Investigations of Student Learning in Thermochemistry and Thermal Physics

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Outline

1. The physics/chemistry connection
2. Difficulties with concept of state function
3. Conceptual confusion regarding free energies
4. Learning of thermochemical concepts in the context of calorimetry

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Students' Evolving Concepts of Thermodynamics

- Most students study thermodynamics in chemistry courses before they see it in physics
  - at Iowa State: ≈ 90% of engineering students
- Ideas acquired in chemistry may impact learning in physics
- Certain specific misconceptions are widespread among chemistry students

Initial Hurdle:

Different approaches to thermodynamics in physics and chemistry

- ***For physicists:***
  - Primary (?) unifying concept is transformation of ***internal energy E*** of a system through heat absorbed and work done;
  - Second Law analysis focuses on ***entropy*** concept, and analysis of cyclical processes.

- ***For chemists:***
  - Primary (?) unifying concept is ***enthalpy H [H = E + PV]*** (ΔH = heat absorbed in ***constant-pressure*** process)
  - Second law analysis focuses on ***free energy*** (e.g., Gibbs free energy G = H – TS)

Conceptual Minefields Created in Chemistry

- The state function enthalpy [H] comes to be identified in students' minds with *heat in general,* which is *not* a state function.

  [$H = E + PV$; ΔH = heat absorbed in ***constant-pressure*** process]

- Contributions to ΔE due to work usually neglected; gas phase reactions de-emphasized

- The distinction between H and internal energy E is explicitly downplayed (due to small proportional difference)

- Sign convention different from that most often used in physics: $\Delta E = Q + W$ (vs. $\Delta E = Q - W$)

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Initial Objectives:
Students' understanding of "*state functions*" and First Law of Thermodynamics

*Diagnostic Strategy: Examine two **different** processes leading from state "A" to state "B":*

Administered in General Chemistry course, Fall 2000
(N = 532)

Consider the following two processes, #1 and #2:

Process #1:

$A + B \rightarrow C + D$
$\underline{C + D \rightarrow G + H}$
Net: $A + B \rightarrow G + H$

Process #2:

$A + B \rightarrow E + F$
$\underline{E + F \rightarrow G + H}$
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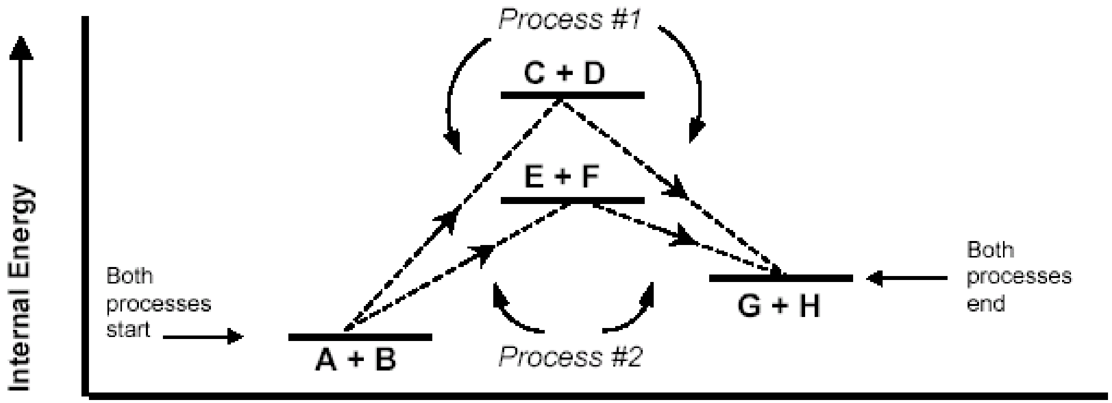

