

Chemistry Education Research and Practice

Accepted Manuscript



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3 A Review of Research on the Teaching and Learning of Thermodynamics at the University
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20 **Abstract**
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22 We review previous research on the teaching and learning of thermodynamics in upper-
23 level, undergraduate settings. As chemistry education researchers we use physical chemistry as a
24 context for understanding the literature. During our synthesis four themes of research emerged:
25 factors that influence student success in learning thermodynamics, understanding
26 thermodynamics through mathematical concepts and representations, student reasoning using the
27 particulate nature of matter, and students' alternative thermodynamic conceptions. We also draw
28 from literature in physics education research, engineering education research, and research on
29 undergraduate mathematics education communities to widen our perspective on the teaching and
30 learning of thermodynamics across disciplines. Following our presentation of studies, we
31 discuss gaps in the literature and directions for new research in line with the recommendations of
32 the National Research Council's (2012) recent report on Discipline-Based Education Research.
33 We also discuss implications for practice which we hope will provide increased pedagogical
34 support for teaching thermodynamics in upper-level, undergraduate settings, especially physical
35 chemistry.
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55 **Purpose**
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3 The purpose of this review is to synthesize recommendations for research regarding
4 thermodynamics education and discuss the implications for physical chemistry practitioners who
5 teach thermodynamics. This work is an important extension of Tsaparlis's (2007) review of the
6 physical chemistry curriculum because many studies regarding thermodynamics education have
7 surfaced since that time. This body of literature spans many of the discipline-based education
8 research (DBER) fields. Consequently, our review integrates many DBER perspectives to
9 learning thermodynamics. After we highlight the literature we discuss recommendations for
10 future research in line with the National Research Council's recent report Discipline-Based
11 Education Research (National Research Council, 2012).
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25 *A comment to the researcher.* This review provides the chemistry education researcher a
26 resource of discipline-based education research within the chemistry education research (CER),
27 physics education research (PER), engineering education research (EER), and research on
28 undergraduate mathematics education (RUME) communities. In addition to key findings we
29 discuss salient features of many research designs. In some cases, these features guided us to
30 make recommendations about theoretical frameworks from the learning sciences literature that
31 may provide new perspectives and lenses for research design, data analysis, and interpretation.
32 In other cases, they guided us to make recommendations about the design and evaluation of
33 assessment instruments in line with the current state of the art of measurement in CER (Arjoon,
34 Xu, & Lewis, 2013).
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49 *A comment to the practitioner.* The discipline-based perspectives included in this review
50 support the physical chemistry practitioner in three ways. First, we discuss thermodynamics
51 education studies across disciplines as a method of highlighting the interdisciplinary nature of
52 the topic. Second, we review many of the thermodynamic conceptions reported in the DBER
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3 literature. Research conducted at the introductory undergraduate level that contributes relevant
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5 results are included, where appropriate. Third, this review promotes the use of valid and reliable
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7 assessment instruments pertaining to thermodynamics in the physical chemistry classroom.
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10 11 12 **Sampling**

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15 Early in our online database searches we agreed on criteria for selecting peer-reviewed,
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17 scholarly work for inclusion in this literature review. The first criterion is our audience. We have
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19 developed this review with an intention of speaking to faculty who teach thermodynamics at the
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21 tertiary level and those who carry out DBER. Every study is in the context of a university-level
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23 or tertiary physical science course with a thermodynamics curriculum. Special attention was
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25 paid to those that studied upper-level university or tertiary student populations in a physical
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27 chemistry course with a thermodynamics curriculum.
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32 The second criterion is the type of scholarly work selected for this review. All the sources
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34 we included present data and report their analysis, which is logically linked to implications for
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36 research and practice. These studies utilized quantitative or qualitative methods, or both, to
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38 address research questions. Many of the studies we reviewed examine student understanding of
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40 thermodynamic concepts, instructional approaches to teaching thermodynamics, or the
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42 development and validation of measurement instruments pertaining to students' conceptions of
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44 thermodynamics. We excluded research that describes the development and implementation of
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46 measurement instruments or the use of innovative curricula or instructional techniques *without*
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48 *providing the results of its effectiveness*. We also excluded articles that suggest changes to
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50 teaching or curricula based solely on experience.
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3 Overall we report on 56 studies from many science education research journals including
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5 *The Journal of Chemical Education*, *Chemistry Education Research and Practice*, *The*
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7 *International Journal of Science Education*, *The Journal of Research in Science Teaching*, *The*
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9 *International Journal of Science and Mathematics Education*, *University Chemistry Education*,
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11 among others. We also included studies from peer-reviewed conference proceedings. Initial
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13 searches were conducted in the Education Resource Information Center (ERIC) database using
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15 key terms, for example, “physical chemistry” in combination with “thermodynamics” or
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17 “entropy.” We then expanded our search to citations within the initially obtained articles. The
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19 book *Advances in Teaching Physical Chemistry* published by the American Chemical Society in
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21 2007 was another important source for this review. We also searched recent issues of science
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23 education research journals throughout the development of the manuscript.
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29 **Outline of the Review**

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31 We discuss key findings from research that examine factors influencing student success
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33 in physical chemistry, the role of mathematics in physical chemistry, the role of students’
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35 reasoning using the particulate nature, and documented alternative thermodynamic conceptions.
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37 We also discuss salient features of research designs, which guided our construction of future
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39 research recommendations. The themes that emerged from our synthesis are then presented.
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41 This is followed by a consideration of implications of the literature for chemistry education
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43 research and physical chemistry practitioners.
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48 **Factors Influencing Success in Physical Chemistry**

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50 Research on factors influencing student success in physical chemistry provides us a
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52 foundation for discussing thermodynamics education. Sözbilir (2004) found overlapping
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54 perceptions of what both students and lecturers identify to be major problems affecting students’
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3 learning in physical chemistry: the abstract nature of concepts, failure to prioritize and thus
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5 overload course content, teacher-centered pedagogies, and lack of student motivation. Students
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8 overwhelmingly call for more promotion of conceptual understanding rather than memorization.
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10 An alarming finding was that lecturers might not give sufficient thought to the most current
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12 models of learning.
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15 Other factors that are commonly investigated as predictors of student success in physical
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17 chemistry are presented in Table 1. Hahn and Polik (2004) measured student success in physical
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19 chemistry in many ways, including free-response exam percentage, ACS exam percentage, and
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21 final grade in physical chemistry, whereas Nicoll and Francisco (2001) and Derrick and Derrick
22
23 (2002) used only final grades. Across this set of studies the findings demonstrate that student
24
25 facility with algebra and calculus are necessary for success in physical chemistry. Nicoll and
26
27 Francisco (2001) found that math ability was important, as measured by a written questionnaire
28
29 designed by the researcher/professor, was an important factor, but that math ability alone was not
30
31 the best predictor of success on mid-term or final exams. Rather, the best predictor of students'
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33 success was their logical thinking skills as measured by their performance on a conceptual
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35 diagnostic instrument.
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41 This is contrary to the findings of Derrick and Derrick (2002) and Hahn and Polik (2004).
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43 Derrick and Derrick (2002) uncovered four key predictors of success. First, they found strong
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45 correlations between students' success in physical chemistry and their final grade in a second
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47 semester calculus course. They also found strong correlations for success in physical chemistry
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49 and both a second semester organic chemistry course and the second semester of a general
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51 physics course. In fact, students' final grade in the second semester general physics course was
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53 the most important variable in their statistical analysis. Surprisingly, students' final grades from
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related chemistry courses were not significantly correlated to student success in physical chemistry. Finally, they found a negative correlation between repeating chemistry, mathematics, and physics courses and success in physical chemistry.

Table 1. Factors investigated as predictors of student success in physical chemistry.

