ELSEVIER

Thermochimica Acta 349 (2000) 153–161

thermochimica
acta

www.elsevier.com/locate/tca

A comparison of values for the entropy and the entropy of formation of selected organic substances of biological importance in the solid state, as determined experimentally or calculated empirically

Edwin H. Battley*, Jonathan R. Stone

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

Received 7 June 1999; received in revised form 5 November 1999; accepted 5 November 1999

Abstract

The entropy of organic substances can be determined experimentally, using low-temperature calorimetry and the Third Law, by means of the equation $S^0_{\mathrm{exp}} = \int_{T=0}^{T^0} C_p\, \mathrm{d}T/T$, where the subscript ‘exp’ indicates that the determination is experimental. The entropy of formation of such substances can be determined by means of the equation $\Delta_f S^0_{\mathrm{exp}} = S^0_{\mathrm{exp}} - \sum S^0_{\mathrm{atoms}}$, where $\sum S^0_{\mathrm{atoms}}$ represents the sum of the standard entropies of the individual atoms in a substance multiplied by their respective coefficients. However, experimental entropy determinations require very special equipment and are difficult to perform, so that at least for purposes of an initial estimate an empirical method for calculating values of entropy and entropy of formation has some advantages. Equations $S^0_{\mathrm{calc}} = 0.187 \sum S^0_{\mathrm{atoms}}$ and $\Delta_f S^0_{\mathrm{calc}} = 0.813 \sum S^0_{\mathrm{atoms}}$ can be used for this purpose, where the subscript ‘calc’ indicates that the values have been calculated empirically rather than determined experimentally. Using these latter values as the standards of comparison, it is shown that, for small molecular weight substances, the average value of S^0_{calc} is 2.03% greater than the average value of S^0_{exp}, although the range is from 28.20 to −28.88%. For the same substances, the average value of $\Delta_f S^0_{\mathrm{calc}}$ is 0.09% less than the average value of $\Delta_f S^0_{\mathrm{exp}}$, with a range of 10.30 to −5.41%. For substances weighing >300 Da, and for cells, the average value of S^0_{calc} is 0.04% less than the average value of S^0_{exp}, with a range of 2.87 to −2.64%. The average value of $\Delta_f S^0_{\mathrm{calc}}$ for these substances is 0.05% less than the average value of $\Delta_f S^0_{\mathrm{exp}}$, with a range of 0.61 to −0.63%. For substances with molecular weights <300 Da, the contributions of individual chemical groups on organic molecules can have a significant entropy effect. For substances with molecular weights greater than this, the entropy contributions of individual chemical groups on molecules appear to average out.

Keywords: Entropy; Entropy of formation; Cellular entropy; Third Law

1. Introduction

One of the problems in studying the thermodynamic changes accompanying biological phenomena is to be able to determine or calculate the thermodynamic properties of complex biological substances, such as biopolymers or cells. For example, a value for $\Delta_f G_{\mathrm{cells}}$ of 1 C-mol (the mass containing 1 g at. of carbon) of biomass cannot be determined by thermal measurements, because it is a non-thermal quantity. A value for $\Delta_f H_{\mathrm{cells}}$ for the same biomass can be obtained by

---

*Corresponding author. Fax: +1-516-632-7626.
E-mail address: battley@life.bio.sunysb.edu (E.H. Battley)

0040-6031/00/$ – see front matter
PII: S0040-6031(99)00509-2

measuring the heat of combustion of a known quantity of rigorously dried cells in a bomb calorimeter and calculating $\Delta_f H_{\text{cells}}$ using an equation representing the combustion reaction, as illustrated in Ref. [1]. For this, the empirical formula for 1 C-mol of cells must be determined, and the thermodynamic properties of all the reactants and products of the combustion other than the cells must be available. If a value for $\Delta_f S_{\text{cells}}$ can be determined, a value for $\Delta_f G_{\text{cells}}$ can be calculated using a variant of the Gibbs free-energy equation, $\Delta_f G_{\text{cells}}=\Delta_f H_{\text{cells}}-T\Delta_f S_{\text{cells}}$.

