Student ideas regarding entropy and the second law of thermodynamics in an introductory physics course

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We report on students' thinking regarding entropy in an introductory calculus-based physics course. We analyzed students' responses to a variety of questions on entropy changes of an arbitrarily defined system and its surroundings. In four offerings of the same course we found that before instruction, no more than 6% of all students could give completely correct responses to relevant questions posed in both general and concrete contexts. Nearly two-thirds of the students showed clear evidence of conservation-type reasoning regarding entropy. These outcomes were little changed even after instruction. Targeted instruction that guided students to recognize that entropy is not a conserved quantity appears to yield improved performance on qualitative questions related to this concept. © 2009 American Association of Physics Teachers.

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I. INTRODUCTION

In this paper we report on student ideas and learning difficulties related to certain aspects of the second law of thermodynamics and its relation to changes in entropy. The goal is to lay the framework for the creation of instructional materials and strategies which can help students improve their understanding of second-law concepts.

The second law of thermodynamics limits the direction of any naturally occurring processes to those that cause an overall increase in the entropy of a system plus its surroundings. This key idea explains the direction of natural phenomena. The concepts of entropy and the second law of thermodynamics are key elements of the introductory curriculum for undergraduate students in a wide variety of science and engineering fields. In nontechnical contexts, ideas related to entropy and the second law are often introduced in the context of energy efficiency and conservation. A central idea is that even under ideal conditions (for example, in a reversible cycle), the usable work that can be gained through a cyclic process from a given amount of energy from heating is less than 100% of the energy. This concept has broad implications but easily leads to misunderstandings and confusion. Some investigators have made preliminary studies of student thinking regarding the energy "degradation" aspect of the second law and notions of the unidirectionality of natural processes such as heat flow.^{1,2} In this paper we explore student thinking on the idea that net entropy increase is a necessary outcome of any natural process.

The idea that entropy increases has been introduced in a variety of ways, depending on the course and the context. It is often discussed in association with terms such as "system," "surroundings" (or "surrounding environment"), "iso-lated system," and "universe," as well as in connection with the phrase "spontaneous process." The meaning of entropy is often associated with both macroscopic and microscopic notions of disorder, although precise definitions are often omit-

ted. At the introductory level most of the emphasis is on changes in entropy, and students are often asked to calculate entropy changes that occur during both reversible and irreversible processes.

In this paper we explore student thinking related to entropy changes in natural processes in a variety of contexts before and after instruction. We also describe the development and initial testing of instructional materials and report preliminary data regarding student learning gains from the use of these materials.

Several papers have reported on student understanding of thermodynamics at the introductory university level, particularly in connection with student thinking regarding the first law of thermodynamics^{3,4} and the ideal gas law.^{5,6} There also have been several brief reports regarding student conceptions in upper-level thermal physics courses,^{7–12} including preliminary reports of some of the work discussed in this paper.¹³ Aside from Refs. 2 and 13, there is little published research on student understanding of entropy and the second law of thermodynamics at the introductory university level.¹⁴

Kesidou and Duit¹ interviewed 15- and 16-year-old students who had received 4 years of physics instruction and asked them questions on concepts related to the first and second laws of thermodynamics. They reported that after instruction, most students had ideas that processes tend to go in one direction only and that energy is in some sense "used up" or becomes less available. These student notions were largely based on intuitive ideas from everyday life and were not phrased within a framework characterized by deep understanding.

There have been several studies on student thinking about entropy in the context of chemistry courses. Granville¹⁵ reported that due in part to ambiguities in the usage of the symbol "*S*," chemistry students sometimes became confused when applying the principle commonly stated as " $\Delta S > 0$ for a spontaneous process." This statement holds when *S* refers to the entropy of the system plus that of its surroundings or equivalently to the entropy of an isolated system. However, in some contexts *S* is used to refer to the entropy of the (nonisolated) system only. Similarly, Thomas and Schwenz¹⁶ reported a strong tendency for physical chemistry students to believe incorrectly that the second law of thermodynamics required the entropy of the system to increase even in a context where the system was not isolated. Conversely, Sözbilir and Bennett¹⁷ found that many students in physical chemistry courses in Turkey did not recognize that entropy must increase in an isolated system undergoing a spontaneous process.

Cochran and Heron² investigated student thinking on entropy and its role in constraining allowed heat-engine efficiencies. They found that for the most part, students did not perceive the connection between constraints on engine efficiencies and increases in total entropy of the system and its surroundings.

II. CONTEXT OF THE INVESTIGATION

The bulk of this study was conducted with students in the second semester of a year-long calculus-based introductory physics course at Iowa State University (ISU). This sequence usually enrolls 700–800 students per calendar year. Most of the students are engineering majors, but a few physics majors and computer science majors are included. The course content varies slightly; the first semester usually covers mechanics and electric fields, and the second semester covers magnetism, ac circuits, waves, fluids, and thermal physics.

Additional data were collected in a sophomore-level physics course at the University of Washington (UW) that covers a wide range of topics on thermal physics. The students in this course are primarily physics majors, all of whom have completed UW's introductory calculus-based physics courses or the equivalent. This thermal physics course is, for most of them, their first exposure to thermodynamics at the university level.

To assess students' previous exposure to entropy, we conducted a brief background survey in the Fall 2006 offering of the ISU course before any instruction on entropy or thermodynamics. We found that of 272 students, 64% self-reported having studied entropy previously, and at least that many reported taking a specific course where entropy was discussed as part of the instruction (primarily in an introductory chemistry course). In many chemistry textbooks students are introduced to entropy and the second law of thermodynamics in the context of spontaneous processes, and it is emphasized that the entropy of the universe must increase in such processes. Chemistry texts are often very explicit in the use of the formulation "system plus surroundings equals universe" (more so than many current physics books).¹⁸

III. QUESTIONS USED TO PROBE STUDENT THINKING

A. Entropy increase in natural processes

We investigated students' thinking regarding the concept of entropy increase in natural processes,¹⁹ as well as the meaning of system and surroundings in the application of this concept. The second law of thermodynamics states that the total entropy of the universe will increase in any real process. In this context the universe can be divided into two arbitrarily defined regions, a system and its surroundings (or surrounding environment). A system is a particular region of For each of the following questions consider a system undergoing a naturally occurring (spontaneous) process. The system can exchange energy with its surroundings.

a) During this process, does the entropy of the <u>system</u> [S_{system}] *increase*, *decrease*, *remain the* same, or is this not determinable with the given information? Explain your answer.

b) During this process, does the entropy of the <u>surroundings</u> [S_{surroundings}] *increase, decrease, remain the same*, or is this *not determinable* with the given information? *Explain your answer.*

c) During this process, does the entropy of the system *plus* the entropy of the surroundings $[S_{system} + S_{surroundings}]$ *increase, decrease, remain the same*, or is this *not determinable* with the given information? *Explain your answer.*



interest that is arbitrarily defined and enclosed by a boundary. The surroundings comprise everything outside that boundary.²⁰ The second-law statement regarding increasing entropy is often closely associated with students' introduction to the entropy concept itself, and this statement has sometimes been referred to as the most general statement of the second law of thermodynamics.²¹

B. General-context question

The general-context question (see Fig. 1) relates to an arbitrary system along with its surroundings; the system and surroundings can exchange energy with each other. The context is any naturally occurring process; no further details are offered regarding either the system or the process. Students are asked whether the entropy of the system will increase, decrease, or remain the same during the process, or whether the answer is not determinable with the given information. That same question is posed regarding the entropy of the surroundings, as well as the total entropy of the system and its surroundings.

The correct answer is that neither the change in entropy of the system nor that of its surroundings is determinable from the given information because no information is provided about the system or the process. The only physical constraint is that the total entropy of the system plus the entropy of the surroundings must increase as a consequence of the second law.

C. Concrete-context question

The concrete-context question (see Fig. 2) relates to an object in a thermally insulated room that contains air. The object and the air are initially at different temperatures and are allowed to exchange energy with each other. Students are asked whether the entropy of the object will increase, decrease, or remain the same during the process, or whether the answer is not determinable with the given information. That same question is posed regarding the entropy of the air in the

An object is placed in a thermally insulated room that contains air. The object and the air in the room are initially at different temperatures. The object and the air in the room are allowed to exchange energy with each other, but the air in the room does not exchange energy with the rest of the world or with the insulating walls.

a) During this process, does the entropy of the <u>object</u> [S_{object}] *increase, decrease, remain the* same, or is this *not determinable* with the given information? *Explain your answer*.

b) During this process, does the entropy of the <u>air in the room</u> $[S_{au}]$ increase, decrease, remain the same, or is this not determinable with the given information? *Explain your* answer.

c) During this process, does the entropy of the object *plus* the entropy of the air in the room $[S_{object} + S_{air}]$ *increase, decrease, remain the same*, or is this *not determinable* with the given information? *Explain your answer.*

d) During this process, does the entropy of the <u>universe</u> [$S_{universe}$] increase, decrease, remain the same, or is this not determinable with the given information? Explain your answer.

Fig. 2. Concrete-context question.

A subsystem A is in thermal contact with its environment B, which together comprise an isolated system. Consider the following situations:

I. Entropy of system increases by 5 J/K; entropy of the environment decreases by 5 J/K.

II. Entropy of system increases by 5 J/K; entropy of the environment decreases by 3 J/K.

III. Entropy of system increases by 3 J/K; entropy of the environment decreases by 5 J/K.

IV. Entropy of system decreases by 3 J/K; entropy of the environment increases by 5 J/K.

Which of the above four situations can actually occur in the real world?

