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Review

On entropy and absorbed thermal energy in biomass; a biologist's perspective

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Abstract

The randomness, probability, organization, and information that are attributed to a greater or lesser entropy of substances are all perceptual manifestations of the same basic phenomenon, which is the absorption of thermal energy. Entropy is a mathematical function not having a physical reality characteristic of material bodies, but when multiplied by the temperature for which the entropy has been calculated the product becomes the quantity of thermal energy that must be absorbed for a substance to exist at that temperature above absolute zero. For the standard temperature, $T^0S^0 = Q^0$. The advantage of visualizing entropy in this respect is discussed, and the suggestion made that the equation $\Delta G^0 = \Delta H^0 - \Delta Q^0$ is a useful and, perhaps, more understandable form of the Gibbs free-energy equation. The distinction is made between changes in absorbed (entropic) thermal energy (ΔQ^0) and exergonic thermal energy ($\Delta G^0{}_{\mathrm{th}}$), resulting from the conversion of non-thermal free energy into heat), the sum of which is the enthalpy change (ΔH^0) of the closed systems being considered, i.e. $\Delta H^0 = \Delta G^0{}_{\mathrm{th}} + \Delta Q^0$. Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

What is entropy? A common answer often given is that entropy is 'randomness', or that entropy is a measure of 'probability', 'organization', or 'information' [1,2]. Something that has a higher entropy per unit mass (otherwise the comparison is useless) than something else is usually considered to be more random, more probable, less organized, and to contain less information. What is meant by these answers in the context of the question is often unclear. In any context, they are unsuitable from the point of view of classical thermodynamics because randomness, probability, organization, and information, per se, have no dimensions. The idea of entropy, S, was originally introduced by Clausius in 1850 [3] in the form of the equation

$$\mathrm{d}S = \frac{\mathrm{d}Q_{\mathrm{rev}}}{T} \tag{1}$$

where S represents an infinitely small increase in entropy, Q the heat absorbed during an infinitely small increase in temperature, and T the absolute ideal gas temperature (thermodynamic temperature on the Kelvin scale). This equation established the relation of S to a quantity of thermal energy and the absolute temperature. At about the same time, evidence suggested that, whenever a spontaneous process takes place, there is always an accompanying increase in entropy. In addition to an increase in entropy, all

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spontaneous processes were observed to be accompanied by an increase in 'disorder', in that the final state of a process always appeared to be more disordered than the initial state; however, this disorder was defined. Such definitions included an increase in randomness and disorganization in the gas phase, and are the source of some of the concepts of entropy at the present time. The idea of probability entered considerations of entropy because it was apparent that a condition of disorder is more probable than one of order, and it is intuitively reasonable that a spontaneous change will involve the passage from a less probable to a more probable condition. This led to the expectation that a connection might exist between the increase in entropy that occurs in a spontaneous process and the increase in probability that occurs at the same time, and it was this kind of consideration that led Boltzmann in 1896 [4] to propose the equation

$$S = k \ln W + \text{const} \tag{2}$$

where S is the entropy of a system, W its thermodynamic probability (defined as the ratio of the probability of a given state of a system to one for the same system for which there is complete order), and k the Boltzmann constant (i.e. the gas constant, R, per single molecule), having the dimensions of $\mathrm{JK}^{-1}\ \mathrm{mol}^{-1}$ (or atom^{-1}). In this manner, the dimensions of energy become related to probability. It was suggested by Planck in 1912 [5] that the undefined constant in Eq. (2) should be zero, resulting in the more familiar form of the equation,

$$S = k \ln W \tag{3}$$

Eq. (3) is retained in this form in modern quantum mechanics, but the symbol W has taken on a modified significance, so that Eq. (3) can be expressed in the following form.

$$S = -k \sum p_i \ln p_i \tag{4}$$

where p_i represents the maximum probability of a gaseous system in terms of the partition functions related to the vibration, rotation, and translation of the atoms or molecules of a gas. However, it is in Eq. (2) that probability was originally linked to entropy, and along with it the ideas of randomness, order, and organization that are still prevalent today.

Entropy has also been related to information following the well-known paper by Shannon, in 1948, on *A mathematical theory of communication* [1]. This theory was based, in part, on the similarity of the equation, $I = \sum p_j \ln_2 p_j$, to Eq. (4). In 1953, the applications of information theory to Biology were explored enthusiastically in a book edited by Quastler [2]. Here, there was an article by Linschitz in which it was calculated that the limiting value of I for one *Escherichia coli* cell was of the order of 10^{13} bits [6]. However, Linschitz also commented that if a cell wastes 99% of its entropy supply in maintenance and metabolic activity, the value of I per cell might be reduced to 10^{10}–10^{11} bits. In the same book, Dancoff and Quastler arrived at a similar range to this latter with respect to germ cells [7]. In 1955, Morowitz calculated that ca. 2×10^{11} bits of information were required to describe a single cell of the bacterium *E. coli* [8]. This later result was considered to be in good agreement with the information content calculated from entropy values *derived* from calorimetric data (see also Refs. [9,10], and a summary in Ref. [11]), although an actual determination of entropy from the Third Law measurements was not made. Still, in a 1966 paper, Gilbert [12] expressed the opinion that the supposed promises of the application of information theory to biology were largely unfounded. A later article by Johnson [13], in 1970, confirmed this, pointing out the difference between purposeful and purposeless information and the problems this presented with respect to the theory. This situation still appears to apply to information theory at the present time, although authors continue to explore its possibilities (see, for example, Refs. [14,15]).

