Student Understanding of Partial Derivatives in Physical Chemistry: A Preliminary Report

Authors:
Nicole Becker and Marcy Towns, Purdue University
Renee Cole, University of Central Missouri
Chris Rasmussen, San Diego State University

Abstract. Upper-level undergraduate physical chemistry courses require students to be proficient in calculus in order to develop an understanding of thermodynamics concepts. Here we present the findings of a study that examines the relationship between math and chemistry in two undergraduate physical chemistry courses. Students participated in think-aloud interviews in which they responded to a set of questions involving mixed second partial derivatives with either abstract symbols or thermodynamic variables. Preliminary findings from the study are discussed.

Background

Physical chemists routinely use mathematical concepts such as exact differentials and partial differentiation to describe thermodynamic properties of chemical systems. Students enrolled in physical chemistry courses are typically required to apply mathematical concepts learned in mathematics coursework by manipulating equations and performing calculations. While some students may develop the ability to apply mathematical manipulations to chemistry problems, not all students develop physical understandings of what the symbols represent. This study is a qualitative investigation of students' understandings of partial derivatives in math and chemistry contexts using think aloud problem-solving interviews that explore undergraduate physical chemistry students' understandings of mathematical expressions across mathematics and physical chemistry contexts.

Typically, physical chemistry courses for upper-division chemistry majors focus on the topic of thermodynamics for approximately a semester. In thermodynamics, concepts such as the thermodynamic state functions and relationships such as the Maxwell relationships play a large role in the thermodynamics curricula. Furthermore, mathematical concepts like that of derivative and integral, and notions of exact derivatives, and relationships such as the equality of mixed second partial derivatives (Clairaut's theorem) are fundamental to understanding physical chemistry concepts. This is in large part due to the fact that many chemical properties such as entropy (denoted by *S*) cannot be observed or measured directly. The equality of mixed second partial derivatives of exact differentials (the Maxwell relations) provides a way to relate macroscopic observable quantities like temperature and pressure to chemical properties like entropy or Gibb's free energy. The Maxwell relations for the Gibb's energy state function is shown in figure 1.

$$dG = -SdT + VdP$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

S = Entropy
G = Gibbs Free Energy
V = Volume
T = Temperature
P = Pressure

Figure 1: Gibbs free energy and corresponding Maxwell's relation

In order to master thermodynamics concepts, students must not only become facile in interpreting symbolic and graphical expressions and performing mathematical manipulations and but must also grasp the physical significance of the symbolic manipulations. Research in student's understanding of chemistry has shown that chemistry students may struggle with mathematical concepts and symbolic representations in chemistry contexts(Tsaparlis, 2007). While a number of studies have looked at students' conceptions of abstract mathematical expressions in introductory-level chemistry and physics courses, relatively few have looked at student understanding of these concepts in upper-division courses such as physical chemistry (Bodner & Weaver, 2008; Greenbowe & Meltzer, 2003; Thomas & Schwenz, 1998; Thompson, Bucy, & Mountcastle, 2005).

Thompson, Bucy, and Mountcastle (2005) developed a written instrument consisting of analogous questions in math and physics contexts in order to probe physics students' understandings of partial derivatives, exact differentials, and the equality of mixed second partial derivatives (Maxwell relations) in an upper division physics course. This instrument examined students understanding of partial and total derivatives and the relationship of mixed second partial derivatives. Students responded to written questions that asked them to reason about partial derivatives in mathematical and physics contexts. Thompson and colleagues' analysis revealed that though some students were able to reason about the math context questions, they did not necessarily apply their mathematical understandings to physics contexts. Furthermore, while some students were able to reason about the physics context questions, some did so without demonstrating an understanding of the underlying mathematics.

Because an understanding of mathematical concepts such as exact differentials and partial derivatives is required to learn physical chemistry, we were interested in exploring students' understanding of these concepts with greater depth within a physical chemistry context. This study focused on upper-division physical chemistry students understanding of partial derivatives.

Methods

Because many of the underlying mathematical concepts examined in Thompson, Bucy, and Mountcastle's (2005) study are similar to the underlying mathematical concepts required to learn physical chemistry, the problem set used in their initial work was adapted as a semi-structured interview to explore physical chemistry student's understanding of partial derivatives. Two sets of interview data using the revised set of questions were collected during the 2008-2009 academic year. Undergraduate students from an interactive classroom using the Process Oriented Guided Inquiry (POGIL) curriculum were interviewed during spring 2009 and students from a lecture-style physical chemistry course from a large Midwestern university were interviewed in fall 2009. The majority of participants were chemistry majors. Five students from the POGIL course and seven from the lecture course participated in the interviews.

