
Gibbs paradox of entropy of mixing: experimental facts, its rejection and the theoretical consequences

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SUMMARY

Gibbs paradox statement of entropy of mixing has been regarded as the theoretical foundation of statistical mechanics, quantum theory and biophysics. A large number of relevant chemical and physical observations show that the Gibbs paradox statement is false. We also disprove the Gibbs paradox statement through consideration of symmetry, similarity, entropy additivity and the defined property of ideal gas. A theory with its basic principles opposing Gibbs paradox statement emerges: entropy of mixing increases continuously with the increase in similarity of the relevant properties. Many outstanding problems, such as the validity of Pauling's resonance theory and the biophysical problem of protein folding and the related hydrophobic effect, etc. can be considered on a new theoretical basis. A new energy transduction mechanism, the deformation, is also briefly discussed.

KEY WORDS Gibbs paradox; entropy of mixing; mixing of quantum states; symmetry; similarity; distinguishability

1. INTRODUCTION

The Gibbs paradox of mixing says that the entropy of mixing *decreases discontinuously* with an increase in similarity, with a zero value for mixing of the most similar or indistinguishable subsystems: The isobaric and isothermal mixing of one mole of an ideal fluid A and one mole of a different ideal fluid B has the entropy increment

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

where R is the gas constant, while

$$(\Delta S)_{\text{indistinguishable}} = 0 \quad (2)$$

for the mixing of indistinguishable fluids [1–10]. It is assumed that **Equations (1) and (2)** are also applicable to the formation of solid mixtures and liquid mixtures.

Gibbs paradox statement of entropy of mixing has been regarded as the theoretical foundation of statistical mechanics [11], quantum theory [12] and biophysics [7]. The resolutions of this paradox has been very controversial for over one hundred years. Many famous physicists confidently claim that they have resolved this paradox, in very diverse and different ways. A sustaining problem is that they do not agree with each other. For example, besides numerous other resolutions [2, 4–9], von Neumann [13] provided a well-known quantum mechanical resolution of this paradox with which not many others are in full agreement [6].

Though the validity of this statement has been taken for granted in all of the textbooks for over a century, and it seems impossible for the present author, like anyone else, to conceive at first sight that

there were any entropy effects when mixing indistinguishable fluids, it is theoretically challenged once the Gibbs paradox statement is finally compared to all of the striking physical realities.

With the establishment of the logarithmic relation of symmetry and entropy [1], it also becomes very straightforward to prove formally, as will be done here, that Gibbs paradox statement, as expressed in the Equations (1) and (2) and other related expressions, is wrong. These formulas of entropy–similarity correlation and the entropy–symmetry correlation constitute a new theory.

A brief overview and descriptive outline of the solution of several outstanding problems of structural relative stabilities and process spontaneities will also be presented. For example, by opposing von Neumann’s conclusion [13], the mixing of quantum states of indistinguishable properties gives the maximum entropy which immediately lends support to the validity of Pauling’s resonance theory. I present these results here in order to arouse the attention of the theoreticians in chemistry and physics: a very fundamental aspect of statistical mechanics has to be reconstructed.

2. ENTROPY EXPRESSIONS

For an ideal gas system of N monatomic particles, from the Maxwell–Boltzmann momentum distribution of free particles, the partition function of any one of these N free particles due to kinetic energy of translational motion in a system of V and T is [14]

$$\begin{aligned} q &= \frac{1}{h^3} \int \int \int dx dy dz \int \int \int e^{-E/k_B T} dp_x dp_y dp_z \\ &= \frac{1}{h^3} \cdot V \cdot (2\pi m k_B T)^{3/2} \end{aligned} \quad (3)$$

where the total energy E includes only the kinetic energy of translational motion, m is the mass, and p_i ($i = x, y, z$) is momenta. The Boltzmann constant k_B will be taken as 1 in most of the following entropy expressions. According to classical statistical mechanics, naturally the partition function of the system of N *independent* particles should be

$$Q = q^N \quad (4)$$

Therefore, entropy should be

$$S(V, T) = k_B N \left[\ln V + \frac{3}{2} \ln \left(\frac{2\pi k_B m T}{h^2} \right) + \frac{3}{2} \right] \quad (5)$$

From this original formula of the classical statistical mechanics, the isobaric isothermal mixing of N subphases of gases $G_1, \dots, G_i, \dots, G_N$ with particle numbers $N_1, \dots, N_1, \dots, N_N$ will have a limited value of entropy increase, provided that the N particles are *independent*, regardless of whether they are different or identical ideal gas particles. Our entropy–similarity correlation conforms with the classical statistical mechanics.

In all modern statistical mechanics texts, however, instead of Equation (4), the formula is

$$Q = \frac{1}{N!} q^N \quad (6)$$

The rejection of the Gibbs paradox statement is the removal of a factor $1/N!$ in the partition function expression (Equation (6)), provided that Equation (3) is still valid.

