

Overcoming Misconceptions about Configurational Entropy in Condensed Phases

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Thermodynamic entropy, S , can be treated as a measure of spontaneous spreading of the available energy, E (e.g., temporally, among the accessible microstates, in a different one each instant, resulting in an averaged distribution) (1, 2). Clausius's fundamental equation,

$$dS = \frac{dq_{\text{rev}}}{T} \quad (1)$$

where dq_{rev} is an energy exchange in the form of heat under conditions of thermal equilibrium with the surroundings and T is temperature, entails the essence of this interpretation in combination with the Boltzmann–Planck equation,

$$S(E) = k \ln W \quad (2)$$

in which W is the number of *equiprobable* microstates (energy distribution modes) accessible by the system via random motion consequent to energy-exchange events¹ and k is the Boltzmann constant.

In light of a view of entropy change as solely involving *energy distributions*, configurational or positional entropy that evaluates numbers of seemingly temperature-independent *locations in space* (using eq 2) may appear to present a problem. Yet, this apparent inconsistency is not due to any case in which configurational entropy has been shown to yield unreliable numerical results. Historically, in a number of cases positional entropy has been the simplest way in which some phenomena could be directly evaluated (e.g., residual entropy; ref 3).

The problem is that entropy change may be perceived to be due solely to an explicit increase in accessible positions in space, a way that W may be interpreted in eq 2. The implication that there are two distinct varieties of entropy (“configurational”, that is, spatial but temperature-independent and “thermal”, that is, space-independent) undermines instruction.

Quantum mechanics is not directly applicable to the systems with defined locations and momenta (particularly, in tightly packed condensed phases), owing to the uncertainty principle. Thus, positional entropy is a *classical* view of the canonical ensemble valid above a high-temperature (classical) limit. However, one of the key challenges to teaching physical chemistry is that the canonical ensemble is mentioned only long after entropy is introduced and widely used (4e, 5f, 6a). A rigorous explanation of configurational entropy using statistical mechanics is, thus, traditionally done in the *graduate* curriculum, using advanced mathematics.

To address this problem at a lower level, classical and quantum mechanics should be connected without involving the complexities of rigorous statistical mechanics. Most importantly, energy quantization may be taken into account via the use of the “spinless” Boltzmann distribution (ignoring the difference between bosons and fermions). Several textbooks

build the entire physical chemistry course upon this concept (7, 8). In my previous publication, I provided a reconciliation of thermal and configurational calculations of the residual entropy in crystals (3).

In the present article, this treatment is expanded to thermally equilibrated condensed phases, primarily liquids. In this case, involving distinguishable and exchangeable particles, configurational entropy is intuitive because different microstates can be obtained by switching the molecules' *positions* because of molecular motion (as opposed to “thermal” *energy* exchange). I shall proceed directly with two cases to illustrate the problem.

The Problem: Two Cases That Frequently Cause Misconceptions

Case 1: Entropy of Neat Liquids

In a blind application of configurational entropy to N distinguishable particles (e.g., in condensed phases) assuming that each particle is unique and distinguishable by its interactions with other unique surrounding particles, that is, configurations, the number of equiprobable microstates, W , may be calculated as

$$W = N! \quad (3)$$

At first glance, this formula, applicable also to a deck of N cards each of them having a different face value, allows for the estimate of molar *configurational* entropy of condensed phases for point-size particles that are *all* distinguishable (N_A is Avogadro's number and R is the gas constant):

$$\begin{aligned} \Delta S_{\text{configurational}} &= k \ln(N_A!) \approx k N_A [\ln(N_A) - 1] \\ &= R \ln\left(\frac{N_A}{e}\right) = 447 \frac{\text{J}}{\text{mol K}} \end{aligned} \quad (4)$$

However, eq 4 is not applicable to real systems: Standard molar entropies of common inorganic solids or liquids are much smaller (4f, 9), whereas the S° values for hydrocarbons greater than C_{12} exceed this “limit” (10). Does the failure of this approach mean that configurational entropy is not applicable?

Case 2: Entropy of Mixing

Configurational entropy of mixing for ideal miscible liquids is due to the independent expansion of two fluids into each other's volume (4a, 5a),

$$\Delta_{\text{mixing}} S = -R \sum_{i=1}^m (X_i \ln X_i) \quad (5)$$

(X_i is the mole fraction of a component); the random, probabilistic nature of eq 5 is underscored by Gibbs' equation involving probabilities instead of X_i (4c).

