19.7198	1.5465	6.8320
130.00	34.4384	22.3609	1.8767	7.9249
140.00	37.1563	25.0135	2.2348	9.0507
150.00	39.7121	27.6651	2.6193	10.2033
160.00	42.1037	30.3053	3.0285	11.3773
170.00	44.3334	32.9255	3.4608	12.5679

112

T (K)	C_p,m	ΔₒᵀSₘ°	ΔₒᵀHₘ°	Φₘ°
180.00	46.4067	35.5190	3.9146	13.7710
190.00	48.3317	38.0803	4.3884	14.9832
200.00	50.1176	40.6053	4.8808	16.2013
210.00	51.7743	43.0912	5.3904	17.4228
220.00	53.3118	45.5357	5.9159	18.6452
230.00	54.7402	47.9374	6.4562	19.8668
240.00	56.0686	50.2955	7.0104	21.0857
250.00	57.3060	52.6097	7.5773	22.3005
260.00	58.4606	54.8800	8.1562	23.5100
270.00	59.5399	57.1068	8.7463	24.7132
280.00	60.5508	59.2906	9.3468	25.9093
290.00	61.4995	61.4321	9.9571	27.0974
298.15	62.2307	63.1468	10.4613	28.0594
300.00	62.3918	63.5323	10.5766	28.2770

Table 4-5: Standard thermodynamics functions of 15-SNDC. $\Delta_0^T S_m°$ is the standard molar entropy at temperature T assuming $S_0 = 0$, $\Delta_0^T H_m°$ is the standard molar enthalpy change on heating from absolute zero to T, $\Phi_m° = \Delta_0^T S - \Delta_0^T H / T$.

T (K)	$C_{p,m}$ (J mol⁻¹ K⁻¹)	$\Delta_0^T S_m°$ (J mol⁻¹ K⁻¹)	$\Delta_0^T H_m°$ (kJ mol⁻¹)	$\Phi_m°$ (J mol⁻¹ K⁻¹)
2.0000	0.0501	0.0041	4.23E-06	0.0019
5.0000	0.0325	0.0146	4.32E-05	0.0060
10.0000	0.1480	0.0612	4.13E-04	0.0200
20.0000	0.9683	0.3603	5.18E-03	0.1014
30.0000	2.9833	1.0921	0.0239	0.2954
40.0000	5.8499	2.3336	0.0677	0.6400
50.0000	9.2897	4.0027	0.1432	1.1390

113

60.0000	12.8667	6.0125	0.2540	1.7798
70.0000	16.3885	8.2616	0.4003	2.5428
80.0000	19.8172	10.6748	0.5814	3.4071
90.0000	23.1551	13.2025	0.7964	4.3541
100.0000	26.3971	15.8109	1.0442	5.3688
110.0000	29.5259	18.4745	1.3239	6.4389
120.0000	32.5197	21.1730	1.6343	7.5541
130.0000	35.3593	23.8892	1.9738	8.7061
140.0000	38.0318	26.6085	2.3409	9.8877
150.0000	40.5315	29.3186	2.7339	11.0929
160.0000	42.8585	32.0097	3.1510	12.3162
170.0000	45.0177	34.6736	3.5905	13.5531
180.0000	47.0173	37.3040	4.0508	14.7997
190.0000	48.8672	39.8963	4.5303	16.0526
200.0000	50.5784	42.4470	5.0277	17.3087
210.0000	52.1621	44.9535	5.5415	18.5656
220.0000	53.6292	47.4144	6.0705	19.8212
230.0000	54.9904	49.8287	6.6137	21.0735
240.0000	56.2553	52.1961	7.1700	22.3212
250.0000	57.4332	54.5168	7.7385	23.5627
260.0000	58.5323	56.7910	8.3184	24.7971
270.0000	59.5602	59.0195	8.9089	26.0235
280.0000	60.5238	61.2032	9.5094	27.2411
290.0000	61.4291	63.3430	10.1192	28.4492
298.1500	62.1277	65.0552	10.6227	29.4265

