The Correlation of Standard Entropy with Enthalpy Supplied from 0 to 298.15 K

Frank L. Lambert*
Department of Chemistry, Occidental College, Los Angeles, CA 90041; **flambert@att.net*

Harvey S. Leff
Department of Physics, California State Polytechnic University, Pomona, CA 91768

It takes energy to heat a substance from near absolute zero to standard room temperature, 298.15 K. As heating progresses, the substance's entropy increases from zero (as dictated by the third law of thermodynamics) to a standard entropy $S°$ for the substance. For each substance, the standard entropy is the sum of reversible small increments dH divided by temperature T for the heating process. That is, the standard entropy $S°$ is a function of the added energy, namely, the total enthalpy $\Delta H°$ delivered during heating. This energy spreads spatially throughout the solid and is stored within it. The entropy function can be usefully interpreted as a *spreading* function, with the symbol S connoting spreading, as clarified below *(1, 2)*. Along similar lines, the term *energy dispersal*, rather than spreading, has been used *(3, 4)*.

In addition to the interpretation of an entropy change ΔS in terms of a *spatial* redistribution of energy in a thermodynamic process, there is a complementary interpretation of S for a thermodynamic equilibrium state: S reflects the extent to which a substance jumps from one accessible quantum microstate to another as time passes—for example, over a measurement's observation time.[1] This is *temporal spreading* of the system's instantaneous microstate over some number, say W, of microstates with energies in a narrow energy range near the internal energy U. The system can be in any of the W microstates for a given thermodynamic macrostate defined by temperature, pressure, and mole number.

The spreading concept has much support, with numerous examples illustrating its validity. Temporal spreading is consistent with, and supported by, the Boltzmann–Planck entropy expression $S° = k_B \ln W°$ *(4)*, where $W°$ is the number of microstates that become occupied sequentially in time under standard temperature and pressure and k_B is the Boltzmann constant. The *spatial spreading* notion has been used to derive the Clausius entropy expression, $dS = Dq_{rev}/T$, which is known to give results that are consistent with the Boltzmann–Planck entropy *(1, 2)*. Because spatial and temporal spreading explicitly entail energy considerations, the concept can be a useful tool for understanding aspects of entropy.

Here, we report an investigation of the entropy–energy connection by examining the energy needed to raise a substance from (nearly) absolute zero temperature to $T° = 298.15$ K reversibly at atmospheric pressure 1.013×10^5 Pa. This energy is $\Delta H°$, the enthalpy delivered to the system,

$$\Delta H^\circ \;=\; \int_0^{T^\circ} C_p(T)\,\mathrm{d}T \qquad (1)$$

$C_p(T)$ is the constant-pressure, temperature-dependent molar heat capacity, which has been measured for diverse substances over many years. Accounting for the third law of thermodynamics statement that a substance's entropy approaches zero as $T \rightarrow 0$ K, the entropy change during the heating process is

$$S^\circ \;\equiv\; S\left(T^\circ\right) \;=\; \int_0^{T^\circ} \frac{C_p(T)}{T}\,\mathrm{d}T \qquad (2)$$

Equations 1 and 2 are used to calculate the enthalpy input $\Delta H°$ for (0, $T°$) and the *standard* entropy at temperature $T°$ and atmospheric pressure. In this article, we focus attention on 77 substances that are solids under standard conditions *(5–23)*.

As a substance is heated, the absorbed energy spreads spatially throughout the volume of the material. From a classical viewpoint, the average kinetic and potential energies within the substance are expected to increase. From a quantum mechanical view, the substance is excited continually to higher system energy states, where the system's density of states is greater and more energy states become accessible. From the first law of thermodynamics, the substance's internal energy change is $\Delta U° = \Delta H° - w$, where w is the net work done *by* the substance. However, for substances that remain solid to 298.15 K, the work w is due to typically small volume changes from thermal expansion (or contraction), so $|w| << \Delta H°$ and to a good approximation $\Delta U° \approx \Delta H°$. Thus, essentially all the energy supplied during heating is stored within a solid as internal energy.