- A. I only
- B. II only
- C. III only
- D. II and III only
- E. II and IV only [correct]

Fig. 3. Spontaneous-process question version A.

room, as well as the entropy of the object and the air. A fourth part of the question asks about the entropy change of the universe.

Because the object and the air in the room are initially at different temperatures, the higher-temperature entity (either object or air) will transfer energy by heating to the lowertemperature entity and thus undergo an entropy decrease. The entity that gains energy will undergo an entropy increase. The question does not specify whether the object temperature is initially higher or lower than that of the air in the room, and so there is insufficient information to determine the sign of the entropy change of the object and the air. As in the general-context question, the only specification that can be made is that the total entropy of the object plus air in the room (and likewise the universe) must increase.

D. Spontaneous-process question

This multiple-choice question describes four processes that involve a change in the entropy of a system and its surrounding environment. In version A (see Fig. 3) students are asked which of the processes can actually occur "in the real world." Version B of this question (see Fig. 4) includes an incorrect answer option [response (E)] that corresponds to the total entropy either increasing or remaining the same. Version A does not include an answer option that combines those two possibilities, that is, no answer corresponds to $\Delta S \ge 0.^{22}$

There is no constraint on the change in entropy of either the system or the environment, so the entropy of either one may increase or decrease. The sum of the two entropy A subsystem A is in thermal contact with its environment B and they together comprise an isolated system that is undergoing an irreversible process. Consider the following situations:

I. Entropy of system increases by 5 J/K; entropy of the environment decreases by 5 J/K.

- II. Entropy of system increases by 5 J/K; entropy of the environment decreases by 3 J/K.
- III. Entropy of system increases by 3 J/K; entropy of the environment decreases by 5 J/K.
- IV. Entropy of system decreases by 3 J/K; entropy of the environment increases by 5 J/K.

Which of the above four situations can actually occur?

- A. I only
- B. II only
- C. III only
- D. II and IV only [correct]
- $E. \ \ \, I, II, and \, IV \, only$

Fig. 4. Spontaneous-process question version B.

changes must be positive, which means that processes II and IV in both versions A and B are possible and all other processes are disallowed.

IV. STUDENTS' REASONING REGARDING THE PRINCIPLE OF INCREASING ENTROPY

A. Responses before instruction

We administered the general-context question during four offerings of the second-semester calculus-based introductory physics course at ISU; in three of those four courses we also administered the concrete-context question. The questions were administered before any instruction on entropy and the second law. Table I shows the proportion of students who provided correct responses on each part of each question.²³

For the general-context question only 19% of the students gave the correct "increase" answer for part (c), the entropy change of the system plus surroundings; 4% gave a correct response for all three parts of the question. The concrete-context question yielded similar results. The percentage of students (14%) who gave a correct response on part (c) of the concrete-context question (see Fig. 2) was similar to the proportion who gave a correct response on the corresponding part (c) for the general-context question.²⁴

The percentage of students (5%) who gave correct answers for parts (a), (b), and (c) of the concrete-context question was nearly identical to the proportion who gave correct answers on all three parts of the general-context question. (We refer to such simultaneous correct responses on parts (a)–(c) as "all-correct" answers.) However, only 44% of those students

Table I. Percentage of preinstruction correct responses on the general- and concrete-context questions. The results shown are mean values and 95% confidence intervals based on score variances among the four samples for the general-context question and three samples for the concrete-context question. See detailed data in Appendices I and II (Ref. 23).

	Preinstruction, general context, N=1184 (four samples) (%)		Preinstruction, concrete context, N=609 (three samples) (%)
(a) Entropy change of system is not determinable.	42 ± 10	(a) Entropy change of object is not determinable.	50 ± 11
(b) Entropy change of surroundings is not determinable.	42 ± 6	(b) Entropy change of air in the room is not determinable.	49 ± 3
(c) Entropy of the system+surroundings increases.	19 ± 5	(c) Entropy of the object+air in the room increases.	14 ± 9
		(d) Entropy of the universe increases.	15 ± 18
All correct, parts (a)–(c)	4 ± 1	First three parts correct, parts (a)-(c)	5 ± 3

Table II. Percentage of responses corresponding to zero total entropy change on the general- and concrete-context questions (see Figs. 1 and 2) before instruction on entropy. Mean values and uncertainties are interpreted as in Table I [see detailed data on EPAPS (Ref. 23) Appendices III and IV]. The first row corresponds to students who answered "remain the same" to part (c) of each question, respectively; "system+surroundings" refers to the general-context question; "object+air in the room" refers to the concrete-context question. The second row (labeled *N-N-S*) corresponds to students who responded "not determinable" to parts (a) and (b), but "remain the same" to part (c) of each question, respectively. The third row (labeled *I-D-S*) corresponds to students who answered either increase or decrease to part (a), but gave the opposite answer (decrease or increase) to part (b), and who also answered "remain the same" to part (c) of each question, *N-N-S* or *I-D-S*.

	Preinstruction, general context, N=1184 (four samples) (%)	Preinstruction, concrete context, N=609 (three samples) (%)
Total entropy of (system+surroundings)/(object+air in the room)		
remains the same.	67 ± 8	71 ± 7
N-N-S: entropy change of (system and surroundings)/(object and air)		
not determinable, but total entropy remains the same.	26 ± 12	38 ± 8
I-D-S: entropy of (system/object) increases (decreases) and entropy of		
(surroundings/air) decreases (increases), but total entropy remains the		
same.	25 ± 10	22 ± 6
Students with one of these notions of entropy conservation (sum of		
<i>N-N-S</i> and <i>I-D-S</i>).	51 ± 7	60 ± 13

who gave an all-correct answer to the concrete-context question were also able to give all-correct answers to the general-context question. 25

Before instruction on the second law of thermodynamics, a clear majority of students gave answers consistent with the belief that entropy is conserved (see Table II). Most students responded that the entropy of the system plus the entropy of the surroundings stays the same. Approximately 80% of the students who gave the "total entropy remains the same" response for the general-context question gave a similar response on the concrete-context question. These consistent yet incorrect responses suggest that most students had a welldefined point of view regarding entropy conservation. This impression is strengthened by further analysis of students' responses as shown in the following.

An analysis of the answers of those students who gave the "total entropy remains the same" responses shows that more than 75% of these students fall into one of two categories on both the general- and concrete-context questions. These categories are referred to as N-N-S and I-D-S, respectively, in Table II. On the general-context question, category N-N-S (26% of all responses) consists of students who state that the change in entropy of the system is not determinable and the change in entropy of the surroundings is not determinable, but the entropy of the system plus that of the surroundings remains the same. Most (65%) of the students in this category cited some type of conservation rule in their reasoning. Many are unclear about what exactly is being conserved, but entropy, energy, and heat are the quantities most often mentioned. On the same question, students in category I-D-S claim that the system's entropy and the surroundings' entropy change in some specified manner, but they too assert that total entropy change is zero. That is, they say that the system's entropy increases (decreases) and the surroundings' entropy decreases (increases), but the entropy of the system plus that of the surroundings remains the same. On the general-context question, the proportions of students in categories N-N-S and I-D-S were almost identical to each other.

As can be seen in Table II, the results for the concretecontext question are very similar to those for the generalcontext question. Most students stated that the entropy of the object plus the entropy of the air in the room (the total entropy) would not change during a spontaneous process. More than half of all responses to the concrete-context question included answers consistent with the total entropy being conserved during a spontaneous process (see the last row in Table II).²⁶ In contrast to the *N-N-S/I-D-S* parity observed for the general-context question, category *N-N-S* was significantly more popular than category *I-D-S* on the concrete-context question. (Categories *N-N-S* and *I-D-S* were defined similarly to those on the general-context question, except that "object" and "air in room" were substituted for system and surroundings, respectively.) The majority of students in category *I-D-S* on either question claimed that the entropy of the surroundings or the air in the room would increase rather than decrease (58% on the general-context question and 71% on the concrete-context question).

B. Comparison of responses pre- and postinstruction

After all instruction on thermodynamics was complete in Spring 2005, we administered free-response questions to students during 1 week of laboratory classes. We compared students' responses on both the general- and concrete-context questions to their preinstruction responses on the same questions for a matched sample of students consisting of the same group both pre- and postinstruction. There was little difference in the proportion of correct responses before and after instruction. For example, correct responses on the "total entropy change" question [part (c)] increased from 25% to 36% on the general-context question and from 20% to 23% on the concrete-context question.²⁷ The proportion of students with all three parts correct increased from 5% to 8% on the general context and from 7% to 13% on the concrete context. (Detailed data and further discussion are given in Sec. VI.)

Responses related to "conservation" thinking on the general- and concrete-context questions are shown in Table III, where students' pre- and postinstruction responses are compared for the Spring 2005 semester. The sample is matched. These students had completed our "entropy state-function ('two-processes') tutorial" during recitation.²⁸ This tutorial was created for use in the Spring 2005 course and was targeted at difficulties regarding the state-function property of entropy and the principle of increasing entropy. It guided students to evaluate and compare changes in *P*, *V*, *T*, and *S* for an ideal gas undergoing either an isothermal ex-

Table III. Percentage of responses corresponding to zero total entropy change on the general-context (Fig. 1) and concrete-context (Fig. 2) questions in Spring 2005. The same group of students responded to the questions both pre- and postinstruction (see Ref. 32).

