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RESEARCH REPORT

Student learning of thermochemical concepts in the context of solution calorimetry

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Student understanding of heat and thermal phenomena has been the subject of considerable investigation in the science education literature. Published studies have reported student conceptions on a variety of advanced topics, but calorimetry – one of the more elementary applications of thermochemical concepts – has apparently received little attention from science education researchers. Here we report a detailed analysis of student performance on solution calorimetry problems in an introductory university chemistry class. We include data both from written classroom exams for 207 students, and from an extensive longitudinal interview series with a single subject who was herself part of that larger class. Our findings reveal a number of learning difficulties, most of which appear to originate from failure to understand that net increases and decreases in bond energies during aqueous chemical reactions result in energy transfers out of and into, respectively, the total mass of the resultant solution.

Introduction

Students' understanding of heat and thermal phenomena has been the subject of considerable investigation in the science education literature. Most of this investigation has been in the context of pre-university students, both at the secondary and pre-secondary levels (e.g., Johnstone *et al.* 1977, Stavy and Berkovitz 1980, Shayer and Wylam 1981, Tiberghien 1983, 1985, Erickson, 1985, Linn and Songer 1991, Kesidou and Duit 1993, Kesidou *et al.* 1995, Lewis and Linn 1994, Harrison *et al.* 1999, Ben-Zvi 1999, Barker and Millar 2000). A few studies have focused on thermodynamics in the context of university-level physics instruction (e.g., Rozier and Viennot 1991, Loverude *et al.* 2002). There have also been a handful of investigations into student learning of chemical thermodynamics at the university level (Granville 1985, Beall 1994, Van Roon *et al.* 1994, Banerjee 1995, Thomas 1997, Thomas and Schwenz 1998). These investigations have reported on student conceptions regarding the first and second laws of thermodynamics, entropy and free energy, spontaneous processes, etc. However, calorimetry – one of the more elementary applications of thermochemical concepts – has apparently received very little attention from researchers in chemical education. A related study on solvation energetics, however, has recently appeared (Ebenezer and Fraser 2001).

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Calorimetry, in the context of chemical reactions in aqueous solutions, is often the very first topic in the chemistry curriculum in which thermodynamic ideas are applied. In view of that fact, it is somewhat ironic that calorimetry has itself received so very little attention in the chemical education literature. Virtually no research data seem to have been published regarding student learning of thermodynamic concepts specifically in the context of solution calorimetry, although some preliminary data have been reported by Keller and Weeks-Galindo (1998). For this reason, in the present investigation we have set for ourselves the following research questions: What are the primary conceptual difficulties faced by college chemistry students in their initial study of calorimetry? How do these relate to other student difficulties with thermodynamic concepts previously identified in the research literature?

Previous work

The science education literature has numerous studies reporting on the difficulties students have with the concepts of heat and temperature (Erickson 1979, 1980, 1985, Tiberghien 1983, 1985, Kesidou *et al.* 1995). Cohen and Ben-Zvi (1992) suggested that misconceptions can develop because of the relatively large number of abstract concepts involved, and Linn and Songer (1991) recommended using a simplified ‘heat-flow’ model in middle-school instruction. In the context of thermochemistry, several investigators have reported student difficulties in understanding and distinguishing between exothermic and endothermic reactions (Johnstone *et al.* 1977, Novick and Nussbaum 1978, Thomas and Schwenz 1998, De Vos and Verdonk 1986). Boo (1998) has reported a detailed investigation of learning difficulties encountered by students in the study of chemical reaction energetics, while Barker and Millar (2000) found that A-level students demonstrated a very weak understanding of the energy changes associated with the breaking and forming of bonds in chemical reactions.

Kesidou and Duit (1993) have discussed the common student confusion between the terms ‘heat’ and ‘temperature’. Heat is frequently viewed as an intensive quantity and temperature interpreted as degree of heat, i.e., as a measure of its intensity. However, heat is a process-dependent variable and represents a transfer of a certain amount of energy between objects or systems due to their temperature difference. Temperature, by contrast, is a measure of the average kinetic energy of molecules in a particular system. Gabel and Bunce (1994) state that:

> . . . although many of these concepts [heat and temperature] are important for understanding science . . . an in-depth understanding of them is not essential for solving many of the chemistry exercises and problems that appear in chemistry textbooks.

However, it seems that no investigations have been reported regarding the possible contribution of such conceptual understanding to college chemistry students’ studies of calorimetry.

Chemical reactions and solution calorimetry

In constant pressure calorimetry experiments involving aqueous solutions, chemists view the *reaction* as the system and the total mass of the solution and the calorimeter as the surroundings. The chemical reaction that occurs, although it can exchange heat with its surroundings, is represented as an abstract entity that does not have mass. The mass of the reactants plus the mass of water, the solvent, are viewed as the total mass of the solution. It is the total mass of solution that absorbs the heat which is released by the forming of bonds during the course of a chemical reaction. Therefore, the reactants in a calorimetry experiment are viewed by chemists in two distinct ways – as the entity that releases heat, and as part of the mass that gains heat. This is a difficult concept for students to understand and apply, and it makes thermochemical experiments more difficult to comprehend than physical processes in which two objects with different temperatures are placed in contact in an insulated container. Most undergraduate students can easily understand that the hotter object in such a process transfers heat to the cooler object until thermal equilibrium is reached.

One ordinarily defines q_A as the amount of heat absorbed by object A, i.e., $q_A > 0$ if energy flows into the object, but $q_A < 0$ if energy flows out of the object. For simple physical processes, any energy that flows *out of* one object must flow into the other, so $q_{hotter} + qcooler = 0$. The formula $q = mc\Delta T$ can then be applied to the two objects simultaneously to find, for example, the final temperature. However, in solution calorimetry problems involving chemical reactions, students have difficulty making the inference that the heat 'absorbed by' the chemical reaction is equal in magnitude but opposite in sign to the heat 'absorbed by' the solution.