114

| 300.0000 | 62.2817 | 65.4400 | 10.7378 | 29.6474 |

SNDC compounds have a residual entropy, due to disorder in arrangement of both cations and anions in the lattice. Each cation lattice position can be occupied by a Ce, Sm or Nd nucleus. Also, each anion position can be occupied by an oxygen atom or a vacancy. Therefore, the residual entropy, S_0, of SNDC consists of two contributions: cationic, $S_{0,cat}$, and anionic, $S_{0,an}$. The residual entropy of SNDC compounds with a general formula $Ce_{1-x}Nd_{x/2}Sm_{x/2}O_{2-x/2}$ was calculated with the approach described in refs. 18 and 19.

$$S_0 = S_{0,cat} + S_{0,an} \tag{7a}$$

$$S_{0,cat} = -N_A k \left[(1-x)\ln(1-x) + \frac{x}{2}\ln\left(\frac{x}{2}\right) + \frac{x}{2}\ln\left(\frac{x}{2}\right) \right] \tag{7b}$$

$$S'_{0,an} = -2N_A k \left[\left(1 - \frac{x}{4}\right)\ln\left(1 - \frac{x}{4}\right) + \frac{x}{4}\ln\left(\frac{x}{4}\right) \right] \tag{7c}$$

where N_A is Avogadro's number, x is the coefficient from the chemical formula of SNDCs (dopant concentration), and $S'_{0,an}$ is the anion contribution to residual entropy assuming all vacancies are disordered. Equation (7) was derived using the Gibbs entropy equation: $S = - k \Sigma_i p_i \ln p_i$, where p_i is probability of microstate i. The factor of 2 in equation (7c) takes into account that there are in total two moles of anions per mole of SNDC. However, due to ordering, not all vacancies contribute equally to residual entropy. Thus, an effective vacancy concentration, n_{eff}, see Table 4-6, has to be taken into account in equation (7c). When this is done, equation (7c) becomes

115

$$S_{0,an} = -\left(2 - \frac{x}{2} + n_{eff}\right) N_A k \left[\left(\frac{2-\frac{x}{2}}{2-\frac{x}{2}+n_{eff}}\right) \ln\left(\frac{2-\frac{x}{2}}{2-\frac{x}{2}+n_{eff}}\right) + \left(\frac{n_{eff}}{2-\frac{x}{2}+n_{eff}}\right) \ln\left(\frac{n_{eff}}{2-\frac{x}{2}+n_{eff}}\right)\right]$$

$$(7d)$$

The factor of 2 from equation (7c) is transformed into $2 - [(x/2) - n_{eff}]$ in (7d) to take into account that the number of particles occupying anionic positions has, in effect, decreased due to vacancy ordering. Thus, combining equations (7a), (7b) and (7d) shows that the residual entropy of 5-SNDC is 3.073 J mol^{-1} K^{-1}, while for 15-SNDC it is 5.054 J mol^{-1} K^{-1}. These values can be compared to those of spinels described in ref. 18, which have a residual entropy originating from similar disorder in two kinds of lattice positions. The slightly lower value reported here arises from lower dopant concentration x in the SNDC samples compared with the spinels studied in ref. 18, as well as the presence of vacancy ordering. The entropies of the two compounds are thus the sum of $\Delta_0^T S$ reported in Table 4-4 and Table 4-5, and the residual entropies. For 5-SNDC the standard entropy at 298.15 K is 66.220 J mol^{-1} K^{-1} and for 15-SNDC it is 70.109 J mol^{-1} K^{-1}.

Using the standard entropies of 5-SNDC and 15-SNDC reported here, together with entropies and enthalpies of the precursor binary oxides,[20] enthalpies of formation from ref. 5, and the standard free energies of formation of the 5-SNDC and 15-SNDC. The entropy of formation of from oxides at 298.15 K for 5-SNDC is 0.0657 J mol^{-1} K^{-1}, while for 15-SNDC it is 0.4566 J mol^{-1} K^{-1}, if residual entropy is excluded. If residual extropy is included, the entropy of formation from oxides for 5-SNDC is 3.1389 J mol^{-1} K^{-1}, while for 15-SNDC it is 5.5103 J mol^{-1} K^{-1}. The standard free energy of formation from the elements at 298.15 K for 5-SNDC is -1097.38 kJ mol^{-1} and for 15-SNDC it is -1082.82 kJ mol^{-1} (residual entropy included into the calculation).