	Spring 2005, matched sample, N=127 (%)				
	Preinstruction, general context	Postinstruction, general context	Preinstruction, concrete context	Postinstruction, concrete context	
Total entropy of (system+surroundings)/(object+air in the room) remains the same.	61 ^a	48 ^{a,b}	69	71 ^b	
<i>N-N-S</i> : entropy change of (system and surroundings)/(object and air) not determinable, but total entropy remains the same.	34 ^a	16 ^{a,b}	39	36 ^b	
<i>I-D-S</i> : entropy of (system/object) increases (decreases) and entropy of (surroundings/air) decreases (increases), but total entropy remains the same.	19	24	21	23	
Students with one of these notions of entropy conservation (sum of <i>N-N-S</i> and <i>I-D-S</i>).	53ª	39 ^{a,b}	60	59 ^b	

^aSignificant difference ($p \le 0.001$) between pre- and postinstruction responses to general-context question, according to binomial proportions test. ^bSignificant difference ($p \le 0.05$) between general-context and concrete-context responses on postinstruction questions.

pansion or a free expansion. The use of this tutorial seemed to help raise students' correct-response rates on certain questions regarding entropy change.²⁹

1. General-context question

On this question nearly half of the students continued to state after instruction that the entropy of the system plus that of the surroundings stays the same; more than 80% of this group (39% of all students) fell into one of the two conservation categories. However, there was a significant decrease from pre- to postinstruction of those in category *N*-*N*-*S*. Among students in category *I*-*D*-*S*, the claim that the surroundings' entropy would increase rather than decrease retained the same majority support it had among the preinstruction group.

Interview data were obtained from 18 student volunteers who agreed to participate in one-on-one interviews after all instruction on thermodynamics was complete. Our interview data confirmed many of the ideas that we observed in the free-response data. Seven of the 18 students provided some type of conservation argument in their answer to the generalcontext question, and none of them gave a correct response for all three parts of this question. (S1 corresponds to Student 1, etc.)

- (a) S1: "I think for the irreversible process... I actually started with step (c). I was thinking that the entropy of the system plus surroundings equals zero, so it would remain the same. I know these two would be opposite of each other... I wasn't 100% sure, but I was thinking the system would decrease, and the surroundings would increase."
- (b) S2: "...[c] it remains the same because the surroundings and system is like the universe and entropy of the universe is constant."

2. Concrete-context question

This question yielded postinstruction responses that were almost unchanged in every category from their preinstruction values (see Table III). After instruction, responses that claimed the total entropy would remain the same were given more frequently on the concrete-context question (71%) than they were by the same students on the general-context question (48%). Of those students that gave a "total entropy remains the same" response to the concrete-context question, 61% gave a similar response on the general-context question. Before instruction this overlap in similar responses between the two contexts was 80%. This decreased consistency of incorrect responses suggests that students' thinking after instruction might have been less well characterized by a notion of entropy conservation than had been the case before instruction.

On both questions a substantial fraction of all students still fell into one of the two conservation categories of the "total entropy remains the same" responses. After instruction, the concrete-context question yielded a higher proportion of conservation arguments (59% of all students) than did the general-context question (39% of all students, difference significant at p=0.001). The proportion of correct responses ("total entropy increases" responses) after instruction in the concrete context (23%) was lower than that in the general context (36%), a difference that is also statistically significant (p=0.02).³⁰

3. Spontaneous-process question

Two versions of the spontaneous-process question were administered after all instruction on thermodynamics in the Fall 2004 and Spring 2005 semesters. After administering version A (Fig. 3) in the Fall 2004 course, we conducted seven interviews in which we asked this question in a freeresponse format. We asked students to identify which of the situations could actually occur in a real process. Four of the seven students stated that the total entropy must either increase or remain the same. We therefore recast the multiplechoice options to reflect this change in version B (Fig. 4), which was given in the Spring 2005 course. Responses to both versions are shown in Table IV.

It is unclear to what extent the students in the Fall 2004 course would have preferred an "increases or remains the same" answer. In any case, in both courses over half of all students gave a response after instruction that was consistent with a belief that entropy would (or at least could) remain unchanged during a spontaneous process.³¹ The proportion of correct responses was not significantly different on the two versions of the question.

Table IV. Percentage of postinstruction responses for each option on versions A and B of the spontaneous-process question. (Only version B includes the option of total entropy either increasing or remaining the same.) Response descriptions in the first column are characterizations of the numerical response options in the original question.

	Fall 2004, postinstruction (version A), <i>N</i> =539 (%)	Spring 2005, postinstruction (version B), N=341 (%)
(A) Total entropy remains the same.	54	36
(B) Total entropy increases and system entropy increases.	5	12
(C) Total entropy decreases and system entropy increases.	7	2
Answers B and C ^a	4	
Total entropy increases and system entropy can increase or decrease		
(correct).	30	27
Total entropy increases or remains the same. ^b		23

^aVersion A only.

^bVersion B only.

V. STUDENT REASONING REGARDING SYSTEM AND SURROUNDINGS

Before instruction 40-50% of all students correctly stated that the changes in entropy of the system/object and of the surroundings/air in the room were not determinable with the information given (see Table V). However, if we look at the preinstruction responses in which students made a specific directional choice (that is, either increases or decreases) we find an asymmetry: in the general context, the students' preferred answer was that the entropy of the system would increase (26%) rather than decrease (19%) or remain the same (10%); the difference between the "increases" and "decreases" responses is significant over our four semesters of data (p < 0.05 using a one-tailed paired two-sample *t*-test). More students expected the entropy of the surroundings to increase rather than decrease or remain the same (p=0.001). Similarly, on the preinstruction concrete-context question, students have a significant preference regarding the entropy of the air in the room (p < 0.001); the responses that the entropy of the air would increase (27%) were nearly triple the responses that stated that the entropy of the air would decrease (9%). On the same question we did not see the same preferential response regarding changes in the entropy of the object (17% increases, 19% decreases). At the outset of our study we expected that students would disproportionately expect entropy to increase rather than decrease, recalling the

often-heard phrase "entropy never decreases." Our findings show that although this expectation may hold in some circumstances, there are contexts in which it does not.

The matched-data sample from the Spring 2005 course shows that the responses before and after instruction are mostly consistent with each other (see Table VI). In most cases students have a preference for the "entropy increases" responses (compared to "decreases" or "remains the same") before and after instruction³² and show a statistically significant preference for stating that entropy of the system, the surroundings, and the air in the room increases. However, for the object in the concrete-context question the matched sample shows no significant difference between the proportions of "increases" and "decreases" responses, either before or after instruction. This result is consistent with our finding from the larger three-semester preinstruction data sample, as discussed at the beginning of this section and as reflected in Table V.

Interviews were conducted throughout our study; 18 were done after all instruction was complete in the Spring of 2005. As noted in Sec. IV B, seven of the 18 students had offered conservation arguments regarding total entropy. By contrast, seven other students in this same group of 18 argued that system entropy would have to increase; however, this latter group of seven varied in the way they treated system and surroundings. Although the students in this subsample said

Table V. Percentage of various preinstruction responses related to system and surroundings as a proportion of all responses. Uncertainties reflect the 95% confidence interval based on response rates and standard deviations observed in four courses for the general-context question, and three courses for the concrete-context question [see EPAPS (Ref. 23) Appendices I and II].

	Preinstruction, general context, N=1184 (four samples)	Preinstruction, concrete context, N=609 (three samples)
Entropy of	System	Object
Increases	$26\pm3\%$	$17 \pm 2\%$
Decreases	$19\pm4\%$	$19 \pm 3\%$
Remains the same	$10\pm4\%$	$6\pm7\%$
Is not determinable (correct)	$42 \pm 6\%$	$50\pm5\%$
Entropy of	Surroundings	Air in room
Increases	$28\pm2\%$	$27\pm2\%$
Decreases	$14\pm2\%$	$9\pm1\%$
Remains the same	$11 \pm 1\%$	$6 \pm 3\%$
Is not determinable (correct)	$42 \pm 4\%$	$49 \pm 1\%$

Table VI. Percentage of various pre- and postinstruction responses related to system and surroundings, general- and concrete-context questions, Spring 2005. The same group of students responded both preinstruction and postinstruction (see Ref. 32).

	Spring 2005, matched sample, N=127					
	Preinstruction, general context	Postinstruction, general context	Preinstruction, concrete context	Postinstruction, concrete context		
Entropy of	Syste	em	Obje	ect		
Increases	28%	35% ^a	20%	$17\%^{\mathrm{a}}$		
Decreases	14%	20%	17%	23%		
Remains the same	3% ^b	$9\%^{a,b}$	2%	3% ^a		
Is not determinable (correct)	51% ^b	35% ^{a,b}	55%	57% ^a		
Entropy of	Surrour	ndings	Air in room			
Increases	29%	31%	25%	29%		
Decreases	10%	17% ^a	10%	6% ^a		
Remains the same	8%	10%	6%	7%		
Is not determinable (correct)	47%	39% ^a	51%	57% ^a		

^aSignificant difference (p < 0.05) between concrete-context and general-context responses on postinstruction questions, according to binomial proportions test. ^bSignificant difference (p < 0.05) between pre- and postinstruction responses on general-context question.

that the system entropy must increase, their answers for the entropy of the surroundings varied among "not determinable" (4), "remain the same" (2), and "increase" (1). Two typical responses categorized as "not determinable," which demonstrate the asymmetry in student thinking regarding system and surroundings, are given here. (I corresponds to Interviewer.)