Equation (6) with the factor $1/N!$ in it is assigned (not derived) subjectively by Gibbs (see the

concluding part of his book [15]) solely due to the argument of particle indistinguishability. This factor asserts explicitly that all $N!$ permutations of the N indistinguishable particles must be counted as 1, because of the permutation symmetry [14].

The effort to design experiments that are pertinent to the question of gaseous phase mixing, to check directly whether the factor $1/N!$ should be removed from Equation (6), is not successful. In many cases the difference between Equation (4) and Equation (6) is not noticeable because most formulas, such as those of pressure

$$P = Nk_B T \left(\frac{\partial}{\partial V} \ln Q \right)_T \quad (7)$$

and of the total energy

$$E = Nk_B T^2 \left(\frac{\partial}{\partial T} \ln Q \right)_V \quad (8)$$

give observable quantities through the derivative of the logarithm of Q , as we understand that a differential of a logarithm of a constant, whether it is 1 or $N!$, is 0. Interestingly, only entropy expressions have a difference: by using Stirling approximation ($N! \approx (N/e)^N$), the use of Equation (6) yields the well-known Sackur–Tetrode equation [16]

$$S(V, T) = k_B N \left[\ln V + \frac{3}{2} \ln \left(\frac{2\pi k_B m T}{h^2} \right) + \frac{3}{2} \right] - Nk_B \ln N + Nk_B \quad (9)$$

From this expression, the entropy increment due to mixing of the same gases is zero. On the contrary, from Equation (5) we find that the entropy of mixing is the same whether the subsystem particles are distinguishable or indistinguishable. But, as elegantly argued by Stern [17], it is also practically impossible by entropy measuring through calorimetry to decide the existence or non-existence of the factor $1/N!$ in the partition function expression and the entropy term $k_B \ln N!$ in the entropy expression. Furthermore, as pointed out by Kaplan [18], all observable quantities are invariant under permutation of identical particles and, consequently, the permutations of identical particles cannot be directly observed.

However, as will be seen in the following section, there are a large number of physical and chemical observations which can be used to check whether the Gibbs paradox statement and the relevant formulas of entropy are valid or not.

3. FACTS

3.1. Mixing of hydrocarbons in water

Note that it is assumed that Equations (1) and (2) are also applicable to solid mixtures as well as gases and liquids.

Two droplets of hydrocarbons in water will spontaneously merge to form a combined phase (Figure 1). Hydrocarbons pentane (A) and hexane (B) mix in water because they are similar in properties. In fact, two identical hydrocarbons pentane (A) merge no less spontaneously than the mixing of A and B (Figure 1) in water.

One may argue that the examples given here are a problem of the interface between oil and water. This problem will be treated very thoroughly elsewhere (see also Section 6.3). However, in fact, really different fluids such as oil and water do not spontaneously mix, and really similar or identical fluids do mix. In a typical phase separation experiment, really different compounds separate as a result that indistinguishable substances most spontaneously ‘mix’.

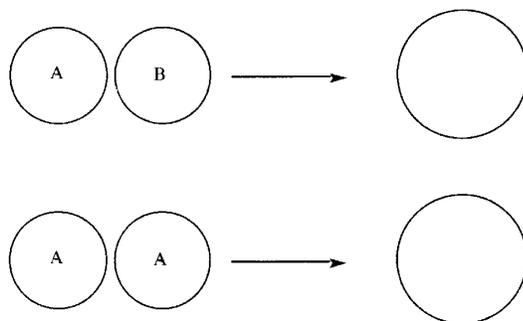


Figure 1. Mixing of hydrophobic fluids of different but similar properties (a) and of indistinguishable properties (b)

Firstly, suppose a drop of hydrocarbon A (say, benzene) and a drop of another hydrocarbon B (toluene) are distributed in the third liquid C (water). As a consequence of their *difference*, A does not mix with C. This means that Equation (1) does not generally conform with the observation. One can expect that the two oil drops A and B will mix to form a homogeneous organic phase and separate from the aqueous phase (C). The spontaneous mixing of A and B should have an entropy of mixing, due to the similarity of A and B, which conforms very well with the correlation of entropy–similarity [1]. Now if both A and B are droplets of *indistinguishable* hydrocarbons (both are toluene droplets, for instance), one would predict, from Equations (1) and (2), that A and B will not mix because there is no entropy of mixing (Equation 2). In fact, the opposite is true: the well-known hydrophobic effect [19, 20]. Phase equilibrium measurements reveal that the entropy of mixing (A mixes with A) from C (water) is always positive (Table 1) [20] and that the entropy increase is the dominant effect contributing to the decrease of the Gibbs free energy (G) [20]. Because the two droplets (A and A) can be originally distributed in water (C) mechanically (or homogeneously at elevated pressure and temperature), this phase separation process is more accurately described as demixing.