Factor Assessed	References			
	Nicoll & Francisco (2001)	Derrick & Derrick (2002)	Hahn & Polik (2004)	Sözbilir (2004)
Student perceptions survey	✓ ^a			✓ ^b
Student perceptions interviews				✓
Course Perception Survey	✓			
Credit hours presently enrolled	✓			
Number of mathematics courses taken	✓		✓	
Math diagnostic (math ability)	✓			
Conceptual diagnostic (blend of FIT and GALT questions)	✓			
Midterm course exams	✓		✓	
Final exam	✓			
Overall point total	✓			
Final course grade	✓	✓	✓	
General chemistry grade		✓ ^c	✓ ^d	
Organic chemistry grade		✓ ^e		
Analytical chemistry grade		✓ ^f		
General physics grade		✓ ^g		
Mathematic course grades		✓ ^h	✓ ⁱ	
Repeating courses		✓		
Homework			✓	
ACS standardized exam			✓ ^j	

^aStudent Perceptions Inventory at beginning and end of physical chemistry course

^bfree-response survey

^cgeneral chemistry 2 grade

^daverage of gen chemistry 1 & 2 grades

^eorganic chemistry 2 grade

^fanalytical chemistry 2 grade

^ggeneral physics 2 grade

^hcollege algebra/trigonometry taken/not taken; calculus 2 grade

ⁱaverage of all mathematics courses

^jraw scores converted to national percentages

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Mathematics performance, as measured by an average of grades from all mathematics courses taken by a given student, was strongly correlated to physical chemistry success and, to a lesser extent, the number of mathematics courses taken (Hahn & Polik, 2004). Hahn and Polik (2004) also found correlations between general chemistry grades (students' average grade in the first and second semesters of general chemistry) and physical chemistry homework scores. The interpretation of the findings point to the importance of students' problem solving abilities and their success in physical chemistry.

Literature relating to factors influencing student success suggests that attitudes, mathematical ability, and logical thinking/problem solving skills are all important to a students' success. It is not uncommon for students to enter physical chemistry courses with negative perceptions and low expectations for personal success (Nicoll & Francisco, 2001). These perceptions may not always be aligned with instructor's perceptions of the physical chemistry curriculum as well (Sözbilir, 2004). Such attitudes should motivate chemistry education researchers to find ways to produce positive and effective learning experiences for all students studying thermodynamics in a physical chemistry context because students' attitudes and perceptions have been shown to affect their achievement (Carter & Brickhouse, 1989).

Mathematics and the Thermodynamics Curriculum

As discussed in the previous section, mathematics understanding and proficiency are connected to student success in physical chemistry (Derrick & Derrick, 2002; Hahn & Polik, 2004; Nicoll & Francisco, 2001). However, very few DBER studies actually examine students' understanding of mathematics in the context of thermodynamics. In order for students to understand thermodynamic concepts, they must be able to translate between mathematical representations and the physical meaning they represent (Becker & Towns, 2012). Below we

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3 discuss the body of literature that examines students' proficiency and understanding of
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5 mathematical concepts in the context of thermodynamics curricula in both undergraduate
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7 chemistry and physics contexts.
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10 Thompson, Bucy, and Mountcastle (2006) investigated students' understanding of partial
11 derivatives and Maxwell's relations in an upper-level thermodynamics course in a physics
12 department. Bucy, Thompson, and Mountcastle (2007) studied upper-level thermal physics
13 students' application of partial derivatives to material properties via an analysis of homework
14 and examination responses. Both inquiries used qualitative methods to analyze in-class
15 assignments, out-of-class assignments, or examination data. These studies suggest that students
16 may have difficulties interpreting physical meaning from the mathematical expressions or
17 creating mathematical expressions based upon a description of a physical process. Furthermore,
18 the findings from these studies illustrate student difficulties with the notion of holding variables
19 fixed in a partial derivative, confusing the meaning of 'constant' and 'fixed.'
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34 Becker and Towns (2012) conducted a study investigating students' understanding of
35 partial derivatives in the context of a physical chemistry curriculum. They found most students
36 accurately interpreted total and partial derivatives and give physical interpretations to
37 mathematical expressions containing thermodynamic variables during individual interviews.
38 Questions that proved most difficult for students were those asking them to apply information or
39 write expressions from described physical situations. Based on their analysis using Sherin's
40 symbolic forms, Becker and Towns (2012) found that some students approached these
41 differential equations in an algebraic manner, similar to the findings in Thompson et al. (2006).
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53 Pollock, Thompson, and Mountcastle (2007) examined students' understanding of work
54 in a physics context and path-dependent functions in a mathematics context. Upper-level
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3 students in a thermal physics course were given both physics questions and the corresponding
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5 mathematical analogs (so-called “physicsless” physics question). The interpretation of the
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7 findings suggests that students hold an isolated understanding of the two subjects rather than an
8
9 integrated framework. For example, work was described as a path independent quantity (state
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11 function) by a significant portion of students, a finding noted elsewhere in literature, e.g.,
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13 Loverude, Kautz, and Heron (2002), Meltzer (2004), Meltzer (2006), and van Roon, van Sprang,
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15 and Verdonk (1994). Students had difficulties comparing the work done by the expansion of a
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17 gas in a closed system based on pressure-volume (P-V) diagrams based on the correct application
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19 of definite integrals. The researchers interpret the results in terms of low mathematical
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21 proficiency rather than a lack of physics conceptual understanding.
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27 Christensen and Thompson (2010) continued the practice of “physicsless” physics
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29 questions to investigate students’ understanding of differentiation, a concept that underlies many
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31 of the mathematical models in thermodynamics. The researchers found upper-level physics
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33 students to have difficulty ranking the magnitude and direction of instantaneous slopes based on
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35 their responses to a question about graphical representations of one-variable functions.
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37 Interestingly, some students ranked the magnitude of average slopes between two points rather
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39 than instantaneous slopes at various points on the curve, a finding that is consistent with previous
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41 RUME studies (Beichner, 1994; Shaffer & McDermott, 2005).
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46 Christensen and Thompson (2010) also examined how students solve problems about gas
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48 expansion work in the context of P-V diagrams. They administered two different surveys to
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50 students in a thermal physics course and a third semester calculus course. Student interviews
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52 were conducted to understand response process to the questions. The researchers found about
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54 half of the student sample could correctly evaluate the physics and “physicsless” physics
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3 questions about work, which required them to compare the magnitudes of the areas under two
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5 different curves. Other students cited related, but inaccurate, reasoning for the difference in
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7 magnitude of the areas under the curves. Wemyss, Bajracharya, Thompson, and Wagner (2011)
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9 extended this study to investigate students' ability to solve problems involving negative integrals.
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13 Student difficulties with mathematical concepts and problem solving reported in this
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15 body of literature are not unprecedented. These procedural and conceptual difficulties in
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17 mathematics are consistent with other DBER studies (i.e. Black & Wittmann, 2009; Cui, Rebello,
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19 & Bennett, 2005; Cui, Rebello, & Bennett, 2007; Orton, 1983a; Orton, 1983b; Zandieh, 2000).
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21 Many of the studies from the PER community provide preliminary evidence that students have
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23 difficulty executing the mathematical operations necessary for use in the study and for
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25 understanding of thermodynamics. Synthesizing across all the studies, we believe the findings
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27 describe a relationship between mathematics and thermodynamic knowledge.
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31 Another interesting aspect of this body of literature is that students may demonstrate
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33 mathematical proficiency even though they lack a conceptual understanding of mathematical
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35 concepts (Becker & Towns, 2012; Hadfield & Wieman, 2010; Thompson et al., 2006).
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39 Problems regarding interpretation arise both in a mathematical context and in a physical
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41 chemistry/physics context (Becker & Towns, 2012; Christensen & Thompson, 2010; Hadfield &
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43 Wieman, 2010; Pollock et al. 2007; Thompson et al., 2006; Wemyss et al., 2011). The
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45 implications of this finding are two-fold. Researchers must make the meaning of 'proficiency'
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47 and 'understanding' explicit in the context of their studies. A clear articulation of one of these
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49 constructs will guide the selection of a theoretical framework and ultimately the interpretation of
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51 student data. For the practitioner, if the goal is to have students develop the ability to understand
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53 thermodynamic concepts *through* mathematical relationships and representations, then we must
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3 explicitly help students learn the meanings of mathematical concepts such as derivatives, partial
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5 derivatives, integrals, state functions, etc. in the context of thermodynamics.
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8 **Student Reasoning using the Particulate Nature of Matter**