Equation 5 can be considered for *equimolar* amounts of two liquids without narrowing the scope of the study, as it has been shown (3, 5a). In this simplified system (two different chemicals mixed in a 1:1 ratio and having $N = N_1 + N_2 = N_A$), the molecules of each kind are considered indistinguishable within the subsets but distinguishable between the subsets. "Configurational" eq 5 yields $\Delta_{\text{mixing}}S = -2R \times \frac{1}{2} \ln \frac{1}{2} = R \ln 2$. However, since neither energy nor temperature are involved in this derivation, it is not obvious that "thermal" entropy is applicable to the process of mixing; particularly, for ideal solutions, when the enthalpy of mixing is zero, $\Delta_{\text{mixing}}H \approx 0$.

The "thermal" way of counting microstates, essential for explaining this apparent lack of application of thermal entropy, is considered in the next section. Then, after linking this approach to configurational considerations via the molecular partition function, these two cases will be revisited.

Thermal Entropy: Reconciliation of Thermodynamics and Statistics

The population of energy levels at thermal equilibrium is described by the Boltzmann distribution (3, 4b, 6b, 11, 12),

$$\frac{N_i}{\sum N_j} = \frac{N_i}{N} = \frac{g_i e^{-\epsilon_i/(kT)}}{\sum g_j e^{-\epsilon_j/(kT)}} \quad (6a)$$

i-th energy-level population fraction

$$\frac{N_{i+n}}{\sum N_j} = \frac{N_{i+n}}{N} = \frac{g_{i+n} e^{-(\epsilon_i + \Delta\epsilon)/(kT)}}{\sum g_j e^{-\epsilon_j/(kT)}} \quad (6b)$$

(i+n)-th energy-level population fraction

$$\frac{N_{i+n}}{N_i} = \frac{g_{i+n}}{g_i} e^{-\Delta\epsilon/(kT)} \quad (6c)$$

where N_i , ϵ_i , and g_i are the population, energy, and degeneracy of a certain *i*-th energy level, respectively, *n* is an integer (so, *i* + *n* refers to a different energy level separated by the energy gap, $\Delta\epsilon$), subscript *j* denotes a *general* energy level, $N = \sum N_j$ is the total number of particles in the system, and $\Delta\epsilon$ is the energy gap separating the energy levels of interest. The denominator in eqs 6a and 6b is called the molecular partition function, which will be considered in the next section.

The most probable, that is, spontaneously achieved, Boltzmann distribution is derived assuming the maximum number of microstates for a closed system ($N = \text{constant}$) under the constraint of constant energy (i.e., the micro-canonical ensemble); normalizing the energies by temperature links it to the statistical canonical ensemble (5b). The physical significance of having exponents in these equations is the randomness of the "choice" made by particles in achieving this distribution (4b, 12). Because of this randomness, eq 6 serves as a connection of "thermal" eq 1 and statistical eq 2 for entropy calculations. It limits the number of possible microstates to those accessible at a given temperature for a given energy gap.

Equiprobability of Configurations: The Rigorous Criterion

The exponential factors in eq 6 account for the unequal probability of the lower-energy and higher-energy states, thus serving as "statistical weights" (11). The other statistical weight is the degeneracy factor for a particular state, g_i (12). Without the use of temperature-dependent exponential factors of eq 6, some values of "entropy" may be calculated using eq 2; however, they would not necessarily be thermodynamically relevant because some of the microstates would not be attainable (13) or would not be taken into account with the correct statistical weights (11).

It is worth mentioning that the unequal accessibility shows up not only as a low population of the upper energy levels but also in terms of real spatial configurations. An example is the head space for a neat liquid in a closed container; the positions within and outside of the liquid's boundaries are not equiprobable for the molecules at temperatures below the boiling point. Thus, "configurational" microstates involving the even distribution of molecules throughout the volume of liquid and head space are not attainable.