3.2. Entropy of a crystal versus entropy of a gas

To divide a certain volume of an ideal gas into half of its original volume with an equal half number of particles, the system of 1 mole of the same fluid (say a gas of the same kind) is finally put into N_A number of chambers, and each particle is confined within a volume of V/N_A (cf. Figure 2), N_A being Avogadro number. The situation is like a lattice structure. The particles are highly strictly confined in space. The release of N_A particles from their individual confinements, so that all of the particles mix and have the whole space of volume V to perform Brownian motion in solution or free translational motion in gaseous state, will unavoidably result in a large entropy increment [21], presumably

$$\Delta S = k_B \ln N_A^{N_A} = R \ln N_A \quad (10)$$

The Gibbs paradox argument of distinguishability is very vulnerable at this point: it is ridiculous to assume that the entropy of an ideal crystal is greater than that of the corresponding ideal gas by including a factor $1/N!$ in the partition function expression for a gas. As everybody knows, particles in a lattice structure are highly constrained (relative to a gas), and the system has a much smaller entropy value than that of the corresponding gas [22, 23]. But, as Gasser and Richards [21] explicitly indicated, the inclusion of $1/N!$ in Equation (6) means that

Table 1. Thermodynamic parameters (kcal mol⁻¹) in the transfer of hydrocarbons from water to organic phases (data from [20]).

Process	<i>T</i> (K)	<i>TΔS</i>	ΔH	ΔG
C ₃ H ₈ in water to liquid propane	298	6.85	1.80	-5.05
<i>n</i> -C ₄ H ₁₀ in water to liquid <i>n</i> -butane	298	6.85	1.00	-5.85
C ₆ H ₆ in water to liquid benzene	291	4.07	0.00	-4.07
C ₇ H ₈ in water to liquid toluene	291	4.65	0.00	-4.65
C ₈ H ₁₀ in water to pure ethylbenzene	291	5.50	0.00	-5.50
<i>m</i> - or <i>p</i> -xylene in water to pure C ₈ H ₁₀	291	5.80	0.00	-5.80

$$\begin{aligned}
 S_{\text{crystal}} - S_{\text{gas}} &= k_{\text{B}} \ln \left(\frac{w_{\text{crystal}}}{w_{\text{gas}}} \right) \\
 &= k_{\text{B}} \ln N! \\
 &= k_{\text{B}} N (\ln N - 1)
 \end{aligned} \tag{11}$$

which in turn means clearly that the solid phase has an entropy content substantially higher than the corresponding gas. This is impossible! The inclusion of $-k_{\text{B}} \ln N!$ in the Sackur–Tetrode equation (Equation (9)) must be wrong.

3.3. No-reaction reactions

In all of the textbooks, racemization is described as a process driven by the entropy of mixing of two enantiomers R and S (Figure 3). In fact, if a racemization happens, there is almost always a similar reaction that leads to the formation of a product which is identical to the educt.

One example is the S_N2 reaction of iodide and ethyl iodide (Figure 4). Because the reactant and the product are indistinguishable, these reactions are the so-called no-reaction reactions. From these phenomena, we see that, if a process of mixing different species spontaneously happens, there must be a similar process that happens no less spontaneously between identical particles.

Consider the reaction in Figure 5. If the compounds A and B are very different in properties, for example their energy levels are very different (here B is much lower) then the resonance reaction will seldom happen. In principle, there will be a reversal reaction, but the reversal reaction can be practically ignored. Therefore, such ‘mixing’ does not happen efficiently, if ever, if they are different in properties. Therefore, once again, *difference* is not the source of the entropy of mixing.

3.4. Combinatorial chemistry and molecular diversity

A mixture of *different* molecules and a mixture of *indistinguishable* compounds must have different entropy increments during the mixing processes. Then, a process to prepare such mixtures should have different entropy and information increments.

Practically, there is a trivial standard about molecular diversity [24] that a collection of many different molecules are certainly more interesting than the collection of the same number but otherwise very similar or indistinguishable compounds. A theoretical explanation for the validity of this standard should be an easy task. However, mathematical relations between entropy (defined as information loss) and

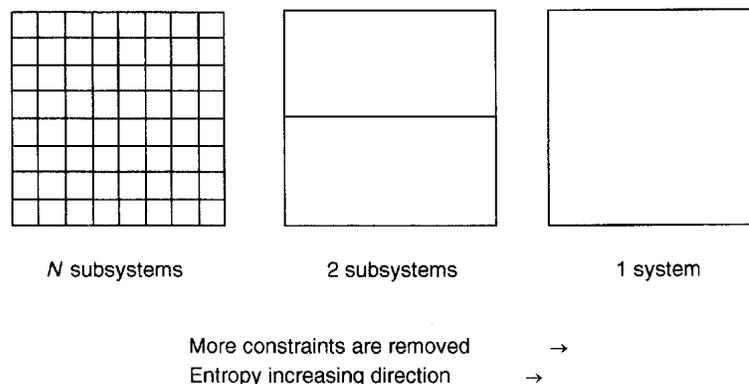


Figure 2. Mixing conceived as a process of removing constraints

diversity, similarity and indistinguishability were never explicitly established in conventional statistical mechanics texts. What is worse, an informational theoretical explanation is confronted with the famous *Gibbs* paradox statement of entropy of mixing [2–13]. The statement says that the mixing of *different* compounds (which should be desirable for a compound library of a high-quality molecular diversity as a mixture) has an entropy of mixing, while mixing of indistinguishable molecules has minimum – which is zero – entropy of mixing. This implies that a mixture (or a combinatorial compound library) of many *different* compounds provides less information than a library consisting of many very similar or *identical* compounds!

