Project Description

Results from Prior NSF Support: David Meltzer has received NSF support for three projects during the past five years, all related to the development of an elementary physics course targeted at education majors and other nontechnical students. (See Biography section for grant numbers and titles.) These projects involved the development and testing of a one-semester activity-centered elementary physics course based on “guided inquiry” instructional methods, given at Southeastern Louisiana University (SLU). Students’ preexisting ideas regarding physical phenomena were determined by pretesting. The pretests formed the basis for a thorough class discussion of the predictions made by students regarding the outcome of various experiments. Investigations to test their predictions were carried out by the students, working in groups of three or four, through guided “mini-research-projects.” Class discussions then centered around the results of the student investigations, making comparisons to the predictions.

The bottom-line result of these projects may be succinctly stated: Before 1994, ***virtually no*** presecondary education majors ever set foot in a physics class at SLU. In the 1997-98 academic year, by contrast, ***twenty-one*** education majors (and eight other nontechnical students) successfully completed this physics course at SLU, with significant learning gains as documented by rigorous assessment, and an ***overwhelmingly positive student response.*** (All students had elected to take this nonrequired course, prompted by recommendations from advisors and fellow students.) An independent study prepared for the NSF’s Division of Undergraduate Education described this project as “very successful” (Whalen, Noonan and Hayes, 1996).

These anonymous comments from students in the Fall, 1997 class tell the story well: “The atmosphere is very laid back and happy. Great class. I loved it”; “I feel I learned a lot about physics. I had ***never*** had any type of physics until now!! Thanks!!!"; "I enjoyed the class. I am glad that I took it. I can now say that I successfully finished a physics class"; "Physics was made interesting and put on a level that could be understood"; "I enjoyed the activities . . . I liked finding out our own answers"; "I really enjoyed this class. I have found many activities I can use when I begin teaching . . ."

Thomas Greenbowe has worked under two contracts with the National Science Foundation during the last five years. One DUE-ILI grant allowed ISU chemistry faculty to work collaboratively with twelve Iowa community colleges and five Iowa private colleges to obtain FT-IR instruments, and to create a mechanism for sending samples to ISU to be run on their NMRs and place the electronic version of the NMR spectra on a WWW site where students could download their sample's spectra. The other grant is a DUE-CCD grant under the "Adapt and Adopt" program. Started one year ago, this grant allows ISU chemistry faculty to work collaboratively with twelve Iowa community colleges and five Iowa private colleges to implement any one of the five NSF systemic curriculum reform chemistry projects in their classrooms. Project leaders from each of the five projects conduct summer workshops for Iowa's chemistry faculty. ISU hosts meetings using the Iowa Communications Network to help faculty with any problems or concerns that arise when they implement these new approaches.

Project Overview: This is a "proof-of-concept" project to create new curricular materials for the study of thermodynamics, which would have a direct impact on instruction both in physics and chemistry at the introductory and intermediate (junior) level. We are in a particularly good position to undertake this development project at Iowa State University, because we are able to combine the capabilities of both the Physics Education Research Group (led by D. Meltzer) and the Chemistry Education Research Group (led by T. Greenbowe). By targeting the subject of thermodynamics – a field that lies precisely on the borderline between Physics and Chemistry – we will be able to bring to bear the extensive experience of both of our groups. Over a two-year period we will create new instructional materials that will be of immediate use both in Physics courses (General Physics, and Intermediate Thermodynamics) and Chemistry courses (such as General Chemistry and Physical Chemistry). Due to the fundamental nature of thermodynamics we expect that the materials will have even broader usage, for example in the engineering curriculum where thermodynamics is a basic subject for mechanical and chemical engineers, and for those in the materials science and engineering program. We have already received support from ISU for preliminary work on this project through a Miller Faculty Fellowship grant for $25,000 awarded in April 1999 to both Project Directors.

