

Correlation of Entropy with Similarity and Symmetry[†]

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Received July 26, 1995[⊗]

Informational entropy is quantitatively related to similarity and symmetry. Some tacit assumptions regarding their correlation have been shown to be wrong. The Gibbs paradox statement (indistinguishability corresponds to minimum entropy, which is zero) has been rejected. All their correlations are based on the relation that less information content corresponds to more entropy. Higher value of entropy is correlated to higher molecular similarity. The maximum entropy of any system (e.g., a mixture or an assemblage) corresponds to indistinguishability (total loss of information), to perfect symmetry or highest symmetry, and to the highest simplicity. This conforms without exception to all the experimental facts of both dynamic systems and static structures and the related information loss processes.

1. INTRODUCTION

The main aim of this paper is to establish the logarithmic relations of entropy and symmetry. The behavior of entropy as a thermodynamic function, the second law of thermodynamics, and the relations of entropy and information have all been well investigated. Therefore the benefit of the entropy-symmetry correlation for characterizing structural stabilities and process spontaneities in chemistry will be obvious.

Factually, the correlation of entropy and symmetry in a qualitative manner was already hinted at by Schrödinger^{1,2} many years ago that negative entropy corresponds to asymmetry, broken symmetry,^{3,4} or less symmetry. However, it remains generally a tacit assumption that higher symmetry of a system implies less entropy. For example, in all statistical mechanics texts, following Gibbs,⁵ the value of the partition function is substantially reduced due to the permutation symmetry number ($N!$) of an ideal gas system of N independent particles by a factor of $1/N!$. Consequently entropy (S) is also reduced by a term of $-\ln N!$ due to the symmetry. By the same reasoning, the rotational partition function is divided by a symmetry number σ , the number of indistinguishable orientations for symmetrical linear molecules and the number of indistinguishable positions through which a molecule may be rotated for other symmetric molecules.⁶ These correlations may be summarized in the following logarithmic function:

$$S = -\ln \sigma \quad (1)$$

where, for simplicity, the positive constant (Boltzmann constant) k is taken as 1.

The symmetry numbers, w for the whole system and σ for an individual molecule, will be defined in the following discussion. Arguments based on the relation that less information content corresponds to more entropy will be given to show that, generally, entropy and symmetry are

simply correlated by a logarithmic expression

$$S = \ln w_a \quad (2)$$

where w_a is the apparent symmetry number—the apparent number of the symmetric or indistinguishable microstates, among them the symmetric transformations can leave the macroscopic state of the system unchanged. Note that the negative sign in eq 1 is removed in eq 2, which means that entropy should increase with the symmetry number.

It appears obvious that various thermodynamic systems have two aspects of properties: dynamic and static properties. Accordingly there should be two types of processes: processes responsible for the conversion between different dynamic modes and processes between different static structures. Their information losses leading to an equilibrium can be considered separately, e.g., intramolecular *dynamics* of individual molecules in crystal and the *static* lattice structure of the crystal. Accordingly there are two types of symmetries: 1. Symmetry due to dynamic motion such as dynamic motion of individual molecules. 2. Symmetry of a static structure generated from phase separation and phase transformation.

The *entropy increase* effect of the first type of process leading to a macroscopically equilibrium state is well recognized (Boltzmann equation). However, ubiquitous effect of *symmetry increase* due to dynamic motion is also clear: A hydrogen atom has spherical symmetry because of the rapid dynamic motion of the electron. If one treats the electron as a particle, the configuration of the hydrogen atom will not be as symmetrical as a sphere at all at any one moment. Similarly, as will be discussed, dynamic motion of individual molecules also contributes to the macroscopic property such as the homogeneity (a symmetry) of a fluid.

For the second type of processes, the *symmetry increase* leading to a macroscopically equilibrium state is obvious. However, as will be pointed out, the corresponding effect of information loss (or *entropy increase*) is also obvious, such as the consequence in the formation of a perfect crystal. Here, information content and symmetry of different static structures are compared and their differences are considered.

[†] Presented at the 6th International Conference of Mathematical Chemistry, Pittlochry, 1995.

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[⊗] Abstract published in *Advance ACS Abstracts*, December 15, 1995.

Therefore, typical examples of these two types of symmetries will be discussed. I found that both cases satisfy the general relation of higher symmetry-higher information loss (or higher entropy), without exception.

2. HIGHER ENTROPY-HIGHER SYMMETRY

Based mainly on the well-known, simple relation of entropy increase = information loss, and on observations, some general and qualitative arguments for the relations of several important chemical concepts are given in the following paragraphs.

Maximum Symmetry at Equilibrium. When transport processes such as heat conduction, diffusion and electrical conduction, etc. take place between several subsystems, the total entropy of these subsystems will increase to the maximum value corresponding to an equilibrium state.⁷ The symmetry of the system composing these subsystems will also increase until the equalization of thermodynamic properties among these subsystems is realized. In more detail, at equilibrium,^{8a} the temperatures at all the locations 1, 2, 3,... are identical, $T^{(1)} = T^{(2)} = T^{(3)} = \dots$; the pressures ($p^{(1)} = p^{(2)} = p^{(3)} = \dots$) and the chemical potentials ($\mu_i^{(1)} = \mu_i^{(2)} = \mu_i^{(3)} = \dots$) as well as electric potentials (and any other potential-like properties or intensive properties) are also all equalized.^{8a} The equalization or equilibrium is the very property of the highest possible symmetry.⁹ In all such cases, one may naturally speculate that higher entropy correlates with higher symmetry.

Generally, if a system at equilibrium or a fully relaxed system, which has of course the maximum entropy,⁷ is subjected to either internal or external constraints, the entropy content will be reduced. It is certain that any such constraints, such as a force or a field, must have *polarity* and will reduce the *isotropicity* of the original structure, hence reduce the symmetry of the original system. Therefore, the reduced symmetry correlates with the reduced entropy. To leave an equilibrium state, both the total entropy and the symmetry will be reduced. One must not be able to find any exception to the following statement: *Any system evolves spontaneously toward a maximal symmetry* of either static or dynamic structures or both.

Symmetry and Orderliness. A seemingly plausible support—and possibly the only support—to the validity of eq 1 is due to the correlation of higher symmetry—higher orderliness. I argue as follows that this is a false conception. Suppose both entropy and symmetry concern the collective behavior of a large number of members of a system. To illustrate the conceptual difference of the *symmetry* and the *order* of such a system, let us treat a society as a system. If all the members are indistinguishable—every one can claim himself to be the president of the country for example. The symmetry of this dynamic society will be really high (at least the permutation), and the society will be in chaos. However, if every member has a specified position and is confined and constrained, so that people are different and distinguishable, then, the symmetry is low and the society is in a state of high orderliness. The social order means asymmetry, not symmetry. The same argument should apply to a dynamic or static molecular system. It is clear that external and internal constraints applied to a system reduce both the symmetry and the entropy of the system. For a dynamic system of many molecules, microscopically and locally, the

applied constraint may confine a molecule in one specific configuration, and the whole system is specifically confined in one of w microstates. Because of the external (e.g., high pressure) and the internal (e.g., van der Waals interactions) constraints, a gas condenses to a liquid and then forms a solid. Therefore, a gas has higher symmetry than a liquid, which is in turn higher than the corresponding solid as elegantly described by Ma.¹⁰ The entropy contents increase during transitions from solid to liquid and to gas.¹⁰ Therefore, the decreased orderliness corresponds to the increased symmetry due to dynamic motions when the temperature is increased, or when the system changes from solid state to fluid state and from condensed state to gaseous state.^{11,12} Various residual entropies remaining in the condensed phase even at zero degree temperature can be exclusively attributed to the requirement of the “residual” symmetry and the disorder.^{13–15} In Pauling’s argument,^{14a} the higher local symmetry (T_d) in ice due to hydrogen-bonding provides a positive contribution to the value of the residual entropy. As Pauling clearly expressed, the T_d symmetry and entropy is due to the “randomness of atomic arrangement”.^{14a} This statement goes against the expression of eq 1 and implies that the symmetry is related to structural randomness, not to structural orderliness. Moreover, many phenomena related to the second-order phase transitions such as ferromagnetism have been observed, where spontaneous formation of a symmetrical pattern (e.g., parallel spin orientations) has never been and can never be satisfactorily explained based on the “higher symmetry-higher order and less entropy” relations, despite great efforts taken to solve this problem over the past decades.^{8b}