In fact, the combinatorial compound library of high diversity is more significant, because it contains more information [24]. The high throughput screening technique uses mixtures of several compounds to perform a biological activity test. A mixture of several very similar compounds will contain less information than that of several different compounds.

3.5. Phase transitions

Consider two static structures: everything is identical, e.g. the same number of molecules, type of molecules, temperature and density, etc., and the only difference is their symmetries (Figure 6), i.e. in one system the molecules have different orientation and molecules in the other system have identical orientation, the structure of a perfect crystal. According to statistical mechanics [25] the one with different spin or molecular orientations has a higher entropy and the spontaneously generated static structure should be the one with different orientations. This is the prediction based on the Gibbs paradox statement, Equation (1). However, at lower temperature, we observe that the spontaneously formed most stable solid structure is always the perfect crystal, where molecules or spins spontaneously orient to an indistinguishable direction. Note, at low temperature, the energy decrease is not a prominent driving force. The entropy increase must be the main factor in relation to the relative stabilities. From basic knowledge of electromagnetism, parallel orientation in solids is higher in energy than non-parallel orientations, irrespective of whether the individuals are polar molecules (electric dipoles) or spins (Figure 6)!

We have treated the phase transitions in a thermodynamic system at a hierarchical level by a thermodynamic temperature T and an informational temperature T_I [26]. Phase transitions at lower values of $|T|$ to form more symmetric static phase, such as a crystal structure with all of the molecules

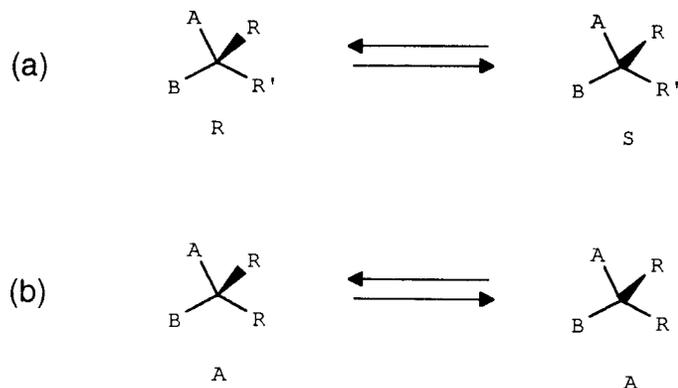


Figure 3. Racemization (interchange of the two enantiomers R and S) (a) and the no-reaction reaction (interchange of A to A) (b)

orienting in one direction, has been conventionally called second-order phase transitions. This process may happen not only in a conventional thermodynamic system, such as a system of many molecules, but also in a system of electrons in an atom or a molecule when the $|T|$ of the local thermodynamic temperature is low [27]. Conventional statistical mechanics would predict the formation of non-perfect static structures. In fact, at such low values of the local thermodynamic temperature $|T|$, the most symmetrical static structures are the most spontaneously formed!

3.6. Mixing of quantum states and valence bond structures

We may apply the term ‘mixing’ as used by von Neumann [13] to a quantum system. We find that resonance among several energetically and configurationally indistinguishable structures [28], such as Kekule structures of benzene, is the most prominent one. Resonance means the time average of several states used to represent a system [29]. The resonance principle has been skilfully used by Pauling (p. 12 of [28]) who attributed the resonance principle to Heisenberg [29].

In quantum mechanics, we distinguish *observables* from *states*. Observables, like momentum and angular momentum, etc., are mathematically described by self-adjoint operators in Hilbert space. We encountered the problem, as indicated in Section 2, that entropy is not an *observable*. States are generally mixed and are represented by a density matrix [30], say ρ , i.e. a Hermitian operator, which is no less than zero and has trace equal to 1. We define the density matrix in a way that the expected value of an observable A in the state ρ is $\langle A \rangle = \text{Tr} \rho A$. The diagonalized density matrix is

$$\rho = \sum_{k=1}^w \mathbf{p} |k\rangle \langle k| \quad (12)$$

where $|k\rangle$ is the k th eigenvector, $\mathbf{p}_k = (0, 0, 0, \dots, p_k, \dots, 0, 0, 0)$, $|k\rangle \langle k|$ is the projection on $|k\rangle$, and the eigenvalue p_k is the probability of finding the system in the k th pure state $|k\rangle$. Then,