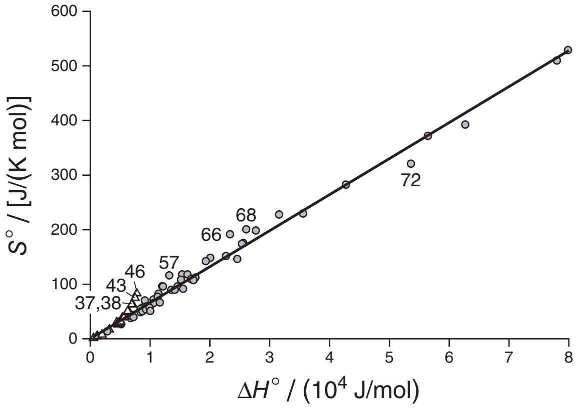

Figure 1. Standard entropy vs enthalpy for solids 1–76 listed in Table 1. Data points for monatomic solids (except iodine, which forms I_2 units) are connoted by triangles and other data points by shaded circles. Substance numbers are shown for six data points that are farthest from the best-fit line. These are discussed explicitly in the online material.

Findings

Beginning this project, we hypothesized that standard entropies would be correlated only crudely with the energy added because various factors might cause $S°$ to increase nonlinearly with greater $\Delta H°$ values. The data in Table 1 indicate that not only was this hypothesis incorrect, but the plot in Figure 1 shows that many of the data points hover near the linear regression best-fit line, defined by

$$\frac{S°}{\Delta H°} = 0.0066\ \mathrm{K}^{-1} \qquad (3)$$

for an extremely broad range of substance sizes and types. The strong linear correlation of entropy and enthalpy supplied is visually evident in Figure 1 and is supported by the value $R^2 = 0.9863$.[2]

It is indeed notable that the standard molar entropy is very nearly proportional to the enthalpy input from 0 → 298.15 K for such a wide variety of solids. Equation 3 can be used to quickly estimate the standard entropy of a solid, within 10 percent for over half the listed substances, given their enthalpy values.[3] Therefore, Figure 1 and eq 3 illustrate important connections between entropy and the concomitant internal energy stored by solids: The standard entropy of many solids is linearly linked to the quantity of energy needed to bring them from near absolute zero to room temperature at atmospheric pressure. The energy added has spread throughout and is stored within the solid. This provides a straightforward *physical* interpretation of entropy, without recourse to "disorder" or "randomness".