Symmetry and the Algorithmic Entropy. Furthermore, an algorithmic entropy concept may be compatible with a conventional informational entropy concept.⁴ If a system evolves to become more symmetrical, the mathematical expression required to describe the system will surely become simpler. Consequently the information content of the system is less and the algorithmic entropy increases, following the well-known relation of information content and entropy.¹⁵

Transformations. Moreover, both symmetry and entropy are related by configurational transformation. It is well-known that the symmetry of a system is defined by invariant transformations in a space spanned by ω microstates. I may call ω the symmetry number.¹⁶ Factually the name “entropy” as created by Clausius¹⁷ means transformation ($\tau\rho\sigma\pi\eta$),^{17,18} where the prefix “en” was used because this concept is related to “energy” transformations in thermodynamics.^{17,18} Entropy (S) is defined by Boltzmann as

$$S = \ln w \quad (3)$$

where w is the number of equivalent microstates¹⁸ which are made accessible through invariant transformations. Based on the observation presented in the previous sections and the foregoing argument, I suggest that w and ω are the same parameter. Microscopic mixing of all the w accessible microstates defines the macroscopic picture or symmetry of a system. Succinctly, symmetry number (w) is the number of the symmetrical microstates,¹⁸ which are all factually accessible in the system with any type of operation.¹⁶

Symmetry and Information. From an argument similar to that for the relation of symmetry and algorithmic entropy, it is certain that the configurations of asymmetric cyclic

molecules, F₄₃₀ and vitamin B₁₂, for example,¹⁹ should have a much higher information content and consequently are much more difficult to synthesize than the symmetrical tetrapyrrole macrocyclic compounds. Highly aperiodic heteropolymers such as DNA and protein have a much higher information content¹⁻⁴ and normally are much more difficult to synthesize than the symmetrical, periodic homopolymers—polymers constructed from indistinguishable monomers. These examples illustrate clearly that lower symmetry is connected with lower entropy or higher information content. If information is registered by an arrangement in space composing many positions occupied by molecules, then in a static structure such as a solid phase, the symmetry of individual molecules determines the symmetry of the whole structure of the molecular ensemble (collection). Even though the symmetry of individual molecules can be considered, one may argue that entropy is normally about an ensemble and becomes meaningless if applied to a single molecule. This problem requires further discussion. Because information registration is much easier to visualize and to discuss, here we should simply recognize the fact that if the symmetry of such individual molecules becomes higher, then more registered information would be lost and entropy would increase.

3. IMPERFECT SYMMETRY, SIMILARITY AND ENTROPY

A discussion on continuous symmetry by Zabrodsky et al.²⁰ revealed significant and stimulating results, and it would therefore be highly desirable to correlate symmetry to informational entropy. According to von Neumann²¹ and Shannon,²² the entropy expression is normally given as

$$S(w) = -\sum_{i=1}^w p_i \ln p_i \quad (4)$$

where p_i is the probability of the i th microstate,¹⁸ with the property that

$$\sum_{i=1}^w p_i = 1 \quad (5)$$

In eq 4, w microstates are different, so that the probability values (p_i) are different. It is plausible to propose that such general situations correspond to imperfect or continuous symmetries; and only if all these w microstates are of indistinguishable property, can we have the corresponding maximum entropy

$$S_{\max} = \ln w \quad (6)$$

corresponding to a perfect symmetry. Therefore, the similarity (Z) is defined as

$$Z = \frac{S}{S_{\max}} = -\frac{\sum_{i=1}^w p_i \ln p_i}{\ln w} \quad (7)$$

We understand that $0 \ln 0 = 0$ and $1 \ln 1 = 0$. By inspection, Z is within the range of 0 and 1.²³ It is obvious that the similarity 1, which means indistinguishability, corresponds to perfect symmetry.

It would be convenient to define w_a as the *apparent* symmetry number (eq 2), which is the *apparent* number of symmetrical microstates. It is easily estimated from eq 4 by

$$w_a = \exp\left(-\sum_{i=1}^w p_i \ln p_i\right) \quad (8)$$

This expression reflects the symmetry-similarity correlation explicitly,²³

$$Z = \frac{\ln w_a}{\ln w} \quad (9)$$

Obviously and generally the apparent symmetry number and the entropy S is related simply as

$$w_a = e^S \quad (10)$$

or as given in eq 2. From the well-known inequality²⁴

$$-\sum_{i=1}^w (p_i \ln p_i) \leq \ln w \quad (11)$$

the entropy content calculated by eq 4 will be equal to or less than the value predicted by eq 6. Consequently, the apparent symmetry number w_a will be equal to or less than w . Because, as a fundamental nature of spontaneous process due to the second law of thermodynamics, that entropy increases until the system is in equilibrium,^{7,17,18} and from eqs 4–11, the apparent symmetry number w_a will assume a value as high as possible.

3. TWO EXAMPLES

Two categories of examples are given in the following to demonstrate that the entropy-symmetry logarithmic function is applicable to both *dynamic* and *static* structures. I will show that, *indistinguishability* (here energy levels) can be responsible for an increase of both entropy and symmetry in the formation of an equilibrium state (section 3.1); and any kind of molecular *differences* (such as chirality) can be used for information registration in a static structure and the reduction of the symmetry (section 3.2).

3.1. “No-Reaction” Reactions. Let us discuss the intramolecular dynamic motions of a molecular system at thermal equilibrium with several simple examples, most of them will be systems of perfect symmetry. Gasser and Richards²⁵ already elegantly described the relation of entropy content and energy-level similarity of multiple degenerate energy states. The occurrence of degeneracy is related to the symmetry of a system.^{26,27} Symmetry is the ability of a system to remain invariant of the macroscopic structure (described by a function Ψ) or parameters (as functions of Ψ) after a set of operations $\{O_i\}$. An operation can be *as complicated as a conventional chemical reaction*.¹⁶ Equation 6 will be applied if the w microstates (designated as $\{\psi_i\}$) are energetically identical or degenerate

$$\epsilon_1 = \epsilon_2 = \dots = \epsilon_i = \dots = \epsilon_w \quad (12)$$

where ϵ_i is the energy of the i th microstate, and the

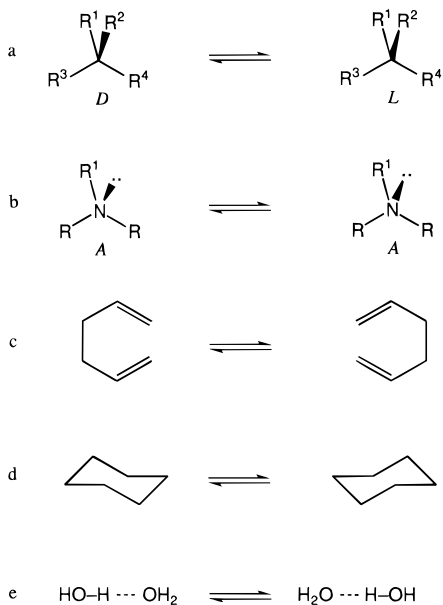


Figure 1. The intramolecular processes (a–d) and hydrogen bond (e). In principle, different configurations (*D* and *L* in process a) and different molecular orientations (b–e) can be used to register information.¹⁵ But the information will be lost due to their interconverting motions, resulting in entropy increase.