Goals and Objectives: The motivation for the creation of these new materials is the now very extensive research base into student learning both in introductory chemistry and introductory physics at the university level. An increasing body of evidence suggests that instruction utilizing ***only*** lecture classes and standard recitations and labs results in relatively small increases in ***most*** students' understanding of fundamental concepts (Brooks, 1984; Barrow, 1991; Black, 1993; Hestenes, Wells, and Swackhamer, 1992; Hake, 1998). It has been pointed out by many experienced researchers that complex scientific concepts are often not effectively communicated to students simply by lecturing about them – however clearly and logically the concepts may be presented (e.g., McDermott, 1991; Redish, 1994; Wells, Hestenes, and Swackhamer, 1995; Arons, 1997). For one thing, students taught exclusively through lecture-based curricula are inclined to short-circuit the highly complex scientific thought process (Reif, 1995). In other words, students do not absorb physics and chemistry concepts simply by being told (***or*** shown) that they are true. They must be guided continually to challenge their present state of understanding, and to resolve conceptual confusion through some process of "active engagement."

By providing new research-based curriculum materials for these courses, using a design model shown to be effective through extensive research (described below), this project will, potentially, significantly strengthen introductory and foundation courses both in Physics and Chemistry. Because the development of these materials is an integral part of the research program carried out by the Physics and Chemistry Education Research Groups, this project develops new programmatic connections between undergraduate curriculum, and the research activities of the faculty. These materials are specifically designed to be used by students working in collaborative groups of two, three, or four – either in "recitation" sections, or during the lecture presentation itself. In this way, they provide small-group learning experiences for first-year students enrolled in the introductory sequences in Physics and Chemistry. By combining the resources of the Departments of Physics and Astronomy, and of Chemistry, this project promotes interdisciplinary collaboration for undergraduate curriculum development. The materials, both in their creation and further refinement, depend directly on student outcomes assessment, in the form of pre- and post-testing utilizing conceptual understanding diagnostics, as well as clinical interviews to assess student learning.

Detailed Project Plan: The specific project we are proposing to carry out is the creation of materials for the study of thermodynamics – both at the elementary and intermediate level – in what is usually called an "active-learning" classroom. In such a classroom, students are required to carry out tasks designed to ***actively*** engage their creative abilities, far beyond merely sitting in a chair and listening to an instructor or teaching assistant. For instance, the students might explore phenomena using lab equipment, or work in groups to solve simple problems posed by the instructor. The materials we plan to develop can be described as guided-inquiry problem sets. These are *not* the same type as those found as end-of-chapter problems in physics and chemistry textbooks. Rather, they are carefully designed both to elicit common student difficulties regarding the subjects under study, and then to lead students to confront these difficulties head-on with a tightly focused and strategically sequenced series of questions and exercises. An integral feature of these exercises is to require students to explain their reasoning process with short written statements. Finally, in the course of working through these questions and exercises, students are guided to resolve their difficulties and confusion and to attain a firm grasp on the targeted concepts. For simplicity's sake, we will call these materials "worksheets."

Pedagogical models that actively engage students in a process of investigation and discovery – often oriented around activities in the instructional laboratory – have been found to be effective in improving students' conceptual understanding of physical principles (Thornton and Sokoloff, 1990, 1998; Hake, 1998; Redish and Steinberg, 1999). The targeted physical concepts are in general not "told" to the students before they have the opportunity to carry out investigations – or follow through chains of reasoning – that might lead them to synthesize the concept on their own. It has been especially challenging to develop effective active-learning materials that do not have the benefit of a simultaneous laboratory component to the instruction.

The instructional model we have described above – known as "elicit, confront, and resolve" – is one that has attained world renown through the decades-long efforts of the Physics Education Group at the University of Washington in Seattle, led by Prof. Lillian McDermott. They have produced the most extensive research-based curricular materials available to date, including the *Tutorials in Introductory Physics* (McDermott, Shaffer, and the Physics Education

Group, 1998). These are designed for the general physics courses (both algebra- and calculus-based), and have been used successfully as the basis of so-called "tutorials" (primarily ***without*** the need for lab equipment), which have partially replaced standard recitations at the University of Washington and elsewhere. In these tutorials, student groups of three or four work through carefully designed worksheets of the type described above. Teaching assistants, instead of lecturing and providing ready-made answers, guide the students with "leading" questions to think through and resolve difficult points. A very extensive body of research has demonstrated the efficacy of these tutorials in increasing student conceptual understanding (e.g. Redish and Steinberg, 1999). Other active-learning materials centered around structured worksheets have been developed and tested by Alan Van Heuvelen (1990a,b; 1991a,b) and others who have been inspired by his work. Van Heuvelen's emphasis is on utilizing "multiple representations" of knowledge – such as "verbal," pictorial, graphical, mathematical-symbolic, etc. – to improve student learning.

