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On the use of ΔQ° rather than $T^\circ\Delta S^\circ$ in the calculation of ΔG° accompanying the oxidation or fermentation of catabolic substrates of biological importance in their standard states[☆]

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Dedicated to Richard B. Kemp on the occasion of his 60th birthday

Abstract

The purpose of this study has been to determine the effect of substituting ΔQ° for $T^\circ\Delta S^\circ$ in the Gibbs free energy equation ($\Delta G^\circ = \Delta H^\circ - T^\circ\Delta S^\circ$, Eq. (1)) so that $\Delta G^\circ_{\Delta Q} = \Delta H^\circ - \Delta Q^\circ$ (Eq. (2)). The result is that values of $\Delta_c G^\circ_{\Delta Q}$ averaged 1.04 ± 0.01 ($n = 5$) times more negative than those of $\Delta_c G^\circ$ for the bomb calorimetric oxidations of five liquid catabolic substrates, with a range 1.02–1.06. Values of $\Delta_c G^\circ_{\Delta Q}$ averaged 1.03 ± 0.01 ($n = 17$) times more negative than those of $\Delta_c G^\circ$ for 17 theoretical bomb calorimetric oxidations of solid catabolic substrates, with a range 1.02–1.05 . While significant, these differences are not large because in bomb calorimetric oxidations the values of $T^\circ\Delta_c S^\circ$ and $\Delta_c Q^\circ$ are small compared to those of $\Delta_c H^\circ$. On the other hand, for six fermentations values of $T^\circ\Delta_p S^\circ$ and $\Delta_p Q^\circ$ are much larger compared to values of $\Delta_p H^\circ$ than those for oxidations. Here, values of $\Delta_p G^\circ$ showed wide variations from $\Delta_p G^\circ_{\Delta Q}$, ranging from 4.88 times greater to 0.88 times less. Clearly, the whole approach to making these calculations using Eq. (2) is fundamentally different and significant to the extent given above. The difference between the use of Eqs. (1) and (2) is not trivial. Eq. (2) represents a different interpretation of the method of calculating the change in the quantity of absorbed thermal energy exchanged by an irreversible system such as a growth process as it passes from an initial to a final state. It is certainly more simple. It may be more correct. Because $\Delta G^\circ_{\Delta Q}$ is *not* the same as ΔG°, it is suggested that the $\Delta G^\circ_{\Delta Q}$ term in Eq. (2) be changed to ΔX°, this letter not being previously used in biological thermochemistry, so that $\Delta X^\circ = \Delta H^\circ - \Delta Q^\circ$.

Keywords: Free energy; Enthalpy; Heat content; Entropy; Microbial growth

1. Introduction

The free energy changes accompanying irreversible chemical reactions or processes such as microbial growth cannot be measured directly, but can be calculated using the Gibbs free energy equation. Conventionally, this equation is related to the standard temperature at 298.15 K, so that

$$\Delta G^\circ = \Delta H^\circ - T^\circ\Delta S^\circ \tag{1}$$

The standard heat of reaction, ΔH°, can be determined experimentally as a thermal measurement. The standard entropy change, ΔS°, cannot be measured

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directly, but can be calculated using the absolute entropies of the reactants and products of a reaction or process. To determine a value for S°, the heat capacities at constant pressure, C_p, of a reactant or product are measured in small increments as a function of temperature between the temperature limits of 0 and 298.15 K. The integration of a plot of C_p against $\ln T$, plus the values for heat absorption during phase transitions divided by the temperature of these transitions, gives S°. Entropy has the dimensions $\mathrm{J\,mol^{-1}\,K^{-1}}$ or $\mathrm{J\,g^{-1}\,K^{-1}}$ and is not energy, although it is related to it. To convert entropy into thermal energy at the standard temperature it must be multiplied by T° to equal $T^\circ S^\circ$, which has the dimensions $\mathrm{kJ\,mol^{-1}}$ or $\mathrm{kJ\,g^{-1}}$. Conventionally, this then becomes the quantity of thermal energy that is necessary for a substance to have absorbed for it to exist physically at 298.15 K, i.e., S° is determined for 298.15 K. The same C_p data used to determine the S° value that is multiplied by T° to equal $T^\circ S^\circ$ can be used in another way to calculate what in the older literature is called the "heat content", represented by the symbol $(H^\circ_T - H^\circ_0)$ and having the dimensions $\mathrm{kJ\,mol^{-1}}$ or $\mathrm{kJ\,g^{-1}}$. At 298.15 K, this quantity becomes $(H^\circ_{298} - H^\circ_0)$. It can be evaluated by integrating the C_p data as a function of temperature between the limits of 0 and 298.15 K and adding to it the values for heat absorption during phase transitions. The symbol Q° is used here in place of the term $(H^\circ_{298} - H^\circ_0)$ because of its traditional association with the absorption of heat. Each of these represents the same quantity of heat and both Q° and $(H^\circ_{298} - H^\circ_0)$ *can* be defined as the quantity of thermal energy that is required for a given substance to exist at 298.15 K.

It might be thought initially that because the same data are used for the same purpose, $Q^\circ = T^\circ S^\circ$, and this was the basis for Ref. [1]. Here, an attempt was made to remove the idea of entropy from the Gibbs free energy equation and to replace it with that of absorbed thermal energy (also termed "entropic thermal energy"), so that $\Delta Q^\circ = T^\circ \Delta S^\circ$. This was considered to involve a more simple concept, in place of the ideas of "randomness", probability, "organization", or "information", so commonly associated with the idea of "entropy." In retrospect, although there may have been some merit to the comments on entropy in Ref. [1] and to the idea of replacing entropy with something more simple, further reflection on the nature of Q° and S° made it apparent that the assumption that $Q^\circ = T^\circ S^\circ$, or that $\Delta Q^\circ = T^\circ \Delta S^\circ$, is basically incorrect. This resulted in a subsequent paper [2] in which it was demonstrated that for a model heat capacity curve represented by $C_p = aT$, where a is a constant, the ratio $T^\circ S^\circ / Q^\circ$ is 2:1. Since there cannot be two different quantities of thermal energy required for a given substance to exist physically at a given temperature, it was proposed that Q° represents a more correct value for the absorbed thermal energy.

Real heat capacity curves are never totally straight over the temperature range 0–298.15 K, therefore a is not constant. In addition, the existence of phase and other transitions over this temperature range can markedly affect the $T^\circ S^\circ / Q^\circ$ ratio. Thus, these ratios would be expected to vary from 2:1, depending on the substance and its state. The question then arises as to what effect the use of ΔQ° (as *not* being equal to $T^\circ \Delta S^\circ$) would have if it is substituted for $T^\circ \Delta S^\circ$ in the Gibbs free energy equation, so that

$$\Delta G^\circ_{\Delta Q} = \Delta H^\circ - \Delta Q^\circ \tag{2}$$

Both S° and Q° for a given substance are derived from the same data. They are different ways of evaluating the changes in heat capacity as a function of temperature, and they result in the calculation of numerically different quantities having different dimensions. It is the purpose of this paper to investigate if $\Delta Q^\circ = T^\circ \Delta S^\circ$ with respect to the oxidation or fermentation of selected catabolic substrates. If it is not, then the free energy change as calculated using Eq. (1) will not have the same value as that calculated using Eq. (2), and consideration should be given as to which equation is the more correct.

2. Methods and calculations

Microorganisms are convenient cells with which to study the process of growth in that many of them can grow using only one organic substance as a source of material and energy, called the substrate. A part of this, the anabolic substrate, is used in the process of anabolism as a carbon source for cellular structure. The other part, the catabolic substrate, is used aerobically by oxidation, or anaerobically by fermentation, to generate energy to bring about anabolism. Anabolism plus catabolism together comprise metabolism which, because of its complexity with respect to growing cells, is better called a “growth process”. In biological growth processes, the free energy change accompanying catabolism is always far greater than that accompanying anabolism and is simpler to represent. Therefore, it is initially catabolic processes that are being studied here. The use of non-aqueous standard states in calculations here may be questioned. In fact, *all* biological processes take place in an aqueous environment, and in most cases biological oxidations of nitrogenous substrates produce ammonia, not nitrogen gas. However, using the aqueous standard states more appropriate to biological catabolic oxidations would introduce a greater initial complexity to the calculations. This study can be more simply addressed at the outset by using non-aqueous standard states for these processes, since the overall conclusions will not be different whether or not they take place in aqueous solution. This is because the energies of formation of substances in the aqueous standard state are for the most part not greatly different from those in the non-aqueous standard state. A subsequent study can then investigate these same oxidations in aqueous environments appropriate to those encountered by living cells. On the other hand, there is at present no evidence suggesting that the energy exchanges involved in the solution of either the reactants or the products of a growth process have anything to do with the thermodynamics of the growth process itself. Water as a solvent serves also as a fluid matrix for the hydration and physical support of internal cellular structure and as a vehicle for the processes of convection (where this can occur in small cells) and diffusion necessary for cellular metabolism. The use of non-aqueous standard states for the biological systems studied here will definitely determine if free energy changes calculated using Eqs. (1) and (2) have different values. Having made this conclusion, it is then appropriate to continue the study using the aqueous standard states encountered by cells in their natural environment.