Boltzmann factor is

$$e^{-(\epsilon_i - \epsilon_j)/T} = 1 \quad (13)$$

which corresponds to a perfect symmetry. A time-independent Hamiltonian (*H*, the energy operator) must be invariant under the transformation $T(O_a)$, or

$$T(O_i)H T^{-1}(O_i) = H \quad (14)$$

or $[T(O_a), H] = 0$, i.e., the Hamiltonian commutes with all the transformations $T(O_a)$.²⁷ Therefore, we can avoid the discussion of the energy aspect of the considered dynamic motions, even though obviously the energy effect is just as important as the entropy effect in many chemical processes.

For a discrete molecule of σ interchangeable degenerate configurations, we have similar relations to the eqs 12–14. The simple relation of σ and w will soon be made clear. If the eqs 12–14 are conformed, σ and w can also be called degeneracies.

Among the intramolecular dynamic processes (see Figure 1),²⁸ there are many truly interesting examples of the so-called “no-reaction” reactions,²⁹ or the degenerate reactions,³⁰ such as the Cope rearrangement (Figure 1c) of bullvalene.^{31,32} Following traditional and standard “cause-effect” reasoning of scientific argument, any process must be driven by some force—the reason for the process to happen. However, as already clearly seen from eqs 13 and 14, there is no energy decrease after these intramolecular reactions; and because the educt and the product are *indistinguishable*, there is no entropy of mixing of *different* molecules³³ according to the conventional statistical mechanics.^{5a} There is simply no advantage of either energy minimization or entropy maximization effects as the thermodynamic driving force according to conventional statistical mechanics and thermodynamics! Therefore, it is not a surprise that, to the present author’s knowledge, so far nobody has been able to tell what the “driving force” for this kind of no-reaction reaction is, even

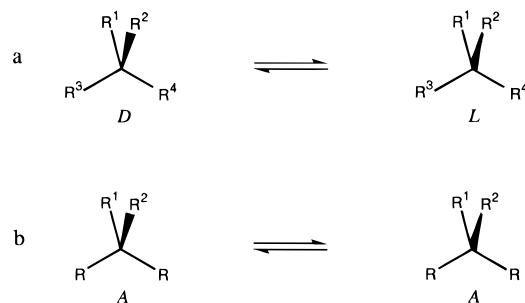


Figure 2. Racemization (a) due to inversion and the similar intramolecular process (b). For the proposal of one-wedge symbolization in stereochemical representation of quadrivalent centers used here, see: Lin, S.-K. A proposal for the representation of stereochemistry of quadrivalent centers. *Chirality* **1992**, *4*, 274–278.

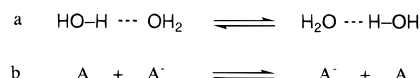


Figure 3. The motion of a proton in a hydrogen bond of water (a) and the similar intermolecular electron transfer process (b).

though such types of reaction have been undergone intensive theoretical considerations.^{28a,b} However, the entropy-symmetry correlation may provide a ready interpretation.

Normally, the process of Figure 1a or eq 15 is regarded as being driven by an entropy of mixing of *D* and *L* as enantiomeric pair—two *different* molecules.³³ This difference may be responsible for information registration in the solid state (see section 3.2). However, it should be emphasized that the two enantiomers *D* and *L* are also (energetically) *indistinguishable* (because eqs 12, 13, and 14 are satisfied).



Because eqs 12, 13, and 14 are satisfied, the racemization of a chiral molecule (Figure 1a or eq 15), where *D* and *L* are molecules of an enantiomer pair, is also a special degenerate reaction. Because of their (energetical) indistinguishability, we say $\sigma = 2$ and the entropy $S = N \ln 2$ for such a system of *N* molecules. The mutual transformation (eq 15) endows to a molecule a factual mirror symmetry (reflection), while an individual enantiomer has lower symmetry. The cause of the symmetry-increase may be due to the same kind of intramolecular process as the inversion of cyclohexane (Figure 1d)¹² or the inversion of a tetrahedral molecule (Figure 2)³⁴ such as an ammonia (Figure 1b)^{34b} molecule.

Another striking example is the dynamic process responsible for hydrogen bonding in ice (Figure 1e).³⁵ The transformation³⁶ is due to the jumping of a proton between the two positions. An isolated water molecule (H₂O) has symmetry C_{2v} in Schönflies notation.³⁶ However the solid state structure indicates the same resident time of the proton H⁺ in both positions, with four half-protons surrounding one oxygen atom, resulting in a local symmetry of T_d in the ice.³⁷ As estimated by Pauling^{14a,36} a residual entropy per molecule

$$S = \ln(3/2) \quad (16)$$

was calculated which matches the known value for H₂O ice^{14b} and later D₂O ice.^{14c}

Both of these two well-known examples (Figure 2a and Figure 3a) can be given explicit correlation of higher symmetry-higher entropy. If a racemization can occur as

shown in Figure 2a, there must be a no-reaction reaction as shown in Figure 2b to occur with exactly the same free energy profile on the potential energy hypersurface. The rationalization of the driving force for the reaction shown in eq 15 is the entropy of mixing of *D* and *L* isomers.³³ A comparison of this process (eq 15) with the similar ones (Figures 1 and 2) provides one of the most striking experimental facts and strong argument for rejecting the Gibbs paradox statement.^{5,38,39}

It should be pointed out that all these systems conform with the entropy additivity. If there are *N* molecules, the entropy content due to the symmetry will be

$$\begin{aligned} S &= N \ln \sigma \\ &= \ln \sigma^N \\ &= \ln w \end{aligned} \quad (17)$$

Generally σ can be defined as the symmetry number and σ_a can be defined as the apparent symmetry number for one molecule.^{40,41} The apparent symmetry numbers σ_a and w_a have logarithmic relations with entropy. On the other hand, molecular diversity (*M*) and apparent molecular diversity (M_a) have a direct logarithmic relation with information.¹⁵ If there are σ interconverting chemical species for a system of *N* molecules, the number of microstates or the symmetry number of the system will be

$$w = \sigma^N \quad (18)$$

Equation 18 gives a relation for σ and w . The apparent symmetry numbers w_a and σ_a have a similar relationship as shown in eq 18.

The ring inversion of cyclohexane (Figure 1d) at an elevated temperature results in a higher symmetry D_{6h} , instead of D_{3d} of the chair conformation.¹²

These examples of intramolecular dynamic processes add more evidence to illustrate clearly that transformations between σ energetically identical configurations, which may be made accessible at elevated temperatures or by catalysis, tremendously increase the symmetry—as indicated by the very large symmetry number w according to eq 18 and accordingly the entropy (eq 17). Note that all these increases of symmetry are due to activated dynamic motion.⁴² Symmetry is then a time-averaged property of the system. It is well-known that entropy as well as other thermodynamic properties are also time-averaged.^{42c}

A microscopic dynamic process, which may be either intermolecular (Figure 3)⁴³ or intramolecular,^{28,30–32} increases symmetry of the system. Recognition of the ubiquitous intermolecular degenerate-reactions is also significant in developing chemical reaction theories, for instance, the Marcus theory,^{43a} where no-reaction reactions,²⁹ such as electron transfer between two ions (Figure 3b) or analogous proton transfer and methyl group transfer, are also frequently encountered. A detailed discussion of the entropies of these reaction systems will be presented elsewhere.

With the development of dynamic NMR,⁴⁴ this kind of phenomena, either degenerate or nondegenerate, has been observed in more and more molecular systems.²⁸ Generally, for a nonsymmetrical intramolecular transformation, where the energy levels of the σ configurations are not degenerate, the entropy content will be calculated by eq 4, and its value will be less than that predicted by eq 6. The apparent

symmetry number w_a , which can be estimated by eq 8, will be less than w . The apparent number of symmetrical configurations (σ_a) will also be less than σ .