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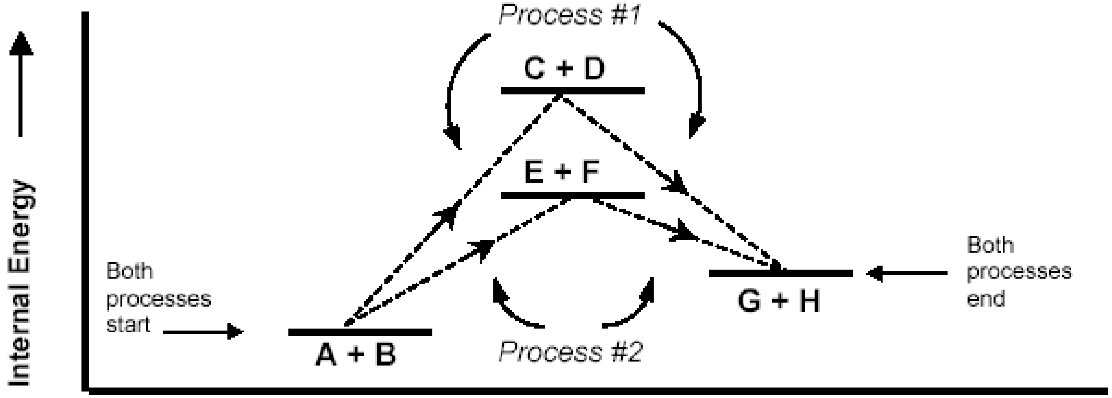

The reactants (**A** and **B**) and the products (**G** and **H**) are ***identical*** in both cases and are in ***<u>identical states</u>***. [**A** + **B**] is the initial state for ***both*** processes #1 and #2, while [**G** + **H**] is the final state for both processes. **However**, the ***intermediate*** reactions are different.

Here we will assume that **<u>the total heat absorbed by the system during Process #1 is larger than the total heat absorbed by the system during Process #2.</u>** *Note that these are* ***not*** *constant-pressure processes,* ***nor*** *are they constant-volume processes; in other words,* ***both*** *the pressure* ***and*** *the volume may vary during each process.*

➡ *Note: The* ***"net change"*** *in a quantity "ΔM" means how much "M" changes from the beginning (initial state) to the end (final state) of a process:*

$$\boxed{\Delta M = M_{final} - M_{initial}}$$

1) *[one point]* Is the ***net change*** in temperature of the system ΔT during Process #1 *greater than, less than,* or *equal to* the ΔT during Process #2?

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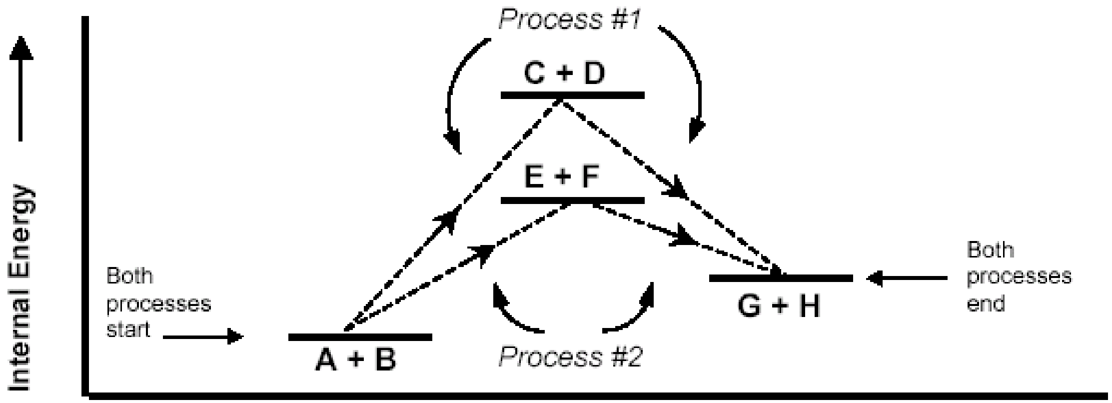

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equal to, *because both processes share the same initial and final states*

Results of Chemistry Diagnostic:

Is the net change in [(a) temperature ΔT; (b) internal energy ΔE] of the system during Process #1 ***greater than, less than,*** *or* ***equal to*** *that for Process #2?*

[*N* = 532]

ΔT during Process #1 is:

greater than: …….48%
less than:…………..3%
➡ **equal to:…………..47%**

ΔT for Process #2.