To compare the results of using Eqs. (1) or (2), theoretical bomb calorimetric oxidations have been carried out on a number of catabolic substrates for the purpose of calculating the free energy changes accompanying these oxidations. The same is done with respect to several fermentations, which represent limited oxidations. To make the appropriate calculations, it is necessary to compile values of Q° for use in Eq. (2), where Q° is defined as the quantity of absorbed thermal energy necessary for a given mass to exist at the standard temperature of 298.15 K. The same definition applies to $T^\circ S^\circ$.

2.1. *Values of Q° for substances in a condensed phase at 298.15 K*

The quantity of thermal energy that has to be absorbed for a given mass to exist at the standard temperature is calculated according to the following equation [3, p. 2–10].

$$\begin{aligned} Q^\circ &= H^\circ_{298.15} - H^\circ_0 \\ &= \int_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} C_p\,\mathrm{d}T + \sum \Delta_{\mathrm{trs}} H^\circ \end{aligned} \tag{3}$$

where the rightmost term represents heat changes accompanying transitions and phase changes. Values of $Q^\circ\,[= (H^\circ_{298.15} - H^\circ_0)]$ for various substances in a condensed phase at 298.15 K are found in the original literature and are given in Table 2.

2.2. *Values of Q° for substances in the gas phase at 298.15 K*

For whatever reason, values of $Q^\circ\,[= (H^\circ_{298.15} - H^\circ_0)]$ listed in the literature for substances in the gas phase are for the gas phase only down to 0 K, and do not include data for the condensed phases [3–6]. In this respect these values differ from those for S°, which are comprised of a summation of data both for condensed and gas phases in accord with Eq. (4). Except for those that sublime at a pressure of 1 bar and for helium, all gases pass from a solid through a liquid state as their temperatures are raised from 0 to 298.15 K, and the heat contents of these condensed phases should be included in the total heat content. For this purpose, the heat content of the condensed phases of the gases used in this study has been calculated from the heat capacity data in the original literature. To these values have then been added the heat content data of the ideal gas phase from the temperature of sublimation, or of the boiling point of the liquid phase, to 298.15 K, and the data comprising both the condensed and gas phases have been included in accord with Eq. (3). These latter data have not been obtained calorimetrically, but have been calculated using statistical mechanics. They are found in several references in the literature such as

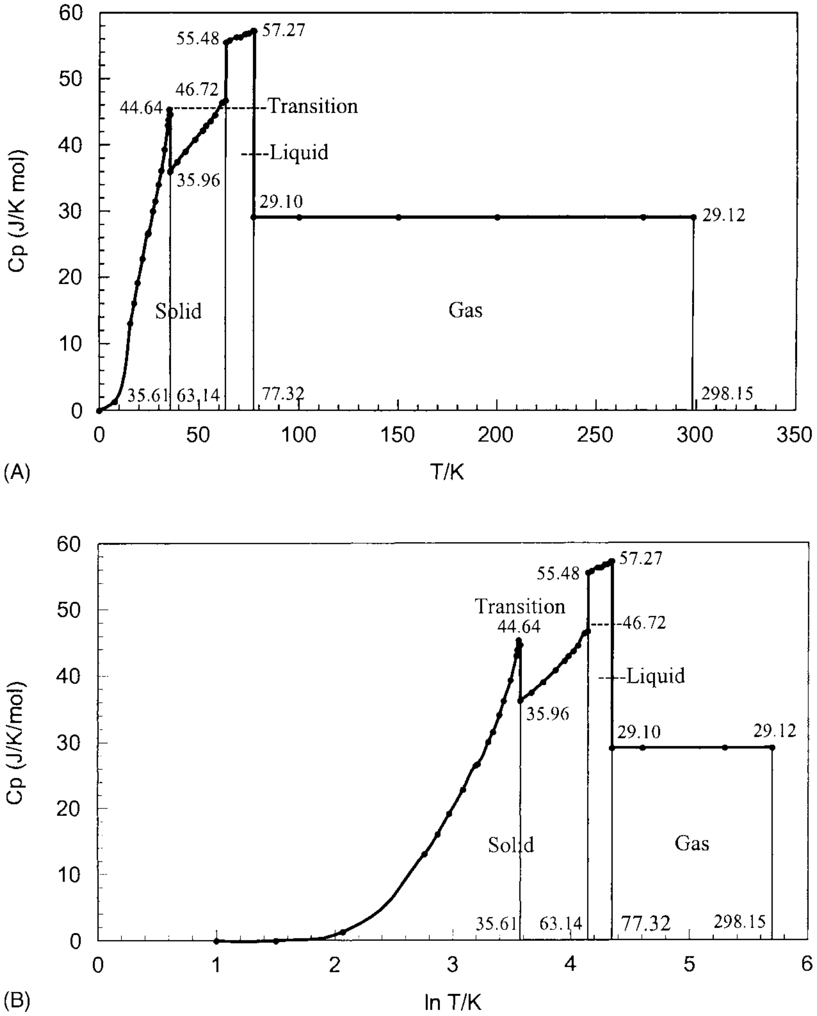

Fig. 1. (A) Determination of the standard heat content (Q°) of nitrogen using Eq. (3) in the text. The graph is of C_p plotted against T (K) for nitrogen. The small numbers at the bottom of the graph refer to values of T; those at various points along the graph refer to values of C_p. Data for the condensed phases were taken from Ref. [8]. Data for the gas phase were taken from Ref. [5, Table 20, p. 92]. (B) Determination of the standard entropy (S°) of nitrogen using Eq. (4) in the text. The graph is of C_p plotted against $\ln T$ for nitrogen. The small numbers at the bottom of the graph refer to values of T, not $\ln T$; those at various points along the graph refer to values of C_p. Data for the condensed phases were taken from Ref. [8]. Data for the gas phase were taken from Ref. [5, Table 20, p. 92]. For both Fig. 1A and B extrapolation of the C_p vs T data was not done using the Debye equation, but as follows. Two data points were introduced into the C_p vs T data set, one having the coordinates 0 C_p:0 T, and the second $C_{p(\mathrm{l})}/10$:$T_{(\mathrm{l})}/2$, where the subscript “(l)” represents the value of the lowest point on the data set. For the six gases studied here the lowest temperatures of the experimental data sets were between 10 and 15 K. This method is simple to use, and the difference between it and the Debye extrapolation is insignificant at very low temperatures. Note that the Y-axis has the same values in both graphs. The quantity Q° has the dimensions of energy (J mol^{-1}). The quantity S° has the dimensions J K^{-1} mol^{-1}. To transform this into energy, the entropy has to be multiplied by T, which here has the value of 298.15 (i.e., the upper limit of the entropy determination). From Fig. 1A, Q° has the value of 15.512 kJ mol^{-1}, and this is the quantity of thermal energy (as determined experimentally for the condensed phases and using statistical mechanics for the gas phase) that is required to raise the temperature of one mol of nitrogen from 0 to 298.15 K From Fig. 1B, S° has the value of 191.61 J K^{-1} mol^{-1}. When this is multiplied by T (K) = 298.15, which is the upper limit of the determination, the quantity of energy that is obtained becomes 57.128 kJ mol^{-1}. This is *conventionally* the quantity of thermal energy that is required to raise the temperature of 1 mol of nitrogen from 0 to 298.15 K. However, this quantity is 3.683 times greater than that determined from Fig. 1A. Since there cannot be two different quantities of thermal energy required to raise the temperature of a given mass of substance from 0 to 298.15 K, consideration must be given as to which determination is more correct.