Eq. (4) has been very useful in calculating values of S^0 (standard entropy) for small atomic or molecular weight gases, these values agreeing well with, and sometimes being more accurate than, the same values as measured using the Third Law. This latter method of determining S^0 does not have any immediate identification with randomness, organization, and probability. These entropy values are determined by integrating heat capacity data obtained by low-temperature calorimetry, using the following equation:

$$S = \int_{T=0}^{T} \frac{C_\mathrm{p} \mathrm{d}T}{T} \tag{5}$$

where S represents the entropy, having the dimensions of J K^{-1} mol^{-1} or J K^{-1} g^{-1}, and C_p the heat capacity at constant pressure, usually taken as 1 bar. Since 0 K is not a practical temperature to achieve, measurements are usually made with a lower bound between 7 and 15 K and an extrapolation to 0 K using the Debye equation. Entropy data are usually listed with $T = 298.15$ K as the upper bound and are referred to as 'standard' entropy values.

Most present-day entropy values are obtained using the Third Law measurements because of the impracticality or impossibility of using Eq. (4). The usual methods of applying statistical mechanics to the calculation of translational and rotational partition functions are not applicable to substances in the solid state [16].

The values of S^0 as determined by Eq. (4), where this can be used, and as determined by Eq. (5) for the same substance are considered to be identical. This again brings up the question of randomness, organization, and probability. As mentioned above, if something has a higher entropy per unit mass than something else, can the former be considered really to be more random, less organized, and its existence to be more probable? For example, one gram of dried *Saccharomyces cerevisiae* cells has an entropy of 1.304 J K^{-1} g^{-1} at 298.15 K [17], and the same mass of crystalline α-D-glucose, which is a common organic substrate used to grow this yeast, has an entropy of 1.161 J K^{-1} g^{-1}[18]. Does this mean that cellular fabric is more random, more probable, and less organized than the substrate from which it was formed? Questions such as this make it apparent that perhaps another way of perceiving entropy may be preferable and easier to understand. One possibility is to regard entropy as being related to the absorption of thermal energy. This is what occurs during Third Law entropy determinations, and the point can be made that the Third Law entropy of a given mass of substance is *related in the form of a mathematical function* to that quantity of thermal energy (heat) that is necessary to be absorbed by this mass for it to exist at a given temperature above absolute zero.

2. Methods

To begin with, a distinction should be made between entropy and entropic (absorbed) thermal energy. Entropy has the dimensions of J K^{-1} g^{-1} or J K^{-1} mol^{-1}. It is a mathematical function which, although it can be calculated to have finite, positive values, by itself has no physical meaning. All modern entropy data are listed at the standard temperature of 298.15 K (25°C). The upper bound of the integration of Eq. (5) is then 298.15 K, and T in the denominator of Eq. (5) then takes on this value in the calculation of S^0. The quantity of thermal energy that has been absorbed or exchanged by a substance or a system under standard conditions can be obtained by multiplying S^0 or ΔS^0, respectively, by $T = 298.15$ K. The symbols T^0S^0 and $T^0\Delta S^0$ then represent a definite quantity of thermal energy. This thermal energy is not entropy, by definition, and should more properly be called 'entropic thermal energy', to distinguish it from exergonic thermal energy (represented by $\Delta G^0{}_{\mathrm{th}}$, resulting from the conversion of non-thermal free energy into thermal energy, and enthalpic thermal energy, (represented by ΔH^0, which is the sum of the values for exergonic and entropic thermal energy (e.g. $\Delta H^0 = \Delta G^0{}_{\mathrm{th}} + T^0\Delta S^0$).

2.1. Conventional methods for calculating quantities of entropic thermal energy

There are two conventional methods for calculating the quantity of entropic thermal energy exchanged by a system during a chemical reaction or process at constant temperature and pressure, nominally taken as standard at 298.15 K and 1 bar.

2.1.1. Method 1

If ΔG^0 and ΔH^0 are known, $T^0\Delta S^0$ and ΔS^0 can be calculated using the Gibbs free-energy equation.

$$\Delta G^0 = \Delta H^0 - T^0\Delta S^0 \tag{6}$$

2.1.2. Method 2

If the entropies of formation of the reactants and products of a reaction or process are known, ΔS^0 can be calculated as follows.

$$\Delta S^0 = \sum \Delta_f S^0_{\mathrm{prod}} - \sum \Delta_f S^0_{\mathrm{react}} \tag{7}$$

In Eq. (7), the subscripts 'prod' and 'react' represent products and reactants, respectively, of a reaction or process. A value for $T^0\Delta S^0$ can then be found by multiplying the value obtained with Eq. (7) by T^0.

To illustrate the above methods, the oxidation of glucose can be used as a simple example. The equation representing this reaction is

$$C_6H_{12}O_6(c) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \tag{8}$$

In Section 2.1.1, values for ΔG^0 and ΔH^0 can be calculated by means of the following equations.

$$\Delta G^0 = \sum \Delta_f G^0_{\text{prod}} - \sum \Delta_f G^0_{\text{react}} \tag{9}$$

$$\Delta H^0 = \sum \Delta_f H^0_{\text{prod}} - \sum \Delta_f H^0_{\text{react}} \tag{10}$$

Using Eqs. (9) and (10) and the appropriate data in Table 1, ΔG^0 and ΔH^0 for the reaction represented by Eq. (8) are calculated as follows.