Yet, the microstates become equally accessible and, thus, equiprobable if the measure of an increment of energy, kT , overcomes the energy gaps between any two of given energy levels (3); this criterion may be re-stated as "dimensionless" energy gaps ($\Delta\epsilon/kT$) are infinitesimal for all accessible *m* energy levels:

$$\frac{\Delta\epsilon}{kT} = \frac{\epsilon_m - \epsilon_1}{kT} \approx 0 \quad (7)$$

Here, $(\epsilon_m - \epsilon_1)$ is the energy gap effectively overcome by the kT heat bath. The physical interpretation of this equation is that overcoming of $\Delta\epsilon$ by kT results in the equipopulation of energy levels.² Henceforth, *m* will be used as both an index number for the maximum energy level for which eq 7 is applied and a total count of such qualified energy levels.

An illustration for the simplest case of $m = 2$ (non-degenerate) and $\epsilon_1 = 0$ is provided in Figure 1. N_2/N_1 is near 1 when $1 \gg \Delta\epsilon/kT \approx 0$ (mode C). By contrast, as shown earlier for this system (3, 6b), the population ratio of the highest and lowest occupied energy levels, N_2/N_1 , is close to zero when either the dimensionless energy gaps are large or, equivalently, when temperature is below the characteristic temperature, $\Theta = \Delta\epsilon/k$. These two cases can be unified by using the condition opposite to that of eq 7, where $\Delta\epsilon/kT \gg 1$ (mode A in Figure 1). In this case, as well as in transitional mode B (occurring within a limited temperature range), configurational entropy is inapplicable because microstates are not equally accessible.

This simple two-level consideration can be readily expanded to the case of any number of populated energy levels, *m*. The application of eq 7 to eqs 6a–c (i.e., assuming $T \gg \Theta$) moves the system to a state similar to mode C in Figure 1. This entails an effectively "infinitely high" temperature and nearly-equal population of *m* accessible levels, which yields N/m for the population of levels (3).

While expanding the two-level case to *m* energy levels, one has to consider degeneracy that may exist as a consequence of states with different sets of quantum numbers having the same energy. This adjustment, essential for the application to various

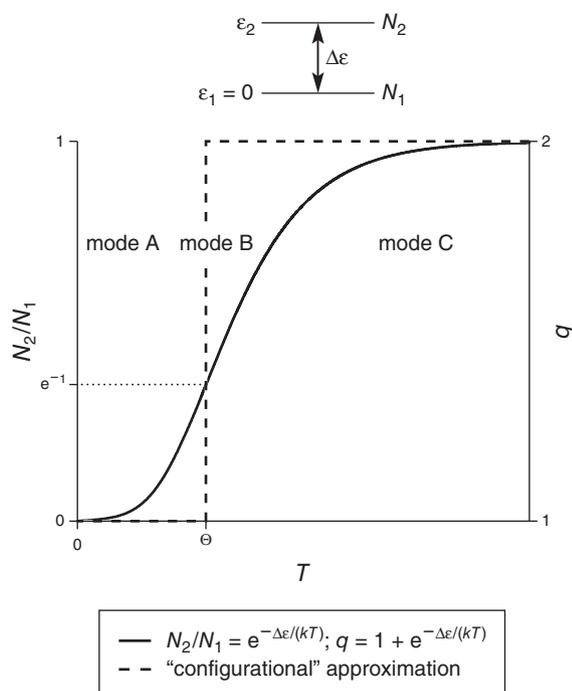


Figure 1. The molecular partition function (right vertical axis) and relative energy-level population (left axis) of a two-level system (with a zero-energy ground state) as a function of temperature.

types of molecular motion (described by the solutions of corresponding quantum mechanical problems) will be represented henceforth by replacing m with a similar parameter, m' (counting all of the different *states* rather than just energy levels).

Equation 7 is too rigorous for practical applications, that is, the limit does not have to be closely approached; this issue is dealt with in the next full section concerning molecular partition functions. However, the approximation used in eq 7 is helpful for conceptual understanding of how equipartitioning enables the application of configurational entropy; this issue is considered now.