Table 1
Calculation of Q° values for O_2(g), CO_2(g), N_2(g), H_2(g), NH_3(g) and CH_4(g)

Calculation of Q° for O_2(g)[a]	Q(kJ mol^{-1})
0–12.97 K, numerical extrapolation	0.018
$\int C_p\,dT$, 12.97–23.66 K	0.127
Heat of transition I at 23.66 K	0.094
$\int C_p\,dT$, 23.66–43.76 K	0.664
Heat of transition II at 43.76 K	0.743
$\int C_p\,dT$, 43.76–54.39 K	0.488
Heat of fusion at 54.39 K	0.445
$\int C_p\,dT$, 54.39–90.13 K	1.913
Heat of vaporization at 90.13 K	6.815
Heat content of gas at boiling point (90.13 K)	11.307
Heat content of gas from 90.13 to 298.15 K	6.083
	$\sum Q = Q^\circ = 17.390$

Calculation of Q° for N_2(g)[b]	Q(kJ mol^{-1})
0–15.82 K, numerical extrapolation	0.062
$\int C_p\,dT$, 10.42–35.61 K	0.559
Heat of transition at 35.61 K	0.228
$\int C_p\,dT$, 35.61–63.14 K	1.138
Heat of fusion at 63.14 K	0.721
$\int C_p\,dT$, 63.14–77.32 K	0.800
Heat of vaporization at 77.32 K	5.576
Heat content of gas at boiling point (77.32 K)	9.084
Heat content of gas from 77.32–298.15 K	6.428
	$\sum Q = Q^\circ = 15.512$

Calculation of Q° for NH_3(g)[c]	Q/(kJ mol^{-1})
0–15.00 K, numerical extrapolation	0.003
$\int C_p\,dT$, 15.00–195.36 K	4.786
Heat of fusion at 195.36 K	5.655
$\int C_p\,dT$, 195.36–239.68 K	3.334
Heat of vaporization at 239.68 K	23.351
Heat content of gas at boiling point 239.68 K	37.129
Heat content of gas from, 239.68–298.15 K	2.048
	$\sum Q = Q^\circ = 39.177$

Calculation of Q° for CO_2(g)[d]	Q(kJ mol^{-1})
0–15 K, numerical extrapolation	0.010
$\int C_p\,dT$, 15–194.67 K	6.652
Heat of sublimation at 194.67 K	26.10
Heat content of gas at sublimation point (194.67 K)	32.762
Heat content of gas from 194.67 to 298.15 K	3.479
	$\sum Q = Q^\circ = 36.241$

Calculation of Q° for H_2(g)[e]	Q(kJ mol^{-1})
0–10.00 K, numerical extrapolation	0.007
$\int C_p\,dT$, 10.00–13.96 K	0.016
Heat of fusion at 13.96 K	0.117
$\int C_p\,dT$, 13.96–20.35 K	0.103
Heat of vaporization at 20.35 K	0.903
Heat content of gas at boiling point (20.35 K)	1.146
Heat content of gas from 20.35–298.15 K	7.842
	$\sum Q = Q^\circ = 8.988$

Calculation of Q° for CH_4(g)[f]	Q(kJ mol^{-1})
0–10.33 K, numerical extrapolation	0.014
$\int C_p\,dT$, 10.33–20.44 K	0.109
Heat of transition at 20.44 K	0.076
$\int C_p\,dT$, 20.44–90.6 K	2.336
Heat of fusion at 90.6 K	0.939
$\int C_p\,dT$, 90.6–111.7 K	0.993
Heat of vaporization at 111.7 K	8.473
Heat content of gas at boiling point 111.7 K	12.940
Heat content of gas from 111.7–298.15 K	6.333
	$\sum Q = Q^\circ = 19.273$

Values of Q° as given in Ref. [3] in kJ mol^{-1} are: $O_2(g) = 8.680$; $H_2(g) = 8.468$; $N_2(g) = 8.669$; $CO_2(g) = 9.360$; $NH_3(g) = 9.991$; $CH_4(g) = 9.991$.

[a] Condensed phase data taken from Ref. [7]. Gas phase data taken from Ref. [5, Table 23, p. 95].

[b] Condensed phase data taken from Ref. [8]. Gas phase data taken from Ref. [5, Table 20, p. 92].

[c] Condensed phase data taken from Ref. [9]. Gas phase data taken from Ref. [5, Table 94, p. 174].

[d] Condensed phase data taken from Ref. [10]. Gas phase data taken from Ref. [5, Table 14, p. 85]. The method of making this calculation differs from that in Ref. [13].

[e] Condensed phase data taken from Ref. [11]. Gas phase data taken from Ref. [5, Table 23, p. 95].

[f] Condensed phase data taken from Ref. [12]. Gas phase data taken from Ref. [5, Table 180, p. 254].

Refs. [3–6] but have here been taken from Ref. [3]. The assumption is made here that at temperatures below 298.15 K the thermodynamic properties of ideal gases are nearly identical with those of real gases. As an example, the calculation of Q° and S° for $N_2(g)$ is illustrated in Fig. 1. This has been chosen because of the presence of a clear transition in the solid state, as well as transitions through the liquid and gas phases. Values of Q° for the gases used here (including the condensed phases) are given in Table 1. These should be compared with the values of $Q^\circ\,[= H^\circ_{298.15} - H^\circ_0]$ listed in Refs. [3–6] and also in Table 1.

2.3. *Values of S° for all substances at 298.15 K*

Values for the entropy are calculated according to the following equation [3, p. 2-9],

$$S^\circ = \int_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} C_p \,\mathrm{d}\ln T + \sum \frac{\Delta_{\mathrm{trs}} H^\circ}{T_{\mathrm{trs}}} \qquad (4)$$

where the rightmost term represents transitions and phase changes. These have all been taken from the literature, and are listed in Table 2.

2.4. *Values of $\Delta_f S^\circ$ and $\Delta_f Q^\circ$ for all substances*

Values of $\Delta_\mathrm{f} S^\circ$ and $\Delta_\mathrm{f} Q^\circ$ for the selected catabolic substrates were calculated using the following equations and data from Table 2, and are listed in Table 3.

$$\Delta_\mathrm{f} S^\circ = S^\circ - \sum S^\circ_{\mathrm{atoms}} \qquad (5)$$

$$\Delta_\mathrm{f} Q^\circ = Q^\circ - \sum Q^\circ_{\mathrm{atoms}} \qquad (6)$$

2.5. *Thermodynamic changes*

Changes in the absorbed heat accompanying the bomb calorimetric oxidations of selected substrates of biological importance in their standard states are given in Table 4, using data from Table 3. They were calculated using the following equations.

$$T^\circ \Delta_\mathrm{c} S^\circ = T^\circ \left[\sum \Delta_\mathrm{f} S^\circ_{\mathrm{prod}} - \sum \Delta_\mathrm{f} S^\circ_{\mathrm{react}}\right] \qquad (7)$$

$$\Delta_\mathrm{c} Q^\circ = \sum \Delta_\mathrm{f} Q^\circ_{\mathrm{prod}} - \sum \Delta_\mathrm{f} Q^\circ_{\mathrm{react}} \qquad (8)$$

where the subscripts ‘prod’ and ‘react’ represent the products and the reactants of the oxidations. Changes in the absorbed heat accompanying fermentations are calculated in the same manner as for Table 4, and are shown in Table 5. The small number of examples of fermentations is due to a lack of good, low temperature heat capacity data on the products of many of these processes, especially for one of the most common products, which is lactic acid.

Changes in free energy accompanying the bomb calorimetric oxidations of selected substrates of biological importance in their standard states are given in Table 6, using data from Table 4. They were calculated using the following equations.

$$\Delta_\mathrm{c} G^\circ = \Delta_\mathrm{c} H^\circ - T^\circ \Delta_\mathrm{c} S^\circ \qquad (9)$$

$$\Delta_\mathrm{c} G^\circ_{\Delta Q} = \Delta_\mathrm{c} H^\circ - \Delta_\mathrm{c} Q^\circ \qquad (10)$$

Changes in free energy accompanying fermentations were calculated in the same manner as for Table 6, and are given in Table 7.

