Teaching entropy to first-year undergraduates: what impact has a microscopic, statistical approach on alternative conceptions?

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Understanding entropy and the second law of thermodynamics presents significant challenges in science education at undergraduate level. While many untested approaches have been proposed to enhance the teaching of these concepts, this study focuses on the testing of a microscopic-oriented introduction to thermodynamics for first-year undergraduates in a scientific curriculum that uses elements from statistical thermodynamics with minimal reliance on mathematics. We investigated the impact of this method on student learning through a conceptual questionnaire featuring multiple-choice questions with and without justification. Our intervention included a two-hour lecture, a two-hour exercise tutorial, and a supplementary text for a thermodynamics laboratory. The results indicate that this approach had a mixed effect on conceptual change. The intervention demonstrated a small effect size in a task addressing entropy comparison in gases, suggesting its potential as a supplementary educational tool in tertiary settings to understand molecular factors affecting entropy. However, the teaching method did not seem to improve alternative conceptions connected to disorder, or to quantum mechanical effects, such as the dependence of rotational entropy on the moments of inertia of particles. These findings underlie the critical need for testing new teaching methods in introductory thermodynamics and provide evidence that a microscopic perspective might complement the traditional teaching of macroscopic thermodynamics.

Keywords: conceptual change; thermodynamics; alternative conception

Introduction

Entropy and the second law of thermodynamics are foundational concepts in thermodynamics, yet they have long been identified in the literature as didactic challenges. These difficulties were recently summarized by Atarés et al. (2021): abstraction, high mathematical complexity, the misuse of disorder as a substitute for entropy, and multiple alternative conceptions (e.g. Sreenivasulu & Subramaniam, 2013 for a list of them). Other obstacles have also been identified in broader domains like thermodynamics and physical chemistry, to which entropy belongs. For example, students often despise physical chemistry (Donnelly & Hernández, 2018). Reasons include abstraction, high mathematical complexity, lack of relevance to everyday life, and the cumulative nature of the concepts (Sözbilir, 2004). In the 19th century, when thermodynamics was first developed, the atomic theory was not yet well established. As a result, macroscopic thermodynamics—which does not depend on atomic theory—was developed and formalized before statistical thermodynamics. This historical sequence has often been used to justify, consciously or not, the traditional order of teaching thermodynamics in higher education. However, since the atomic theory is now for a long time well established, there is no longer a compelling scientific argument to teach macroscopic thermodynamics before introducing its microscopic foundation.

The present study aims at contributing to the field of conceptual change research. A recent review by Potvin et al. (2020) highlighted the richness and diversity of this field by cataloguing 86 models of conceptual change, along with their respective literature supports. Our two primary references are Vosniadou’s (1994) framework theory and Chi’s ontological shift theory (2005), respectively the second and third most supported approaches according to Potvin et al.’s review. Though it is not the aim of this article to try to summarize the major contributions from both theories to conceptual change, we lay out here two key elements that guided the development of the teaching intervention and the analysis of the results.

1. In this study, we employ the term “alternative conception” (AC) to denote the underlying rationales or mental models that students hold. These can lead to incorrect responses in conceptual questionnaires. It’s important to note that these are distinct from the erroneous answers themselves. While alternative conceptions can lead to errors, not all errors stem from alternative conceptions. Other words have often been used, such as mental models (Vosniadou, 1994, 2019), misconceptions (e.g. Barke et al., 2009), or conceptual resources (e.g. Sabella and Redish, 2007), though all these terms point to slightly different versions of the beliefs, rationales and mental systems that researchers ascribe to students to account for their erroneous answers and faulty justifications. According to Vosniadou (2019), alternative conceptions can be synthetic or fragmented, denoting respectively a high or low degree of coherence with one’s other conceptions of the physical world.
2. In her seminal article on the AC of emergent processes, where she refers to the diffusion of a blue dye in water as an example, Chi (2005) argues that *emergent* processes (such as diffusion) induce more robust AC in students than *direct* processes (such as blood circulation in the body), because the students do not learn the causal mechanism that connects the components (e.g. in diffusion, the molecules) and the macroscopic phenomenon (e.g. a localized drop of dye spreads out in water, making it slightly blue). Since entropy is an emergent property of matter, a specific attention was given to alternative conceptions that indicated the presence of a misclassification, or a lack of comprehension of the underlying causal mechanism, at the particulate level.

The two theories provide different frameworks for analyzing alternative conceptions highlighting different characteristics of ACs, i.e. their level of coherence or their erroneous ontological categorization, among others, and therefore, we believe both theories are useful for the discussion of alternative conceptions that are connected to emergent processes such as entropy and the second law of thermodynamics.

The subjects of this study are mostly 18-year-old students starting tertiary education at a university. Consequently, we will not be identifying preconceptions, which are intuitive, naïve mental models of the physical world. Instead, we will focus on synthetic and fragmented AC. These are AC that blend preconceptions with correct, school-taught conceptions. Synthetic AC represent a coherent amalgamation of preconceptions and school-taught conceptions while fragmented AC lack internal consistency (Vosniadou, 2019).

Since conceptual change is difficult to track and proposes a diversity of research methods (e.g. interviews, cognitive tasks, questionnaires), we will provide an explanation of our method to track conceptual change in students in the methodology section.

A review by our research team has scoped the literature solutions to improve the teaching of entropy (Natalis & Leyh, 2025) and underscores the need to

(i) focus research on testing the numerous methods that have been proposed in the literature: such research does exist but is rare, e.g. Malgieri et al. (2016), who implemented a teaching sequence connecting the microscopic and macroscopic aspects of the first and the second laws in high school with high success;

(ii) improve the quality of reporting and the quality of methodology of studies designed for improving the conceptual teaching of entropy;

(iii) investigate the use of microscopic methods to help students bridge the gap between macroscopic and microscopic representations of entropy due to its emergent nature: research has already shown that students can use both representations coherently (Leinonen et al., 2015).

These findings justify the aim of the present study: to test a microscopic teaching method with 1st year undergraduate students engaged in a scientific study program. The goal is to foster conceptual change while focusing on the quality of the testing method and of reporting. This approach ensures that this study can be compared with others and included in secondary literature (e.g., in a meta-review). We articulate this aim in the following research question: how and to what extent do the alternative conceptions of the students in the intervention group and in the control group evolve when they are taught an introduction to the statistical thermodynamics approach to entropy during a general chemistry course at university, compared to the traditional, classical thermodynamics approach?

Methods

Population characteristics

The subjects were N = 185 students (N = 8 geologists, N = 22 chemists and N = 155 pharmacists) in their 1st undergraduate year at the University of Liège (Belgium) registered for the General Chemistry course, part 2 (CHIM0737) which covers atoms, molecules, orbitals, thermodynamics, and equilibria in solution (acid-base and redox reactions). They were divided into two groups based on the alphabetical order of their family names, because sub-groups for exercise tutorials were based on this list, which greatly eased the organization of the intervention. Thus, this can be considered convenience randomization. However, we did not have any a priori evidence of a correlation between the alphabetical order of family names and performance in thermodynamics, and we carefully controlled for pre-test performance at the conceptual questionnaire as well as with other variables known to influence success at university: (i) grades in the General Chemistry course, part 1 (CHIM0737), that ended just before General Chemistry, part 2, started, (ii) the number of weekly hours of science, mathematics and Latin in secondary school, and (iii) the secondary school socio-economic index. These criteria were established following guidance in a working paper analysis of socio-economic factors in Wallonia (French-speaking Belgium) conducted at the Université Libre de Bruxelles (Bruffaerts et al., 2011). All data was collected based on informed consent and following GDPR guidance (General Data Protection Regulation, 2016).

Teaching sequence

Both groups were given 30 hours of lectures, 36 hours of laboratory work, and 18 (geologists) to 24 (chemists and pharmacists) hours of exercise solving tutorials. The intervention group received additional teaching: one 2-hour theoretical lecture, one 2-hour problem solving tutorial, and a homework following a laboratory recalling concepts from the lecture and the tutorial. The lecture and the tutorial were recorded and broadcasted to all students after the post-test to ensure equity of access to pedagogical material. None of these pedagogical events were mandatory, to mimic the usual requirements of the course and eliminate that variable. This pedagogical material aimed at emphasizing the microscopic and symbolic approach of entropy and the second law. It is briefly described here but can be accessed fully via contact with the first author. An outline is provided in the Supplementary Information, Appendix I.

The two-hour lecture provided a nearly mathematics-free introduction to statistical thermodynamics. This served to introduce the statistical nature of entropy and its definition, $S = k \cdot ln(W)$. The lecture then explored how a chemical system can distribute energy in space (e.g., across particles) and within individual degrees of freedom (translation, rotation, vibration, and chemical bonds within molecules). The influence of temperature on entropy was also discussed. To supplement this discussion, we presented diagrams of the Boltzmann distribution for different degrees of freedom (fig. 1).

The second half of the lecture provided a systematic overview of the effects of various thermodynamic parameters. This included both macroscopic parameters (volume, temperature, colligative properties) and microscopic parameters (molecular mass, moment of inertia, symmetry, vibrational wave numbers).

The two-hour tutorial focused on solving the same exercises than those proposed to the control group, but with the theoretical microscopic approach taught in the lecture. This included, but was not limited to, a qualitative discussion of the relative entropies of different compounds or computing residual entropy, The estimation of the relative importance of the contributions of the different degrees of freedom was highlighted.

Questionnaire and alternative conceptions repertoire

Performance and AC evolution were observed via a pre-test, post-test design. The same questionnaire was used in both instances. All multiple-choice questions (MCQ) are summarized in the results and can be found with full text in the Supplementary Information, appendix II, along with the correct answers and argued justifications. The first two MCQ did not require any justification from the students. The next four ones required written justification. The questions with justifications were divided into two categories: questions about systems assumed as ideal (abbreviated “CO_2 vs. propane”, “Noble gases” and “Seawater”), which were expected to measure the direct effect of our intervention, since they aligned precisely with what was taught, and a system evolution question (abbreviated “Supercooled liquid”), which was more focused on the evolution of the entropy of the system, and which required more knowledge transfer from the taught concepts, that is, moving from the comparison of two different systems to the evolution of one system from an initial to a final state. All questions were likely to identify some alternative conceptions, as listed in table 1, adapted from a submitted article by our research team (Natalis et al., 2024) and from literature research papers listing common alternative conceptions (Atarés et al., 2021; Bain et al., 2014; Sreenivasulu & Subramaniam, 2013). The 2 MCQ without justification were graded out of 4 points (2 for the ontological question, because there are three correct answers out of seven possible ones, and 2 for the isolated/closed system question, since there is one correct answer for each system). The 4 MCQ with justification were graded one point each and the justifications were not graded. They were only used for AC identification.