4.5   Discussion

Schliesser and Woodfield's linear term model[8] assumes a random distribution of vacancies, an assumption that can be tested by comparison of the vacancy concentrations calculated from sample stoichiometry (equation 1) and from the coefficient of the linear term in the fit to the heat capacity (equation 3). This comparison is given in Table 4-6. For 5-SNDC, the calculated and measured vacancy concentrations agree reasonably well (0.0239 vs. 0.0260). But the calculated vacancy concentration (0.012) for 15-SNDC, is much smaller than the actual vacancy concentration (0.077). This difference is most likely due to vacancy ordering in 15-SNDC, since vacancy ordering becomes more extensive as the dopant concentration increases.[5] Equation (3) thus gives quantitative results for samples with random vacancies, but when the vacancies interact and are ordered, equation (3) underpredicts the concentration because the vacancies no longer have a random distribution. However, if the total vacancy concentration is known, as is the case here, the disordered vacancy concentration as measured by heat capacities can be used to calculate the actual concentration of ordered vacancies, which has not been possible previously. In this case for the 15-SNDC sample, the ordered vacancy concentration would be 0.065.

Table 4-6: Vacancy concentrations of 5-SNDC and 15-SNDC found from the linear term in the heat capacity fit, γ, compared with the values found from stoichiometry of the samples.

	5-SNDC	15-SNDC
γ (J mol^{-1} K^{-2})	0.00361	0.00186
$n_{stoichiometric}$	0.0260±0.0005	0.077±0.002
n_{eff}	0.0239	0.0123
error (%)	-8	-84

117

Another interesting feature in the heat capacity occurs in the low temperature region between 2 and 4 K as shown in the inset in Figure 4-1. The sizeable upturn with decreasing temperature in the 15-SNDC heat capacity is significantly smaller in 5-SNDC. The coefficient of the T^{-2} term, A in Table 4-3, quantifies this difference with A being an order of magnitude greater in 15-SNDC than in 5-SNDC. The T^{-2} term originates from nuclear magnetic contributions to the heat capacity, and the upturn is the high temperature tail of a nuclear Schottky anomaly arising from ordering of nuclear magnetic moments.[7] The Nd nuclei in 5-SNDC are less numerous than in 15-SNDC, so the effect is less pronounced. (See refs. 21 and 22 for details.) The paramagnetic Nd nuclei are immersed in an electric field from the electrons surrounding the nucleus causing splitting of the nuclear energy levels. At higher temperatures, both higher and lower energy levels are equally populated, but as the temperature decreases, the Nd nuclei transition to the lower energy level. The transition leads to the Schottky anomaly in the heat capacity,[7] the upper tail of which is seen as the upturn in the 15-SNDC heat capacity.

The coefficient of the T^{-2} term, A, is related to the local magnetic field at Nd nuclei, H_{hyp}, through the equation

$$A = y \frac{N_A k}{3} \left(\frac{I+1}{I}\right) \left(\frac{\mu_I H_{hyp}}{k}\right)^2 \qquad (7)$$

where y is the concentration of nuclei with non-zero spin, N_A is Avogadro's number, I is the nuclear spin, and μ_I is the nuclear magnetic moment.[22,23] Both ^{143}Nd and ^{145}Nd have non-zero nuclear spins both with $I = 7/2$.[23] ^{143}Nd has an abundance of 12.18% and $\mu_I = -1.208\mu_N$, while ^{145}Nd has an abundance of 8.29% and $\mu_I = -0.744\mu_N$, where $\mu_N = 5.05 \cdot 10^{-27}$ J/T is the nuclear magneton. ^{143}Nd and ^{145}Nd have the same nuclear spins and H_{hyp}, since they are surrounded by identical

electron clouds. However, they have different abundances and magnetic moments, resulting in different contributions to A. Thus, the observed value of A is a sum of the two contributions. ^{143}Nd and ^{145}Nd have y values of 12.18% ($x/2$) and 8.29% ($x/2$), respectively. Thus equation (7) becomes

$$A = \frac{x}{2}\frac{N_A}{3k}\left(\frac{I+1}{I}\right)\left\{12.18\%\left[\mu_I(^{143}Nd)\right]^2 + 8.29\%\left[\mu_I(^{145}Nd)\right]^2\right\}H_{hyp}^2 \qquad (8)$$