$$\begin{aligned}\Delta G^0 &= 6(-394.36) + 6(-237.18) \\ &\quad - (-910.56) - 6(0) \\ &= -2878.68\,\text{kJ mol}^{-1}\end{aligned} \tag{11}$$

and

$$\begin{aligned}\Delta H^0 &= 6(-393.51) + 6(-285.83) \\ &\quad - (-1274.45) - 6(0) \\ &= -2801.59\,\text{kJ mol}^{-1}\end{aligned} \tag{12}$$

Using Eq. (6), the quantity of absorbed (entropic) thermal energy exchanged by the system is then

$$T^0\Delta S^0 = -2801.59 + 2878.68 = 77.09\,\text{kJ mol}^{-1} \tag{13}$$

from which

$$\begin{aligned}\Delta S^0 &= 77.09\,\text{kJ mol}^{-1}/298.15\,\text{K} \\ &= 258.56\,\text{J K}^{-1}\,\text{mol}^{-1}\end{aligned} \tag{14}$$

In Section 2.1.2, Eq. (7) is used with the appropriate values from Table 1:

$$\begin{aligned}\Delta S^0 &= 6(2.85) + 6(-163.17) - (-1220.48) \\ &\quad - 6(0) = 258.56\,\text{J K}^{-1}\,\text{mol}^{-1}\end{aligned} \tag{15}$$

from which

$$\begin{aligned}T^0\Delta S^0 &= 258.56\,\text{J K}^{-1}\,\text{mol}^{-1} \times 298.15\,\text{K} \\ &= 77.09\,\text{kJ mol}^{-1}\end{aligned} \tag{16}$$

The calculation using Eq. (16) should provide the same value as that using Eq. (13), and does.

2.2. *Using Q to calculate quantities of entropic thermal energy.*

Nowhere in the foregoing two methods for calculating $T\Delta S^0$ is it directly evident in the symbols used that we are dealing with entropic thermal energy, which can be represented by Q. In addition to Eqs. (1) and (2), the calculation of S^0 can be accomplished as follows:

$$S^0 = \frac{Q^0}{T^0} \tag{17}$$

Here, the symbol Q^0 represents the entropic thermal energy that must be absorbed for a given mass of substance to exist at the standard temperature of 298.15 K above absolute zero. From Eq. (17)

$$Q^0 = T^0 S^0 \tag{18}$$

Values of Q^0 for several substances of biological interest are listed in Table 1.

2.2.1. *Method 3*

If Q^0 does indeed represent the *absorbed thermal energy* necessary for a given mass of substance to exist at a given temperature (K) above absolute zero (here, 298.15 K), it should be possible to calculate the quantity of this thermal energy that is exchanged by a closed system as it passes from an initial to a final state. This provides another method for calculating $T^0\Delta S^0$. Thus,

$$\Delta Q^0 = T^0\Delta S^0 = \sum Q^0_{\text{prod}} - \sum Q^0_{\text{react}} \tag{19}$$

Using Eq. (19) and the appropriate values for Q^0 from Table 1, ΔQ^0 for the reaction represented by Eq. (8) is calculated as follows:

$$\begin{aligned}\Delta Q^0 &= 6(63.682) + 6(20.837) - (63.236) \\ &\quad - 6(61.120) = 77.16\,\text{kJ mol}^{-1}\end{aligned} \tag{20}$$

Accepting a slight difference in the result of the calculation due to the use of fractional numbers, this value is the same as that for $T^0\Delta S^0$ obtained with methods 1 and 2 with respect to the reaction represented by Eq. (8), and represents the exchange of entropic thermal energy by the system as the reactants represented in Eq. (8) pass from the initial to the final state. Consequently,

$$\Delta Q^0 = T^0\Delta S^0 \tag{21}$$

Table 1
Thermodynamic data on biomass and selected substances of biological importance, arranged in order of decreasing values of the mass related entropy

Substance	Formula	M.W./Da	$\Delta_f G^0$/ (kJ mol^{-1})	$\Delta_f H^0$/ (kJ mol^{-1})	$\Delta_f S^0$/ (J K^{-1} mol^{-1})	S^0/ (J K^{-1} g^{-1})	$Q^{o,e}$/ (kJ g^{-1})	Q^0/ (kJ mol^{-1})
Nitrogen[a]	N_2(g)	28.01	0	0	0	6.837	2.038	57.084
Oxygen[a]	O_2(g)	32.00	0	0	0	6.407	1.910	61.120
Carbon dioxide[a]	CO_2(g)	44.01	−394.36	−393.51	2.85	4.854	1.447	63.682
Water[a]	H_2O(l)	18.01	−237.18	−285.83	−163.17	3.882	1.157	20.837
Sulfur trioxide[a]	SO_3(g)	93.21	−371.08	−395.72	−82.64	2.753	0.820	76.432
Palmitic acid[b]	$C_{16}H_{32}O_2$(cr), II	256.42	−315.05	−890.77	−1930.97	1.775	0.529	135.646
L-Methionine[b]	$C_5H_{11}O_2NS$(cr)	149.21	−508.35	−761.07	−847.63	1.551	0.462	68.935
L-Valine[b]	$C_5H_{11}O_2N$(cr)	117.14	−358.99	−617.98	−868.66	1.526	0.455	53.299
Glycine[b]	$C_2H_5O_2N$(cr)	75.07	−377.69	−537.22	−535.07	1.379	0.411	30.854
Chymotrypsinogen A[c]	$CH_{1.612}O_{0.318}N_{0.282}S_{0.011}$(cr)	23.03	−26.88	−67.87	−139.96	1.350	0.402	9.258
Bovine zinc insulin[c]	$CH_{1.480}O_{0.295}N_{0.256}S_{0.024}Zn_{0.002}$(cr)	22.71	−17.58	−55.74	−128.21	1.315	0.392	8.902
Saccharomyces cerevisiae[d]	$CH_{1.613}O_{0.557}N_{0.158}P_{0.012}S_{0.003}K_{0.022}Mg_{0.003}Ca_{0.001}$	26.20	−85.95	−131.08	−151.37	1.304	0.389	10.192
L-Aspartic acid[b]	$C_4H_7O_4N$(cr)	133.10	−729.35	−972.53	−815.63	1.278	0.381	50.711
α-D-Glucose[b]	$C_6H_{12}O_6$(cr)	180.16	−910.56	−1274.45	−1220.48	1.177	0.351	63.236
Potassium oxide[a]	K_2O(cr)	94.20	−321.84	−363.15	−138.55	0.999	0.298	28.072
Phosphorous decoxide[a]	P_4O_{10}(cr)	283.89	−2697.84	−2984.03	−959.88	0.806	0.240	68.134
Calcium oxide[a]	CaO(cr)	56.08	−604.04	−635.09	−104.14	0.709	0.211	11.833
Magnesium oxide[a]	MgO(micro cr)	40.31	−565.97	−597.98	−107.36	0.692	0.206	8.304
Zinc oxide[a]	ZnO(cr)	81.37	−318.32	−348.28	−100.48	0.536	0.160	13.019