Analysis

Quantitative statistics

Baseline pre-test equivalence. To ensure equivalence between the control and test groups at the pre-test stage, we measured five variables in addition to the pre-test performance. These variables were all numeric, either continuous (e.g., score on the General Chemistry, Part 1 exam, CHIM0737) or discrete (e.g., number of weekly hours of science, math, and Latin in secondary school; score on a 1 to 20 scale of the socio-economic index of the secondary school).

We conducted a Shapiro-Wilk test to determine if the distributions of the variables of the control group and of the test group could be assumed to be normal, and an F-test to check for equality of variances. If the distributions were assumed to be normal and the variances were equal, we performed a Student’s t-test to compare the means. If these conditions were not met, we used an unpaired Wilcoxon signed-rank test instead.

Change in student responses. Measurement of changes in student responses was performed as a McNemar paired test with Yates continuity correction between pre-test and post-test and effect size Φ as in eq. 2.

$$\Phi = \sqrt{\frac{\chi^2}{N}} \, (2)$$

where χ^2 is the Chi Square test statistic, and N is the sum of the number of participants at pre-test and post-test (since it is a paired sample, N is just twice the number of participants in either instance). Values are interpreted as follows: $\varphi=0.1$, small, $\varphi=0.3$, medium and $\varphi=0.5$, large.

Alternative conceptions

The identification of alternative conceptions in the justifications for some questions was based on an analysis published in another submitted article (Natalis et al., 2024). This analysis provided experimental evidence supporting some alternative conceptions from the literature and proposed new ones (table 1). In this current study, these alternative conceptions (AC) serve as indicators or outcomes of conceptual change. In addition to tracking the evolution of these known AC, we were interested in seeing if the microscopic teaching approach could induce or uncover new alternative conceptions related to concepts such as macrostates, microstates, and probability. This is particularly relevant since both macroscopic-oriented and microscopic-oriented teachings were introduced concurrently for the test group.

Results

Pre-test verification of the similarity of the intervention group and the control group (baseline alignment)

The pre-test took place during the first lecture of the course. Attendance for the theoretical lecture was optional. Out of the N = 354 students registered for the course, N = 286 (81%) of students were present and participated. At the post-test, students were invited via mail to attend the lecture and complete the post-test; N=206 (58%) students attended and completed the post-test. The attendance is comparable to the usual one for lectures, as evidenced by an unannounced roll call during one lecture, which also recorded a 58%

attendance rate. A total of N = 185 (52%) students participated in both instances, forming the paired sample for our statistical analysis.

Table 2 presents the results of the statistical comparison between the control group and the test group based on their performance at the conceptual pre-test and the General Chemistry exam, part 1 (CHIM0737). The latter serves as a baseline comparison for the pre-test. Both measurements indicate no significant difference between the two groups. Furthermore, the weekly number of Latin hours, the weekly number of science hours, and the socio-economic index of the secondary school are not significantly different between the two groups (see Appendix III in the Supplementary Information for statistical tests). The only difference is in the number of weekly hours of mathematics (Wilcoxon signed rank test, p = 0.01). This statistically significant difference (test group: M = 5.29 hours per week, SD = 1.59; control group: M = 5.93 hours per week, SD = 1.84) remains in absolute terms relatively small and will probably not impact our results since the teaching intervention employs only basic mathematics and focuses more on conceptual topics.

Analysis of alternative conceptions

MCQ with justifications

CO_2 vs. propane. In this question, students were asked to compare the entropies of one mole of gaseous CO_2 and one mole of gaseous propane (C_3H_8) at identical volume and temperature.

Given that both the theoretical lecture and the exercise tutorial explicitly discussed entropy comparisons between chemical substances, we anticipated that the “CO_2 vs. propane” and the “Noble gases” questions would best demonstrate the teaching’s impact on conceptual change. For instance, the lecture explained how mass impacts translational entropy, how symmetry and the magnitude of the moment of inertia of molecules affect rotational entropy, and how the number and type of vibrational normal modes influence vibrational entropy.

It’s important to note that the quantitative statistics and graphs are reported for the paired sample of students who participated in both the pre-test and the post-test ($N_T = 98$, $N_C = 87$). However, the qualitative discussions (types of justifications, use of certain terms) are reported for the entire unpaired cohorts ($N_{T,\text{ pre}} = 144$, $N_{T,\text{ post}} = 94$, $N_{C,\text{ pre}} = 140$, $N_{C,\text{ post}} = 93$).

As can be observed from the percentages of answers and Φ values (table 3), the test group improved more than the control group at post-test on this conceptual question.

The correct answer, $S(C_3H_8) > S(CO_2)$, chosen by 29% of students at pre-test in the control group, and 30% in the test group, was not explained correctly and completely by any student’s justification, except one student in the control group (“There are also more possible molecular movements for C_3H_8 due to its geometry.”). Most of the rationales posited that “more atoms/bonds/carbon atoms/movement/agitation leads to more disorder, and thus more entropy,” without further explanation. The post-test justifications from both groups were nearly identical. In the control group, 24% of the justifications were correct, with 16% primarily relying on degrees of freedom and 8% on micro-states and the Boltzmann formula. In the test group, 25% of the rationales were correct, with 17% focusing more on degrees of freedom and 8% on micro-states and the Boltzmann formula.

The more significant increase in correct answers in the test group compared to the control group, as reported in Table 3, is attributable to students who did not justify their answer choices. The nearly identical percentages of types of justification mentioned in the previous paragraph might suggest that the intervention teaching method did not prevail. However, we suspect this could be due to some undesired transmission of material from the test group students to the control group students, who might have thought that access to the supplementary material was crucial for their exam, overlooking the fact that we would give access to this material after the post-test. To support this claim, we noted that in previous instances of this conceptual test in the same course (2019 and 2020), but without intervention (thus, comparable to the control cohort of this study), only 2 out of 43 students mentioned the term “micro-state,” and only one student mentioned the concept of “degree of freedom.”

The wrong answer chosen by a majority of students, “$S(C_3H_8) = S(CO_2)$”, dropped significantly in both groups, but more so in the test group ($\Phi = 0.38$ in the test group vs. $\Phi = 0.29$ in the control group). In the explanations, we observed erroneous answers attributable to AC-substance: “Entropy is independent of the nature of the pure substance contained in a system”, which leads logically to $S(C_3H_8) = S(CO_2)$, with justifications stating that some thermodynamical parameter being equal (“conditions”, pressure, volume, temperature, number of moles, the ideal gas condition, etc.), the entropies of the two gases should be equal. In the control group, 80% of justifications at pre-test and 61% at post-test used that kind of reasoning and in the test group, 53% at pre-test and 60% at post-test in the control group. This could be caused by an improvement for AC-substance in the test group but needs further exploration (since the percentages reported here are for unpaired cohorts).

Testing a new teaching method in a conceptual change perspective also means being wary of possible new fragmented or synthetic AC (Vosniadou, 2019), which are respectively incoherent or coherent combinations of new teaching with former preconceptions. For example, in the $S(CO_2) = S(C_3H_8)$ answer, in the post-test of the test group, one student argues:

“*If [CO_2 and C_3H_8] have the same mass, they have the same moment of inertia and the more you increase the moment of inertia, the more entropy increases. So the entropy of CO_2 = the entropy of C_3H_8.*”

This reveals a fragmented AC linking a correct argument (the impact of the moment of inertia on the rotational entropy) and an AC (ignoring that the moment of inertia depends on both the masses of the atoms and their internuclear distances).

Also in the post-test of the test group, but in the "S(CO_2) > S(C_3H_8)" answer, another student states:

"*The CO_2 molecule has higher degrees of freedom than the C_3H_8 molecule (greater possibility of rotation) and therefore has* $\Delta S_{CO_2} > \Delta S_{C_3H_8}$*.*" Here, the ''greater possibility of rotation'' might probably be a loose formulation for a larger moment of inertia (As a side note, you can observe in the answer a common mistake: confusing ΔS with S.)

These two answers might result from a misconception about the moment of inertia, though further investigation is needed to detect if this kind of reasoning is attributable to an AC combining entropy and the moment of inertia, or simply of a lack of knowledge about this physical concept from these students.

Other quotes from the test group post-test justifications in the correct answer "S(CO_2) < S(C_3H_8)" might signal that AC-disorder is still interfering with answers, even if students have studied microstates and degrees of freedom, which is consistent with the prevalence model (Potvin et al., 2015) that states that AC never disappear from students' mental models, and that teaching can only train the mind to make the correct conception prevail:

"*More degrees of freedom for propane, so more disorder*."

"*Because there are more atoms in C_3H_8 and therefore more disorder => related to the number of microstates*."

AC-levels, AC-collisions, AC-stability, and AC-freedom were not detected enough in students' answers to be used as monitoring variables of conceptual change, because of the small number or respondents in each answer. For example, AC-stability was chosen by 3 students out of 17 respondents in the control group justifying their choice in the "$S(C_3H_8) > S(CO_2)$" answer, then 0 out of 45 in the post-test. In the test group, 0 students out of the 11 respondents chose this AC-stability rationale in the pre-test, 2 out of 48 in the post-test. On the contrary, AC-disorder and AC-spatial were used by all students in all cohorts with a high prevalence, with no noticeable evolution, except for some justifications mentioning "microstates" in both cohorts in the post-test, which might indicate that some of them stopped using AC-spatial and understood the relationship between energy and entropy, but this evidence remains anecdotal.

Noble gases. In this question, students were asked to compare the entropies of one mole of each of the first four noble gases at identical volume and temperature. The relationship between mass of the particles and entropy is not often taught (but exceptions exist, e.g. Tro , 2019), probably because (a) it cannot be explained straightforwardly by macroscopic thermodynamics, and because (b) in this case, the disorder metaphor cannot fulfill its role of illustrating, without mathematical or conceptual burden, the statistical nature of entropy. To observe this relationship, the Sackur-Tetrode equation can be used to derive the following equation for the translational entropy of gases of molar mass M (in g·mol^{-1}), which is the only degree of freedom that contributes to entropy for monoatomic gases:

$$\bar{S}_{trans} = R\left\{\frac{3}{2}lnT + \frac{3}{2}lnM + lnV + ln\left[\frac{(2\pi k_B)^{3/2}e^{5/2}}{h^3 N_A^{5/2}}\right]\right\} \quad (1)$$

Where $\bar{S}_{trans}$ is the molar translational entropy (J·mol^{-1}·K^{-1}), R the gas constant (8.3145 J·mol^{-1}·K^{-1}), T the temperature (K), V the volume (m^3), k the Boltzmann constant ($1.3807\cdot10^{-23}$ J·K^{-1}), e the charge of the electron ($1.6022\cdot10^{-19}$ C), h Planck constant ($6.6261\cdot10^{-34}$ J·s) and N_A Avogadro constant ($6.0221\cdot10^{23}$ mol^{-1}). Paños and Pérez (2015) listed important assumptions underpinning the derivation of eq. 1, i.e. (a) that "*the phase space has been* *discretized in elementary regions of volume h^n, where n is the number of degrees of freedom of the system*" (p. 3), (b) that the demonstration of eq. 1 relies on the fact that the canonical partition function must be divided by N!, a mathematical choice which can be discussed, and (c), that the function does not equal 0 when T = 0K, requiring some discussion concerning its relationship with the Third Law. Still, eq. 1 (used to produce fig. 2) can be applied to compare the entropies of monoatomic gases, such as Helium or Krypton, at the same T and V, and thus to probe students' understanding of the relationship between the mass of the particles and entropy.