3. Results

Table 1 shows that the values of Q° for the six gases studied are significantly higher than those for the same gases given in compilations such as Refs. [3–6]. This is because the heat capacities of the solid and liquid phases have been included in the calculations. The ratios of (data given in Table 1/data taken from Ref. [3]) are, in $\mathrm{kJ\,mol^{-1}}$, $O_2(g)$ 17.390/8.680; $N_2(g)$ 15.512/8.669; $NH_3(g)$ 39.177/9.991; $CO_2(g)$ 36.241/9.360; $H_2(g)$ 8.988/8.468; $CH_4(g)$ 19.273/9.991.

In Table 2, it is shown that the value of $T^\circ S^\circ$ for a given substance is always greater than Q°, the ratio of $T^\circ S^\circ/Q^\circ$ being highly variable. For the diatomic gases studied this ratio averages 3.845, with a range 3.517–4.335. For the five organic liquids studied, this ratio averages 1.718, with a range 1.508–1.980. For the 17 solid organic substances studied it averaged 1.955, with a range 1.877–2.025. For non-organic substances in different states, this ratio ranges from 1.467 for ammonia, to 4.335 for hydrogen. An average of these data would not be meaningful.

The data in Table 2 illustrate that carrying out a numerical integration of the C_p curves gives a more accurate estimate of the ratio of $T^\circ S^\circ/Q^\circ$ than does the mathematical model used in Ref. [2]. Nevertheless, the averaged data show a ratio of 1.955 with respect

Table 2
A comparison of values of $T^\circ S^\circ$ and Q°[a]

Substance	Formula	S° ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$T^\circ S^\circ$ ($\mathrm{kJ\,mol^{-1}}$)	Q° ($\mathrm{kJ\,mol^{-1}}$)	$T^\circ S^\circ/Q^\circ$
Elements					
Carbon(c)	C	5.74	1.711	1.050	1.629
Hydrogen(g)	H_2	130.68	38.962	8.988[b]	4.335
Nitrogen(g)	N_2	191.61	57.128	15.512[b]	3.683
Oxygen(g)	O_2	205.15	61.165	17.390[b]	3.517
					Average for diatomic gases: 3.845
Inorganic					
Ammonia(g)	NH_3	192.77	57.474	39.177[b]	1.467
Carbon dioxide(g)	CO_2	213.79	63.741	36.241[b]	1.759
Methane(g)	CH_4	186.26	55.533	19.273[b]	2.881
Water(l)	H_2O	69.95	20.855	13.273	1.569
Organic					
Liquids					
Acetic acid	$C_2H_4O_2$	158.0 [14]	47.108	28.150 [14]	1.673
n-Butyric acid	$C_4H_8O_2$	225.3 [14]	67.173	39.320 [14]	1.708
Ethanol	C_2H_6O	161.21 [15]	48.065	24.275 [15]	1.980
Glycerol	$C_3H_8O_3$	206.3 [16]	61.508	40.776 [16]	1.508
n-Propionic acid	$C_3H_6O_2$	191.0 [14]	56.946	33.090 [14]	1.721
					Average: 1.718 ± 0.169, $n = 5$
Solids					
L-Alanine	$C_3H_7O_2N$	29.20 [17]	38.521	20.034 [17]	1.923
L-Aspartic acid	$C_4H_7O_4N$	170.12 [18]	50.721	25.810 [18]	1.965
Glucose	$C_6H_{12}O_6$	209.16 [19]	62.361	32.556 [19]	1.915
Glycine	$C_2H_5O_2N$	103.51 [17]	30.861	16.179 [17]	1.907
L-Glutamic acid	$C_5H_9O_4N$	188.20 [18]	56.111	28.766 [18]	1.951
L-Glutamine	$C_5H_{10}O_3N_2$	195.06 [18]	58.157	30.051 [18]	1.935
Glycylglycine	$C_4H_9O_3N_2$	180.29 [20]	53.753	27.394 [20]	1.962
L-Leucine	$C_6H_{13}O_2N$	211.79 [21]	63.145	31.623 [21]	1.997
Palmitic acid	$C_{16}H_{32}O_2$	452.37 [22]	134.874	68.621 [22]	1.965
L-Phenylalanine	$C_9H_{11}O_2N$	213.63 [23]	63.694	31.447 [23]	2.025
L-Proline	$C_5H_9O_2N$	164.05 [23]	48.911	24.437 [23]	2.018
L-Serine	$C_3H_7O_3N$	149.16 [24]	44.472	22.653 [24]	1.963
Succinic acid	$C_4H_6O_4$	167.32 [25]	49.886	25.233 [25]	1.977
Sucrose	$C_{12}H_{22}O_{11}$	392.4 [26]	116.994	62.340 [26]	1.877
L-Tryptophan	$C_{11}H_{12}O_2N_2$	251.04 [23]	74.847	37.211 [23]	2.011
L-Tyrosine	$C_9H_{11}O_3N$	214.01 [23]	63.807	33.369 [23]	1.912
L-Valine	$C_5H_{11}O_2N$	178.87 [21]	53.330	27.581 [21]	1.933
					Average: 1.955 ± 0.042, $n = 17$

[a] The numbers in brackets represent references. Entropy values for elements and for inorganic substances were taken from Ref. [4].

[b] See Table 1.

to solid substances, as opposed to 1.993 obtained with this model.

Table 3 provides data for Table 4. Table 3 also shows that for the 17 solid substances studied, the ratio $T^\circ \Delta_f S^\circ/\Delta_f Q^\circ$ is remarkably constant at 4.72 ± 0.27. It is less so at 8.62 ± 1.03 for the five liquid substances studied, presumably due to differences in the quantity of heat absorbed during the phase change from the solid to the liquid state.

Table 4 provides data for Table 6. Table 4 also shows that the quantities of absorbed heat exchanged with the environment during bomb calorimetric oxidations

Table 3
Comparative values of $T^\circ\Delta_f S^\circ$ and $\Delta_f Q^\circ$

Substance	Formula	$\Delta_f S^{\circ a}$ ($JK^{-1}\,mol^{-1}$)	$T^\circ\Delta_f S^\circ$ ($kJ^{-1}\,mol^{-1}$)	$\Delta_f Q^{\circ b}$ ($kJ^{-1}\,mol^{-1}$)	$T^\circ\Delta_f S^\circ/\Delta_f Q^\circ$
Elements [2]					
Carbon(c)	C	0	0	0	
Hydrogen(g)	H_2	0	0	0	
Nitrogen(g)	N_2	0	0	0	
Oxygen(g)	O_2	0	0	0	
Inorganic [2][c]					
Ammonia(g)	NH_3	−99.055	−29.533	17.939	−1.69
Carbon dioxide(g)	CO_2	2.900	0.865	17.801	0.05
Methane(g)	CH_4	−80.836	−24.101	0.247	−97.57
Water(l)	H_2O	−163.305	−48.689	−4.410	11.04
Organic					
Liquids					
n-Acetic acid	$C_2H_4O_2$	−320.00	−95.408	−9.316	10.24
n-Butyric acid	$C_4H_8O_2$	−525.53	−156.686	−18.222	8.60
Ethanol	C_2H_6O	−344.89	−102.829	−13.484	7.63
Glycerol	$C_3H_8O_3$	−641.36	−191.221	−24.411	7.83
n-Propionic acid	$C_3H_6O_2$	−423.41	−126.240	−14.414	8.76
					Average: 8.62 ± 1.03, $n = 5$
Solids					
L-Alanine	$C_3H_7O_2N$	−646.35	−192.709	−39.720	4.85
L-Aspartic acid	$C_4H_7O_4N$	−816.32	−243.386	−52.384	4.65
Glucose[d]	$C_6H_{12}O_6$	−1224.81	−365.177	−79.842	4.57
Glycine	$C_2H_5O_2N$	−535.62	−159.696	−33.537	4.76
L-Glutamic acid	$C_5H_9O_4N$	−934.66	−278.669	−59.466	4.69
L-Glutamine	$C_5H_{10}O_3N_2$	−968.37	−288.719	−61.736	4.68
Glycylglycine	$C_4H_9O_3N_2$	−930.06	−277.297	−584.355	4.71
L-Leucine	$C_6H_{13}O_2N$	−973.02	−290.106	−58.215	4.98
Palmitic acid	$C_{16}H_{32}O_2$	−1935.50	−577.069	−109.377	5.27
L-Phenylalanine	$C_9H_{11}O_2N$	−857.72	−225.729	−52.583	4.29
L-Proline	$C_5H_9O_2N$	−753.66	−224.704	−46.405	4.05
L-Serine	$C_3H_7O_3N$	−728.97	−217.342	−45.796	4.74
Succinic acid	$C_4H_6O_4$	−657.98	−196.176	−40.711	4.82
Sucrose	$C_{12}H_{22}O_{11}$	−2242.28	−668.535	−144.773	4.62
L-Tryptophan	$C_{11}H_{12}O_2N_2$	−992.94	−296.045	−61.169	4.84
L-Tyrosine	$C_9H_{11}O_3N$	−959.92	−286.200	−59.356	4.84
L-Valine	$C_5H_{11}O_2N$	−869.52	−259.247	−52.249	4.96
					Average: 4.72 ± 0.27, $n = 17$

[a] $\Delta_f S^\circ = S^\circ_{sub} - \sum S^\circ_{atoms}$. The subscript 'sub' refers to the given substance. Data for calculations taken from Table 2.