Most textbooks, including the one used by the students in this study (Brown *et al.* 2000), discuss the relationship of the law of conservation of energy to calorimetry experiments:

> One of the most important observations in science is that energy can be neither created nor destroyed: *energy is conserved.* Any energy that is lost by the system must be gained by the surroundings, and vice versa. (Brown *et al.* 2000: 149)

> If we assume that the calorimeter perfectly prevents the gain or loss of heat from the solution to its surroundings, the heat gained by the solution must be produced from the chemical reaction under study. In other words, the heat produced by the reaction, q_{rxn}, is entirely absorbed by the solution; it does not escape the calorimeter. For an 'exothermic' reaction, heat is 'lost' by the reaction and 'gained' by the solution, so the temperature of the solution rises. The opposite occurs for an endothermic reaction. The heat gained by the solution, q_{soln}, is therefore equal in magnitude and opposite in sign from q_{rxn}: $q_{soln} = -q_{rxn}$. The value of q_{soln} is readily calculated from the mass of the solution, its specific heat, and the temperature change. (Brown *et al.* 2000: 160)

Silberberg's (1996) general chemistry textbook discusses the source of the heat:

> *The energy released or absorbed during a chemical change is due to the difference in potential energy between the reactant bonds and the product bonds* . . . energy does not really 'come from' anywhere; it exists in the different energies of the bonds of the substances. In an exothermic reaction, $E_{p\,(\mathrm{bond})}$ of the products is *less* than that of the reactants, so $\Delta E_{p\,(\mathrm{bond})} < 0$ and the system *releases* the energy difference. (Silberberg 1996: 231, emphasis in original)

Qualitative research, think-aloud interviews, and case studies

The think-aloud interview technique has been used to elicit student understanding of chemistry and physics concepts and approaches to problem solving (Clement 1979, Champagne *et al.* 1985, Larkin and Rainard 1984, Herron and Greenbowe

1986, Nakhleh and Krajcik 1993, Bowen 1994, Welzel and Roth 1998). With respect to thermodynamics, Thomas (1997) and Thomas and Schwenz (1998) reported a study in which they interviewed 16 college students enrolled in a physical chemistry course about their understanding of equilibrium and thermodynamics. Even though the students were in an advanced chemistry course, most of them showed a lack of understanding of basic thermochemistry principles, including the meaning of 'heat' and 'temperature' (Thomas 1997: 80–81). Harrison *et al.* (1999) reported a case study of one student's understanding of heat and temperature from observations made over an eight-week period. Qualitative data collected for this study included transcripts of all classroom discussions and a student portfolio containing all written work. Through class activities which employed the *Physics by Inquiry* curriculum (McDermott 1996), the subject became better able to distinguish the meaning of the terms heat and temperature.

Our instructional experience had persuaded us that a number of serious and widespread thermochemical misconceptions are developed among college chemistry students, even those who are successful in solving algorithmic calorimetry problems. This is consistent with previous research which found that students use algorithms to help solve chemistry problems but fail to exhibit conceptual understanding (Bodner 1987, Gabel *et al.* 1987, Nurrenbern and Pickering 1987). To examine this issue, our study included *both* quantitative and qualitative problems; data sources included both student interviews and written work on students' exam papers.

Method

This study incorporates both detailed analysis of student performance on written exams for a moderately large sample of students ($n = 207$) and extensive longitudinal interview data from a single subject who was herself part of the same class from which that larger sample was drawn. We were able to 'calibrate' our single subject, so to speak, by comparing her performance on the various written exam questions with the performance of her classmates in the larger sample. This allowed us to make a judgment regarding the likelihood of her views being representative of a significant portion of the larger sample.

The students in this study were enrolled in an introductory chemistry course for science and engineering majors at a large mid-western university in the USA. The primary data source for the study was an analysis of students' work on two calorimetry problems for a subset of the entire class. The first problem was on the second hour examination and the second problem was on the final examination. Prior to the second hour examination, as part of the normal course work, students had the opportunity to attend three lectures on thermochemistry and calorimetry. They had the opportunity to do the assigned readings in the textbook (Brown *et al.* 2000), work homework problems, and participate in recitation and laboratory sessions on calorimetry and enthalpy.

A subset of student examination papers was selected for detailed analysis. These samples were randomly selected from the work of the entire class of students enrolled in the course ($n = 541$); the sample represents more than one third of the entire class (second hour exam, $n = 185$; final exam, $n = 207$). The appropriate pages from each student's examination were photocopied.

A letter was attached to about 50 students' second hour examination paper when it was returned to them, asking if they would volunteer to discuss their responses. These students had exhibited a range of problem-solving performance and conceptual understanding and none had received a grade of 'A' or 'F' on that exam. Ten students showed up for the initial interview and from this group, an individual we refer to as 'Sophia' agreed to a series of interviews. Her work and performance were compared to students from her class who solved the same calorimetry problems. Over a three-month period, observations of Sophia's work and thinking were made and two instances of instructional intervention were provided. Hence, a longitudinal case study of Sophia's understanding of calorimetry was generated.

Sophia was chosen for the case study because of her ability to clearly state her conceptions and problem solving methods. Her examination scores in the introductory chemistry course indicated she was an above-average student. Overall, we believe that she is a student who is representative of her classmates. She was asked to explain what she did on the calorimetry exam problems by thinking aloud. She gave permission for a tape recorder to be used to record her voice and she signed a voluntary informed consent form agreeing to the conditions of the interviews, including the analysis of her work on the course examinations. She regularly volunteered her opinions and willingly expressed her views during the interview sessions.

There were four interview sessions with Sophia, an average of two hours each. Sessions 1, 2, and 3 occurred between the second hour examination and the final examination; Session 4 occurred after the final examination and focused on her work on that examination. Sessions 1 and 4 involved neutral observations and interactions, while Sessions 2 and 3 involved some instructional intervention, engaging Sophia in an interchange involving 'the juxtaposition of conflicting ideas, forcing reconsideration of previous positions' (Guba and Lincoln 1989: 90). The principal interviewer was one of the authors of this paper, and neither author was the instructor for Sophia's introductory chemistry course.