[a] These data were taken from Ref. [19].

[b] These data were taken from Ref. [20], except for K_2O(cr), which were taken from Ref. [21].

[c] Anhydrous. These unit-carbon formulas as well as the entropy data were calculated from the empirical formulas, $C_{508}H_{752}O_{150}N_{130}S_{12}Zn$ and $C_{1077}H_{1736}O_{343}N_{304}S_{12}$ from Ref. [22]. The enthalpy data were calculated with Thornton's Rule using the value of −111.14 kJ eq^{-1} [23]. The values for $\Delta_f G^0$ were calculated from these using the Gibbs free-energy equation.

[d] Anhydrous. This unit-carbon formula was taken from Ref. [24]. The enthalpy data were obtained from Ref. [24] and the entropy data from Ref. [17].

[e] $Q^0 = T^0 S^0$.

2.3. *Calculation of Q^0 with respect to biomass*

This is important with respect to considering ideas of randomness, probability, and organization in that a cell has such a complex structure of a great many kinds of molecules, perhaps more than any other substance. The absolute entropy of any form of biomass, $S^0{}_{\mathrm{biomass}}$, has only been determined recently with a study on a sample of specially prepared dried cells of *S. cerevisiae* that did not contain intracellular storage products [17]. The unit-carbon formula (UCF) for the composition of the cellular fabric has been taken as $\mathrm{CH_{1.613}O_{0.557}N_{0.158}P_{0.012}S_{0.003}K_{0.022}Mg_{0.003}Ca_{0.001}}$, so that one unit-carbon formula weight (also more frequently referred to as one carbon-mol, or C-mol) of cells weighs 26.202 Da [24]. The value for S^0 was measured at $1.304\,\mathrm{J\,K^{-1}\,g^{-1}}$, or $34.167\,\mathrm{J\,K^{-1}\,C\text{-}mol^{-1}}$ [17]. The value of Q^0 for this biomass is then

$$T^0S^0 = 298.15\,\mathrm{K} \times 34.167\,\mathrm{J\,K^{-1}\,C\text{-}mol^{-1}} \times 10^{-3}\,\mathrm{kJ\,J^{-1}} = 10.186\,\mathrm{kJ\,C\text{-}mol^{-1}} \tag{22}$$

and represents the quantity of entropic thermal energy that one C-mol of this biomass must absorb for it to exist at a temperature of 298.15 K above absolute zero.

Calculations with respect to biomass are the same as those for less complex substances, as demonstrated with glucose, above. Although any reaction or process would do, an equation representing the bomb-calorimetric oxidation of yeast cells can be used as an example of one involving biomass, as follows [24].

$$\begin{aligned}&\mathrm{CH_{1.613}O_{0.557}N_{0.158}P_{0.012}S_{0.003}K_{0.022}Mg_{0.003}}\\&\quad \mathrm{Ca_{0.001}(biomass) + 1.151O_2(g)}\\&\quad \rightarrow \mathrm{1.000CO_2(g) + 0.806H_2O(l)}\\&\quad + \mathrm{0.079N_2(g) + 0.003P_4O_{10}(cr)}\\&\quad + \mathrm{0.003SO_3(g) + 0.011\,K_2O(cr)}\\&\quad + \mathrm{0.003MgO(cr) + 0.001CaO(cr)}\end{aligned} \tag{23}$$