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10 Classical thermodynamics deals with the macroscopic interactions between matter and
11 energy. The application of classical thermodynamics to study chemical systems naturally
12 requires one to think at the microscopic level in certain contexts. Consider comparing three
13 macroscopic systems containing only water at three different temperatures such that water in one
14 system is in the solid phase, then next in the liquid/vapor phase, and the third only vapor exists.
15 Research has demonstrated that students discuss the movement of particles in different phases as
16 a way of rationalizing and understanding the relative entropy of each system (Becker, Rasmussen,
17 Sweeney, Wawro, Towns, & Cole, 2013). Therefore, students may use a particulate nature of
18 matter (PNOM) model to describe and rationalize phase changes and physical properties, which
19 are part of the physical chemistry thermodynamics curriculum.
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34 The PNOM is a difficult concept to understand and apply for students of all levels. Many
35 pioneering studies involved determining and documenting students' alternative conceptions of
36 the PNOM from primary students to tertiary students (Gabel, Samuel, & Hunn, 1987; Nakhleh,
37 1992; Novick & Nussbaum, 1978; Novick & Nussbaum, 1981). However, less research
38 considers upper-level, undergraduate science courses. One example is Al-Balushi (2009) who
39 found that students explain and predict chemical phenomena using their mental models of the
40 particulate nature of matter.
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50 Cole, Becker, Towns, Sweeney, Wawro, and Rasmussen (2011) adapted Toulmin's
51 argumentation model, a well-established method in the RUME community, as a means to
52 document and analyze students' conceptual development and collective production of meaning
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3 by examining classroom interaction during the thermodynamics curriculum in a Process Oriented
4 Guided Inquiry Learning (POGIL) physical chemistry classroom (Spencer & Moog, 2008).
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8 Video recordings of small group discussions were analyzed to see how arguments became part of
9 the classroom community's normative ways of reasoning. This methodology moved forward to
10 identify a classroom chemistry practice: reasoning using particulate-level descriptions of
11 different phases of matter to discuss, describe, or compare physical properties.
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18 In their case study of a small group discussion in the same POGIL classroom, Becker et
19 al. (2013) found that students used particulate-level explanations to describe chemical and
20 physical phenomenon (but not without difficulty). Argumentation, a specific genre of classroom
21 discourse, in this particular POGIL classroom was found to be guided by particulate level
22 descriptions of matter. Common claims involved motion and spacing of a collection of particles
23 and descriptions of molecular structure as justification. The researchers made sense of the
24 PNOM justifications as an emerging sociochemical norm, or the criteria that regulate classroom
25 discourse that are particular to the study of chemistry.
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37 The investigation of student explanation and reasoning by Cole et al. (2011) and Becker
38 et al. (2013) brings the conclusions drawn by Al-Balushi (2009) to a new level. These findings
39 may be surprising to many practitioners, as there is rarely a conscious or explicit awareness of
40 sociochemical norms and normative ways of reasoning. Rather, they likely go unnoticed since
41 experts' conceptual networking is more organized and sophisticated (Al-Balushi, 2009).
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49 Appealing to our present models of learning, we should be actively conscious of students'
50 conceptions of the particulate nature of matter and how they are using it to explain and predict
51 chemical phenomena.
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Students' Conceptions of Thermodynamics

The most prominent type of education research regarding thermodynamics curricula is the measurement of student learning. As an area of inquiry, this body of research is characterized by quantitative and qualitative methods, which are used to elicit students' conceptions or alternative conceptions of thermodynamics. We purposefully choose to use the term alternative conceptions in this review to represent student understandings, which are inconsistent with accepted scientific explanations or descriptions. The term misconceptions is associated with pedagogical approaches of replacement of incorrect understandings with correct ones, which is inconsistent with our current understanding of how students learn (Bransford, Brown, & Cocking, 2000; Mickiewicz & Line back, 2013; Smith, diSessa, & Roschelle, 1993).

The First Law

The literature presented here focuses on students' understanding of work, heat, internal energy, and enthalpy in the context of the First Law of Thermodynamics. A list of the alternative conceptions reported in this body of literature is presented in Table 2.

Table 2. Main findings from the literature regarding students' alternative conceptions of the First Law of Thermodynamics and related concepts.

References	Alternative Conceptions
van Roon et al. (1994)	Scientific and phenomenological understandings of heat and work
van Roon et al. (1994); Meltzer (2004); Meltzer (2006)	Heat and work are state functions
Carson and Watson (1999); Nilsson and Niedderer (2013)	Enthalpy, entropy, internal energy, and activation energy are forms of energy
Greenbowe and Meltzer (2003)	Heat transfers between reactants, rather than being consumed and generated by the breaking and forming of bonds
Thomas and Schwenz (1998)	According to the first law, energy is always conserved because the internal energy of the system in the initial state equals the internal energy of the system in the final state $\Delta U = w + q$ was not used to understand how the first law applies to the reaction The enthalpy change ΔH is the same as the internal energy change ΔU Heat is energy that is added to something No heat occurs under isothermal conditions
Hadfield and Wieman (2010)	$w = -P\Delta V$, $q = \Delta H$, and $\Delta U = q + w$ are restatements of the first law
Miller, Streveler, Nelson, Geist, and Olds (2005); Miller, Streveler, Olds, Chi, Nelson, and Geist (2006); Nottis, Prince, and Vigeant (2010)	The rate of energy transfer causes macroscopic changes in temperature

van Roon et al. (1994) inquired into students' understanding of heat, work, and the first law in a traditional lecture-based introductory level chemistry course. Specifically, researchers observed tutorial sessions consisting of approximately 20 students, divided into four to five

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3 smaller groups, as they practiced thermodynamics problems. The researchers sought to evaluate
4 the students' acquisition of heat and work concepts. They discovered that many students treated
5 heat as a state function rather than a process-dependent function wherein students attempted to
6 conserve heat energy according to naive interpretations of the First Law of Thermodynamics. In
7 addition, students struggled to differentiate between kinetic energy or mechanical energy and the
8 thermodynamic internal energy. The authors argued that these difficulties source from students'
9 understanding of the terms 'heat' and 'work' that they acquire in their everyday lives, as the
10 students entered the course already possessing concepts of heat and work (van Roon et al., 1994).

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13 Carson and Watson (1999) investigated how introductory chemistry students'
14 conceptions of enthalpy and related thermodynamic concepts developed through a series of
15 lectures. They assumed participating students were familiar with the mathematical definition of
16 enthalpy ($\Delta H = \Delta U + P\Delta V$), work ($w = -P\Delta V$), and heat ($q = \Delta H$). To evaluate students'
17 conceptions, the researchers conducted 20 individual interviews before and after the lectures on
18 thermodynamics. During each interview the researcher demonstrated three chemical reactions to
19 the participating student. Each chemical reaction (neutralization of hydrochloric acid with
20 sodium hydroxide, the reaction between solid magnesium and hydrochloric acid, and the
21 dissolution of ammonium chloride in water) illustrated a specific thermodynamic principle, such
22 as enthalpy change, heat, and work. Students were asked to make observations while they
23 interacted with the reactions, comment on the source of temperature change measured by
24 thermometer or temperature probe, and explain the thermochemistry. To analyze the results,
25 students' explanations in the interviews were compared with expert responses. This data was also
26 compared with the lecture content.

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Prior to instruction, many of the participating students were unable to identify whether work was done on or by the system for each of the chemical reactions, a finding supported by Nilsson and Niedderer (2012). Further, they viewed enthalpy, entropy, internal energy, and activation energy as ‘forms’ of energy, which was also identified by van Roon et al. (1994). The learning gains after instruction were of mixed results. Students’ responses regarding enthalpy did not improve for the second interview. Most students provided incomplete or imprecise explanations of enthalpy. More students were able to correctly describe the work done by the expansion of a gas (P-V work) and to recognize work being done by the system. However, many were still working with conceptions of entropy, internal energy, and activation energy as ‘forms’ of energy. Many of these conceptions were not further developed after the lectures based on students’ responses to the same questions during the second interview. The interpretation of the findings was that students’ alternative conceptions of enthalpy did not change, as they persisted to the end of the semester.

Greenbowe and Meltzer (2003) identified introductory chemistry students’ conceptions of heat transfer, enthalpy of reaction, and relationship between system and surroundings in the context of solution chemistry. An analysis of examination data and one longitudinal interview series showed mixed results. Students often correctly identified reactions as endothermic or exothermic. However, students’ responses described heat as transferring between reactants, rather than being consumed and generated by the breaking and forming of bonds. Similar conceptions about the chemical bond were reported in Galley (2004).

