Commentary

Distinguishability in Entropy Calculations: Chemical Reactions, Conformational and Residual Entropy

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Abstract: By analyzing different examples of practical entropy calculations and using concepts such as conformational and residual entropies, I show herein that experimental calorimetric entropies of single molecules can be theoretically reproduced considering chemically identical atoms either as distinguishable or indistinguishable particles. The broadly used correction in entropy calculations due to the symmetry number and particle indistinguishability is not mandatory, as an ad hoc correction, to obtain accurate values of absolute and relative entropies. It is shown that, for any chemical reaction of any kind, considering distinguishability or indistinguishability among identical atoms is irrelevant as long as we act consistently in the calculation of all the required entropy contributions.

Keywords: particle distinguishability; chemical reactions; conformational entropy; residual entropy; Gibbs paradox

1. Introduction

In the statistical treatment of a system of \(N\) identical particles, it is customary to divide the partition function by \(N!\) in order to avoid the overcounting of states due to particle indistinguishability [1]. Analogously, the single molecule partition function is divided by the external symmetry number \(\sigma_{\text{ext}}\) that corresponds to the number of indistinguishable molecular orientations, and by the internal symmetry number \(\sigma_{\text{int}}\) that accounts for the number of indistinguishable conformers (see [2] for a convincing discussion on symmetry numbers). In all cases, the reduction in microstates is related to the concept of indistinguishability: since chemically identical atoms are considered as indistinguishable, any permutation among them would lead to the same state.
The solution of the so-called Gibbs paradox [3–8], is probably the most famous example where the same kind of correction has been applied. Gibbs proposed an ad hoc reduction in the entropy of an $N$-particle system by the amount $-k_B \ln N!$, where $k_B$ is Boltzmann’s constant. This entropy diminution, which corresponds to a reduction in the number of microstates accessible to the system by the permutation symmetry number $N!$, was able to correct what Gibbs considered as an unphysical situation, that is, the fact that entropy increases after mixing two (identical) ideal gases both being initially at the same temperature and pressure.

The unphysical situation that Gibbs tried to avoid in mixing processes is consistent with the concept of entropy as extensive property as held by Gibbs himself. However, it may be interesting to remember that the thermodynamic definition of entropy proposed by Clausius in 1865 does not reveal anything about how the entropy behaves as the number of particles $N$ changes. The Clausius definition only allows us to compute the difference in entropy between two thermodynamics states of a closed system. Pauli noticed this incompleteness and showed what additional condition must be imposed in order to define an extensive entropy, suggesting that entropy, as defined by Clausius, is not intrinsically an extensive property [4,9]. In any case, the extensivity and the indistinguishability are concepts closely connected to each other in the context of the Gibbs arguments, which have been supported and rejected more than once in an ongoing debate [3,4,7,10,11].

From the point of view of classical statistics, whenever identical particles are distinguishable (Maxwell–Boltzmann statistics), it turns out that the entropy reduction by a term of $-k_B N \ln \sigma$ is in contrast with the idea of a magnitude that grows with the number of microscopic complexions compatible with the macroscopic state of the system [6], because ultimately, the result of any symmetry operation including any permutation is another microscopic complexion. Nevertheless, it is well known that the experimental 3$^{rd}$ law entropies of small molecules can be reproduced with extreme accuracy if the entropy reduction is employed. It therefore appears that the experimental values can be reproduced only by using this correction, or equivalently, by adopting truly quantum statistics from which the entropy reduction emerges naturally due to the symmetry of the wave function [12].

The residual entropy [13–15] is another concept that can be linked to the indistinguishability. When we assert that a perfect crystal at 0K has null entropy, we are implicitly assuming from the statistical standpoint that any permutation of two identical particles does not lead to a new microstate. Although the residual entropy is only relevant when is empirically detectable [13,14] and can be related to a potentially measurable latent head [15], the concept will be helpful when we analyse absolute entropies in the context of distinguishable particles. Because in this scenario, the residual entropy would be present even if a reversible path to the solid state at 0K were available.