From equation (8), for 5-SNDC H_{hyp} = 2683 T and for 15-SNDC H_{hyp} = 4756 T. The calculated H_{hyp} values are high when compared with fields surrounding Mn nuclei in $La_{1-x}Sr_xMnO_{3+\delta}$.[21] However, similar local fields surrounding Nd nuclei have been reported. Villuendas *et al.*[17] used low temperature calorimetry to study magnetic properties of Nd_5Ge_3 and reported fields of 2722 T and 2761 T surrounding Nd nuclei at two different positions in the crystal lattice.

Typically, heat added to a solid sample first excites phonons which then equilibrate with other electronic and atomic modes of motion. However, at low temperatures, the number of accessible phonons becomes so small that there is often no longer an effective transfer of energy between phonons and nuclear levels. Such a situation appears in the 15-SNDC sample and can be seen as the abrupt heat capacity drop near 2 K. This phenomenon is detected indirectly by the calorimeter, the heat from equilibration of the nuclei is first transferred to phonons, and then transferred to the calorimeter. However, when the number of phonons is small, heat from the nuclei cannot reach the calorimeter. The heat becomes essentially "trapped" in the nuclei, is not measured by the calorimeter, and the measured heat capacity drops off sharply.

119

4.6 Summary

The heat capacities of $Ce_{0.948}Nd_{0.0260}Sm_{0.0260}O_{1.9740}$, and $Ce_{0.847}Nd_{0.077}Sm_{0.077}O_{1.924}$ were determined from 1.8 to 300 K. Standard entropies from 0 to 300 K were calculated from the heat capacity data. Free energies of formation at 298.15 K were determined. Residual entropy was found to be for 5-SNDC 3.073 J mol^{-1} K^{-1} and for 15-SNDC 5.054 J mol^{-1} K^{-1}. Vacancy ordering was found to decrease the influence of vacancies on heat capacity. For samples with disordered vacancies, a linear term gives a quantitative estimate of vacancy concentration. A nuclear Schottky effect due to ordering of the paramagnetic Nd nuclei was observed between 2 and 4 K in the 15-SNDC sample, but not in the 5-SNDC sample. The 15-SNDC heat capacity exhibited a sharp drop-off below 2 K, which is caused by uncoupling of the paramagnetic Nd nuclei from lattice phonons. Entropy of heating the samples was calculated from 0 to 300 K (Table 4-4 and Table 4-5). Residual entropy of the samples was calculated to be 3.073 J mol^{-1} K^{-1} for 5-SNDC and 5.054 J mol^{-1} K^{-1} for 15-SNDC. The sum of the entropy of heating and residual entropy - standard entropy at 298.15 K is 66.220 J mol^{-1} K^{-1} for 5-SNDC and 70.109 J mol^{-1} K^{-1} for 15-SNDC. The Gibbs free energies of formation at 298.15 K of the samples are -1097.38 kJ mol^{-1} for 5-SNDC and -1082.82 kJ mol^{-1} for 15-SNDC.

4.7 References:

[1]   C. Kittel and P. McEuen, *Introduction to Solid State Physics* (Wiley, Hoboken, NJ, 2005).

[2]   R.M. Ormerod, Solid oxide fuel cells, Chemical Society Reviewes **32**, 17-28 (2003).

[3]   M. Morgensen, N.M. Sammes and G.A. Tompsett, Physical, chemical and electrochemical properties of pure and doped ceria, Solid State Ionics **130**, 69-76 (2000).