Consider the following two processes, #1 and #2:

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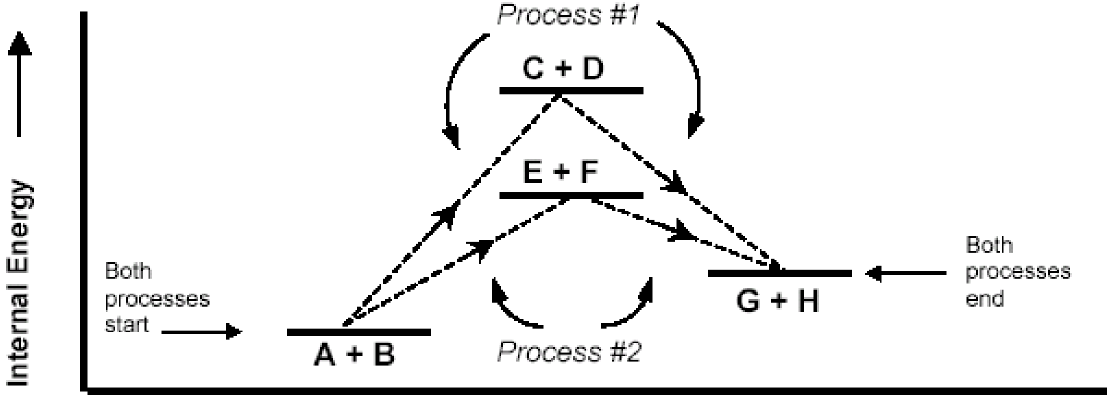

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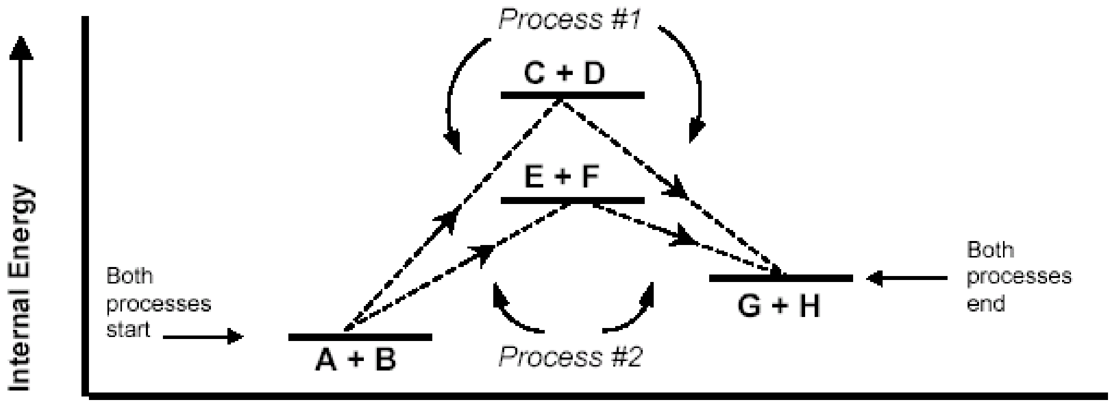

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2) *[one point]* Is the ***net change*** in internal energy of the system ΔE during Process #1 *greater than, less than,* or *equal to* the ΔE during Process #2? Explain your answer.

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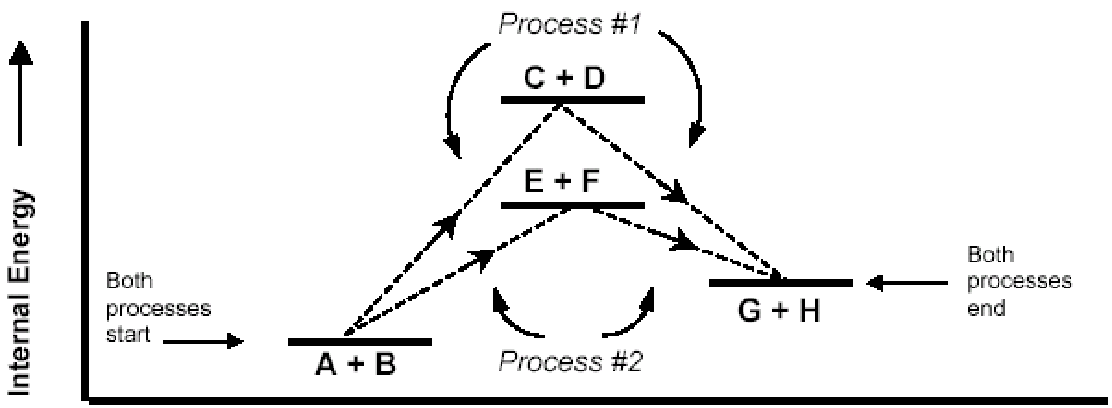

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> ***equal to,*** *because both processes share the same initial and final states. The fact that the ΔE's are equal can also be read directly off of the diagram*

Results of Chemistry Diagnostic:

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[*N* = 532]

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greater than: …….48%
less than:…………...3%
➡ equal to:…………..47%

ΔT for Process #2.

