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Review

On the inequality of Q° and $T^{\circ}S^{\circ}$ with respect to solid state organic substances of biological importance

Edwin H. Battley*, Jonathan R. Stone[1]

Department of Ecology and Evolution, State University of New York at Stony Brook, Stony Brook, NY 11794-5245, USA

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Abstract

The conventional method of determining the quantity of thermal energy that must be absorbed by a substance for it to exist at the standard temperature, T° (=298.15 K), is to multiply the standard entropy, S° of that substance, by T°. The standard entropy is determined by calculating the area under a curve comprising incremental C_p values plotted against ln T, where the lower limit is $T\approx10$ K and the upper limit of $T=T^{\circ}$. Extrapolation of the curve to 0 K usually is achieved using the Debye T^3 equation. The total quantity of heat, Q°, that must be introduced into a sample in a low temperature calorimeter to raise it from 0 K to T° can be determined by calculating the area under a curve comprising the same incremental C_p values plotted against T. Conventionally, $T^{\circ}S^{\circ}=Q^{\circ}$. However, in this paper it is demonstrated that for solid state organic substances $T^{\circ}S^{\circ}\approx2Q^{\circ}$.

Keywords: Entropy; Enthalpy; Free energy; Absorbed heat; Third law

1. Introduction

In a recent paper on entropy and absorbed thermal energy in biomass [1], it was suggested that Q°, representing the quantity of thermal energy absorbed by a given mass in order for it to exist at the standard temperature, T° (=298.15 K) could be substituted for the quantity $T^{\circ}S^{\circ}$ relative to the same mass. It was further suggested that ΔQ° represents the change in the quantity of absorbed thermal energy required to maintain the temperature of a system at 298.15 K as it passes from an initial to a final state. This could be substituted for $T^{\circ}\Delta S^{\circ}$ relative to the same system, so that the Gibbs free energy equation could be modified into the form:

$$\Delta G^{\circ} = \Delta H^{\circ} - \Delta Q^{\circ} \qquad (1)$$

from

$$\Delta G^{\circ} = \Delta H^{\circ} - T^{\circ}\,\Delta S^{\circ} \qquad (2)$$

No proposal was made that Q° represents a new quantity. Conventionally, the quantities involved in Eqs. (1) and (2) are the same (i.e. $Q^{\circ}=T^{\circ}S^{\circ}$). The rationale for proposing the suggestions was to acknowledge explicitly the fact that, for a given mass to exist at any temperature, it must have absorbed thermal energy. The suggestions also removed from Eq. (2) the symbol for entropy, together with the accompanying ideas of randomness, probability, and information that have become associated with it. There is justification for such ideas, as the entire field of statistical mechanics has been based on

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* Corresponding author. Fax: +1-631-632-7626.
E-mail address: battley@life.bio.sunysb.edu (E.H. Battley)

[1] Present address: Department of Animal Ecology, Evolutionary Biology Center, Uppsala University, Norbyvägen 18D, S-752 36 Uppsala, Sweden.

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thermodynamic probabilities (especially theory concerning gases). Nevertheless, most published entropy values are derived from Third Law measurements, because of the impracticality of using statistical mechanical methods.

Consequently, entropy determinations are reduced to measuring heat capacities between 0 and 298.15 K and integrating these using the equation:

$$S = \int_{T=0}^{T} \frac{C_p \, dT}{T} \tag{3}$$

For solid substances, integrating C_p as a function of ln T between the limits of ln 1 and ln 298.15 yields a value for the standard entropy, S^o.

All the quantities in Eqs. (1) and (2) have the dimensions J mol^{-1} or J g^{-1} and represent energy per unit mass of substance reacted. It is evident from Eq. (3) that entropy differs from energy. Classically, entropy is a mathematical function having no physical reality characteristic of material bodies; it cannot be measured directly and must be calculated numerically [1]. The T in Eq. (3) represents an interval, so that S is a thermodynamic quantity related to heat capacity averaged over a temperature range. If S is multiplied by T, then the product becomes a quantity of thermal energy. Conventionally, T^oS^o is considered to be the quantity of absorbed thermal energy required for a substance to exist at 298.15 K and to be identical with Q^o.

However, there remains the question as to whether, in fact, Q *is* equivalent to TS. It is the purpose of this paper to investigate this issue.