The Algebra of Permutations: How Molecules Let the Dice Fly

For N particles distributed among m' states at a given temperature, the number of available microstates, $W(T)$, in the system can be calculated:

$$W(T) = \frac{N!}{N_1! N_2! \dots N_{m'}!} \quad (8)$$

For any $N_i = N/m'$ (i.e., equipopulation at “infinitely high” T , T_∞), eqs 2 and 8 may be combined. Upon the application of Stirling’s approximation, the entropy change reflecting the system’s transfer from $T = 0$ to T_∞ can be found,

$$\begin{aligned} \Delta S &= k \ln \left[W(T_\infty) / W(T=0) \right] = k \ln \left\{ \left[\frac{N!}{\left(\frac{N}{m'} \right)!} \right] / 1 \right\} \quad (9) \\ &= kN \ln m' \end{aligned}$$

where $W(T=0) = 1$ is the single microstate when all of the particles are on the ground energy level.

On the other hand, by an algebraic rearrangement of $kN \ln m'$, the following equation can be obtained:

$$\Delta S(T_\infty) = kN \ln m' = k \ln (m'^N) \quad (10)$$

This equation shows the inherent coupling of the “thermal” approach to configurational permutations (combinations of finite sets of objects) because m'^N in eq 10 can be visualized as the number of possible combinations while tossing a hypothetical die—with m' equal sides— N times. Figuratively speaking, each molecule “rolls a die” to “decide” which quantum state it will go to upon an energy exchange event. The use of a die is consistent with eqs 6 and 7. A die whose imperfection is infinitesimally small still generates equiprobable combinations, within the margin of statistical errors. When this condition is met, m' in eq 10 represents the number of both available energy-distributing states and spatial configurations (3). By contrast, when eq 7 is not valid, the die is significantly skewed; some sides are “heavier” than the others. The microstates with significantly smaller Boltzmann exponential “statistical weights” that disobey eq 7 would be as likely as the landing of a die on its corner and staying in this precarious position.

The Molecular Partition Function as an Effective Value of m'

Equation 7 sets a rather rigorous requirement that seems to be unattainable. However, Scott showed that a large percentage of the calculated vibrational and, particularly, rotational heat capacity is accounted for by the accessibility of just a few energy levels higher than the ground state (11), that is, the *effective* m to satisfy eq 7 tentatively is lower than the actual number of populated energy levels.

This problem may be addressed by revisiting the molecular partition function, $q(T)$, the denominator in the Boltzmann distribution formula (eqs 6a and 6b),

$$q(T) = \sum g_j e^{-\epsilon_j/(kT)} \quad (11)$$

which will be considered below separately for two important subsets.

Limited Number of Energy Levels

Each exponential term in eq 11 is varied from 0 to 1. A simple illustration for a non-degenerate two-state system (i.e., $1 < q < 2$) is shown in Figure 1. One can see that $q(T)$, similar to the population ratio N_2/N_1 , changes nearly stepwise with temperature, from approximately 1 in mode A (the two exponential terms in the denominators of eqs 6a and 6b being near 1 and 0, respectively) to near 2 in mode C (both terms yielding exactly 1 with $q = 2$ at T_∞).

The logical expansion to a more general case of multiple (yet limited) accessible energy levels (eq 6) leads to a well-known conclusion that the value of q is tentatively equal to the number of accessible states, m' , for an average molecule (5c). Figure 1 illustrates that this condition becomes mathematically rigorous at T_∞ , that is, assuming eq 7 (mode C). In this case, the molecular partition function has a clear physical significance as a *probabi-*

istic value for equally populated states (4c),

$$m' = \lim_{T \rightarrow \infty} q(T) = \frac{1}{p_i} = \frac{1}{p} \quad (12)$$

where p_i is the probability of a molecule to occur in state i and p is the probability of a molecule being in a particular equipopulated state in general.

Unlimited Stack of Energy Levels

For an unlimited number of available energy levels, Figure 1, applicable to *limited* values of m , needs to be adjusted. Textbooks show that upon changing summation to integration in eq 11, $q(T)$ becomes a continuous function proportional to $T^{x/2}$ where x is the number of independent kinetic and potential energy terms for a given mode of motion (4e, 5g, 6c). Similar to the case of a limited number of states, this treatment is valid only above the effective characteristic temperature, thus imposing the assumptions of eq 7, for example, infinitesimal “dimensionless” energy gaps, $\Delta\epsilon/kT$. Such an assumption defines this state of the system as a *classical* limit because the quantization is effectively negated.