Herein, through the careful analysis of various practical cases, I support the idea that considering identical atoms as indistinguishable particles is not mandatory in order to compute entropy values that are in agreement with experiment [10,16,17]. I show that classical treatment (distinguishable particles) can reproduce experimental entropy values without the need for any adjustment due to weaknesses of the classical model. All that is required is to be consistent with all the implications arising from distinguishability, including the consequences for the residual and conformational entropy (if any) of the involved molecules. I also show with two examples the innocuous effect of the distinguishability
on the entropy change in chemical reactions obtaining for all cases the same result as that obtained by considering identical atoms as indistinguishable.

The entropy of mixing and the Gibbs paradox, however, is out of the scope of this work because the problem has recently been solved for distinguishable particles without any ad hoc correction [8,17]. In this respect, the present work tries to generalize the idea to any other chemical transformation of any kind, where symmetry changes might take place. The implications of these ideas could be particularly relevant for approximate calculations of absolute entropies in which quantum mechanical and classical statistics are mixed in order to estimate different entropic contributions.

2. Discussion

2.1. Indistinguishable Particles and Third Law Entropies

Nowadays, 3rd law entropies of small molecules in the gas-phase can be computed easily and with remarkable precision by feeding thermodynamic statistical formulae with molecular properties computed with quantum chemical methods [18]. For example, Table 1 shows both theoretical and experimental entropy values reported in the literature for small alkanes [19]. For simplicity, the examples in Table 1 are selected so that the \( \omega \) possible conformers for each molecule, if any, are not only isoenergetic, but also chemically identical. Thus, the conformational entropy would be zero, depending whether or not we are considering indistinguishability or distinguishability among identical conformers.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( \sigma_{ext} )</th>
<th>Theory</th>
<th>Experiment</th>
<th>Abs. Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane</td>
<td>12</td>
<td>186.20</td>
<td>186.37</td>
<td>0.17</td>
</tr>
<tr>
<td>ethane</td>
<td>6</td>
<td>228.50</td>
<td>229.16</td>
<td>0.66</td>
</tr>
<tr>
<td>propane</td>
<td>2</td>
<td>270.20</td>
<td>270.31</td>
<td>0.11</td>
</tr>
<tr>
<td>methylpropane</td>
<td>3</td>
<td>295.50</td>
<td>295.70</td>
<td>0.20</td>
</tr>
<tr>
<td>dimethylpropane</td>
<td>12</td>
<td>306.74</td>
<td>306.00</td>
<td>0.74</td>
</tr>
<tr>
<td>2,2-dimethylbutane</td>
<td>1</td>
<td>358.70</td>
<td>358.40</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Since molar entropies are being dealing with, the number of particles is chosen to be the Avogadro Number (\( N_a \)), expressing the entropy corrections preferably in terms of the gas constant \( R = k_B N_a \). The theoretical values in Table 1 are Rigid-Rotor Harmonic-Oscillator (RRHO) entropies obtained from standard statistical thermodynamic formulae at the B3LYP/cc-pVTZ level of theory, where B3LYP is a hybrid density functional and cc-pVTZ denotes the correlation consistent basis set used [20]. Standard formulae refers to the fact that in all cases the reported theoretical entropies are reduced due to the symmetry including the permutation symmetry (i.e., reduced by the terms \(-R \ln \sigma_{ext} \) and \(-k_B \ln N_a ! \)) [12]. In principle, we should also correct the entropy due to the internal symmetry number \( \sigma_{int} = \omega \) by adding \(-R \ln \omega \). However, it is well known that RRHO entropies do not capture all the intramolecular entropy, as they lack the purely conformational part of the entropy [21–23], which is in our case exactly \( R \ln \omega \) and, therefore, the last correction is automatically done due to the deficiencies of the RRHO
2.2. Distinguishable Particles and Third Law Entropies