2. Methods

The justification for equating Q^o with T^oS^o is apparent on consideration of any small organic molecule, one example of which would be glucose, α-D-$C_6H_{12}O_6$(cr). For this substance, $\Delta_f G^o = -910.56$ kJ mol^{-1}, $\Delta_f H^o = -1274.45$ kJ mol^{-1}, and $S^o = 212.13$ J K^{-1} mol^{-1} [2]. Another form of Eq. (2) is

$$\Delta_f G^o = \Delta_f H^o - T^o \Delta_f S^o \tag{4}$$

from which, using the preceding values,

$$T^o \Delta_f S^o = \Delta_f H^o - \Delta_f G^o = -1274.45 + 910.56 = -363.89 \tag{5}$$

and

$$\Delta_f S^o = -\frac{363.89}{298.15} = -1220.49 \tag{6}$$

$\Delta_f S^o$ is related to S^o through the equation

$$\Delta_f S^o = S^o - \sum S^o_{\text{atoms}} \tag{7}$$

where $\sum S^o_{\text{atoms}}$ represents the sum of the standard entropies of the atoms comprising a substance multiplied by their respective coefficients in that substance. Thus, for glucose,

$$\begin{aligned} S^o &= \Delta_f S^o + \sum S^o_{\text{atoms}} \ \ (\text{all at } T^o = 298.15\,\text{K}) \\ &= -1220.49 + 5.74n\text{C} + 65.34n\text{H} + 102.57n\text{O} \\ &= -1220.49 + (5.74 \times 6) + (65.34 \times 12) \\ &\quad + (102.57 \times 6) = -1220.49 + 34.44 + 784.08 \\ &\quad + 615.42 = 213.45\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1} \end{aligned} \tag{8}$$

where the constant 5.74 is the standard entropy of solid graphite, and the constants 65.34 and 102.57 are one-half the standard entropies of H_2(g) and O_2(g), respectively [3].[2] This value closely approximates that of 212.13 J K^{-1} mol^{-1} found in the literature [2].

In practice, $\Delta_f G^o$ values are obtained using Eq. (4), $\Delta_f H^o$ values are calculated from measured heats of combustion in the conventional manner, and $\Delta_f S^o$ values are calculated using Eq. (7) and Third Law heat capacity measurements using Eq. (3). The term T^oS^o can be used to calculate the quantity $T^o\Delta S^o$ in Eq. (2) directly, without using the values for ΔG^o and ΔH^o. For example, the oxidation of glucose can be represented by the following equation:

$$C_6H_{12}O_6(\text{cr}) + 6O_2(\text{g}) \rightarrow 6CO_2(\text{g}) + 6H_2O(\text{l}) \tag{9}$$

for which

$$\begin{aligned} T^o \Delta S^o &= \sum T^o S^o_{\text{prod}} - \sum T^o S^o_{\text{react}} \\ &= T^o \left(\sum S^o_{\text{prod}} - \sum S^o_{\text{react}} \right) \end{aligned} \tag{10}$$

where ‘prod’ and ‘react’ represent the products and

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[2] This is a compilation of selected values taken from D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schuum, S.M. Bailey, I. Halow, K.L. Churney, R.L. Nuttall, National Bureau of Standards Notes 270–273, 270–274, 270–275, 270–276, 270–277, and 270–278, Superintendent of Documents, U.S. Government Printing Office, Washington, DC, 20402.

Table 1
Thermodynamic data relative to the oxidation of glucose

Substance	Formula	M.W. (D)	$\Delta_f G^o$ (kJ mol^{-1})	$\Delta_f H^o$ (kJ mol^{-1})	$\Delta_f S^o$ (J K^{-1} mol^{-1})	S^o (J K^{-1} mol^{-1})	T^oS^o (kJ^{-1} mol^{-1})
Carbon dioxide[b]	CO_2(g)	44.01	−394.37	−393.51	2.85	213.63	63.694
α-D-Glucose[a]	$C_6H_{12}O_6$(cr)	180.16	−910.56	−1274.45	−1220.48	212.13	63.253
Oxygen[b]	O_2(g)	32.00	0	0	0	205.00	61.120
Water[b]	H_2O(l)	18.01	−237.18	−285.83	−163.17	69.91	20.843

[a] These data were taken from Ref. [2].
[b] These data were taken from Ref. [3].

reactants, respectively, of a reaction or process. Appropriate T^oS^o values can be calculated from data in Table 1, where S_1^o, S_3^o, and S_4^o represent the standard entropies of $C_6H_{12}O_6$(cr), CO_2(g), and H_2O(l), respectively, and S_2^o represents one-half the standard entropy of O_2(g), in Eq. (9). Thus,

$$\begin{aligned} T^o\,\Delta S^o &= T^oS_3^o + T^oS_4^o - T^oS_1^o - T^oS_2^o \\ &= T^o(S_3^o + S_4^o - S_1^o - S_2^o) \\ &= 298.15[6(213.63) + 6(69.91) \\ &\quad - (209.2) - 6(204.99)) \\ &= 298.15\,(1281.78 + 419.46 - 209.2 \\ &\quad - 1229.94) \\ &= 298.15(262.1) \\ &= 78.15\,\text{kJ mol}^{-1}\ \text{of glucose oxidized} \end{aligned} \tag{11}$$