Connections to particular kinds of molecular motion are provided by Scott who showed that the classical limit is reached when only a few lowest energy levels or states are intensely populated (11). This outcome is because the above considerations, made for a limited number of states, still apply to an unlimited stack, except that the slope of the asymptotic line for high-temperature limit in Figure 1 becomes positive (Figure 2). Using eq 11, several consecutive exponential terms (reflecting the highly populated low-energy levels) are still near 1, the rest are near zero; the number of those near 1 increases with temperature and is tentatively equal to q (5c, 6c). Thus, q provides the *effective* value of m' for which eq 7 is valid at a given temperature. Note that q , as an effective value, does not have to be an integer.

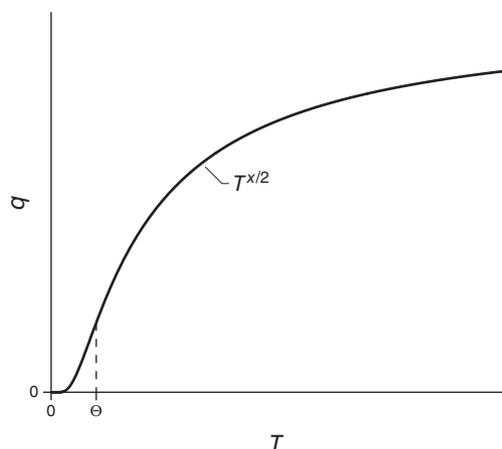


Figure 2. The molecular partition function as a function of temperature ($T^{x/2}$) for a system with an unlimited stack of energy levels.

It is important to recall that the molecular partition function is the sum of “statistical weights” for each particular state ($e^{-\epsilon_i/kT}$) for all of the energy levels ($g_i e^{-\epsilon_i/kT}$).³ Thus, its calculation is an essential step to defining an *effective/average* particle having an equal probability of occupying any of the accessible energy levels [$p = 1/q(T)$, as in eq 12] (4c, 5f). Considering the system as N identical average particles (to which eqs 8–10 are also applicable) provides a “bridge” between the microcanonical and canonical ensembles by calculating the entire system’s partition function, $Q(T)$, which reflects the *statistical* number of equiprobable microstates in the system at a given temperature:

$$Q(T) = W(T) = [q(T)]^N \quad (13)$$

In eq 13, $q(T)$ (calculated as a product of partition functions for the available modes of motion) can be viewed as the *effective* number of attainable configurations at a given temperature (as m' in eq 10). Whenever this assumption is used, configurational entropy is applicable [e.g., “configurational integrals” (6e), residual entropy (3), or activation entropy (14)]. However, as shown in the next section, uncoupling either q or W from their thermal nature leads to errors.

Returning to Case 1: Pure Condensed Phases

Configurational entropy, in its application to distinguishable particles (e.g., in condensed phases) approximates the exponential curve shown in Figure 1 as a stepwise switch between just two modes, A and C. In mode A, there is only one microstate, $W = 1$ yielding $S = 0$ (eq 2). In mode C, assuming that each particle is unique and distinguishable (i.e., $N_1 = N_2 = N_m = 1$ and $m' = N$), the number of equiprobable microstates may be calculated using eq 3 ($W = N!$), which turns out to be incorrect for real neat liquids.

Thus, configurational entropy cannot be decoupled from $q(T)$, the number of attainable configurations per molecule at a given temperature. The assumption of eq 3 (distinguishability of *all* particles) is valid only if $m' \approx q = N_A$ whereas the values of vibrational and rotational $q(T)$ at room temperature are significantly smaller (4e, 6c, 12).

This consideration does not mean that the application of configurational entropy necessarily leads to errors; it does so only if the value of characteristic temperature is ignored. An example can be offered on intermolecular vibrations. HCl dipoles are known to be present in virtually 100% “head-to-tail” configuration near its freezing point, so it freezes as a “perfect” crystal. This means that, at this temperature, $q(T) = 1$ for intermolecular vibrations, that is, the system is below the characteristic temperature for this type of motion (mode A, Figure 1). If either temperature increases or the energy gap ($\Delta\epsilon$) between the “head-to-tail” and “head-to-head” configurations decreases (e.g., as is true of CO, in contrast to HCl, near *its* freezing point), the choice of configuration is nearly random, so $q(T) \approx 2$ (3).