- (a) S3: "Entropy of the system will increase because it's irreversible and you have to have an increase in entropy if it's irreversible... second one [the entropy of the surroundings] I wasn't sure of... entropy must either stay the same or increase... because you can't achieve order from disorder, but it can go the other way around."
- (b) S4: "[For surroundings] I said remain equal or increase, and that depends on whether the heat is transferred to the system."

I: Could it decrease?

S4: "It [the surroundings] would always remain the same or increase. [Part c] remain[s] the same because the universe can't possibly become more ordered... it's one of the laws of thermodynamics."

Approximately 15% of the explanations on part (d) of the concrete-context question included a claim that the entropy of the universe is unaffected by the process, or that the universe is isolated from the process; some argued that the entropy of the universe would be unaffected "because it's too big." We developed a "metal in the ocean" question to provide clearer evidence of student thinking on this issue. The problem describes a 1 cm³ piece of hot metal thrown into an ocean. The hot metal was initially at a higher temperature than the ocean. The students are asked to consider the entropy change of the metal, the ocean, and the ocean plus the metal after several hours have elapsed.

The question was first developed in Spring 2006 and was used during 20 postinstruction interviews during that semester. The most surprising finding is that three out of the 20 students claimed that although the metal would decrease in entropy, the entropy of the ocean would remain the same. Their explanation hinged on some type of ocean-size argument and led to their conclusion that the total entropy of metal plus ocean would actually decrease. Excerpts from the interview with one of these three students are given in the following:

S5: "...entropy of the metal is going to decrease because it's losing heat, once it reaches equilibrium it will have lost entropy because it's also lost heat; the entropy of the surroundings I think means the ocean, then the ocean remains the same, it's a law or it's a frame of reference... a very small change in entropy into a very large surroundings isn't going to result in any measurable change in entropy in the surroundings because of the size difference between the two... It [the change in entropy of the metal piece plus the surroundings] would decrease because the entropy in the ocean is going to remain the same but the entropy of the very hot piece of metal will decrease drastically to come in equilibrium with the ocean...In the object in the room the object was large enough to create a change in entropy in the room; then there would be enough to determine if it's the same. In this problem there wasn't a noticeable change in entropy of the ocean but there was in the metal."

Our study did not assess the full extent of this error among our sample.

We documented specific student difficulties regarding the entropy changes in a spontaneous process. Before and after instruction most students failed to recognize the correct answers on questions regarding the change in entropy during a naturally occurring process. The most common responses suggest belief in a conservation principle that requires the total entropy to remain the same. Among those students who assert a direction for entropy change even when none can be specified, a significantly higher proportion of students claim that entropy will increase rather than decrease for both the system and surroundings. For the most part we found that

Table VII. Percentage of correct responses on the general-context question, matched samples, Spring 2005 and Spring 2006. The Spring 2005 class used the entropy state-function [two-processes] tutorial, and the Spring 2006 class used the entropy spontaneous-process [two-blocks] tutorial.

	Spring 2	2005, N=127 (%)	Spring 2006, N=191 (%)	
	Preinstruction	Postinstruction with two-processes tutorial	Preinstruction	Postinstruction with two-blocks tutorial
(a) Entropy change of system not determinable	51	35 ^a	42	74 ^a
(b) Entropy change of surroundings not determinable	47	39 ^a	42	75 ^a
(c) Entropy of (system+surroundings) increases	25	36 ^a	21	68 ^a
All correct, (a)–(c)	5	8^{a}	6	55 ^a

^aSignificant difference (p < 0.0001) between Spring 2005 and Spring 2006 on postinstruction responses, according to binomial proportions test. (Differences between 2005 and 2006 on preinstruction responses are not significant.)

students' responses to questions posed both in a general context and in a concrete context were very similar in the two contexts.³³

VI. CURRICULUM DEVELOPMENT

A. Entropy spontaneous-process "two-blocks" tutorial

Based on our finding that many students overgeneralized the notion of conservation to questions regarding total entropy change during real processes, we developed curricular materials to help students address this difficulty. Our strategy was to guide students to consider a physical situation that allows them to affirm their understanding of energy conservation³⁴ and challenges the notion that entropy is conserved in the same process. It was also important to choose a system and process in which the outcome of entropy increase is easy to deduce.

We developed a tutorial based on a set of two large, insulated metal blocks connected by a thin insulated metal rod of negligible heat capacity; we refer to this as our "entropy spontaneous-process [two-blocks] tutorial."³⁵ (This replaced the entropy state-function [two-processes] tutorial.) The two blocks are initially at different temperatures, and students are asked to consider net changes in the energy and entropy of the two blocks during the heat-transfer process. The dimensions of the blocks are shown to be so small as to be negligible. The relation $\Delta S \equiv \int_{\text{initial state}}^{\text{final state}} \delta Q_{\text{rev}}/T$ simplifies for the blocks (which act as thermal reservoirs) to $\Delta S = Q/T$, where Q is the heat transfer to the block and T is the temperature of the block. (Heat transfers to the thin rod are stated to be negligible.)

Students are asked questions at the beginning of the tutorial on the change in entropy of the low-temperature block and the net change in entropy of both blocks together. They are asked whether there are any conserved quantities for this process and whether energy and/or entropy are conserved. Because most students are likely to apply an inappropriate conservation argument to questions of this type, we wanted to elicit these difficulties at the beginning so that students could address and resolve them over the course of the tutorial.³⁶

Students are asked to consider the magnitudes and signs of the heat transfers to the two blocks and are led to recognize that these heat transfers are equal in magnitude and opposite in sign and that the net energy change is zero. Students are then asked to consider the magnitudes and signs for the entropy changes of each block and the net change in entropy. Students are guided to realize that the entropy increase of the cooler block is larger in magnitude than the entropy decrease of the warmer block, and so the net change in entropy is positive.

The tutorial continues by guiding students to explore the relations among the system, surroundings, and the universe. Our goal is to get students to realize that regardless of how the system and surroundings are defined (for example, no matter which block is taken to be the system and which the surroundings), the total entropy of the system plus the surroundings will increase during this process. Additional sections in the tutorial guide students to consider the consequences of negative entropy changes, as well as the limiting case of zero entropy change for an ideal reversible process as the temperatures of the two blocks approach each other arbitrarily closely.

In the Spring of 2006 we administered the two-blocks tutorial to all students ($N \approx 200$) who attended recitation during the week in which entropy was covered in class. Postinstruction testing took place on the midterm exam, which covered all thermodynamics topics (using multiple-choice questions), and also during 1 week of laboratories conducted 2 weeks after the midterm was complete (using free-response questions). As seen in Tables VII (general-context question) and VIII (concrete-context question), student performance gains (pretest to post-test) on both questions are much better in the Spring 2006 course compared to the matched sample in the Spring 2005 course.³⁷ There was also a dramatic improvement in the proportion of students answering all three parts correctly (55% and 53%, respectively, on the general- and concrete-context questions, postinstruction, compared to only 6% preinstruction). After tutorial instruction a much higher proportion of students who were able to answer (a), (b), and (c) correctly on the concrete-context question also answered all three parts correctly on the general-context question. This overlap proportion rose from 45% to 90% (pre- to postinstruction), indicating far greater consistency in correct-answer responses after use of the two-blocks tutorial.³⁸ (In 2005, by contrast, no shift in the overlap proportion was observed even after instruction had taken place.) Those students who gave incorrect responses did not do so as consistently as before instruction, and the overlap proportion for incorrect answers to part (c) dropped from 83% to 69%.

A third version of the spontaneous-process multiplechoice question was designed that was almost identical to version B, which had been used in Spring 2005. The proportion of correct responses (61%) to this question was signifi-

Table VIII. Percentage of correct responses on the concrete-context question, matched samples, Spring 2005 and Spring 2006. The Spring 2005 class used the two-processes tutorial, and the Spring 2006 class used the two-blocks tutorial.

	Spring 2	Spring 2005, N=127 (%)		006, N=191 (%)
	Preinstruction	Postinstruction with two-processes tutorial	Preinstruction	Postinstruction with two-blocks tutorial
(a) Entropy change of object not determinable.	55	57 ^a	53	73 ^a
(b) Entropy change of air in the room not determinable.	51	$57^{\rm a}$	52	73 ^a
(c) Entropy of (object+air in the room) increases.	20	23 ^b	16	69 ^b
(d) Entropy of universe increases.	26 ^c	26^{a}	15 ^c	44^{a}
(a), (b), and (c) correct	7	13 ^b	6	53 ^b

^aSignificant difference (p < 0.001) between Spring 2005 and Spring 2006 on postinstruction responses, according to binomial proportions test.

^bSignificant difference (p < 0.0001) between Spring 2005 and Spring 2006 on postinstruction responses.

^cSignificant difference (p < 0.05) between Spring 2005 and Spring 2006 on preinstruction responses.

cantly higher after instruction with the two-blocks tutorial than it had been without its use in 2004 (30% correct) and 2005 (27% correct).