For the reaction represented by Eq. (9),

$$\Delta G^o = \sum \Delta_f G^o_{\text{prod}} - \sum \Delta_f G^o_{\text{react}} \tag{12}$$

and

$$\Delta H^o = \sum \Delta_f H^o_{\text{prod}} - \sum \Delta_f H^o_{\text{react}} \tag{13}$$

Using Eqs. (12) and (13) and the appropriate data from Table 1, ΔG^o and ΔH^o values for the reaction represented by Eq. (9) are calculated to be −2878.68 and −2801.59 kJ mol^{-1}, respectively. Using Eq. (2), the value for $T\Delta S^o$ then is 77.09 kJ mol^{-1}. This value closely approximates 78.15 kJ mol^{-1}, obtained using Eq. (11).

From the two preceding examples, it is apparent that, when making calculations involving S^o, the usual convention is to multiply S^o by T^o to determine the quantity of thermal energy required for a given mass to exist at T^o, and that $T^o\Delta S^o$ represents the quantity of *absorbed* thermal energy that is exchanged with the environment during the passage from an initial to a final state, as represented by Eq. (2). So, the justification in equating Q^o with $T^o\Delta S^o$, or ΔQ^o with $T^o\Delta S^o$, as previously proposed [1], is merely that it is conventional to do so. The advantage of using Q is that it represents only a quantity of thermal energy and eliminates the uncertainties associated with S concerning probability, randomness, and information.

3. Results

In the calculation of a value for the entropy of a given substance, C_p is measured as a function of T in a low-temperature calorimeter from ≈10 K as the lower limit, to 298.15 K, as the upper limit (the conventional standard temperature T^o). C_p values at <10 K are inferred conventionally using the Debye T^3 equation. This process can be modeled, the simplest model being one in which C_p varies proportionately with T. In this case use of the Debye equation is unnecessary, as the line intersects the origin.

Two graphs are shown in Fig. 1, Fig. 1A depicting C_p plotted against T and Fig. 1B depicting C_p plotted against ln T. The dimensions of C_p are J K^{-1} g^{-1}. The lower limit of T in Fig. 1A is 0 K and in Fig. 1B it is 1.00 K (ln (1.00)=0); the upper limit in both graphs is 298.15 K (=T^o). Both figures depict similar data; however, the areas under the curves represent different quantities. The area under Fig. 1A represents Q^o, having the dimensions J g^{-1}, which is the quantity of thermal energy required for 1 g of substance to exist at T^o=298.15 K. The area under Fig. 1B represents S^o, having the dimensions J K^{-1} g^{-1}. Both figures apply to a hypothetical substance in which