The value for $\Delta_f S_{\text{cells}}$ is related to cellular entropy (S_{cells}) as follows:

$$\Delta_f S_{\text{cells}} = S_{\text{cells}} - \sum S^0_{\text{atoms}} \tag{1}$$

where $\sum S^0_{\text{atoms}}$ represents the sum of the entropies of the atoms comprising the biomass, multiplied by their respective coefficients per C-mol. The superscript ‘0’ is not used with respect to biomass, because biomass is not a pure substance. The entropies of the atoms are well known, but that of the biomass must be determined using a low-temperature calorimeter to obtain a heat capacity curve between the limits of 0 K and T^0, from which data S^0 can be calculated.

Low-temperature calorimetry requires expensive equipment and measurements are not easy to make. In a recent publication [2], an empirical method was proposed for calculating values of S. The purpose of the present publication is to explore within what limits this method is useful and valuable.

2. Methods

Living cells are best regarded as precipitates. Most of the water associated with cells constitutes a fluid matrix that supports the cellular structure and provides for the movement of solutes within the cells by diffusion, or by convection as the result of cyclosis. In its natural state cellular biomass is hydrated, but only to a small degree. It has been shown [3] that the heat of cellular hydration for dried yeast cells is $<90\ \text{J g}^{-1}$. or ca. $2.36\ \text{kJ C-mol}^{-1}$ of cells. This is only ca. 0.46% of the heat of combustion of 1 C-mol of cells (-509.37 kJ as measured by Larsen in Ref. [1]), and well within the standard error of most cellular combustion analyses. Thus, the assumption is made that the heat of hydration can be ignored, and the heat of combustion used directly in calculations of $\Delta_f H_{\text{cells}}$. The same assumption can be applied to calculations of $\Delta_f S_{\text{cells}}$

Dry biomass can be represented by a formula in which the quantity of the constituent atoms is given relative to a single carbon atom. For example, the unit carbon formula for yeast cells can be written as [1]

$$\begin{aligned}&\mathrm{CH_{1.613}O_{0.557}N_{0.158}P_{0.012}S_{0.003}K_{0.022}Mg_{0.003}}\\ &\quad\times \mathrm{Ca_{0.001}}\ \text{(cells)}\end{aligned} \tag{2}$$

A value for $\Delta_f S_{\text{cells}}$ yeast cells as represented by Formula (2) can then be calculated using Eq. (1) as follows.

$$\begin{aligned}\Delta_f S_{\text{cells}} = {} & S_{\text{cells}} - 5.74n\mathrm{C}_{\text{cells}} - 65.34n\mathrm{H}_{\text{cells}}\\ & - 102.57n\mathrm{O}_{\text{cells}} - 95.81n\mathrm{N}_{\text{cells}}\\ & - 41.09n\mathrm{P}_{\text{cells}} - 31.80n\mathrm{S}_{\text{cells}}\\ & - 64.18n\mathrm{K}_{\text{cells}} - 32.68n\mathrm{Mg}_{\text{cells}}\\ & - 41.42n\mathrm{Ca}_{\text{cells}}\end{aligned} \tag{3}$$

where S_{cells} is the entropy of 1 C-mol of lyophilized *Saccharomyces cerevisiae* cells, and n represents the subscript for each atom in Formula (2). The constants 65.34, 102.57, and 95.81 are one-half the standard entropies of H_2(g), O_2(g), and N_2(g), respectively [4]. The other constants are the standard entropies of solid graphite, white phosphorus, rhombic sulfur, potassium, magnesium, and calcium [4]. For lyophilized *S. cerevisiae* cells, as represented in Formula (2), the calculation becomes

$$\begin{aligned}\Delta_f S_{\text{cells}} = {} & S_{\text{cells}} - 5.74(1) - 65.34(1.613)\\ & - 102.57(0.557) - 95.81(0.158)\\ & - 41.09(0.012) - 31.80(0.003)\\ & - 64.18(0.022) - 32.68(0.003)\\ & - 41.42(0.001)\\ = {} & S_{\text{cells}} - 5.74 - 105.39 - 57.13 - 15.14\\ & - 0.49 - 0.09 - 1.41 - 0.10 - 0.04 \equiv S_{\text{cells}}\\ & - 185.53\ \text{J K}^{-1}\ \text{C-mol}^{-1}\end{aligned} \tag{4}$$

It is, however, necessary to obtain a value for either $\Delta_f S_{\text{cells}}$or S_{cells}. Conventionally, a value for $\Delta_f S_{\text{cells}}$ can be calculated only by using Eq. (1). The remaining thermodynamic quantity to be determined then becomes S_{cells}.