A description of the calorimetry problem on the second hour examination

This problem (figure 1) was a modified version of an end-of-chapter problem from the course textbook; it involves the mixing of two aqueous solutions of known concentration and volume. The initial and final temperatures of the solutions are measured. The goal is to determine the heat of reaction, and then the molar enthalpy change of the reaction. The format of this problem appears in several general chemistry textbooks as in-chapter examples and end-of-chapter exercises (Zumdahl and Zumdahl 2000, Brown *et al.* 2000, Chang 1998).

Individuals solving this problem are expected to realize that there is a transfer of energy from the chemical reaction to the mass of the resultant solution. (It is assumed that no heat is released or absorbed by the calorimeter.) The equation $q = mc\Delta T$ is used to calculate q_{soln}, the heat absorbed by the solution, and the relation $q_{rxn} + q_{soln} = 0$ is applied to determine the heat of reaction. Since the process occurs at constant pressure, $\Delta H_{rxn} = q_{rxn}$; therefore, dividing the heat of reaction by the number of moles of the limiting reagent

Calorimetry problem on the second hour examination

In a constant-pressure calorimeter with negligible heat capacity, 50.0 mL of 2.00 M HCl and 50.0 mL of 2.00 M NH_3 were combined. The initial temperature of both solutions was 22.4°C. The temperature of the combined solutions rose to 34.8°C after mixing. Assume that the specific heat of all the solutions is 4.18 J/g-°C, and assume that all solutions have a density of 1.01 g/mL.

a. How much heat did this reaction generate in the calorimeter?

b. What is ΔH for this reaction in kJ/mol?

Calorimetry problem on the final examination

The following reaction takes place at constant pressure in an insulated calorimeter: 1.00 L of 2.00 M $Ba(NO_3)_2$ solution at 25.0°C was mixed with 1.00 L of 2.00 M Na_2SO_4 solution at 25.0°C. The final temperature of the solution after mixing was 31.2°C. Assume that all solutions had a density of 1.00 g/mL and a specific heat of 4.18 J/g-°C.

a. What is the system?

b. What are the surroundings?

c. Calculate the heat of reaction (in kJ).

d. Is the reaction endothermic or exothermic?

e. Write a balanced chemical equation for the reaction.

f. Calculate the change in enthalpy (ΔH) for the reaction with units of kJ per mole of $Ba(NO_3)_2$ that reacts.

g. If 0.500 L of 2.00 M $Ba(NO_3)_2$ solution at 25.0°C is mixed with 0.500 L of 2.00 M Na_2SO_4 solution at 25.0°C, the final temperature of this solution will be ________________ (more than, less than, or equal to) 31.2°C (within experimental error).

Figure 1. Calorimetry problems on the second hour examination and final examination.

determines the molar enthalpy change for the reaction. Specifically, we have for parts (a) and (b):

$$\text{(a)}\quad m = \rho V = (1.01\,\text{g/mL})(100.0\,\text{mL}) = 101\,\text{g}$$

$$q_{soln} = mc\Delta T = (101\,\text{g})(4.18\,\text{J/g-°C})(+12.4\,\text{°C}) = +5.24\,\text{kJ}$$

$$q_{rxn} = -q_{soln} = -5.24\,\text{kJ}$$

a. The chemical reaction

b. The solution, consisting mostly of water, and the calorimeter. (Calorimeter can be assumed to have negligible heat capacity, and so may be ignored in the calculation.)

c. $m = \rho V = (1.00\,\text{g/mL})(2 \times 10^3\,\text{ml}) = 2 \times 10^3\,\text{g}$

$q_{soln} = mc\Delta T = (2 \times 10^3\,\text{g})(4.18\,\text{J/g-°C})(+6.2\text{°C}) = +\ 52\,\text{kJ}$

$q_{rxn} = -q_{soln} = -52\,\text{kJ}$

d. Exothermic.

e. $Ba(NO_3)_2\ (aq) + Na_2SO_4\ (aq) \rightarrow 2NaNO_3\ (aq) + BaSO_4(s)$

f. $1.00\,\text{L} \times 2.00\,\text{mol/L} = 2.00\,\text{mol}\ Ba(NO_3)_2$

$1.00\,\text{L} \times 2.00\,\text{mol/L} = 2.00\,\text{mol}\ Na_2SO_4$

$$\Delta H_{rxn} = \frac{q_{rxn}}{n_{limiting\ reagent}} = \frac{-52\,\text{kJ}}{2.00\,\text{mol}} = -\ 26\,\text{kJ/mol}$$

g. $0.500\,\text{L} \times 2.00\,\text{mol/L} = 1.00\,\text{mol}\ Ba(NO_3)_2$

$0.500\,\text{L} \times 2.00\,\text{mol/L} = 1.00\,\text{mol}\ Na_2SO_4$

$q_{rxn} = \Delta H_{rxn} \times n_{limiting\ reagent} = -26\,\text{kJ/mol} \times 1.00\,\text{mol}\ Ba(NO_3)_2$
$= -26\,\text{kJ}$

$q_{soln} = -q_{rxn} = +26\,\text{kJ}$

$m = \rho V = (1.00\,\text{g/mL})(10^3\,\text{mL}) = 10^3\,\text{g}$

$$\Delta T = \frac{q_{soln}}{mc} = \frac{+26\,\text{kJ}}{(10^3\,\text{g})(4.18\,\text{J/g-°C})} = +6.2\text{°C}$$

$T_{final} = 25.0\text{°C} + 6.2\text{°C} = 31.2\text{°C}$

Figure 2. Solution to calorimetry problem on final examination.

(b) $0.0500\,\text{L} \times 2.00\,\text{mol/L} = 0.100\,\text{mol HCl}$

$$\Delta H_{rxn} = \frac{q_{rxn}}{n_{limiting\ reagent}} = \frac{-5.24\,\text{kJ}}{0.100\,\text{mol}} = -52.4\,\text{kJ/mol}$$

A description of the calorimetry problem on the final examination

This problem (figure 1) is similar to the one described above; a solution is shown in figure 2. Students are asked to identify the system and the surroundings, and

Table 1. Types of approaches used by students when calculating the heat of reaction on the second hour examination part (a), and the final examination part (c).