There were other substantial changes in the content of instruction during the Spring 2006 course compared to the Spring 2005 course. The same instructor taught both courses and the form of instruction was consistent, but the instructor drastically modified his lectures on entropy. He modeled some of the same steps that were used in the two-blocks tutorial and incorporated a number of related questions, which he posed to the class using clickers.³⁹

We also administered the two-blocks tutorial in a sophomore-level physics course at the UW. Before instruction the UW students performed at a level similar to that of the ISU students, although a higher proportion of UW students gave all-correct answers on the general- and concrete-context questions (13% and 19%, respectively; N=32) than did ISU students in the two matched samples ($\approx 6\%$). The students' postinstruction performance was significantly better than that of students in the Spring 2005 ISU course, with a higher proportion of students giving all-correct answers for the general-context (63%) and concrete-context (69%) questions. These high postinstruction performance in the Spring 2006 course at ISU.⁴⁰

B. Student performance on "universe equals system plus surroundings" concept

We assessed students' thinking on the commonly used terminology in which an arbitrarily defined system and that system's surroundings are taken together to define the universe. Our concrete-context question shed light on their thinking by asking for the change in entropy inside the insulated room and the change in entropy of the universe. Both before and after the Spring 2005 course, students' responses on these two questions were consistent with each other. After instruction with the two-blocks tutorial in the 2006 course, the proportion of students who claimed incorrectly that the entropy of the universe would stay the same (53%) was far higher than those who gave the corresponding answer on part (c) of the concrete-context question (24%).⁴¹ Student explanations that justified the "entropy of the universe remains the same" response often described the universe as being isolated from the room, which is contrary to the meaning employed in the tutorial. Despite the substantial improvement in overall student understanding (see Tables VII and VIII and

discussion in Sec. VI A), this use of the two-blocks tutorial increased student difficulties in consistently interpreting the meaning of universe in the context used here. This shortcoming will need to be addressed in future versions of this tutorial.

VII. CONCLUSION

We conducted an extensive analysis of student thinking on certain aspects of the principle of increasing entropy, including those that relate to the meaning of system and surroundings. Analysis of data from four semesters of classes demonstrated that before instruction, students have well-defined and consistent lines of thinking and reasoning. These lines include the popular notion that total entropy remains unchanged during a real process, implicitly based on an assumption that entropy is a conserved quantity. These ideas can lead to difficulties in understanding the role of entropy in the second law of thermodynamics.

Before instruction fewer than 10% of the students were able to correctly respond to questions on entropy changes, and there was very little dependence on whether these questions were posed in a general or a concrete context.³³ Almost two-thirds of the students showed evidence of conservation-type reasoning regarding entropy.

Many students showed a strong tendency to claim, even when lacking the required information, that the entropy change of the system or surroundings would have a specific sign; most of this group asserted that entropy would increase. It appeared as if many students were attempting to reconcile two popular ideas: the common perception that "entropy always increases" and a belief that the total entropy must be conserved.

Results from matched samples of students assessed by pre- and postinstruction testing showed that some of these difficulties persist despite instructor awareness of the difficulties and deliberate attempts to overcome them. We subsequently developed a research-based tutorial that explicitly addressed some of these difficulties. Early indications are that instruction using this tutorial is effective in improving students' performance on questions regarding the principle of entropy increase in spontaneous processes, at least in processes that involve energy transfer by heating.⁴²

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- ¹⁸See, for example, N. J. Tro, *Chemistry, A Molecular Approach* (Prentice-Hall, Upper Saddle River, NJ, 2008), pp. 783–785.
- ¹⁹In general, we use the terms "natural," "spontaneous," "real," and "naturally occurring" synonymously when modifying the word "process."
- ²⁰ For practical purposes and to facilitate analysis, we ordinarily specify a particular system along with a separate region or reservoir referred to as the surroundings; both this system and the surroundings are then isolated from the rest of the universe. See discussion of the "concrete-context" question in Sec. III C.
- ²¹D. Giancoli, *Physics for Scientists and Engineers*, 3rd ed. (Prentice-Hall, Upper Saddle River, NJ, 2000), p. 539; D. Halliday, R. Resnick, and J. Walker, *Fundamentals of Physics*, 6th ed. (Wiley, New York, NY, 2001), p. 500; R. D. Knight, *Physics for Scientists and Engineers* (Addison-Wesley, San Francisco, CA, 2004), p. 566; R. A. Serway, *Physics for Scientists and Engineers*, 4th ed. (Saunders, Philadelphia, PA, 1996), pp. 629–632.
- ²²The instructor for the course in which this question was first used employed the terminology "isolated system," so the question was written to include that language in version A. Student understanding of this terminology was not a focus of our research. We also discovered that the distracters in version A might not have fully represented students' thinking on this question, and so we created version B. See discussion in Sec. IV B 3.
- ²³ See EPAPS Document No. E-AJPIAS-77-013909 for appendices. Appendix I contains detailed responses to all questions in each course. This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (http://www.aip.org/ pubservs/epaps.html).
 ²⁴ Almost all students (90%) who gave a "not determinable" response on
- ²⁴Almost all students (90%) who gave a "not determinable" response on part (a) (system/object) also gave a "not determinable" response on part (b) (surroundings/air) on both the general-context and concrete-context questions.
- ²⁵ After instruction in Spring 2005, this overlap proportion was almost unchanged at 41%. After use of specially designed curricular materials, this overlap proportion increased sharply; see Sec. VI A.
- ²⁶ It is conceivable that some students may confuse the word "entropy" with the word "energy." The words are spelled similarly and sound similar, and the two concepts are closely linked. Although there may be some confusion regarding words, there is no significant evidence from their responses that students actually believe energy and entropy to be the same entity.
- ²⁷ These correspond to normalized gains of $\langle g \rangle = 0.15$ and 0.04, respectively, using Hake's definition of normalized gain. See R. R. Hake, "Interactive engagement versus traditional methods: A six-thousand-student survey of mechanics test data for introductory physics courses," Am. J. Phys. **66**, 64–74 (1998). Note, however, that correct ("not determinable") responses regarding system entropy change on the general-context question actually *declined* after instruction (p=0.01).
- ²⁸This tutorial is shown in Appendix IX on EPAPS. See Ref. 23.
- ²⁹W. M. Christensen, "An investigation of student thinking regarding calorimetry, entropy, and the second law of thermodynamics," Ph.D. dissertation, Iowa State University, 2007, UMI No. 3274888, Chap. 5.
- ³⁰We used a binomial-proportions test as described in J. P. Guilford, Fun-

damental Statistics in Psychology and Education, 4th ed. (McGraw-Hill, New York, 1965), pp. 185–187. On the postinstruction "entropy of the system" general-context question (considering only those students who made a directional choice), the "increases" response is more common than the "decreases" response (p < 0.001). Similarly, the postinstruction general-context response that the entropy of the surroundings increases is more popular than the response that the entropy of the surroundings decreases (p < 0.01); a similar preference is expressed on the concretecontext question for the entropy of the air in the room (increases preferred over decreases, p < 0.0001).

- ³¹ Student responses are consistent with the most general form of the entropy inequality and might be considered to be partially correct. However, the questions explicitly referred to irreversible processes, or process that can actually occur, for which the total entropy always increases. The patterns of student responses we have reported appear to be independent of the specific terminology used in a particular question. That is, whether one or another term is used, the proportion of correct responses remains essentially unchanged.
- 32 The complete data are provided in Appendix V on EPAPS. See Ref. 23.
- ³³Other studies have explored the role of context-dependence of students' responses, mostly in the form of different problem representations. See D. E. Meltzer, "Relation between students' problem-solving performance and representational format," Am. J. Phys. **73**, 463–478 (2005), and references therein.
- ³⁴See Ref. 29, Chaps. 2 and 4.
- ³⁵The tutorial is shown in Appendix X on EPAPS. See Ref. 23.
- ³⁶L. C. McDermott, "Bridging the gap between teaching and learning: The

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- ³⁷For a breakdown of the matched-sample data, see Appendix VI on EPAPS. See Ref. 23.
- ³⁸Analogous results were found in a different context by D. E. Meltzer, "Analysis of shifts in students' reasoning regarding electric field and potential concepts," Proceedings of the 2006 Physics Education Research Conference, Syracuse, NY, 2006, edited by Laura McCullough, Leon Hsu, and Paula Heron [AIP Conf. Proc. 883, 177–189 (2007)].
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- ⁴¹See Appendix XI on EPAPS. See Ref. 23.
- ⁴²In contrast, we and others have found that students' conceptual difficulties regarding processes that do not involve heat transfer, for example, the free expansion of a gas, persist to some extent. See Refs. 8 and 12.