Thomas and Schwenz (1998) conducted an exploratory, qualitative study inquiring into students’ understanding of equilibrium and fundamental thermodynamics. They interviewed 16 students from four different physical chemistry classes. The interview consisted of questions

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3 relating to the chemical reaction, $\text{energy} + \text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$, taking place in a
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5 “perfect” cylinder with a movable piston. All interview questions aimed at eliciting students’
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7 conceptions of the thermodynamics underlying the hypothetical situation. We discuss the results
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9 related to internal energy and enthalpy here.
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12 The interviews were transcribed and coded relating to macroscopic and microscopic
13 descriptions of thermodynamics and equilibrium. The responses were then ranked for
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15 correctness on a 6-point rubric. Average scores were calculated for each student. Thomas and
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17 Schwenz (1998) identified alternative conceptions as those differing from accepted scientific
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19 understanding and reported those conceptions held by 25% of the students in their sample.
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22 Among their findings was that students do not use $\Delta U = q + w$ to understand how the
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24 first law applies to a chemical reaction (closed system). Some students’ interpretations of the
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26 first law suggested they believe internal energy is always conserved between changes in initial
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28 and final states. Furthermore, some students generalize internal energy and enthalpy as the same
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30 thing. This finding is confirmed by Nilsson and Niedderer in a similar study inquiring into upper
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32 level students’ conceptions of enthalpy and related concepts (2014). Finally, some students
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34 reported alternative conceptions about heat and temperature: Heat is energy that is added to
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36 something and no heat occurs under isothermal conditions.
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39 Many of the studies we have reviewed so far utilized mathematical problem solving in
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41 their evaluation of students’ conceptual understanding of the First Law of Thermodynamics and
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43 related concepts. Hadfield and Wieman (2010) explicitly examined students’ interpretations of
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45 the mathematics related to the First Law of Thermodynamics. The authors presented 55 students
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47 with three equations: $w = -\int PdV$; $q = \int C_v dT$; $\Delta U = q + w$, and asked whether the three
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49 equations were restatements of the First Law of Thermodynamics. Only the third statement
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($\Delta U = q + w$) regarding internal energy is a restatement of the first law. However, many of the students responded that the definitions of either work (49%) or heat (32%) were restatements of the first law. Students also responded that the change in internal energy was a restatement of the first law. The researchers then interviewed ten students about their response process to the questionnaire. Some students had difficulty describing how the mathematical equation, $\Delta U = q + w$, modeled both the conversion and conservation of energy. They found that students frequently resorted to the assumption that change in internal energy was zero.

The results from this study complemented others that argued students struggled to distinguish between heat, work, and internal energy (Carson & Watson, 1999; Greenbowe & Meltzer, 2003; Thomas & Schwenz, 1998; van Roon et al., 1994). In addition, students have difficulty identifying the direction of heat flow and describing work as an interaction between system and surroundings both of which involve a mislabeling or ambiguity of identifying the system and the surroundings. This could also emerge from a failure to differentiate between process and state variables and how that informs problem solving in chemistry (van Roon et al., 1994; Carson & Watson, 1999).

Literature from the PER community suggest similar findings, although many of the studies are embedded in students' understanding of classical thermodynamics, which is distinct from chemical thermodynamics in that it is not specific to chemical systems. Loverude et al. (2001) examined how students relate the First Law of Thermodynamics to physical scenarios (a bicycle pump). A majority (~75%) of the 36 students interviewed were able to predict the outcome of the scenario, but they did not provide explanations that correctly considered expansion work. When the interviewers prompted the students to consider the role of energy in the bicycle pump, many argued that energy played no role in the working of the bicycle pump.

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3 Further, after being presented with the equation $\Delta U = q + w$, only 25% of the students
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5 correctly identified the role of work.
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8 Meltzer (2004) conducted a study that investigated student reasoning regarding work,
9
10 heat, and the First Law of Thermodynamics in an introductory calculus-based general physics
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12 course. The data were collected in the form of an open-ended questionnaire (N=653) and a
13
14 multiple-choice survey (N=407). Interviews were also conducted with a subset of 32 students.
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16 Like van Roon et al. (1994) and Nilsson and Niedderer (2012), Meltzer observed students having
17
18 difficulty applying the concept of work to solve problems, especially in the context of energy
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20 transfer. Both work and heat were thought to be a state function rather than a process-dependent
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22 function by a significant portion of the sample. Three quarters of the students interviewed
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24 thought either net work, or total heat transferred, or both, would be zero for the entire process.
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29 Meltzer (2006) reported a continuation of his investigation with participants coming from
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31 an introductory calculus-based general physics course (N=653), an upper-level thermal physics
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33 course (N=33), and an upper-level physical chemistry course (N=8). Based on his analysis of
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35 student responses to an open-ended questionnaire, substantial portions (21-30%) of students from
36
37 each of the courses treated work as a state function. Less than a third of any student population
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39 correctly identified heat as a process-dependent function. Meltzer also found that a majority of
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41 the students in both of the upper-level courses had considerable trouble applying energy
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43 conservation principles when solving problems.
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48 Turning to the EER community, Miller, Streveler, Nelson, Geist, and Olds (2005) report
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50 an alternative conception regarding heat using the Thermal and Transport Concept Inventory
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52 (TTCI)¹. Miller and colleagues assessed that 13% of engineering students in their sample use the
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58 ¹ <http://www.thermalinventory.com>
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3 alternative conception that the rate of energy transfer caused macroscopic changes in temperature
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5 rather than the amount of energy transferred during a physical process.
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8 In a later study, Miller, Streveler, Olds, Chi, Nelson, and Geist (2006) extended their
9
10 study to focus specifically on the observed “rate versus amount” alternative conception held by
11
12 engineering students (and probably similar proportions of undergraduate science majors).
13
14 Twenty-nine senior level chemical engineering students responded to questions from the TTCI
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16 regarding heat plus new questions constructed specifically for this study. Students’ responses
17
18 indicated that this sample was working with the same alternative conception of heat, specifically
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20 regarding their understanding of the amount and rate of energy transfer during a process. Similar
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22 findings are reported in Nottis, Prince, and Vigeant (2010).
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27 When we consider the literature as a whole we find a recurring theme: some students’
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29 conceptions of energy, enthalpy, and related concepts are not driven toward more scientifically
30
31 accurate notions after formal instruction. Such a finding is not unprecedented, as it is well known
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33 that alternative conceptions are resistant to change and difficult to alter (Bransford et al., 2000).
34
35 An added source of difficulty with many thermodynamic concepts, such as work, heat, and
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37 energy, is the presence of these terms in students’ frameworks of everyday phenomena (Thomas
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39 & Schwenz, 1998; van Roon et al., 1994). A new and interesting research design by Miller,
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41 Streveler, Yang, and Santiago Roman (2011) applies Chi’s (2005) framework of emergent
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43 processes to make meaning about students’ alternative conceptions of heat transfer. This may be
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45 a productive framework from the learning sciences for modeling student’ understanding of
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47 thermodynamics because it brings the ontology of heat transfer (i.e., an emergent process) into
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49 perspective.
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55 **The Second Law**

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The literature presented here focuses on students' understanding of entropy in the context of the Second Law of Thermodynamics. Alternative conceptions are reported in Table 3.

Table 3. Main findings from the literature regarding students' alternative conceptions of the Second Law of Thermodynamics and related concepts.

References	Alternative Conceptions
Bucy, Thompson, and Mountcastle (2006); Sözbilir and Bennett (2007); Smith, Christensen, and Thompson (2009)	System/universe confusion in $\Delta S_{\text{universe}} \geq 0$ Entropy of the system increases during a spontaneous process
Bucy, Thompson, and Mountcastle (2006); Sözbilir and Bennett (2007)	Entropy is a measure of disorder Physical/ statistical/thermodynamic meaning of "disorder" compared to ordinary language
Meltzer (2006)	Entropy always increases
Sözbilir and Bennett (2007)	Entropy of pure substance is greater than mixture Entropy increases due to increased intermolecular interactions Entropy increases due to increased collisions between particles Absolute entropy of carbon dioxide is greater than that of propane; absolute entropy of carbon dioxide and propane are equal Physical meanings of enthalpy and entropy and how they relate to energy
Christensen, Meltzer, and Ogilvie (2009)	$\Delta S_{\text{universe}}$ remains unchanged during a real process Entropy is a conserved quantity

The content of Meltzer's (2006) study discussed in the previous section overlaps with topics traditionally associated with the Second Law of Thermodynamics. Both introductory and thermal physics students demonstrated difficulty with the concept of entropy when solving problems. Often, they had the tendency to argue that the entropy of a *system* always increases, no