The standard entropy of organic substances can be determined experimentally, using low-temperature calorimetry and the Third Law convention, by means of the equation

$$S^0_{\mathrm{exp}} = \int_{T=0}^{T^0} \frac{C_\mathrm{p}}{T}\,\mathrm{d}T \qquad (5)$$

where the superscript '0' represents standard conditions and the subscript 'exp' indicates that the determination has been carried out experimentally. The entropy of formation of such substances can be calculated using Eq. (1). However, experimental entropy determinations require very special equipment and have been made only once for cellular substance [5].

Historically, entropy calculations (as opposed to Third Law determinations) have been restricted largely to statistical mechanics as applied to ideal gases. Ideal gases are considered to consist of point particles at equilibrium in an isolated system, independent of structure. However, as with solid substances, the entropy of real gases increases as a function of atomic or molecular weight. Even for the 'noble gases', which approximate ideal gases as closely as possible, there is a logarithmic relation between entropy and atomic weight (Fig. 1A). A logarithmic relation also applies

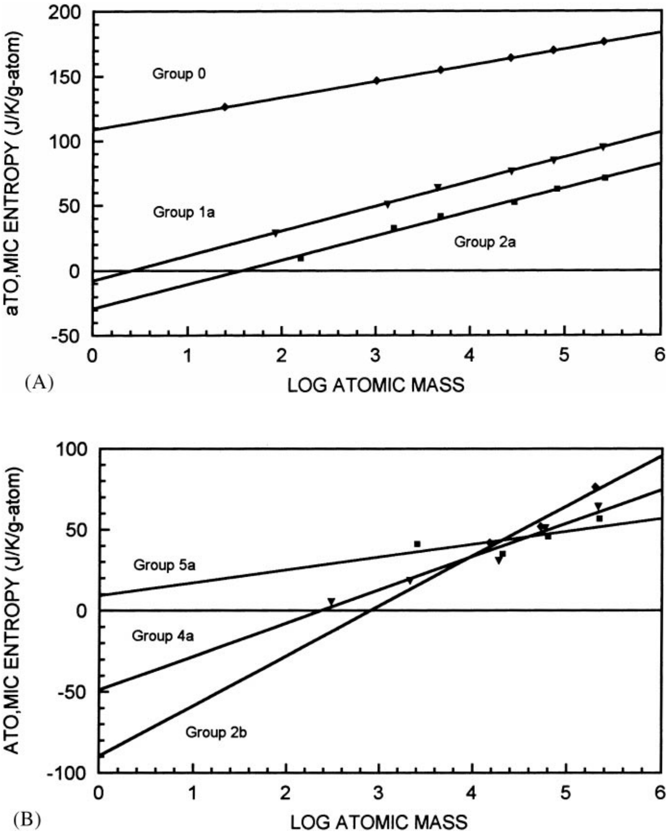


Fig. 1. Linear regressions of the entropies of selected atoms plotted against the logarithms of their atomic masses. (A) Data for Groups 0 (noble gases), 1a (all monovalent elements, excluding hydrogen), and 2a (all divalent elements) in the Periodic Table. For Group 0, $y=108.75+12.47x$, with $r^2=0.999$; for Group 1a, $y=-7.603+19.057x$, with $r^2=0.998$; and for Group 2a, $y=-29.20+18.62x$, with $r^2=0.992$. (B) Data for Groups 2b, 4a, and 5a elements, but excluding nitrogen, in the Periodic Table, illustrate that the relationships in (A) do not necessarily hold as accurately for other groups. For Group 2b (◆), $y=-89.37+30.80x$, with $r^2=0.955$; for Group 4a (▼), $y=9.14+7.95x$, with $r^2=0.513$; and for Group 5a (■), $y=-48.73+20.56x$, with $r^2=0.956$. In general, entropy increases with mass for all groups.

to some solid-state atoms (Fig. 1A), although other solid-state atoms deviate from this (Fig. 1B). Atomic entropy generally increases as a function of atomic mass, whether the atoms comprise gases, liquids, or solids.