$$C_p = 0.10T \tag{14}$$

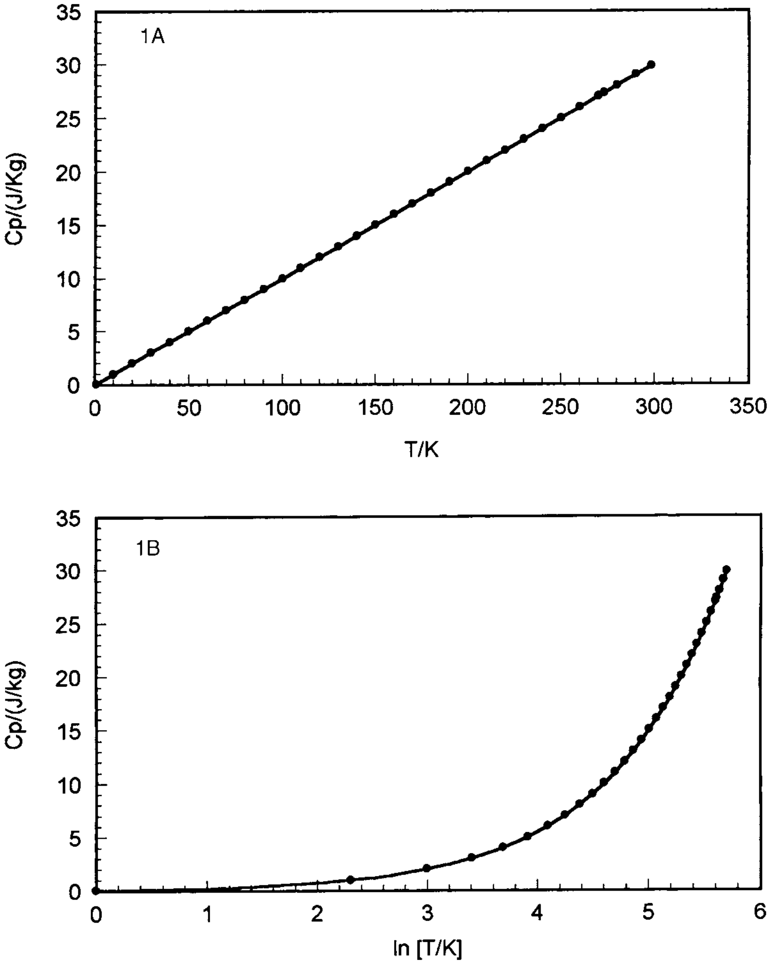

Fig. 1. Model graphs illustrating the calculation of Q^o and T^oS^o for the relationship C_p=0.10T. In Fig. 1A, the area under the curve is Q^o=4442.92 J g^{-1} (average from Section 3.1). In Fig. 1B, the area under the curve is S^o=29.53 J K^{-1} g^{-1} (average from Section 3.2). The value for T^oS^o is then 8804.37 J g^{-1}, which is effectively twice that of Q^o.

3.1. Calculating the area under the curve in Fig. 1A to determine Q^o

The area under the line in Fig. 1A can be calculated using three methods.

3.1.1. Method 1, geometrical calculation

The most direct method of calculating the area under the line in Fig. 1A is to recognize it as a right-angled triangle.

$$Q^o = \frac{[(C_p \text{ at } T^o) \times T^o]}{2} = \frac{(29.81 \times 298.15)}{2} = 4443.93 \text{ J g}^{-1} \qquad (15)$$

3.1.2. Method 2, numerical integration

In this method, the area under the curve in Fig. 1A is integrated numerically, as shown in Table 2. This gives the area as $\Sigma\overline{C}_p\Delta T^o$=$Q^o$=4440.17 J g^{-1}, which closely approximates 4443.93 J g^{-1}, the value obtained with the method described in Section 3.1.1.

3.1.3. Method 3, algebraic integration

For the general equation Y=aX, the indefinite integral is (aX)=(aX^2/2)+c, where a and c are constants. For the equation C_p=0.10T, the solution of the indefinite integral becomes $aT^2/2$ where

Table 2
Numerical integration of C_p against T for the relationship C_p=0.10T with 0 K as the lower bound and 298.15 K as the upper bound

T (K)	C_p (J K^{-1}g^{-1})	ΔT (K)	$\overline{C}_p$ (J K^{-1} g^{-1})[a]	$\overline{C}_p\Delta T$ (J g^{-1})	$\Sigma\overline{C}_p\Delta T$ (J g^{-1})
0	0.0000				0.0000
		10.0000	0.5000	5.0000	
10	1.0000				5.0000
		10.0000	1.5000	15.0000	
20	2.0000				15.5000
		10.0000	2.5000	25.0000	
30	3.0000				40.5000
		10.0000	3.5000	35.0000	
40	4.0000				75.5000
		10.0000	4.5000	45.0000	
ad continuum					
260	26.0000				3375.5000
		10.0000	26.5000	265.0000	
270	27.0000				3640.5000
		3.1500	27.1575	85.5461	
273.15	27.3150				3726.0461
		6.8500	27.6575	189.4539	
280	28.0000				3915.5000
		10.0000	28.5000	285.0000	
290	29.0000				4200.5000
		8.1500	29.4075	239.6711	
298.15	29.8150				4440.1711[b]

[a] By $\overline{C}_p$ is meant the average of the two C_p values in the 2nd column on the lines above and below each average.
[b] Q^o=4440.17 J g^{-1}.

a=0.10 J K^{-2} g^{-1}. The constant c accounts for particular conditions (so-called boundary conditions, usually initial conditions). The c denotes that the solution of the indefinite integral is one member of a family of parabolas $aT^2/2+c$. In this case the parabola intersects the origin, so c=0. If there are limits to the integration (i.e. between temperatures T_1 and T_2) then the indefinite integral becomes a definite integral with the solution $a(T_2^2 - T_1^2)/2$, and the constant c cancels out because it is subtracted from itself. In Fig. 1A the limits are between 0 K (T_1) and 298.15 K (T_2), so

$$Q^o = 0.10\,\frac{[(298.15)^2 - (0)^2]}{2} = \frac{0.10 \times 88893.42}{2} = 4444.67 \text{ J g}^{-1} \tag{16}$$

This area closely approximates those obtained in Sections 3.1.1 and 3.1.2. The average value of the three areas is 4442.92 J g^{-1}.

3.2. Calculating the area under the curve in Fig. 1B to determine S^o

The area under the curve in Fig. 1B can be calculated using two methods.