$$S = - \sum_{k=1}^w p_k \ln p_k \quad (13)$$

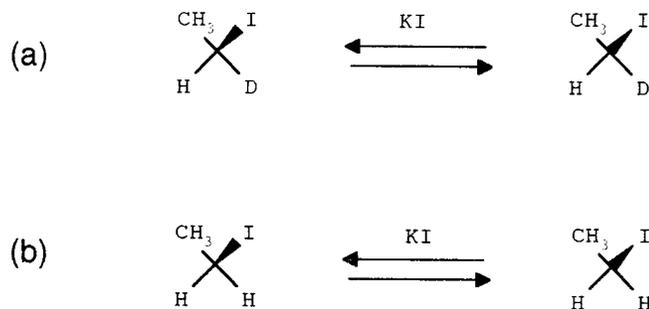


Figure 4. Examples of racemization and the no-reaction reaction catalyzed by iodide.

More generally, following von Neumann,

$$S(\rho) = -\text{Tr} \rho \ln \rho \quad (14)$$

If all of the w pure states have *indistinguishable* properties (e.g. their eigenvalues of certain operators are of same value), we have the familiar Boltzmann formula:

$$S = \ln w \quad (15)$$

which represents the maximum entropy, based on the famous Gibbs inequality:

$$-\sum_{k=1}^w p_k \ln p_k \leq \ln w \quad (16)$$

More historical background [30] and more detailed definitions [31] can be found in literature.

Then, *without exception*, the practical example of the calculations indicates that only when the w pure states have *indistinguishable* properties (such as configurations and energy states, etc.) can we have the most prominent *mixing* of states (to give the best ‘resonance hybrid’ (p. 12 of [28])! Only when the w pure states have *indistinguishable* properties, can the w pure states make equal contributions to the normal state of the quantum system. If the w pure states are of *indistinguishable* properties, only when they make equal contributions can they achieve the maximum stability. Note in practical calculation, that the w pure states can be taken as w microstates or w valence bond structures (p. 12 of [28]), etc. *All* of the examples of resonance given in Pauling’s book [28] support this conclusion. Two examples of such perfect mixing are given in Figure 7.

Pauling also gives examples of the efficiency of resonance and the energy state similarities of several considered structures (p. 22 of [28]).

4. DISPROOF OF GIBBS PARADOX STATEMENT

The disproof of the Gibbs paradox statement as expressed in Equations (1) and (2) can be done in the following ways: first from the symmetry argument, then the similarity argument. Two additional arguments are also given afterwards.



Figure 5. Reaction in one direction, provided that their energies are very different and that the reaction is not carried out at a very high temperature

4.1. Symmetry number and entropy

Starting from the von Neumann–Shannon entropy expression, [Equations \(13\)](#) and Boltzmann formula [\(15\)](#) we prove that this statement is wrong: Gibbs paradox statement implies that the entropy decreases with an increase in symmetry (as represented by a symmetry number σ ; see any statistical mechanics textbook) [\[1\]](#). This can be expressed as

$$S = -\ln \sigma \quad (17)$$

From group theory any system has at least a symmetry number $\sigma = 1$, which is the identity operation for a strictly asymmetric system: $\sigma \geq 1$. It follows that the entropy of a system is equal to, or *less* than, zero:

$$S \leq 0 \quad (18)$$

However, from either von Neumann–Shannon entropy formula [\(13\)](#) or the Boltzmann entropy formula [\(15\)](#) and the original definition, entropy is not negative. Therefore, this statement is false.

4.2. Similarity and Gibbs inequality

From the Gibbs inequality ([Equation \(16\)](#)),

$$-\sum_{i=1}^w p_i \ln p_i \leq \ln w$$

and the general expression ([Equation \(13\)](#))

$$S = -\sum_{i=1}^w p_i \ln p_i$$

and the expression for the maximum entropy ([Equation \(15\)](#))

$$S = \ln w$$

and the conditions for a mixing process to gain maximum entropy, i.e. indistinguishability, the Gibbs paradox statement ([Equations \(1\)](#) and [\(2\)](#)) must be false. The conclusions in [Equations \(1\)](#) and [\(2\)](#) violate the inequality [\(16\)](#). There is a famous discontinuity in changing from [Equation \(1\)](#) to [Equation \(2\)](#). From the general expression of entropy ([Equation \(13\)](#)), the variation of entropy of mixing is continuous, depending on the similarity of the relevant properties [\[24\]](#).