[4]   H. Inaba and H. Tagawa, Ceria-based solid electrolytes, Solid State Ionics **83**, 1-16 (1996).

[5]   S. Buyukkilic, T. Shvareva and A. Navrotsky, Enthalpies of formation and insights into defect association in ceria singly and doubly doped with neodymia and samaria. Solid State Ionics **227**, 17-22 (2012).

[6]   D.A. McQuarrie, *Statistical Mechanics* (University science books, Mill Valley, CA, 2000).

[7]   E.S.R. Gopal, *Specific heats at low temperatures* (Plenum press, New York, NY, 1966).

[8]   J.M. Schliesser and B.F. Woodfield, Lattice vacancies responsible for the linear dependence of the low-temperature heat capacity of insulating materials, Phys. Rev. B **91**, 024109 (2015).

[9]   Q. Shi, C.L. Snow, J. Boerio-Goates and B.F. Woodfield, Accurate heat capacity measurements on powdered samples using a Quantum Design physical property measurement system, J. Chem. Thermo. **42**, 1107-1115 (2010).

[10]   Q. Shi, J. Boerio-Goates and B.F. Woodfield, An improved technique for accurate heat capacity measurements on powdered samples using a commercial relaxation calorimeter, J. Chem. Thermo. **43**, 1263-1269 (2011).

[11]   R. Stevens, J. Boerio-Goates, Heat capacity of copper on the ITS-90 temperature scale using adiabatic calorimetry. Journal of Chemical Thermodynamics **36**(10), 857-863 (2004).

[12]   D.L. Martin, Specific Heats of Copper, Silver, and Gold below 30°K. Phys. Rev. **146**, 614 (1966).

[13]   J. Majzlan, A. Navrotsky, B.F. Woodfield, B.E. Lang, J. Boerio-Goates and R.A. Fisher, Phonon, Spin-Wave, and Defect Contributions to the Low-Temperature Specific Heat of a-FeOOH, Journal of Low Temperature Physics **130**, 69-76 (2003).

[14]   A.I. Smith, J.-C. Griveau, E. Colineau, P.E. Raison, G. Wallez and R.J.M. Konings, Low temperature heat capacity of Na_4UO_5 and Na_4NpO_5, J. Chem. Thermo. **91**, 245-255 (2015).

[15]   J.M. Schliesser and B.F. Woodfield, Lattice vacancies responsible for the linear dependence of the low-temperature heat capacity of insulating materials, Phys. Rev. B **91**, 024109 (2015).

[16]   J.M. Schliesser, S.J. Smith, G. Li, L. Li, T.F. Walker, T. Perry, J. Boerio-Goates and B.F. Woodfield, Heat capacity and thermodynamic functions of nano-TiO_2 anatase in relation to bulk-TiO_2 anatase, J. Chem. Thermo. **81**, 298-310 (2015).

[17]   B.F. Woodfield, J. Boerio-Goates, J.L. Spahiro, Molar heat capacity and thermodynamic functions of zirconolite $CaZrTi_2O_7$. Journal of Chemical Thermodynamics **31**, 245-253 (1999).

122

[18]   J.M. Schliesser, B. Huang, S.K. Sahu, M. Asplund, A. Navrotsky, B.F. Woodfield, Experimental heat capacities, excess entropies, and magnetic properties of bulk and nano Fe_3O_4-Co_3O_4 and Fe_3O_4-Mn_3O_4 spinel solid solutions. Journal of Solid State Chemistry **259**, 79-90 (2018).

[19]   A. Navrotsky, O.J. Kleppa, The thermodynamics of cation distributions in simple spinels. J. Inorg. Nucl. Chem. **29**, 2701-2714 (1967).

[20]   R.J.M. Konings, O. Benes, A. Kovacs, D. Manara, D. Sedmidubsky, L. Ghorkhov, V.S. Iorish, V. Yungman, E. Shenyavskaya, E. Osina, The thermodynamic properties of the f-elements and their compounds. Part 2. The lanthanide and actinide oxides. Journal of Physical and Chemical Reference Data **43**, 013101 (2014).