Lead Bells. These two small bells, cast in lead, came to the Greenslade Collection from Wellesley College. Normally, they give a dull *clunk* when shaken, but after being soaked in liquid nitrogen, they give out a pleasant chime. (Photograph and Notes by Thomas B. Greenslade, Jr., Kenyon College)

	Fall 2004 Pre-Instruction	Spring 2005 Pre-Instruction	Fall 2005 Pre-Instruction	Spring 2006 Pre-Instruction	Pre-Instruction General Context Cumulative Results
	N = 406	N = 171	N = 360	N = 247	N = 1184
Entropy of system					
increases	30%	26%	24%	24%	$26\pm4\%$
decreases	19%	14%	25%	18%	$19\pm7\%$
remains the same	9%	5%	13%	13%	$10 \pm 6\%$
is not determinable [correct]	39%	50%	35%	43%	$42\pm10\%$
Entropy of surroundings					
increases	26%	26%	31%	28%	$28 \pm 4\%$
decreases	16%	11%	14%	14%	$14 \pm 4\%$
remains the same	12%	9%	11%	11%	$11 \pm 2\%$
is not determinable [correct]	42%	47%	38%	42%	$42\pm6\%$
Entropy of system + surroundings					
increases [correct]	19%	23%	16%	19%	$19 \pm 5\%$
decreases	2%	1%	3%	2%	$2 \pm 1\%$
remains the same	67%	60%	69%	71%	$67 \pm 8\%$
is not determinable	8%	12%	7%	4%	$8\pm5\%$
All Correct	5%	4%	4%	5%	4 ± 1%

Appendix I. Itemized response data, general-context question, pre-instruction, all semesters

Appendix II. Itemized response data, concrete-context question, pre-instruction, all semesters

	Spring 2005 Pre-Instruction Concrete Context	Fall 2005 Pre-Instruction Concrete Context	Spring 2006 Pre-Instruction Concrete Context	Pre-Instruction Concrete Context Cumulative Results
	N = 155	N = 207	N = 237	N = 609
a. Entropy of object				
increases	19%	15%	17%	$17 \pm 5\%$
decreases	16%	20%	21%	$19 \pm 6\%$
remains the same	3%	14%	3%	$6 \pm 16\%$
is not determinable [correct]	54%	45%	52%	$50 \pm 11\%$
b. Entropy of air in the room				
increases	25%	27%	28%	$27 \pm 3\%$
decreases	8%	10%	10%	$9\pm2\%$
remains the same	7%	9%	3%	$6\pm8\%$
is not determinable [correct]	48%	48%	50%	$49 \pm 3\%$
c. Entropy of object + air in the room				
increases [correct]	17%	11%	15%	$14 \pm 9\%$
decreases	1%	5%	4%	$3 \pm 6\%$
remains the same	68%	71%	74%	$71 \pm 7\%$
is not determinable	5%	4%	3%	$4\pm2\%$
d. Entropy of universe				
increases [correct]	23%	9%	14%	$15 \pm 18\%$
decreases	1%	2%	0%	1 ± 2%
remains the same	61%	73%	72%	69 ± 17%
is not determinable	6%	7%	8%	7 ± 3%
a, b, and c correct	6%	3%	5%	5 ± 3%

Appendix III. Responses related to overall entropy change, general-context question, preinstruction, all semesters

	Fall 2004 Pre-Instruction N = 406	Spring 2005 Pre-Instruction N = 171	Fall 2005 Pre-Instruction N = 360	Spring 2006 Pre-Instruction N=247	Pre-Instruction General Context Cumulative Results N = 1184
Total entropy [of (system + surroundings / (object + air in the room)] remains the same	67%	60%	69%	71%	67 ± 8%
A. Entropy of (system and surroundings)/ (object and air) not determinable, but total entropy remains the same	27%	33%	16%	29%	26 ± 12%
B. Entropy of (system/object) increases [decreases] and entropy of (surroundings/air) decreases [increases], but total entropy remains the same	30%	16%	31%	25%	25 ± 10%
C. Students with one of these notions of entropy conservation (sum of A and B above)	57%	49%	46%	53%	51 ± 7%

Appendix IV. Responses related to overall entropy change, concrete-context question, pre-instruction, all semesters

	Spring 2005 Pre-Instruction N = 155	Fall 2005 Pre-Instruction N = 207	Spring 2006 Pre-Instruction N = 237	Pre-Instruction Concrete Context Cumulative Results N = 609
Total entropy <i>[of</i> (system + surroundings)/ (object + air in the room)/ remains the same	68%	71%	74%	71 ± 7%
A. Entropy of (system and surroundings)/ (object and air) not determinable, but total entropy remains the same	37%	35%	41%	38 ± 8%
B. Entropy of (system/object) increases [decreases] and entropy of (surroundings/air) decreases [increases], but total entropy remains the same	19%	22%	24%	22 ± 6%
C. Students with one of these notions of entropy conservation (sum of A and B above)	56%	57%	65%	60 ± 13%

Appendix V. Itemized response data, general- and concrete-context questions, pre- and post-instruction, spring 2005 matched sample

Spring 2005 Matched Sample N = 127	Pre-Instruction General Context	Post-Instruction General Context	Pre-Instruction Post-Instruct Concrete Context Concrete Cor		
a. Entropy of	Syste	em	Object		
increases	28%	35%	20%	17%	
decreases	14%	20%	17%	23%	
remains the same	3%	9%	2%	3%	
is not determinable [correct]	51%	35%	56%	57%	
b. Entropy of	Surroun	dings	Air in the Room		
increases	29%	31%	25%	29%	
decreases	10%	17%	10% 6%		
remains the same	8%	10%	6%	7%	
is not determinable [correct]	47%	39%	51%	57%	
c. Entropy of	System + Surroundings		Object + Air in the Room		
increases [correct]	25%	36%	20% 23%		
decreases	1%	3%	0%	0%	
remains the same	61%	48%	69%	71%	
not determinable	10% 12%		5%	6%	
d. Entropy of			Universe		
increases [correct]				27%	
decreases			1%	0%	
remains the same			62%	65%	
is not determinable			5%	5%	
<i>a</i> , <i>b</i> , and <i>c</i> correct	5%	8%	7%	13%	

Appendix VI. Itemized response data, general- and concrete-context questions, pre- and post-instruction, spring 2006 matched sample

Spring 2006 Matched Sample N = 191	Pre-Instruction General Context	Post-Instruction General Context	Pre-Instruction Concrete Context	Post-Instruction Concrete Context		
a. Entropy of	Syste	em	Object			
increases	25%	13%	16%	15%		
decreases	18%	12%	23%	12%		
remains the same	14%	2%	3%	1%		
is not determinable [correct]	42%	74% 53%		73%		
b. Entropy of	Surrour	adings	Air in the	Air in the Room		
increases	28%	17%	29%	16%		
decreases	14%	6%	8%	8%		
remains the same	12%	3%	4%	2%		
is not determinable [correct]	42%	75% 52%		73%		
c. Entropy of	System + Su	rroundings	Object + Air	Object + Air in the Room		
increases [correct]	21%	68%	16%	69%		
decreases	2%	2%	4%	2%		
remains the same	71%	21%	73%	24%		
is not determinable	4%	8%	3%	5%		
d. Entropy of	-	-	Universe			
increases [correct]				44%		
decreases			1%	1%		
remains the same			73%	54%		
is not determinable			8%	1%		
<i>a</i> , <i>b</i> , and <i>c</i> correct	6%	55%	6%	53%		

Appendix VII. Correct responses, pre- and post-instruction, general-context question, ISU 2005 and UW 2007

	Iowa State Introducto	University ory Course	University of Washington Sophomore Course		
	Pre-Instruction Pre-Instruction Processes Tutorial		Pre-Instruction	Post-Instruction with Two-Blocks Tutorial	
	Spring 2005WintMatched SampleMatched $N = 127$ N			er 2007 ed Sample = 32	
a. Entropy change of system not determinable	51%	35%	50%	84%	
<i>b</i> . Entropy change of surroundings not determinable	47%	39%	53%	84%	
c. Entropy of system + surroundings increases	25%	36%	34%	72%	
All Correct	5%	8%	13%	63%	

Appendix VIII. Correct responses, pre- and post-instruction, concrete-context question, ISU 2005 and UW 2007

	Iowa State Introducto	University ory Course	University of Washington Sophomore Course		
	Post-Instruction Pre-Instruction with Two- Processes Tutorial		Post-Instruction with Two-Blocks Tutorial		
	Spring 2005 Matched Sample N = 127		Winter 2007 Matched Sample N = 32		
<i>a</i> . Entropy change of object not determinable	55%	57%	47%	88%	
<i>b</i> . Entropy change of air in the room not determinable	51%	57%	47%	88%	
c. Entropy of object + air in the room increases	20%	23%	34%	78%	
<i>a</i> , <i>b</i> , and <i>c</i> correct	7%	13%	19%	69%	

Appendix IX. Entropy State-Function ["Two-Processes"] Tutorial

A system consisting of one mole of a monatomic *ideal gas* goes through two different processes as shown below. The initial values of volume (V_i), pressure (P_i), and temperature (T_i) are the same for each process. Also note that the final volume (V_f) is the same for each process.

Process #1 occurs very slowly so that it is always at the same temperature as the surroundings, and the pressure applied to the piston may vary. Note that the piston for Process #1 slides without friction. (Processes #1 is reversible.)

The system is thermally insulated from its surroundings in Process #2. In Process #2, the gas is initially trapped in one half of the container by a thin partition; the other half of the container contains vacuum. The partition is suddenly removed, and the gas quickly fills the rest of the volume.



#2: Free Expansion into a Vacuum



1.1 Consider Process #1: Explain the meaning of "isothermal."

- 1.2 During this process, state whether the following quantities increase, decrease, or remain the same:
 - a. temperature
 - b. volume
 - c. pressure
- 1.3 For an ideal gas, internal *[thermal]* energy is directly dependent on temperature by the equation $E_{th} = 3/2 \ nRT$. Does the internal energy of the system in Process #1 (the system consists of the gas only) *increase, decrease, or remain the same*? Explain.
- 1.4 In Process #1, the gas molecules exert a force on the piston by colliding with it while the piston is moving. Does this mean work done by the system on the surroundings is *positive*, *negative*, or *zero*?
- 1.5 According to the first law of thermodynamics, is the heat transfer to the system from the surroundings in Process #1 *positive*, *negative*, or *zero*? Explain.