4.3. Entropy additivity

Moreover, it is clear that the Gibbs paradox statement of entropy of mixing contradicts the entropy additivity principle suggested by Gibbs himself. From Gibbs entropy additivity principle (or law) [\[32\]](#), the entropy of a mixture of ideal gases is equal to the sum of the entropies that each gas separately would have if they each occupied the volume of the mixture. For an ideal gas, if only the translational

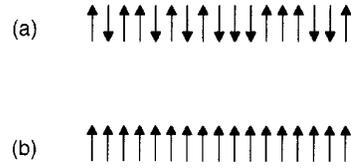


Figure 6. Molecular or spin orientations. According to conventional statistics, the solid mixture at (a) has an entropy of mixing while that at (b) has no entropy of mixing. We have always observed (b) as a much more stable structure

motion is considered, the Gibbs entropy additivity

$$S = \sum_{i=1}^N S_i \quad (19)$$

and the Dalton pressure additivity

$$P = \sum_{i=1}^N P_i \quad (20)$$

take the same form as Gibbs explicitly indicated [32]. Obviously, as should be agreed by everybody, the pressure additivity is suitable for ideal gases, regardless of whether they are distinguishable or *indistinguishable*. Then, it is unreasonable that the entropy additivity is suddenly not suitable for *indistinguishable* ideal gases. Shown in Figure 8 is a cycle related to such a mixing process. The Gibbs entropy additivity law, being applicable to gases of the same particles, is equivalent to $(\Delta S)_1 = 0$ (step 1 in the cycle). Step 2 is trivially an isothermal expansion which gives $(\Delta S)_2 = 2R \ln 2$ for the volume increase from V to $2V$. Then step 3 must give a non-zero entropy increment,

$$(\Delta S)_3 = (\Delta S)_1 + (\Delta S)_2 \quad (21)$$

or

$$(\Delta S)_{\text{samefluids}} = 2R \ln 2 \quad (22)$$

for mixing the same (indistinguishable) ideal fluids. Facing the clear contradiction of the entropy additivity law and the Gibbs paradox statement, we have to defend the entropy additivity principle and deny the latter. Consequently Equation (6) is wrong.

4.4. Ideal gas defined as independent particles

Note that the inclusion of the term $-k_B \ln N!$ in the Sackur–Tetrode equation (Equation (9)) will imply that the N particles in consideration are *not* independent. This contradicts what was required for the definition of ideal gas: the entropy contribution of a particle

$$S/N = \frac{3}{2}k_B + k_B \ln q - \frac{k_B \ln N!}{N} \quad (23)$$

depends on the presence of other particles or *depends* on the total number of particles (N) if the total entropy is calculated by Sackur–Tetrode equation (Equation (9)). The partial molar entropy in an ideal gas mixture will also depends on the total number of particles in the container.

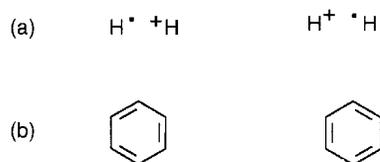


Figure 7. The perfect resonance in the description of the one-electron bond in the hydrogen molecule ion and the stability of benzene [28]

5. RESULTS

From the facts (Section 3) and the logical arguments (Section 4), we present the following results.

5.1. The term $\ln N!$

As the relation between particle indistinguishability and the permutation symmetry of a many-particle system remains a topic of debate [18], it will be practically pertinent to treat the term $\ln N!$ as a residual entropy [1]. Following the tradition of Pauling (his treatment of the entropy discrepancy between the measured and the calculated values for water vapor [33] by including a residual entropy due to the local *symmetry* of water molecules [33], the random orientational disorder and the local tetrahedral symmetry of ice [1]), we suggest that, for the *real* particles, there is a *residual* entropy

$$S_0 = \ln N! \quad (24)$$

due to the residual permutation symmetry in a perfect crystal of the system of N identical particles at $T = 0$.

The ideal gas model assumes that the ideal gas state equation

$$PV = nRT \quad (25)$$

is, in principle, valid throughout the whole temperature and volume range $(0, \infty)$. The calculation based on the ideal gas model never expects a condensed phase when T approaches 0. A system of real particles, however, has a limited (non-zero) intrinsic volume, as implied in the van der Waals' equation. However, in definition, the ideal gas particle has no volume. Then, in principle, all of the N ideal gas particles can be packed into a space of infinitely small volume (or into an element of phase space smaller than that defined by the Planck constant), or a mathematical point – a ‘singularity’, presumably with $w = 1$:

$$S_{\text{ideal}} = \ln w = 0 \quad (26)$$

Therefore, it is not unreasonable that the Nernst entropy, which can be measured by calorimetry for real gases, is connected to the ideal gas entropy as

$$S_{\text{Nernst}} = S_{\text{ideal}} - S_0 \quad (27)$$

where S_0 (Equation (24)) is the calorimetrically unmeasurable quantity which we call, following tradition, a residual entropy, which is temperature independent.