It has been shown recently that the following equations can be used to calculate values of S^0 and $\Delta_f S^0$ for organic substances of biological importance in the solid state [2]:

$$S^0_{\text{calc}} = 0.187 \sum S^0_{\text{atoms}} \tag{6}$$

$$\Delta_f S^0_{\text{calc}} = 0.813 \sum S^0_{\text{atoms}} \tag{7}$$

where the subscript 'calc' indicates that the values have been calculated empirically rather than determined experimentally using Eq. (5). Obviously, the use of these equations is far easier than carrying out an experimental determinations, but the values obtained empirically may be less accurate than those obtained experimentally.

The number of critically determined values of S^0_{exp} for substances of biological importance available from the literature is not very large. Most of the values used in this study were obtained from the compilation of entropy data in Domalski et al. [6]. Of these, only entropy data rated 'A' have been used. These were obtained with the lower bound of the entropy determination being within the range of 7 to 20 K, and the upper bound in the 298.15–310 K range. An extrapolation to 0 K is usually made using the Debye equation. Values for $\Delta_f S^0_{\text{exp}}$ were calculated with Eq. (1). Values for S^0_{calc} and $\Delta_f S^0_{\text{exp}}$ were obtained from Eqs. (6) and (7), respectively. The two sets of values were then compared for the percent agreement of the calculated values with those obtained experimentally with Third Law determinations.

3. Results

The results of the comparison described in Section 2 are presented in Table 1. These are far better illustrated by graphs. Fig. 2 shows the percent differences for the substances listed in Table 1 from those for the same substances that were determined calorimetrically using the Third Law, plotted against their molecular weight. In Fig. 2A, there is a wide excursion of values for the lower molecular weight molecules, with a range of 28.20 to −28.88%, which becomes less as the molecular weight increases toward 300 Da. In spite of these wide fluctuations, the average difference between S^0_{calc} and S^0_{exp} for the substances listed is only 2.03%, with a standard deviation of ±11.45% (n=28). Fig. 2B shows the same plot, but including only substances having a molecular weight >300 Da. Here, the average per cent difference between S^0_{calc} and S^0_{exp} is only −0.26% (n=7), with a range of 2.87 to −2.64% and a standard deviation of ±1.69%. The accuracy of S^0_{calc} then begins to approach that of S^0_{exp}, although values for the standard deviations of experimental heat capacity determinations are generally not found in the literature. The value for *S. cerevisiae* could not be shown here because it does not have a true molecular weight, this latter being usually represented as the weight of a C-mol of dried cells.

On the other hand, it is not values of S^0 that are used in calculations of $\Delta_p S^0$ for a given process, but values of $\Delta_f S^0$. These latter are always 4–5 times more negative than the corresponding entropy values are positive. Fig. 3 shows the percent differences of calculated entropy of formation values for the substances listed in Table 1 from those for the same substances that were determined calorimetrically using the Third Law, plotted against their molecular weight. In Fig. 3(A), there is again a wide excursion of values for the lower molecular-weight molecules, although not so great as in Fig. 2A. The average difference between $\Delta_f S^0_{\text{calc}}$ and $\Delta_f S^0_{\text{exp}}$ for organic substances up to 300 Da is −0.09% (n=28) with a range of 10.30 to −5.41% and a standard deviation of ±3.00%. These differences also tend to become less as the molecular weight increases. Fig. 3B shows the same plot, but with high molecular-weight substances included from Table 1 except for *S. cerevisiae.* Here, the average difference is only 0.01%, with a range of 0.61 to −0.63% and a standard deviation of only ±0.44% (n=7). This is a good indication of the agreement between $\Delta_f S^0_{\text{calc}}$ and $\Delta_f S^0_{\text{exp}}$ with respect to high molecular-weight substances. It is important to note that these percentage agreements are relative to $\Delta_f S^0_{\text{exp}}$ being taken as a standard, and the higher the molecular or formula weight, the lower the relative error. The absolute error of the calculations, i.e. the difference of number of joules between the standard and the calculated values can be quite high.

