

What if entropy were dimensionless?

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One of entropy's puzzling aspects is its dimensions of energy/temperature. A review of thermodynamics and statistical mechanics leads to six conclusions: (1) Entropy's dimensions are linked to the definition of the Kelvin temperature scale. (2) Entropy can be defined to be dimensionless when temperature T is defined as an energy (dubbed *tempergy*). (3) Dimensionless entropy per particle typically is between 0 and ~ 80 . Its value facilitates comparisons among materials and estimates of the number of accessible states. (4) Using dimensionless entropy and tempergy, Boltzmann's constant k is unnecessary. (5) Tempergy, kT , does not generally represent a stored system energy. (6) When the (extensive) heat capacity $C \gg k$, tempergy is the energy *transfer* required to increase the dimensionless entropy by unity. © 1999 American Association of Physics Teachers.

I. INTRODUCTION

Entropy has many faces. It has been interpreted as a measure of disorder,¹ the unavailability of work,² the degree of energy spreading,³ and the number of accessible microstates⁴ in macroscopic physical systems. While each of these interpretations has a logical basis, it is unclear why *any* of them should have the dimensions of energy per unit temperature. Indeed the common entropy unit, J K^{-1} , is as mysterious as entropy itself. The goal here is to answer the following questions: (i) Why does entropy have the dimensions of energy per unit temperature? (ii) Are these dimensions necessary and/or physically significant? (iii) How would thermal physics differ if entropy were defined to be dimensionless and temperature were defined as an energy? (iv) What range of values does dimensionless entropy per particle have? (v) If temperature is defined as an energy, called *tempergy*, does it have a meaningful physical interpretation? An examination of thermal physics books⁵⁻¹⁰ shows that although some authors define entropy as a dimensionless quantity and some define temperature as an energy, no in-depth discussion of questions (i)-(v) seems to exist. What follows is in part a review and synthesis of ideas that are scattered throughout textbooks, with the goal of filling this gap.

In Sec. II, we review common definitions of entropy in thermodynamics, statistical mechanics, and information theory. In Sec. III we observe that in each case one can replace S by a dimensionless entropy S_d and that, in a sense, entropy is inherently dimensionless. We show how handbook entropy values can be converted to dimensionless entropies per particle, assess the range and meaning of the latter numerical values, and use them to estimate the number of accessible states. Defining entropy as a dimensionless quantity leads naturally to a definition of temperature as an energy (tempergy). In Sec. IV, we argue that although in very *special* cases, tempergy is a good indicator of the internal energy per particle, per degree of freedom, or per elementary excitation, no such property holds in general. Thus tempergy *cannot* be interpreted generally as an identifiable *stored* energy. In Sec. V we show that under typical laboratory conditions, tempergy is the energy transfer needed to increase a system's dimensionless entropy by unity. In addition, tempergy shares with temperature the property of determining the internal energy (quantum statistical average energy) and

thus the energy spectrum region where the system spends most time executing its "entropy dance." Section VI contains a recapitulation and main conclusions.

II. DEFINITIONS OF ENTROPY AND THE "ENTROPY DANCE"

Clausius defined the entropy change dS of a system at temperature T , in terms of an infinitesimal reversible heat process during which the system gains energy δQ_{rev} . His famous entropy algorithm is¹¹

$$dS = \frac{\delta Q_{\text{rev}}}{T}. \quad (1)$$

Extending this process along a finite path with a finite energy transfer, integration of (1) leads to an entropy difference $S_{\text{final}} - S_{\text{initial}}$. This procedure is commonly used as a calculation tool to obtain path-independent entropy differences. It is evident from Eq. (1) that S has the dimensions of energy per unit temperature (common units are J/K).

Notably, Clausius used the Kelvin temperature T in (1). This can be traced to the definition of the Kelvin temperature scale and the following property of dilute gases. If an N particle dilute gas has pressure p and volume V , then

$$\frac{pV}{N} = \tau = \text{function of temperature}. \quad (2)$$

The Kelvin temperature T is defined to be proportional to τ and to have the value $T_3 = 273.16 \text{ K}$ at the triple point of H_2O . It follows that

$$\tau = kT, \quad (3)$$

where the constant of proportionality, $k = 1.3807 \times 10^{-23} \text{ J K}^{-1}$, is Boltzmann's constant. Extrapolation of (2) to low temperatures shows that $T = t + 273.15$, where t is the Celsius temperature. The above-mentioned specification of T_3 assures that the Kelvin and Celsius scales have equal degree sizes. An interpretation of Eq. (3) is that k is a conversion factor that links temperature and energy. The product kT , which is ubiquitous in thermal physics, enables correct dimensions whenever an energy, heat capacity, or pressure is expressed as a function of T in Kelvins.

Modern-day values of Boltzmann's constant are obtained from data on the universal gas constant $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$, evaluated from dilute gas data, and Avogadro's number, N_A .¹²⁻¹⁵ That is, combining (2) and (3) with the corresponding standard molar equation $pV = nRT$, where n is the mole number, gives $k = R/(N/n) = R/N_A$. We note that k and R are two versions of the *same* constant using different unit systems.

Given the definition of temperature above and the fact that *all* reversible Carnot cycles operating between fixed reservoir temperatures T_c and T_h have efficiency $1 - T_c/T_h$, one finds that for any such Carnot cycle,

$$\frac{Q_h}{T_h} + \frac{Q_c}{T_c} = 0, \quad (4)$$

where (Q_h, Q_c) are the energies gained by the working fluid at (T_h, T_c) . In many textbooks, these properties are used to obtain the Clausius inequality, $\sum_i Q_i/T_i \leq 0$, for a cycle with segments $i = 1, 2, \dots$, and this inequality is then used to obtain the entropy algorithm, Eq. (1).^{16,17}

In Callen's modern formulation of classical thermodynamics,¹⁸ the entropy function S is postulated to exist for equilibrium thermodynamic states. It is specified to be extensive, additive over constituent subsystems, and to vanish in a state for which $(\partial U/\partial S)_{V,N} = 0$. Here U is the internal energy and the derivative is taken holding particle numbers and external parameters fixed. The dimensions of S come from the requirement that the latter derivative be identified as the Kelvin temperature; i.e.,

$$(\partial U/\partial S)_{V,N} = T, \quad (5)$$

and this gives S the dimensions energy/temperature. Again the dimensions of S are linked to the definition of temperature.

In statistical physics, entropy is usually defined using the Boltzmann form,

$$S = k \ln W. \quad (6)$$

The factor k is Boltzmann's constant, which was actually introduced into Eq. (6) by Planck. Using radiation data, Planck obtained the first numerical value of k .¹⁹ In classical statistical mechanics, W is proportional to the total phase space volume accessible to the system. This volume is in the $6N$ -dimensional phase space consisting of the position and momentum coordinates for the N particles. If there are internal degrees of freedom, say, for diatomic molecules that can rotate and vibrate, the dimensionality of the phase space is increased accordingly. In the quantum framework, W represents the number of quantum states that are accessible to the system. Evaluation of W to obtain S is a main task of the microcanonical ensemble formalism of statistical mechanics.