Table 1. Enthalpy ($\Delta H°$ for 0 → 298.15 K) and $S°$ for Solids

Substance	Name	Formula	$\Delta H°$/ (J mol^{-1})	$S°$/ (J K^{-1} mol^{-1})	Lit Citation
1	Carbon (diamond)	C	520	2.36	*6*
2	Carbon (graphite)	C	1060	5.7	*7*
3	Boron	B	1220	5.9	*5*
4	Beryllium	Be	1950	9.5	*5*
5	Beryllium oxide	BeO	2840	13.8	*5*
6	Silicon	Si	3180	18.8	*8*
7	Magnesium oxide	MgO	5160	27.0	*5*
8	Aluminum	Al	4610	28.3	*9*
9	Lithium	Li	4630	29.1	*5*
10	Titanium	Ti	4820	30.7	*5*
11	Germanium	Ge	4640	31.1	*5*
12	Sulfur	S	4410	32.1	*5*
13	Magnesium	Mg	5000	32.7	*5*
14	Copper	Cu	5070	33.2	*9*
15	Calcium oxide	CaO	6750	38.1	*5*
16	Germanium dioxide	GeO_2	7230	39.7	*5*
17	Phosphorus	P	5360	41.1	*5*
18	Silicon dioxide	SiO_2	6920	41.5	*5*
19	Calcium	Ca	5740	41.6	*5*
20	Zinc	Zn	5660	41.6	*5*
21	Platinum	Pt	5730	41.7	*8*
22	Silver	Ag	5750	42.6	*5*
23	Zinc oxide	ZnO	6930	43.7	*5*
24	Stannic dioxide	SnO_2	8380	49.0	*5*
25	Uranium	U	6360	50.2	*5*
26	Titanium dioxide	TiO_2	8680	50.6	*5*
27	Aluminum oxide	Al_2O_3	10020	50.9	*5*
28	Tin	Sn	6320	51.2	*5*
29	Sodium	Na	6460	51.3	*5*
30	Thorium	Th	6350	51.8	*5*
31	Cadmium	Cd	6250	51.8	*5*
32	Boric oxide	B_2O_3	9300	54.0	*5*
33	Cadmium monoxide	CdO	8410	54.8	*5*
34	Stannic oxide	SnO	8740	57.2	*5*
35	Magnesium fluoride	MgF_2	9910	57.2	*5*
36	Lithium chloride	LiCl	9420	59.3	*8*
37	Potassium	K	7090	64.7	*5*
38	Lead	Pb	6940	64.8	*10*
39	Thorium oxide	ThO_2	10560	65.2	*5*
40	Aluminum fluoride	AlF_3	11620	66.5	*5*
41	Mercury oxide	HgO	9120	70.3	*5*
42	Sodium chloride	NaCl	10560	72.1	*11*
43	Rubidium	Rb	7490	76.8	*5*
44	Uranium dioxide	UO_2	11280	77.0	*5*
45	Potassium chloride	KCl	11400	82.6	*12*
46	Cesium	Cs	7770	85.2	*8*
47	Magnesium chloride	$MgCl_2$	14120	89.6	*13*
48	Boric acid	H_3BO_3	13520	90.0	*5*
49	Magnesium sulfate	$MgSO_4$	15500	91.6	*14*
50	Potassium bromide	KBr	12150	95.9	*11*
51	Uranium trioxide	UO_3	14590	96.1	*5*
52	Silver chloride	AgCl	12030	96.3	*5*
53	Ferrous sulfate	$FeSO_4$	17250	107.6	*14*
54	Calcium chloride	$CaCl_2$	15170	108.4	*13*
55	Copper sulfate	$CuSO_4$	16860	109.2	*5*
56	Manganese sulfate	$MnSO_4$	17580	112.1	*14*
57	Iodine	I_2	13200	116.1	*5*
58	Ferrous chloride	$FeCl_2$	16220	118.0	*13*
59	Manganese chloride	$MnCl_2$	15340	118.2	*13*
60	Ferric chloride	$FeCl_3$	19300	142.3	*15*
61	Ferrous oxide	Fe_3O_4	24550	146.4	*16*
62	Lead sulfate	$PbSO_4$	20050	148.5	*5*
63	Uranium fluoride	UF_4	22670	151.7	*17*
64	1,4-Dichlorobenzene	$C_6H_4Cl_2$	25340	174.0	*18*
65	Potassium sulfate	K_2SO_4	25570	175.6	*14*
66	Mercurous chloride	Hg_2Cl_2	23350	191.6	*5*
67	1,3,5-Trichlorobenzene	$C_6H_4Cl_2$	27670	198.0	*18*
68	Mercurous sulfate	Hg_2SO_4	26070	200.7	*5*
69	Uranium hexafluoride	UF_6	31570	227.6	*17*
70	Cadmium sulfate	$CdSO_4 \cdot 8/3H_2O$	35560	229.7	*5*
71	Triuranium octoxide	U_3O_8	42740	282.6	*5*
72	Uvarovite	$Ca_3Cr_2Si_3O_{12}$	53600	320.9	*19*
73	Tridecanol	$C_{13}H_{27}OH$	56450	371.7	*20*
74	Sucrose	$C_{12}H_{22}O_{11}$	62690	392.4	*21*
75	Nonadecane	$C_{19}H_{40}$	78000	510.0	*22*
76	Eicosane	$C_{20}H_{42}$	79880	529.0	*22*
77	Tripalmitin	$C_{51}H_{98}O_6$	204020	1365.0	*23*

Why the Correlation Line Has a Slope of 0.0066 K^{-1}

The reason that the value of the slope in eq 3 is 0.0066 K^{-1}, at least in broad-brush strokes, is as follows. Because the maximum heat capacity of solids increases with Z, the number of atoms or ions per unit, complex solids with $Z > 1$ per unit have higher heat capacity, entropy, and enthalpy at room temperature. The data in Figures 2 and 3 show that for sufficiently complex solids, the maximum heat capacity is not reached until temperatures much higher than 300 K, and C_p becomes roughly a straight line beginning at the origin, as dictated by the third law of thermodynamics. In such cases, where $C_p \approx AT$, with A = constant, the implied entropy-to-enthalpy ratio is