Using Method 1, Eqs. (23), (9) and (10), and the appropriate data in Table 1:

$$\begin{aligned}\Delta G^0 &= 1.000(-394.36) + 0.806(-237.18)\\&\quad + 0.079(0) + 0.003(-2697.84)\\&\quad + 0.003(-371.08) + 0.011(-321.84)\\&\quad + 0.003(-565.97) + 0.001(-604.04)\\&\quad - (-85.95) - 1.151(0)\\&= -514.98\,\mathrm{kJ\,C\text{-}mol^{-1}}\end{aligned} \tag{24}$$

$$\begin{aligned}\Delta H^0 &= 1.000(-393.51) + 0.806(-285.83)\\&\quad + 0.079(0) + 0.003(-2984.03)\\&\quad + 0.003(-395.72) + 0.011(-363.15)\\&\quad + 0.003(-597.98) + 0.001(-635.09)\\&\quad - (-131.08) - 1.151(0)\\&= -509.37\,\mathrm{kJ\,C\text{-}mol^{-1}}\end{aligned} \tag{25}$$

$$\begin{aligned}T^0\Delta S^0 &\equiv \Delta H^0 - \Delta G^0 = -509.37\,\mathrm{kJ\,mol^{-1}}\\&\qquad - (-514.64\,\mathrm{kJ\,mol^{-1}})\\&= 5.27\,\mathrm{kJ\,C\text{-}mol^{-1}}\end{aligned} \tag{26}$$

from which

$$\begin{aligned}\Delta S^0 &\equiv 5.27\,\mathrm{kJ\,mol^{-1}} \times 298.15\,\mathrm{K^{-1}}\\&= 17.67\,\mathrm{J\,K^{-1}\,C\text{-}mol^{-1}}\end{aligned} \tag{27}$$

Using Method 2, Eqs. (23) and (7), and the appropriate data in Table 1:

$$\begin{aligned}\Delta S^0 &= 1.000(2.88) + 0.806(-163.17)\\&\quad + 0.079(0) + 0.003(-959.88)\\&\quad + 0.003(-82.64) + 0.011(-138.55)\\&\quad + 0.003(-108.33) + 0.001(-104.14)\\&\quad - (-151.37) - 1.151(0)\\&= 17.65\,\mathrm{J\,K^{-1}\,C\text{-}mol^{-1}}\end{aligned} \tag{28}$$

from which

$$\begin{aligned}T^0\Delta S^0 &= 298.15\,\mathrm{K} \times 17.655\,\mathrm{J\,K^{-1}\,C\text{-}mol^{-1}}\\&\qquad \times 10^{-3}\,\mathrm{kJ - J^{-1}} = 5.26\,\mathrm{kJ\,C\text{-}mol^{-1}}\end{aligned} \tag{29}$$

Using Method 3, Eqs. (23) and (19), and the appropriate data in Table 1:

$$\begin{aligned}\Delta Q &= 1.000(63.682) + 0.806(20.837)\\&\quad + 0.079(57.084) + 0.003(68.134)\\&\quad + 0.003(76.432) + 0.011(27.072)\\&\quad + 0.003(8.304) + 0.001(11.833)\\&\quad - 10.186 - 1.151(61.120)\\&= 5.22\,\mathrm{kJ\,C\text{-}mol^{-1}}\end{aligned} \tag{30}$$

Again accepting a slight difference in the results of the calculation due to the use of fractional numbers, this value is the same as that obtained with Eqs. (26) and (29).

Table 2

Comparison of ΔQ^0 and $T^0\Delta S^0$ values relative to the oxidation to $CO_2(g)$, $N_2(g)$, $P_4O_{10}(cr)$, $O_2(g)$, $K_2O(cr)$, MgO(cr), CaO(cr), ZnO(cr), and $H_2O(l)$ of representative substances of biological interest[a]

Substance	Method 1 $T^0\Delta S^0$/(kJ mol^{-1})	Method 2 $T^0\Delta S^0$/(kJ mol^{-1})	Method 3 ΔQ^0/(kJ mol^{-1})
L-Aspartic acid(cr)	−76.31	−76.31	−76.29
α-D-Glucose(cr)	−77.09	−77.09	−77.20
Glycine(cr)	−39.61	−40.25	−39.62
L-Methionine(cr)	−35.24	−35.24	−35.26
Palmitic acid(cr)	−189.08	−189.08	−189.10
L-Valine(cr)	−4.33	−4.33	−4.30
Bovine zinc insulin(cr)	2.37	2.42	2.34
Chymotrypsinogen A(cr)	3.11	3.10	3.10
Saccharomyces cerevisiae (dried cells)	5.27	5.26	5.22

[a] Data for these calculations have been taken from Table 1.

3. Results

It is apparent that, even with substances as apparently complex as yeast cells, the above three methods of calculation give the same result, and that, for the oxidation represented by Eq. (23), $\Delta Q^0 = T^0\Delta S^0$. The results using equations representing any other kind of spontaneous chemical reaction or process would be expected to be the same. Examples involving the oxidation of several kinds of substances of biological interest for which good entropy data are available, are presented in Table 2. These all show the same identity of ΔQ^0 with $T^0\Delta S^0$.

4. Discussion

The concept of entropy has proven to be one that is difficult to understand, and it has been interpreted in many different ways. The reason for this may be the problem of comprehending it in terms that are related to some form of reality. This latter actually exists within the framework of the concept, but it appears to have been obscured because of the mathematics involved. As pointed out by Klotz "Ultimately one must realize that entropy is essentially a *mathematical function*." (the italics are the present author's) [25]. As such, it does not have a true physical meaning, being in effect a numerical value representing the average heat capacity of a substance per degree K within the range of 0 K and the upper bound of the temperature used in determining the entropy, usually 298.15 K. It acquires a physical meaning when it is multiplied by the temperature which is the upper bound, whereupon the product becomes the quantity of thermal energy that must be absorbed for a given mass to exist at that temperature above absolute zero. Usually this is listed as the standard temperature of 298.15 K. For the chemical systems presented here, distinctions can be made with respect to exergonic thermal energy, entropic thermal energy (so designated because of historical reasons) and enthalpic thermal energy.