	Second hour examination (n = 185)	*Final examination* (n = 207)	
Correct or nearly correct magnitude of q_{rxn}√†	50%	40% *negative value 14%* √ *positive value 26%* †	
Errors using formula			
Set $q = \Delta T$ (or $q = T$)	8%	5%	[Final exam:] *negative value 13%* *positive value 41%*
Did not use $q = mc\Delta T$ *or* $q = \Delta T$	11%	9%	
Errors in value for mass			
Used mass of the reactants only	15%	21%	
Used mass of one solution only	8%	5%	
Other responses	7%	15%	
No answer	2%	6%	

Notes: All values are in percent of total n for respective exam.
A √ indicates the correct response.
A † indicates the response of Sophia on that category.
'Nearly correct' means there was only a simple math error.
'Other response' means *did* use $q = mc\Delta T$, but error did not fall into other categories.

whether the reaction is exothermic or endothermic. They are also asked to calculate the heat of reaction, and then the molar enthalpy change for the reaction. Finally, students are asked to consider the final temperature for a system involving the mixing of 500 mL of each reactant, instead of 1.00 L of each: Would T_{final} be more than, less than, or equal to that observed in the original system?

Results

It is notable that none of the students in this study acknowledged the fact that since the reactions occurred under conditions of constant pressure, the heat of reaction (q_{rxn}) is equal to the enthalpy change of the reaction (ΔH_{rxn}). Also, fewer than 1% of the students stated explicitly that $q_{rxn} + q_{soln} = 0$. (One might suggest that the common practice of tolerating students' failure to explicitly state fundamental assumptions and constraints in exam solutions may be, ironically, a factor that contributes to hindering students' understanding.)

Analysis of students' responses to questions on heat of reaction

Table 1 shows the categories of responses contained in students' work on the parts of the calorimetry problems dealing with the heat of reaction, along with the percentage of the student sample corresponding to each response. Because of the way this problem was worded on the second hour exam ('How much heat did this reaction generate in the calorimeter?'), only the magnitude (and not the sign) of the students' responses was considered in the case of the second hour exam.

On the second hour exam, we counted as correct or nearly correct student answers for part (a) that had the correct magnitude for q_{rxn}, or that contained only very minor mathematical errors. Only 50% of the students were able to successfully calculate the magnitude of q_{rxn}. The major problem seems to be the use of an incorrect mass for the entity (the surroundings) that is absorbing the heat from the system (the chemical reaction).

Table 1 also includes a summary of students' responses to part (c) of the final examination problem (i.e., a very similar question about heat of reaction). Only 40% of the students were able to apply the equation $q = mc\Delta T$ with use of the correct mass to generate a correct or nearly correct magnitude for the heat of reaction, compared to 50% on the second hour exam. Overall, there was a significant decrease in performance in comparison with the second hour exam (according to a two-sample test for binomial proportions: $z = 1.99$, $p < 0.05$). Only 14% of the students provided both a correct magnitude and correct (negative) sign, while 26% provided a correct magnitude but incorrect sign. Again, the major error exhibited by students was that of using the mass of chemical reactants and not including the mass of the water, for the total mass m in the formula $q = mc\Delta T$. It is also notable that, between the second hour exam and the final exam, there was a significant increase ($z = 1.99$, $p < 0.05$) in the number of 'no answer' responses, and also in the number of 'other' responses ($z = 2.50$, $p < 0.01$) that did not correspond to any of the other listed categories. The results suggest that students' confusion on at least some calorimetry principles actually may have increased in the time between the second hour exam and the end of the course.

Taken at face value, the determination of the heat of reaction appears to be a straightforward calculation. Using the formula $q = mc\Delta T$, students need only plug in the correct values for mass, specific heat, and the change in temperature to calculate q. Students then had to recognize that they had actually found q_{soln}, and then apply the relation $q_{rxn} = -q_{soln}$. However, the students' exam responses indicate severe difficulties in a number of areas.

On the final exam question regarding heat of reaction, 20% of the sample either failed to provide any response, or failed even to realize that they would need to make use of the relation $q = mc\Delta T$. Of the remainder of the sample, about one third did not understand which physical quantity corresponded to the m. Only about one student in seven could calculate a correct value for the heat of reaction accompanied by a correct sign. Some of the students equated the heat of reaction with the change in temperature, indicating that these students were quite unable to distinguish between the terms 'heat' and 'temperature'.

Analysis of students' responses to questions on molar enthalpy

Common errors exhibited by the students on part (b) of the calorimetry problem on the second hour examination are shown in table 2.

This part of the problem asks the students to calculate ΔH for this reaction in kJ/mol; only 4% of the students provided the correct magnitude and sign for the value of ΔH_{rxn}. In this case both the sign and magnitude are required. Using the formula $q = mc\Delta T$, students need only plug in the correct values for mass, specific heat, and the change in temperature to calculate a value for q. However, most

Table 2. Responses on the second hour examination to part (b) of the calorimetry problem, calculation of the molar enthalpy change of the reaction, ΔH_{rxn} [molar].