Several things should be kept in mind. First, the term *accessible* means accessible under specified experimental conditions, e.g., the system's temperature is fixed, which implies that the system's quantum state is likely to be in a specific region of the energy spectrum (we discuss this further in Sec. V). Second, if states are accessible, this implies that the system can be in any of them. Classically, this means that the system's phase point, (r, p) , which consists, say, of $6N$ position and momentum components, moves through the accessible phase space as time increases. Quantum mechanically, the system's state can make transitions between the accessible states. With this view, S has the interpretation of being

a "spreading" function.³ This "spreading" can usefully be envisioned as a *dance* over the system's accessible states. When the dance involves more states (or phase space volume) then the entropy is greater; thus we call it an *entropy dance*. Last, but not least, we observe that although the factor k in Eq. (6) gives S its conventional dimensions of energy/temperature, S/k contains all the essential physics. In this sense, entropy is inherently a dimensionless entity.

In information theory, the *missing information*, MI, is defined as

$$\text{MI} = -c \sum_i P_i \ln P_i, \quad (7)$$

where P_i is the probability of finding the system in state i , with energy eigenvalue E_i , and c is an arbitrary multiplicative constant.²⁰ Equilibrium statistical mechanics at constant temperature can be obtained by maximizing the function MI under the constraint that the average energy is fixed.²¹ This procedure leads to the conclusion that if one makes the identifications $S = \text{MI}$ and $c = k = \text{Boltzmann's constant}$, then consistency with classical thermodynamics is obtained, and

$$P_i = Z^{-1} \exp(E_i/\tau) \quad \text{with} \quad Z = \sum_i \exp(E_i/\tau). \quad (8)$$

Z is the canonical partition function of statistical mechanics. Notably, in both P_i and Z , temperature occurs *only* through the product $\tau = kT$. As in the microcanonical formalism, entropy's dimensions come solely from the factor k . Here the essential physics is contained within the set $\{P_i\}$. In this sense, the canonical ensemble entropy is inherently dimensionless.

III. DIMENSIONLESS ENTROPY AND TEMPERGY

The arguments above suggest that the tempergy, $\tau = kT$, has significance. Nevertheless, it is the temperature T , and not τ , that is commonly used as a thermodynamic variable.²² Recall that τ is traditionally written as kT in order to obtain an absolute temperature scale with a degree size equal to the Celsius degree. Had the temperature been defined as τ , then T_h and T_c in Eq. (4) would have been replaced by τ_h and τ_c , respectively. Similarly, the Clausius algorithm, (1), would have taken the form

$$dS_d = \frac{\delta Q_{\text{rev}}}{kT} = \frac{\delta Q_{\text{rev}}}{\tau}, \quad (9)$$

where S_d is the dimensionless entropy,

$$S_d = \frac{S}{k}. \quad (10)$$

Use of (10) in Eq. (6), gives the dimensionless Boltzmann form

$$S_d = \ln W. \quad (11)$$

It might seem that using τ rather than T would upset thermodynamics as we know it, but this is not so because it is possible to view the Kelvin as an energy,²³ i.e., $1 \text{ K} \equiv 1.3807 \times 10^{-23} \text{ J}$. It should be kept in mind, however, that although tempergy and internal energy have the same dimensions, they are very different entities, and we show in Sec. IV that in general, tempergy cannot be related to a stored system energy. Had the previously described steps been followed

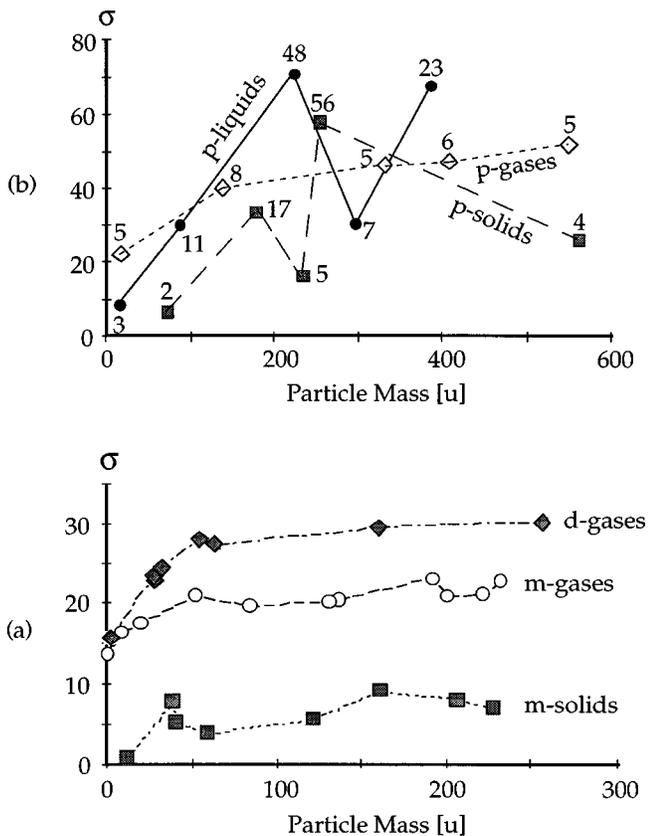


Fig. 1. Dimensionless entropy per particle σ vs particle mass, in mass units (u). (a) Monatomic solids (*m*—solids; gray squares), monatomic gases (*m*—gases; open circles) and diatomic gases (*d*—gases; gray diamonds). (b) Polyatomic solids (*p*—solids; gray squares), liquids (*p*—liquids; black circles), and gases (*p*—gases; open diamonds). Integers printed near data points are numbers of atoms per molecule, e.g., the polyatomic liquid water has (approximate) mass 18 u and 3 atoms per molecule, while the polyatomic liquid $C_{16}H_{32}$ has mass 224 u and 48 atoms per molecule. The polyatomic gases each have approximately the same number of atoms per molecule and their sequence shows that entropy increases with mass. Entropy-increasing effects of larger numbers of atoms per molecule are evident for the polyatomic liquids and solids. Lines connecting data points are included to help identify materials of a given type; they do not necessarily indicate the positions of other data points.

historically, entropy would have been dimensionless by definition and we might never have encountered the Kelvin temperature scale or Boltzmann's constant.