Check that you and your group members have the same answers and consistent explanations for the questions above. If not, reconcile the responses and enter the group explanation.



- 2.1 Consider Process #2: According to the information, the system in Process #2 is thermally insulated. Explain what "thermally insulated" means.
- 2.2 In Process #2, is the heat transfer to the system from the surroundings positive, negative, or zero?
- 2.3 In Process #2, the gas is expanding but there is nothing for the molecules to collide against therefore there is no force exerted during the expansion. Is the work done by the system on the surroundings *positive, negative, or zero?* Explain.
- 2.4 According to the first law of thermodynamics, does the internal energy of the system in Process #2 *increase, decrease, or remain the same*? Explain.
- 2.5 During this process, state whether the following quantities increase, decrease, or remain the same:
 - a. temperature
 - b. volume
 - c. pressure
- 2.6 Is the final volume of the system in Process #2 greater than, less than, or equal to the final volume of the system in Process #1? Answer the same question for the initial volumes. *HINT: Check the information at the top of page 1*.
- 2.7 Is the final temperature of the system in Process #2 greater than, less than or equal to the final temperature of the system in Process #1? Explain.
- 2.8 Is the final pressure of the system in Process #2 *greater than, less than* or *equal to* the final pressure of the system in Process #1? Explain.

Check that you and your group members have the same answers and consistent explanations for the questions above. If not, reconcile the responses and enter the group explanation.

3. Draw points to represent the initial and final states of the two processes on the same P-V diagram; label each state 1_i, 1_f, 2_i, and 2_f, respectively. (e.g. 1_i is the initial state of Process #1, etc.)



Note: Check that the final volumes of both processes are the same.

Is your diagram consistent with your answer to Questions 2.6, 2.7, and 2.8 on the previous page?

- 4. Which process has the greatest magnitude of heat transfer to the system? If the two are equal, indicate with an "=" symbol.
- 5. Is S_{1(initial state)}, the initial entropy of the system in Process #1, *greater than*, *equal to*, or *less than* S_{2(initial state)}, the initial entropy of the system in Process #2?

The change in the entropy of a system that begins in initial state *i* and ends in final state *f* can be expressed as $\Delta S = \frac{Q_{reversible}}{T}$. Here, $Q_{reversible}$ represents the heat transfer to the system **only** during a process from *i* to *f* that is reversible; the *T* in this equation is related to the average temperature of the system during the process.

6. Does the entropy of the system *increase*, *decrease*, or *remain the same* for Process #1?

Is your answer to Question #6 consistent with $\Delta S = \frac{Q_{reversible}}{T}$? Explain.

Do NOT continue until you check your answers with the recitation instructor.

7. Consider ΔS_2 and ΔS_1 , the *changes* in the entropy of the system during Process #2 and Process #1, respectively; $\Delta S = S_{\text{(final state)}} - S_{\text{(initial state)}}$. Three students are discussing whether ΔS_2 is *greater than*, *equal to*, or *less than* ΔS_1 . Read through the discussion and follow the directions below.

Student A: "*I think that the entropy for Process #2 is going to stay the same. The system is thermally insulated so if there is no heat transfer to the system from the surroundings there is*

no change in the entropy of the system because $\Delta S = \frac{Q_{reversible}}{T}$."

Student B: "That makes sense from the ΔS equation we were given, but that is only correct for a reversible process. We must remember that entropy is a state function. Process #2 has the exact same final pressure, volume, and temperature as Process #1, so I think that the entropy in Process #2 will increase the same amount that entropy in Process #1 increases."

Student C: "I think you are on the right track, but Process #2 can't go back to its initial state like Process #1; that means that it's not reversible. So even though it has the same final state as Process #1, I think the change in entropy for Process #2 will be different from that in Process #1."

Student B responds to Student C: "I agree that #2 is irreversible, but we already determined that the initial entropy for both processes was the same in Question #5. The change in entropy is $\Delta S = S_{(final \ state)} - S_{(initial \ state)}$, so if the initial AND final states of Process #2 and Process #1 are the same the change in entropy in Process #2 has to be the same as Process #1 regardless of whether it's reversible or irreversible."

Re-read each student's statement and comment on the parts with which you agree, and identify the statements that you believe are incorrect. Explain your reasoning.

Discuss your reasoning and that of your group with the recitation instructor before continuing.

Continue to Page 5

- 8. Is $\Delta S_{\text{system 1}}$, the change in entropy of the system for Process #1, *greater than*, *equal to*, or *less than* $\Delta S_{\text{system 2}}$, the change in entropy of the system for Process #2? *Explain*.
- 9. Is $\Delta S_{\text{surroudings 1}}$, the change in entropy of the **surroundings** for Process #1, greater than, equal to, or less than $\Delta S_{\text{surroundings 2}}$, the change in entropy of the **surroundings** for Process #2? *Explain.* Hint: $Q_{\text{system}} = -Q_{\text{surroundings}}$
- 10. Using your answers from Questions 8 and 9, is the magnitude of $|\Delta S_{system 1}|$ greater than, equal to, or *less than* the magnitude of $|\Delta S_{surroudings 1}|$? *Hint:* $Q_{system} = -Q_{surroundings} \& \Delta S = \frac{Q_{reversible}}{T}$
- 11. Is $\Delta S_{\text{universe 1}}$, the change in entropy of the **universe** for Process #1, greater than, equal to, or less than $\Delta S_{\text{universe 2}}$, the change in entropy of the **universe** for Process #2? Explain your answers. (Note that $\Delta S_{\text{universe}} \equiv \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$)
- 12. Use the results from the worksheet to fill out the Table below

	Process #1	Process #2
Reversible or Irreversible?		
Q _{to system} > 0, Q _{to system} < 0, or Q _{to system} = 0?		
$\Delta S_{system} > 0,$ $\Delta S_{system} < 0, \text{ or}$ $\Delta S_{system} = 0?$		
$\begin{array}{l} Q_{to \; surr} > 0, \\ Q_{to \; surr} < 0, \; or \\ Q_{to \; surr} = 0? \end{array}$		
$\Delta S_{surr} > 0,$ $\Delta S_{surr} < 0, \text{ or}$ $\Delta S_{surr} = 0?$		
$\Delta S_{universe} > 0,$ $\Delta S_{universe} < 0, \text{ or }$ $\Delta S_{universe} = 0?$		

In any real (or irreversible) process, does the entropy of the **universe** *increase*, *decrease*, *remain the same*, or is this *not determinable* without additional information?

I. Energy Reservoir

A metal cube, one meter on each side, is enclosed in a thermally insulating jacket. Another metal cube of the same size is enclosed in its own insulating jacket. The temperature of this second cube is higher than the temperature of the first cube. We'll refer to the high-temperature cube as "H," and the other as "L," and their temperatures as $T_{\rm H}$ and $T_{\rm L}$, respectively. The only connection between the cubes is through a narrow metal rod that has a very small mass. Heat transfer to or from the cubes can take place only through this narrow metal rod. We will assume that when heat transfer does take place, the rate of energy change is so small that neither of the metal cubes undergoes any measurable change in temperature.



Is it reasonable to assume the temperature of the two cubes will remain constant? <u>A quantitative argument</u>: Suppose we have two different copper blocks each with volume of 1 m^3 ; assume that the temperature difference between the blocks is 50 K and that they are connected by a copper rod 20 cm long, with diameter 1 cm. There would be 8 joules of energy transferred each second through heat conduction. However, given the mass of the blocks (each weighs roughly 10 tons), it would take almost 12 days before the temperature of the blocks changed even by *one* kelvin.

Definition: The term used for a system so massive that it does not change temperature even when heat transfer takes place is "energy reservoir" or "thermal reservoir."

Does the high-temperature cube fit the definition of an energy reservoir? Why or why not?

Does the low-temperature cube fit the definition? Why or why not?

The following questions refer to the process that takes place when the cubes are connected by the metal rod; consider a process with duration of one minute.

- **II. What do you expect will happen?** (*These questions are meant to get you thinking about the problem, don't be concerned if you are unsure of your answers.*)
 - a) Consider the system consisting *only* of the low-temperature cube. While the two cubes are connected with the rod, does the entropy of this system *increase*, *decrease*, or *remain the same*?
 - b) During the same process, does the total entropy of the high- and low-temperature cubes <u>together</u> *increase, decrease, or remain the same*? Explain your reasoning.

c) State whether the following quantities are conserved during this process: (i) energy; (ii) entropy.

 \rightarrow On the diagram above, draw an arrow to indicate the direction of *positive* heat transfer.

III. Heat transfer and entropy

1. During a process with duration of one minute, consider $Q_{\rm H}$ and $Q_{\rm L}$, the heat transfers *to* the high-temperature and low-temperature cubes, respectively.

- a) Is $Q_{\rm H}$, the heat transfer to the high-temperature cube, positive, negative, or zero?
- b) Is Q_L, the heat transfer to the low-temperature cube, positive, negative, or zero?
- c) Compare the magnitudes (absolute values) of $Q_{\rm H}$ and $Q_{\rm L}$; is one larger than the other? If so, which one?
- d) Is the sum $[Q_{\rm H} + Q_{\rm L}]$ positive, negative, or zero?
- e) For this process, is energy a conserved quantity? Explain.