Even though the influence of mass on the entropy of translation was explicitly addressed during the lecture and the exercises tutorial (see fig. 2), no significant change was observed in the test group nor in the control group (table 4). In addition to a possible lack of insistence towards this concept in the intervention, we believe this is because the influence of mass on entropy is a very counterintuitive concept which highlights the pitfalls of the very prevalent AC-disorder, which has little to say about the influence of mass on "disorder". How can "heavy objects" be more disordered than "light objects" ? Might the opposite also be true ?

For example, no student even mentions microstates or degrees of freedom in the correct answer that Krypton gas has the highest entropy. In the same correct answer, instead, students prominently use AC-levels: "Entropy is linked to the number of particles, whatever the level (subatomic, atomic, molecular, or macroscopic)." For the test group, 37% referred to it in the post-test, while only 13% used it in the pre-test. A tentative explanation is that putting the focus on the internal structure of molecules enforced this AC. Our detailed analysis of the impact of the internal structure of molecules (bonds, moment of inertia) on the entropy contributions might have misled students, who then transposed this approach to the internal structure of atoms (protons, electrons, and neutrons) and incorrectly connected it to the loose concept of disorder. In the “entropies are all equal” answer, the dominant AC is AC-substance: in the control group, 34% (pre-test) to 45% (post-test) of students use it, while in the test group, 27% (pre-test) to 28% (post-test) employ it.

Phase change questions

The intervention only partially addressed phase change. The lecturer offered microscopic explanations to clarify colligative properties, linking statistical thermodynamics entropy with freezing point depression, for instance. The goal was to help students understand why the temperature of a phase change changes when a non-volatile solute is added to a solvent.

In the “seawater” question the students were asked to compare the entropy change upon freezing for a pure water and a seawater sample, being informed that seawater freezes at a lower temperature. In the lecture, the argument started from the cause (entropy increase of the solution compared to the pure solvent) and led to the experimental consequence (freezing point depression or boiling point elevation). The contextualized test question required to argue in the opposite direction: from the experimental observation to the conceptual cause. Most students in both groups opted for the correct answer, in the pre-test (control: 61% and test: 69%) and in the post-test (control: 76% and test: 75%), but neither improved significantly (control: $\chi^2 = 3.17$, $p = 0.08$ and test: : $\chi^2 = 0.372$, $p = 0.54$). AC-ordering, which states that “crystallization requires an energy input to order liquid molecules into an orderly solid”, can be found in the justifications of both the correct and in the incorrect answers, depending on the way they estimated the energy input required for the “ordering” crystallization. For example, combining AC-ordering with “seawater requires more ordering because it contains more particles” yields the right answer (with the wrong justification), and combining AC-ordering with “seawater requires less energy to crystallize because it does so at a lower temperature and is thus already more orderly” yields the wrong answer. The incoherence between these rationales might be indicative of the fact that AC-ordering is a fragmented AC.

In the correct answer “$|\Delta S_{seawater} | > |\Delta S_{pure\ wate}r|$”, the frequency of use of AC-ordering is constant across cohorts, pre-test and post-test (control group: pre-test, 31% and post-test, 25%; test group: pre-test, 30% and post-test, 29%), showing the probable absence of conceptual change on this subject in the test group. In the groups that chose the wrong answer “$|\Delta_{Sseawater} | < |\Delta S_{pure\ water}|$”, about the same percentages of students used AC-ordering, but reached the opposite conclusion (control group: pre-test, 20% and post-test, 44%, test: pre-test, 36% and post-test, 35%). These descriptive statistics do not support evidence of conceptual change, but also signals that our intervention did not impede students’ understanding of phase changes phenomena compared to macroscopic-oriented teaching, since both groups performed the same way, and justified their answers with the same kind of rationale.

Similar results were found in the “supercooled” question, where students were asked how the entropy of an isolated system containing supercooled water evolves when the liquid spontaneously crystallizes following the addition of a negligeable quantity of ice. The distribution of frequencies of answers does not change between the pre-test and the post-test for the test group (table 5), and the control group significantly worsens (correct answer goes from 34% to 18%, $\chi^2 = 4.38$, $p = 0.04$, $\Phi = 0.16$). The justifications for the correct answer in both groups in the post-test are mostly incorrect and/or incomplete, with a minority of students mentioning that freezing is exothermic and increases the extent of thermal agitation, and thus, entropy. For this answer, no student in the post-test mentions the second law, the number of microstates, or the impact of degrees of freedom.

The “entropy stays constant” answer allows monitoring of the AC-constant1: “$\Delta S = 0$ for an adiabatic process (system or universe)” (control : pre-test, 15%, post-test, 7%, no significant change, test: pre-test, 13%, post-test, 8%, no significant change), which is not modified by the classical thermodynamics course or our intervention. Finally, the “entropy decreases” answer, picked by a large majority of students in both groups, without significant change between the pre-test and post-test for the test group, and with a significant worsening in the control group ($p < 0.001$, $\Phi = 0.23$), relies on the justification that crystallization makes entropy decrease, since solids have a lower entropy than liquids. In this question more than others, students use AC-disorder, explicitly equating entropy with spatial disorder (control: 22% at pre-test, 42% at post-test, test: 18% at pre-test, 32% at post-test). Similarly to some answers in the “CO2 vs. propane” question, we observed some fragmented AC between AC-disorder and the newly taught concepts of microstates and molecular degrees of freedom to justify the “entropy decreases” answer, showing that disorder continues to coexist with these new concepts:

“*Order increases because a solid has fewer degrees of freedom than a liquid, so* $S_{solid} < Sl_{iquid}$.”

“*When a crystal is added, there is a phase change: the molecules go from a liquid to a solid state. The molecules become more ordered, molecular disorder decreases = entropy decreases. In the solid phase, the molecules are more organized, so they have fewer degrees of freedom => we have access to fewer microstates => entropy decreases*.”

MCQ without justification

AC-disorder

The definition question (fig. 3), which proposed several possible concepts to define entropy, allowed students to add their own definition of entropy. In the paired sample of the control group, 18% of students mentioned “disorder” as a definition for entropy in the pre-test, and 15% in the post-test. In the paired sample of the test group, these figures become, respectively, 11% and 13%. Since the students could add their definition but were not required to do so, no conclusion can be drawn on the efficiency of the intervention for this AC, but its resilience can nevertheless be mentioned since >10% in both groups took the time to mention it in the post-test.

AC-energy

This AC could be traced in the “entropy is a form energy” definition (fig. 3). This AC recedes significantly, but not more in the test group than the control group: 54% to 36% ($p = 0.015$, $\Phi = 0.17$) in the test group, and 48% to 24% for the control group ($p = 0.002$, $\Phi = 0.24$), the effect size being greater in the latter group. Though the intervention teaching explicitly addressed the link between energy and entropy at the molecular level, it might not have really helped distinguish the two concepts. In addition, the repeated use of entropy vs energy graphs in our intervention lecture could possibly have reinforced the conception that energy and entropy are similar concepts (see for example fig. 1b), contrarily to the classical thermodynamics course which did not present such graphs.

Students had to answer the following two-fold question: “Which ΔS is (are) always positive when a spontaneous process occurs in (a) an isolated, (b) a closed system? Multiple answers are in each case allowed.” We did not expect any specific evolution of the three AC that could be targeted by these question (AC-universe1, AC-increase1, AC-increase2, see table 1 for statements) because the focus of the intervention was on molecular degrees of freedom and the influence of thermodynamic parameters (temperature, volume, …) on the absolute entropies of substances, and these three AC rather focus on the evolution of entropy between an initial state and a final state. We wanted to ensure that our intervention did not worsen the prevalence of these AC.

AC-universe1: “Entropy of the universe does not change or decrease.”

We monitored this AC in the three choices that do not include the term "universe" among the seven possible options for the entropy increase: system only, environment only, system and environment, across the two tiers of the question. We observed no significant changes in either the control group or the test group (McNemar paired test, “isolated system” (fig. 4): test group, 55% to 19%, p = 0.16, control group, 46% to 37%, p = 0.49; “closed system” (fig. 5): test group, 46% to 37%, p = 0.37, control group, 43% to 41%, p = 0.95).

AC-increase1: “In an irreversible process, all entropies increase (system, environment, universe)”

We tracked this AC in the frequencies of the “system, environment and universe” option: we observed no change in the test group nor in the control group (McNemar paired test, “isolated system”: test group, 0% to 14%, p not acquired because the McNemar test does not compute “0” values, control group, 0% to 6%, p not acquired; “closed system”: test group, 4% to 11%, p = 0.22, control group, 8% to 4%, p = 0.64).

AC-increase2: “Entropy of the system always increases during a spontaneous process”

This AC was monitored via the frequencies of all options that include “system” (i.e. system, system and environment, system and universe, all three) in the “closed system” tier of the question. Again, no change was observed in both groups (McNemar paired test, test group, 43% to 42%, p = 0.89, control group, 47% to 41%, p = 0.62).

Discussion

Overall, the teaching intervention proposed in this study had a quasi-null quantitative effect on the conceptions of students, since only one piece of data supports a partial conceptual change (of AC-substance). Some qualitative data reveal nuanced effects of this microscopic approach, positive and negative, on some conceptions, such as AC-levels or AC-disorder, which will be discussed in this section.