Table 1

Comparison of experimentally determined and empirically calculated entropies and entropies of formation at 298.15 K and 1 bar[a]

Substance[a]	Formula	Molecular weight	S^0_{exp}	S^0_{calc}	$\Delta_f S^0_{\mathrm{exp}}$	$\Delta_f S^0_{\mathrm{calc}}$	$(S^0_{\mathrm{calc}}-S^0_{\mathrm{exp}})/(S^0_{\mathrm{exp}})\times 100$	$(-\Delta_f S^0_{\mathrm{calc}}+\Delta_f S^0_{\mathrm{exp}}/-\Delta_f S^0_{\mathrm{exp}})\times 100$
			($\mathrm{J\,K^{-1}\,mol^{-1}}$)					
Urea	CH_4ON_2	60.05	104.60	104.96	−456.69	−456.63	0.34	−0.01
Glycine	$C_2H_5O_2N$	75.07	103.51	119.52	−535.62	−519.61	15.47	−2.99
L-Alanine	$C_3H_7O_2N$	89.09	129.21	145.03	−646.34	−630.52	12.24	−2.45
Oxalic acid	$C_2H_2O_4$	90.03	115.6	103.3	−436.84	−449.13	−10.64	2.81
L-Serine	$C_3H_7O_3N$	105.09	149.16	164.2	−728.96	−713.91	10.12	−2.06
L-Proline	$C_5H_9O_2N$	115.13	164.06	171.80	−753.65	−746.10	4.72	−1.00
L-Valine	$C_5H_{11}O_2N$	117.15	178.87	196.05	−869.52	−852.34	9.60	−1.98
Succinic acid	$C_4H_6O_4$	118.08	167.32	154.33	−657.96	−670.95	−7.76	1.97
Benzoic acid	$C_7H_6O_2$	122.12	167.73	119.19	−469.63	−518.17	−28.88	10.30
L-Leucine	$C_6H_{13}O_2N$	131.17	211.79	221.54	−973.02	−963.25	4.60	−1.00
L-Isoleucine	$C_6H_{13}O_2N$	131.17	207.99	221.54	−976.82	−963.25	6.51	−1.31
Glycyl glycine	$C_4H_8O_3N_2$	132.12	180.30	195.42	−864.71	−849.59	8.38	−1.75
L-Aspartic acid	$C_4H_7O_4N$	133.10	170.12	184.46	−816.31	−801.97	8.43	−1.76
L-Glutamine	$C_5H_{10}O_3N_2$	146.15	195.06	220.92	−986.37	−960.50	13.26	−2.62
L-Glutamic acid	$C_5H_9O_4N$	147.13	188.20	209.97	−934.65	−912.88	11.57	−2.33
L-Methionine	$C_5H_{11}O_2NS$	149.21	231.46	201.99	−848.73	−878.19	−12.73	3.47
L-Asparagine hydrate	$C_4H_8O_3N_2\ H_2O$	150.13	209.62	239.04	−1068.64	−1039.22	14.03	−2.75
L-Phenylalanine	$C_9H_{11}O_2N$	165.19	213.64	200.34	−857.71	−871.00	−6.22	1.55
α-D-Glucose[b]	$C_6H_{12}O_6$	180.16	209.16	268.15	−1224.78	−1165.79	28.20	4.82
L-Tyrosine	$C_9H_{11}O_3N$	181.19	214.01	219.52	−959.91	−954.40	2.57	−0.57
L-Histidine.HCl	$C_6H_{10}O_2N_3Cl$	191.62	276.10	225.72	−930.95	−981.33	−18.24	−5.41
L-Tryptophan	$C_{12}H_{11}O_2N_2$	204.23	251.04	232.62	−927.60	−958.23	−7.34	3.30
Citric acid monohydrate	$C_6H_8O_7{\cdot}H_2O$	210.14	283.5	282.10	−1224.90	−1226.33	−0.49	0.12
L-Arginine.HCl	$C_6H_{15}O_2N_4Cl$	210.66	286.31	304.73	−1343.25	−1324.83	6.43	−1.37
L-Cystine	$C_6H_{12}O_4N_2S_2$	240.29	280.58	277.51	−1203.44	−1206.51	−1.09	−0.25
n-Octadecane	$C_{18}H_{38}$	254.50	480.20	483.63	−2105.94	−2102.53	0.71	−0.16
Palmitic acid	$C_{16}H_{32}O_2$	256.43	452.37	446.53	−1935.49	−1941.33	−1.29	0.30
Methyl palmitate	$C_{17}H_{34}O_2$	270.45	495.09	472.04	−2029.19	−2052.24	−4.66	1.14
Sucrose[c]	$C_{12}H_{22}O_{11}$	342.29	392.26	396.77	−1729.52	−1725.01	1.15	−0.26
n-Hexacosane	$C_{26}H_{54}$	366.71	667.00	687.00	−3010.60	−2989.89	3.00	−0.69
Trimyristin[d]	$C_{45}H_{86}O_6$	723.14	1247.	1214.	−5246.	−5278	−2.65	0.61
Anhydous bovine zinc insulin	$C_{508}H_{752}O_{150}N_{130}S_{12}Zn$	11530.41	15161.9	15019.0	−65153.7	−65296.61	−0.94	0.22
Hydrated bovine zinc insulin	$C_{508}H_{732}O_{150}N_{130}S_{12}Zn\ 26.7\ H_2O$	12011.44	16347.5	16183.6	−70195.9	−70359.8	−1.00	0.23
Anhydous chymotrypsinogen A	$C_{1077}H_{1736}O_{343}N_{304}S_{12}$	24816.11	33501.6	34464.4	−150800.0	−149837.2	2.87	−0.64