$$\frac{S^\circ}{\Delta H^\circ} = \frac{\int_0^{T^\circ} \left(C_p/T\right) \mathrm{d}T}{\int_0^{T^\circ} T\left(C_p/T\right) \mathrm{d}T} \approx \frac{\int_0^{T^\circ} A \,\mathrm{d}T}{\int_0^{T^\circ} A\,T \,\mathrm{d}T} \qquad (4)$$

$$= \frac{1}{T^\circ/2} = 0.0067 \ \ \mathrm{K}^{-1}$$

This result is in good agreement with the entropy-to-enthalpy ratio for points on the best-fit line in Figure 1. We conclude that solids for which the heat capacity can be approximated by a linear heat capacity will have their (ΔH°, S°) points close to the best-fit line.

Notably, this group primarily consists of complex organic substances. More generally, to describe any solid substance, the ratio $S^\circ/\Delta H^\circ$ can be written as

$$\frac{S^\circ}{\Delta H^\circ} = \frac{S^\circ}{\int_0^{T^\circ} T\left(C_p/T\right) \mathrm{d}T} = \frac{1}{\int_0^{T^\circ} T\, f(T) \,\mathrm{d}T} = \frac{1}{\langle T \rangle} \qquad (5)$$

where

$$\langle T \rangle = \int_0^{T^\circ} T\, f(T)\, \mathrm{d}T$$

$\langle T \rangle$ is an *average* temperature and calculated using the (unconventional, but mathematically convenient) "distribution function",

$$f(T) \equiv \frac{C_p(T)}{T\,S^\circ} \quad \text{for} \quad 0 \le T \le T^\circ \qquad (6)$$

Empirical data show that $C_p(T)/T \propto T^2$ for $T \rightarrow 0$, then peaks at some value of T and decreases as T increases further.

A simple, albeit coarse, estimate $\langle T \rangle_{\mathrm{est}}$ is the *arithmetic mean* of the minimum and maximum temperatures during heating, that is, $\langle T \rangle_{\mathrm{est}} = ½(0 + 298.15) = 149.57$ K, which immediately yields $1/\langle T \rangle_{\mathrm{est}} = 0.0067$. This is not surprising because if $C_p = AT$ (as discussed above), the distribution function $f(T)$ is constant, which implies that $\langle T \rangle$ is given by the arithmetic mean above. Solids whose data points lie near the best-fit line in Figure 1 have heat capacities and corresponding distribution functions $f(T)$ that imply average temperatures $\langle T \rangle \approx 149$ K.

Because C_p is in both the numerator and denominator of eq 4, the entropy-to-enthalpy ratio is relatively insensitive to small changes in $C_p(T)$, which contributes to the phenomenon of many solids having their data points near the best-fit line in Figure 1.[4] It is also true that changes in $C_p(T)$, especially at higher temperatures, typically change ΔH° more than S° because of the factor $1/T$ in the integrand of eq 2. Deviations from the best-fit line are extensively addressed in the online material.

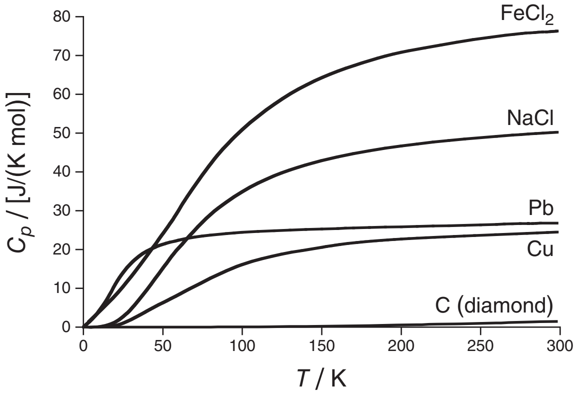

Figure 2. Molar heat capacity vs temperature for three monatomic solids, a solid with $Z = 2$ atoms per unit, and a solid with $Z = 3$ atoms per unit, as described in the text. Note that the maximum molar heat capacity, $C_p(T^\circ) < 80$ J K^{-1}mol^{-1}.