3.2.1. Method 1, numerical integration

In this method the area under the curve in Fig. 1B is integrated numerically, as shown in Table 3. This area is S^o=30.16 J K^{-1} g^{-1}.

3.2.2. Method 2, algebraic integration

Fig. 1B is derived from the data comprising Fig. 1A but with the abscissa values transformed logarithmically. The result is that the curve in Fig. 1B is described by the equation Y=ae^Z, where Z=ln (X). For the general equation Y=ae^Z, the indefinite integral (ae^Z)=ae^Z+c. The corresponding definite integral between temperatures T_1 and T_2 is $a(\mathrm{e}^{\ln T_2} - \mathrm{e}^{\ln T_1}) = a(T_2 - T_1)$. In Fig. 1B, the limits

Table 3
Numerical integration of C_p against ln T for the relationship C_p=0.10 ln T, with 1.00 K as the lower bound and 298.15 K as the upper bound

T (K)	ln T	C_p ($\mathrm{J\,K^{-1}\,g^{-1}}$)	Δ ln T	$\overline{C}_p$ ($\mathrm{J\,K^{-1}\,g^{-1}}$)[a]	$\overline{C}_p\Delta$ ln T ($\mathrm{J\,K^{-1}\,g^{-1}}$)	$\Sigma\overline{C}_p\Delta$ ln T ($\mathrm{J\,K^{-1}\,g^{-1}}$)
1	0.0000	0.1000				0.0000
			2.3026	0.5500	1.2664	
10	2.3026	1.0000				1.2664
			0.6931	1.5000	1.0396	
20	2.9957	2.0000				2.3060
			0.4055	2.5000	1.0137	
30	3.4012	3.0000				3.3197
			0.2877	3.5000	1.0069	
40	3.6889	4.0000				4.3266
			0.2231	4.5000	1.0039	
ad continuum						
260	5.5607	26.0000				26.3434
			0.0377	26.5000	0.9991	
270	5.5984	27.0000				27.3425
			0.0116	27.1755	0.3152	
273.15	5.6100	27.3150				27.6550
			0.0248	27.6575	0.6859	
280	5.6348	28.0000				28.3409
			0.0351	28.5000	1.0003	
290	5.6699	29.0000				29.3412
			0.0277	0.4075	0.8146	
298.15	5.6976	29.8150				30.1558[b]

[a] By $\overline{C}_p$ is meant the average of the two C_p values in the 3rd column on the lines above and below each average.
[b] S^o=30.16 $\mathrm{J\,K^{-1}\,g^{-1}}$.

are 0 and 298.15 K and a=0.10 $\mathrm{J\,K^{-2}\,g^{-1}}$, so

$$S^o = 0.10\,(298.15 - 1.00) = 29.71\,\mathrm{J\,K\,g^{-1}} \tag{17}$$

This value closely approximates 30.16 $\mathrm{J\,K^{-1}\,g^{-1}}$ obtained with the method described in Section 3.2.1. The average of the two being 29.93 $\mathrm{J\,K^{-1}\,g^{-1}}$.

3.3. Converting S^o into energy

The quantity S^o has the dimensions $\mathrm{J\,K^{-1}\,g^{-1}}$, which differ from but are related to those of energy. If the average S^o value obtained with the methods described in Sections 3.2.1 and 3.2.2 is multiplied by 298.15 K (the upper limit of the temperatures for which the heat capacities have been determined), the result is

$$29.93 \times 298.15 = 8923.63\,\mathrm{J\,g^{-1}} \tag{18}$$

Supposedly, this is the quantity of thermal energy, Q^o that is required to raise the temperature of 1 g of the hypothetical substance from 0 to 298.15 K, calculated on the basis of integration in Section 3.1. However, it is apparent that the mean value for T^oS^o of 8923.63 $\mathrm{J\,g^{-1}}$ obtained in Section 3.3 is almost exactly twice 4442.93 $\mathrm{J\,g^{-1}}$, the mean of the values obtained in Section 3.1.

3.4. The mathematical relationship between Q and S

Given a linear relation between C_p and T, as represented by the equation C_p=0.10T

$$Q = \frac{a(T_2^2 - T_1^2)}{2} = \frac{a(T_2 - T_1)(T_2 + T_1)}{2} \tag{19}$$

where Q is the area under the line in Fig. 1A. But, $a(T_2-T_1)=S$ is the area under the curve in Fig. 1B. Therefore,

$$Q = \frac{S(T_2 + T_1)}{2} = S(T_{\mathrm{avg}}) \tag{20}$$

It should be emphasized that Eq. (20) applies if there is a linear relationship between C_p and T. Although most graphs of C_p plotted against T are nonlinear, those for some organic substances are approximately linear. Consequently, in Section 3.5 numerical integration is used to demonstrate that, in fact, for some solid state organic substances of biological importance, Q^o and T^oS^o values are different and to corroborate the mathematical relation between them derived in this subsection.