Description of the response	*Percentage of students exhibiting this response* *(n = 185)*			
Correct or nearly correct magnitude for ΔH_{rxn} √	**18%**			
(Divided q_{rxn} by 0.1 mol)				
negative sign for the value of ΔH_{rxn} √		4%		
positive sign for the value of ΔH_{rxn}		14%		
Incorrect magnitude for ΔH_{rxn}	**68%**			
negative sign for the value of ΔH_{rxn}		17%		
positive sign for the value of ΔH_{rxn}		51%		
Used incorrect number of moles				
Divided q_{rxn} by 2 mol			8%	
negative sign for the value of ΔH_{rxn}				*5%*
positive sign for the value of ΔH_{rxn}				*3%*
Divided q_{rxn} by 0.2 mol			14%	
negative sign for the value of ΔH_{rxn}				*3%*
positive sign for the value of ΔH_{rxn}				*11%*
Equated enthalpy and temperature				
ΔH_{rxn}[molar] = ΔT			3%	
Equated molar enthalpy and heat				
ΔH_{rxn}[molar] = q_{rxn}			12%	
negative sign for the value of ΔH_{rxn}				*4%*
positive sign for the value of ΔH_{rxn}				*8%*
Math errors			3%	
Other responses			29%	
negative sign for the value of ΔH_{rxn}				*5%*
positive sign for the value of ΔH_{rxn}†				*24%*
No answer	**13%**			

Notes: A √ indicates the correct response.
A † indicates the response of Sophia on that category.
'Other responses' includes those using incorrect number of moles but which don't fall into specific categories listed above.

students seemed not to recognize that the value of 'q' calculated from the experimental data is q_{soln}, not q_{rxn}, and that the signs of those two quantities must differ. Beyond that, the major problem with this calculation seems to be dividing the heat of reaction by an incorrect number of moles.

Students' responses on the final exam question related to molar enthalpy (part (f)) are shown in table 3. Only 18% of the students were able to determine a correct (or nearly correct) magnitude along with a correct sign for the molar enthalpy change of the reaction, although this was a significant improvement ($p < 0.001$) over the 4% who succeeded on the second hour exam.

Table 3. Responses on the final examination to part (f) of the calorimetry problem, calculation of the molar enthalpy change of the reaction, ΔH_{rxn} [molar].

Description of the response	*Percentage of students exhibiting this response (n = 207)*			
Correct or nearly correct magnitude for ΔH_{rxn} √ † (Divided q_{rxn} by 2 mol)	**34%**			
negative sign for the value of ΔH_{rxn} √ †		18%		
positive sign for the value of ΔH_{rxn}		16%		
Incorrect magnitude for ΔH_{rxn}	**39%**			
negative sign for the value of ΔH_{rxn}		12%		
positive sign for the value of ΔH_{rxn}		27%		
Used incorrect number of moles				
Divided q_{rxn} by 4 mol			2%	
negative sign for the value of ΔH_{rxn}				*0.4%*
positive sign for the value of ΔH_{rxn}				*2%*
Equated enthalpy and temperature				
ΔH_{rxn}[molar] = ΔT			2%	
Equated molar enthalpy and heat				
ΔH_{rxn}[molar] = q_{rxn}			10%	
negative sign for the value of ΔH_{rxn}				*4%*
positive sign for the value of ΔH_{rxn}				*5%*
Other responses			25%	
negative sign for the value of ΔH_{rxn}				*7%*
positive sign for the value of ΔH_{rxn}				*17%*
No answer	**27%**			

Notes: A √ indicates the correct response.
A † indicates the response of Sophia on that category.
'Other responses' includes those using incorrect number of moles but which don't fall into specific category listed above.

Table 4 outlines the responses given by students to parts (a), (b), (d) and (g) of the calorimetry problem on the final examination. With the exception of the identification of the reaction as an 'exothermic reaction', for which 71% of the students were correct, more than 50% of the responses to these questions were incorrect. The chemical reaction was identified as the system by only 22% of the students, while only 6% of the students correctly identified the solution and the calorimeter as the surroundings. (If the students identified the mass of the resultant solution as the surroundings, they received a rating of 'correct'.)

Sophia's work on the calorimetry problems

Sophia earned six points out of eight on the calorimetry problem on the second hour exam. In trying to calculate the molar enthalpy change, Sophia divided the

Table 4. Responses on the final examination to parts (a), (b), (d) and (g) of the calorimetry problem.

Description of the response	*Students' answers*	*Percentage of students exhibiting this response (n = 207)*	
(a) What is the system?			
Correct answer	the chemical reaction √	22%	
Partially correct	the reactant(s)/reactant solution †	7%	
Incorrect answers		71%	
	Everything inside the calorimeter		14%
	The calorimeter		23%
	The solution		22%
	Calorimeter and Contents		5%
	Other		6%
	No answer		1%
(b) What are the surroundings?			
Correct answer	The solution and calorimeter √ The solution or the water	6%	
Partially correct	The calorimeter †	32%	
Incorrect answers		62%	
	Everything outside the calorimeter		31%
	The calorimeter and everything else		8%
	The air		5%
	Other		18%
	No answer		1%
(d) Is the reaction exothermic or endothermic?			
Correct answer	exothermic √ †	71%	
Incorrect answer	endothermic	29%	
(g) [Comparison of the change in temperature of the two systems]			
Correct answer	equal to √	44%	
Incorrect answer	more than †	10%	
Incorrect answer	less than	43%	
No answer		2%	

Notes: A √ indicates the correct response.
A † indicates the response of Sophia on that category.

heat of reaction by the 'moles of solution' instead of dividing by the number of moles of limiting reagent. On the final examination calorimetry problem, Sophia correctly identified the two reactants as part of the system, but she did not indicate that it is the entire chemical reaction that is considered to be the system. She identified the calorimeter as being part of the surroundings, but she did not identify the solution as being part of the surroundings. She correctly used the total mass of the solution to calculate the heat absorbed by the solution, and then correctly inferred that this must be the heat that was transferred from the system. She correctly divides the heat of reaction by the number of moles of limiting reagent involved to generate a correct value for the molar enthalpy change of the reaction. Sophia did have a negative value for ΔH_{rxn}. She did not, however, realize that the 'heat of reaction' must also have a negative sign. Sophia incorrectly stated that the system in part (g) would produce a greater change in temperature in comparison with the original problem. She does not explicitly write down the relation $q_{rxn} = -q_{soln}$, yet she succeeds in correctly solving all but the last part of this problem.

Excerpts from Sophia's interviews

In order to confirm and to elaborate on why Sophia answered some of the parts of the calorimetry problem the way she did, an interview session (Session 4) was scheduled five days after her final examination. In this session, the interviewer was trying to assess why Sophia did not identify the solution as part of the surroundings, to assess Sophia's understanding of the term 'exothermic', and to assess her understanding of the use of positive and negative signs to indicate endothermic and exothermic processes respectively.