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3 matter the circumstance. While problem solving, some introductory level students were reluctant
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5 to apply the concept that for naturally occurring processes the total entropy (system and
6
7 surroundings) must always increase. Many physical chemistry students in this study also
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9 asserted that total entropy would not change.
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13 Sözbilir and Bennett (2007) examined students' understanding of entropy in the context
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15 of physical chemistry. They designed an open-ended diagnostic questionnaire to assess student
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17 learning before and after an instructional intervention. The questionnaire was administered to
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19 two groups of students (91 students total) in two different physical chemistry courses. This
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21 occurred twice over a seven month time period. The content of the questionnaires was validated
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23 by the researchers' colleagues. Individual interview data was collected immediately following
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25 the test and retest events and was used to support findings from the questionnaire.
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30 Evidence from the pre/post-assessment indicated that students' conceptions about entropy
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32 were tightly associated with ordinary meanings of "randomness", "chaos", or metaphors of
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34 "disorder." For some students the concept of entropy was often associated with movements of
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36 particles, for example, the collisions and intermolecular interactions between particles. In other
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38 cases, students argued that the absolute entropy of carbon dioxide was greater than or equal to
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40 that of propane. Other alternative conceptions stem from the Clausius statement of the second
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42 law ($\Delta S_{\text{universe}} \geq 0$). For example, some students responded that the entropy of an isolated
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44 system decreases or does not change when a spontaneous change occurs. Similar findings are
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46 also reported in Carson and Watson (2002) with a student sample from an introductory chemistry
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48 course.
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53 Perhaps unsurprisingly, similar findings have emerged in the PER literature. Bucy et al.
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55 (2007) investigated 7 upper-level students' understanding of entropy and state functions in the
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3 context of an isothermal and free expansion of an ideal gas. They analyzed student responses to
4
5 an in-class questionnaire before instruction and a modified version of the questionnaire on a
6
7 comprehensive exam after instruction. Lecture-based instruction included a discussion about the
8
9 statistical formulation of entropy in addition to the thermodynamic definition.
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13 Prior to instruction, the students responded to questions about entropy in a comparable
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15 fashion using terms such as “disorder” with no evidence of reasoning that links “disorder” to
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17 entropy. Furthermore, responses revealed a tendency to apply the Clausius statement of the
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19 second law to isolated systems rather than the universe. After instruction, most students applied
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21 the correct thermodynamic definition to predict the entropy changes for the isothermal expansion
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23 of an ideal gas and others applied the correct statistical definition. Difficulty was observed when
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25 students’ applied incorrect physical concepts to the free expansion of an ideal gas. The
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27 interpretation of the findings was that the instructional intervention did not yield a more complex
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29 and nuanced understanding of the concept of state functions or entropy.
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35 Christensen, Meltzer, and Ogilvie (2009) investigated students’ ideas regarding entropy
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37 and the Second Law of Thermodynamics in introductory physics courses at two large research
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39 universities. More than half of the sample reported having taken previous classes that introduced
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41 the concept of entropy. Students completed an open-ended questionnaire regarding entropy prior
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43 to instruction in the physics course. Nineteen percent of the 1,184 students gave a correct
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45 response regarding the overall increase of entropy of the system plus surroundings. Some
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47 responses to the questionnaire suggested that students’ understanding was consistent with the
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49 alternative conception that entropy is conserved, as discussed in Meltzer (2006).
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54 Following lecture-based instruction the same questionnaire was administered to the
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56 students. A comparison of student responses to their pre-instruction responses led to the
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3 researchers to conclude there was little improvement in student understanding pertaining to
4 entropy. Another question regarding spontaneous processes was also administered after the
5 instruction. The interpretation of the findings was that a majority of students were working with
6 a conception that the sum of the entropy changes in the system and surroundings would (or at
7 least could) remain unchanged during a spontaneous process (Christensen et al., 2009). Interview
8 data supported these findings. However, among the interviewed students that did assert a
9 direction for entropy change, most declared that entropy would increase.

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20 Based on the preliminary evidence Christensen et al. (2009) designed guided-inquiry
21 conceptual worksheets (called tutorials) to facilitate student learning of state properties of
22 entropy (Entropy Two-Process Tutorial) and entropy changes during spontaneous processes
23 (Entropy Two-Blocks Tutorial). The Entropy Two-Process Tutorial guides students to use the
24 state function property of entropy to calculate the change in entropy for a reversible isothermal
25 expansion and an irreversible free expansion of an ideal gas. The Entropy Two-Blocks Tutorial
26 guides students to reason about heat transfer between two large, insulated, metal blocks acting as
27 thermal reservoirs and concludes that the total entropy of the universe always increases. The
28 worksheets were implemented during two semesters (N=127 and N=191, respectively). Binomial
29 proportions tests measured significant improvements post tutorial instruction. The tutorials can
30 be found in the Supplemental Material to Christensen et al. (2009).

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46 Smith, Christensen, and Thompson (2009) designed a guided-inquiry conceptual
47 worksheet, called the Heat Engines Tutorial, to guide students in an upper-level thermodynamics
48 course as they derive the Kelvin-Planck statement of the second law and Carnot's theorem using
49 $\Delta S_{\text{universe}} \geq 0$. The tutorial was designed with the assumption that it is administered after the
50 tutorials developed in Christensen et al. (2009). Prior to administering the tutorial, but after
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3 lecture-based instruction, the researchers administered a pre-test, open-ended questionnaire, to
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5 assess students' prior knowledge. Student responses revealed alternative conceptions about
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7 entropy, heat engines, and the second law, in particular that the entropy of the system undergoing
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9 a cyclic process increases. A pre/post analysis and interview data suggests the tutorial supports
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11 the development of a more accurate understanding of entropy, heat engines, and the Second Law
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13 of Thermodynamics.
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17 Similar to our findings in the previous section, when we consider the literature as a whole
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19 we find a recurring theme: students' conceptions of entropy associated with spatial motion are
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21 not further developed into more scientifically accurate conceptions during formal instruction.
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23 We discovered from some of the PER studies that designed guided-inquiry conceptual
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25 worksheets helped many of the thermal physics students address some of the common
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27 difficulties many experience when learning about entropy. However, further evaluation of these
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29 assessment instruments is needed in order to translate the data into meaningful instructional
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31 practice. The literature also suggests that students struggle with working with state variables. In
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33 addition, students often apply $\Delta S_{\text{universe}} > 0$ to all systems. Finally, when considering abstract
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35 concepts, such as entropy, students often use analogies to make sense of them (e.g. disorder).
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40 41 **The Third Law** 42

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44 The literature presented here focuses on students' understanding of entropy in the context
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46 of the Third Law of Thermodynamics. Alternative conceptions are reported in Table 4.
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49 Table 4. Main findings from the literature regarding students' alternative conceptions of the
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51 Third Law of Thermodynamics and related concepts.
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53 54 Reference	55 56 Alternative conceptions
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Sreenivasulua and
Subramaniam (2013)

In purely crystalline and purely amorphous solids, there is no disorder, hence its entropy is zero

For a perfectly ordered pure solid, there is no freedom of motion

When a solid is in the elemental form, there is no disorder and entropy is zero

Sreenivasulua and Subramaniam (2013) diagnosed three alternative conceptions held by second-year chemistry majors (N=106) regarding the solid state, using the Thermodynamics Diagnostic Instrument (THEDI). The authors found that nearly a third of the sample held an alternative conception about thermal properties of the solid state. Similar to the findings in Sözbilir and Bennett (2007), a relation between entropy and spatial “disorder” was persistent in students’ conceptual understanding of thermodynamics. This was diagnosed for about 24% of the sample. THEDI also measured a relatively high confidence rating related to students’ alternative conception. Almost one third of the sample responded to items on THEDI that suggest they are working with the conception that in a perfectly ordered pure solid there is no freedom of motion at all. A smaller portion of the sample (12%) responded in a way that suggests they are working with the conception that when a solid is in its elemental form there is no disorder and thus, the entropy is zero. Both of these findings are correlated with relatively high confidence ratings.

There is noticeably less literature regarding students’ conceptions of absolute entropy and pure solids compared to topics related to the First and Second Laws of Thermodynamics. We believe this is in part reflects the nature of the thermodynamics curriculum in physical chemistry. In our experience, the application of the Third Law of Thermodynamics is given less attention

than other concepts. Nonetheless, we found the recurring pattern that students often associate entropy with spatial disorder and this influences how students reason about the behavior of solids.

Spontaneity and Equilibrium

As an extension of the laws of thermodynamics, free energy, spontaneity, and equilibrium are crucial to explaining chemical processes and physical changes. The literature presented here focuses on students' understanding of these topics. Alternative conceptions are reported in Table 5.

Table 5. Main findings from the literature regarding students' alternative conceptions of spontaneity and equilibrium.