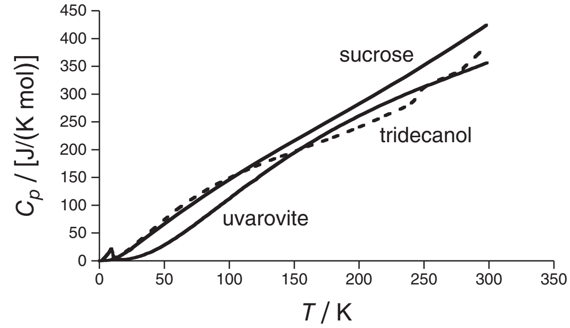

Figure 3. Molar heat capacity vs temperature for three polyatomic solids: uvarovite ($Ca_3Cr_2Si_3O_{12}$); sucrose ($C_{12}H_{22}O_{11}$); and tridecanol ($C_{13}H_{27}OH$). For each solid substance, the Debye temperature is much larger than 300 K. Note that the maximum molar heat capacity is over 400 J K^{-1}mol^{-1}, compared with the maximum less than 80 J K^{-1}mol^{-1} in Figure 2.

Influence of Variations in Heat Capacity on Standard Entropy

Given that both ΔH° and S° depend critically on the behavior of the molar heat capacity[5] of substances as a function of T, it is useful to examine differences between the heat capacities of five solids for the temperature interval, 0 → 298.15 K. A graph of $C_p(T)$ versus T for these archetypal solids is shown in Figure 2.

The solid with the smallest heat capacity in this temperature range is diamond, which has the smallest volume per atom and exceptionally strong forces between adjacent atoms. Because of its relatively low mass and closely spaced atoms, quantum effects exist from near 0 K to diamond's unusually high Debye temperature, $\Theta_{\mathrm{D}} = 2230$ K.[6] Diamond's high Debye temperature results from its vibrational energy being dominated by high-frequency oscillations. Put differently, diamond's lattice is stiff, as indicated by its exceptional hardness. The relatively small heat capacity in (0, T°) shows that only a correspondingly small energy input is needed to raise diamond's temperature from near 0 K to T°, and diamond's data point (not labeled) in Figure 1 lies below the best-fit line.

Copper's larger atoms are farther apart and less tightly bound to one another, and therefore its heat capacity lies well above that for diamond. Furthermore, for temperatures near 300 K, $C_p(T)$ has nearly reached its classical plateau of $3R + \Delta$, where $\Delta = C_p - C_v > 0$ and C_v is the constant-volume molar heat capacity.[7] This is consistent with the equipartition of energy, namely, each degree of freedom contributes ½R per mole to the heat capacity. Because a 3D oscillator has six degrees of freedom (three each from space and momentum coordinates), the total contribution is $3R$. Copper's data point in Figure 1 lies 1% below the best-fit line.

Lead, with larger atoms than copper, also has a larger volume per atom, weaker interatomic forces, and the relatively low Debye temperature, $\Theta_D \approx 85$ K. In Figure 2, heat capacity of lead can be seen to rise much more rapidly between 0 K and 50 K than that of copper, or that of other substances, such as cesium ($\Theta_D \approx 45$ K) and rubidium ($\Theta_D \approx 60$ K). The larger quantity of energy required at these low temperatures also causes an unusually great entropy increase because C_p/T is relatively large at lower temperatures (see eq 2) and thus, lead's standard entropy is 41% above the best-fit line.

We now consider solids in which there are $Z \geq 2$ atoms or ions per formula unit. The first example is NaCl, with $Z = 2$, which implies that the total number of degrees of freedom is double that for a monatomic solid. Thus, for sufficiently high temperatures, equipartition of energy implies that the maximum constant-volume heat capacity C_v is expected to be $6R$ per mole of di-ionic units.[8] That is, the maximum $C_p = 6R + \Delta$, which is consistent with NaCl in Figure 2. For $FeCl_2$, with 3 ions per unit, the maximum $C_p \approx 9R + \Delta$, which is also evident in Figure 2. The data points for NaCl and $FeCl_2$ in Figure 1 lie 3.4% and 10.3% respectively above the best-fit line.