It is instructive to examine the *intensive* dimensionless entropy per particle,^{24,25}

$$\sigma \equiv \frac{S_d}{N}. \quad (12)$$

In what follows, unless stated otherwise, we focus on one-component, single-phase systems. What are typical values of σ ? Consider graphite, with entropy $5.7 \text{ J K}^{-1} \text{ mol}^{-1}$ at standard temperature and pressure. Equation (12) implies the dimensionless entropy per particle, $\sigma = 0.68$. Similarly, one finds that diamond has $\sigma = 0.29$ while lead has $\sigma = 7.79$. At $T = 1 \text{ K}$, solid silver has $\sigma = 8.5 \times 10^{-5}$, which seems consistent with σ approaching zero for T (or τ) $\rightarrow 0$.²⁶ It turns out that the dimensionless entropies per particle of monatomic solids are typically < 10 , as illustrated in Fig. 1(a).

Table I. Typical dimensionless entropy ranges for solids, liquids, and gases for $T = 298.15 \text{ K}$ and pressure $= 0.101 \text{ MPa}$. Higher (but atypical) values exist.

Type of matter	Typical range for σ
Monatomic solids	0.3–10
Monatomic gases	15–25
Diatomic gases	15–30
Monatomic and polyatomic solids	10–60
Polyatomic liquids	10–80
Polyatomic gases	20–60

For monatomic dilute gases in the classical domain, the Sackur–Tetrode formula for entropy²⁷ implies that the dimensionless entropy per particle is

$$\sigma = -1.16 + 1.5 \ln(M_a) + 2.5 \ln(T) \quad (13)$$

at pressure 0.101 MPa, where M_a is the atomic mass in mass units, and T is the Kelvin temperature. At $T = 298.15 \text{ K}$, this implies $\sigma = 15.2$ for helium gas and $\sigma = 21.2$ for the relatively massive radon gas. Figure 1(a) shows that at standard temperature and pressure, $15 < \sigma < 25$ for most monatomic gases. This range is above that for monatomic solids because gas atoms are less constrained than solids and gases have more accessible states. Figure 1(a) also shows that $15 < \sigma < 30$ for most diatomic gases. For a given particle mass, diatomic gases have higher entropy because their entropy dance involves more states. Entropy tends to increase with particle mass, as in (13), because the density of states (number of energy states per unit energy) is greater for more massive particles.³

Figure 1(b) shows that entropy is larger for more complex molecules. Again entropy tends to increase with particle mass, but this tendency can be overshadowed by the sensitivity of σ to the number of atoms per molecule. For example the solid $C_{18}H_{38}$ (octadecane), with molecular mass 254 u and 56 atoms per molecule has considerably higher σ than the solid Br_2Hg_2 , with more than twice the molecular mass 561 u, but only four atoms per molecule. The octadecane molecules have many more degrees of freedom and accessible states. Approximate ranges of σ for gases, liquids, and solids are summarized in Table I.

Overall, a helpful rule of thumb is that σ is typically between 0 and (roughly) 80 at ordinary temperatures and pressures. We may gain a deeper understanding of the numerical information in Table I and Fig. 1 using Eqs. (11) and (12) to obtain

$$\sigma = \ln(W^{1/N}), \quad (14)$$

or equivalently,²⁸

$$W = \exp(N\sigma). \quad (15)$$

We now estimate W when $N = 2 \times 10^{19}$ (roughly the number of air molecules in 1 cm^3 of air) for small and large values of σ . For solid silver's relatively small value $\sigma = 8.5 \times 10^{-5}$ at $T = 1 \text{ K}$, (15) implies $W = 10^{7.4 \times 10^{14}}$. For the hydrocarbon gas icosane, with $\sigma = 112$ under standard conditions,²⁹ (15) implies $W \approx 10^{10^{21}}$. A range of σ and W values is given in Table II.

We close this section with two observations. The first is that use of τ leads naturally to a dimensionless heat capacity

Table II. Number of accessible states W for an N particle system for $\sigma = 10^{-10}, 0.1, 1, 10,$ and 100 when $N = 2 \times 10^{19}$.

σ	W (order of magnitude)
10^{-10}	10^{109}
0.1	10^{1018}
1	10^{1019}
10	10^{1020}
100	10^{1021}

as well as dimensionless entropy. Notably, the American Institute of Physics Handbook contains tabular data for both dimensionless specific entropy and dimensionless specific heat capacities. Second, S_d and σ satisfy the relations

$$\left(\frac{\partial S_d}{\partial U}\right)_{V,N} = \frac{1}{\tau}, \quad \left(\frac{\partial \sigma}{\partial U}\right)_{V,N} = \frac{1}{N\tau}, \quad (16)$$

where the derivatives hold particle numbers and externally variable parameters fixed.

IV. TEMPERGY IS NOT GENERALLY A STORED SYSTEM ENERGY

In general, tempergy τ cannot be linked to an energy per particle, per degree of freedom, or per excitation. Despite this fact, we enumerate some very *special* cases for which τ is so related. The equipartition theorem implies that for monatomic and diatomic ideal gases in the classical domain, namely at sufficiently high τ and/or low density, each degree of freedom (including rotations and/or vibrations when these modes are active) stores $\frac{1}{2}\tau$ of energy on average. A sufficient condition for equipartition in the classical domain is that each degree of freedom have an energy that is quadratic in its variable, e.g., momentum for translational kinetic energy and displacement for vibrational energy.³⁰ Thus, even for classical nonideal gases with position-dependent forces, each translational degree of freedom stores energy $\frac{1}{2}\tau$. For the Einstein and Debye (quantum) models of solids, each degree of freedom stores $\frac{1}{2}\tau$ of energy on average for sufficiently high τ .

Another *special* case is an ideal Bose–Einstein gas below its critical temperature τ_c . The total number of particles can be written as $N = N_0 + N_{\text{exc}}$, where N_0 and N_{exc} are the numbers of particles in the ground state and in excited states, respectively. It can be shown that³¹

$$N_{\text{exc}} = N - N_0 = 2.612 \frac{V}{\lambda^3} \quad \text{with} \quad \lambda = \left(\frac{h^2}{2\pi m \tau}\right)^{1/2}, \quad (17)$$

and

$$\frac{U}{N_{\text{exc}}} = \frac{2.012\tau(V/\lambda^3)}{2.612(V/\lambda^3)} = 0.77\tau \quad \text{for} \quad \tau < \tau_c. \quad (18)$$

Thus, below the critical temperature, the tempergy τ is within 30% of the average energy per *excited* particle. However, because the particles in the ground state contribute zero energy, τ is *not* a good indicator of U/N .