3.5. Q^o and S^o values for some substances of biological importance

The number of solid state organic substances of biological importance for which the heat capacity has been measured from 7–10 to 298.15 K is limited. Q^o and S^o values are determined most easily by numerical integration using a computer, the software used here being MATHEMATICA (v.2.2, Wolfram Research. Inc., Champaign, IL). In the integration calculations, 0 K was taken as a data point, and no effort was made to use the Debye T^3 equation to establish Q^o and S^o values below 10 K. This was because for sucrose [15] Q^o and S^o values calculated using experimental data with T as low as 5 K were 63 937 J mol^{-1} and 420.77 J K^{-1} mol^{-1}, respectively, whereas those calculated down to 10 K were 62 920 J mol^{-1} and 420.65 J K^{-1} mol^{-1}, respectively. These differences are considered to be insignificant, as were those that would apply additionally were data to be calculated below 5 K using the Debye T^3 equation.

Q^o and S^o values and related quantities for several solid state organic substances of biological importance are presented in Table 4. The entropies of the substances listed were given an 'A' rating in Ref. [4],

Table 4
A comparison of values for T^oS^o and Q^o values

Substance+Ref.	S^o_{rep} (J K^{-1} mol^{-1})	$T^oS^o_{rep}$ (J mol^{-1})	S^o_{calc} (J K^{-1} mol^{-1})	$T^oS^o_{calc}$ (J mol^{-1})	Q^o_{calc} (J mol^{-1})	$(S^o_{calc}/S^o_{rep})\times 100$	$T^oS^o_{rep}/Q^o_{calc}$	$T^oS^o_{calc}/Q^o_{calc}$
L-Alanine [5]	129.21	39521	130.17	38810	19470	100.75	2.029	1.993
L-Asparagine monohydrate [6]	209.62	62498	217.31	64791	32504	103.70	1.923	1.993
L-Arginine HCl [7]	286.31	85363	278.42	83011	41645	97.24	2.049	1.993
L-Aspartic acid [6]	170.12	50721	166.25	49567	24868	97.73	2.040	1.993
L-Cystine [8]	280.58	83654	278.82	83130	41704	99.37	2.006	1.993
α-D-Glucose [9]	209.2	62373	220.60	65772	32996	105.40	1.890	1.993
Glycine [5]	103.51	30861	105.15	31350	15728	101.56	1.962	1.993
Glycyl glycine [10]	180.29	53753	176.36	52581	26380	97.82	2.038	1.993
L-Glutamic acid [6]	188.20	56111	186.13	55495	27840	98.90	2.015	1.993
L-Glutamine [6]	195.06	58157	195.15	58184	29189	100.00	1.992	1.993
Histidine HCl [7]	276.10	82319	264.99	79006	39636	95.98	2.076	1.993
L-Isoleucine [11]	207.99	62012	200.41	59752	29977	96.35	2.068	1.993
L-Leucine [11]	211.79	63145	205.48	61264	30735	97.02	2.054	1.993
Lysine HCl [7]	264.47	78852	254.62	75915	38085	96.27	1.038	1.993
L-Methionine [8]	231.46	69009	235.95	70348	35292	101.90	1.955	1.993
L-Phenylalanine [12]	213.63	63694	208.54	62176	31193	97.62	2.041	1.993
L-Proline [12]	164.05	48912	158.19	47164	23662	96.43	2.067	1.993
L-Serine [13]	149.16	44472	145.06	43250	21818	97.25	2.038	1.982
Succinic acid [14]	167.32	49886	162.30	48390	24277	97.00	2.055	1.993
Sucrose [15]	392.4	116994	420.65	125416	62920	107.20	1.859	1.993
L-Tryptophan [12]	251.04	75742	243.59	72626	36435	97.03	2.079	1.993
L-Tyrosine [12]	214.01	63807	220.62	65777	32999	103.08	1.933	1.993
L-Valine [11]	178.87	53330	179.67	53569	26874	100.44	1.984	1.993
Anhyd. Bovine zinc insulin [16]	131.55	39221	129.27	38542	19336	98.27	2.028	1.993
Hyd. Bovine zinc insulin [16]	132.00	39356	134.97	40241	20188	102.30	1.949	1.993
Anhyd. Chymotrypsinogen A [16]	135.02	40256	133.15	39698	19915	98.60	2.021	1.993
Hyd. Chymotrypsinogen A [16]	152.09	45345	157.57	46979	23569	103.60	1.924	1.993
Dried *S. cerevisiae* cells [17]	130.4	38879	132.7	39564	19855	101.80	1.958	1.993
Average						99.66±3.04	1.965±0.19	1.993