Profoundly inspired by the work of McDermott, Van Heuvelen, and their collaborators and followers, the Physics and Chemistry Education Research Groups at Iowa State University have recently embarked on our own separate programs of curriculum development. T. Greenbowe (Co-PI of this proposal) has led development during the past semester of *Tutorials in Introductory Chemistry*, a groundbreaking attempt to begin to do for chemistry that which has been achieved in significant part by McDermott's group for physics. These chemistry tutorials have been tested out successfully during the Fall 1998 semester. Meanwhile, D. Meltzer (PI of this proposal), in collaboration with K. Manivannan at Southeastern Louisiana University, has produced and utilized a *Workbook for Introductory Physics – Electricity and Magnetism*. This *Workbook* has been specifically designed to be useful both in large-enrollment classrooms, and in the algebra-based sequence of introductory physics. Both of these latter features set it apart from most currently available active-learning materials. The *Workbook* has received very enthusiastic reviews from several independent experts solicited by a leading textbook publisher, and is under consideration for publication. It has already been used with great success both at Southeastern Louisiana, and here at Iowa State in the Fall 1998 semester of Phys. 112. All four recitation sections of that course were converted to the "tutorial" model, and both instructor and teaching assistants helped guide student groups as they worked through the worksheet materials.

The materials described above – as well as those to be developed in this project – are designed with a guiding theme. This theme is the premise that the solution of even very simple physics and chemistry problems invariably hinges on a lengthy chain of concepts and reasoning, much of which is often glossed over, or which is simply unstated "tacit" knowledge gained through experience (Reif, 1995). Worksheet activities guide the student to lay bare these chains of reasoning. They help students construct in-depth understanding of physical concepts through step-by-step confrontation with conceptual "sticking points" and counterintuitive ideas. One has to illuminate in a stark and glaring light, so to speak, the phases in the student's thought process where the concept is lacking, so that in the student's own mind the gap to be filled by the missing concept is clearly sensed. Then, the eventual synthesis of the concept by the student becomes ***dramatically*** apparent to them.

This is accomplished through carefully linked sequences of activities that first lead the student to confront the conceptual difficulties, and then to resolve them. The strategy is to break down complex physical problems into conceptual elements, allowing students to grapple with each one in turn, and then returning to synthesize a unifying perspective. Frequently, we return to re-explore difficult concepts in varied contexts, in order to reinforce students' understanding and confidence.

Nearly all topics treated in intermediate-level courses both in thermodynamics and physical chemistry have yet to be addressed by the type of curriculum reform outlined here. (A rather different approach by R. Chabay and B. Sherwood will soon be in press.) Our proposal is to create an integrated set of worksheet "tutorial" materials, which eventually will be synthesized into a full-scale workbook. This workbook will then be ready for use in several different courses both in physics and chemistry. As a practical matter – due to differences in notation commonly used in chemistry and physics, etc. – it will probably be necessary to create two separate "tracks." That is, the final workbook might have a "Physics" track and a "Chemistry" track, or it might actually be necessary to create two separate (though closely related) workbooks.

Based on published research regarding learning of concepts in thermodynamics, and our own extensive teaching experience, we will begin to draft sequences of questions and exercises focused on our targeted topics. The material will consist of a tightly linked set of (1) brief textual expositions in highly "interactive" format, (2) multiple-choice, concept-oriented questions for use with classroom communication systems in large classes, (3) structured series of questions that lead students to elicit and then resolve conceptual difficulties, and finally (4) exercises to strengthen understanding. The emphasis throughout will be on qualitative reasoning and mastery of fundamental concepts. A great deal of pictorial, diagrammatic, and graphical material will be incorporated. ***Detailed descriptions of each of these types of materials are given in Appendix A; included in the descriptions are references to lengthy samples of each type, which are provided in Appendices D, E, F, G, and H.***