If some modes of molecular dynamic motion remain even at $T = 0$, the corresponding symmetry (with $w > 1$) will also remain.⁴⁵ Then there will be residual entropies. As I have mentioned, the symmetry and the residual entropy of ice due to the dynamic process (Figure 1e) considered by Pauling is a well-known example (vide supra). I may refer to the local symmetry T_d in ice as the residual symmetry, because this remains as T approaches zero.⁴⁶ However, normally at extremely low temperatures it is the symmetry of static structure (vide infra) that mainly contributes to the stability.

3.2. Informational Entropy and Symmetry of Static Structures. Based on the following observations it is even more obvious that the application of w_a – S relation to static molecular aggregation relies on the consideration of the entropy-information relation. Self-organization phenomena in nature repeatedly demonstrates that, at reasonably low thermodynamic temperatures, the spontaneously formed most stable static structures are the most symmetrical *perfect crystals* or as symmetrical as possible. These include phenomena as diverse as the arrangements of microorganisms,⁴⁹ living cells,⁵⁰ colloidal hard spheres,⁵¹ and globular proteins,⁵² the formation of micelles by molecular self-assembling,⁵³ amphiphilic bilayer molecular packing,⁵⁴ protein folding to form a more symmetrical spherical shape⁵⁵ which is responsible for many enzyme functions, the π - π stacking which stabilizes the double helical structure of DNA,⁵⁶ the formation of enantiomerically pure phases from a racemic mixture,³³ where all the *D* molecules aggregate together and all the *L* molecules crystallize together,^{3,4,57a} and finally the crystallization of identical molecules to form one bulky chiral phase.^{57b}

Moreover, the amazing phenomenon of ferromagnetism⁵⁸ is characterized by the fact that all the spins in the solid state are parallel, reaching the highest symmetry of the perfect crystal at zero temperature. It seems obvious that nothing should prevent these spins from orientating antiparallel. On the contrary, the well-established principles of electromagnetic theory,^{59,60} quantum mechanics,^{61,62} and thermodynamics and statistical mechanics⁶³ predict the formation of a structure of a nonperfect crystal where all the molecular orientations and spin orientations remain different.

As has been recognized by many reputable scientists,⁶⁴ theoretical considerations of many related phenomena need to resort to the consideration of symmetry. Furthermore, as these problems are basically statistical mechanics problems or thermodynamic problems of phase transition, it would be more conceivable if the symmetry consideration were to be directly connected to a familiar thermodynamic parameter such as entropy.

Because the Clausius definition of entropy

$$dS = \frac{\delta Q}{T} \quad (19)$$

is a function of temperature, and because it would be inconvenient to compare the structural stabilities of a perfect and a nonperfect crystal at zero temperature, we prefer to employ the Boltzmann expression (eq 6) and the expression

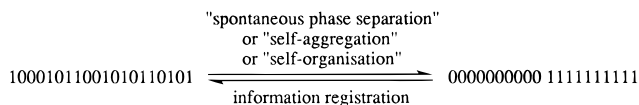


Figure 4. Informational registration as a binary string and the information loss due to a possible spontaneous process.

of von Neumann²¹ and Shannon (eq 4).^{22,15} These expressions can be readily used to evaluate the symmetry number of the concerned system (vide supra).⁶⁵ It is also very clear that at zero temperature the kinetic energy of molecules is no longer disposable, and the consideration of energy minimization is not pertinent. The only factor able to determine the relative structural stabilities of assemblage must be entropy, and, more specifically, informational entropy.^{15,65}

Note the comparison of static structural stabilities discussed here is different from that of the dynamic system equilibrium discussed in section 3.1, where a transformation can be carried out physically. Despite the difference, the contribution of symmetry to the stabilities of static structures is just as important as that of symmetry to the stabilities of systems of dynamic motions. As observed by several authors,^{1-4,66} neither a perfect crystal (a *static* structure of highest possible symmetry) nor an ideal gas (a *dynamic* structure of very high symmetry¹⁰) can be used for information processing⁶⁶ or as biological construction material;¹⁻⁴ both cases require the relevant molecular assemblage to be maintained at considerable low entropy.^{1-4,66} Just as entropy-increasing dynamic motions (vide supra) increased the symmetry of the system, the highest symmetry of a static structure correlates to the most stable solid state (perfect crystal) as a state of complete information loss and the highest informational entropy. This statement conforms well with the observation of Teich and Mahler⁶⁶ and all the related facts.⁴⁹⁻⁵⁷ An example is outlined below.

Given a molecular assemblage of $2N_A$ molecules with D and L as two enantiomers. Then this is a system with molecular diversity (M) value 2 if the chirality difference is our sole consideration.¹⁵ Suppose also that each molecule occupies one cell in a solid. Then the maximum information registered for a system of N molecules is, from Shannon²² expression¹⁵

$$\begin{aligned} I_{\max}(M,N) &= I_{\max}(2,2N_A) \\ &= \ln M^N = N \ln M \\ &= 2 \times 6.022 \times 10^{23} \ln 2 \\ &= 8.35 \times 10^{23} \text{ nats} \end{aligned} \quad (20)$$

where nat, corresponding to bit in a binary system,²² is the natural logarithmic unit, which we prefer to use. From a linear relation of information (I) and entropy (S)

$$I = S_{\max} - S \quad (21)$$

there will be a maximum entropy if the information is totally lost:

$$S_{\max}(2,2N_A) = 8.35 \times 10^{23} \text{ nats} \quad (22)$$

An information registration and a spontaneous self-organization to induce information loss in the one-dimensional case is depicted in Figure 4. The system where a

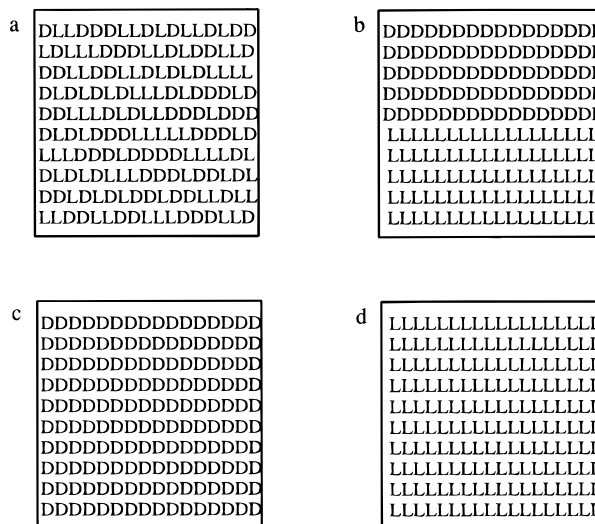


Figure 5. Schematic representations of molecular assemblage of $2N_A$ molecules (N_A is the Avogadro number) and its entropy in a very heterogeneous arrangement (a) after the formation of two phases (b) and the formation of only one phase (c and d).

large amount of information is coded must be extremely heterogeneous and of a highly aperiodic and asymmetrical arrangement (Figure 5a), as there is no translational symmetry in the solid. If two phases are formed from this system, where information is coded, one is pure D , the other is pure L (Figure 5b),^{57a} then a large loss of information will be the consequence. The apparent molecular diversity number (M_a) in each phase is 1, corresponding to virtually zero information content (relative to Figure 5a) in each phase. The entropy is $S = 2S_{\max}(2, N_A)$ which is virtually the same value as given in eq 22. The resulting system of two phases can be used to register at the most 2 bits of information—as there are two phases, and if each phase is regarded as a unit device,²² or

$$I_{\max}(2,2) = 2 \ln 2 = 1.39 \text{ nats} \quad (23)$$

The remaining information is transformed to entropy. Compared to the information (8.35×10^{23}) in Figure 5a, as given in eq 20, this number (1.39 nats) is negligible. There are two homogeneous phases. Due to the symmetry and homogeneity in the two separate phases, the information content registrable is the same as two of the $2N_A$ cells in the original structure: If I have the knowledge of one cell, I can claim that I have the full knowledge of all the other $N - 1$ cells in a phase. For information storage in a computer, if the phase separation occurred—for example, all “0” form one phase and all “1” give the other phase—presumably we lose all but 2 bits (or 1.39 nats) (Figure 4).