If the particles are distinguishable, the entropy correction is not justified and there are new entropy terms that should be taken into account. The conformational entropy, for instance, is now not canceled and consequently the corresponding term $R \ln \omega$, as well as the one due to the external symmetry $R \ln \sigma_{ext}$, must be added to each of the theoretical values in Table 1. By doing so, the agreement of the theoretical data with the experimental values apparently worsens. However, we realize that standard experimental calorimetric entropies are ultimately an entropy change from $T = 0K$ to $T = 298K$. This change is equal to the absolute entropy if the 3rd law holds, i.e.,

$$S_{T=298K} = S_{T=0K} + \int_{T=0K}^{T=298K} \frac{\delta Q}{T}$$

(1)

To interpret the experimental results assuming distinguishable particles, it can be noted first that, in the examples, any formal conformational change of a single molecule near 0K, as well as any rotational symmetry operation, will lead to a different microscopic complexion compatible with the macroscopic state [13]. Therefore, a residual entropy should be considered for these molecules having a value of $R \ln (\omega \sigma_{ext})$. This quantity must be added to the original experimental values and the resulting entropy values, which assume particle distinguishability, maintain the agreement between theory and experiment (see Table 2).

Table 2. Theoretical (B3LYP/cc-pVTZ) and experimental entropy values in $JK^{-1}mol^{-1}$ augmented by $R \ln (\omega \sigma_{ext})$ due to the distinguishability.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\omega$</th>
<th>$\sigma_{ext}$</th>
<th>Theory</th>
<th>Experiment</th>
<th>Abs. Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane</td>
<td>1</td>
<td>12</td>
<td>206.86</td>
<td>207.03</td>
<td>0.17</td>
</tr>
<tr>
<td>ethane</td>
<td>3</td>
<td>6</td>
<td>252.53</td>
<td>253.19</td>
<td>0.66</td>
</tr>
<tr>
<td>propane</td>
<td>$3^2$</td>
<td>2</td>
<td>294.23</td>
<td>294.34</td>
<td>0.11</td>
</tr>
<tr>
<td>methylpropane</td>
<td>$3^3$</td>
<td>3</td>
<td>332.03</td>
<td>332.23</td>
<td>0.20</td>
</tr>
<tr>
<td>dimethylpropane</td>
<td>$3^4$</td>
<td>12</td>
<td>363.93</td>
<td>363.19</td>
<td>0.74</td>
</tr>
<tr>
<td>2,2-dimethylbutane</td>
<td>$3^5$</td>
<td>1</td>
<td>404.37</td>
<td>404.07</td>
<td>0.30</td>
</tr>
</tbody>
</table>

At this point the reader might wonder why, if all particles are taken as distinguishable, the uncertainty due to the permutation symmetry in the solid state at 0K has not been considered. After all, any permutation would give a new different microstate. In fact, it could have been done, but it would have changed nothing, because in such a case the term $k_B \ln N_a!$ needs to also be added to the theoretical value because the translational part of the entropy is computed in its corrected form $S_t = R(\ln q_t + \frac{5}{2})$, where $q_t$ is the translational partition function [1]. Note that the corrected form is conceptually equivalent to the “reduced” entropy used by Cheng [17]. In general any other intra- or extra-molecular permutation between identical but distinguishable atoms can both be considered in the gas phase and in the solid state nearby 0K, and the agreement between theory and experiment would be unaffected.
2.3. Entropy Changes in Chemical Reactions: Is There Any Difference?

The statement that the absolute entropy of a system depends on a subjective decision, to consider or not that identical atoms or particles are indistinguishable, most likely seems awkward. It is no less subjective, however, than setting an arbitrary reference in order to transform a relative magnitude into an absolute one. There are an infinite number of possible functions that would give the correct experimental entropy change, and therefore they all meet the original Clausius thermodynamic definition. The entropy change is the magnitude that must be invariant regardless of any considerations. Through two simple examples, both points of view discussed above (considering identical particles distinguishable or not) will be shown as totally equivalent.