[b] $\Delta_f Q^\circ = Q^\circ_{sub} - \sum Q^\circ_{atoms}$. The subscript 'sub' refers to the given substance. Data for calculations taken from Table 2.

[c] Values for inorganic substances taken from Ref. [4] except for methane, which was taken from Ref. [3]. All values for organic substances taken from Ref. [27].

[d] $C_p\,dT$ data integrated numerically by the author.

can vary widely and may even have a different sign, when calculated as $T^\circ\Delta_c S^\circ$ or as $\Delta_c Q^\circ$. The most extreme example of this is that of palmitic acid, which is $-188.13\,kJ\,mol^{-1}$ for $T^\circ\Delta_c S^\circ$ and $323.634\,kJ\,mol^{-1}$ for $\Delta_c Q^\circ$.

Table 5 provides data for Table 7. It also shows differences similar to those in Table 4 with respect to $T^\circ\Delta_c S^\circ$ and $\Delta_c Q^\circ$.

In Table 6, the data indicate that for the bomb calorimetric oxidation of five organic liquids, values for

Table 4
A comparison of the values for $T^{\circ}\Delta_{c}S^{\circ}$ and $\Delta_{c}Q^{\circ}$ accompanying the oxidation in their standard states of organic substances of catabolic importance

Substance	Reaction	$T^{\circ}\Delta_{c}S^{\circ}$[a] (kJ^{-1} mol^{-1})	$\Delta_{c}Q^{\circ}$[b] (kJ^{-1} mol^{-1})
Liquids			
Acetic acid	$CH_3COOH(l) + 2O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$	−0.24	36.10
n-Butyric acid	$C_4H_8O_2(l) + 5O_2(g) \rightarrow 4CO_2(g) + 4H_2O(l)$	−34.61	71.79
Ethanol	$C_2H_6O(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$	−41.51	35.86
Glycerol	$C_3H_8O_3(l) + 3.5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$	−0.94	60.17
n-Propionic acid	$C_3H_6O_2(l) + 3.5O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l)$	17.23	54.59
Solids			
L-Alanine	$C_3H_7O_2N(c) + 3.5O_2(g) \rightarrow 3CO_2(g) + 3.5H_2O(l) + 0.5N_2(g)$	24.89	77.69
L-Aspartic acid	$C_4H_7O_4N(c) + 3.75O_2(g) \rightarrow 4CO_2(g) + 3.5H_2O(l) + 0.5N_2(g)$	76.43	108.15
Glucose	$C_6H_{12}O_6(c) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$	78.23	160.19
Glycine	$C_2H_5O_2N(c) + 2.25O_2(g) \rightarrow 2CO_2(g) + 2.5H_2O(l) + 0.5N_2(g)$	39.70	58.11
L-Glutamic acid	$C_5H_9O_4N(c) + 5.25O_2(g) \rightarrow 5CO_2(g) + 4.5H_2O(l) + 0.5N_2(g)$	63.89	128.63
L-Glutamine	$C_5H_{10}O_3N_2(c) + 6O_2(g) \rightarrow 5CO_2(g) + 5H_2O(l) + N_2(g)$	49.59	128.69
Glycylglycine	$C_4H_9O_3N_2(c) + 4.75O_2(g) \rightarrow 4CO_2(g) + 4.5H_2O(l) + N_2(g)$	61.65	110.21
L-Leucine	$C_6H_{13}O_2N(c) + 8.25O_2(g) \rightarrow 6CO_2(g) + 6.5H_2O(l) + 0.5N_2(g)$	−21.19	136.36
Palmitic acid	$C_{16}H_{32}O_2(c) + 23O_2(g) \rightarrow 16CO_2(g) + 16H_2O(l)$	−188.13	323.63
L-Phenylalanine	$C_9H_{11}O_2N(c) + 10.75O_2(g) \rightarrow 9CO_2(g) + 5.5H_2O(l) + 0.5N_2(g)$	−4.28	188.54
L-Proline	$C_5H_9O_2N(c) + 6.25O_2(g) \rightarrow 5CO_2(g) + 4.5H_2O(l) + 0.5N_2(g)$	9.92	124.55
L-Serine	$C_3H_7O_3N(c) + 3.75O_2(g) \rightarrow 3CO_2(g) + 4.5H_2O(l) + 0.5N_2$	0.83	79.35
Succinic acid	$C_4H_6O_4(c) + 3.5O_2(g) \rightarrow 4CO_2(g) + 3H_2O(l)$	53.57	98.68
Sucrose	$C_{12}H_{22}O_{11}(c) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)$	143.33	309.87
L-Tryptophan	$C_{11}H_{12}O_2N(c) + 13O_2(g) \rightarrow 11CO_2(g) + 6H_2O(l) + 0.5N_2(g)$	13.42	230.52
L-Tyrosine	$C_9H_{11}O_3N(c) + 10.25O_2(g) \rightarrow 9CO_2(g) + 5.5H_2O(l) + 0.5N_2(g)$	26.19	195.31
L-Valine	$C_5H_{11}O_2N(c) + 6.75O_2(g) \rightarrow 5CO_2(g) + 5.5H_2O(l) + 0.5N_2(g)$	−4.22	117.00

[a] $\Delta_{c}S^{\circ}$ was calculated using the equation $\Delta_{c}S^{\circ} = \sum \Delta_{f}S^{\circ}_{prod} - \sum \Delta_{f}S^{\circ}_{react}$.

[b] $\Delta_{c}Q^{\circ}$ was calculated using the equation $\Delta_{c}Q^{\circ} = \sum \Delta_{f}Q^{\circ}_{prod} - \sum \Delta_{f}Q^{\circ}_{react}$.

Table 5
Values for $T^{\circ}\Delta_{p}S^{\circ}$ and $\Delta_{p}Q^{\circ}$ accompanying the theoretical fermentation in their standard states of organic substances of catabolic importance[a]

Fermentation		$T^{\circ}\Delta_{p}S^{\circ}$[b] (kJ mol^{-1})	$\Delta_{p}Q^{\circ}$[c] (kJ mol^{-1})
Ethanolic[d]	$C_6H_{12}O_6(c)_{Glucose} \rightarrow 2CO_2(g) + 2C_2H_6O(l)_{Ethanol}$	161.25	88.48
Methanogenic[e]	$C_2H_4O_2(l)_{Acetic\ acid} \rightarrow CH_4(g)_{Methane} + CO_2(g)$	72.17	27.36
Homoacetate[f]	$C_6H_{12}O_6(c)_{Glucose} \rightarrow 3C_2H_4O_2(l)_{Acetic\ acid}$	78.95	51.89
Stickland[g]	$C_3H_7O_2N(c)_{Alanine} + 2C_2H_5O_2N(c)_{Glycine} \rightarrow 3NH_3(g) + 3C_2H_4O_2(l) + CO_2(g)$	138.14	150.46
Propionate[h]	$C_6H_{12}O_6(c)_{Glucose} \rightarrow C_2H_4O_2(l)_{Acetic\ acid} + C_3H_6O_2(l)_{Propionic\ acid} + CO_2(g)$	144.39	73.91
Butyrate[i]	$C_2H_6O(l)_{Ethanol} + C_2H_4O_2(l)_{Acetic\ acid} \rightarrow C_4H_8O_2(l)_{Butyric\ acid} + H_2O(l)$	−7.14	0.17

[a] The subscript 'p', for 'process' is used here because the subscript 'f', which might have been used to represent fermentation, is already used to represent 'formation'.