The formation of a homochiral phase of either D or L (Figure 5 (parts c and d, respectively)) is not impossible. A very pertinent example of such a case is observed by Kondepudi et al.,^{57,67} where the information left is

$$I_{\max}(2,1) = \ln 2 = 0.69 \text{ nats} \quad (24)$$

This means that, due to the symmetry and homogeneity in the whole phase, the information content is the same as in only one of the $2N_A$ cells: If the information of one of these $2N_A$ cells is known, we have full knowledge of all the remaining $2N_A - 1$ cells. Again, comparing the information content given in eq 20, the remaining 0.69 nats is negligible.

This could give an interpretation of why, at equilibrium, we observe perfect crystals as the most stable static structures such as solid phases. Clearly, nature does not tend to form a complicated heterogeneous solid phase lacking symmetry, because such a solid of a very complicated structure might presumably be used to register a tremendous amount of information and the information loss is a spontaneous process of entropy increase.

The discussion of static structures also shows that generally a higher symmetry can be correlated with a higher simplicity or less complexity.

4. INFORMATION THEORY OF STATIC STRUCTURE

As clearly pointed out by Gibbs in his statistical mechanics text, as the subtitle of the book,^{5b} statistical mechanics is the foundation of thermodynamics. More and more people have accepted the viewpoint that information theory is the foundation of statistical mechanics.⁶⁹ Unfortunately so far only the *dynamic* aspect of information loss and the corresponding entropy increase due to dynamic motion has been introduced. For example, if a typewriter of 35 keys was used to record information, and if all the 35^N combinations (equivalent to 35^N microstates of a *dynamic* system) appeared with identical probability, then a maximum entropy would result if all these combinations were printed out with an identical chance on an alphabetical string of length N .^{22a} Further practical examples of a thermodynamic system information loss were given in section 3.1.

However, as indicated in section 3.2, because information must be recorded on a *static* supporting material or as a static structure of molecular array, it is more important to give an information content formula for static structures. Because the information loss is the entropy increase, it follows that the relative stabilities can be estimated quantitatively. Unfortunately, to the knowledge of the present author, there is no such formula which can be used here. We have noticed that, for an array of N *different* molecules in N positions, if only N different molecules are available and are exhaustively used, then the maximum information registered is

$$I_{\max} = \ln N! \quad (25)$$

because there are $N!$ combinations. If all of these molecules are not different at all but very similar or factually *indistinguishable*, the total permutation symmetry number is $N!$, and the supposed information registration system has a total information loss of

$$S_{\max} = \ln N! \quad (26)$$

Shannon pointed out that the constant used in the logarithmic expression of entropy is a positive constant (K).^{22a} Because information can be registered by both simple (as simple as a spin) or composite entities (as composed of millions of molecules), whether the constant K defined by Shannon²² might be different from or the same as the Boltzmann constant, is a very important problem still open in the theory of information loss and entropy increase of static structures.

5. THE REJECTION OF THE GIBBS PARADOX STATEMENT

A careful reader may have already discerned that from both the interpretation of experimental observations (either

dynamic processes or static structures as shown in Figures 1–5) and the theoretical analyses,^{38,39,46,63} it is necessary to reject the statement of the Gibbs paradox of entropy of mixing.

The Gibbs paradox statement says that the isobaric and isothermal mixing of 1 mol of an ideal fluid A and 1 mol of a different ideal fluid B has the entropy increment

$$(\Delta S)_{\text{distinguishable}} = 2R \ln 2 = 11.53 \text{ JK}^{-1} \quad (27)$$

where R is the gas constant, while

$$(\Delta S)_{\text{indistinguishable}} = 0 \quad (28)$$

for mixing of indistinguishable fluids.^{5,70–72} It is assumed that eqs 27 and 28 are also applicable to solid mixtures^{5a} as well as gases and liquids.

If we want to reject this statement, it is sufficient to observe the fact that air bubbles in a liquid (which served as container for the air bubbles) of an identical component will spontaneously merge to achieve a gas–liquid phase separation; the fact that in a fluid system, oil droplets (same fluids) originally distributed in water (which served as container for the oil droplets) will *spontaneously* mix, and truly different fluids (oil and water) do not *spontaneously* mix. It has been routinely observed that in a system of a saturated solution with tiny crystals, the tiny crystals will slowly disappear to give larger crystals.⁷³ This is a very spontaneous process of forming a larger solid phase from initial smaller solids of identical composition.⁷³ These are simply facts of most spontaneous processes of “mixing” most similar (or identical) subsystems, whether they are *gases*, *liquids*, or *solids*.

The rejection is also obviously necessary based on the entropy-similarity relations, where the indistinguishability is correlated to the maximum entropy. One can illustrate this easily. If the information registration is a process of putting inks of different colors on paper, then the information loss process can be envisaged as a process whereby inks of different colors return to their respective ink chambers. This information-loss process is just like the phase separation, where identical substances merge together to achieve information loss at equilibrium.

The entropy term in eq 1 due to the Gibbs paradox statement, which cannot be included in the Nernst entropy calculation and cannot be measured by calorimetry, can be taken as a residual entropy due to the permutation symmetry (see eq 26).³⁹ This can be regarded as a treatment similar to that of the residual entropy of ice.

6. SYMMETRY AND ASYMMETRY

It is now clear that higher symmetry correlates with less orderliness, more simplicity and less complexity, because higher symmetry means less information content (eq 21). With these correlations established, it is worthwhile commenting that the frequent correlation of symmetry with beauty, and the consequent emphasis on certain aspects of symmetry, may be inadequate, incorrect, and sometimes misleading.⁷⁴ Life is beautiful but is full of asymmetry in all of its hierarchical structures.^{1–4} As mentioned previously, some coenzymes such as vitamin B₁₂ and F₄₃₀ are highly asymmetrical molecules,¹⁹ which may be more beautiful and

more significant⁷⁵ than artificial—in most cases symmetrical tetrapyrroles or other highly symmetrical macromolecules.⁷⁶ The enantiomerically selective synthesis remains an active research field in organic chemistry; it is full of challenges because of the asymmetry of the target compounds. Theoreticians have a strong tendency to destroy symmetry (mainly degeneracy), both in thermodynamics⁷⁸ and in quantum mechanics,^{79,34,61,64,68} with their powerful variational treatments. In consideration of any interactions, one may still finally have to resort to symmetry reductions introduced by perturbations. Thus, the search for asymmetry will be very important for both practical chemistry (organic synthesis) and theoretical chemistry (theories for spontaneous symmetry breaking phenomena in thermodynamics and quantum mechanics).^{34,64,68} We have revealed that symmetry and its increase are only a natural character of spontaneous processes by an obvious connection with the second law of thermodynamics. It is helpful for us to be clearly aware of the ubiquitous existence of symmetry and its increase and to find rational ways to interfere and prevent its increase or reduce it locally by imposing interactions, perturbations and confinements with the sacrifice of the symmetry increase of the surroundings.

7. CONCLUDING REMARKS

The logarithmic relations of entropy and symmetry have been established and used to quantitatively interpret dynamic stereochemical phenomena in chemical reactions and spontaneous symmetry-breaking phenomena in phase transitions such as crystallization. At higher temperatures, various activated modes of *dynamic* motion increase the symmetry of the system as indicated by the increased symmetry number. When temperature is lowered, the system keeps *static* symmetry as high as possible as indicated by a large information loss and a very high symmetry number. Thus, nature has a stubborn tendency to remain as symmetrical as possible regardless of whatever the temperature. Even at zero degrees, any equilibrium state must overwhelmingly prefer the highest symmetry.