The residual entropy due to the symmetry of permutation (Equation (24)) is tremendous. For 1 mol of particles, $S_0 = \ln N_A! \approx N_A(\ln N_A - 1) = 3.24 \cdot 10^{25}$. Therefore, if we prefer to treat a real gas by the ideal gas model (for a substance has no other residual entropy except for the residual permutation

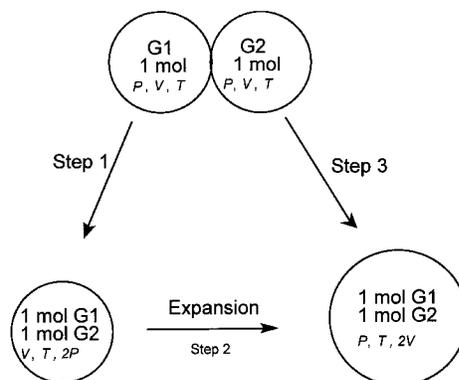


Figure 8. Gibbs entropy additivity principle (step 1), isothermal expansion (step 2) and isothermal isobaric mixing (step 3) with observable mechanical work output

entropy at $T = 0$, one should include the term S_0 :

$$S_{\text{ideal}} = S_{\text{Nernst}} + S_0 \quad (28)$$

where S_{ideal} is calculated by Equation (5), an entropy formula without the term $\ln N_A!$.

5.2. Entropy and symmetry

Whether the system is in dynamic motion or is a static structure, we observed that the most stable structure is the one at equilibrium which has either the highest *dynamic* symmetry or/and *static* symmetry [1]. Therefore, the entropy calculated as the amount of information loss can always be quantitatively estimated according to $S = \ln w$ or generally

$$S = \ln w_a \quad (29)$$

where w_a is the apparent symmetry number [1]. Entropy always increases with an increase in symmetry.

5.3. Entropy and similarity

Entropy of all kinds of mixing processes increases with an increase in the similarity of the relevant properties of the individuals to be mixed. This conclusion can be expressed by a definition of the similarity index [1, 24]:

$$Z = \frac{S}{S_{\text{max}}} = \frac{\sum_{i=1}^w p_i \ln p_i}{\ln w} \quad (30)$$

Therefore, entropy increases continuously with an increase in similarity:

$$S = S_{\text{max}} Z \quad (31)$$

6. APPLICATIONS

In all of the chemical and physical observations given in Section 3 and the logical analysis given in Section 4, we have shown that the most spontaneous process also gives a maximum entropy increase.

This conforms perfectly with the second law of thermodynamics. The entropy increase as an indication of process spontaneity and state stability can be used in many applications, including both practical and theoretical problems.

6.1. Mixing and separation

The rejection of Gibbs paradox and the recognition of maximum entropy of mixing of most similar (or indistinguishable) substances enable us to invent a quite general technique of facile organic synthesis [34]. The essential point of the correlation of entropy of mixing and substance similarity is that substances of really different properties will separate (or demix) with the result that substances of really indistinguishable properties will mix or self-aggregate driven by the entropy effect. Obviously temperature and pressure are conditions which can be varied to adjust the property similarities among the components in a reaction vessel [34]. Self-organization patterns can be controlled by changing property similarities of the constituent individuals.

6.2. Hydrophobic effects

A satisfactory explanation of the hydrophobic effect is possible only if the Gibbs paradox of entropy of mixing is rejected. Hydrophobic effect is observed in the protein folding phenomena. A large number of various theories have been published in recent years about the hydrophobic effect in general and protein folding in particular. Many authors believe that entropy of mixing plays an important role in the hydrophobic effect [35]. The phenomena of the hydrophobic effect is simple: fluids of identical or very similar properties mix spontaneously. Fluids of very different properties (oil and water) separate. A theory in contrast to the conclusions of Gibbs paradox statement can offer a perfect explanation to these phenomena.

6.3. Deformation as energy transduction

The mixing of fluids of very similar or identical properties is the most spontaneous one as indicated by its maximal entropy increase. We consider a model of an ideal gas as the working fluid in a balloon. An *isobaric*, *isothermal* and *isochoric* process can be characterized by Gibbs free energy increment

$$\Delta G = -T\Delta S \quad (32)$$

if $\Delta H = 0$. Mixing (or the combination) of indistinguishable gases, which we believe has an entropy increase, may be regarded as a deformation. This is illustrated by change of the N smaller enclosures of identical shapes to a final total volume

$$V = \sum_{i=1}^N V_i \quad (33)$$

of the same shape to give

$$\Delta S = k \sum_{i=1}^N N_i \ln(V/V_i) \quad (34)$$

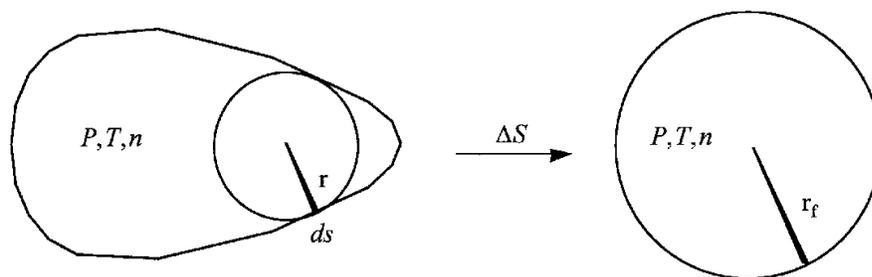


Figure 9. Calculation of the entropy effect of a shape change on the system of n mol ideal gas. The particles in the volume corresponding to ds , originally confined in an imaginary maximal inscribed sphere of radius r , are released into a common sphere of radius r_f after the deformation