Our last *special* case is a gas of photons in an otherwise empty box of volume V , with wall temperature τ . For this photon gas, the total internal energy is known from statistical mechanics to be³¹

$$U = \frac{8\pi\tau^4 V}{(hc)^3} \int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{8\pi\tau^4 V J_U}{(hc)^3}, \quad (19)$$

where $J_U = \pi^4/15 = 6.494$ is the integral in (19). The average number of photons, which depends upon both the container volume V and the temperature τ , is

$$N_{\text{photons}} = \frac{8\pi\tau^3 V}{(hc)^3} \int_0^\infty \frac{x^2}{e^x - 1} dx = \frac{8\pi\tau^3 V J_N}{(hc)^3}, \quad (20)$$

where $J_N = 2.404$ is the integral in (20). The combination of Eqs. (19) and (20) gives

$$\frac{U}{N_{\text{photons}}} = \left(\frac{J_U}{J_N}\right) \tau = 2.7\tau. \quad (21)$$

The average energy per photon is seen to be 2.7τ , despite the fact that $U \propto \tau^4$. This is true because $N_{\text{photons}} \propto \tau^3$. These results hold for all $\tau > 0$.

In order to understand how very *special* the above-mentioned cases are, we take a closer look at the Debye model of a solid, which accounts for small oscillations of coupled atoms. Using normal coordinates, the model reduces to a collection of independent linear oscillators. Debye assumed the distribution of the oscillators' frequencies coincides with the distribution of sound wave frequencies in the solid, and that there is a maximum frequency, ν_D . For $\tau \gg h\nu_D$, the model predicts that the system energy (relative to the ground state) $\rightarrow 3N\tau$. This reflects energy equipartition, i.e., average energy $\tau/2$ for each of the $6N$ degrees of freedom ($3N$ from kinetic and $3N$ from potential energies). In the low temperature limit, $\tau \ll h\nu_D$, quantum behavior prevents equipartition, and it is interesting to examine the average energy *per excitation*. These excitations, called phonons, are usefully viewed as independent, identical *quasiparticles* that obey Bose–Einstein statistics. Using the canonical ensemble, the average energy of the phonons can be written³²

$$U_{\text{phonons}} = \frac{9N\tau^4}{(h\nu_D)^3} \int_0^{(h\nu_D/\tau)} \frac{x^3}{e^x - 1} dx = \frac{9N\tau^4 I_U}{(h\nu_D)^3}, \quad (22)$$

and the average number of phonons is

$$N_{\text{phonons}} = \frac{9N\tau^3}{(h\nu_D)^3} \int_0^{(h\nu_D/\tau)} \frac{x^2}{e^x - 1} dx = \frac{9N\tau^3 I_N}{(h\nu_D)^3}. \quad (23)$$

The quantities I_U and I_N are shorthand notations for the integrals that appear in Eqs. (22) and (23), respectively. Notice that the number of phonons depends on the temperature, which is reminiscent of the photon gas. Combining these equations gives

$$\frac{U_{\text{phonons}}}{N_{\text{phonons}}} = \left(\frac{I_U}{I_N}\right) \tau. \quad (24)$$

Numerical evaluations of the integrals I_U and I_N show that for values of τ between 0 and $h\nu_D$, the right-hand side of (24) ranges from 2.7τ to 0.64τ , as illustrated in Fig. 2. Notice that the factor 2.7 arises in the zero temperature limit, for which $I_U/I_N = J_U/J_N$ [see Eqs. (19)–(21) for the photon gas]. We conclude that for sufficiently low temperatures, the

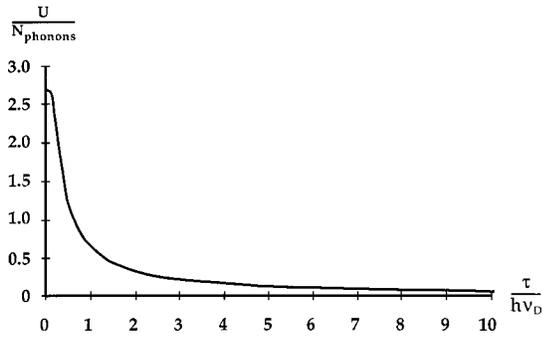


Fig. 2. Average energy per phonon vs $\tau/h\nu_D$ for the Debye model.

tempergy τ is a rough indicator of the average energy *per phonon*, but is a poor indicator of the energy per particle, U/N .

In contrast, for $\tau \gg h\nu_D$, $N_{\text{phonons}} \rightarrow (9N\tau)/(2h\nu_D)$, while $U_{\text{phonons}} \rightarrow 3N\tau$, so $U_{\text{phonons}}/N_{\text{phonons}} \rightarrow 0.67(h\nu_D/\tau)\tau$. That is, the average energy per phonon becomes a small fraction of τ . In this limit energy equipartition ($\pi/2$ per degree of freedom) holds and $U \rightarrow 6NkT$. In the intermediate region, where quantum effects are more subtle, there is no known way to interpret τ as a stored energy.

Before closing this section, we consider another model for which τ cannot be related to a stored system energy. Consider a collection of independent particles, each with two accessible states, having energies 0 and $\epsilon > 0$. Figure 3 shows graphs of $U/(N\epsilon)$ vs τ/ϵ and $U/(N\tau)$ vs τ/ϵ . For $\tau/\epsilon < 1$, relatively few particles are in the excited states and the average energy per particle $U/N \ll 0.5\epsilon$. For $\tau/\epsilon \gg 1$, the fraction of particles in the excited state approaches 0.5. Thus, when τ increases without bound, $U/N \rightarrow 0.5\epsilon$ while $U/(N\tau) \rightarrow 0$. Figure 3 shows that $U/N < 0.28\tau$ for all values of τ . Also, because $U = N_{\text{exc}}\epsilon$, where N_{exc} is the average number of particles in the higher energy state, it follows that $U/N_{\text{exc}} = \epsilon$, independent of τ . Thus, for this simple model of two-state independent particles, τ is neither a good indicator of the average energy per particle nor the average energy per excitation.

For the *special* cases where tempergy *can* be related to the average energy per particle, per degree of freedom, or per excitation, the total energy can be written as the sum of the energies of similar, independent particles or quasiparticles, or degrees of freedom. In some cases the special result follows because the particle energy is quadratic in a momentum or position variable and the temperature is sufficiently high. In other cases, the special result seems to be related to Bose-Einstein statistics. However, when such special conditions do *not* exist, we cannot relate τ to a stored system energy.

Except for special cases, τ is a poor indicator of the internal energy per particle, per degree of freedom, or per elementary excitation, and no universal interpretation of tempergy as a meaningful stored energy is known.