These logarithmic relations can also be used in many other cases involving various phenomena of structural stability and process spontaneity as diverse as the justification of the resonance theory in chemical bonding (where the spontaneously formed stable ground state has higher symmetry and higher informational entropy) and the hydrophobic effect of protein folding (where odd shaped hydrophobic molecular bodies will spontaneously evolve into more symmetrical globular shapes), encouraged by the following profound observations, whether it is a process of elementary chemical reaction,⁸⁰ a phase transition,^{64,68} or a coupling of several irreversible processes,⁷ the symmetries of the involved subsystems are at least conserved. More broadly, these logarithmic relations can be readily used to investigate any many-body systems of complicated hierarchical dynamic and static structures. I may finally speculate that, perhaps without exception, for any process, the system will evolve spontaneously toward the highest dynamic or static symmetry. On reading the Clausius statement about entropy⁸¹ I may claim that *the universe evolves toward a maximum symmetry*.

ACKNOWLEDGMENT

The author wishes to thank Professor David Avnir and Dr. Edward Kirby for their encouragements and Dr. Gerald A. Murphy for English corrections.

REFERENCES AND NOTES

- (1) Schrödinger, E. *What Is Life? The Physical Aspect of Living Cell*; Cambridge University Press: London, 1945.
- (2) In Schrödinger's booklet 'What Is Life?' the spatial static asymmetry of genetic structure is repeatedly addressed.¹ The asymmetric geometrical arrangement of biopolymers (DNA or protein), in Schrödinger's own words, is an *aperiodic crystal* different from the symmetric "periodic crystals" (italics belong to Schrödinger¹). His famous statement is "life feeds on negative entropy".¹
- (3) Kondepudi, D. In *Entropy, Information, and Evolution*; Weber, B. H., Depew, D. J., Smith, J. D., Eds.; MIT Press: Cambridge, 1988; p 41.
- (4) Kondepudi, D. *Non-Equilibrium Polymers, Entropy, and Algorithmic Information*, In *Complexity, Entropy and the Physics of Information*; Zurek, W. H., Ed.; Addison-Wesley: Redwood City, CA, 1990; pp 199–206.
- (5) (a) Wannier, G. H. *Statistical Physics*; Dover: New York, 1987; p 167. (b) Gibbs, J. W. *The Collected Works of J. W. Gibbs*, Vol. II, *Elementary Principles in Statistical Mechanics*; Yale University Press: New York, 1948. (c) Gibbs, J. W. *The Collected Works of J. W. Gibbs*, Vol. I, *Thermodynamics*; Yale University Press: New York, 1948; pp 150–172.
- (6) (a) The symmetry numbers are defined, for example, in Mislow, K. *Introduction to Stereochemistry*; Benjamin: New York, 1965. See, also: Stoddart, J. F. *Stereochemistry of Carbohydrates*; Wiley-Interscience: New York, 1971; p 11. (b) Atkins, P. W. *Physical Chemistry*, 4th ed., reprinted with corrections; Oxford University Press: Oxford, 1992, p 596.
- (7) Onsager, L. Reciprocal relations in irreversible processes. I. *Phys. Rev.* **1931**, *37*, 405–425.
- (8) (a) Chandler, D. *Introduction to Modern Statistical Mechanics*; Oxford University Press: New York, 1987; p 31. (b) Reference 8a, p 154.
- (9) (a) Latal, H. *Parity Violation in Atomic Physics*, in *Chirality, from Weak Bosons to the α -Helix*; Janoschek, R., Ed.; Springer: Berlin, 1991, Chapter 1. (b) Pearson, R. G. *Symmetry Rules for Chemical Reactions*; Wiley: New York, 1976; p 1.
- (10) Ma, S.-K. *Statistical Mechanics*; World Scientific: Singapore, 1985; pp 505–508.
- (11) Generally, dynamic motions will increase the symmetry.^{10,12,13} The homogeneity and isotropicity of a gas are symmetry properties.¹⁰
- (12) (a) Eliel, E. L. Book review comment. *J. Am. Chem. Soc.* **1994**, *116*, 6994. (b) Heilbronner, E.; Dunitz, J. D. Reflections on Symmetry in Chemistry; VCHCA and VCH: Basel and Weinheim, 1993.
- (13) A well-known example is the residual entropy of ice due to the dynamic motion of a proton in between the two oxygen atoms. This increases the symmetry of an individual molecule (C_{2v}) to T_d .¹⁴
- (14) (a) Pauling, L. The structure and entropy of ice and of other crystals with some randomness of atomic arrangement. *J. Am. Chem. Soc.* **1935**, *57*, 2680–2684. (b) Giaque, W. F.; Stout, J. W. The entropy of water and the third law of thermodynamics. The heat capacity of ice from 15 to 273 K. *J. Am. Chem. Soc.* **1936**, *58*, 1144–1150. (c) Long, E. A.; Kemp, J. D. The entropy of deuterium oxide and the third law of thermodynamics. Heat capacity of deuterium oxide from 15 to 298 K. The melting point and heat of fusion. *J. Am. Chem. Soc.* **1936**, *58*, 1829–1834.
- (15) Lin, S.-K. Molecular diversity assessment and preservation strategies. *Molecules* **1996**, *1*, to be published.
- (16) So far the symmetry number is used only for rotations—the so called proper symmetry operation.⁶ I propose that a "proper" (or allowed) operation can be *any* transformation, for example, a rotation, inversion, reflection, permutation, or a *complicated process such as a chemical reaction*. Normally only rotation is regarded as a proper operation,⁶ because the transformation can be properly realized. But if another transformation occurred in the concerned system, it should also be treated as an operation to increase the symmetry of the system and to make more microstates accessible. For example, the inversion of the cyclohexane molecule¹² can be treated as a proper operation or transformation which may make a contribution to the entropy, because such an inversion is very similar to the racemization (which has an effect of entropy increase, see: Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates, and Resolutions*; Wiley: New York, 1981; p 47.) of enantiomers due to the inversion. It should be emphasized that it is *not* the specific type of transformation (rotation or permutation or whatever else) that determines the symmetry number of the system.