I: Would you walk me through what you were doing and thinking on this calorimeter problem on your final exam.

Sophia: I thought that the system is the two solutions reacting and the surroundings was the calorimeter because it was at constant pressure and that the calorimeter was insulated, so anything outside the calorimeter was not going to affect the reaction . . .

I said it was exothermic because the temperature increased . . . For the change in enthalpy, I took the heat of reaction that we had found and it asked for per moles of barium nitrate. I found moles of barium nitrate by using litres and molarity. I divided the heat of reaction by those moles because I figured that the heat had to be the same so the change in enthalpy was the same as up here . . .

I: You have a negative ΔH, ΔH equals negative 25.9 kilojoules per mole . . .

Sophia: Yes, I have it negative because it is an exothermic reaction.

Sophia seems to have a good understanding of when to use positive and negative signs to indicate endothermic and exothermic process, and she elaborates a bit on the responses she gave on the final examination regarding the questions of 'what is the system' and 'what is the surroundings'. Later in this interview she also demonstrated understanding of the concept of molarity despite confusion about its application to specific heat problems. Additional excerpts from her interviews will be presented and discussed in the next section.

Students' conceptual misunderstandings uncovered by the investigation

In this section, we will summarize the specific conceptual difficulties regarding calorimetry encountered by the students in our sample, as reflected by our analysis of the data. This includes both the written exam data and the interviews conducted with the subject Sophia.

> *Lack of recognition that energy flow out of reactants and into solution implies a negative 'heat of reaction', which, for constant-pressure processes, has the same meaning as a negative change in enthalpy of the reactants, i.e. that* $\Delta H_{rxn} < 0$

On both the second hour examination (question part b) and the final examination (question parts c and f), students had been asked to consider an exothermic reaction under constant-pressure conditions in which net energy is transferred from the chemical bonds in the reactants and products *to* the solution. The direction of energy flow can be recognized simply from the fact that the temperature of the solution increases. The conclusion should be that both the heat of reaction and the enthalpy change are negative in both cases, i.e. that both $q_{rxn} < 0$ and $\Delta H_{rxn} < 0$. However, on all three relevant questions, a large majority of the students who responded gave a positive value for their answer.

It is not clear how many of these errors in the sign of q_{rxn} and ΔH_{rxn} can be attributed to simple carelessness, and how many actually reflect a fundamental physical misunderstanding. A large majority (71%) of the students correctly identified the reaction as 'exothermic' on the final exam question, part (d). However, this may simply reflect a learned recognition that an increase in solution temperature corresponds to an exothermic reaction. (This is precisely the reasoning given by Sophia in Interview Session 4; see below.) Textbooks often make reference, rather loosely, to the heat 'released by', 'produced by', or 'evolved by' the reaction, but these terms are sometimes – not always! – assumed to refer to the absolute value of the heat of reaction – i.e., to $|q_{rxn}|$, which is defined to be a positive quantity (e.g., Zumdahl and Zumdahl 2000: 253). This obviously increases the potential confusion for the student.

Students do not necessarily give consistent answers to this type of question. On the final exam question Sophia, for example, correctly identified the reaction as exothermic and ΔH as negative; however she gave a positive value for the heat of reaction. From Interview Session 4, it is obvious that Sophia is well aware of the chain of reasoning that goes *increase in solution temperature* $\Rightarrow$ *exothermic reaction* $\Rightarrow$ $\Delta H < 0$. Here is how she explains her answer to part (f) of the final exam question during this interview:

> Sophia: . . . I said it was exothermic because the temperature increased . . .
>
> I: You have a negative ΔH, ΔH equals negative 25.9 kilojoules per mole . . .
>
> Sophia: Yes, I have it negative because it is an exothermic reaction.
>
> I: And you have written '$\Delta H = -q_{rxn}$'?
>
> Sophia: Yes, I was not so sure about that. I was trying to show that it was going to be negative because it was exothermic.

In contrast to her reasoning above, she explains her answer to part (c) as follows:

> Sophia: When it said to calculate heat of reaction I used the equation $q = mc\Delta T$. I found the mass by adding the two volumes, the litres, one of each solution. Then I put the values into the equation. I did the calculation on my calculator and got 51.8.

The issue of the sign of the heat of reaction – positive or negative – seems never to have entered her considerations. It appears that for Sophia, as for many other students, the fact that the 'heat of reaction' may have a positive or a negative sign – and that in fact, for constant-pressure processes, the heat of reaction is really just the same thing as the change in enthalpy ΔH – is simply an idea that has never been fully understood.

Identifying the 'heat of reaction' or 'heat generated by reaction' as simply the temperature change that results from that heat flow

Perhaps the most well-known and widely discussed student misunderstanding in the field of heat and thermodynamics is the confusion of 'heat' and 'temperature' (e.g., Kesidou *et al.* 1995). In calorimetry problems the distinction is made explicit, at least in quantitative terms, through application of the equation $q = mc\Delta T$. None the less, when asked to find the amount of heat generated by the reaction (on the second exam), and the heat of reaction (on the final exam), some students simply responded with the value of the temperature change ΔT of the solution, i.e., 12.4 °C on the second hour exam (response given by 8% of the students), and 6.2 °C on the final exam (response given by 5% of the students). In response to a question about an amount of heat – which should be measured in joules or calories – these students responded with a temperature, measured in degrees. Sophia expressed a related confusion during Session 4:

I: Good. Now, one last question, what is the difference between heat and temperature?

Sophia: Heat is energy being released or absorbed by something. Like 'q' here is the energy being released. Temperature is just a way to measure it.

I: When you use a thermometer in a calorimeter experiment, are we measuring heat or temperature when a reaction takes place?

Sophia: Heat.

The word 'heat' is properly used to represent an energy transfer into or out of a system due to a temperature difference, and it is a quantity for which a larger magnitude necessarily corresponds to a larger absolute amount of energy. The mistaken idea that temperature (an intensive quantity) is merely a measure of an amount of heat, rather than a measure of the average kinetic energy per molecule – a quantity distinctly different from heat – is clearly a misunderstanding that lingers on in many students' minds.