[21]   G.H. Fuller, Nuclear spins and moments, Journal of Physical and Chemical Reference Data **5**, 835-1092 (1976).

[22]   B.F. Woodfield, M.L. Wilson, J.M. Byers, Low-Temperature Specific Heat of $La_{1-x}Sr_xMnO_{3+\delta}$, Phys. Rev. Lett. **78**(16), 3201-3204 (1997).

[23]   D. Villuendas, T. Tsutaoka, J.M. Hernandez Ferras, Heat capacity study of the magnetic phases in a Nd_5Ge_3 single crystal. Journal of Magnetism and Magnetic Materials **405**, 282–286 (2016).

5 CONCLUSIONS AND FUTURE RESEARCH

The entropy concept is unavoidable in many scientific disciplines, resulting in inconsistencies in its application and interpretation. The analysis leads to the conclusion that:

1. The original Clausius' definition of entropy seems to be the most appropriate. Entropy is in physical sciences a measure of the part of internal energy that cannot be converted into work, or in practical terms it represents useless energy.

2. Thermal entropy should be considered as an objective parameter. Residual entropy should also be considered as an objective parameter.

3. Living organisms increase their entropy during life, due to processes of accumulation and entropy generation. The negentropy concept represents a mathematically correct manipulation of the Boltzmann equation, which however has no physical sense.

Based on the general principle of enumerating microstates, the work posited a paradigm wherein adaptation and evolution are stochastically deterministic, i.e. having a specific direction arising from many random events. Natural selection over time, resulting from random events governed by deterministic constraints, minimizes the difference in the information describing the local environment and the biological system. Therefore, this paradigm lays the foundation for an information theory formulated on the immensely powerful statistical concept of enumerating microstates that provides summary statistics similar to thermodynamic entropy. To avoid confusion of thermodynamic entropy with various other "entropies", it has been proposed the summary statistics for the environment and for the population demographics be called the "envotropy" and the "demotropy", respectively, and that a similar nomenclature be developed for

124

the summary statistics of other systems. This work thus proposes a foundation for a quantitative theory for summary statistics of information systems including biological systems, economics, markets, and health systems.

Hydrolysis of cellulose to glucose is a key reaction in renewable energy from biomass and in mineralization of soil organic matter to CO_2. Conditional thermodynamic parameters, $\Delta_{hyd}G'$, $\Delta_{hyd}H'$, and $\Delta_{hyd}S'$, and equilibrium glucose concentrations are reported for the reaction *$C_6H_{10}O_5(cellulose)+H_2O(l) \rightleftarrows C_6H_{12}O_6(aq)$* as functions of temperature from 0 to 100⁰C. Activity coefficients of aqueous glucose solution were determined as a function of temperature. The reaction free energy $\Delta_{hyd}G'$ becomes more negative as temperature increases, suggesting that producing cellulosic biofuels at higher temperatures will result in higher conversion. Also, cellulose is a major source of carbon in soil and is degraded by soil microorganisms into CO_2 and H_2O. Therefore, global warming will make this reaction more rapid, leading to more CO_2 and accelerated global warming by a positive feedback.

Vacancy ordering was found to decrease the influence of vacancies on heat capacity. For samples with disordered vacancies, the model developed by Schliesser and Woodfield (chapter 4) gives a quantitative estimate of vacancy concentration from the linear term in the low temperature heat capacity. Vacancy ordering decreases the influence of vacancies on low temperature heat capacity, causing the model to give only an order of magnitude estimate of vacancy concentration.

Starting from the assumption that age represents biological and thermodynamic state of an organism, and that aging as an integral part of life is a biological and thermodynamic process, the future goal for research is formulation of an equation of state of an idealized cell. If the currency

125

of change of state is entropy, then an equation of state should express entropy change that encompasses all contributions.

Similarly, to thermodynamic state, an organism should also have an information state. During evolution, there is a change in information content (mutations of nucleic acids) and information state. Then the goal of the second direction of research is to quantitatively formulate changes in information state of an organism during evolution. This represents a step in quantification of theory of evolution.