- The rotation, which is the only transformation regarded as the proper operation so far, can also become strictly hindered, resulting in rotational isomers, see: Oki, M. *The Chemistry of Rotational Isomers*; Springer-Verlag: Berlin, 1993.
- (17) Clausius, R. Ueber verschiedene für die Anwendung bequeme Formen der Hauptgleichungen der mechanischen Wärmetheorie. *Ann. Phys.* **1865**, *125*, 353–400.
- (18) Wehrl, A. General Properties of entropy. *Rev. Mod. Phys.* **1978**, *50*, 221–260.
- (19) Eschenmoser, E. Chemistry of corphinoids. *Ann. N. Y. Acad. Sci.* **1986**, *471*, 108–129.
- (20) Zabrodsky, H.; Peleg, S.; Avnir, D. Continuous symmetry measures. *J. Am. Chem. Soc.* **1992**, *114*, 7843–7851; Zabrodsky, H.; Peleg, S.; Avnir, D. Continuous symmetry measures. 2. Symmetry groups and the tetrahedron. *J. Am. Chem. Soc.* **1993**, *115*, 8278–8289; Zabrodsky, H.; Avnir, D. Continuous symmetry measures. 4. Chirality. *J. Am. Chem. Soc.* **1995**, *117*, 462–473.
- (21) von Neumann, J. *Mathematical Foundations of Quantum Mechanics*; Princeton University Press: Princeton, 1955; p 347.
- (22) (a) Shannon, C. E. A mathematical theory of communication. *Bell Sys. Tech. J.* **1948**, *27*, 379–423; 623–656. (b) Shannon, C. E.; Weaver, C. E. *The Mathematical Theory of Communication*; University of Illinois Press: Urbana, IL, 1949.
- (23) Conventionally a similarity index is defined as a number within the range of 0 and 1: Kubinyi, H. *QSAR: Hansch Analysis and Related Approaches*, Weinheim: VCH, 1993, p 172; Richards, W. G. Computer-aided drug design. *Pure Appl. Chem.* **1994**, *66*, 1589–1596.
- (24) The proof of this inequality can be found in the literature: Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989; pp 255–258. Hansen, J. P.; McDonald, I. R. *Theory of Simple Liquids*; Academic Press: London, 1976; p 149.
- (25) Gasser, R. P. H.; Richards, W. G. *Entropy and Energy Levels*; Clarendon, Oxford, 1974.
- (26) Reference 6b, p 324.
- (27) Pelliott, J. T.; Dawber, P. G. *Symmetry in Physics*; reprinted with corrections, Macmillan: London, 1985.
- (28) (a) Brocas, J.; Gielen, M.; Willem, R. *The Permutational Approach to Dynamic Stereochemistry*; McGraw-Hill: New York, 1983. (b) Sokolov, V. I. *Introduction to Theoretical Stereochemistry*; Gordon and Breach Science Publishers: New York, 1991; Chapter 5. (c) M. Oki, *The Chemistry of Rotational Isomers*; Springer-Verlag: Berlin, 1993. (d) Minkin, V. I.; Nivorozhkin, L. E.; Korobov, M. S. Stereodynamics and degenerate ligand exchange in solutions of tetracoordinate chelate complexes of nontransition metals. *Russ. Chem. Rev.* **1994**, *63*, 289–311.
- (29) “No-reaction” stands for the fact that the educt and the product are both energetically and configurationally the same.
- (30) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; Chapter 18.
- (31) Doering, W. von E.; Roth, W. R. A rapidly reversible degenerate Cope rearrangement. Bicyclo[5.1.0]ocza-2,5-diene. *Tetrahedron* **1963**, *19*, 715–737.
- (32) (a) See p 1133 of ref 30. (b) Huang, Y.; Macura, S.; Ernst, R. R. Carbon-13 exchange maps for the elucidation of chemical exchange networks. *J. Am. Chem. Soc.* **1981**, *103*, 5327–5333. (c) Titman, J. J.; Luz, Z.; Spiess, H. W. Solid-state reactions studied by carbon-13 rotor-synchronized magic angle spinning two-dimensional exchange NMR. 2. The Cope rearrangement and molecular reorientation in bullvalene. *J. Am. Chem. Soc.* **1992**, *114*, 3765–3771.
- (33) Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates, and Resolutions*; Wiley: New York, 1981; p 47.
- (34) (a) Barron, L. D. Can a magnetic field induce absolute asymmetric synthesis? *Science* **1994**, *266*, 1491–1492, and the citations. Quack, M. Molecular quantum dynamics from high resolution spectroscopy and laser chemistry. *J. Mol. Struct.* **1993**, *292*, 171–196. (b) Anderson, P. W. More is different. *Science* **1972**, *177*, 393–396.
- (35) Perrin, C. L. Symmetries of hydrogen bonds in solution. *Science* **1994**, *266*, 1665–1668, and references cited therein.
- (36) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, 1960; Chapter 12.
- (37) Mak, T. C. W.; Zhou, G.-D. *Crystallography in Modern Chemistry*; Wiley: New York, 1992; p 106.
- (38) But reactions shown in Figure 2b also happen and have all the same kinetic features as a normal reaction (requiring activation energy, for example) and as an energetically degenerate process as all the remaining processes depicted in Figures 1–3. Therefore, these reactions must have the driving force due to the entropy of mixing *indistinguishable* chemical entities.
- (39) I comment that, if the conventional entropy concept can be used to interpret an energetically degenerate process,³⁸ I can also apply this argument to other energetically degenerated dynamic processes, such as the permutation transformations between the $N!$ equivalent microstates in an ideal gas system of N particles. Therefore, these experimental facts of “no-reaction” reaction (Figures 1–3) lend one more strong support to our rejection of Gibbs paradox statement⁵ (vide infra).
- (40) (a) We encounter a noninteger symmetry number in the case of the residual entropy of ice. Therefore, it is better to use w_a instead of w in eq 17 for ice. Incidentally, a straightforward application of eq 4 may lead to an easier estimation of the residual entropies.
- (41) The increase of symmetry due to the dynamic motion reduces the apparent molecular diversity M_a from its maximum value M to its minimum value 1^{15} and increases the apparent symmetry number per molecule (σ_a) from 1 to its maximum value σ . For example, the interconversion of D and L (Figure 1a) will reduce M_a from 2 to 1; the molecule appears as D at one moment and as L at another moment and is averaged to 1. This process also increases σ_a from 1 to 2.
- (42) (a) A problem may arise in this context about the symmetry-number (w and σ) accounting for the corresponding entropy calculation. Suppose different configurations of a molecule are used to register information. This requires the system to remain in originally designed microstates *forever*. In turn, this means that it will be desirable that the microstate be surrounded by an infinitely high energy barrier. In the word of conventional potential surface, this microstate is situated in an infinitely deep potential-well and so assumes a local minimum potential energy forever. Otherwise, if the energy threshold surrounding the configuration of a molecule on the potential surface is finite, the information registered as a specified microstate will be lost. In this sense, the estimation of the entropy and the symmetry number is subjective.^{42b} Because entropy function (or the information loss) is independent of time^{42c} and in order to avoid any further and complicated philosophical dispute here, we assume that there is an infinitely high potential barrier (the wall) surrounding the territory where the w microstates or σ configurations are situated and the energy barrier among these w microstates (σ configurations) are finite. (b) Denbigh, K. G.; Denbigh, J. S. *Entropy in Relation to Incomplete Knowledge*; Cambridge University Press: London, 1985. (c) Lin, S.-K. Time symmetry and thermodynamics. *Computers Math. Applic.* **1991**, *22*, 67–76, and the citations.
- (43) (a) Marcus, R. A. Electron transfer reactions in chemistry. Theory and experiment. *Rev. Mod. Phys.* **1993**, *65*, 599–610. Marcus, R. A. Chemical and electrochemical electron-transfer theory. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155–196. (b) Ebersson, L.; Gonzalez-Luque, R.; Lorentzon, J.; Merchan, M.; Roos, B. O. Ab Initio calculation of inner-sphere reorganization energies of inorganic redox couples. *J. Am. Chem. Soc.* **1993**, *115*, 2898–2901, and references cited therein.
- (44) E.g., ref 32b.
- (45) There are many reports on such types of dynamic processes in solid state, which might be a surprise, as solid state is normally assumed to be of static structure, for example, see ref 32c.
- (46) Similarly, the entropy-symmetry correlation permits us to attribute the large discrepancy between the experimentally measured Nernst entropy (e.g., see ref 47) and the absolute entropy calculated by an ideal gas model⁴⁸ to a residual entropy, which is $S_0 = \ln N!$, with the residual symmetry number $w = N!$ existing in the perfect crystal of N particles at zero temperature.
- (47) Giaque, W. F.; Ashley, M. Molecular rotation in ice at 10 K. Free energy of formation and entropy of water. *Phys. Rev.* **1933**, *43*, 81–82.
- (48) Kittel, C.; Kroemer, H. *Thermal Physics*; Freeman: San Francisco, 1980; pp 165–168.
- (49) E.g., see: Skvarla, J. A physico-chemical model of microbial adhesion. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 2913–2921.
- (50) E.g., see: Fisher, L. Forces between biological surfaces. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 2567–2582.
- (51) E.g., see: Bartlett, P.; Ottewill, R. H.; Pusey, P. N. Freezing of binary mixtures of colloidal hard spheres. *J. Chem. Phys.* **1990**, *93*, 1299–1312. Several authors thought this is an entropy-driven process. But no explanation was provided: Eldridge, M. D.; Madden, P. A.; Frenkel, D. Entropy-driven formation of a superlattice in a hard-sphere binary mixture. *Nature* **1993**, *365*, 35–37. See also: Jackerson, B. J. When order is disordered. *Nature* **1993**, *365*, 11–12.
- (52) E.g., see: Young, L. R. D.; Fink, A. L.; Dill, K. A. Aggregation of globular proteins. *Acc. Chem. Res.* **1993**, *26*, 614–620.
- (53) E.g., see: Menger, F. M.; Littau, C. A. Gemini surfactants: A new class of self-assembling molecules. *J. Am. Chem. Soc.* **1993**, *115*, 10083–10090.
- (54) E.g., see: Jeffrey, G. A. Carbohydrate liquid crystals. *Acc. Chem. Res.* **1986**, *19*, 168–173.
- (55) E.g., see: Chan, H. S.; Dill, K. A. The protein folding problem. *Phys. Today* **1993**, (2), 24–32. Dill, K. A. Dominant forces in protein folding. *Biochemistry* **1990**, *29*, 7133–7155.
- (56) E.g., see: Dahl, T. The nature of stacking interactions between organic molecules elucidated by analysis of crystal structures. *Acta Chem. Scand.* **1994**, *48*, 95–106.
- (57) (a) E.g.: Eckhardt, C. J.; Peachey, N. M.; Swanson, D. R.; Takacs, J. M.; Khan, M. A.; Gong, X.; Kim, J. H.; Wang, J.; Uphaus, R. A.;