V. A PHYSICAL INTERPRETATION OF TEMPERGY

Given that τ generally cannot be associated with a meaningful *stored* energy, it is natural to ask if it has any general and useful physical interpretation. We know that temperature

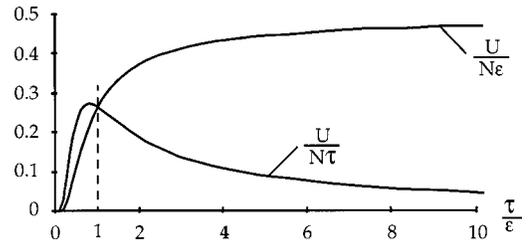


Fig. 3. $U/(N\tau)$ and $U/(N\epsilon)$ as functions of τ/ϵ for a system with N particles, each with possible energies 0 and $\epsilon > 0$. Because $U/(N\tau)$ is never near unity (its maximum is ~ 0.28), τ never represents the average internal energy per particle. Similarly, because $U/(N\epsilon)$ is never near unity, τ never represents the average internal energy per excitation.

represents the degree of hotness for objects, and when two objects interact thermally, energy flows from hotter to colder.^{33,34} This very useful interpretation holds for tempergy as well as temperature but provides no particular insights for τ .

In search of such insights, we consider an energy transfer $Q > 0$ to a system by a heat process. In terms of the (extensive) heat capacity $C(T)$,

$$Q = \int_T^{T+\Delta T} C(T') dT' = \bar{C} \Delta T, \quad (25)$$

where the last step defines the average heat capacity \bar{C} for the interval $(T, T+\Delta T)$, with $\Delta T > 0$. \bar{C} is well defined unless $\Delta T = 0$ and $Q \neq 0$. This special case, which occurs for two coexisting phases, is treated separately later. If we make the *special* choice $Q = kT$, and also assume that $\bar{C} \gg k$ (because \bar{C} is extensive and k is a constant) it follows that

$$\frac{\Delta T}{T} = \frac{k}{\bar{C}} \ll 1. \quad (26)$$

The dimensionless entropy change of the system when its temperature increases from T to $T+\Delta T$ is

$$\Delta S_d = \int_T^{T+\Delta T} \frac{C(T')}{kT'} dT'. \quad (27)$$

Because $C(T') > 0$, we may establish lower and upper bounds on ΔS_d by replacing $1/T'$ by $1/(T+\Delta T)$ and $1/T$, respectively, as follows:

$$\begin{aligned} \frac{1}{k(T+\Delta T)} \int_T^{T+\Delta T} C(T') dT' &\leq \Delta S_d \\ &\leq \frac{1}{kT} \int_T^{T+\Delta T} C(T') dT'. \end{aligned} \quad (28)$$

The equalities hold in the limit $\Delta T \rightarrow 0$.

Using Eq. (25) in (28), we obtain $Q/[k(T+\Delta T)] \leq \Delta S_d \leq Q/(kT)$. For the special case $Q = kT$, this becomes $T/(T+\Delta T) \leq \Delta S_d \leq 1$. Application of Eq. (26) then gives

$$\frac{1}{(1+k/\bar{C})} \leq \Delta S_d \leq 1$$

when

$$Q = \tau = kT. \quad (29)$$

Because we assume $\bar{C} \gg k$, expansion of the left-hand side in (29) to order k/\bar{C} leads to the conclusion $|\Delta S_d - 1| < k/\bar{C}$, and this brings us to our desired result,

$$\Delta S_d = 1$$

when

$$Q = \tau = kT, \quad \bar{C} \gg k. \quad (30)$$

Equation (30) is very general, and is satisfied whenever \bar{C} is well defined. We now show that it holds for various real and model systems over a wide range of temperatures.

For an isothermal transfer $Q = \tau$, (30) obviously holds because $\Delta S_d = Q/\tau = 1$. This is true even if the system consists of two coexisting phases at constant pressure, in which case $Q \neq 0$, $\Delta T = 0$, and \bar{C} —defined in Eq. (25)—does not exist. It is instructive to examine this interesting case. If L is the ‘‘heat of transformation’’ per mole, then $Q = \Delta n L = kT$ when Δn moles get transformed. This gives $\Delta n = k/(L/T) = k/\Delta s_{\text{mol}}$, where Δs_{mol} is the entropy of transition per mole. In particle language this implies $\Delta N = R/\Delta s_{\text{mol}} = 1/(\sigma_2 - \sigma_1)$.²⁵ Here σ_2 and σ_1 refer to the higher and lower entropy phases, respectively. To see the implications of this, consider a transition from liquid to vapor (assuming no dissociation upon vaporization). In this case $\sigma_2 - \sigma_1 = \Delta \sigma_{\text{vap}}$, the dimensionless entropy of vaporization per particle. For many such liquids, it is known that $\Delta \sigma_{\text{vap}} \approx 10$ at atmospheric pressure.³⁵ Notably, this implies $\Delta N < 1$, i.e., not even one molecule goes from liquid to vapor when $Q = \tau$. In fact the condition $\Delta N > 1$ requires that $\Delta \sigma_{\text{vap}} < 1$. Although this condition is satisfied for any saturated liquid at pressures and temperatures sufficiently close to its critical point, the *typical* result $\Delta N < 1$ for atmospheric pressure underscores the *smallness* of the energy transfer τ . If indeed $\Delta N > 1$, the result $\Delta S_d = 1$ is independent of both ΔN and the amount of liquid and vapor in the system because the process is isothermal. If $\Delta N < 1$ there is no phase transition and the liquid–vapor system acts as a system with heat capacity $C = C_{\text{liquid}} + C_{\text{vapor}}$. If $\bar{C} \gg k$ our earlier argument implies $\Delta S_d = 1$ for the almost-isothermal process in the two-phase system.

Another almost-isothermal process entails the heating of 1 g of copper, initially at $T = 1$ K and with constant-pressure heat capacity, $C = 1.2 \times 10^{-5}$ J/K. When energy $Q = \tau = kT$ is added to this system, Eq. (26) implies that $\Delta\tau/\tau = \Delta T/T = k/\bar{C} = 10^{-18}$, and Eq. (30) is valid. For higher temperatures, C is larger and thus $\Delta\tau/\tau$ is even smaller. Evidently for copper, Eq. (30) holds over a wide range of temperatures.

The derivation of Eq. (30) fails when \bar{C} is comparable with k . Because \bar{C} is proportional to the system’s mass, this happens if the system is sufficiently small. It happens also if the system is sufficiently cold because $C \rightarrow 0$ for $T \rightarrow 0$. We now investigate how low T must get to make (30) invalid for a given sample size.