2. During the heat transfer process, consider $\Delta S_{\rm H}$ and $\Delta S_{\rm L}$, the change in entropy of the high-temperature cube and low-temperature cube, respectively.

a) Is $\Delta S_{\rm H}$, the change in entropy of the high-temperature cube, *positive*, *negative*, or *zero*?

Does this mean the entropy of the high-temperature cube increases, decreases, or remains the same?

b) Is ΔS_L , the change in entropy of the low-temperature cube, *positive*, *negative*, or *zero*?

Does this mean the entropy of the low-temperature cube increases, decreases, or remains the same?

- c) Consider the magnitudes (absolute values) of $\Delta S_{\rm H}$ and $\Delta S_{\rm L}$. Is the absolute value of one larger than the other? If so, which one? Explain.
- d) If we consider the actual values, is the sum $[\Delta S_{\rm H} + \Delta S_{\rm L}]$ positive, negative, or zero?
- e) For this process, is entropy a conserved quantity? Justify your answer. Explain any differences between this answer and your answer to 1(e) above.

IV. Outside the Insulation...

3. In Question #2, we determined the change in entropy of everything inside the insulating jackets, (i.e. the cubes). We must now consider the change in entropy of *everything else* apart from the cubes and the rod.

If you were to physically describe "everything else," what are some things that would be considered to be part of "everything else?" Discuss this with your group (and don't be afraid to think big).

- a) If we assume the jackets that surround the cubes and the rod are perfectly insulating, is there any heat transfer to the outside world from the metal cubes or rod? Why or why not?
- b) Calculate the change in entropy of everything outside the insulation due to heat transfer from the metal cubes and rod. $\Delta S_{\text{EVERYTHING ELSE}} =$
- c) Based on your answer to (b), does the entropy of everything else due to heat transfer from the cubes and rod *increase*, *decrease* or *remain the same*?

V. System and surroundings

4. For now, let us refer to the high-temperature cube *alone* as the thermodynamic "system." We will define "surroundings" (same as "surrounding environment") as *everything that is <u>not</u> the system*.

a) If we define the high-temperature cube as the system, describe what would be considered the "surroundings." Would the surroundings include the low-temperature cube? *Hint:* What criteria are we using to determine whether or not something should be considered as part of the surroundings?

b) With this definition of system and surroundings, and considering the same one-minute time interval,

i) does the entropy of the system increase, decrease, or remain the same?

ii) does the entropy of the surroundings increase, decrease, or remain the same?

Be sure to explicitly address the change in entropy of everything that is <u>not</u> the system.

V. System and surroundings (cont.)

5. Now, let us refer to the *low*-temperature cube alone as the "system."

- a) Using our previously stated definition, describe what would be considered the "surroundings," or "surrounding environment." Would the surroundings include the high-temperature cube?
- b) With this new definition of system and surroundings,

i) does the entropy of the system increase, decrease, or remain the same?

ii) does the entropy of the surroundings increase, decrease, or remain the same?

6. Given our definition of system and surroundings in Question #4, can one determine the sign of entropy change of the [system + surroundings]? If no, why not? Answer the same question for the case of Question #5.

If you can determine the sign in both cases, is the sign the same in both, or different? Explain.

	Question #4	Question #5
System consists of		
Surroundings consist of		
Entropy of system <i>increases</i> , <i>decreases</i> , or <i>remains the same</i> ?		
Entropy of surroundings increases, decreases, or remains the same?		
Entropy of system + surroundings <i>increases</i> , <i>decreases</i> , or <i>remains the same</i> ?		

Summarize the results from Question #4 and Question #5 in the following table.

Discuss the results with your group. What can you say about the entropy of the system + surroundings for these two processes?

V. System and surroundings (cont.)

7. You overhear a group of students discussing the above problem. Carefully read what each student is saying.

Student A: Well, the second law says that the entropy of the system is always increasing. Entropy always increases no matter what.

Student B: But how do you know which one is the system? Couldn't we just pick whatever we want to be the system and count everything else as the surroundings?

Student C: I don't think it matters which we call the system or the surroundings, and because of that we can't say that the system always increases. The second law states that the entropy of the system plus the surroundings will always increase.

Analyze each statement and discuss with your group the extent to which it is correct or incorrect. How do the students' ideas compare with your own discussion about the table on the previous page?

8. For both Questions #4 and #5, we made a specific designation for the "system" and considered the "surroundings" to include *everything* that was <u>not</u> the system.

a) If we wanted to describe the "system," and the "surroundings" with one word—where surroundings refers to everything outside the system—what word could we use? *Hint:* Remember to think big!

Write this word in the box in part (c) below.

b) Review your answers from Question #6: did you determine that the S_{system} + S_{surroundings} *increases, decreases, or remains the same*, for the case in Question #4? What about for the case in Question #5?

Would these answers change whether or not we included objects outside the insulation in "the surroundings?" Why or why not?

VI. Heat flow from low to high?

9. Suppose for a moment that heat transfer occurred spontaneously from low-temperature objects to high-temperature objects; draw an arrow to indicate the direction of *positive* heat transfer in this case.



a) Could such a situation actually occur "spontaneously" (that is, without any outside intervention)?

If it did occur, how would it affect your answers to Question #2? Explain in detail for each part a-d.

b) In real processes where high- and low-temperature objects are in thermal contact, is there ever actually *zero* heat transfer?

Suppose heat transfer between the high- and low-temperature cubes *were* zero; how would that affect your answers to Question 2?

c) Based on your answers to (a) and (b), can you make any specific statements regarding the change in $[S_{system} + S_{surroundings}]$ that could occur in any *real* process? (For example, could that total change be negative or zero?) Explain.

VII. Reversible Processes

10. Let's now consider a situation that is similar to our original problem. The temperature of the L cube is the same as it was before, but the temperature of the H cube is *lower* than its previous value and is designated by $T'_{\rm H}$. Although the H cube now has a lower temperature, it is still higher than that of the L cube.



We'll designate the heat transfers to the high- and low-temperature cubes in this case as $Q'_{\rm H}$ and $Q'_{\rm L}$, respectively. Consider that the heat transfer process, that originally lasted one minute, now lasts sufficiently long to ensure that the heat transfer to the higher-temperature cube is exactly the same as it was before, that is, $Q'_{\rm H} = Q_{\rm H}$.

- a) Is $Q'_{\rm L}$, greater than, less than, or equal to $Q_{\rm L}$?
- b) Consider the magnitudes (absolute values) of the entropy changes in the high-temperature cube, $|\Delta S'_{\rm H}|$, and the low temperature cube, $|\Delta S'_{\rm L}|$, and compare them to the values in the original case $|\Delta S_{\rm H}|$ and $|\Delta S_{\rm L}|$ (see Question #2):
 - i) is $|\Delta S'_{\rm H}|$ greater than, less than, or equal to $|\Delta S_{\rm H}|$?
 - ii) is $|\Delta S'_{\rm L}|$ greater than, less than, or equal to $|\Delta S_{\rm L}|$?
- c) Is the total entropy change in this present case $[\Delta S'_{\rm H} + \Delta S'_{\rm L}]$ greater than, less than, or equal to the total entropy change in the original case $[\Delta S_{\rm H} + \Delta S_{\rm L}]$ (when the temperature difference between the cubes was larger)?

VII. Reversible Processes (Cont.)

Suppose the temperature of the L cube remains the same, and the H cube drops to a temperature that is still higher, but infinitesimally close to the temperature of the L cube.

- d) For this case, what will happen to the *total entropy change* of the two cubes during the process, assuming that the heat transfers continue to remain the same as before? What can you say about the time required for this new process, compared to those before?
- e) As the temperatures of the cubes come closer together, what happens to the total entropy change of the universe, compared to that in the previous cases?
- f) In *reversible* heat transfer processes, all temperature differences are infinitesimally small (and there is no frictional dissipation). Such processes are idealizations of real processes; no real process is completely reversible.
 - i) Based on your answers to the questions above, what would be the entropy change of the universe in a completely reversible process?
 - ii) Could this be the entropy change of any real process? Why or why not?

Check that your answer is consistent with your statements in Question #9, part c.

	Pre-Ins Spring Matched	Pre-Instruction Spring 2005 Matched Sample		Post-Instruction with Two-Processes Tutorial Spring 2005 Matched Sample		Pre-Instruction Spring 2006		Post-Instruction with Two-Blocks Tutorial Spring 2006	
	N = 131		N = 131		N = 223		N=231		
	Entropy of the object + air	Entropy of Universe	Entropy of the object + air	Entropy of Universe	Entropy of the object + air	Entropy of Universe	Entropy of the object + air	Entropy of Universe	
Increases	20%	27%	23%	26%	15%	14%	68%*	44%* ^{,†}	
Remains the same	69%	62%	70%	66%	74%	72%	24%*	53%* ^{,†}	

Appendix XI. Pre- and post-instruction, concrete-context question, entropy of "object + air in the room" vs. entropy of the "universe" responses, spring 2005 and 2006

* Statistically significant difference compared to *pre*-instruction response on same item (p < 0.0001)

[†] Statistically significant difference compared to "object + air" response on same question (p < 0.0001)