- Separation of chiral phases in monolayer crystals of racemic amphiphiles. *Nature* **1993**, *362*, 614–616. (b) Kondepudi, D. K.; Bullock, K. L.; Digits, J. A.; Yarborough, P. D. Stirring rate as a critical parameter in chiral symmetry breaking crystallization. *J. Am. Chem. Soc.* **1995**, *115*, 401–404. Kondepudi, D. K.; Bullock, K. L.; Digits, J. A.; Hall, J. K.; Miller, J. M. Kinetics of chiral symmetry breaking in crystallization. *J. Am. Chem. Soc.* **1995**, *115*, 10211–10216.
- (58) Ma, S.-K. *Modern Theory of Critical Phenomena*; W. A. Benjamin: London, 1976.
- (59) Wangsness, R. K. *Electromagnetic Fields*, 2nd ed.; John Wiley & Sons: New York, 1986.
- (60) Antiparallel orientation of spins are obviously energetically more favorable because the structure would have lower energy.⁵⁹
- (61) (a) Atkins, P. W. *Molecular Quantum Mechanics*, 2nd ed.; Oxford University Press: Oxford, 1983. (b) The persistence of symmetry in a quantum system is embedded in the Pauli principle.^{62a} But any such symmetry can be easily removed by variational methods if one would like to do so. For example, a system of two degenerate states can easily be made non-degenerate by an interaction of the two degenerate states.
- (62) (a) The Pauli principle (see p 365, 382, and 611 of ref 6b and Pauli, W. Exclusion principle, Lorentz group and reflection of space-time and charge. In *Niels Bohr and the Development of Physics*, Pergman Press: London, 1955, pp 30–51.) will be justified based on the logarithmic relations of entropy and symmetry.^{62b} (b) Lin, S.-K. Negative temperature of electronic motion in atoms and molecules. To be submitted.
- (63) The antiparallel orientations of all the spins would result in an entropy of mixing; see ref 5a, pp 332–333. If all spins are parallel, such entropy of mixing does not exist, based on the Gibbs paradox statement of entropy of mixing.
- (64) For example, see Wilson's Nobel Prize award address: Wilson, K. G. The renormalization group and critical phenomena. *Rev. Mod. Phys.* **1983**, *55*, 583–600, and citations.
- (65) (a) The discussions on compatibility of thermodynamic entropy (eq 19) and informational entropy can be found in the literature.^{18,65b,65c} (b) *Entropy, Information, and Evolution*; Weber, B. H., Depew, D. J., Smith, J. D., Eds.; MIT Press: Cambridge, 1988. (c) *Complexity, Entropy and the Physics of Information*; Zurek, W. H., Ed.; Addison-Wesley: Redwood City, CA, 1990.
- (66) Teich, W. G.; Mahler, G., in ref 65c, p 289, especially p 291.
- (67) Kondepudi et al.^{57b} observed the formation of chiral crystal from nonchiral molecules. One may observe the formation of such a homochiral phase from a real racemic mixture of two enantiomers which are interchangeable. The formation of one of the two homochiral phases with slightly higher probability is discussed by several authors.^{3,4,34a,68}
- (68) Chela-Flores, J. The origin of chirality in protein amino acids. *Chirality* **1994**, *6*, 165–168. Salam, A. The role of chirality in the origin of life. *J. Mol. Evol.* **1991**, *33*, 105–113.
- (69) Jaynes, E. T. Information theory and statistical mechanics. *Phys. Rev.* **1957**, *106*, 620–630.
- (70) Gibbs, J. W. On the equilibrium of heterogeneous substances. *Trans. Conn. Acad.* **1875–1876**, *3*, 108; especially pp 227–229.
- (71) Lin, S.-K. Gibbs paradox and its resolutions. *Ziran Zazhi (Nature Journal, China)* **1989**, *12*, 376–379.
- (72) The resolutions of this paradox has been very controversial. Some recent debates are: Lesk, A. M. On the Gibbs paradox: what does indistinguishability really mean? *J. Phys. A: Math. Gen.* **1980**, *13*, L111-L114. van Kampen, N. G. *The Gibbs Paradox*, In *Essays in Theoretical Physics*; Parry, W. E., Ed.; Pergamon: Oxford, 1984, 303–312. Kemp, H. R. Gibbs' paradox for entropy of mixing. *J. Educ. Chem.* **1985**, *62*, 47–49. Kemp, H. R. Gibbs' paradox: Two views on the correction term. *J. Educ. Chem.* **1986**, *63*, 735–736. Dieks, D.; van Dijk, V. Another look at the quantum mechanical entropy of mixing. *Am. J. Phys.* **1988**, *56*, 430–434. Richardson, I. W. The Gibbs paradox and unidirectional fluxes. *Eur. Biophys. J.* **1989**, *17*, 281–286; Wantke, K.-D. A remark on the Gibbs-paradox of the entropy of mixing of ideal gases. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *94*, 537.
- (73) This phenomenon is observed and the corresponding technique of unit operation is used routinely in solid chemicals production plants.
- (74) (a) See ref 12b. (b) Zee, A. *Fearful Symmetry, The Search for Beauty in Modern Physics*; Collier Books: New York, 1986; p 13.
- (75) Cornforth, J. W. *Asymmetry and Enzyme Action*; The Nobel prize in chemistry lecture, In *J. Mol. Catal.* **1975–1976**, *1*, pp 145–157.
- (76) This is said without any disparagement of the studies of supramolecular chemistry which is valuable for many other obvious reasons.⁷⁷
- (77) Lehn, J.-M. From coordination chemistry to supramolecular chemistry. In *Perspectives in Coordination Chemistry*; Williams, A. F., Floriani, C., Merbach, A. E., Eds.; VHC: Basel, 1992; pp 447–62, and the citations.
- (78) See ref 8, p 135.
- (79) For example, the treatment of degenerated intramolecular processes depicted in Figure 1a.
- (80) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie and Academic Press: Weinheim, 1970; Fukui, K. *Theory of Orientation and Stereo Selection*; Springer Verlag: Berlin, 1975.
- (81) "Die Energie der Welt ist constant. Die Entropie der Welt strebt einem Maximum zu". See: Clausius, R. Ueber verschiedene für die Anwendung bequeme Formen der Hauptgleichungen der mechanischen Wärmetheorie. *Ann. Phys.* **1865**, *125*, 353–400; especially p 400.

CI950077K