Not recognizing and applying the relationship between heat flow, specific heat, and temperature change (i.e., not making use of equation $q = mc\Delta T$*)*

A significant number of students were simply unaware that they needed to apply the relationship $q = mc\Delta T$ in order to find the heat of reaction. About 10% of students on both the second hour exam and the final exam attempted unsuccessfully to calculate the heat of reaction without using the relevant equation.

Not recognizing that the 'm' *in the relationship* $q = mc\Delta T$ *refers to the total mass of the solution contained within the calorimeter, and does not refer merely to the mass of the molecules that react to generate the heat flow*

The single most common confusion found among our student sample was that related to the meaning of 'm' – the mass – in the equation $q = mc\Delta T$. The 'ΔT'

in this case refers to the temperature change of the entire contents of the calorimeter, which is to say the total mass of the solution. The *m*, then, refers to the mass of that solution. However, about one-quarter of all students, on both exams, expressed confusion on this point. The most frequently expressed student idea (15% of students on the second exam, and 21% on the final) was that this mass refers in some fashion only to the molecules that are engaged in the chemical reaction that produces the heat. This misunderstanding led to a wide variety of incorrect numerical answers.

A significant number of students, although realizing that the *m* referred to the mass of the solution, did not realize that it was the entire mass of solution that had to be considered. As a result, 8% of students on the second hour exam and 5% on the final exam set *m* equal to half the mass of the total solution. Apparently, they were misled by the fact that there were two reacting species, each of which originally represented half of the total solution.

> *Not understanding that in solution calorimetry, the thermodynamic 'system' refers to the reacting molecules and their products – more precisely, to the chemical bonds (assumed to be massless) that are both made and broken (i.e., the 'reaction') – and that the 'surroundings' refers to the entire mass of material contained within the calorimeter (and, in principle at least, that which is outside the calorimeter as well)*

Although it is admittedly a subtle point, the meaning of the terms 'system' and 'surroundings' in the context of calorimetry often presents students with their first opportunity to try to relate thermodynamic terminology to an actual laboratory set-up. The interpretation of these terms in the context of calorimetry was stressed during the lectures in this course. However, on the final exam, fewer than one-third of students were able to give anything close to an acceptable answer to the question 'What is the system?' Similarly, fewer than 40% of the students could properly identify the 'surroundings'.

> *Not understanding that the molar enthalpy change refers to the relevant quantity (i.e.,* ΔH_{rxn}*) divided by the number of moles of one of the reacting species, and that for constant-pressure processes,* $\Delta H_{rxn} = q_{rxn}$

Part (f) of the final exam question clearly asks for the change in enthalpy ΔH per mole of one of the reactants. Therefore, a correct response would be to divide the heat of reaction q_{rxn} (i.e., the answer to part (c)) by the number of moles of this reactant (i.e., 2.00). A large number of students answered this question incorrectly. 10% of the students simply copied their numerical answer from part (c), while 29% of the students made other types of errors in this calculation (not including those who merely carried over an incorrect answer from part (c)). Twenty seven per cent of students gave no response to this question at all.

> *Believing that the heat flow is produced by an energy transfer from one reactant to another, rather than from the breaking and forming of chemical bonds to the total mass of material contained within the calorimeter*

This extremely interesting confusion was expressed by Sophia during Interview Session 1. On the one hand, she seems to understand that the solution is absorbing heat. On the other hand, she quite clearly is under the impression that heat is flowing *from* the solution containing one of the reacting species, *to* the solution containing the other, and is not sure about which is the source and which is the recipient. She also appears to express a confusion between a system where a chemical reaction is the source of heat, and a quite different system in which one physical object (such as hot metal) is a source of heat that flows into a surrounding liquid.

I: What are you measuring with the thermometer?

Sophia: The heat is rising in the solution because something is letting off heat but it is going into solution. There is a transfer of heat. It is going from one object to another.

I: And what is that object to the other?

Sophia: It is from one chemical to the other but I am not sure which is giving it off and which is absorbing it.

I: So, identify the chemicals that are in that solution.

Sophia: Hydrochloric acid and ammonia

I: Any other chemicals in there?

Sophia: Water. So I think water is the one absorbing the heat when the temperature is given off. I don't think water is part of the reaction. That is why we can exclude it in this problem. It is not part of the equation for finding heat.

I: So, is there water in this 101 grams?

Sophia: There is water in the 101 grams? I don't know this. Because if we had a solid . . . [Sophia looks at the chemicals on the nearby table and picks up a jar of magnesium metal], say we had the magnesium and we pour HCl(aq) on it. I would then know where one thing is going to the other. Because if the solution gains heat when you put Mg in the hydrochloric acid, then we know that the liquid solution is absorbing the heat, from the solid to the aqueous solution. But, when we have two aqueous solutions, then I don't know which is giving the heat and which one is absorbing the heat.

We were able to confirm Sophia's thinking on this issue through her explanation of the heat of reaction produced during the reaction of magnesium metal and hydrochloric acid:

I: What is this q?

Sophia: 'q' is heat. Heat of the reaction. So this heat is what is given off by the magnesium and transferred to the hydrochloric acid solution. The magnesium gives or transfers heat to the 6 M HCl solution and that is why the solution gets warm. And you can see it happening because the magnesium reacts with the HCl and gives bubbles. The magnesium is where the reaction is taking place because you can see it happening!

It is very clear that Sophia does not have a concept of energy being transferred due to the breaking and forming of bonds within the reacting species; rather, she is convinced that energy flows from one of the reactants, to the other. It is difficult to say at this time just how widespread this belief may be among students in general. However, it seems likely that it forms an important component of many students' thinking, and it certainly merits additional investigation.

Belief that the total amount of heat generated depends on the concentration of the reacting solutions, rather than on the total mass of reactants

On part (g) of the final exam question, although the mass of reactants was cut in half, Sophia assumed that since the concentrations remained unchanged (at 2.0 molar), the total heat generated would also be unchanged. Here is how she expressed her thinking (using the idea of 'micro-heaters' previously introduced as a metaphor for the chemical reaction):

Sophia: So you have the same amount of concentration but you have less water. So you have the same number of micro-heaters. Just less water . . . I assumed that the heat was going to be the same.