In general, as the number of atoms, Z, increases, the maximum heat capacity rises and the Debye temperature becomes larger. This is suggested in Figure 2 for substances with $Z = 1$, 2, and 3; that is, one to three atoms per unit. However, for more complex polyatomic solids, especially covalent substances with 20 or more atoms ($Z \geq 20$), the molar heat capacities approach their maximum values only for temperatures far greater than $T°$. Typical heat capacities in the temperature range $(0, T°)$ for three complex polyatomic solids, with $Z = 20$, 42, and 45, are shown in Figure 3. For each, the Debye temperature, $\Theta_D >> 300$ K.

Despite some wiggles for tridecanol and a small cusp associated with an unexplained low-temperature anomaly for uvarovite, the heat capacity curves can be approximated by straight lines to calculate $\Delta H°$ and $S°$. For eicosane ($C_{20}H_{42}$) with $Z = 62$ (substance 76 in Table 1), a graph of heat capacity versus temperature and a linear approximation are shown in Figure 4. Eicosane's entropy lies only 0.3% above the best-fit line. In what follows, we show that the nearly linear behavior of $C_p(T)$ can help us understand why the highly complex polyatomic solids have data points near the best-fit line for $S°$ versus $\Delta H°$ in Figure 1.

The Debye model of a solid depicts a monatomic solid as N atoms linked to other atoms by harmonic forces. Clever mathematics (i.e., a normal mode transformation) transforms the problem into a set of independent 3D harmonic oscillators with an unknown distribution of frequencies, ν. Debye assumed this distribution to be that of continuous acoustic waves, proportional to ν^2, with a maximum "Debye" frequency, ν_D. The corresponding Debye temperature is defined as $\Theta_D \equiv h\nu_D/k_B$, where h is Planck's constant. This definition shows that solids with relatively low Debye temperatures, for example, lead, are limited to relatively low-frequency lattice vibrations. In contrast, diamond, with Debye temperature 2230 K, is dominated by higher-frequency and higher-energy vibrations.

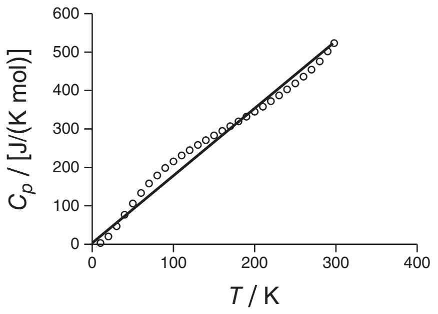

Figure 4. $C_p(T)$ vs T for eicosane (circles) and linear approximation $C_p(T) \approx 1.76\ T$ (solid line). The data imply $S° = 523$ J K^{-1}mol^{-1} and $\Delta H° = 77972$ J mol^{-1}. The approximation implies $S° = 526$ J K^{-1}mol^{-1} and $\Delta H° = 79884$ J mol^{-1}.

In polyatomic covalent solids, individual atoms within each polyatomic molecule are closer together than the larger polyatomic molecules are to one another, and the forces between atoms within a molecule are typically stronger than forces between molecules. Thus, lattice vibrations are excited at lower temperatures and internal vibrations of atoms within molecules are excited significantly only at higher temperatures. At sufficiently low temperatures a system containing N polyatomic molecules, each with Z atoms, behaves similarly to N atoms in the sense that each molecule vibrates about its own lattice site, with internal vibrations within molecules being negligible.[9] As temperature increases, lattice vibrations are accompanied by internal vibrations within the covalent molecules. Consistent with energy equipartition, the maximum molar heat capacity C_v for these atoms is max $C_v = 3ZR$, and thus, max $C_v > 3ZR$. This picture does not account for coupling between the lattice and internal vibrations. It also does not address existing anharmonic forces.[10]

Conclusions and Their Importance in General Chemistry

The stimulus for investigating the data for a number of solids at room temperature was to see how well the entropy of a solid at room temperature correlates with the enthalpy that must be added to the solid from a hypothetical near 0 K to 298.15 K. It is stunning that some monatomic, diatomic, triatomic, and heavy polyatomic ionic solids, as well as complex covalent solids (e.g., tripalmitin[2]) have data points on or near the best-fit line with a slope of 0.0066 K^{-1} in Figure 1. Clearly there is a strong linear correlation between standard entropy $S°$ and energy input $\Delta H°$ over the temperature interval $(0, T°)$.