Table 1 (*Continued*)

Substance[a]	Formula	Molecular weight	S^0_{exp}	S^0_{calc}	$\Delta_\mathrm{f}S^0_{\mathrm{exp}}$	$\Delta_\mathrm{f}S^0_{\mathrm{calc}}$	$(S^0_{\mathrm{calc}}-S^0_{\mathrm{exp}})/(S^0_{\mathrm{exp}})\times 100$	$(-\Delta_\mathrm{f}S^0_{\mathrm{calc}}+\Delta_\mathrm{f}S^0_{\mathrm{exp}}/-\Delta_f S^0_{\mathrm{exp}})\times 100$
			($\mathrm{J\,K^{-1}\,mol^{-1}}$)					
Hydrated chymotrypsinogen A	$C_{1077}H_{1736}O_{343}N_{304}S_{12}$ 165 H_2O	27788.75	42266.7	41661.3	−180521.1	−181126.5	−1.43	0.34
Saccharomyces cerevisiae[e]	$CH_{1.613}O_{0.557}N_{0.158}P_{0.012}S_{0.003}K_{0.022}Mg_{0.003}Ca_{0.001}$	26.20	34.17	34.69	−151.36	−150.83	1.52	−0.35

[a] All substances with defined structures are crystalline solids; except where indicated, all entropy values have been taken from Ref. [3], and have been given a rating of ‘A’, indicating data that were obtained experimentally between 7–20 and 298.15–310 K.

[b] Data taken from Ref. [7].

[c] Data taken from Ref. [8].

[d] Data taken from Ref. [9].

[e] Dried cells have no standard state. However, this preparation of *S. cerevisiae* was grown so as not to contain any storage substances [1].

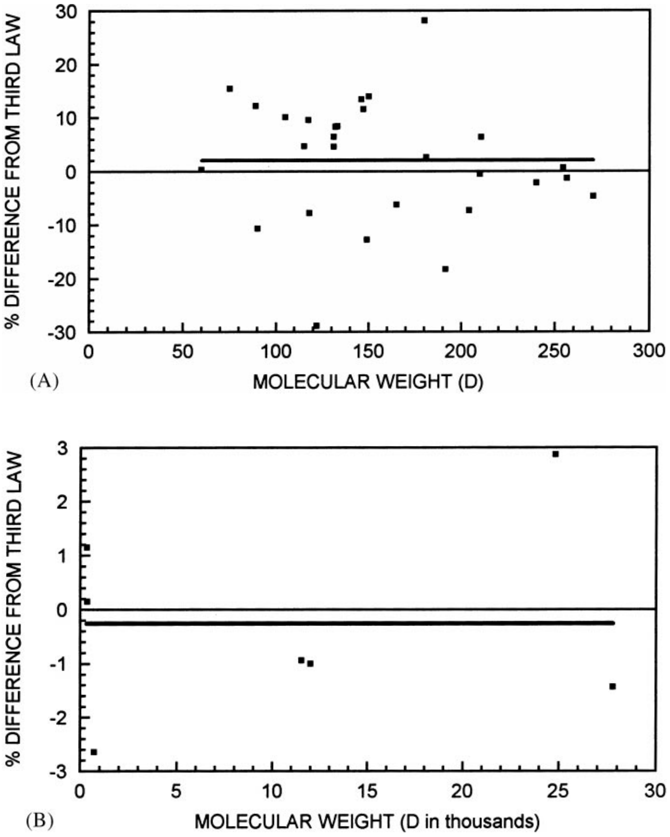
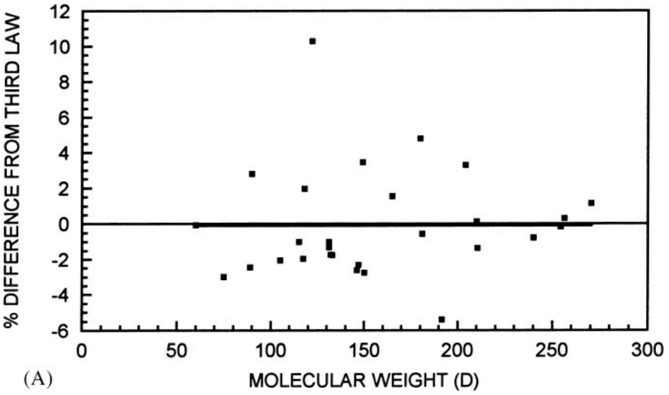