References	Alternative Conceptions
Banerjee (1995)	<p>There are no equilibrium constants associated with reactions that go to completion or reactions that do not occur</p> <p>Systems change spontaneously because they tend toward lower energy</p> <p>Gibbs free energy increases or decreases linearly to make a reaction spontaneous</p>
Thomas and Schwenz (1998)	<p>ΔS° & ΔH° are not mentioned as factors that determine the value of equilibrium constants</p> <p>The amount of pure solid affects the position of heterogeneous equilibria</p> <p>With high enough temperature or low enough pressure, all CaCO_3 would be consumed at equilibrium</p> <p>Pressure affects the value of equilibrium constant</p> <p>At equilibrium, most if not all chemical reaction ceases</p> <p>Temperature affects equilibrium composition because it affects the rate of reaction</p>
Sözbilir (2002)	<p>The slower the reaction the smaller change in Gibbs free energy</p> <p>The bigger Gibbs free energy change means the faster the reaction occurs</p> <p>The bigger/smaller $\Delta_r G^0$ the faster the reaction occurs; the reaction with bigger $\Delta_r G^0$ goes towards full completion</p> <p>If a reaction occurs fast it goes towards full completion</p>

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Incorrect graphical representations of Gibbs free energy as a function of extent of reaction

Sreenivasulu and Subramaniam (2013)	At the boiling point, increasing heat supply increases both the rate of vaporization and the temperature A substance cannot exist in the vapor phase below its boiling point Freezing involves heat absorption and is endothermic
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Azizoglu, Alkan, and Geban (2006) identified alternative conceptions of phase equilibrium held by 59 pre-service chemistry teachers enrolled in a physical chemistry class. The researchers developed an instrument with eight open-ended questions testing the pre-service teachers' understanding of equilibrium vapor pressure, phase diagrams, state changes, among other things. Common alternative conceptions were identified relating to simple definitions, such as not having correct definitions for vaporization, condensation, sublimation, or freezing points (Azizoglu et al., 2006). Some students held that "equilibrium vapor pressure depends on the volume of the container in which the liquid is present", which was also identified by Canpolat, Pinarbasi, and Sözbilir (2006).

There were numerous alternative conceptions originating from incorrect relationships between vapor pressure and other variables. For example, some students argued that dissolving sodium chloride decreases the vapor pressure because it causes an increase in intermolecular forces. In reference to a graph of the pressure and temperature carbon dioxide at constant volume, students argued that an increase in pressure contributes to an increase in melting temperature, which makes carbon dioxide easy to melt. Other alternative conceptions relate to an incorrect relationship between vapor pressure and molecule size, miscibility, solution purity, and colligative properties (Azizoglu et al., 2006).

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3 Boudreaux and Campbell (2012) conducted a qualitative study of introductory physics
4 and chemistry students' understandings of vapor pressure as it relates to other variables in liquid-
5 vapor phase equilibrium using written responses to exam and quiz data. Their analysis found
6 students have great difficulty understanding the conditions under which a liquid and vapor
7 coexist in equilibrium. For example, students had difficulty defining the system and recognize
8 that vapor pressure is controlled solely by temperature. Students tended to focus on variables
9 that differed from one situation to another (whether they influence the vapor pressure or not),
10 failed to distinguish between multiple usages of technical terms (such as equilibrium), and
11 struggled to construct a coherent description of how equilibrium is established.
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25 Banerjee (1995) designed and administered a diagnostic questionnaire intended to
26 measure students' conceptions of thermodynamic equilibrium and problem solving abilities after
27 12 weeks of instruction in a third semester general chemistry course. The content was validated
28 by an expert reviewer. Sixty students responded to the questionnaire. Alternative conceptions
29 reported in this study are listed in Table 5. Sözbilir (2002) designed and administered a
30 diagnostic questionnaire that identified and classified 45 undergraduate students' alternative
31 conceptions of Gibbs free energy using methods similar to Sözbilir and Bennett (2007). Based on
32 analysis of student responses to the questionnaire, the authors compiled students' conceptual
33 difficulties, which are listed in Table 5. Sözbilir (2002) and Banerjee (1995) reported a very
34 similar finding about students understanding of Gibbs free energy in relation to the extent of a
35 chemical reaction. Both groups of students showed similar difficulty in representing or
36 recognizing the graphical representation of Gibbs free energy as a function of extent of reaction.
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53 Sreenivasulu and Subramaniam (2013) identified two alternative conceptions about phase
54 equilibrium using THEDI. The authors found that 11% of the sample indicated additional heat
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3 sources would increase the rate of vaporization *and* temperature of a liquid while it is boiling.
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5 This finding is in agreement with Thomas and Schwenz (1998), Miller et al. (2005; 2006), and
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7 Nottis et al. (2010). The THEDI instrument also provided evidence that students were highly
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9 confident in their incorrect understanding of phase equilibria. Over half of the sample (53.8%)
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11 indicated with high confidence that a substance could not exist in the vapor phase below its
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13 boiling point.
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17 Turányi and Tóth (2013) identified physical chemistry students' alternative conceptions
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19 relating to thermodynamics and kinetics. Students' conceptions were assessed using ten tasks
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21 gathered from research and researcher's experience. The researchers paid special attention to
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23 misunderstandings that arise from confusing kinetics and thermodynamics. The authors
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25 established content validity of the task sheet. In addition, some of the tasks were piloted with
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27 both secondary and university students. The authors established reliability by calculating
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29 Cronbach-alpha ($\alpha=0.758$). The task was administered to 424 students (11.3% chemistry, 42.5%
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31 biology, 27.4% pharmacy, 18.9% environmental). The tasks were graded on a 3-point scale, 0
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33 given for a wrong answer and 2 given for a perfect answer.
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40 Descriptive statistics suggests that chemistry students who had received the most physical
41
42 chemistry instruction performed best on the instrument. Students who answered incorrectly
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44 tended to use everyday analogies for solving scientific problems and applied macroscopic
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46 properties to the microscopic level, a prominent finding also noted in the PNOM literature
47
48 (Talanquer, 2006).
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51 In a study related to spontaneity and equilibrium, Sözbilir, Pinarbasi, and Canpolat
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53 (2010) investigated third-year pre-service chemistry teachers' conceptions of the differences
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55 between chemical thermodynamics concepts and chemical kinetics concepts. A diagnostic test
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3 was piloted in an undergraduate physical chemistry course and content validity was assessed by
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5 four chemistry lecturers. Understanding of 53 of these pre-service teachers was probed under
6
7 normal class conditions through a diagnostic test containing five open-ended questions. If the
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9 students showed any alternative conceptions in their responses without providing an in depth
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11 explanation of their reasoning, they were interviewed (N=13) to clarify their reasoning. Upon
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13 analysis of students' responses, those that were prevalent in over 20% of the tests were reported
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15 as alternative conceptions.
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20 Sözbilir et al. (2010) found that students tended to confuse thermodynamic and kinetic
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22 concepts, as Turányi and Tóth (2013) found above. When students considered a substance
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24 dissolving they confused the effect of temperature on the rate of dissolving with the effect on
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26 solubility. The most frequent mistake was the use of the equilibrium constant to predict rate of
27
28 the reaction. One student argued that if a reaction has a larger equilibrium constant, products are
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30 more favored; therefore, reactions take place faster. Another student argued that with a smaller
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32 equilibrium constant, fewer products are formed (a correct conception), but stated that the
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34 reaction would take less time because less product is created. Students also incorrectly applied
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36 shifts attributed to LeChatelier's principle to the rate of the reaction. For example, one student
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38 explained that if the equilibrium shifts towards the reactants, the rate of formation of product
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40 should increase because there are fewer products. The researchers also identified alternative
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42 conceptions due to the relationship between spontaneity and the equilibrium constant. Students
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44 reasoned that if a reaction were very spontaneous, it would have a faster rate, because it will
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46 proceed more "easily." This reasoning also applies to relating enthalpy to rate. For example, a
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48 reaction that is largely exothermic will be faster as it will go forward "easily" (Sözbilir et al.,
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3 2010). Sozibilir and Bennett reported similar reasoning in an earlier study about students'
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5 understanding of enthalpy and spontaneity (2006).
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8 Although faculty recognize that thermodynamics and kinetics are distinct intellectual
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10 areas with specific connections, students attempt to forge relationships between these areas in
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12 ways that are not scientifically accurate.
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15 We found that researchers collectively document students' ability to describe chemical
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17 equilibrium and factors affecting the state of equilibrium. It is interesting that many of these
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19 studies focus on findings regarding students' understanding of cause-and-effect relationships
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21 between thermodynamic and state variables rather than underlying causal mechanism of
22
23 equilibrium. While some studies did pursue students' understanding of free energy in the context
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25 of chemical equilibria, we found less research that examines students' understanding of the
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27 thermodynamics underlying chemical equilibria.
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32 **Discussion**