In general chemistry courses, the standard molar entropy of a substance is usually presented as a number among many in a routine table, with the statement that the liquid and gaseous forms of a solid have successively higher entropy values. We believe the striking visual impact of Figure 1 can help students gain a considerably greater understanding of the nature of entropy. The main point is that the data in Figure 1 show that standard entropy reflects the quantity of energy stored within solid substances at a given temperature.[11] More specifically, the entropy $S°$ of a solid at temperature 298 K and atmospheric pressure is proportional to the quantity of energy stored within it at that temperature, with the proportionality constant

0.0066 K^{-1}. This stored energy has been spread spatially throughout the substance's molecules and is stored in the substance's accessible energy storage modes. Quantum mechanically, the standard entropy can be usefully viewed in terms of the sequential temporal spreading of a substance's instantaneous microstate to any of the other accessible microstates. The spreading metaphor, which entails energy, provides a more accurate picture of entropy than attempts to relate it to the unfortunately vague concept of "disorder". For more advanced students, the latter points can be accompanied by discussions of molar heat capacities, Debye temperatures, and energy storage by lattice vibrations, and internal vibrational and rotational modes within polyatomic units.

In response to some general chemistry texts that emphasize "configurational entropy" by focusing on the "probability of locations" without including the importance of energy, we close with the following observation: Without energy, there would be no thermodynamics and no entropy. Entropy and energy are intimately related concepts that form the underpinning of thermodynamics. Examination of the $S°$ versus $\Delta H°$ graph for solids showcases the energy–entropy relationship.

Acknowledgment

We thank the reviewers for their incisive comments, which led to significant improvement of the manuscript.

Notes

1. Energy exchanges to and from the surroundings cause a solid's instantaneous system microstate to change continually, which constitutes *temporal* spreading. The standard entropy in thermodynamic equilibrium at a given temperature and pressure reflects the number of system states over which the system's instantaneous microstate spreads sequentially during typical observation times.

2. R^2, the square of the correlation coefficient between $S°$ and $\Delta H°$, is one indicator of the goodness of fit. Tripalmitin, $C_{51}H_{98}O_6$, not shown in Figure 1 because its inclusion would have unduly compressed other data points, has the very large values of $\Delta H° = 204022$ J mol^{-1} and $S° = 1365$ J mol^{-1} K^{-1}. Nevertheless, for the latter enthalpy value, the entropy deviates from that predicted by the best-fit line by 1.4%.

3. Some readily explicable deviations from eq 3 exceeding 30% exist. These are reflected in the standard deviation $\sigma = 12.2$ J K^{-1} mol^{-1} for the best-fit line relative to empirical $S°$ values. These deviations are discussed in the online material.

4. Furthermore, under the scale transformation $C_p(T) \rightarrow \lambda C_p(T)$, with $\lambda > 0$, $S°/\Delta H°$ does not change.

5. A good exposition of the heat capacity of ideal gases can be found in ref *24*.

6. Θ_D can be viewed (roughly) as the temperature that separates the heat capacity's classical plateau of approximately $3R$ from the lower temperature quantum region over which $C_p(T)$ increases from 0 K.

7. Typically $\Delta < 0.05\ C_p$.

8. For metals, $C_v(T)$ can exceed $3R$ because of contributions from conduction electrons. This effect is typically less than 0.01 C_v, and is not dealt with explicitly here. $C_v(T)$ can also exceed $3R$ because of anharmonic forces. See note 10.

9. The Debye model has been applied with moderate success to many polyatomic solids for which the atoms in a unit have nearly equal masses, the solid is isotropic, and near-neighbor force constants are of similar strength. In other cases, the Debye model fails, and it is common to assign a Debye temperature $\Theta_D(T)$ to match measured heat capacities for each temperature T.

10. Anharmonicity is necessary to explain theoretically why solids undergo thermal expansion and are thermal conductors. Furthermore, anharmonic forces are needed to explain measured $C_v(T)$ values in excess of $3R$ for some monatomic solids, including Cu at room temperature.

11. This statement is based upon the *specific* comparison of $S°$ and $\Delta H°$ for the *specific* temperature interval (0, 298.15). Figure 1 makes it clear that different solids store energy differently from one another. Generally, in a thermodynamic equilibrium state, S reflects not only the quantity of energy stored, but also *how* that energy is stored.

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