[b] $\Delta_{p}S^{\circ}$ was calculated using the equation $\Delta_{p}S^{\circ} = \sum \Delta_{f}S^{\circ}_{prod} - \sum \Delta_{f}S^{\circ}_{react}$.

[c] $\Delta_{p}Q^{\circ}$ was calculated using the equation $\Delta_{p}Q^{\circ} = \sum \Delta_{f}Q^{\circ}_{prod} - \sum \Delta_{f}Q^{\circ}_{react}$.

[d] *Saccharomyces cerevisiae.*

[e] *Methanosarcina barkeri.*

[f] *Clostridium thermoaceticum.*

[g] *Clostridium* sp.

[h] *Veillonella* sp.

[i] Many gram-negative, anaerobic bacteria.

Table 6

A comparison of the free energy changes accompanying the oxidation in their standard states of organic substances of catabolic importance as calculated using $T^\circ\Delta_c S^\circ$ or $\Delta_c Q^{\circ a}$

Reaction		$\Delta_c H^{\circ b}$ (kJ mol^{-1})	$\Delta_c G^{\circ c}$ (kJ mol^{-1})	$\Delta_c G^{\circ}_{\Delta Q}{}^{d}$ (kJ mol^{-1})	$\Delta_c G^{\circ}_{\Delta Q}/\Delta_c G^\circ$ (kJ mol^{-1})
Liquids					
Acetic acid	$CH_3COOH(l) + 2O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$	−874.54	−874.30	−910.64	1.04
n-Butyric acid	$C_4H_8O_2(l) + 5O_2(g) \rightarrow 4CO_2(g) + 4H_2O(l)$	−2183.50	−2148.89	−2255.29	1.05
Ethanol	$C_2H_6O(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$	−1366.83	−1325.32	−1402.70	1.06
Glycerol	$C_3H_8O_3(l) + 3.5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$	−1655.40	−1654.46	−1715.57	1.04
n-Propionic acid	$C_3H_6O_2(l) + 3.5O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l)$	−1527.28	−1544.51	−1581.87	1.02
					Average: 1.04 ± 0.01, *n* = 5
Solids					
L-Alanine	$C_3H_8O_2N(c) + 4O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) + 0.5N_2(g)$	−1620.46	−1645.35	−1698.15	1.03
L-Aspartic acid	$C_4H_7O_4N(c) + 3.75O_2(g) \rightarrow 4CO_2(g) + 3.5H_2O(l) + 0.5N_2(g)$	−1601.80	−1678.23	−1709.95	1.02
Glucose	$C_6H_{12}O_6(c) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$	−2803.03	−2881.26	−2963.22	1.03
Glycine	$C_2H_5O_2N(c) + 2.25O_2(g) \rightarrow 2CO_2(g) + 2.5H_2O(l) + 0.5N_2(g)$	−973.49	−1013.19	−1031.60	1.02
L-Glutamic acid	$C_5H_9O_4N(c) + 5.25O_2(g) \rightarrow 5CO_2(g) + 4.5H_2O(l) + 0.5N_2(g)$	−2243.46	−2307.35	−2372.09	1.03
L-Glutamine	$C_5H_{10}O_3N_2(c) + 6O_2(g) \rightarrow 5CO_2(g) + 5H_2O(l) + N_2(g)$	−2571.07	−2620.66	−2699.76	1.03
Glycylglycine	$C_4H_9O_3N_2(c) + 4.75O_2(g) \rightarrow 4CO_2(g) + 4.5H_2O(l) + N_2(g)$	−1970.45	−2032.10	−2080.66	1.02
L-Leucine	$C_6H_{13}O_2N(c) + 8.25O_2(g) \rightarrow 6CO_2(g) + 6.5H_2O(l) + 0.5N_2(g)$	−3583.13	−3561.94	−3719.49	1.04
Palmitic acid	$C_{16}H_{32}O_2(c) + 23O_2(g) \rightarrow 16CO_2(g) + 16H_2O(l)$	−9977.83	−9789.70	−10301.46	1.05
L-Phenylalanine	$C_9H_{11}O_2N(c) + 10.75O_2(g) \rightarrow 9CO_2(g) + 5.5H_2O(l) + 0.5N_2(g)$	−4645.49	−4641.21	−4834.03	1.04
L-Proline	$C_5H_9O_2N(c) + 6.25O_2(g) \rightarrow 5CO_2(g) + 4.5H_2O(l) + 0.5N_2(g)$	−2727.97	−2737.89	−2852.52	1.04
L-Serine	$C_3H_7O_3N(c) + 3.75O_2(g) \rightarrow 3CO_2(g) + 4.5H_2O(l) + 0.5N_2(g)$	−1454.78	−1455.61	−1534.13	1.05
Succinic acid	$C_4H_6O_4(c) + 3.5O_2(g) \rightarrow 4CO_2(g) + 3H_2O(l)$	−1491.01	−1544.58	−1589.69	1.03
Sucrose	$C_{12}H_{22}O_{11}(c) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)$	−5640.87	−5784.20	−5950.74	1.03
L-Tryptophan	$C_{11}H_{12}O_2N(c) + 13O_2(g) \rightarrow 11CO_2(g) + 6H_2O(l) + 0.5N_2(g)$	−5551.67	−5639.23	−5856.33	1.04
L-Tyrosine	$C_9H_{11}O_3N(c) + 10.25O_2(g) \rightarrow 9CO_2(g) + 5.5H_2O(l) + 0.5N_2(g)$	−4430.02	−4456.21	−4625.33	1.04
L-Valine	$C_5H_{11}O_2N(c) + 6.75O_2(g) \rightarrow 5CO_2(g) + 5.5H_2O(l) + 0.5N_2(g)$	−2919.59	−2915.37	−3036.59	1.04
					Average: 1.03 ± 0.01, *n* = 17

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[a] Values for $T^\circ\Delta_c S^\circ$ or $\Delta_c Q^\circ$ have been taken from Table 4.

[b] Values for $\Delta_c H^\circ$ have all been taken from Ref. [27].

[c] Values for $\Delta_c G^\circ$ were calculated using the equation $\Delta_c G^\circ = \Delta_c H^\circ - T^\circ\Delta_c S^\circ$.

[d] Values for $\Delta_c G^\circ_{\Delta Q}$ were calculated using the equation $\Delta_c G^\circ_{\Delta Q} = \Delta_c H^\circ - \Delta_c Q^\circ$.

Table 7
A comparison of the free energy changes accompanying the theoretical fermentation in their standard states of organic substances of catabolic importance as calculated using $T^\circ\Delta_p S^\circ$ or $\Delta_p Q^\circ$

Fermentation		$\Delta_p H$[a] (kJ mol^{-1})	$\Delta_p G^{\circ}$[b] (kJ mol^{-1})	$\Delta_p G^{\circ}_{\Delta Q}$[c] (kJ mol^{-1})	$\Delta_p G^{\circ}/\Delta_p G^{\circ}_{\Delta Q}$ (kJ mol^{-1})
Ethanolic[d]	$C_6H_{12}O_6(c)_{\text{Glucose}} \rightarrow 2CO_2(g) + 2C_2H_6O(l)_{\text{Ethanol}}$	−69.38	−230.63	−157.86	1.46
Methanogenic[e]	$C_2H_4O_2(l)_{\text{Acetic acid}} \rightarrow CH_4(g)_{\text{Methane}} + CO_2(g)$	15.81	−56.36	−11.55	4.88
Homoacetate[f]	$C_6H_{12}O_6(c)_{\text{Glucose}} \rightarrow 3C_2H_4O_2(l)_{\text{Acetic acid}}$	−179.37	−258.32	−231.26	1.11
Stickland[g]	$C_3H_7O_2N(c)_{\text{Alanine}} + 2C_2H_5O_2N(c)_{\text{Glycine}} \rightarrow 3NH_3(g) + 3C_2H_4O_2(l)_{\text{Acetic acid}} + CO_2(g)$	−367.03	−505.17	−517.49	0.98
Propionate[h]	$C_6H_{12}O_6(c)_{\text{Glucose}} \rightarrow C_2H_4O_2(l)_{\text{Acetic acid}} + C_3H_6O_2(l)_{\text{Propionic acid}} + CO_2(g)$	−115.36	−259.75	−189.27	1.37
Butyrate[i]	$C_2H_6O(l)_{\text{Ethanol}} + C_2H_4O_2(l)_{\text{Acetic acid}} \rightarrow C_4H_8O_2(l)_{\text{Butyric acid}} + H_2O(l)$	−57.85	−50.71	−57.68	0.88