The development of these initial drafts will be assisted by Graduate Student Research Assistants, one a member of the Physics Education Research Group, and the other a member of the Chemistry Education Research Group. Draft worksheets will be class-tested in recitation sections, labs, and during lecture presentations. Feedback obtained through the class testing will be immediately utilized for revision and redesign. We have already obtained agreement in principle with some of the instructors in the targeted courses to cooperate with the testing of these materials. ***A detailed description of the actual process we have carried out to create some of the sample materials included in this proposal is contained in Appendix B. This provides a model that will guide our future activities as this project evolves.***

The Graduate Student R.A.'s participate in all aspects of this work. They assist in formulating initial drafts, help to test them out in recitation sections, and give input for revisions and rewrites. They help carry out extended "interview" questioning to probe student understanding in depth. They also contribute to the creation of high-quality graphic materials (diagrams, drawings, etc.) that form an integral part of the worksheets. (This is one of the more labor-intensive aspects of this type of curriculum development.)

In addition to graduate student involvement in this work, we will be drawing in selected advanced undergraduate students to participate in the process of testing and assessing the curricular materials. We will focus in particular on students who plan to become high-school physics and chemistry teachers. These students can benefit tremendously by participating in the instructional activities in the tutorial sessions (whether these occur during recitations, labs, or "lectures"). As they walk around the room, listening to students' comments as they work through the materials and providing guidance by asking leading questions, these future teachers will gain first-hand experience with common learning difficulties and strategies for confronting them. As a result, they will be able to make valuable contributions to the curriculum development work by providing insight into student learning difficulties. They will also help in directly monitoring student responses to the new materials. In work at Southeastern Louisiana University (as well as at the University of Washington), this type of participation by undergraduate students has been extremely beneficial to all concerned (as well as being very cost effective.)

The thermodynamics topics to be covered will include all those normally discussed in introductory general physics and general chemistry courses, as well as a core of advanced topics typically covered in junior-level thermodynamics and physical chemistry courses. This is our core list of planned topics (more may be added later):

1. Kinetic theory of gases, ideal gas equation of state, equipartition of energy
2. First law of thermodynamics: heat, work, internal energy and enthalpy
3. Heat Engines, Carnot cycle
4. Entropy and the Second Law of Thermodynamics
5. Free energy, Maxwell's relations; third law of thermodynamics
6. Non-mechanical work: voltaic cells, magnetism
7. Phase transitions, Clausius-Clapeyron equation, Van der Waals theory
8. Chemical potential, phase equilibria, phase rule
9. Gibbs-Duhem equation, colligative properties

With the exception of an introductory section on kinetic theory of ideal gases, our approach will be almost entirely macroscopic. We feel that this is a more accessible approach for most introductory students, and we will not at this time be focusing on the statistical approach to thermodynamics concepts.

Research on Learning Thermodynamics: Although we will take (and in fact already have taken) our starting point from already published research in the extant literature, the fact remains that there has not been a great deal of research on teaching and learning of thermodynamics at the undergraduate level. This is particularly true for advanced (junior) level courses such as Thermal Physics and Physical Chemistry. Erickson (1985) has reviewed a number of studies that demonstrate the great confusion younger students have when trying to distinguish the concepts of heat, temperature, and energy. Tiberghien (1985), in another such review, points out that even after extended instruction on these topics, much confusion remains. Warren (1972) describes similar difficulties among university students. In other studies with university students, van Roon, van Sprang, and Verdonk (1994) have observed difficulties in distinguishing heat as a "process quantity," in contrast to a "state quantity" (i.e., a state function). Rozier and Viennot (1991) have discussed students' difficulties in appreciating and interpreting the fact that thermodynamic quantities are usually functions of ***several*** variables (not just one). In a somewhat similar vein, Gréa and Viard (1995) point out that students generally ignore the ***momentum*** component in phase-space interpretations of the entropy concept. Kesidou and Duit (1993) have given detailed descriptions of German students' (rather confused) interpretations of various thermodynamic concepts. An ongoing series of investigations by the Physics Education Group at the University of Washington (e.g., Heron, 1996; Shaffer, 1997; Loverude et al., 1999; Kautz, et al., 1999) has demonstrated convincingly that students' confusion with concepts in classical ***mechanics*** lies at the root of many learning difficulties related to thermodynamic ideas. Recently, Harrison, Grayson and Treagust (1999) have described students' evolving concepts during use of the "Heat and Temperature" module of the *Physics by Inquiry* curriculum (McDermott et al., 1996) developed at the University of Washington. In the field of chemical thermodynamics, a short but very useful paper by Granville (1985) points out several significant conceptual subtleties that are usually misunderstood by introductory chemistry students.