During the interviews students were asked to describe their prior coursework in math, chemistry, and physics, and were then asked to think aloud as they worked through five interview questions. The initial interview protocol adapted from Thompson, Bucy, and Mountcastle's (2005) work contained three questions in an abstract mathematical context, and two in physical chemistry contexts. These interview questions are shown below in figure 2.

1a. R is a function of the independent variables C and F, that is $R = R(C, F)$. The total differential of R can be written as

$$dR = BdC + EdF$$

Interpret the above equation in order to determine an expression for B.

1b. Is the following statement sometimes true, always true, or always false? Please explain your reasoning.

$$\left(\frac{\partial B}{\partial F}\right)_C = \left(\frac{\partial E}{\partial C}\right)_F$$

2a. G is the Gibbs Function. The total differential of G can be written as

$$dG = -SdT + VdP$$

Where S is the entropy, T is the temperature, V is the volume, and P is the pressure. In a certain experiment, it is found that

$$\left(\frac{\partial V}{\partial T}\right)_P = 4.2 \times 10^{-6}\ \mathrm{m^3/K}$$

Is this a reasonable result? Please explain your reasoning.

2b. From this data, is it possible to determine $\left(\frac{\partial S}{\partial P}\right)_T$?

If so, explain how and give a value. If not, explain what additional information you would need to do so.

Figure 2: Pilot Study Interview Protocol

After initial testing of the interview protocol, two additional questions were added in order to assess students' ability to write mathematical representations of change in math and physics contexts. In the first question, students were asked to write an equation for how height changes with respect to time if the height of the object is given by the equation $h(t) = -16t^2 + v_0 t + h_0$. Students who were unable to complete this task were then asked to evaluate a hypothetical response to the question. In the second question, students were given the diagram shown in Figure 3 and were asked to write an expression for how the pressure of the gas would change as it is heated. As in the first question, students were asked evaluate a response from a hypothetical response if unable to complete the task.

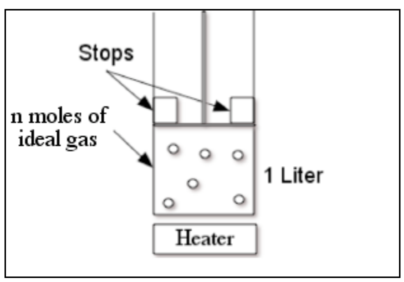

Figure 3: Diagram from interview

Interviews were audio recorded and student work papers were collected after the interviews. Additionally, in some interviews students were asked to write using a Livescribe Pulse Pen (Livescribe.com) rather than a traditional pen. This device uses an infrared camera to record the students' writing and the written work is then linked to the audio recording.

Interviews were transcribed and analyzed using open coding and grounded theory methodology to explore general themes in our data (Strauss & Corbin, 1990). Student work papers and/or Livescribe pen recordings were analyzed as secondary data sources along with transcripts. We compared participants' responses to each question across the two groups of students.

Results and Discussion

Our preliminary analysis has revealed that even students with advanced mathematical backgrounds and extensive prior coursework in physics and chemistry struggle to connect mathematical and chemistry concepts. Our findings indicated that students did not transfer their math knowledge to chemistry in a straightforward fashion and in many instances students did not demonstrate a solid understanding of mathematical notions such as partial derivatives.

Several themes emerged from our preliminary analysis, two of which will be described in this paper. First, students struggled with differences in the notations used in math and physical chemistry. For instance, Jocelyn, when asked to write an expression for how $f(x) = -16x + c_1 x + c_2$ would change as x changes, wrote $\Delta f(x) = -32x + c_1$. When asked to comment on a hypothetical response written by another student ($\frac{df}{dx} = -32x + c_1$), she responded:

Jocelyn: Um, I suppose I could have written it that way also.

Interviewer: Is there a difference?

Jocelyn: Um, to me, no. (laughs) No, there's not a difference to me, but I know they're supposed to be a difference (…)

Jocelyn commented that she recalled several different notations having been used interchangeably in her physical chemistry course. In physical chemistry, delta is typically reserved for discussions of change in state functions (exact differentials). While it is likely Jocelyn may have seen several different types of notation used in physical chemistry, it is not likely that the instructor used them interchangeably. However, without a clear and explicit discussion of notational differences between physical chemistry and calculus students could easily become confused.