The only piece of quantitative data underscoring a positive, yet limited effect on the conceptions of students is the effect size difference in the “C_3H_8 vs CO_2” question (correct answer: test, $\Phi = 0.30$, control, $\Phi = 0.21$ and incorrect answer, test, $\Phi = 0.38$, control, $\Phi = 0.29$), which can be considered small, but was also supported by data from the qualitative analysis of students’ answers. This small value might be caused by known limitations such as the general small effect sizes of teaching intervention in tertiary education (see e.g. Hill et al., 2008), or a lack of alignment between the concepts covered in the intervention and the concepts addressed by the conceptual test. For comparison with relevant literature, to the best of our knowledge, the only studies that have implemented pre-test/post-test designs with a test cohort and a control cohort of undergraduate students, to improve entropy teaching, are Teichert & Stacy (2002) and Christensen et al. (2009), who both achieved high effect sizes, as calculated by Natalis & Leyh (2025). However, given the distinct goals of these two articles, the different focus of the current study, and the limited number of intervention studies available, comparing effect sizes might not indicate so much the lack of efficiency of the microscopic method rather than clear-cut differences in objectives.

As for mixed effects on conceptual change, our evidence points to the worsening of AC-levels in the “Noble gases” question. We believe both the positive aforementioned improvement, and the present worsening, can be attributed to a shift from transition-focused, macroscopic-oriented teaching to system-focused, microscopic-oriented teaching, where the entropies of pure substances are explicitly discussed. We showed that all other AC either had a too small occurrence in answers to allow analysis, or that their evolution between pre-test and post-test did not appear to be more impacted by the teaching intervention than the regular teaching.

Given these contrasted results, we ponder whether the shift from transition-focused, macroscopic-oriented teaching to a system-focused, microscopic-oriented approach that highlights the internal degrees of freedom of the molecules might be or not the key to introductory entropy, and if other connections could be more explicitly made, for example with phase space connection between the Clausius and the Boltzmann definition (e.g., Bhattacharyya & Dawlaty, 2019).

Additionally, in the "CO_2 vs. propane" question, we provided arguments for a new AC created by the mixing of AC-disorder with new concepts like microstates. Some justifications showed that students, after equating entropy with disorder, were willing to equate entropy, disorder and microstates, without nuance, and used the three words interchangeably. This supports the existence of a synthetic AC (Vosniadou, 2019) between AC-disorder and these newly taught concepts, since the students use them coherently in lieu of one another. We presented data showing the stability of AC-disorder (in the "MCQ without justification" section), supporting well-established results that, both in teaching methods, and in students' minds, disorder is the core metaphor that explains all phenomena related to entropy (Abell & Bretz, 2019; Bucy, 2006; Carson & Watson, 2002; Langbeheim et al., 2013). The hybridization of "disorder" with "microstates" in post-test answers also supports Haglund's proposal that the disorder metaphor should maybe not be discarded, or, in the case of this study, not be conceptually replaced by "microstates", but rather explicitly put in perspective in a broader set of metaphors used to describe entropy (e.g. disorder, spreading, freedom, and microstates) (Haglund, 2017). For another example, in the "seawater" question, we showed that students could use AC-ordering with other rationales, bringing them either to the correct or to the incorrect answer, revealing the fragmented, incoherent nature of the AC.

Given the *emergent* nature of entropy, Chi's ontological shift theory, as presented in the introduction, can help interpret some ACs. We believe our teaching intervention effectively addressed the causal mechanism underlying entropy values, by showing how the number of microstates for each type of degree of freedom (translation, rotation, vibration) governs the magnitude of their contributions to entropy. We started from the components: counting the number of microstates (W), i.e. the number of ways energy can be partitioned among a set of distinguishable particles, enabled us to highlight the maximum likelihood of a specific energy distribution, the Maxwell-Boltzmann distribution. The number of microstates could then be directly linked to the macroscopic property known as entropy ($S = k.ln(W)$). While quantitative improvements in students' understanding (AC-substance improvement) suggest a better grasp of this causal mechanism, data from other questions might rebut this positive finding (e.g. connection of the moment of inertia and rotational entropy). The concept of density of states in the Boltzmann distribution, which is used in our lecture to explain some entropic effects (e.g. the influence of particle mass on entropy), might not be such an intuitive concept to grasp for students relatively unfamiliar with quantum mechanics. Also, it is possible that the idea that the mass of an atom determines the entropy of an entire system of atoms, creates a direct causal schema (i.e., property of one atom – the density of its energy levels - causes the properties of the system - its entropy) and prevents students from realizing the emergent scheme, namely, that entropy emerges from many possible ways to partition energy quanta among particles.

Given the nuanced effects of our teaching intervention on students' conceptions, as presented in the discussion, this article presents a few perspectives for future research on the conceptions of entropy and the second law of thermodynamics.

a. *Provide additional causal mechanisms* to students, starting with specific phenomena and gradually connecting them to macroscopic effects. For instance, to enhance understanding of the "noble gases" question, a supplementary explanation could be offered. Currently, students are told that an increase in particle mass induces a decrease in $\Delta E_{translation}$ and an entropy increase, without conceptual justification of the effect of the mass on the translational quanta. Providing such a justification would lead to a direct insight on how mass affects the energy spectrum, and to a deeper understanding of the entropy evolution as a function of mass, as illustrated in fig. 2. This approach would also complement Malgieri et al.'s (2016) microscopic method for teaching the second law in high school. Introducing energy quantization could alleviate the counterintuitive nature of entropy's dependence on particle mass. However, as already stated in this discussion, introduction of quantum mechanics concepts to support entropy explanation should be done with great caution to avoid fostering the ACs that are have been documented in that field (e.g. Krijtenburg-Lewerissa, et al., 2020).

b. *Employ more diverse methods* to investigate how students reason about this causal mechanism, such as multiple-tiered questions (as in Atarés et al., 2024) or, ideally, interviews. This would provide deeper insights into how students conceptualize the relationship between "energy distribution" and the "entropy" outcome.

c. *Incorporate the dynamic nature of energy distribution,* an aspect currently missing from our teaching sequence. An analogous situation arises with chemical equilibria where the system appears macroscopically static with constant concentrations of reactants and products, whereas it is in fact dynamic with molecules continuously reacting at equal forward and reverse rates. A similar misunderstanding may arise with entropy, where students might assume that energy is shared between particles once and for all. The stable entropy values in reference tables may reinforce this misconception. Improvements to our teaching method could include games (Michalek and Hanson, 2006) or simulations, such as Einstein solids (Moore and Schroeder, 1997) or ideal gases (Jameson and Brüschweiler, 2020), with greater emphasis on showing the ongoing distribution of energy among particles and its direct connection to entropy by displaying both simultaneously in the simulation.

d. To the best of our knowledge, a study of a the impact of a *statistical thermodynamics "only"* introduction on undergraduate students' conceptions has yet to be done and would be an important point of comparison with the usual, macroscopic-oriented tested methods.

Concerning limitations, this study was not a randomized control trial since it used convenience randomization (family names). Since we operated in a single cohort of students, in a single university, we fit the description for the "single unit" confounding factor. Also, we mentioned in the "CO2 vs. propane" question some evidence of undesired transmission of the pedagogical material (PowerPoint slides, exercise resolutions, etc.) between the test group and the control group, even though we asked the students not to give the control group any material, since they would gain access to it after the post-test (and before the exam). This might have biased the results and weakened the measured difference between the two groups at post-test. An additional limitation of this study is the absence of a clear-cut distinction between lack of knowledge and alternative conception. An interesting yet simple tool used recently in entropy education research is the use of scales of confidence in answers, which allows for a detection of lack of knowledge (Atarés et al., 2024). Though in our intervention, we modified an exercise session and added a homework to the thermodynamics laboratory, we focused primarily on modifying the theoretical lecture, which showed ultimately a small impact on one conception and a mixed effect on overall conceptual change. In comparison, Atarés et al. (2024) and Maglieri et al. (2016) showed a greater effect by focusing primarily on practical sessions in addition to theoretical lectures, pointing to another potential methodological limitation of this work.

Conclusion

In this work, we have studied how a microscopic-oriented method impacts the learning of entropy and the second law of thermodynamics, by using a conceptual questionnaire of multiple-choice questions with and without justification to observe the evolution of student performance and alternative conceptions. We demonstrated that a two-hour lecture, accompanied by a two-hour exercise tutorial and a textual complement to a thermodynamics laboratory might promote conceptual change, especially for the analysis of molecular factors that impact entropy. The effect size of the intervention on the "CO_2 vs. C_3H_8" question was considered small but promising for a time-limited supplementary intervention in tertiary education without replacement of the usual course. Still, the evolution of some ACs were the same in the test group and the control group, and some data show (a) possible synthetic ACs between the microscopic concepts and documented ACs (such as "AC-disorder" with "microstates") and (b) a possible misclassification of some emergent causal schemas as direct schemes. Both results underpin the idea that *if* introductory statistical thermodynamics can promote conceptual change in thermodynamics education, this study lacks enough data to support it, and that the connections of entropy ACs to quantum mechanics ACs are crucial. The modest AC evolution of AC-substance, as well as the possible worsening of AC-levels, also raise questions about the best strategy to extend our system-focused statistical approach (comparison of different systems, e.g. why do samples of $CO_{2\,(g)}$ and $C_3H_{8\,(g)}$ have different values of S°?) to a transition-focused view of entropy (evolution of a given system, e.g. how does the entropy of one mole of $CO_{2\,(g)}$ change when it is adiabatically compressed?).

Declaration of interest statement

The authors report there are no competing interests to declare.

Ethics statement

Students were informed that the completion of the survey was non-mandatory. Informed consent for the questionnaire was obtained by a signed agreement in compliance with the University of Liège GDPR guidelines (General Data Protection Regulation, 2016), since the Fédération Wallonie-Bruxelles does not require an ethics committee approval for educational studies when no personal data is gathered.

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Table 1. List of entropy alternative conceptions. In the identification column, the original references are mentioned: 1 for (Bucy, 2006), 2 for (Bennett & Sözbilir, 2007), 3 for (Carson & Watson, 2002), 4 for (Gabriela et al., 1990), 5 for (Ribeiro, 1992), 6 for (Granville, 1985), 7 for (Brown & Singh, 2021), 8 for (Meltzer, 2007), 9 for (Smith et al., 2015), 10 for (Natalis et al., 2024), 11 for (Christensen et al., 2009), 12 for (Ulloa Lugo, 2006), 13 for (Brosseau & Viard, 1992), 14 for (Atarés et al., 2024), 15 for (Velasco et al., 2022), 16 for (Leinonen et al., 2015), 17 for (Erceg et al., 2019), 18 for (Erceg et al., 2016), 19 for (Brundage & Singh, 2023). AC-constant2 and AC-free-energy are mentioned for the sake of exhaustion and are not studied herein since we the study is limited to ideal gases (for AC-constant2), and since no question aims at free energy (for AC-free-energy).