[a] $\Delta_p H^\circ = \sum \Delta_f H^\circ_{\text{prod}} - \sum \Delta_f H^\circ_{\text{react}}$. The $\Delta_f H^\circ$ data were taken from Ref. [27].
[b] $\Delta_p G^\circ_{T\Delta S} = \Delta_p H^\circ - T^\circ \Delta_p S^\circ$. The data for the last term were taken from Table 5.
[c] $\Delta_p G^\circ_{Q} = \Delta_p H^\circ - \Delta_p Q^\circ$. The data for the last term were taken from Table 5.
[d] *Saccharomyces cerevisiae.*
[e] *Methanosarcina barkeri.*
[f] *Clostridium thermoaceticum.*
[g] *Clostridium* sp.
[h] *Veillonella* sp.
[i] Many gram-negative, anaerobic bacteria.

$\Delta_c G^\circ_{\Delta Q}$ averaged 1.04±0.01 times more negative than those for $\Delta_c G^\circ$, with a range 1.02–1.06. For the 17 solids studied, values for $\Delta_c G^\circ_{\Delta Q}$ averaged 1.03±0.01 times more negative than those for $\Delta_c G^\circ$, with a range 1.02–1.05.

In Table 7, for fermentative processes these differences can be vastly greater. Here the symbol $\Delta_p Q^\circ$ is used rather than $\Delta_f Q^\circ$ ('f' for "fermentations") because this latter has already a different meaning. The data show that for the six fermentations studied, the values for $\Delta_p G^\circ$ average 1.61 ± 1.62 times more negative than those for $\Delta_p G^\circ_{\Delta Q}$, with a range 4.87–0.88. These differences are large compared to those obtained with bomb calorimetric oxidations.

4. Discussion

In Ref. [2], the function Nintegrate in the computer program Mathematica (v. 2.2 Wolfrom Research, Inc., Champaign, IL, USA) was used for integrating the curves of C_p vs T and C_p vs $\ln T$ for the substances cited, with the result that the ratio $T^\circ S^\circ/Q^\circ$ was in all but one case equal to 1.993. Nintegrate applied to a function $f(x)$ provides a numerical approximation of the integral of $f(x)$, resulting in best fit curves of the linear and the exponential relation and yielding the above ratio. This is close to the theoretical value of 2.000 obtained for this ratio if C_p vs T is a straight line. However, it was noted in Ref. [2] that the value of 1.993 was only in good approximate agreement with the experimental values. The C_p vs T curves for the substances studied here are not linear, although for solid substances this may be closely approximated. In Table 2, the values for Q° and S° were obtained by numerical integration, not by mathematical modeling. The result is that the values for $T^\circ S^\circ/Q^\circ$ in column 6 of Table 2 are not 1.993 for the solid organic substances studied, as in Ref. [1], but can vary from 1.877 to 2.025 (ave. = 1.955). For organic liquids this ratio varies from 1.508 to 1.980, and for gases from 1.467 to 4.335. Thus, although there is clearly an inequality between $T^\circ S^\circ$ and Q°, as emphasized in Ref. [2], this inequality is highly variable with respect to different substances and will have an effect on the calculation of $\Delta_f Q^\circ$ values as compared to $T^\circ \Delta_f S^\circ$.

4.1. Absorbed thermal energy exchange

During a spontaneous reaction or process, there is an exchange of absorbed thermal energy with the environment because the physical qualities of the products of a reaction are different from those of the reactants. Each reactant or product requires a certain quantity of thermal energy to be absorbed for it to exist at a given temperature. As reactants disappear from the reaction system, their absorbed thermal energy becomes released into the environment. As products are formed within the reaction system, they must absorb thermal energy from the environment in order to exist at the temperature of the system. At a constant T and p with regard to the initial and final states of a reaction, the difference between the quantity of thermal energy released into the environment by the reactants and that absorbed by the products is the total quantity of absorbed thermal energy exchanged with the environment. One way of expressing this is the following, which relates C_p to T (K) with the upper bound being $T^\circ = 298.15\,\mathrm{K}$.

$$\begin{aligned}\Delta H^\circ_{\mathrm{ab}} &= \sum\left(\int_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} C_p\,\mathrm{d}T + \sum \Delta_{\mathrm{trs}} H^\circ\right)_{\mathrm{prod}} \\ &\quad - \sum\left(\int_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} C_p\,\mathrm{d}T + \sum \Delta_{\mathrm{trs}} H^\circ\right)_{\mathrm{react}} \\ &= \sum (H^\circ_{298.15\,\mathrm{K}} - H^\circ_{0\,\mathrm{K}})_{\mathrm{prod}} \\ &\quad - \sum (H^\circ_{298.15\,\mathrm{K}} - H^\circ_{0\,\mathrm{K}})_{\mathrm{react}} \\ &= \sum Q^\circ_{\mathrm{prod}} - \sum Q^\circ_{\mathrm{react}} = \Delta Q^\circ \end{aligned} \tag{11}$$

where $\Delta H^\circ_{\mathrm{ab}}$ represents the change in the absorbed thermal energy, which is equivalent to ΔQ°. This last is the most simple way of representing the absorbed heat exchange. All values are in $\mathrm{kJ\,mol^{-1}}$.

Another way of calculating $\Delta H^\circ_{\mathrm{ab}}$ is first to calculate the change in entropy of a system as the result of a reaction or process, and to then multiply it by the temperature for which the entropy change has been calculated. This method relates heat capacity as a function of $\ln T$ (K) rather than T (K) as is done above.

$$\begin{aligned}\Delta S^\circ &= \sum\left(\int_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} C_p\,\mathrm{d}\ln T + \sum \Delta_{\mathrm{trs}} S^\circ\right)_{\mathrm{prod}} \\ &\quad - \sum\left(\int_{0\,\mathrm{K}}^{298.15\,\mathrm{K}} C_p\,\mathrm{d}\ln T + \sum \Delta_{\mathrm{trs}} S^\circ\right)_{\mathrm{react}} \\ &= \sum S^\circ_{\mathrm{prod}} - \sum S^\circ_{\mathrm{react}} \end{aligned} \tag{12}$$

Because $\ln T$ is dimensionless, ΔS° has the dimensions of C_p, which are $\mathrm{J\,K^{-1}\,mol^{-1}}$ or $\mathrm{J\,g^{-1}\,mol^{-1}}$ and does not represent energy. It becomes a quantity of energy when multiplied by the upper limit of T for which the entropy value was calculated. For standard conditions $T = T^\circ$. Thus, using entropy

$$\Delta H^\circ_{\mathrm{ab}} = T^\circ\left(\sum S^\circ_{\mathrm{prod}} - \sum S^\circ_{\mathrm{react}}\right) = T^\circ \Delta S^\circ \tag{13}$$

From an inspection of Eqs. (11) and (13) it might appear that $\Delta Q^\circ = T^\circ \Delta S^\circ$, since they both represent the exchange of absorbed heat with the environment (i.e., $\Delta H^\circ_{\mathrm{ab}}$) and both make use of the same C_p. However, as shown in Tables 4 and 5, the quantity of absorbed heat that is exchanged is greatly different depending on whether Eqs. (11) or (13) is used for the calculation and can even be different in sign. Obviously, there cannot be two different quantities of absorbed heat exchanged during the same reaction at the same T and p.

4.2. Generated thermal energy exchange

For combustion processes, the absorbed thermal energy exchange accounts for only a small part of the total thermal energy exchange comprising ΔH°, although this is not true for many fermentation processes. Most of the thermal energy comprising ΔH° is the result of the conversion of chemical, non-thermal energy into thermal energy as a result of a spontaneous reaction or process, and can be called ‘generated’ thermal energy. The quantity of heat exchanged with the environment is thus the sum of the absorbed thermal energy exchange and the generated thermal energy exchange. The non-thermal energy equivalent of the generated thermal energy is called the free energy, or free enthalpy.