ΔE during Process #1 is:

greater than: …….30%
less than:…………..2%
➡ equal to:…………..66%

ΔE for Process #2.

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} ΔT **for Process #2.**

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greater than: ……..30%
less than:…………….2%
➡ **equal to:…………..66%**

} ΔE **for Process #2.**

Students answering correctly that *both* ΔT *and* ΔE are equal: *33%*

Results from Chemistry Diagnostic

[*Given in general chemistry course for science majors, Fall 2000, N =532]*

- 66% of students recognized that change in internal energy was same for both processes.
  - But many students fail to grasp meaning of diagram

- Only 47% of students recognized that change in temperature must be the same for both processes (since initial and final states are identical).

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Previous Investigations of Learning in Chemical Thermodynamics

(upper-level courses)

- A. C. Banerjee, “Teaching chemical equilibrium and thermodynamics in undergraduate general chemistry classes,” J. Chem. Ed. **72**, 879-881 (1995).

- M. F. Granville, “Student misconceptions in thermodynamics,” J. Chem. Ed. **62**, 847-848 (1985).

- P. L. Thomas, and R. W. Schwenz, “College physical chemistry students’ conceptions of equilibrium and fundamental thermodynamics,” J. Res. Sci. Teach. **35,** 1151-1160 (1998).

Student Understanding of Entropy and the Second Law of Thermodynamics in the Context of Chemistry

- Second-semester course; covered standard topics in chemical thermodynamics:
  - Entropy and disorder
  - Second Law of Thermodynamics:

$$\Delta S_{universe}\ [= \Delta S_{system} + \Delta S_{surroundings}] \geq 0$$

  - Gibbs free energy: $G = H - TS$
  - Spontaneous processes: $\Delta G_{T,P} < 0$

- Written diagnostic administered to 47 students (11% of class) last day of class.

- In-depth interviews with eight student volunteers

Students' confusion: apparently conflicting criteria for spontaneity

- $\Delta G_{T,P} < 0$ criterion, and equation $\Delta G = \Delta H - T\Delta S$, refer only to properties of the ***system;***

- $\Delta S_{universe} > 0$ refers to properties ***outside*** the system;

→ *Consequently, students are continually confused as to what is the "system" and what is the "universe," and* ***which one*** *determines the criteria for spontaneity.*

Student #2: I assume that ΔS [in the equation $\Delta G = \Delta H - T\Delta S$] is the total entropy of the system and the surroundings.

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Student #3: " . . . I was just trying to recall whether or not the surroundings have an effect on whether or not it's spontaneous."

Student #2: I assume that ΔS [in the equation $\Delta G = \Delta H - T\Delta S$] is the total entropy of the system and the surroundings.

Student #3: " . . . I was just trying to recall whether or not the surroundings have an effect on whether or not it's spontaneous."

Student #6: "I don't remember if both the system and surroundings have to be going generally up . . . I don't know what effect the surroundings have on it."

Overall Conceptual Gaps

- There is no recognition of the fact that change in G of the ***system*** is directly related to change in S of the ***universe*** (= ***system*** **+** ***surroundings***)

- There is uncertainty as to whether a spontaneous process requires entropy of the ***system*** or entropy of the ***universe*** to increase.

- There is uncertainty as to whether $\Delta G < 0$ implies that entropy of the ***system*** or entropy of the ***universe*** will increase.

Lack of awareness of constraints and conditions

- There is little recognition that ΔH equals *heat absorbed* ***only*** for constant-pressure processes

- There appears to be no awareness that the requirement that $\Delta G < 0$ for a spontaneous process only holds for ***constant-pressure, constant-temperature*** processes.