Consider a Debye solid with $T \ll T_D$, the Debye temperature. In this region, $C(T)$ is well approximated by³² $C(T) = bNk(T/T_D)^3$ where $b = 12\pi^4/5 = 234$. Defining $\xi \equiv \Delta T/T$, it follows that when $T \rightarrow T + \Delta T$,

$$Q = \frac{bNkT^4}{4T_D^3} [(1 + \xi)^4 - 1]. \quad (31)$$

Similarly

$$\Delta S_d = \frac{\Delta S}{k} = \frac{bNT^3}{3T_D^3} [(1 + \xi)^3 - 1]. \quad (32)$$

Setting $Q = kT$, solving for $(1 + \xi)$ and substituting the result in (32), we find that

$$\Delta S_d = \frac{bNT^3}{3T_D^3} \left[\left(1 + \frac{4}{bN} \left(\frac{T_D}{T} \right)^3 \right)^{3/4} - 1 \right]. \quad (33)$$

Expansion of the first term in the square brackets leads to

$$\Delta S_d = 1 - \frac{(T_D/T)^3}{2bN} + \dots \quad (34)$$

For any $T \ll T_D$, the second term on the right-hand side becomes negligible for sufficiently large N .³⁶ If we demand that this term be no larger, say, than 0.001, the implied condition is

$$NT^3 > \frac{T_D^3}{0.47}$$

when

$$|\Delta S_d - 1| < 0.001. \quad (35)$$

This condition is most restrictive for small samples of solids with relatively high Debye temperatures. For diamond, with the exceptionally high Debye temperature $T_D = 2200$ K, (35) becomes $NT^3 > 2.3 \times 10^{10}$. Choosing the relatively small sample size 10^{-6} mol or $N = 6.02 \times 10^{17}$ and mass = 1.2×10^{-8} kg, this is satisfied for $T > 0.003$ K. Given diamond’s high Debye temperature, this example suggests that $\Delta S_d = 1$ is a good approximation when $Q = \tau = kT$ for most macroscopic solids over all but the very lowest attainable temperatures.

In addition to the lattice vibrations, electrons contribute to the heat capacity in metals. Using the free electron model, at low temperatures the electronic heat capacity is proportional to T . Therefore the total low-temperature heat capacity has the form $C = AT + BT^3$, where the linear and cubic terms come from the electrons and lattice, respectively. Using data for metals,³⁷ one can explicitly confirm whether $C \gg k$ for a sample of a given size. For example, at $T = 10^{-6}$ K, a calculation for 10^{-6} mol (9×10^{-9} kg) of beryllium shows that for $Q = \tau$, $\Delta S_d = 1.000$ (to four digits). Even more convincing results hold for other metals and also for larger sample sizes.

Yet another example is a Bose–Einstein (BE) ideal gas below its critical temperature for BE condensation. A cubic centimeter of material with the density of liquid helium has $N = 2.2 \times 10^{22}$ atoms and $|\Delta S_d - 1| < 0.001$ for $T > 2 \times 10^{-13}$ K.

The above-mentioned examples indicate that $\Delta S_d = 1$ for $Q = \tau$ typically holds for all but the most extreme low temperatures. Because a sufficient condition for $\bar{C} \gg k$ is $C \gg k$ in the interval $(T, T + \Delta T)$, the above findings can be summarized as follows.

For macroscopic systems with heat capacities $C \gg k$, tempergy τ is the energy transfer required to increase the dimensionless entropy by unity, i.e., $\Delta S_d = 1$. This

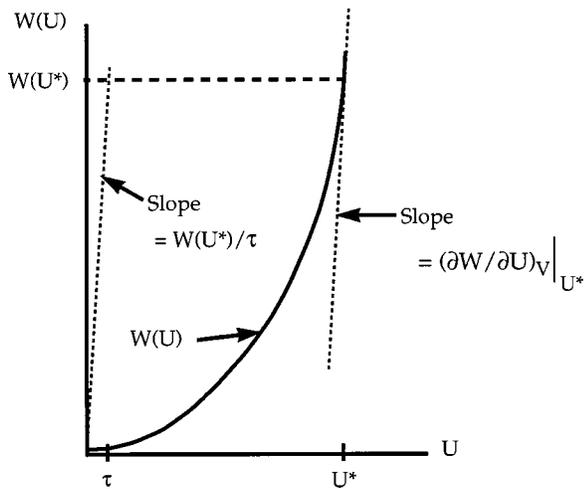


Fig. 4. A plot showing $W(U) \propto U^Y$ vs U , as described in the text, and a geometrical view of Eq. (36). The slopes of the two dotted lines represent the left- and right-hand sides of Eq. (36). The tempergy $\tau > 0$ and the fixed external parameters, including volume V , determine the system's internal energy U^* . To enable a graphical view of Eq. (36), this sketch is not drawn to scale. In real systems, τ typically is many orders of magnitude smaller than U .

holds to an excellent approximation for macroscopic systems over nearly all attainable temperatures.

Because S_d is of order N , the number of system particles, the entropy change $\Delta S_d = 1$ is typically a very small relative change for S_d . Examination of Eq. (11) shows that increasing S_d by unity corresponds to multiplying the total number of accessible states by the factor $e = 2.718\dots$, the base of natural logarithms.³⁸

The fact that an added energy $Q = \tau$ induces $\Delta S_d = 1$ is a consequence of Eq. (16), $(\partial S_d / \partial U)_V = 1/\tau$, which relates tempergy to the *rate of change* of S_d with U . For a system whose dimensionless entropy S_d has continuous first and second derivatives with respect to U , and whose heat capacity C_v is *finite*, the concavity condition for entropy³⁹ implies that $(\partial^2 S_d / \partial U^2)_V < 0$. The latter condition assures that $C_v > 0$, and that Eq. (16) has a unique solution U^* for any $\tau > 0$.⁴⁰

For a one-component, single phase system with fixed volume, whose entropy has continuous first and second derivatives, tempergy—like temperature—determines the internal energy. Quantum statistically, this pinpoints the average energy and thus, the neighborhood of the system's energy spectrum where the entropy dance spends most time.

Using Eqs. (6), (10), and (16), we obtain

$$\left(\frac{\partial}{\partial U} W(U^*) \right)_V = \frac{W(U^*)}{\tau}. \quad (36)$$

A graphical interpretation of Eq. (36) is given in Fig. 4, assuming that $W(U) \propto U^Y$. This form satisfies the concavity condition above and, for the special case of a classical monatomic ideal gas, it is well known⁴¹ that $Y \propto N$.

VI. CONCLUSIONS

Entropy's conventional units, J/K, can be traced to the definition of the Kelvin temperature scale. The exercise of

defining and examining dimensionless entropy and dimensionless entropy per particle inspires a healthy rethinking of the foundations of thermodynamics and statistical mechanics. It provides a natural setting in which to compare values of dimensionless entropy per particle for different materials, which can give a better *sense* of entropy's role as a measure of the temporal entropy dance of the system over its accessible states. Typically, the dimensionless entropy per particle σ lies between 0 and (roughly) 80. These findings imply that the number of accessible states is $W \sim 10^{10^x}$ for macroscopic systems under standard temperature and pressure conditions, with $10 < x < 21$. W is indeed impressively large.