Name	**Statement**	**Identified by**
AC-disorder	Entropy is a measure of disorder, in the sense of randomness, and not in the statistical thermodynamic precise sense.	1, 2, 3, 4, 10
AC-energy	Entropy is another ‘form’ of energy, like kinetic or potential energy.	3, 10
AC-universe1	Entropy of the universe does not change or decrease.	5, 10, 16, 19
AC-constant1	$\Delta S = 0$ for an adiabatic process (system or universe).	6, 10, 16, 19
AC-constant2	$\Delta S_{unvierse} = 0$ in a real process	2, 10, 11
AC-increase1	In an irreversible process, all entropies increase (system, environment, universe).	7, 10
AC-increase2	Entropy of the system always increases during a spontaneous process.	1, 2, 3, 4, 6, 8, 9, 10, 15, 16, 19
AC-free-energy	Entropy is confused with free energy	17
AC-collisions	If molecules have a higher chance to collide, their entropy is higher.	2, 10, 18
AC-substance	Entropy is independent of the nature of the pure substance contained in a system.	10
AC-levels	Entropy is linked to the number of particles, whatever the level (subatomic, atomic, molecular, or macroscopic).	
AC-freedom	Entropy is proportional to the freedom of movement of particles.	
AC-stability	Molecules that have a higher chemical stability have a lower entropy.	
AC-ordering	Crystallisation requires an energy input to organize liquid molecules into an ordered solid.	
AC-spatial	Entropy depends solely on spatial distribution of particle (and not on energy dispersion between particles)	10, 12, 13, 14

Table 2. Statistical comparison of the test group and the control group on the conceptual pre-test and the General Chemistry exam, part 1, that occurred before the study began and serves as pre-test comparison. N for the number of participants, M for mean, SD for standard deviation, SW test for Shapiro-Wilk test of distribution normality (H0 is that the distribution is normal), W test for unpaired Wilcoxon signed rank test (H0 is that true mean difference is equal to 0), F test for variance difference test (H0 is that true variance difference is equal to 0), T test for Student's t-test (H0 is that the true mean difference is equal to 0). Level of significance $\alpha = 0.05$.

	N	Conceptual pre-test				General Chemistry, part 1 (CHIM0737) exam				
		M	SD	SW test	W test	M	SD	SW test	F test	T test
Test group	98	2.26	1.21	$W = 0.93$ $p < 0.001$	$W = 4562$ $p = 0.4$	10.02	3.62	$W = 0.97$ $p = 0.09$	$F = 0.83$ $p = 0.40$	$t = 0.81$ $p = 0.42$
Control group	87	2.40	1.12	$W = 0.93$ $p < 0.001$		10.49	3.24	$W = 0.98$ $p = 0.34$		

Table 3. Pre-test and post-test percentages of answers of students to the “CO2 vs. propane” question, as well as McNemar paired tests, χ^2 statistics, p-value and effect size Φ value. Correct answers in bold green characters**.**

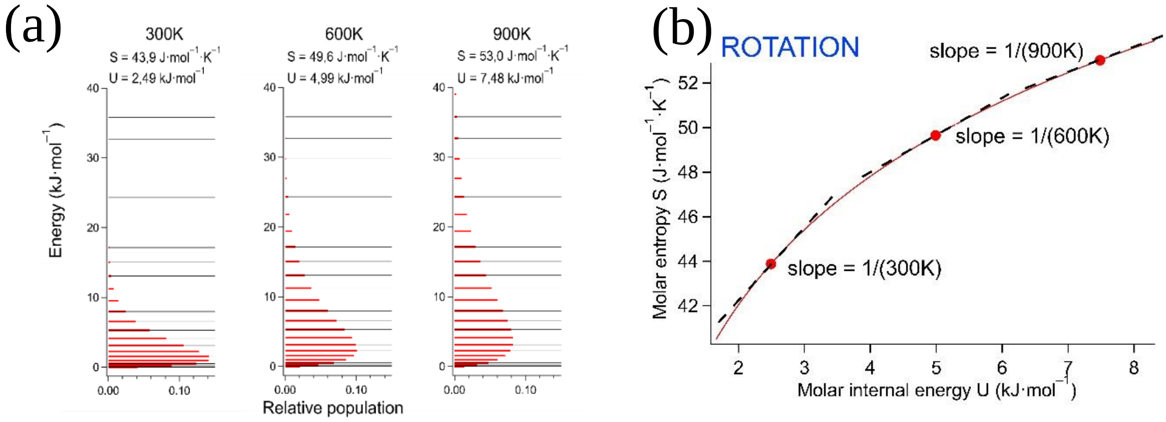
Answer	Control group					Test group				
	Pre	Post				Pre	Post			
	%	%	χ^2	p	Φ	%	%	χ^2	p	Φ
$S(CO_2) > S(C_3H_8)$	2	10	2.66	0.10	/	4	12	1.91	0.17	/
$S(C_3H_8) > S(CO_2)$	30	52	6.21	0.01*	0.21	29	60	14.0	<0.001*	0.30
$S(C_3H_8) = S(CO_2)$	68	38	12.0	<0.001*	0.29	67	28	21.9	<0.001*	0.38

Table 4. Pre-test and post-test percentages of answer of students to the “Noble gas” question, as well as McNemar paired tests, χ^2 statistic, p-value and effect size Φ value. Correct answer in green bold characters.

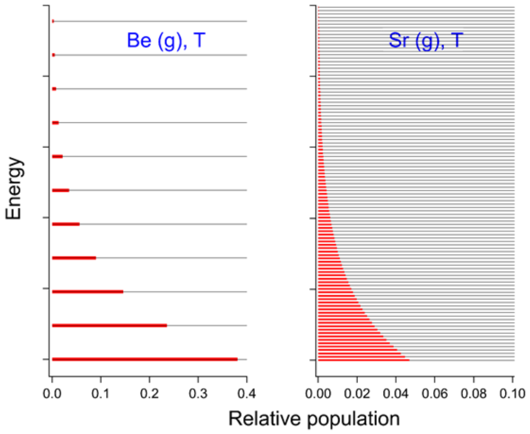
Answer	Control					Test				
	Pre	Post				Pre	Post			
	%	%	χ^2	p	Φ	%	%	χ^2	p	Φ
S(He) > S(Ne) > S(Ar) > S(Kr)	14	6	1.42	0.23	/	14	14	0.044	0.83	/
S(Kr) > S(Ar) > S(Ne) > S(He)	20	19	0.003	0.96	/	19	27	0.881	0.35	/
S(He) = S(Ne) = S(Ar) = S(Kr)	66	75	1.00	0.32	/	67	59	0.642	0.42	/

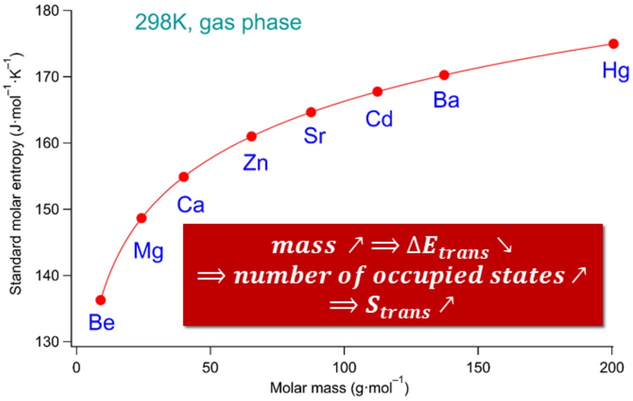
Table 5. Pre-test and post-test percentages of answer of students to the “Supercooled liquid” question, as well as McNemar paired tests, χ^2 statistic, p-value and effect size Φ value. Correct answer in green bold characters.

Answer	Control					Test				
	Pre	Post				Pre	Post			
	%	%	χ^2	p	Φ	%	%	χ^2	p	Φ
Entropy increases	34	18	4.38	0.04	0.16	26	19	0.936	0.33	/
Entropy decreases	51	74	8.82	<0.001	0.23	58	73	2.568	0.11	/
Entropy stays constant	15	7	1.96	0.16	/	13	8	0.787	0.38	/


(a)
300K
S = 43,9 J·mol⁻¹·K⁻¹
U = 2,49 kJ·mol⁻¹
600K
S = 49,6 J·mol⁻¹·K⁻¹
U = 4,99 kJ·mol⁻¹
900K
S = 53,0 J·mol⁻¹·K⁻¹
U = 7,48 kJ·mol⁻¹
Energy (kJ·mol⁻¹)
40
30
20
10
0
0.00
0.10
Relative population
(b)
ROTATION
slope = 1/(900K)
slope = 1/(600K)
slope = 1/(300K)
Molar entropy S (J·mol⁻¹·K⁻¹)
52
50
48
46
44
42
2
3
4
5
6
7
8
Molar internal energy U (kJ·mol⁻¹)

How does the mass of the particles influence the translational entropy?