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Learning of Thermochemical Concepts in Context of Calorimetry

T. J. Greenbowe and D. E. Meltzer, Int. J. Sci. Educ. *25, 779 (2003)*

- Investigated students' misunderstanding of role of bond breaking and forming in determining heats of reaction
  - *belief that heat flows <u>from</u> one reactant <u>to</u> the other*
- Uncovered students' misinterpretation of role of mass in relationship $Q = mc\Delta T$
  - *tendency to associate "*m*" with reactants only, instead of with total mass undergoing temperature change*

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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.

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Calorimetry Problem on Final Exam

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.

Calculate the heat of reaction (in kJ).

Very similar question included on second hour exam

Solution to Final Exam Question

$$m = \rho V = (1.00\,\mathrm{g/\,mL})\left(2\times 10^{3}\,\mathrm{mL}\right) = 2\times 10^{3}\,\mathrm{g}$$

$$\begin{aligned} q_{soln} &= mc\Delta T \\ &= \left(2\times 10^{3}\,\mathrm{g}\right)\left(4.18\,\mathrm{J/\,g{-}^{\circ}C}\right)\left(+6.2^{\circ}\mathrm{C}\right) \\ &= +52\,\mathrm{kJ} \end{aligned}$$

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

Responses on Heat of Reaction Questions

	Second Hour Exam	**Final Exam**
	$n = 185$	$n = 207$
Correct or nearly correct magnitude of q_{rxn}	50%	40%
Errors using formula		
Set $q = \Delta T$ (or $q = T$)	8%	5%
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%

Difficulties with Calorimetry Problems

- Most students did not provide correct sign (negative) for heat of reaction in this exothermic process.
- About 15-20% of students did not realize the need to use $q = mc\Delta T$.
- About 25% of all students did not realize that mass m refers to total mass of solution in container.

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Examples from Interviews

Q: *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.

***Q:** 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.

Examples from Interviews

Sophia: …say we had the magnesium and we pour $HCl(aq)$ on it. I would then know where one thing is going to the other.

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Examples from Interviews

Sophia: …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.

Examples from Interviews

Q: *What is this* q*?* [heat of reaction produced during reaction of magnesium metal and hydrochloric acid]

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.

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Other Reports of Student Difficulties Regarding Bond Breaking and Forming

- Martins and Cachapuz (1993): high-school and college chemistry students in Portugal
- Boo (1998) and Boo and Watson (2001): Grade 12 students in UK
- Barker and Millar (2000): high-school graduates in the UK
- Ebenezer and Fraser (2001): university engineering students in South Africa