The study of dimensionless entropy suggests that temperature can be replaced by tempergy, $\tau = kT$, and this leads naturally to an investigation of the occurrence and significance of τ in thermal physics. Despite the existence of simple models for which tempergy is proportional to internal energy per particle, per degree of freedom, or per excitation, no such property holds generally. Two reasonably *general* energy-specific interpretations of tempergy are known. One entails an energy *transfer*, rather than a *stored* energy, namely: tempergy is the amount of energy needed to increase a system's dimensionless entropy by unity. This property holds for macroscopic systems that are not at ultralow temperatures, i.e., when $C \gg k$. The second interpretation is for single-phase systems, for which $W(U)$ has the shape in Fig. 4. In this case, τ —like temperature—determines the average energy and thus, the region of the energy spectrum where the system spends most time doing its entropy dance over states. The fact that this dance occurs for thermodynamic equilibrium highlights the dynamic microscopic nature of macroscopic equilibrium.

It is possible to circumvent Boltzmann's constant by defining entropy as a dimensionless quantity and working with tempergy rather than temperature. This leads one to question whether k is really a *fundamental* constant of nature. We can compare it to the speed of light in vacuum, c , which is fundamental in that it applies to *all* electromagnetic radiation. We can also compare it with Planck's constant h , which is fundamental in that it links a particle property (energy) and a wave property (frequency) for *all* electromagnetic radiation and *all* de Broglie particle waves. Boltzmann's constant can be considered fundamental in the sense that it provides a linear link between tempergy and temperature, where temperature is a fundamental measure of hotness and tempergy represents a well-defined stored energy for *all* sufficiently dilute gases. It is important to realize however that despite this property of dilute gases, tempergy does *not* represent a known stored system energy for macroscopic matter in general.

Finally, we observe that although many people seem comfortable with their understanding of temperature, fewer seem comfortable with entropy. This is true in part because we can *feel* when objects have higher or lower temperatures, but we cannot usually sense entropy directly. To the extent that one's comfort with temperature stems from the incorrect belief that temperature is always proportional to the average kinetic energy per particle, it gives a false sense of security. Baierlein^{33,34} has emphasized that temperature does *not* tell us how much energy a system stores, but rather, reflects a system's *tendency to transfer* energy via a heat process. The

findings here agree with that assessment and, in addition, show that the specific energy transfer $Q = \tau$ induces the dimensionless entropy change $\Delta S_d = 1$.

This article began as an attempt to clarify an aspect of entropy, but has led inadvertently to a rethinking of temperature. Although entropy can be related *very generally* to the entropy dance described here and dimensionless entropy can help us better understand that dance, no such system-independent picture emerges for temperature or tempergy. The general definition of T in thermodynamics is given by Eq. (15), which relates T to the rate of change of energy with entropy. This suggests that temperature is *at least* as elusive as entropy, i.e., *at least* as difficult to understand on microscopical grounds.

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- ⁷J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (Wiley, New York, 1977), 2nd ed., p. 90.
- ⁸C. Kittel and H. Kroemer, *Thermal Physics* (Freeman, New York, 1980), 2nd ed. See also the first edition (Wiley, New York, 1969), pp. 29, 132–133, and C. Kittel, *Elementary Statistical Physics* (Wiley, New York, 1958), p. 27.
- ⁹B. K. Agrawal and M. Eisner, *Statistical Mechanics* (Wiley, New York, 1988), pp. 40–47.
- ¹⁰See also B. H. Lavenda, *Statistical Physics: A Probabilistic Approach* (Wiley, New York, 1991), pp. 14–15. He defines the Boltzmann statistical entropy in the conventional way but then writes, “In most of the subsequent formulas, Boltzmann’s constant will be omitted implying that the temperature will be measured in energy units. This introduces a greater symmetry in the formulas, especially in regard to dual Legendre functions.”
- ¹¹Strictly speaking the reversibility implied by $dS = \delta Q_{rev}/T$ is sufficient, but not necessary. It is necessary only that the system in question undergo a *quasistatic* process, which can occur even if the system interacts irreversibly with its environment (see Ref. 2).
- ¹²Planck calculated N_A in 1900 (see Ref. 19) using data on radiation. A “direct” determination of N_A , using Einstein’s theory of Brownian motion, was published in J. B. Perrin, *Ann. Chim. (Paris)* **18**, 1 (1909); an English translation is in F. Soddy, *Brownian Motion and Reality* (Taylor & Francis, London, 1910). See also A. Einstein, *Investigations on the Theory of the Brownian Movement* (Dover, New York, 1956), especially pp. 60–62.
- ¹³A student laboratory experiment for measuring Boltzmann’s constant was developed by M. Horne, P. Farago, and J. Oliver, “An experiment to measure Boltzmann’s constant,” *Am. J. Phys.* **41**, 344–348 (1973). This paper also contains interesting historical information.
- ¹⁴The modern value of N_A is known from measurements of the lattice constant, density, and atomic mass of silicon. See R. D. Deslattes, “Recent estimates of the Avogadro constant,” in *Atomic Masses and Fundamental Constants*, edited by J. H. Sanders and A. H. Wapstra (Plenum, New York, 1975), Vol. 5.
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Petley, *The Fundamental Physical Constants and the Frontier of Measurement* (Hilger, Bristol, 1985), pp. 94–99. The best modern values of Boltzmann’s constant utilize $k = R/N_A$.