Let us first consider the following equilibrium reactions in the gas phase:

\[
\text{CH}_3\text{Cl} + \text{Cl}_2 \rightleftharpoons \text{CH}_2\text{Cl}_2 + \text{HCl} \quad \text{(R-1)}
\]

If a quantum chemical program is used to optimize the molecular geometries, carry out the corresponding frequency calculations and compute the RRHO entropies without considering any symmetry operation except the identity, the entropy values, say, \(S_{\text{CH}_3\text{Cl}}^{\text{RRHO}}, S_{\text{Cl}_2}^{\text{RRHO}}, S_{\text{CH}_2\text{Cl}_2}^{\text{RRHO}},\) and \(S_{\text{HCl}}^{\text{RRHO}}\) would be obtained. For convenience the required entropy corrections are introduced explicitly, then the estimated entropy change in (R-1) is

\[
\Delta S = \Delta S_{\text{nosym}}^{\text{RRHO}} + \Delta \left( - R \ln \sigma_{\text{ext}} \right)
\]

\[
= \Delta S_{\text{nosym}}^{\text{RRHO}} - R \ln \frac{\sigma_{\text{ext}}(\text{CH}_2\text{Cl}_2)\sigma_{\text{ext}}(\text{HCl})}{\sigma_{\text{ext}}(\text{CH}_3\text{Cl})\sigma_{\text{ext}}(\text{Cl}_2)}
\]

\[
= \Delta S_{\text{nosym}}^{\text{RRHO}} + R \ln 3 \tag{2}
\]

where \(\Delta S_{\text{nosym}}^{\text{RRHO}} = S_{\text{CH}_2\text{Cl}_2}^{\text{RRHO}} + S_{\text{HCl}}^{\text{RRHO}} - S_{\text{CH}_3\text{Cl}}^{\text{RRHO}} - S_{\text{Cl}_2}^{\text{RRHO}}\). In principle, \(\Delta S\) would reproduce the experimental entropy change provided that the level of theory in the calculations is adequate.

Considering distinguishability in the same reaction (R-1), it is now obvious that the \(\text{CH}_3\text{Cl}\) molecule can be formed by any of the 3 distinguishable Cl atoms involved, furthermore, the three numerable H atoms can be reordered in two different forms not superimposable by rotations, being the atoms in \(\text{Cl}_2\) completely determined by our first selection. Hence, the reactants would have an additional uncertainty that contributes to the entropy in \(R \ln (2 \times 3)\). On the other hand, the \(\text{CH}_2\text{Cl}_2\) molecule can be formed by any two of the three Cl and any two of the three H atoms, and once selected, there are two possible arrangements to be chosen between. Note that the atoms are numerable and we could obtain two enantiomeric configurations. The atoms in HCl will be determined once again by the previous selection and finally the entropy estimation under this new formalism is

\[
\Delta S = \Delta S_{\text{nosym}}^{\text{RRHO}} + R \ln \left\{ 2 \binom{3}{2} 2 \binom{3}{2} \right\} - R \ln (2 \times 3)
\]

\[
= \Delta S_{\text{nosym}}^{\text{RRHO}} + R \ln 18 - R \ln 6
\]

\[
= \Delta S_{\text{nosym}}^{\text{RRHO}} + R \ln 3 \tag{3}
\]

which is exactly the same result obtained above.
Let us consider a more complex example where the conformational entropy is also involved. In (R-2), the symmetry number is three for the methylpropane, one in the methylcyclopropane and two for the H, being \( \Delta(-R \ln \sigma_{ext}) = R \ln (3/2) \).

\[
\begin{align*}
\text{CH}_3 & \quad \iff \quad \text{MeCp}^+ \quad + \quad \text{H}_2 \\
\end{align*}
\]

(R-2)

Considering identical atoms as indistinguishable, there is no conformational entropy either in the methylpropane or in the methylcyclopropane molecules. The entropy change involved is \( \Delta S = \Delta S_{RRHO}^{nosym} + R \ln (3/2) \).

If, on the contrary, identical atoms are distinguishable, the H atoms can be arranged in multiple different ways and the entropy value is not lower due to symmetry, but higher. Additionally, the conformational entropy must be taken into account since any conformational change in any methyl group would give a new different conformer. The uncertainty due to the arrangements of the carbon atoms (excluding the connectivity) is the same in reactant and products and will not be considered.