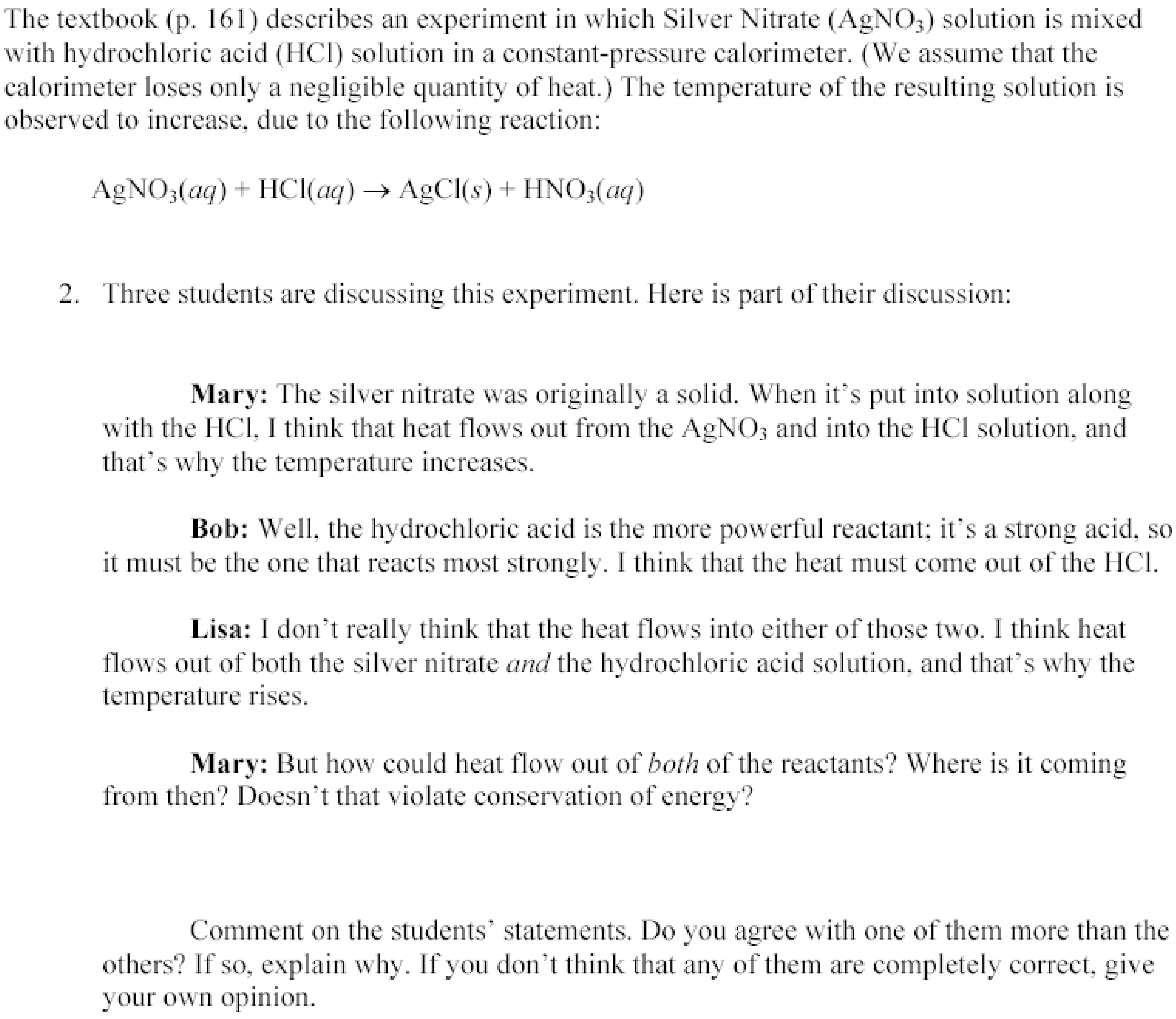
Thermochemistry Instructional Strategy

"Elicit, Confront, Resolve"

(Model developed by University of Washington Physics Education Group)

- Elicit students' explanations for source of heats of reaction.
- Allow students to grapple with common misconception that heat of reaction arises through heat flow ***from*** one reactant ***to*** another.
- Guide students to resolve discrepancies by using concept of bond forming and breaking.

Thermochemistry Tutorial



The textbook (p. 161) describes an experiment in which Silver Nitrate ($AgNO_3$) solution is mixed with hydrochloric acid (HCl) solution in a constant-pressure calorimeter. (We assume that the calorimeter loses only a negligible quantity of heat.) The temperature of the resulting solution is observed to increase, due to the following reaction:

$$AgNO_3(aq) + HCl(aq) \rightarrow AgCl(s) + HNO_3(aq)$$

2. Three students are discussing this experiment. Here is part of their discussion:

Mary: The silver nitrate was originally a solid. When it's put into solution along with the HCl, I think that heat flows out from the $AgNO_3$ and into the HCl solution, and that's why the temperature increases.

Bob: Well, the hydrochloric acid is the more powerful reactant; it's a strong acid, so it must be the one that reacts most strongly. I think that the heat must come out of the HCl.

Lisa: I don't really think that the heat flows into either of those two. I think heat flows out of both the silver nitrate *and* the hydrochloric acid solution, and that's why the temperature rises.

Mary: But how could heat flow out of *both* of the reactants? Where is it coming from then? Doesn't that violate conservation of energy?

Comment on the students' statements. Do you agree with one of them more than the others? If so, explain why. If you don't think that any of them are completely correct, give your own opinion.

Excerpt from Worksheet

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During this reaction, does energy flow *into* the resulting solution (if so, where did the energy come from?), *out of* the solution (if so, where did it go?), or is there *no net flow of energy* into or out of the solution (if so, how do you know?).

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Summary

- In our sample, most introductory students in both chemistry and physics courses had inadequate understanding of fundamental thermodynamic concepts.
- Curriculum development will probably need to target very basic concepts in order to be effective.
- Interaction between chemistry and physics instruction on development of understanding of thermodynamics merits additional study.