- ¹⁶See, for example, M. W. Zemansky and R. H. Dittman, *Heat and Thermodynamics* (McGraw-Hill, New York, 1997), 7th ed., pp. 186–191.
- ¹⁷Clausius used a similar, but less well known, method to obtain Eq. (1). His method also required the definition of absolute temperature given in the text. See R. J. E. Clausius, *The Mechanical Theory of Heat* (John Van Voorst, London, 1867), pp. 134–135. Interesting discussions of Clausius’s method can be found in W. H. Cropper, “Rudolf Clausius and the road to entropy,” *Am. J. Phys.* **54**, 1068–1074 (1986) and P. M. C. Dias, S. P. Pinto, and D. H. Cassiano, “The conceptual import of Carnot’s theorem to the discovery of entropy,” *Arch. Hist. Exact Sci.* **49**, 135–161 (1995).
- ¹⁸See Ref. 5, pp. 27–32.
- ¹⁹See M. Planck, *The Theory of Heat Radiation* (Dover, New York, 1991). This is an English translation by Morton Masius of Planck’s second edition of *Vorlesungen über die Theorie der Wärmestrahlung* (1913). Planck wrote (p. 120), “... Boltzmann’s equation lacks the factor k which is due to the fact that Boltzmann always used gram-molecules, not the molecules themselves, in his calculations.” Planck’s numerical calculation of k along with Planck’s constant is given on pp. 172–173. Notably, Planck also calculated Avogadro’s number and the electron charge. References to the relevant original (1901) articles are on p. 216.
- ²⁰See, for example, R. Baierlein, *Atoms and Information Theory* (Freeman, San Francisco, 1971), Chap. 3.
- ²¹The information theory development of statistical mechanics was pioneered by E. T. Jaynes, “Information theory and statistical mechanics,” *Phys. Rev.* **106**, 620–630 (1957); “Information theory and statistical mechanics. II,” **108**, 171–190 (1957). A good summary is in K. Ford, Editor, *Statistical Physics—1962 Brandeis Summer Institute Lectures in Theoretical Physics* (Benjamin, New York, 1963), Vol. 3, pp. 181–218.
- ²²One exception is Ref. 8, in which τ is used throughout.
- ²³Callen (Ref. 5) and Landau and Lifshitz (Ref. 6) adopt this view. A contrasting view is taken in F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965), pp. 99, 136–137. Here, T is defined to be *dimensionless*, and the unit *degree* is taken to be “... a unit in the same sense as the degree of angular measure; it does not involve length, mass, or time.”
- ²⁴In Refs. 6–9, the *extensive* dimensionless entropy is labeled σ , which is related to the Clausius (extensive) entropy S by $S = k\sigma$. In contrast, we use the *lower case* σ for the *intensive* dimensionless entropy per particle and S_d for the *extensive* dimensionless entropy.
- ²⁵ σ can be expressed in terms of the entropy per mole, $s_{mol} = S/n$ and the entropy per unit mass, $s_{mass} = S/M$ as follows: $\sigma = Ms_{mass}/(Nk) = ns_{mol}/(Nk) = s_{mol}/R$. The latter expression shows that if one knows the molar entropy in $\text{J K}^{-1} \text{mol}^{-1}$, then $\sigma = s_{mol}/8.314$. If s_{mol} is in calories/mol, then $\sigma = s_{mol}/2$ to a good approximation.
- ²⁶The third law of thermodynamics implies that entropy, and thus dimensionless entropy, approaches the same value for all paths leading toward absolute zero temperature. By convention, this value is defined to be zero.
- ²⁷R. P. Bauman, *Modern Thermodynamics with Statistical Mechanics* (Macmillan, New York, 1992), p. 345. In this book, the Sackur–Tetrode equation is written $S = R[1.5 \ln M + 2.5 \ln T - \ln P] + 172.298$, where M is the mass, in kg, of one mole (6.02×10^{23} particles). For example, for neon, $M = 0.02018 \text{ kg}$. In contrast, in our Eq. (13), $M = 20.18 \text{ mass units}$.
- ²⁸If an exact expression for W is used to obtain σ using Eq. (14) and small terms are dropped for large N , then use of the inversion formula (15) cannot recover the exact W . For example, if $W = N^g q^N$, where g and q are constants, then $\sigma = \ln q + (g/N) \ln N$ and the second term on the right is negligible for sufficiently large N . Taking antilogarithms of the first term, we recover $W = q^N$, but not the factor N^g . Thus, Eq. (15) is useful for obtaining the order of magnitude of W rather than its exact value.
- ²⁹Icosane (also called eicosane), with molecular formula $\text{C}_{20}\text{H}_{42}$, has 62 atoms per molecule. Although it is a solid at room temperature, Lange’s Handbook of Chemistry lists an entropy value that implies $\sigma = 112$ for icosane gas under standard conditions.
- ³⁰R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford U.P., Oxford, 1938; reprinted by Dover, New York), pp. 95–98. Tolman derives a *general equipartition principle* and shows that a form of equipartition holds even for a relativistic gas of noninteracting particles, whose energy is *not* quadratic in momentum. Specifically, if u is particle speed and m rest mass, then $[(mu^2)/(1 - u^2/c^2)^{1/2}]_{\text{average}} = 3kT$. Equipartition holds for the *kinetic* energy per particle only in the nonrelativistic limit.

- ³¹R. K. Pathria, *Statistical Mechanics* (Butterworth-Heinemann, Oxford, 1996), 2nd ed., Chap. 7.
- ³²K. Huang, *Statistical Mechanics* (Wiley, New York, 1987), 2nd ed., pp. 283–286.
- ³³R. Baierlein, “The meaning of temperature,” *Phys. Teach.* **28**, 94–96 (1990).
- ³⁴R. Baierlein, *Thermal Physics* (Cambridge U.P., New York, 1999), pp. 6–8, 177–178, 347–349.
- ³⁵This is known as Trouton’s rule. See, for example, M. Sprackling, *Thermal Physics* (American Institute of Physics, New York, 1991), p. 242. The value $\Delta s_{\text{mol}} \approx 85 \text{ J mol}^{-1} \text{ K}^{-1}$ cited by Sprackling implies $\Delta \sigma_{\text{vap}} \approx 10$.
- ³⁶The second term in (34) is much less than 1 if $(T/T_D)^3 \gg 1/(2bN)$. Using the heat capacity, $C(T) = bNk(T/T_D)^3$, this implies $C(T) \gg k/2$. The latter

agrees (in an order of magnitude sense) with the condition $\bar{C} \gg k$ for $Q = kT$ to induce the change $\Delta S_d = 1$.

³⁷See Ref. 16, p. 355, Table 13.4.

³⁸In “bit language,” the dimensionless entropy is $S_d[\text{bits}] = S_d/\ln 2 = S_d/0.693$, and Eq. (30) becomes $\Delta S_d[\text{bits}] = 1.44$ bits upon addition of energy $Q = \tau$. This reflects the additional missing information associated with 2.718... times as many accessible states.

³⁹See Ref. 5, pp. 203–207.

⁴⁰A unique solution would *not* exist if $(\partial^2 S_d / \partial U^2)_{V,N}$ vanished over a finite U interval, which would imply infinite C_V for this range of U values. Empirically, for a single-phase system, C_V diverges when a critical point is approached.

⁴¹See Ref. 32, pp. 138–140.

SEVERITY AND FLABBINESS

That is the severity of the criterion that science sets for itself. If we are to be honest, then we have to accept that science will be able to claim complete success only if it achieves what many might think impossible: accounting for the emergence of everything from absolutely nothing. Not almost nothing, not a subatomic dust-like speck, but absolutely nothing. Nothing at all. Not even empty space.

How different this is from the soft flabbiness of a nonscientific argument, which typically lacks any external criterion of success except popular acclaim or the resignation of unthinking acceptance. One typical adipose arch-antireductionist argument may be that the world and its creatures were created (by something called a God), and that was that. Now, that may be true, and I cannot prove that it is not. However, it is no more than a paraphrase of the statement that ‘the universe exists’. Moreover, if you read into it an active role for the God, it is an exceptionally complex explanation, even though it sounds simple, for it implies that everything (or almost everything, even if the God supplied no more than electrons and quarks) had to be provided initially.

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