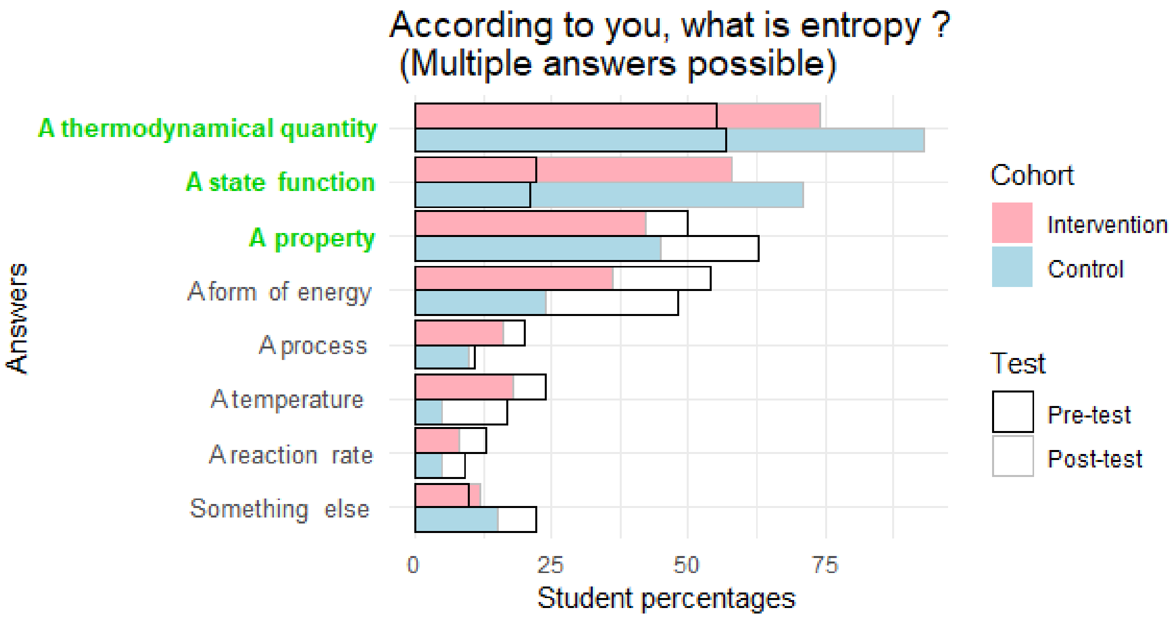


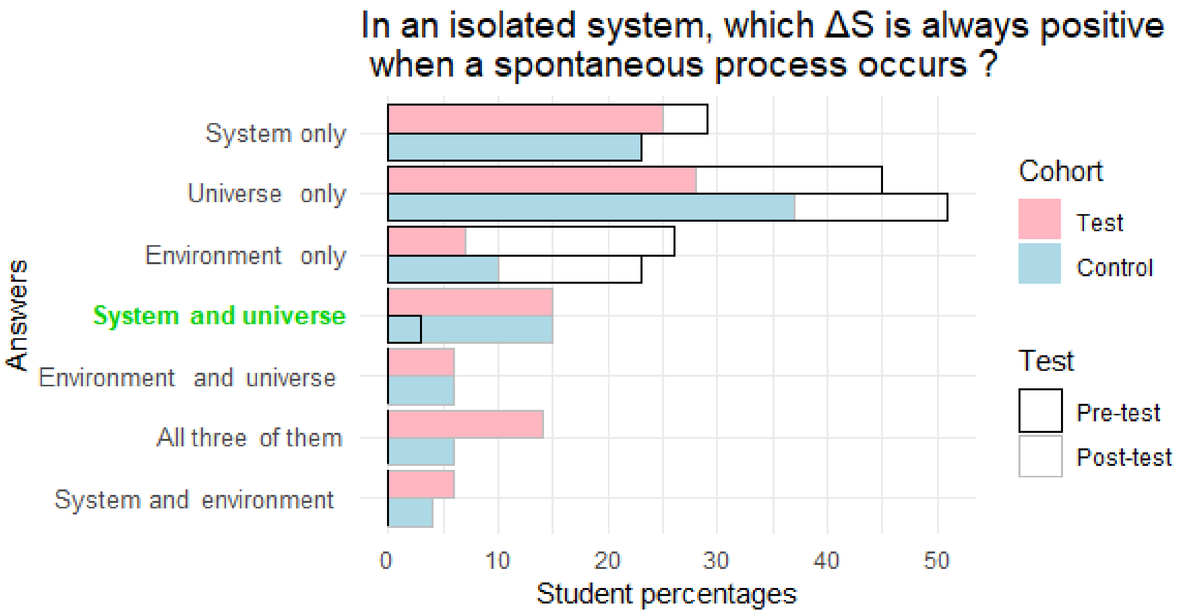


$mass \nearrow \Longrightarrow \Delta E_{trans} \searrow$

$\Longrightarrow number\ of\ occupied\ states \nearrow$

$\Longrightarrow S_{trans} \nearrow$


According to you, what is entropy ?
(Multiple answers possible)
Answers
A thermodynamical quantity
A state function
A property
A form of energy
A process
A temperature
A reaction rate
Something else
0
25
50
75
Student percentages
Cohort
Intervention
Control
Test
Pre-test
Post-test


In an isolated system, which ΔS is always positive when a spontaneous process occurs ?
Answers
System only
Universe only
Environment only
System and universe
Environment and universe
All three of them
System and environment
0
10
20
30
40
50
Student percentages
Cohort
Test
Control
Test
Pre-test
Post-test

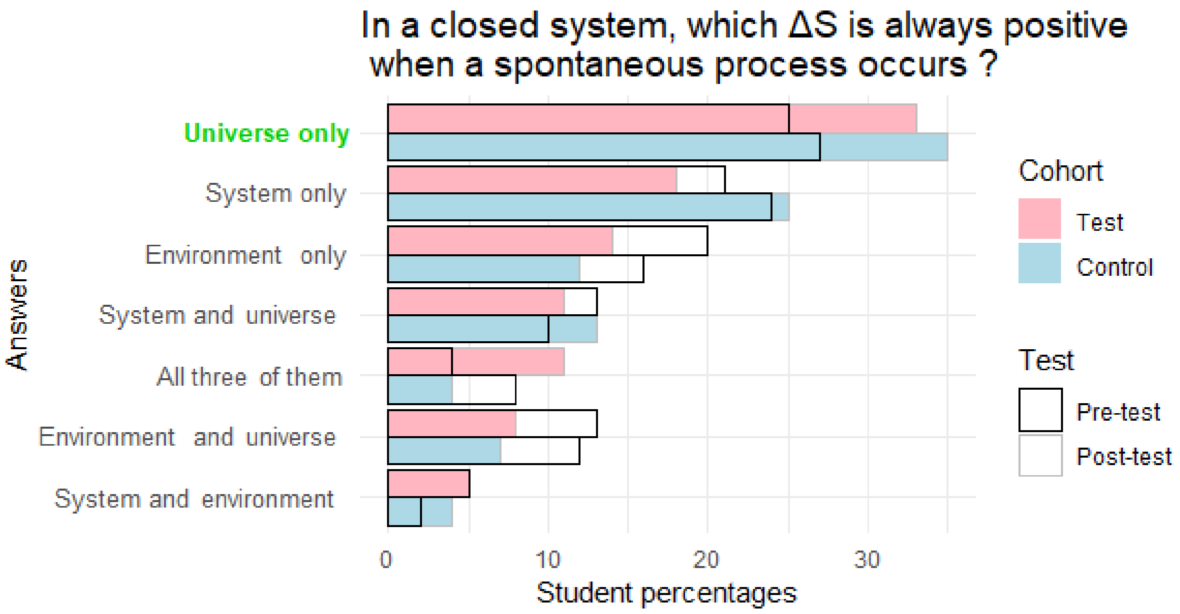

In a closed system, which ΔS is always positive when a spontaneous process occurs ?
Answers
Universe only
System only
Environment only
System and universe
All three of them
Environment and universe
System and environment
0
10
20
30
Student percentages
Cohort
Test
Control
Test
Pre-test
Post-test

Figure 1. (a) Boltzmann distributions of the relative populations of $O_{2\ (g)}$ molecules on their rotational states at three temperatures, to highlight the larger increase between 300K and 600K compared to the change from 600K to 900K. (b) Graph of molar entropy of rotation as a function of internal molar energy, showing the 1/T dependence of the slope.

Figure 2. Example of a PowerPoint slide from the theoretical lecture, which illustrates the impact of mass on translational entropy.

Figure 3. Pre-test and post-test results for the test group and the control group for the “definitions” question. Correct answer in green bold characters.

Figure 4. Pre-test and post-test results for the test group and the control group for the “isolated system” question. Correct answer in green bold characters.

Figure 5. Pre-test and post-test results for the test group and the control group for the “closed system” question. Correct answer in green bold characters.

Appendix I : a two-hour lecture introducing basic concepts of statistical thermodynamics by a nearly mathematics-free approach

1. **Short review of pre-requisites**
    - 1.1. Review of basic ideas of classical thermodynamics
        - 1.1.1. 1st law, internal energy, heat, work
        - 1.1.2. 2nd law, entropy, Clausius definition ($\Delta S = \int_i^f \frac{dq_{rev}}{T}$)
    - 1.2. Review of basic concepts of atomic and molecular structure: energy quantization
2. **Introductory statistical physics: fundamental concepts**
    - 2.1. Definitions: macrostate, microstate, number of microstates (W) + simple example with 3 particles
    - 2.2. More complex example with 30 particles to reach the conclusion that *"The equilibrium macrostate of a system is the most probable one, that is, the one corresponding to the largest number of microstates"* (assuming equal probability for all microstates)
    - 2.3. Revisiting the definition of entropy through a statistical interpretation: $S = k \cdot ln(W)$; entropy measures the dispersion (spreading) of energy over the accessible particle states; short discussion of the meaning of the widespread (but heavily criticized) disorder metaphor
    - 2.4. Simple application examples: heat transfer through space, temperature equalization, free gas expansion
    - 2.5. Detailed analysis of the molecular entropy contributions: energy spreading over the states associated with the molecular degrees of freedom (translation, rotation, vibration) (electronic contribution mentioned but not discussed at this stage)
        - 2.5.1. Description of the molecular degrees of freedom: examples of simple linear (CO_2) and non-linear (H_2O) molecules (dynamic visualizations of the vibrational modes)
        - 2.5.2. Comparison of the sizes of the energy quanta for translation, rotation and vibration based on experimental data (and not derived from theoretical models) : $\Delta E_{trans} \lll \Delta E_{rot} \ll \Delta E_{vib}$
        - 2.5.3. Effect of temperature on the translational entropy; graphical representation of S_{trans} vs. U (internal energy)
        - 2.5.4. Effect of temperature on the rotational entropy; graphical representation of S_{rot} vs. U (diatomic case)
        - 2.5.5. Effect of temperature on the vibrational entropy; graphical representation of S_{vib} vs. U (diatomic case)
    - 2.6. Summary
        - 2.6.1. $S_{trans} \gg S_{rot} > S_{vib}$ in general
        - 2.6.2. $\left(\frac{\partial S}{\partial U}\right)_{N,V} = T^{-1}$: *the same energy absorption at higher temperature induces a smaller entropy increase*
        - 2.6.3. Connection with Clausius entropy definition
        - 2.6.4. Quantitative application to heat transfer from a hot to a cold water system: connection with the 2nd law
3. **Applications of the basic concepts: influence of external and molecular parameters on the entropy, based on a discussion of the size of the energy quanta, the number of accessible states and the energy spreading**
    - 3.1. Influence of the temperature + connection with classical thermodynamics (heat capacity)
    - 3.2. Effect of volume change + connection with classical thermodynamics
    - 3.3. Gas mixing
    - 3.4. Mass of the particles: impact on S_{trans}
    - 3.5. Molecular moment of inertia: impact on S_{rot}

  3.6. Molecular symmetry: impact on S_{rot}
  3.7. Vibrational modes: impact of the number of modes and of their frequencies (influence of masses and bond strengths) on S_{vib}. Extension from molecules to crystals.
  3.8. Addition of a non-volatile solute to a solvent: colligative properties

4. **Final summary. Take home message: How can entropy be increased? By increasing the number of accessible states over which energy can be spread.**

- By increasing T (other parameters constant)
- By decreasing the size of the energy quanta (ΔE) at constant T
    - By increasing V
    - By increasing the mass of the particles
    - By increasing the molecular moment of inertia
    - By decreasing the vibrational frequencies
- By increasing the number of degrees of freedom
    - By increasing the number of atoms in the molecules
    - By decreasing the molecular symmetry (upon deuteration, e.g.)
    - By adding particles to the system (colligative properties, e.g.)