A second theme that became evident from our preliminary analysis was that though many students were able to successfully manipulate symbolic expressions in physical chemistry contexts to obtain the appropriate Maxwell relation, few were able to demonstrate an understanding of the foundational mathematics. For example, one participant enrolled in the large lecture section of physical chemistry, Taylor, when asked to obtain a value for $\left(\frac{\partial S}{\partial P}\right)_T$ when given only a value for $\left(\frac{\partial V}{\partial T}\right)_P$, immediately wrote the correct expression $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$. When asked how he obtained his result he replied as follows:

Interviewer: *Now how did you get that expression, you seem to almost have it memorized.*

Taylor: Um, I do have it memorized. (laughs) Um, yeah, I'm trying to remember back to those, like when he was telling us all of those rules. We did have a um, derivation for this, and I remember it was kind of like, troublesome.

Taylor continued to describe how he obtained the Maxwell relationships using a mnemonic device that he learned in physical chemistry class. While he recalled having derived the Maxwell relations at some point in class, he believed that it was more important to be able to reproduce the necessary Maxwell relation than to understand the mathematical basis for the relationship.

Future Work

Further data collection is planned from a lecture course in fall of 2010 and subsequent data analysis will explore trends in how students transfer between information learned in mathematics courses to chemistry contexts. We plan to adopt a contemporary transfer perspective, such as the dynamic transfer perspective developed by Rebello, Zollman, and

Allbaugh (2005) and the actor-oriented transfer perspective (Lobato & Ellis, 2002), as a theoretical lens for subsequent data collection and analysis. We hope to reformulate our interview questions prior to additional data collection in order to use more open-ended problems and graduated prompting, as is consistent with methodologies used in contemporary transfer studies (Cui, Rebello, & Bennett, 2005).

Conclusions

Our preliminary work thus that has explored upper-division students understanding of total and partial derivatives and the Maxwell relations in mathematical and physical chemistry contexts. Our initial findings indicate that despite years of coursework students may fail to develop sophisticated understandings of foundational concepts like derivatives. These findings echo what has been found in other research (Thompson, et al., 2005; Yeatts & Hundhausen, 1992). Further work in this area to explore upper-division students' mathematical understandings in chemistry contexts is needed to inform curricula and pedagogy so students can be better equipped to succeed in their future careers.

Acknowledgements

This research is supported by the NSF under DUE-CCLI (TUES) 0817467. Any opinions, findings, and conclusions, or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation. Thanks to Megan Wawro (SDSU), George Sweeney (SDSU) for their helpful feedback.

References

Bodner, G. M., & Weaver, G. C. (2008). Research and practice in chemical education in advanced courses. *Chemistry Education Research and Practice, 9*, 81-83.

Cui, L., Rebello, N. S., & Bennett, A. G. (2005). *College students' transfer from calculus to physics*. Paper presented at the Physics Education Research Conference, Salt Lake City, UT.

Greenbowe, T. J., & Meltzer, D. E. (2003). Student learning of thermochemical concepts in the context of solution calorimetry. *International Journal of Science Education, 25*(7), 779-800.

Lobato, J., & Ellis, A. B. (2002). The teacher's role in supporting students' connections between realistic situations and conventional symbol systems. *Mathematics Education Research Journal, 14*(2), 99-120.

Rebello, N. S., Zollman, D. A., & Allbaugh, A. R. (2005). Dynamic transfer: A perspective from physics education research. In J. P. Mestre (Ed.), *Transfer of learning from a modern multidisciplinary perspective*. Greenwich, CT: Information Age Publishing.

Strauss, A., & Corbin, J. (1990). *Basics of qualitative research: Grounded theory procedures and techniques.* Newbury Park, CA: Sage.

Thomas, P. L., & Schwenz, R. W. (1998). College physical chemistry students' conceptions of equilibrium and fundamental thermodynamics. *Journal of Research in Science Teaching, 35*(10), 1151-1191.

Thompson, J. R., Bucy, B. R., & Mountcastle, D. B. (2005). *Assessing student understanding of partial derivatives in thermodynamics*. Paper presented at the Physics Education Research Conference, Salt Lake City, UT.

Tsaparlis, G. (2007). Teaching and learning physical chemistry: A review of educational research. In M. D. Ellison & T. A. Schoolcraft (Eds.), *Advances in teaching physical chemistry* (pp. 75-112). Washington D.C.: American Chemical Society.

Yeatts, F. R., & Hundhausen, J. R. (1992). Calculus and physics: Challenges at the interface. *American Journal of Physics, 60*(8), 716-721.