The second problem with the application of eq 3 to neat liquids is that molecules, instead of being of “point-size”, possess multiple degrees of freedom, each having an unlimited stack of energy levels (thus, illustrated by Figure 2 rather than by Figure 1). For instance, molar entropies exceed the $k \ln N!$ value for

large flexible molecules with low-energy internal rotations (e.g., hydrocarbons greater than C_{12}). This result is due to low characteristic temperatures of internal rotations around the C–C bonds (5ϵ) leading to large values of q at room temperature (as illustrated in Figure 2). From the standpoint of configurational entropy, some of the *parts* of such molecules become distinguishable, thus increasing the number of microstates above the perceived $N!$ limit.

Why Are Molecules Not Like Cards?

This consideration sets the rigorous limit to the use of a 52-card deck to illustrate entropy change (2a). The “information entropy” ($S = k \ln 52!$) calculated for possible sequences in this card deck does not represent a thermodynamic entity. First, this model misrepresents the entropy of a real molecular system by omitting any equivalent to molecular motion at a given temperature. Second, being temperature-independent, this model does not obey the third law and definition of the micro-canonical ensemble. The root of the problem is that the “particles” within a card deck (having $\Delta\epsilon = 0$) are unlike the molecular systems (where $\Delta\epsilon \approx 0$ is a useful approximation only above the characteristic temperature, that is, $\Delta\epsilon \ll kT$). Switching particles present in the same state (e.g., having the same energy) within a micro-canonical ensemble does not generate new microstates, so $W = 0$ and $S = 0$. This system is neither thermal nor dynamic.

By contrast, in real condensed phases interactions of different atoms in different configurations lead to different energy gaps, thus yielding different values of $\Delta\epsilon_i$ to mark their *thermodynamically relevant* distinguishability. It is the difference in energy that serves as a distinguishability marker, no matter how small the dimensionless energy gap, even at T_∞ (eq 7).

Thus, in thermodynamic applications, not *every* $\ln W$ may be allowed to be multiplied by k in eq 2 to yield a valid thermodynamic value; W must be temperature-dependent in accordance with eqs 6 and 13. As shown in the next section, this limitation is also true for the entropy of mixing.

Returning to Case 2: Mixing from the Standpoint of Thermal Entropy

Consider two liquids mixed to reach equilibrium. The two-state model (Figure 1) can be applied assuming a single average energy for the “ground state” of separated species only and a single average energy for the “excited” solution state ($\Delta\epsilon$ being the energy difference between the averaged homomolecular and solute–solvent interactions). When $m = 2 = q_{\text{mixing}}$, meaning that the liquids are fully miscible, the locations within the former two liquids (i.e., before mixing, with one liquid on top of the other) become totally equiprobable for each particle regardless of its origin, $p = 1/2$. Figuratively speaking, the multifaceted die to be rolled (eq 10) becomes a two-sided coin that each molecule “tosses” to “decide” whether it will stay in the original region or move to the other one.

For m equimolar components, the entropy of mixing can be expressed as

$$\Delta_{\text{mixing}}S = -Rm \frac{1}{m} \ln\left(\frac{1}{m}\right) = R \ln m \quad (14)$$

This equation justifies the applicability of eqs 9 and 10 [$W = (m)^N$] to the entropy of mixing. As has been noted before, eq 9 (of “thermal” origin”) and eq 10 (of “configurational” origin) are the same thus underscoring the inherent coupling of these two approaches when eq 7 is valid. Hence, the spreading of matter in spontaneous thermal motion is tantamount to energy spreading (because energy is carried by particles).

The fundamental problem, so far as thermodynamic entropy is concerned, is that viewing $W = (m')^N$ as a purely statistical statement (where m' includes degenerate energy levels) means that *all* of these substates can be degenerate with no energy difference ($\Delta\epsilon = 0$, as in macro objects such as a perfect die or coin). As has been shown here, this condition may be valid in mathematics, but it does not rationalize an observable physical change in macro thermodynamics as does the micro-thermodynamic view of mobile molecules constantly moving among different energy arrangements and randomly exploring available space as well.⁴

Generally, one may safely assume that different chemicals to be mixed are energetically non-equivalent with the presumed exception of isotopes. However, Levine (6d) pointed out that the appearance of entropy of mixing for different isotopes is also due to the small difference in the energy of intermolecular interactions. Isotopes are usually miscible at the melting point but become immiscible at very low T ; with a notable exception, pointed out by Noggle, of ^3He and ^4He that are immiscible even in the liquid phase because of the difference in nuclear spins (5a).