Appendix II: full text of multiple-choices questions, with explanations of the correct answer

Correct answer are signalled with an asterisk (*)

1. What is entropy? (multiple answers allowed)[1]

A temperature

A form of energy

A thermodynamical quantity*

A state function*

A reaction rate

A system property*

A process

Something else: ....

Explanation

Entropy is

- A thermodynamic quantity: a quantity is a property of nature that can be measured. In thermodynamics, the entropy of a system can be determined indirectly, through heat capacity measurements.
- A state function: a state function is a thermodynamic quantity whose variation between two states of a system does not depend on the path taken or the method used. For example, the entropy variation of a one-ton block of steel from 0°C (initial state) to 100°C (final state) is the same whether the block is heated rapidly, slowly, cooled and then reheated, or vice versa: only the initial and final states define the entropy variation between the two systems.
- A property of a system: entropy is the value of a quantity that describes a system, like other properties (temperature, amount of matter, for example).

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[1] Adapted from (Bain, Moon, Mack, & Towns, 2014)

Entropy is not :

- A temperature: temperature is the quantity that measures the average kinetic energy of particles in a system.
- Energy: entropy is a concept linked to energy, but distinct from it. Energy refers to a system's capacity to produce work (of various kinds: mechanical, electrical, magnetic) or to release heat. Entropy is a quantity that qualifies the way energy is organized. It indicates how little or how much energy is distributed among the energy-storing degrees of freedom of the particles of the system. If these particles are polyatomic molecules, for example, energy can be stored in their movement in space (translation), in the vibrations of atomic bonds, and in the rotations of the molecule. Whatever the amount of energy possessed by the system, it is the entropy that will describe whether this energy is concentrated in a few degrees of freedom (low entropy), or whether, on the contrary, the energy is distributed over many degrees of freedom (high entropy).
- A reaction rate: Entropy is a state function (see above), which means that its variation is not altered by the rate at which a reaction takes place.
- A process: the notion of process is closely linked to that of transformation. In chemistry, we often speak of entropy variation between two states of a system, for example, if we transform one mole of A into one mole of B. This does not mean that entropy itself is a process: it is a property that varies between two equilibrium states. If we subtract the entropy of the initial system from that of the final system, we obtain the entropy variation between the two states, which is denoted ΔS, but the respective entropy of each state is not a process: it's a property. Heat, on the other hand, is a process: it's the transfer of thermal energy from a hot body to a cold one.

2. Which of the entropy variations mentioned in the table below is always positive when a spontaneous process occurs in an (a) isolated system and (b) closed system? (Multiple answers allowed in both sub questions)[2]

---

[2] Adapted from (Christensen, Meltzer, & Ogilvie, 2009)

	ΔS_{system}	$\Delta S_{environment}$	$\Delta S_{universe = environment + system}$
(a) Isolated system	*		*
(b) Closed system			*

Explanation

Whatever the nature of the system considered (open, closed, isolated), if a spontaneous process takes place, then the entropy of the universe increases. This is the second law of thermodynamics. So, in both cases, you can tick the third column.

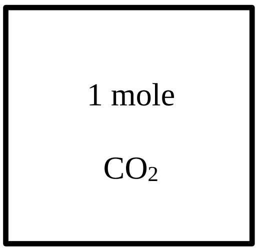
In an isolated system, there is no possibility of transferring either matter or energy to the environment. This means that if a spontaneous process occurs in the system, entropy increases. As no matter or energy is supplied to the environment, its entropy remains a priori unaffected.

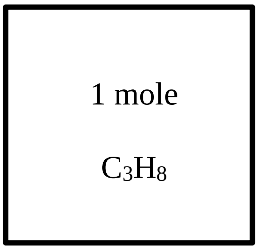
In a closed system, on the other hand, the system can exchange energy (in the form of heat, for example), but not matter, with the environment. So we can't say whether it's the system or the environment whose entropy increases. We can be sure that the sum of the two entropies (system and environment) has increased, since the entropy of the universe must increase to comply with the second law, but we can't say in all generality that one or the other will always increase in a spontaneous process.

3. CO_2 vs. C_3H_8

Carbon dioxide (CO2) and propane (C3H8) have the same molecular weight. Assume two closed, non-deformable and identical chambers. One contains 1 mole of CO2 and

the other 1 mole of C3H8. The two gases are at the same temperature. How do the entropies of the two gases compare? Assume the gases are ideal.[3]





- S (CO_2) > S (C_3H_8)
- S (CO_2) < S (C_3H_8)*
- S (CO_2) = S (C_3H_8)
- None of the above

Justify your answer as precisely as possible:

Explanation

For a given total energy, if the particles in a system all have roughly the same energy, the entropy will be low. If, on the other hand, the energy distribution over the particles is very broad, entropy will be high, because there will be many equivalent ways of achieving such a broad distribution, by exchanging the energy of different particles. The number of such possible arrangements, also known as microstates, is denoted by W, and the entropy is given by the statistical thermodynamics formula $S = k_B \cdot \ln (W)$ (Boltzmann's formula).

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[3] Adapted with permission from Bennett, J. M., & Sözbilir, M. (2007). A Study of Turkish Chemistry Undergraduates’ Understanding of Entropy. *Journal of Chemical Education*, *84*(7), 1204. https://doi.org/10.1021/ed084p1204. Copyright 2007 American Chemical Society.

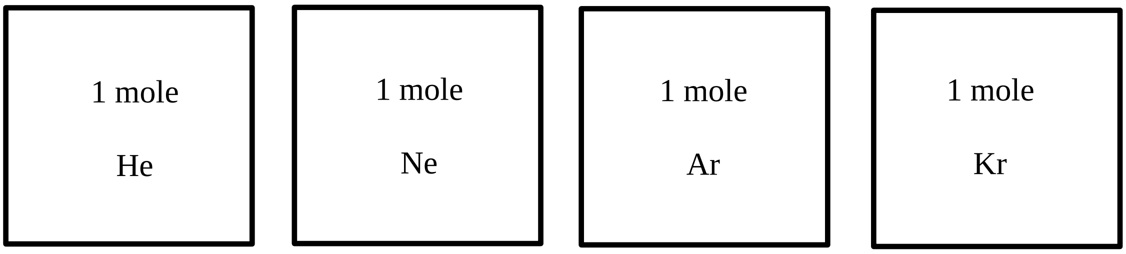
It follows from the above discussion that the more chemical bonds a molecule has, the more different possibilities there are for distributing energy. This is because chemical bonds can be compared to small springs that perform low-amplitude vibrational movements. These movements can therefore store energy.

The contribution to W of the rotation and translation of the two molecules under consideration (CO_2 and C_3H_8) are very similar, as their masses and mass distributions relative to the centre of mass are almost identical (for the influence of mass on entropy, see the “noble gases” answer). What is very different here, however, is the $W_{vibration}$ contribution of the number of possible vibrations to the total number of microstates (W), and therefore to the entropy (S). In $CO_{2,}$ there are two C=O bonds. In C_3H_8, there are 2 C-C bonds, and 8 C-H bonds. There are many more possible energy distributions on the vibrations of propane atoms than on the vibrations of CO_2: the entropy of C_3H_8 is larger than that of CO_2.

4. Noble gases

Assume four closed, non-deformable and identical chambers, each containing 1 mole of one of the first 4 noble gases of the periodic table, in ascending order of atomic number.

The temperature T is identical in all four chambers, and we assume that the gases behave like ideal gases. How do the entropies of these four samples compare?[4]



- S (He) > S (Ne) > S (Ar) > S (Kr)
- S (Kr) > S (Ar) > S (Ne) > S (He)*
- S (Kr) = S (Ar) = S (Ne) = S (He)
- None of the above

Justify your answer as precisely as possible:

Explanation

In this exercise, the important point to note is that entropy depends on the mass of the noble gas. For atoms, the only contribution comes from the translational motion (electronic excitation can be neglected at reasonable temperatures). The larger the atomic mass, the higher the entropy. The only way to justify this relationship is through statistical thermodynamics, using the formula $S = k_B.\ln (W)$.

Both a classical and a quantum mechanics interpretations are possible. Even though we focussed on the counting of microstates which implies energy quantization, we outline briefly the classical point of view to show the convergence of both approaches. Classically, entropy

---

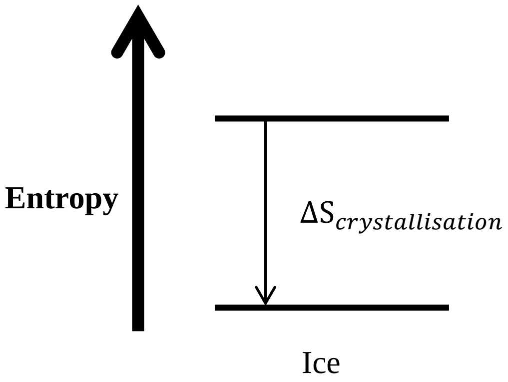
[4] Adapted from (Jungermann, 2006)

is proportional to the logarithm of the phase space volume, which includes both configuration and linear momentum components. If the temperature is the same for all gases, the average kinetic energy per particle (ε_k) is also identical. But because ε_k is equal to $\frac{p^2}{2m}$, the momentum distribution must be broader for larger masses to keep the kinetic energy distribution unchanged. This leads to a broader sampling of the momentum space and thus of phase space and, accordingly, to a larger entropy. In quantum mechanics, translational energy is quantized, even if the quanta (energy difference between two levels) are minute. It turns out that these quanta become even smaller as the mass of the particles (atoms or molecules) increases. Consequently, for a given temperature, there will be more populated levels and therefore more possibilities for distributing particles over the energy levels, i.e. more microstates, if the mass of the particles is higher. This corresponds to a higher entropy according to Boltzmann's formula $S = k_B.\ln(W)$.

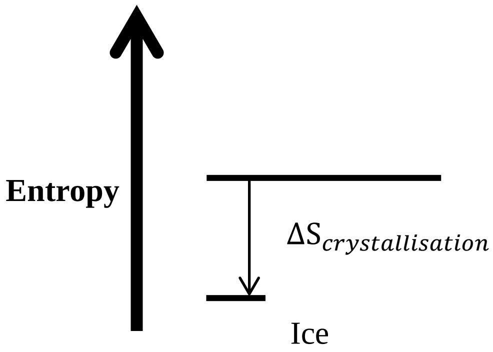
$W_{\text{translation, Kr}} > W_{\text{translation, Ar}} > W_{\text{translation, Ne}} > W_{\text{translation, He}}$. So S (Kr) > S (Ar) > S (Ne) > S (He).