Fig. 2. Plots of the percent difference between empirical calculations of values of S^0 for organic substances of biological importance calculated mathematically (S^0_{calc}) with those determined experimentally (S^0_{exp}), using Third Law calorimetry, against their molecular weights. The data are taken from columns 1, 2, and 3 in Table 1. (A) Comparisons of S^0_{calc} with S^0_{exp} for organic substances up to 300 Da to show the spread of data at the lower molecular weights and how this difference tends to become less pronounced as the molecular weight increases. As indicated by the horizontal line, the average value is 2.03±11.45 % (n=28), with a range of 28.20 to −28.88.%. (B) The same comparisons with substances having a molecular weight >300 Da. Here, the average value is −0.26±1.69% (n=7) with a range of 2.87 to −2.64%.

4. Discussion

From Fig. 2, it is apparent that using Eq. (6) to calculate entropy values for crystalline substances, having molecular weights <300 Da, is not sufficiently accurate for most purposes. The most accurate method for determination of the entropy of these substances is low-temperature calorimetry. However, if the structure as well as the composition of a substance of this weight is known, as it usually is, then the entropy can often be obtained with approximations using various methods of group contribution [10]. Therefore, Eq. (6) may be considered useful for entropy calculations provided that the molecular weight of a substance is over 300 Da, especially if only the empirical composition is known, or if the structure is not amenable to using group contribution methods. Such substances would include nucleic acids, proteins, lipoproteins, glycoproteins, phospholipids, lipids, polyglycosides, lipopolysaccharides, etc. Eq. (6) can also be used for studies on isolated organelles in the same manner as for studies on cells, and can even be extended to studies on small, dried animals, the composition of which can also be expressed in terms of C-mol of biomass.

Fig. 3 shows that, for substances having a molecular weight <300 Da, the values for $\Delta_f S^0_{calc}$ agree with those for $\Delta_f S^0_{exp}$ within a range of ±3%, except for three