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34 The DBER literature regarding factors influencing student success in physical chemistry,
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36 student performance and understanding of mathematical concepts, students' reasoning with the
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38 particulate nature of matter, and conceptions of thermodynamic concepts (in introductory and
39
40 upper-level courses) synergistically contribute to our understanding of how students learn
41
42 thermodynamics. This body of literature yields implications for DBER researchers, CER in
43
44 particular, and for faculty teaching physical chemistry courses or courses in other disciplines
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46 such as physics (wherein the course "physical chemistry" may be titled "thermal physics") that
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48 focus on similar content.
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53 *Success in physical chemistry.* An ongoing question in the CER community deals with
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55 how students' prior coursework impacts their performance in physical chemistry. The existing
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3 body of literature provides a surface-level description of factors affecting students' success in
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5 physical chemistry. It appears strong predictors of student success are mathematical proficiency
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7 and logical thinking skills. The research also suggests that some students have negative
8
9 perceptions of the physical chemistry curriculum. More troublesome is the clashing perceptions
10
11 held by students and their physical chemistry instructor found by Sözbilir (2004). Sözbilir also
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13 reports a very important aspect of faculty professional development; one physical chemistry
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15 instructor appeared to be working with outdated models of learning and had limited resources to
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17 promote effective changes to his curriculum. This has consequences for students' success in a
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19 physical chemistry course.
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25 *Mathematics in physical chemistry.* We observed little to no articulation of two
26
27 constructs: mathematics understanding and proficiency. Some of the literature reads as though
28
29 student difficulties are due to low mathematical proficiency rather than an issue of *transfer*,
30
31 referring to the acquisition of knowledge in one contexts and its applications in other contexts
32
33 (Singley & Anderson, 1989). But we must be careful before we generalize these findings because
34
35 many of these studies do not explain why transfer may or may not occur. Dziembowski and
36
37 Newcombe (2005) point out salient features of transfer studies that make them difficult to control,
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39 including the nature of the problem tasks for assessing transfer and the instructional intervention
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41 given to students, which should be considered in future studies of this nature.
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46 Of the studies in the literature that did apply the appropriate framework for learning, the
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48 interpretations of the findings offered insight into how mathematics influenced the teaching and
49
50 learning of thermodynamics. Specifically, the research suggests that students do not always use
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52 the requisite mathematics knowledge in new contexts, as practitioners would expect. This is
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54 reported for the physical chemistry setting (Becker & Towns, 2012) and researchers also found
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3 preliminary evidence of this thermal physics settings (Thompson et al., 2006; Bucy et al., 2007;
4 Christensen & Thompson, 2010). We anticipate the same to be true in the engineering discipline
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6 as well.
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10 *Student reasoning and the particulate nature of matter.* The research demonstrates that
11 students use the particulate nature of matter to reason about thermodynamic concepts. This is
12 important for researchers and practitioners alike as these findings may be surprising considering
13 the macroscopic nature of classical thermodynamics. Appealing to our present models of
14 learning, we should be actively conscious of students' conceptions of the particulate nature of
15 matter and how they are used to explain and predict chemical phenomena.
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19 *Student understanding of the First, Second, and Third Law of Thermodynamics,*
20 *spontaneity, and equilibrium.* The current literature in the learning sciences has moved beyond a
21 model where incorrect concepts are to be eradicated and replaced because this model is not
22 reflective of our current understanding of how students learn (Bransford et al., 2000; Maskiewicz
23 and Lineback, 2013; Smith, diSessa, Roschelle, 1993). Student's alternative conceptions are
24 what they can use (perhaps only in part) as a foundation for future understanding. Recognizing
25 these foundations and considering how to effectively leverage specific components of them to
26 build more scientifically accurate understandings is a challenge for researchers, practitioners, and
27 curriculum designers.
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31 The extensive literature on students' conceptions of thermodynamics across disciplines
32 signifies that the DBER community is aware of many starting points that our students may use
33 before constructing more scientifically-based conceptions of energy, enthalpy, entropy, free
34 energy and equilibrium. Furthermore, students struggle to identify state variables, path-
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3 dependent processes, systems and surroundings, and the meanings beyond their mathematical
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5 representations.
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8 Many of the studies reviewed here utilized some form of written assessment (e.g. a
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10 survey, assessment instrument, etc.) in many different ways giving the research findings varying
11
12 degrees of validity. For example, some researchers employed measures of content validity, face
13
14 validity, and/or reliability of the interpretations of data they collected when using an assessment
15
16 instrument or survey. Assessment instruments specifically designed to diagnose students'
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18 thermodynamic conceptions have been introduced to the chemistry and engineering communities,
19
20 including THEDI (Sreenivasulua & Subramaniam, 2013), Thermodynamics Concept Inventory
21
22 or TCI (Wren & Barbera, 2013; Wren & Barbera, 2014), and TTCI (Streveler, Miller, Santiago
23
24 Roman, Nelson, Geist, Olds, 2011). These instruments were specifically identified here because
25
26 they meet many of the standards for measurement in CER outlined by Arjoon et al. (2013). The
27
28 corresponding citations include descriptions about how practitioners or education researchers
29
30 may obtain the instrument for use in their classroom.
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36 **Directions for Future Research and Implications for Practitioners**

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38 From our review of the literature it is clear that research at the intersection of chemistry,
39
40 physics, engineering, and mathematics where thermodynamics lies is a stimulating area for
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42 inquiry in the undergraduate curriculum. To drive forward this research and translate findings
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44 into effective classroom practices a number of recommendations should be considered.
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48 **Design, Development, and Evaluation of Assessment Instruments and Their Dissemination** 49 50 **to Practitioners**

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54 *Recommendations for research.* Assessment instruments designed to diagnose alternative
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56 conceptions in the way they are intended to be are necessary to publish findings that can be
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3 translated into meaningful instructional practice and be used to build on in future research
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5 (Arjoon et al., 2013). Many of the assessment instruments that appear in the literature have one
6
7 or two sources of evidence for validity, if any. Measurements beyond content and construct
8
9 validity are necessary to improve our understanding about how an instrument works in certain
10
11 setting. Evidence for some degree of internal structure, knowledge of how the intended measure
12
13 correlates with other variables, temporal stability, and internal consistency beyond an expert
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15 review and information about how students respond to assessment items are desired. We offer
16
17 five suggestions to improve measurements of students' alternative conceptions.
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23 First, student interviews can support and provide context for psychometric data from
24
25 multiple-choice and open-ended questionnaires. Second, robust statistical analyses with the
26
27 appropriate sample sizes can inform researchers about the ways items function on questionnaires.
28
29 For example, Wren and Barbera (2014) report elsewhere in this special issue on their findings
30
31 from a Rasch analysis of items on the Thermodynamics Concept Inventory or TCI. Third, not
32
33 any one study needs to collect, analyze, and report all the necessary sources of evidence for the
34
35 validity and reliability. Instead, it can be a collective effort within the community with
36
37 contributions extending over a period of time. Fourth, when an assessment instrument such as the
38
39 THEDI, TCI, or TTCI is used in a different setting other than the one intended by the developing
40
41 researchers, the interpretations of data collected should be monitored, as they are functions of the
42
43 data rather than the instrument itself (Wren & Barbera, 2013). This means re-evaluating how the
44
45 instrument works in the new settings and collecting evidence that it functions the way it was
46
47 intended to. Finally, with the development and evaluation of assessment instruments in the
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49 research communities comes the responsibility to make them accessible to practitioners.
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3 Beyond investigating the presence or absence of specific alternative conceptions, we
4 would be remiss if we did not encourage researchers to develop pedagogical approaches and
5 curricula that facilitate students developing more scientifically correct conceptions. For example,
6 if we can demonstrate that students believe that the entropy of the universe is conserved after
7 formal instruction, then this should drive us to modify our instruction and continue to measure
8 changes in student conceptions in the hope that we develop more effective ways to facilitate
9 learning. Over 20 years ago Smith, diSessa, and Roschelle (1993) wrote that, “It is time to move
10 beyond the identification of misconceptions.” Continuing to identify misconceptions will not
11 advance our understanding of student learning and will not help practitioners develop more
12 effective classroom practices that allow for the refinement of knowledge into more sophisticated
13 and expert like understandings.
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29 *Implications for practitioners.* Practitioners may use the instruments as a means of
30 formative and summative assessment in their course. Instruments such as THEDI, TCI, and
31 TTCI have shown to be effective tools for assessing students’ understanding and may provide
32 instructors with a sense of students’ alternative conceptions to treat as a starting point for
33 discussion in their classes. Many alternative conceptions have conditions under which they may
34 function appropriately by providing reasonable “roots” for students to construct knowledge. The
35 challenge for practitioners is to help students discuss, consider, and refine their knowledge into
36 more sophisticated structures that function appropriately in a broader variety of contexts.
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48 In terms of summative assessments of student learning, the American Chemical Society
49 Physical Chemistry Thermodynamics examination for 2013 is a method by which faculty in the
50 United States, Puerto Rico, and Canada can assess student learning at the end of a course
51 focusing on thermodynamics. The ACS Exams Institute posts norms for these exams so that an
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3 exam score can be connected to a percentile ranking considering a larger population of test-
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5 takers.
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8 **Emergent Processes as a Framework for Understanding Thermodynamic Concepts**