indicating that they were obtained within temperature ranges of 7–15 to 298.15 K or higher. In Table 4, the symbol $S^{\mathrm{o}}_{\mathrm{rep}}$ represents entropy values reported in the literature. The method of integration by which these data were obtained usually is unspecified. The symbols $S^{\mathrm{o}}_{\mathrm{calc}}$ and $Q^{\mathrm{o}}_{\mathrm{calc}}$ represent entropy and absorbed heat values, respectively, that were obtained by numerical integration of the original data used to obtain the $S^{\mathrm{o}}_{\mathrm{rep}}$ values. The accuracy of $S^{\mathrm{o}}_{\mathrm{calc}}$ values with respect to $S^{\mathrm{o}}_{\mathrm{rep}}$ values is 99.66 ± 3.04 ($n=28$), although the deviation with respect to an individual pair is as much as 7%. This indicates that computer determined values are consistent with those obtained by other methods. No such comparisons can be made for $Q^{\mathrm{o}}_{\mathrm{calc}}$ values because these are not reported in the literature. The computer determined integrations of curves of C_{p} plotted against T and C_{p} plotted against $\ln T$ yield $T^{\mathrm{o}}S^{\mathrm{o}}_{\mathrm{calc}}/Q^{\mathrm{o}}_{\mathrm{calc}}=1.993$ (except for serine), indicating that this ratio is ≈ 2.000. More accurately, the average ratio $T^{\mathrm{o}}S^{\mathrm{o}}_{\mathrm{rep}}/Q^{\mathrm{o}}_{\mathrm{calc}}=1.967\pm0.191$ ($n=28$). The average might more closely approximate 2.000, but experimentally determined Q^{o} values are unavailable for comparison. Nevertheless, the data in Table 4 indicate clearly that $T^{\mathrm{o}}S^{\mathrm{o}}$ values calculated from experimental C_{p} data are twice the Q^{o} values calculated according to the mathematical analyses described in Section 3.

4. Discussion

Obviously, there cannot be two different quantities of heat required to raise a given mass of a solid state organic substance from 0 to 298.15 K. The dilemma, then, is which quantity is it: Q^{o} or $T^{\mathrm{o}}S^{\mathrm{o}}$? We propose that the answer is Q^{o}! Entropy, having the dimension of thermal energy/temperature/unit mass, must be multiplied by a temperature to yield a quantity of thermal energy/unit mass (ostensibly the quantity that is required to raise the temperature of a substance by a given number of degrees on the Kelvin scale). The standard entropy, S^{o}, is determined using Eq. (3), by integrating C_{p} plotted against $\ln T$ from 1 to $\ln 298.15$ K. In the calculation of TS^{o}, the value for T is T^{o}, as, conventionally, this is the upper bound in the integration of the C_{p} data. However, as shown by Eq. (20), $Q^{\mathrm{o}}=S^{\mathrm{o}}\,(T_2+T_1)/2$, and if $T_1=0$ K, then $T_2/2=298.15\text{ K}/2=149.07$ K. Thus, the appropriate quantity of heat required for a given mass to exist at 298.15 K is $S^{\mathrm{o}}(T^{\mathrm{o}}/2)$, which is equal to Q^{o}.

It has been pointed out previously by Klotz [18] (and undoubtedly others) that "Ultimately one must realize that entropy is essentially a *mathematical function*." (the italicization has been done by the present authors.) It was emphasized in Ref. [1] that, classically, entropy has no physical reality, cannot be measured, and can only be calculated. Thus, it cannot be transported, 'produced' or 'consumed'. This does not mean that increases or decreases in the numerical value of entropy as a mathematical function cannot be calculated, if there is some reason for doing this.

In contrast, thermal energy (heat) does have a physical reality and can be measured directly, as is done during heat capacity measurements in Third Law entropy determinations. However, these heat capacities are measured as the result of heat added to a sample electrically by means of a resistance wire over a large number of small incremental temperature rises, to ensure 'reversibility'. Of the two methods of calculation demonstrated in Fig. 1, that involving Q^{o} indicates the quantity of heat required to raise the temperature of a given mass of substance from 0 to 298.15 K more accurately than does that involving $T^{\mathrm{o}}S^{\mathrm{o}}$. This is amenable to experimental verification. The total quantity of electricity used to elevate the temperature of the sample from 0 interval during which current passes through the resistance wire may be converted into the total quantity of heat required to raise the temperature of the sample over this temperature range. It is important to know whether Q^{o} or $T^{\mathrm{o}}S^{\mathrm{o}}$ is the appropriate value. If it is Q^{o}, then Eq. (7) will become

$$\Delta_{\mathrm{f}}Q^{\mathrm{o}} = Q^{\mathrm{o}} - \sum Q^{\mathrm{o}}_{\mathrm{atoms}} \tag{21}$$

and Eq. (4) will become

$$\Delta_{\mathrm{f}}G^{\mathrm{o}} = \Delta_{\mathrm{f}}H^{\mathrm{o}} - \Delta_{\mathrm{f}}Q^{\mathrm{o}} \tag{22}$$