I: . . . Why would the heat be the same up here? . . .

Sophia: Because it is the same reaction taking place. So the molarities are the same. But the only thing that changes is the volume, so the mass changes.

Implications for instruction

In the introductory chemistry curriculum, solution calorimetry problems are often the first practical application in which ideas about heat, temperature, energy changes in chemical reactions, and conservation of energy are combined. Because of the relatively simple calculations involved in calorimetry, it is tempting for both students and instructors to overlook the need for careful attention both to straightforward matters (such as the positive or negative sign of the heat of reaction), and more subtle concepts (such as the bond-forming origin of reaction heats).

The results of this investigation suggest a number of specific areas in which increased attention by instructors may yield a significant return in improved student understanding of thermochemistry and calorimetry:

Students' inattention to the sign of an energy change is a common error. This may represent a more serious misunderstanding of just how a change in a physical quantity is ordinarily defined (i.e., change is equal to final value minus initial value). In any case, consistent attention to sign conventions is important in reducing unnecessary calculation errors that are potentially wasteful of students' time and energy. Students might be advised to make the very first step in a calorimetry calculation a consideration of the sign – positive or negative – of the quantity being determined. In some cases (such as the problems described here), the sign can be determined as a matter of inspection. In other cases, a calculation will first have to be carried out.

The commonly misunderstood distinction between 'heat' and 'temperature' often first becomes an issue in the context of calorimetry. Our data support a widely reported finding: students' belief that these terms are essentially synonymous is not easily dislodged. We suggest that the realm of physical calorimetry, i.e., where physical changes only are involved, offers the best opportunity to clarify the distinction between heat and temperature. Numerous curricular approaches have been developed to achieve this goal (e.g., McDermott 1996). Once the complication of a chemical reaction is introduced, analysis of the system becomes considerably more challenging. We suggest therefore that the heat-temperature distinction is best treated before reaction energetics is introduced.

It is important to counter students' tendency to misunderstand the meaning of the mass m in the relationship $q = mc\Delta T$. Most commonly, students' errors reflected a misapprehension that the mass m referred only to the reacting species, and not to the entire quantity of material that was undergoing the temperature change. One must help students understand that in the equation $q = mc\Delta T$ the temperature change ΔT is that of the entire contents of the calorimeter, and so the mass m, the specific heat c, and the heat absorbed q must also refer to that contents.

The key to understanding energy changes in chemical systems is that reaction energies result from the breaking and forming of chemical bonds. In calorimetry, energy flows into or out of an aqueous solution as a result of bonds forming and breaking. In a physical system, by contrast, energy flows from a hotter object (such as a piece of hot metal) into a cooler object (a water solution, for instance). No changes in chemical bonds are involved. There is evidence both from the present study, and in the research literature, that confusion on this concept may be widespread among introductory students. The serious misconception expressed by Sophia that energy is transferred from one of the reacting species to the other may well underlie errors made on such questions as the meaning of 'system' and 'surroundings', and the temperature change resulting from a system that contains only half of the original quantity of reactant solutions. Because of the central importance of this issue, we will discuss it in some detail.

Martins and Cachapuz (1993) interviewed both high school and college chemistry students in Portugal to determine how they would explain the temperature increase observed in a water solution when a piece of sodium metal is placed in it. The most popular explanation was that energy was being transferred from the sodium to the water: '. . . the sodium gives out energy and the water takes in that energy . . . it becomes hotter . . .' (This is virtually the same explanation given by Sophia in the case of Mg and HCl.) In an earlier study Cachapuz and Martins (1987) had found that students often invoke a 'principle reactant' explanation in which one of the reactants plays a more important role than the others. (Similarly, Brosnan (1992) has suggested that students view chemical reactions as being caused by an active agent acting on a passive substance.) What is missing from these explanations is an appreciation of the central role of the breaking and forming of chemical bonds, and the associated absorption and release of energy, respectively.

Boo (1998) and Boo and Watson (2001) interviewed Grade 12 students in the UK to elicit their understanding of, among other things, the system in which magnesium is added to dilute hydrochloric acid and the temperature of the solution is observed to increase. They found that only a small minority (15%) of the students were able to give an explanation based on understanding that the bonds being made in the reaction are stronger than those which are being broken, and that therefore there is a net release of energy from the reaction, into the solution. A majority of the students were under the impression that bond making requires input of energy and bond breaking releases energy (i.e., the exact opposite of the chemist's view), or instead that both the processes of bond breaking and bond making required the input of energy. That this is a common belief was also noted by Ross (1993) and (in South Africa) by Ebenezer and Fraser (2001). Barker and Millar (2000) collected questionnaire data from UK students several months after they had completed the General Certificate of Secondary Education exams. They found only a very small proportion of students (about 10%) with a full or partial understanding of the basic energetics of chemical reactions, including an understanding of the role of bond breaking and formation. Several authors cited here have pointed out that confusion on this concept may be aggravated by the common notion that 'energy is stored in chemical bonds'.

A grasp of the law of conservation of energy and of the energetics associated with bond breaking and bond making plays a fundamental role in student understanding of chemical reactions and thermochemical phenomena (Boo 1998, Barker and Millar 2000, and references therein). The findings of the various investigators cited above, as well as our own – thereby representing four different countries – are rather striking in their consistency. It seems that students in widely disparate settings encounter a common set of conceptual difficulties related to the energetics of chemical reactions. We suspect that significant curricular enhancements and additional instructional time will be needed to improve student learning of these important concepts. Barker and Millar (2000), for instance, report very significant improvements in student learning of these concepts with the SAC curriculum, in which the exothermicity of bond formation is given explicit, extended attention. We have developed both tutorial worksheets and a computer animation[1] that guide students to confront very directly these conceptual difficulties, and we are in the process of assessing the effectiveness of these materials.

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Note

[1] http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/animations/index.htm

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