Just as $T^0\Delta S^0$ represents the entropic thermal energy exchanged between a system and its environment, because $T^0\Delta S^0 = \Delta Q^0$, this latter quantity can be substituted for $T^0\Delta S^0$ in the Gibbs free-energy equation.

$$\Delta G^0 = \Delta H^0 - \Delta Q^0 \tag{31}$$

The principal advantage of this is that ΔQ^0 represents a thermal exchange of the system with its environment, which is a representation that is possibly easier to understand than $T^0\Delta S^0$. Eq. (31) also has another aspect. In the determination of Third Law entropy values, a sample is placed in a low-temperature calorimeter that is well equipped with adiabatic heat shields to prevent the exchange of thermal energy with the environment of the calorimeter. The temperature of the sample is then lowered to ca. 7 K, following which the temperature of the sample is raised in small increments by means of an electrical resistance inside the calorimeter vessel, with enough time in between the electrical pulses to allow the sample to come to a temperature equilibrium (relaxation time). This ensures the 'reversibility' that theory demands. The total quantity of thermal energy put into the system to raise the temperature of the sample from ca. 7 to 298.15 K can be determined from the total amount of current passed through the known resistance in the calorimeter, with corrections being made for the heat capacity of the calorimeter vessel. The quantity of thermal energy required to raise the temperature of the sample from 0 to 7 K can be extrapolated using the Debye equation. The sum of these two values equals Q^0. Using values of Q^0 obtained by this method for the appropriate substances, Eq. (19) can then be used to calculate values for ΔQ^0.

An interesting aspect with respect to Eq. (31) is that both ΔH^0 and ΔQ^0 are thermal quantities that can be measured directly, and therefore that ΔG^0 can be calculated without any recourse at all to entropy and the concepts of randomness, probability, and organization that are associated with this latter. Does this mean that going through the mathematical calculation of entropy is not necessary?

Returning to the ideas of randomness, probability, and organization as identified with entropy, an inspection of columns 7 and 8 in Table 1 is also interesting. Here S^0 and Q^0 are arranged in order of decreasing values with respect to the substances listed. As would be expected from Eq. (17), these decreases parallel one another, and if Q^0 is converted from kJ g^{-1} to J g^{-1}, the ratio of $1000Q^0$ to S^0 is always 298 K This is true, independently of the molecular weight of a substance; whether it is a solid, liquid, or gas; or whether it appears to be extremely complex as in dried cells, or as simple as a metal oxide. Certainly, one conclusion to be made is that the absorption of thermal energy has a constant effect on the entropy that is a function only of the temperature, and therefore no influence on what we perceive as randomness, probability, and organization. Can we regard these perceptions as representing qualities that are independent of Q^0? A most interesting consideration in this respect is that of the triple point of water, where $1000Q^0/S^0$ is the same for the three phases that exist in equilibrium at that temperature.

Questions such as those above can at least be asked, irrespective of whether there are good answers. For example, in solids, where the principal partition function is the entropy of vibration, does the absorption of thermal energy increase their randomness, probability, and organization? One answer is that it likely does not, as long as the structure of the substance does not change. What will happen is that the density of the solid will decrease, but can this be considered to change the structure, and therefore the organization? And with respect to the common perception that a larger entropy per unit mass is indicative of a greater randomness, a greater probability, and a lesser organization, a comparison between the entropies of L-methionine and *S. cerevisiae* in Table 1 is revealing. Can we really say that the extremely complex *S. cerevisiae* cells with an entropy of 1.304 J K^{-1} g^{-1} are less random, less probable, and more organized, than the crystal lattice of L-methionine crystals with an entropy of 1.551 J K^{-1} g^{-1}? Comparisons of this kind do not seem to make sense, at least with solids. Comparisons with liquids and gases in this respect is another matter that will not be specifically addressed here, except to suggest that what we perceive with respect to randomness, probability, and organization, may be different from a thermodynamic perspective. For example, if a constant volume of gas is heated, although the pressure will increase the mean free path of the molecules will not, and we can then say with good reason that the 'organization' of the gas molecules has not changed. On the other hand, the mean probability of a single gas molecule occupying a point location over a given interval of time will have increased, due to the increase in kinetic energy. But does not the simple concept of the absorption of heat cover all situations, without the necessity of considering whether something is more random, more probable, or more organized, not only with respect to the existence of a substance at a given temperature, but also with respect to reactions or processes that are carried out at constant temperature and pressure?

The idea that we may relate biological order and complexity to thermodynamic entropy has not gone uncriticized. For example, it was emphasized by McGlashan [26] that only with respect to statistically well-defined systems, such as small molecular weight gases, can we imagine an entropic order. Wright [27] felt that it is a 'highly contentious opinion' to connect entropy quantitatively with disorder. Landsberg [28] offered arguments which "cast doubt on existing discussions on entropy of living things." Landsberg was also of the opinion that what we consider to be biological order is not entropy [29]. Lwoff [30] was emphatic in his statement that, "It is clear, however, that this functional [biological] order cannot be measured in terms of entropy units, and is meaningless from a purely thermodynamic point of view." On the other hand, at the time such criticisms were made cellular entropy had not yet been physically measured, and they must be regarded more as intuitive comments than as statements based on experimental information.

Is there any real need for the idea of 'entropy', except with respect to the creation of a formal mathematical function? Would it not be equally correct simply to state that, for example, in order to exist at a temperature of 298.15 K one gram of L-methionine crystals just happens to have to absorb more thermal energy than one gram of dried yeast cells in order to exist at 298.15 K, and this has little or nothing to do with randomness, probability, or organization?