It is perhaps unfortunate that the symbol “H” is used in two different ways. With respect to absorbed heat, the symbol appears in the term $(H^\circ_{298.15\,\mathrm{K}} - H^\circ_{0\,\mathrm{K}})$ representing the heat content. This term does not involve any heat exchange resulting from the degradation of chemical energy to heat. With respect to the heat of reaction, ΔH° equals either $\Delta G^\circ + T^\circ \Delta S^\circ$, using Eq. (1), or $\Delta G^\circ_{\Delta Q} + \Delta Q^\circ$, using Eq. (2). The heat exchange measured during a combustion or fermentation is then the sum of two thermal energy exchanges. Conventionally, in chemical thermodynamics ΔG° represents non-thermal chemical energy that becomes converted to thermal energy during a spontaneous process as this passes from an initial to a final state. ΔQ° represents the change in heat content of the system, i.e., the change in the quantity of thermal energy that is necessary for the system to exist physically at T°, during the same process. This can be represented by the combustion of glucose.

$$C_6H_{12}O_6(c) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \quad (14)$$

As glucose and oxygen are consumed as reactants, the thermal energy required for them to exist at the initial temperature of 298.15 K, $\sum Q^\circ_{\text{react}}$, is released from their masses as heat. As carbon dioxide and water are formed as products, the quantity of thermal energy required for them to exist at the final temperature of 298.15 K, $\sum Q^\circ_{\text{prod}}$, is absorbed as heat. The difference, $\sum Q^\circ_{\text{prod}} - \sum Q^\circ_{\text{react}}$, equals ΔQ°. The thermal exchange accompanying the reaction represented by Eq. (14) is then

(1) The heat formed during the degradation of non-thermal chemical energy (ΔG° or $\Delta G^\circ_{\Delta Q}$) to thermal energy. This is a manifestation of a chemical change

$$\Delta H^\circ = + \quad (15)$$

(2) The exchange of absorbed heat ($T^\circ\Delta S^\circ$ or ΔQ°) resulting from the change in the absorbed heat of the reactants to that of the products during the course of the reaction.

4.3. *Calculating free energy changes*

In the Gibbs free energy equation, the generated thermal energy exchange accompanying combustion under standard conditions is represented as ΔG° and the absorbed thermal energy exchange is represented as $T^\circ\Delta S^\circ$ (Eq. (13)). This results in Eq. (1).

$$\Delta G^\circ = \Delta H^\circ - T^\circ \Delta S^\circ \quad (1)$$

The absorbed thermal energy can also be represented as ΔQ° (Eq. (11)), rather than $T^\circ\Delta S^\circ$, so that

$$\Delta G^\circ_{\Delta Q} = \Delta H^\circ - \Delta Q^\circ \quad (2)$$

For irreversible processes such as catabolic oxidations or fermentations, ΔH° has the same value with respect to either Eqs. (1) or (2). Thus, because of the inequality of $T^\circ\Delta S^\circ$ and ΔQ°, the value for ΔG° as calculated with Eq. (1) will be different from $\Delta G^\circ_{\Delta Q}$ as calculated using Eq. (2). This is shown in columns 4 and 5 of Tables 6 and 7. Obviously, there cannot be two different values for ΔG° accompanying the same process. The question then arises as to which is more correct. Certainly Eq. (2) represents the most direct approach to calculating ΔG°. Both ΔH° for a process and the values of Q° for the reactants and products of the process can be determined by direct thermal analyses. With Eq. (1), whereas ΔH° can be determined directly, even though the same C_p data are used, values of S° must be calculated and then multiplied by T°. This is less direct. Also, as emphasized in Refs. [1,2], S° is a mathematical function. The multiplication of S° by T° gives a thermal quantity that is different from Q° simply because the calculation of S° is a different mathematical operation. It is not that either *calculation* is wrong, per se.

4.4. *ΔG° or $\Delta G^\circ_{\Delta Q}$?*

From the results of calculations in Table 6, it is evident that using Eq. (2) gives free energy changes that average about 4% more negative than when using Eq. (1) for the liquids studied, and about 3% more negative for the solids studied. Are these significant enough average differences that in calculating free energy changes Eq. (2) should be used rather than Eq. (1)? A reasonable answer is, “possibly not”, based on the data in Table 6 alone. These differences might be expected to be small because the ΔH° for oxidative reactions is very much larger than either $T^\circ\Delta S^\circ$ or ΔQ°. This is not true for fermentative processes. The data in Table 7, while involving a small number of examples, certainly show that there can be highly significant differences between the use of Eqs. (1) and (2). In addition, with these fermentation examples, in four cases the free energy changes are calculated to be less negative when using Eq. (2) than they are when using Eq. (1), in contrast to the oxidative examples in Table 6. Clearly, the whole approach to making these two calculations is fundamentally different, and significant to the extent that this is shown in Tables 6 and 7. In this respect, different symbols should be used for the free energy changes calculated using Eqs. (1) and (2).

4.5. *The choice of a symbol to replace $\Delta G^\circ_{\Delta Q}$*

The symbol $\Delta G^\circ_{\Delta Q}$ does not represent Gibbs free energy, which should continue to be represented conventionally by ΔG°. The symbol $\Delta G^\circ_{\Delta Q}$ represents a different thermodynamic quantity from ΔG°, is calculated in a different way, and if possible should be represented by a single letter symbol. The symbol least used in the “Green Book” [28] is the symbol ‘X’, representing only two entities, electrical reactance and the ‘x-unit’. This symbol can hardly be confused with anything in chemical or biological thermodynamics. Therefore, its adoption is suggested as a replacement for $\Delta G^\circ_{\Delta Q}$. Eq. (2) then becomes

$$\Delta X^\circ = \Delta H^\circ - \Delta Q^\circ \tag{16}$$

Here ΔX° represents the free energy change calculated using ΔQ° rather than $T^\circ \Delta S^\circ$, and taken as the quantity of non-thermal chemical energy that becomes converted into thermal energy during the course of a reaction or process. The data in Tables 6 and 7 indicate that, at least for the spontaneous reactions and fermentations studied, $\Delta G^\circ_{\Delta Q}$ $(= \Delta X^\circ)$ is always negative, just as is ΔG°. Thus, empirically it is possible, although not proven, that a negative ΔX°, just as a negative ΔG°, is an indicator of a spontaneous reaction. This might be predicted in that both $T^\circ \Delta S^\circ$ and ΔQ° for a given reaction are derived from the same data. It seems reasonable to suggest that for a spontaneous process as calculated either with $T^\circ \Delta S^\circ$ or ΔQ°, some chemical or physical non-thermal energy *must* be converted into heat, which then becomes a part of the thermal energy exchanged between the system and the environment. ΔH° has its usual meaning of the total quantity of thermal energy exchanged between the system and its environment. For a spontaneous process, the sign of ΔH° can be either positive, negative, or zero, but is usually negative. ΔQ° represents the change in the quantity of thermal energy absorbed by the system (heat content) because the quantity of heat absorbed by the reactants at a given temperature is different from that absorbed by the products at the same temperature. For a spontaneous process, the sign of ΔQ° can be positive, negative, or zero. Symbols other than X for the free energy can also be considered, if there is a good reason for doing so. In any case, it is important to represent non-thermal chemical energy that becomes transformed into thermal energy as being different from a change in absorbed thermal energy.

Eq. (16) is certainly more simple both in construction and use than Eq. (1). Whether W. Gibbs would approve of this is conjectural, although in a letter to the National Academy of Sciences in January of 1881 he wrote, “One of the principal objects of theoretical research in any department of knowledge is to find the point of view from which the subject appears in its greatest simplicity”. [29].

The information presented above has been presented previously in a more brief form, and at an earlier stage at in its evolution [30]. The results of this study suggest strongly that a further study of the thermodynamics of microbial growth using Eq. (16) is worth doing, using biological, aqueous standard states [31].

5. Conclusion

The use of the equation $\Delta X^\circ = \Delta H^\circ - \Delta Q^\circ$, where ΔX° represents the free energy change calculated using ΔQ° rather than $T^\circ \Delta S^\circ$, is an alternate method of calculating free energy changes. This is based on the interpretation that Q° is a more accurate measure of the quantity of heat absorbed in order that a mass can exist at the standard temperature than is $T^\circ S^\circ$.

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