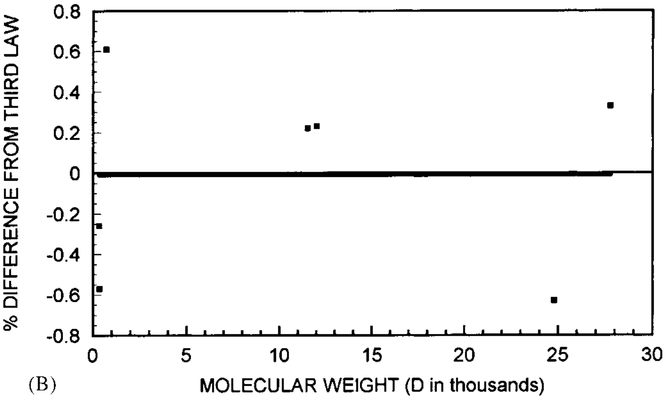


Fig. 3. Plots of the percent agreement of empirical calculations of values of $\Delta_f S^0$ for organic substances of biological importance calculated empirically ($\Delta_f S^0_{calc}$) with those determined experimentally ($\Delta_f S^0_{exp}$), using Third Law calorimetry, against their molecular weights. The data are taken from columns 1, 2, and 3 in Table 1. (A) Comparison of $\Delta_f S^0_{calc}$ with $\Delta_f S^0_{exp}$ for organic substances <300 Da showing the spread of data at the lower molecular weights, and how this agreement tends to improve as the molecular weight increases. As indicated by the horizontal line, the average value is $-0.09\pm3.00\%$ ($n=28$) with a range of 10.30 to -5.41%. (B) The same comparisons with substances having a molecular weight >300 Da. Here, the average value is $0.01\pm0.44\%$ ($n=7$), with a range of 0.61 to -0.63%.

outliers. For substances >300 Da, this agreement is excellent, averaging 0.09%. This is highly indicative that Eq. (7) may be used freely in calculating values for $\Delta_f S^0$ for substances of this size.

Explanation as to why the percent difference between calculated and experimental entropy values at molecular weights <300 Da is so erratic is at present purely conjectural. One reason might be that the effect of individual chemical groups (i.e. hydroxyl, amino, carboxyl, ketone, alcohol, etc.) on the entropy of the whole molecule is much greater at lower, than at higher molecular weights. The principal entropy partition function in solid substances is certainly that of vibration. The electronic partition function is less significant; whereas those of translation and rotation are negligible. With higher molecular weight substances, the effects of individual chemical groups tend to average out so that the interatomic entropy for all the atoms assumes a relatively constant value. This conjecture offers an explanation for the presence of the constant (i.e. a coefficient of proportionality) in Eqs. (6) and (7).

The foregoing discussion does not intend to ignore the possibility that Third Law entropy values may not include the configurational disorder that many scientists would regard as being most certainly present in biomass, such as cells. Viewed in this manner Third Law measurements represent a lower bound to S_{cells}.

5. Conclusions

The use of Eq. (7) for the calculation of $\Delta_f S$ values for organic substances of biological importance having a molecular or formula weight >300 Da is practical and accurate to within 1% of the value obtainable with Third Law low temperature calorimetry. Values of $\Delta_f S$ for similar substances weighing less than this would better be determined by Third Law calorimetry or by group contribution methods.

Acknowledgements

The authors wish to thank Prof. Dr. Ingolf Lamprecht for his kindness in offering to present this paper at the 11th ISBC Conference when the first author (E.H. Battley) was unable to do so. Thanks are also expressed by E.H. Battley to Mr. Lee Najman for several enthusiastic discussions on the nature of entropy.

References

[1] E.H. Battley, Thermochim. Acta 309 (1998) 17.
[2] E.H. Battley, Thermochim. Acta 326 (1999) 7.
[3] U. von Stockar, L. Gustafsson, C. Larsson, I.W. Marrison, P. Tissot, E. Gnaiger, Biochim. Biophys. Acta 1183 (1993) 221.
[4] D.D. Wagman, V.B. Parker, R.H. Schumm, S.M. Bailey, I. Halow, K.L. Churney, R.L. Nuttall, in: R.C. Weast, M.J. Astle (Eds.), CRC Handbook of Chemistry and Physics, Selected Values of Chemical Thermodynamic Properties, CRC Press, Inc., Boca Raton, Florida, 1983, National Bureau of Standards Technical Notes 270–273, 270–274, 270–275, 270–276, 270–277, and 270–278.
[5] E.H. Battley, R.L. Putnam, J. Boerio-Goates, Thermochim. Acta 298 (1997) 37.
[6] E.S. Domalski, W.H. Evans, E.D. Hearing, J. Phys. Chem. Ref. Data 13, Suppl. 1, 1984.
[7] J. Boerio-Goates, J. Chem. Thermodyn. 23 (1991) 403.
[8] R.L. Putnam, J. Boerio-Goates, J. Chem. Thermodyn. 25 (1993) 607.
[9] R.C. Wilhoit, in: H.D. Brown (Ed.), Biochemical Microcalorimetry, Academic Press, New York, 1969, Appendix, p. 305.
[10] I.M. Klotz, Chemical Thermodynamics, Basic theory and Methods., Prentice Hall, New York, 1950.