Generally,

$$\Delta S = \frac{P}{T} \int \int_s \left(\ln \frac{r_f}{r} \right) \mathbf{r} \cdot d\mathbf{s} \quad (35)$$

for the deformation from an odd-shaped balloon to give a final shape of a single sphere, where $\mathbf{r}(s)$ is the radius of the maximal inscribed sphere intersecting the interface at s on the interface, and r_f is the radius of the final sphere (Figure 9). The differential geometry problem will be treated in more detail elsewhere.

If carried out reversibly, this step will perform non-expansion mechanical work in a quantity of $-\Delta G = T\Delta S$, with ΔS calculated, e.g. we predict that the deformation of an ideal gas in a balloon from a shape of two identical spheres (each of $0.5V$) to a final single sphere of volume V can perform mechanical work as great as that of an isothermal expansion from a volume of $0.5V$ to a final volume V (Figure 10), with ΔS being calculated by Equation (34).

Gibbs statement that the deformation of a fluid is immaterial [36] is incorrect. Like the Carnot cycle, the working substance in the balloon model is also an ideal gas. From the general expression for the deformation (Equation 35), ΔS is related to the area as well as the curvature of the flexible interface enclosing the working gas. The *isobaric*, *isothermal* and *isochoric* deformation processes discussed here are much more pertinent in the discussion of the mechanism of biological energy transduction as encountered in muscle contraction and relaxation than that of a heat engine which converts chemical energy to expansion work over a large range of pressure, temperature and volume changes in processes such as the Carnot cycle. Analogously, by consuming chemical energy, the flexible proteins unfold and separate in the muscle relaxation step. Muscle contraction is a process of protein folding and protein combination to perform mechanical work.

6.4. Resonance theory

Again, if we apply the term ‘mixing’ as used by von Neumann [13] to a quantum system such as atoms and molecules, we will find that all of the results of practical calculations must contradict with the Gibbs paradox of mixing. However, they will conform with our conclusion, irrespective of whether the calculations are carried out according to very approximate but useful MO (‘mixture’ of AO or other MOs) and VB theories (mixture of several valance structures) or many sophisticated theories (mixtures of a vast number of analytical functions to represent quantum states). Recently, the concept of mixing VB configurations or MO configurations [37, 38] has proven useful for elucidating a large number of organic reactions of different types. Our theory may provide support to the validity of such principles.

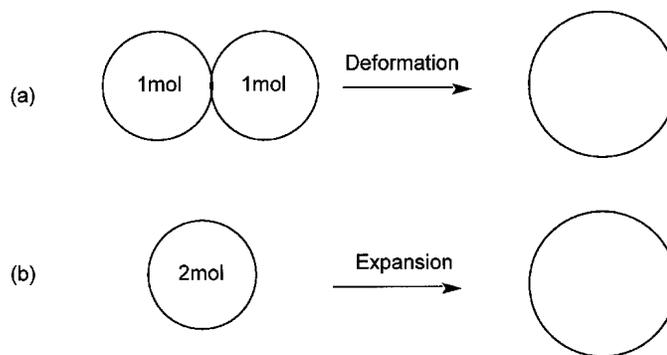


Figure 10. Deformation (a) as an isobaric, isothermal and isochoric energy transduction. It can be as efficient as an expansion (b) of an ideal gas to perform an identical amount of mechanical work in a thermal engine working over a large range of pressure, temperature and volume changes

Because symmetry and similarity are related to entropy [1], a calculation might be simplified based on these correlation. Furthermore, the explanation of the results are much more clear. After the rejection of Gibbs paradox statement, one will believe that the second law of thermodynamics can be perfectly applied to quantum systems to judge the structural stability and process spontaneity.

7. CONCLUDING REMARKS

When we read physicists' discussions about the general properties of entropy [30], we see that they should have easily found the correlation that higher symmetry means higher entropy [1]. They failed to discover this truly very significant and general relation because of the prestigious Gibbs paradox statement. Now we can call w , in the Boltzmann formula, the symmetry number only because the facts and logical reasoning reject Gibbs paradox statement.

Much theoretical work needs to be done after the Gibbs paradox statement is rejected, and it will be very worthwhile. So far the Gibbs paradox statement has been factually a very fundamental assumption in statistical mechanics [4–10]; hence, it will not be a surprise if the rejection of this statement results in tremendous theoretical consequences in theoretical physics, physical chemistry [39–42] and biophysics.

Acknowledgements

The author thanks Professor W. Graham Richards (Oxford University) and Professor David Avnir (The Hebrew University, Jerusalem, Israel) for their kind encouragement.

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