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10 *Recommendations for research.* One possible area of inquiry is the implementation of
11 Chi (2005) and Chi, Roscoe, Slotta, Roy, and Chase's (2012) domain-general explanation for
12 students' understanding of emergent processes. Heat and temperature are examples of concepts
13 that students often confuse and need a strong concept of the emergent properties to understand
14 appropriately. Emergent processes can be described by fundamental attributes that include
15 randomness and simultaneous independent interactions between components. These are
16 characteristics of chemical systems viewed at the particulate level. Yang, Roman, Strevler,
17 Miller, Slotta, and Chi (2010) used Chi's distinction between direct and emergent processes to
18 design curricula to impact engineering students understanding of diffusion, microfluidics, and
19 heat transfer. Statistically significant results were found for students studying diffusion and
20 microfluidics, but not heat transfer. However, one study is not the final word and we believe
21 Chi's perspectives could prove important for researchers in designing their studies. We
22 encourage researchers to use it as a framework to understand alternative conceptions and to
23 derive implications for building on students' knowledge.
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44 *Implications for practitioners.* Although classical thermodynamics is the realm of the
45 macroscopic, students will seek to use multiple cognitive resources from their prior experiences
46 to understand the information presented in physical chemistry. In the cases where a PNOM
47 perspective may be useful and appropriate we encourage practitioners to have students draw their
48 understandings. There is a vast amount of peer-reviewed literature across DBER and cognitive
49 science pointing toward the importance and impact of student drawing (Ainsworth, Prain, &
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3 Tytler, 2011; Harle & Towns, 2012; Harle & Towns, 2013; Leopold & Leutner, 2012; Van
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5 Meter & Garner, 2005). If student drawings are collected or volunteered anonymously, then
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7
8 practitioners can use them as exemplars for class discussion and an exploration of PNOM
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10 concepts under consideration. Student interactions with computer simulations have also shown to
11
12 be effective pedagogical tools (Wieman, Adams, Loeblein, & Perkins, 2010; Podolefsky, Perkins,
13
14 & Adams, 2010). These may support pedagogy and provide students with additional resources
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16 for thinking about the PNOM.
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19 20 **Collaborations Across Disciplines**

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22 *Recommendations for research.* Student understanding of mathematics in a physical
23
24 chemistry context is an issue of *transfer*, referring to the transfer of learning. Fields such as the
25
26 learning sciences and PER have carried out transfer research for quite some time (Mestre, 2005);
27
28 however, it is greatly understudied in CER. The student use of mathematics in physical
29
30 chemistry is fundamentally a question about *transfer* and should be investigated as such.
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34 We recommend CER members to become familiar with theories in the literature that may
35
36 provide greater analytical power for investigating student understanding of mathematics in
37
38 physical chemistry. For example, diSessa and Wagner (2005) developed the notion of a *concept*
39
40 *projection* within a theory pertaining to conceptual change that has implications for how transfer
41
42 takes place. They also discuss *classes* of transfer as a way to describe the preparedness of
43
44 students' knowledge (diSessa & Wagner, 2005). With this more nuanced view of prior
45
46 knowledge and transfer of knowledge, we agree with diSessa and Wagner that adequate
47
48 performance on a single task should not be the only measure of transfer in research studies.
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53 Another recommendation is for CER members to use existing theoretical frameworks
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55 from RUME that may be used to study students' understanding of mathematical concepts in
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3 physical chemistry. Only with a model of learning can we model students' *understanding* of a
4
5 concept. One example is Zandieh's (2000) model of understanding the concept of derivative.
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8 The model is centered on two constructs: multiple representations and process-object
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10 conceptions of mathematical entities (e.g. ratio, function, limit). Zandieh exemplifies the
11
12 process-object conception of the mathematical function as, "Functions may be seen as the
13
14 process of taking an element in the domain and acting on it to produce an element in the range.
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16 Functions may also be viewed statically as a set of ordered pairs." Students may build initial
17
18 understandings of derivative using process-objects, but sometimes they may be using pseudo-
19
20 objects. These cognitive entities are best described as "intuitive understanding that does not
21
22 involve an understanding of the process underlying the object" (Zandieh, 2000). The multi-layer
23
24 conception of derivative together with the context-dependence of using these layers explains why
25
26 some students have partial understandings, as noted in the science education literature (Becker &
27
28 Towns, 2012; Thompson et al., 2006; Bucy et al., 2007; Christensen & Thompson, 2010). As
29
30 students progress in their understanding they construct additional layers in the form of process-
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32 object relationships.
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39 We believe Zandieh's (2000) model is a framework for discipline-based education
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41 researchers to apply in their research that focuses on the transfer of mathematics knowledge to
42
43 thermodynamic contexts because it spans the many definitions and representations that are
44
45 consistent with the thermodynamics curriculum. We note this model of understanding may be
46
47 applied as a framework to make sense of student data regarding their conceptions of derivatives
48
49 and their representations and not as a tool for measuring proficiency at problem solving.
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54 Finally, physical chemistry is situated at the interface of chemistry, physics, mathematics,
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56 and engineering offering discipline-based education research unique opportunities to collaborate
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3 across disciplines. We recommend initiating and sustaining discussions across disciplinary lines
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5 that may help researchers develop studies, curricula, and assessments for use in thermodynamics.
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7
8 Researchers are encouraged to read broadly in the DBER and learning sciences literature for
9
10 studies that inform their research. For example we recommend a new “resource letter” article in
11
12 PER that focuses on introductory level thermodynamics in first year chemistry, physics, and
13
14 biology due to the nearly 200 articles across disciplines abstracted in it that can inform and
15
16 enrich research (Dreyfus, Geller, Meltzer, & Sawtelle, 2014) Beyond reading the literature,
17
18 attending PER and RUME conferences is a mechanism to develop a network of interdisciplinary
19
20 collaborators.
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24
25 *Implications for Practitioners.* If we want our students to take away concepts *through* an
26
27 understanding of the mathematical relationships and representations in our thermodynamics
28
29 curriculum, it would be best to assess their prior knowledge of the requisite mathematics and
30
31 scaffold their continued learning of mathematics in new contexts. This is one way to facilitate the
32
33 construction of accurate conceptual and operational understandings in physical chemistry.
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35 Additionally, if faculty are concerned with student mathematical abilities, then support within the
36
37 class itself through additional mathematical resources may be warranted (see Barrante, 2003;
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39 McQuarrie & Hansen, 2008; or Francl, 2002).
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44 Many resources are available in the DBER journals, but understanding how a
45
46 thermodynamic curriculum functions beyond the local needs of a physical chemistry classroom
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48 and a chemistry department also requires effective communication with members from
49
50 mathematics, physics, and engineering departments in your own institution. Thus, we encourage
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52 practitioners to take three bold and intellectually energizing actions: collaborate effectively with
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54 faculty in other departments to build a more coherent curriculum across the disciplines, read
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3 articles pertaining to teaching and learning thermodynamics outside the chemistry education
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5 journals, and engage in interdisciplinary activities and cultivate collaborators by attending DBER
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7 conferences.
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10 **Closing Statement**

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14 Four themes emerged in the scholarly literature pertaining to the teaching and learning of
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16 thermodynamics in undergraduate or tertiary settings: factors influencing student success in
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18 physical chemistry, the mathematics of physical chemistry, students' reasoning using the PNOM,
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20 and students' alternative conceptions of the First, Second, and Third Laws of Thermodynamics,
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22 spontaneity, and equilibrium. Based upon our analysis across this body of literature we
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24 synthesized recommendations for future research and implications for practitioners who teach
25
26 this subject. Above all, we encourage researchers and practitioners to collaborate across
27
28 disciplinary lines with mathematicians, physicists, and engineers who also seek to help students
29
30 understanding the challenging topics in thermodynamics.
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37
38
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44
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46
47 from the PER literature so that it could be cited in this review. We extend additional thanks to
48
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