5. Seawater

Seawater contains several types of dissolved minerals and therefore freezes at a lower temperature than pure water. The energy released during the transition to the solid state is assumed to be the same for seawater as for pure water. The diagrams below illustrate two entropy changes, one corresponding qualitatively to seawater, the other to pure water.[5]



(a)



(b)

Choose the correct statement:

- Diagram (a) corresponds to pure water, diagram (b) corresponds to seawater
- Diagram (a) corresponds to seawater, diagram (b) corresponds to pure water*

Justify your answer as precisely as possible:

Explanation

The aim is to identify whether crystallization of pure water or seawater leads to the greatest decrease in entropy of the system.

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[5] Adapted with permission from Bennett, J. M., & Sözbilir, M. (2007). A Study of Turkish Chemistry Undergraduates' Understanding of Entropy. *Journal of Chemical Education*, *84*(7), 1204. https://doi.org/10.1021/ed084p1204. Copyright 2007 American Chemical Society.

Three pieces of information are provided in the statement:

1) Seawater contains dissolved minerals.
2) The melting temperature of seawater is lower than that of pure water.
3) The enthalpy of solidification (crystallization), i.e. the enthalpy change that accompanies the crystallization process, is assumed identical for seawater and pure water.

The correct answer is “diagram (a) corresponds to seawater, (b) corresponds to pure water”. In other words, the crystallization of seawater is accompanied by a greater decrease in the entropy of the system. There are at least three possible explanations:

1. Classical thermodynamics (macroscopic) reasoning based on the entropy of a reversible process at constant T and P. We use the definition of entropy and information (2) and (3). This is a crystallization at equilibrium (reversible process), so :

   $$\Delta_{cr}S_{syst} = \frac{Q_{cr}}{T_{cr}} = \frac{\Delta_{cr}H_{syst}}{T_{cr}}$$

   The subscript 'cr' stands for 'crystallization'. Q_{cr} denotes the amount of heat released during crystallization. Given information (2) and (3), $|\Delta_{cr}S_{seawater}| > |\Delta_{cr}S_{pure\ water}|$ because $T_{cr,seawater} < T_{cr,pure\ water}$

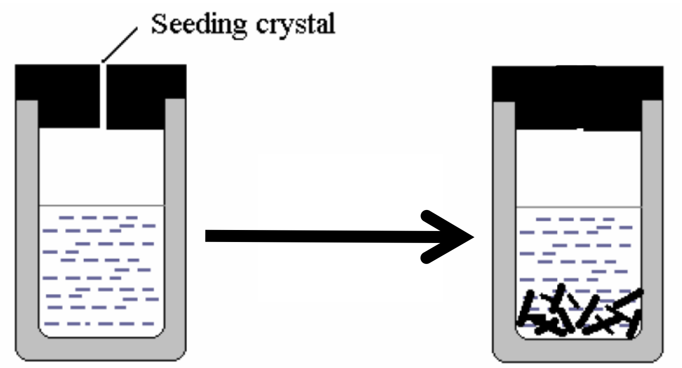
2. Classical (macroscopic) thermodynamics reasoning based on the free enthalpy of a reversible process at constant T and P. This is crystallization at equilibrium, so $\Delta_{cr}G_{syst} = \Delta_{cr}H_{syst} - T_{cr}\Delta_{cr}S_{syst} = 0$. We deduce that $\Delta_{cr}S_{syst} = \frac{\Delta_{cr}H_{syst}}{T_{cr}}$.

   Given information (2) and (3), $|\Delta_{cr}S_{seawater}| > |\Delta_{cr}S_{pure\ water}|$

3. Statistical (microscopic) thermodynamics reasoning: the presence of solute particles in a solution increases the number of accessible states compared to the pure solvent, leading to a larger number of microstates and, therefore, an increased entropy. Crystallisation will then decrease entropy to a larger extent for the solution than for the pure water.

6. Supercooled water

When water is very pure, it can be kept supercooled down to -10°C at atmospheric pressure, which means that it is still liquid even though it should be solid. When an ice crystal is added to supercooled water, crystallization starts immediately. This phase change is exothermic. To study this process in detail, some supercooled water is placed in a box made of Styrofoam (a thermal insulator): there is therefore no possible exchange of heat with the environment. Then a small ice crystal is added through a hole in the lid, which is immediately closed. The ice crystal immediately triggers spontaneous crystallization. The mass of the added crystal is small enough that its contribution to the entropy can be neglected. How does the entropy of the system change after the addition of the ice crystal?[6]



- It increases*
- It decreases
- It stays the same
- None of the above

Justify your answer as precisely as possible:

---

[6] Adapted with permission from Bennett, J. M., & Sözbilir, M. (2007). A Study of Turkish Chemistry Undergraduates' Understanding of Entropy. *Journal of Chemical Education*, *84*(7), 1204. https://doi.org/10.1021/ed084p1204. Copyright 2007 American Chemical Society.

Explanation

A first possibility is to simply apply the second principle of thermodynamics, as recalled in question 3: when a spontaneous process takes place in an isolated system, then the entropy of the system increases. Supercooled water is a metastable state that eventually relaxes to the equilibrium state of ice, for which the entropy of the system and its surroundings will be maximal. According to the second law, the entropy of the system and its surroundings increases as the metastable state transitions to equilibrium (in this case, the system is isolated, and therefore, only the entropy of the system increases). The microscopic view adds some physical insight. The situation can indeed be described as follows. As soon as the crystallization of the supercooled water begins, the heat released, which cannot escape to the outside because the system is isolated, increases the temperature of the water-ice system (and also that of the air above the water-air interface, but this contribution is quite negligible). However, the amount of released heat is not large enough for the temperature of this mixture to exceed the melting temperature of ice at atmospheric pressure, i.e. 273.15K. At this temperature, equilibrium is reached, corresponding to a water-ice mixture.

This conclusion can be checked by solving a numerical example based on thermochemistry data available from reliable databases[7].

Let us assume an isolated system of 100g of supercooled water at $T\ =-10\ °C\ (263.15K)$. Pressure is assumed to be 1 bar ≈ 1 atm. Relevant data is reported in the following table.

	$\boldsymbol{T=263,15K}$	$\boldsymbol{T=273,15K}$
$\Delta_{fus}H°\ (J.mol^{-1})$	5620	6008

---

[7] National Institute of Standard and Technology (2023) *NIST Chemistry Webbook*. Available at https://webbook.nist.gov/chemistry/

$\Delta_{fus}S°\ (J.mol^{-1}.K^{-1})$	20,58	22,00
$C_{p,ice}\ (J.mol^{-1}.K^{-1})$	36,94	37,84
$C_{p,liquid\ water}\ (J.mol^{-1}.K^{-1})$	77,65	76,41

Using Hess' law, we split the overall irreversible process in three reversible steps.

I. Crystallization of supercooled water at 263,15K (based on the data of the Table above)

a. The released heat is $Q_1 = n_{water}\Delta_{cristallisation}H° = -n_{water}\Delta_{fus}H° = -\frac{100\ g}{18.02\ g\cdot mol^{-1}} \cdot 5620\ J \cdot mol^{-1} = -31188\ J$

b. Entropy variation is $\Delta S_1 = -\frac{100\ g}{18.02\ g\cdot mol^{-1}} \cdot 20.58\ J \cdot mol^{-1} \cdot K^{-1} = -114.2\ J \cdot K^{-1}$

II. The released heat of $31188\ J$ is more than enough to heat the ice up to 273.15K.

a. The absorbed heat is

$$Q_2 = n_{ice}C_{p,ice}\Delta T = \frac{100\ g}{18.02\ g\cdot mol^{-1}} \cdot 37.39\ J \cdot mol^{-1} \cdot K^{-1} \cdot 10\ K = 2075\ J$$

Here, we assumed an average value of $C_{p,ice}$ since it does not vary much on the considered temperature range.

b. Entropy variation is

$$\Delta S_2 = n_{ice}C_{p,ice}ln\left(\frac{T_f}{T_i}\right) = \frac{100\ g}{18.02\ g\cdot mol^{-1}} \cdot 37.39\ J \cdot mol^{-1} \cdot K^{-1} \cdot ln\left(\frac{273.15\ K}{263.15\ K}\right) = +7.74\ J \cdot K^{-1}$$

III. Only part of the released heat has been used to bring ice to 273.15K. The remaining heat will lead to partial reversible ice melting at 273.15K.

a. The remaining heat available to make ice melt at 273.15K is equal to $Q_3 = -Q_1 - Q_2 = 31188 - 2075 = 29113\ J$.

Indeed, since the system is isolated and that no work has been done, $\Delta U = Q_1 + Q_2 + Q_3 = 0$. This heat induces the melting of the following amount of ice $n = \frac{29113\ J}{6008\ J \cdot mol^{-1}} = 4.846\ mol$, which corresponds to $87.32\ g$ of water. The final state is therefore a mixture of water and ice in proportions 87.32:12.68 ≈ 7:1 at 273.15 K

b. The entropy variation of this third step is

$\Delta S_3 = 4.846\ mol \cdot 22.00\ J \cdot mol^{-1} \cdot K^{-1} = +106.6\ J \cdot K^{-1}$

c. The total entropy variation is therefore equal to $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = -114.2 + 7.74 + 106.6 = +0.14\ \mathrm{J} \cdot \mathrm{K}^{-1}$, which is, as expected, positive.

Appendix III: supplementary statistical results

Table 1. Statistical comparison of the test group and the control group on four secondary school parameters. N for the number of participants, M for mean, SD for standard deviation, SW test for Shapiro-Wilk test of distribution normality (H^0 is that the distribution is normal), W test for unpaired Wilcoxon signed rank test (H^0 is that true mean difference is equal to 0). Level of significance $\alpha = 0.05$

	N	Socio-economic index				Weekly science hours				Weekly latin hours				Weekly mathematics hours			
		M	SD	SW test	W test	M	SD	SW test	W test	M	SD	SW test	W test	M	SD	SW test	W test
Test group	98	12.74	5.22	W = 0.90 p < 0.001	W = 3195 p = 0.55	7.03	2.54	W = 0.92 p < 0.001	W = 4208 p = 0.51	0.19	0.82	W = 0.23 p < 0.001	W = 4200 p = 0.60	5.29	1.59	W = 0.81 p < 0.001	W = 4925 p = 0.01
Control group	87	12.25	5.27	W = 0.91 p < 0.001		7.36	2.72	W = 0.85 p < 0.001		0.25	0.92	W = 0.28 p < 0.001		5.93	1.84	W = 0.91 p < 0.001	