Third Law and the Enthalpy of Mixing

This example illustrates the limitation of using configurational entropy to describe mixing because the configurational approach fails to obey the third law. To avoid this pitfall, the adjustment to a temperature-dependent number of effective configurations (eq 13) has to be made (thus, $\Delta\epsilon = 0$). The low-temperature limit of $\Delta_{\text{mixing}}S$ is zero because chemicals become immiscible, even those that “are supposed to mix”.⁵ Accounting for the enthalpy of mixing can be addressed by using the “thermal” treatment, which couples the entropy and enthalpy of mixing for *partially* miscible liquids.

When eq 7 (i.e., $T \gg \Theta$) is not valid, that is, the chemicals are not miscible at a certain temperature, this system is either in mode A in Figure 1 (with the “mixing” molecular partition function near 1) if the mutual solubility is near zero (as for a long-chain aliphatic hydrocarbon in water) or in mode B if the solubility is noticeable (as for a mid-size alcohol in water, $1 < q_{\text{mixing}} < 2$). Thus, unlike mode C, the locations within two phases are not equiprobable with the Boltzmann exponents (eq 6) being the statistical weights. The solubility is near zero below the threshold value of temperature, $\Theta = \Delta\epsilon/k$. Increase of temperature, normally, increases mutual solubility according to eq 6.

If the characteristic temperature (or $\Delta\epsilon$) is known, the population of the higher energy level (N_2/N , the mutual solubility of components) may be calculated, as a function of temperature, using the Boltzmann distribution (eq 6b). Once the value of N_2 is known, the entropy change for *partial* mixing can be calculated using eq 8 combined with the mass balance equation ($N = N_1 + N_2$).

Conclusion

Configurational entropy calculations for distinguishable particles are significant and valid as long as their fundamental connection to random energy dispersion is maintained. This connection may be ensured by considering the molecular partition function, that is, the number of effectively equipopulated energy levels or, equivalently, the number of effective configurations for an average molecule attainable at a given temperature.

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Notes

1. This is merely an illustration; according to the ergodic hypothesis, there is no preference for any particular temporal path.

2. Equation 7 does not necessarily state that the interactions between the particles are weak, although it could be the case when applied to the ideal gas. By contrast, for liquids, eq 7 (e.g., mode C in Figure s1) implies that there is no “preference” (i.e., no significant difference in energy) among m types of intermolecular interactions for m miscible liquids thus making an “ideal solution” (6a).

3. While focusing on energy gaps described by the exponential Boltzmann terms, one should stress that degeneracy integers, g_j , may also make a significant impact on the value of $q(T)$ if the low-lying energy levels are substantially degenerate, thus partially offsetting a relatively large energy gap (e.g., rotation).

4. This treatment helps explain the Gibbs’ paradox, which is based on the assumption that, from a configurational viewpoint, mixing two identical volumes of *the same* liquid would generate $\Delta S = kN \ln 2$ (eq 10). However, there is no paradox from the “thermal” view because, since $\Delta \epsilon = 0$ between the two subsets, m pertaining to mixing remains equal to 1; thus, $W_2 = W_1$ and $\Delta S = 0$. An insightful discussion of the Gibbs paradox has been provided by Spencer and Lowe (15).

5. The corresponding heat of mixing may be recovered if, instead of the direct irreversible mixing, a reversible path is taken, along which eq 1 applies. Such a path for “unmixing” at low T is often unavailable because the mixture is usually a solid at $T = \Theta$, and so the molecules cannot change their configurations upon cooling (16). However, Levine suggested an isothermal reversible path for *mixing* liquids that involves vaporizing each liquid at its equilibrium vapor pressure with the concomitant gas expansion; then, the gases (which could be mixed reversibly using selectively permeable membranes) are isothermally con-

densed into the solution (6f). As pointed out by Levine, mixing several liquids (e.g., water and amines) yields *negative* $\Delta_{\text{mixing}} S$ in a reversible process, owing to weaker hydrogen bonding in pure chemicals than in the mixture (6f). This observation emphasizes the energetic aspect of mixing when applied to liquids.

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