If Eq. (22) is considered with respect to Eq. (21), $\Delta_{\mathrm{f}}G^{\mathrm{o}}$ as a thermodynamic property will have a different value than it does in Eq. (4) and the quantity $(\Delta_{\mathrm{f}}H^{\mathrm{o}}-\Delta_{\mathrm{f}}Q^{\mathrm{o}})$ cannot represent the true Gibbs free energy of formation. Perhaps a different symbol should be used. The values represented by the symbols in Eq. (22) can be used in Eq. (1) to calculate the energy changes accompanying a reaction of process.

Classically, for a given mass S^o and Q^o values are both associated with the absorption of heat and have nothing to do with probability, information, and organization. It cannot be said, for example, that α-D-glucose, *by itself,* having a standard entropy of $1.161\ \mathrm{J\ K^{-1}\ g^{-1}}$ [9] is more probable, contains more information, or is more organized than is bovine serum albumin, *by itself*, having a standard entropy of $1.315\ \mathrm{J\ K^{-1}\ g^{-1}}$ [16]. What can be stated with certainty is that per unit mass, glucose has to absorb less heat to exist at T^o than does bovine serum albumin, and this is what is reflected in their S^o and Q^o values. Every organic solid, *by itself*, at any T, has a probability of 1 in the sense that its state or condition could not be other than it is at that temperature and pressure. It contains no information and possesses no organization in the sense that, were its structure unknown, its S^o and Q^o values would still be the same.

5. Conclusion

Q^o is not equal to T^oS^o. With respect to the organic substances in the solid state that are investigated herein, $Q^o \approx S^o(T^o/2)$. This relationship would not be expected to be the same for substances in the liquid or gaseous state at T^o because of the phase changes that take place during the absorption of thermal energy required to reach this temperature. It is concluded that Q is a more accurate measure of the quantity of thermal energy that must be absorbed by a substance in the solid state for it to exist at a given T than is TS.

References

[1] E.H. Battley, Thermochim. Acta 331 (1999) 1.
[2] R.C. Wilhoit, in: H.D. Brown (Ed.), Biochemical Microcalorimetry, Appendix, Academic Press, New York, p. 305.
[3] R.C. Weast (Ed.), Handbook of Biochemistry and Biophysics, 63rd Edition, CRC Press, Boca Raton, FL, 1982, p. D-45.
[4] E.S. Domalski, W.H. Evans, E.D. Hearing, J. Phys. Chem. Ref. Data 25 (1996) 1.
[5] J.O. Hutchens, A.G. Cole, J.W. Stout, J. Am. Chem. Soc. 82 (1960) 4813.
[6] J.O. Hutchens, A.G. Cole, R.A. Robie, J.W. Stout, J. Biol. Chem. 238 (1963) 2407.
[7] A.G. Cole, J.O. Hutchens, J.W. Stout, J. Phys. Chem. 67 (1963) 2245.
[8] J.O. Hutchens, A.G. Cole, J.W. Stout, J. Biol. Chem. 239 (1964) 591.
[9] J.B. Boerio-Goates, J. Chem. Thermodyn. 23 (1991) 403.
[10] J.O. Hutchens, A.G. Cole, J.W. Stout, J. Biol. Chem. 244 (1969) 33.
[11] J.O. Hutchens, A.G. Cole, J.W. Stout, J. Phys. Chem. 67 (1963) 1128.
[12] A.G. Cole, J.O. Hutchens, J.W. Stout, J. Phys. Chem. 67 (1963) 1852.
[13] J.O. Hutchens, A.G. Cole, J.W. Stout, J. Biol. Chem. 239 (1964) 4194.
[14] C.E. Vanderzee, E.F. Westrum, J. Chem. Thermodyn. 2 (1970) 681.
[15] R.L. Putnam, J. Boerio-Goates, J. Chem. Thermodyn. 25 (1993) 607.
[16] J.O. Hutchens, A.G. Cole, J.W. Stout, J. Biol. Chem 244 (1969) 26.
[17] E.H. Battley, R.L. Putnam, J. Boerio-Goates, Thermochim. Acta 298 (1997) 37.
[18] I.M. Klotz, Chemical Thermodynamics: Basic Theory and Methods, W.A. Benjamin, New York, 1963, p. 129.