4.1. *On entropy-driven processes*

The idea that processes can be 'entropy-driven' has become prevalent in recent years. Two familiar examples of these are phase changes and thermally-induced, reversible protein denaturation. Whether or not these are actually entropy-driven can be considered still a matter of interpretation.

The words 'entropy-driven' convey the idea of a 'force' being exerted to accomplish something, the force being entropy. The concept of 'force' brings into consideration that of 'work'. However, work is *non-thermal energy* that is exchanged between two masses because of a force that is exerted between them[1]. Clearly, this is not what happens with entropy changes, during which it is thermal energy, not non-thermal energy, that is involved. On the other hand, heat is *thermal energy* that is exchanged between two masses because of a temperature difference between them (see Footnote 1), and this is what takes place if the environment of a closed system can be considered one of the masses. Whether the absorption or loss of heat from a system can be considered to be 'driven' is questionable, especially in phase changes which take place at a constant temperature. Another difficulty with the use of the words 'entropy-driven' is the implication that entropy as a force is energetically active, i.e. that entropy is energy. Entropy is *not* energy. The idea emphasized in this paper is that entropy is a mathematical function that has a positive value at all temperatures above 0 K. Within a closed system, changes in entropy, ΔS, can occur with signs that can be $+$, $-$, or 0, but these changes are also those of mathematical constructs having values which, per se, cannot 'drive' anything. Entropy or entropy changes cannot be measured; they can only be calculated. On the other hand, values of S or ΔS do reflect (as mathematical functions) the absorption or loss of heat, and it is only this latter which can be measured physically. It is understandable why phase changes might be considered to be 'entropy-driven.' As stated previously, an increase in entropy has come to be associated with an increase in randomness and probability, and this is certainly the case with the conversion of ice to water, or water to water vapor. There is also the prevalent idea that heat *is* entropy (which it is not), and that the only function of heat is to provide a means of transport of thermal energy across the limiting boundary of a system, after which it becomes absorbed. On the other hand, the absorption or loss of heat from a system may be one of the few, perhaps the only truly reversible process in that there is no loss of thermal energy. The conversion of water to ice can be represented by the following equation:

$$\begin{aligned}&\mathrm{H_2O(cr, 273.15\,K, 1\,bar)}\\&\quad\leftrightarrow \mathrm{H_2O(\mathit{l},\ 273.15\,K, 1\,bar)}\end{aligned} \tag{32}$$

The equation representing the change in entropy accompanying the melting of one mole of ice is

$$\begin{aligned}\Delta S &= S_{\text{water}} - S_{\text{ice}} = \frac{\Delta Q_{\text{rev}}}{T} = \frac{L_{\text{cl}}}{T}\\ &= \frac{6009.48\,\mathrm{J\,mol^{-1}}}{273.15\,\mathrm{K}} = 22.01\,\mathrm{J\,mol^{-1}\,K^{-1}}\end{aligned} \tag{33}$$

where L_{cl} represents the latent heat absorbed in the phase change from crystal to liquid water, and the other symbols have been defined previously. The change in entropy accompanying the freezing of one mole of water at this temperature would be equal but opposite in sign. The process is, therefore, completely reversible (i.e. $\Delta G = 0$) and not spontaneous if both the system and the environment are at this temperature. The only way that ice can be converted into water is for the environment to have a temperature that is >273.15 K, whereupon heat will pass from the

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[1] The author is not aware of the origin of these definitions, and they do not originate with him. They were acquired at some time during his studies over the past 40 years, and have always seemed to be intirely appropriate.

environment into the system.. The environment must have a temperature <273.15 K if ice is to be formed from water, whereupon heat will pass from the system into the environment. The question is whether the heat exchange can be considered active or passive. It is not entropy that is exchanged. Entropy is a quantity that is acquired or lost. It does not perform a function or do work. It seems completely reasonable to accept that the term 'heat of fusion' (actually, the term 'heat of liquefaction' would be better) adequately describes the thermal exchange that accompanies the process represented by Eq. (32). It is not necessary to make use of the mathematical formalism of entropy.

In the determination of Third Law entropy values, the introduction of heat into the sample chamber of a low-temperature calorimeter by means of an electrical resistance is not usually regarded as representing an introduction of entropy, nor is the rise in temperature exhibited by the sample considered to be a process that is entropy-driven. In the case of the determination of the Third Law entropy of water by this method, the water passes through a phase change from ice to water, as demonstrated by Eq. (32). Again, this particular part of the entropy determination need not be considered to be entropy-driven. What is going on here is simply that heat is being added to the system and, after the system has reached a temperature of 273.15 K, the system just happens to undergo a phase change and remains at 273.15 K until the heat of fusion has been added to the system. What is measured during this determination is the change in heat capacity, not the entropy. The entropy can be calculated at any time during this determination. One interpretation of this is certainly that the system is not entropy-driven and that the absorption of heat in these measurements can be considered passive.

Similar observations can be made with respect to the reversible denaturation of certain proteins in aqueous colloidal suspension. Here, the temperature of the colloidal suspension can be raised to the point where not only is the thermal activity of the protein increased, but, more importantly, the Brownian motion of the water molecules becomes sufficiently so high that they no longer bind to the protein with the same strength as at a lower temperature. At this point the configuration of the protein molecules becomes changed, and they may even precipitate from suspension. With some proteins this process can be reversed by lowering the temperature of the aqueous environment, whereupon the water molecules again become bound to the protein to support it in the aqueous matrix. The process of reversible protein denaturation is different from that of phase changes in that it is probably more the activity of the aqueous environment of the protein that changes as a result of heat absorption, and not that of the system (the protein), per se. But again, this can be considered simply a passive phenomenon brought about by a temperature difference.

