Students' Conceptual Difficulties in Thermodynamics for Physics and Chemistry:
Focus on Free Energies

David E. Meltzer
Department of Physics and Astronomy
Iowa State University
Ames, Iowa

Supported by Iowa State University Miller Faculty Fellowship
and by National Science Foundation grant DUE #9981140

Collaborator

Thomas J. Greenbowe
Department of Chemistry
Iowa State University

Our Goal: Investigate learning difficulties in thermodynamics in both chemistry and physics courses

- First focus on students' ***initial*** exposure to thermodynamics (i.e., in chemistry courses), then follow up with their ***next*** exposure (in physics courses).

- Investigate learning of same or similar topics in two different contexts (often using different forms of representation).

- Devise methods to directly address these learning difficulties.

- Test materials with students in both courses; use insights gained in one field to inform instruction in the other.

Outline

1. The physics/chemistry connection

2. First-semester chemistry:
    - *state functions*
    - *heat, work, first law of thermodynamics*

3. Second-semester physics:
    - *heat, work, first law of thermodynamics*
    - *cyclic process*

4. Second-semester chemistry:
    - second law of thermodynamics
    - Gibbs free energy

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)

How might this affect physics instruction?

- For many (most?) physics students, initial ideas about thermodynamics are formed during ***chemistry*** courses.

- In chemistry courses, a particular state function (enthalpy) comes to be identified -- in students' minds -- with ***heat in general***, which is ***not*** a state function.

Sample Populations

- ***CHEMISTRY*** *[N = 426]:* Calculus-based course; first semester of two-semester sequence. *Written diagnostic administered after completion of lectures and homework regarding heat, enthalpy, internal energy, work, state functions, and first law of thermodynamics; also, small number of student interviews.*

- ***PHYSICS*** *[N = 186]:* Calculus-based course; second semester of two-semester sequence. *Written diagnostic administered after completion of lectures and homework regarding heat, work, internal energy, state functions, and first law of thermodynamics.*

Initial Research Objective: How well do students understand the "*state function*" concept?

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

- What is the *same* about the two processes?
- What is *different* about the two processes?

- How well do students distinguish between changes in ***state functions*** such as internal energy (same for any process connecting states A and B), and ***process-dependent quantities*** (e.g., heat [Q] and work [W])?

- Can students identify temperature as a prototypical state function?

Results of Chemistry Diagnostic:
Question #1a and 1b

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

DT **during Process #1 is:**

greater than: …….61%
less than:…………..3%
equal to:…………..34%

DT **during Process #2.**

DE during Process #1 is:

greater than: …….51%
less than:…………..2%
equal to:…………..43%

DE **during Process #2.**

Students answering correctly that <u>*both*</u> DT *and* DE are equal: ***20%***

Common Basic Misunderstandings (chemistry students)

- No clear concept of ***“state”*** or ***“state function”***
- No clear idea of what is meant by ***“net change”***
- Difficulty interpreting standard diagrammatic representations
- Association of ***“enthalpy”*** with ***“heat”*** even when pressure is ***not*** constant

Most common errors

(chemistry students)

- Do not recognize that work done ***by*** the system is equal to $P\Delta V$ (≈ 70%)
- Do not recognize that work done ***on*** the system is ***negative*** if $P\Delta V > 0$ (≈ 90%)
- Are unable to make use of the relation between Q, W, and ΔE (i.e., First Law of Thermodynamics) (≈ 70%)
- Believe that $W \propto \Delta E$ regardless of ΔV (≈ 40%)
- Believe that $Q \propto \Delta E$ regardless of ΔV (≈ 40%)
- Believe that $Q \propto \Delta V$ regardless of ΔE (≈ 20%)

Results of Physics Diagnostic: *Question #1*

Is W for Process #1 ***greater than, less than,*** *or* ***equal to*** *that for Process #2?* **[Answer: greater than]**

Greater than:	**73%**
Less than:	**2%**
Equal to:	**25%**

[25% of the class cannot recognize that ***work done by the system*** depends on the process, or that *"work equals area under the p-V curve."]*

Results of Physics Diagnostic: *Question #2*

Is Q for Process #1 ***greater than, less than,*** *or* ***equal to*** *that for Process #2?* **[Answer: greater than]**

Greater than: 56%

Less than: 13%

Equal to: 31%

[Most students who answer ***“equal to”*** explicitly state that ***heat absorbed by the system*** is ***independent*** of the process]

Results of Physics Diagnostic: *Question #3*

Can you draw another path for which Q is larger than either Process #1 or Process #2? **[Answer: Yes]**

Yes [and draw correct path with <u>correct</u> explanation]: …15%

Yes [and draw correct path with incorrect explanation]: . 36%

Yes [and draw incorrect path]: ………………………15%

No, not possible: ……………………………29%

No response: ………………………………….6%

Most common errors

(physics students)

- Q and/or W are path independent (≈ 30%)
- larger pressure Þ larger Q (≈ 15%)
- Q = W [*or :* $Q \propto W$ *]* (≈ 15%)
- Q = -W (≈ 10%)

Summary results of preliminary study

- Most first-semester chemistry students in our sample lack rudimentary understanding of thermodynamic concepts.