In order to build the reactant molecule (methylpropane), 10 H atoms need to be distributed into 4 “boxes” of capacities 3, 3, 3 and 1, where, in the boxes of capacity 3 (methyl groups), there are two possible enantiomeric arrangements. Also, each methyl group will contribute to the conformational entropy with 3 conformers, being the total number of complexions

\[
\frac{10!}{3!3!3!1!} \times 2^3 \times 3^3 = 10!
\]

For the products (methylcyclopropane and \( \text{H}_2 \)), the carbon atoms which will close the cycle are selected first (there are \( \binom{3}{2} \) possibilities), then we have 10 H atoms for 5 boxes of capacities 3, 2, 2, 1 and 2, where we included the \( \text{H}_2 \) molecule as the last box. Once again the methyl groups as well as the \(-\text{CH}_2-\) groups have two possible arrangements and each methyl group generates three different conformers. As a consequence, the total number of complexions is

\[
\binom{3}{2} \times \frac{10!}{3!2!2!2!1!} \times 2^3 \times 3 = \frac{3}{2} \times 10!
\]

and therefore the computed entropy is

\[
\Delta S = \Delta S_{RRHO}^{nosym} + R \ln (10! \times (3/2)) - R \ln 10!
\]

obtaining again the same result under both formalisms.

However, two examples do not equate to a formal proof, the idea needs to be extended to any chemical reaction. To this end, notice that for distinguishable particles, those permutations that lead to a different arrangement, i.e., not superimposable with the original one by rigid rotations are being considered. For a given system, a systematic way to compute the required number of permutations would be to consider all the possible permutations and then reduce this value taking into account the total symmetry number. For example, it is known that there are only two possible arrangements of the distinguishable atoms in the \( \text{CH}_4 \) molecule, this quantity is equal to the number of permutations of the H atoms \( (4!) \) divided by the symmetry number of a tetrahedral molecule \( (\sigma = 12) \).
In general, the number of permutations not superimposable by rotations (internal or external) of a system that have \( n_1 \) atoms of type 1, \( n_2 \) atoms of type 2, and so on, is equal to

\[
\frac{\prod_i n_i!}{\prod_j \sigma_j}
\]

where the denominator is the product of all the symmetry numbers of the system (reactants or products). If, for instance, the last expression in the reaction (R-1) is applied, it results in \((3!3!1!)/(2 \times 3) = 6\) and \((3!3!1!)/(2 \times 3) = 18\) complexions for the reactants and products respectively, the same results obtained above (see Equation (3)).

For a general reaction \( \text{React} \Rightarrow \text{Prod} \), since the number and type of atoms is conserved, the numerator in (5) always cancels out in the difference \( R \ln \frac{\prod_i n_i!}{\prod_j \sigma_j,\text{prod}} - R \ln \frac{\prod_i n_i!}{\prod_j \sigma_j,\text{react}} \), where \( \sigma_j,\text{react} \) and \( \sigma_j,\text{prod} \) are respectively the symmetry number of reactants and products. Consequently, the effect is equivalent to correcting the entropy change by \( \Delta(-R \ln \sigma) \), being \( \sigma = \prod_j \sigma_j \) the total symmetry number on each side of the chemical reaction. Note that the correction is the same as that for indistinguishable particles except for one point; in the above two examples when indistinguishable particles were considered, only external symmetry numbers were used, not because the internal symmetry was not present, but simply because of the flaws of the RRHO approach taken as “reference”. In other words, considering whether identical atoms are distinguishable or not has no effect on the entropy change in chemical reactions.

3. Conclusions

It has been explicitly shown through practical examples that, for all practical applications, it is irrelevant to consider indistinguishable particles or not in entropy calculations. The classical statistical treatment (distinguishable particles) is equally valid provided that the new degrees of freedom involved are taken into account properly. These arguments could be of particular interest for computing entropies in biochemical reactions where the classical treatment is ubiquitous. Even though in such systems it is quite common to observe chemical reactions like binding processes where no symmetry change takes place [21,22], care must be taken, because as we have seen, even under a classical formalism the symmetry should be considered for a proper entropy estimation.

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References


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