The very brief discussion here attempts to show that phase changes and reversible protein denaturation are not the result of being entropy-driven. The two interpretations remaining are that these processes are 'heat-driven', or that they are the result of a purely passive absorption or loss of heat as the result of a temperature difference with the environment. The present author prefers the latter as being the most parsimonious interpretation[2]. When we boil water to make tea, we usually consider this process to be the result of heating the water on a stove.

4.2. *The process of microbial growth*

The process of microbial growth can be represented by a process equation, one of which is as follows [24]:

$$\begin{aligned} &\mathrm{C_6H_{12}O_6(aq)} + 0.302\,\mathrm{NH_3(aq)} + 4.050\,\mathrm{O_2(aq)} \\ &+ 0.023\,\mathrm{H_2PO_4^-(aq)} + 0.006\,\mathrm{SO_4^{2-}(aq)} \\ &+ 0.042\,\mathrm{K^+(aq)} + 0.006\,\mathrm{Mg^{2+}(aq)} \\ &+ 0.002\,\mathrm{Ca^{2+}(aq)} + 0.023\,\mathrm{OH^-(aq)} \\ &\rightarrow 4.086\,\mathrm{CO_2(aq)} + 4.975\,\mathrm{H_2O(l)} \\ &+ 1.914\,\mathrm{CH_{1.613}O_{0.557}N_{0.158}P_{0.012}S_{0.003}K_{0.022}} \\ &\mathrm{Mg_{0.003}Ca_{0.001}(biomass)} \qquad (34) \end{aligned}$$

Unlike the processes discussed in Section 4.1, the process of microbial growth *does* take place at a constant temperature. In order to proceed from the initial state to the final state, it is not required that the temperature of the environment be different from that of the system. In the final state the temperature of the environment is still that of the system. Such systems

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[2] *Essentia non sunt multiplicanda praeter necessitatem.* (Essentials should not be multiplied except of necessity), attributed to William of Ockham. (b.12 ??–d.c. 1349).

are truly spontaneous, and result in the conversion of non-thermal chemical free energy into heat. This quantity of generated heat can be called exergonic thermal energy (ΔG_{th}) because of its origin in non-thermal free energy (ΔG) and is always negative for a spontaneous process. In the opinion of this author, it is the chemical or physical events causing the change in free energy that actually drive the process of microbial growth, the most important of these being the transfer of electrons from a less probable condition in the initial state to a more probable condition in the final state, as a result of oxidation–reduction reactions. The equivalent quantity of heat becomes lost from the system during a transient rise in the temperature of the system above that of the environment, which falls back to that of the environment in the final state. The other quantity of thermal energy that is also exchanged with the environment is the entropic thermal energy, ΔQ, which is the change in the total Q of the system as it passes from its initial to its final state. However, this quantity can have a sign of $+$, $-$, or 0 in a closed system at constant T and p. This being so, it seems unlikely that entropy has anything to do with 'driving' the system. Rather, it is more parsimonious to consider that entropy changes are purely passive, at least in spontaneous systems such as those involving microbial growth. They are the result of the chemical or physical changes that have brought about the change in free energy. The sum of the exergonic thermal energy and the entropic thermal energy is equal to the enthalpic thermal energy, i.e. for standard conditions $\Delta H^0 = \Delta G^0{}_{\mathrm{th}} + \Delta Q^0$. It should be emphasized that in making this statement thermal energy is taken to be a form of kinetic energy that is synonymous with heat (i.e. the absorption of thermal energy can raise the thermodynamic temperature of a given mass). Exergonic, enthalpic, and entropic thermal energy are all quantities of heat, and the designations 'exergonic'. 'enthalpic', and 'entropic' thermal energy simply refer to the source of the heat.

5. Conclusions

Entropy is a mathematical function which, when multiplied by the temperature at which it is defined, gives the quantity of entropic thermal energy that must be absorbed for a given mass to exist at a given temperature above absolute zero. At the standard temperature, this quantity can be represented by Q^0 and is the amount of entropic thermal energy that must be absorbed by a given mass in order for it to exist at 298.15 K It is equivalent to T^0S^0. $\Delta Q^0$is the quantity of entropic thermal energy that becomes exchanged between a closed system and the environment at 298.15 K, as the system passes from an initial to a final state. It is equivalent to $T^0\Delta S^0$, and can have a sign of $+$, $-$, or 0. The advantage of this kind of consideration is not that it represents a new definition, but that it calls attention to the fact that, in order for a mass to exist at any temperature, it must absorb thermal energy. For the chemical systems being considered here, the distinction is made between exergonic, entropic and enthalpic thermal energy. This latter can be represented by the equation $\Delta H^0 = \Delta G^0{}_{\mathrm{th}} + \Delta Q^0$ (see also Ref. [24]). Viewed in this light, it is hard to believe that the absorption or loss of entropic thermal energy is anything other than a purely passive phenomenon, and that the driving force behind a spontaneous reaction or process is not the entropy change, but the chemical and physical events that cause the change in free energy. The absorption of thermal energy is basic to all our considerations of entropy, but may not necessarily contribute to a greater randomness, a greater probability, or a lesser organization, depending on how we as observers conceive these terms to mean.

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