- Most physics students in our sample ***either*** (1) misunderstand *process-dependent* nature of work and/or heat, ***or*** (2) do not grasp process-*independent* nature of ΔE $(= Q - W)$, ***or both (1) and (2).***

Follow-up study: Second-semester Chemistry students

- Course covered standard topics in chemical thermodynamics:
  - Entropy and disorder
  - Second Law of Thermodynamics: $\Delta S_{universe}$ [= $\Delta S_{system} + \Delta S_{surroundings}$] ≥ 0
  - Gibbs free energy: $G = H - TS$
  - Spontaneous processes: $\Delta G_{T,P} < 0$
  - Standard free-energy changes
- Written diagnostic administered to 47 students (11% of class) last day of class.
- In-depth interviews with eight student volunteers

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 Interviews

- Eight student volunteers were interviewed within three days of taking their final exam.
- The average course grade of the eight students was above the class-average grade.
- Interviews lasted 40-60 minutes, and were videotaped.
- Each interview centered on students “talking through” a six-part problem sheet.
- Responses of the eight students were generally quite consistent with each other.

Students' Guiding Conceptions
(what they "know")

- DH is equal to the heat absorbed by the system.
- "Entropy" is synonymous with "disorder"
- Spontaneous processes are characterized by increasing entropy
- $DG = DH - TDS$
- DG must be ***negative*** for a spontaneous process.

Difficulties Interpreting Meaning of "ΔG"

- Students often do ***not*** interpret "$\Delta G < 0$" as meaning *"G is **decreasing**"* (nor "$\Delta G > 0$" as *"G is **increasing**"*)

- The expression "ΔG" is frequently confused with "G"
  - *"DG < 0" is interpreted as "G is negative," therefore, conclusion is that **"G must be negative for a spontaneous process"***
  - *Frequently employ expression **"DG [or DS] is becoming more negative"** (or "more positive")*

Examples from Interviews

Q: *Tell me again the relationship between G and "spontaneous"?*

Student #7: I guess I don't know, necessarily, about *G*; I know ΔG.

Q: *Tell me what you remember about ΔG.*

Student #7*:* I remember calculating it, and then if it was negative then it was spontaneous, if it was positive, being nonspontaneous.

Q: *What does that tell you about G itself. Suppose ΔG is negative, what would be happening to G itself?*

Student #7: I don't know because I don't remember the relationship.

Student Conception: If the process is spontaneous, *G* must be ***negative.***

Student #1: If it's spontaneous, *G* would be negative . . . But if it wasn't going to happen spontaneously, *G* would be positive. At equilibrium, *G* would be zero . . . if *G* doesn't become negative, then it's not spontaneous. As long as it stays in positive values, it can decrease, but [still be spontaneous].

Student #4: Say that the Gibbs free energy for the system before this process happened . . . was a negative number . . . [then] it can still increase and be spontaneous because it's still going to be a negative number as long as it's increasing until it gets to zero.

Students' confusion:
apparently conflicting criteria for spontaneity

- $DG_{T,P} < 0$ criterion, and equation $DG = DH - TDS$, refer only to properties of the ***system****;*

- $DS_{universe} > 0$ 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 DS [in the equation $DG = DH - TDS$] 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.”

Difficulties related to mathematical representations

- There is confusion regarding the fact that in the equation $DG = DH - TDS$, all of the variables refer to properties of the ***system*** (and not the surroundings).

- Students seem unaware or unclear about the definition of DG (i.e., $DG = G_{final} – G_{initial}$)

- There is great confusion introduced by the definition of *standard free-energy change of a process:*

$$\Delta G^{\circ} = \sum n \, \Delta G_{f}^{\circ}(\text{products}) - \sum m \, \Delta G_{f}^{\circ}(\text{reactants})$$

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.

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.

Summary

- In our sample, the ***majority*** of students held incorrect or confused conceptions regarding ***fundamental*** thermodynamic principles following their introductory courses in physics and chemistry.

- The tenacity and prevalence of these conceptual difficulties suggest that instruction must focus sharply upon them to bring about significant improvements in learning.