Evaluation Plan: Central to the development process of these curricular materials is an intensive cycle of ongoing assessment and research, aimed at testing and improving their effectiveness. Conceptual quizzes based on the materials will be given both as pretests and posttests. On these quizzes, students are frequently asked to explain the reasoning they used to arrive at their answers. Along with results from in-class discussions and group work making use of the materials, these provides real-time feedback and allow the repair of unclear or confusing passages, addition of activities (hard or easy as the situation demands), and occasionally thorough rewrites of whole sections. Conceptual diagnostic questions will be presented on midterm and final exams; student answers and written explanations allow comparison with results in previous courses, and with results that have been reported by other researchers in physics and chemistry education. This comparison provides information about the pedagogical efficacy of the curricular materials. ***A detailed description of our evaluation and assessment methods, including examples of ongoing work, is contained in Appendix C. Dr. Barbara Sawrey, Professor of Chemistry at the University of California at San Diego and Vice-Chair for Education, has agreed to serve as an external evaluator for this project. Prof. Sawrey is a leader in the development of multimedia to assist student learning of scientific concepts. In addition, Prof. Lillian C. McDermott and Prof. Paula R. L. Heron of the University of Washington, Seattle, have agreed to consult with us on an informal basis during the course of this project. Prof. Alan Van Heuvelen (Ohio State Univ.) has also agreed to be a consultant.***

Dissemination of Results: We plan three major forms of dissemination: (1) Workshops at conferences of the American Association of Physics Teachers, and American Chemical

Society, in which we will describe the design and methods of use of the materials, and will guide participants through sample activities based on the materials. The PI has already given two AAPT workshops (with a third scheduled for this August) centered around the *Workbook for Introductory Physics – Part I, Electricity and Magnetism* (Meltzer and Manivannan, 1997, 1998). (2) Publications and presentations at conferences in which we discuss the development of our curricular materials, and our assessment of the results of their use. We have given many such presentations related to our previous curriculum development work. (3) Publication and national distribution; we have already discussed our project with acquisitions editors of three major textbook publishers and have received indications of potential interest in publication of our final product. ***Letters from the publishers are included in Appendix I.***

Timeline for the Project:

January 2000 – December 2000: During this period we will complete the work we have already begun on topics covered in introductory courses in general physics and general chemistry, and will begin work on advanced topics normally covered in junior-level courses. During this time, all materials will be extensively and repeatedly tested in labs, recitation sections, and lecture sections of both physics and chemistry courses. We expect to see positive evidence on our various assessments that the materials have resulted in actual learning gains. We will be able to check this by comparing performances of students who use the materials, to those who do not. (This is described in greater detail in Appendix C, Assessment.) We will begin beta testing of the materials by releasing them for use by our collaborators at other institutions, e.g., K. Manivannan (Physics) at Southeastern Louisiana University, and M. Sanger (Chemistry) at the University of Northern Iowa. ***(See letters describing collaborations in Appendix I.)*** We will also begin preliminary dissemination of material for more advanced topics during this year.

During this time, and throughout the rest of the project, we will be giving presentations at professional meetings about our work, and will incorporate some of the materials in workshops we conduct related to our active-learning teaching methods.

January 2001 – December 2001: During this period we will complete our work on the core material for the advanced topics, and will continue testing the material in courses on thermal physics and physical chemistry. One of the PI's will either himself instruct an advanced-level thermodynamics course, or will work closely with the instructor of that course in order to carry out extended testing of the curricular materials. We will seek additional collaborators at other institutions to test individual sections or parts of sections and report back to us about their results. Outside evaluators will examine the materials and our assessment data. We will begin assembling our materials into a preliminary version of a complete Workbook (or two separate Workbooks, one each for physics and chemistry), and we will actively seek out a publisher (or publishers) for the completed work.

Experience and Capabilities of the Principal Investigators: David E. Meltzer, Assistant Professor of Physics, received a Ph.D. in theoretical physics from S.U.N.Y. at Stony Brook in 1985, and carried out postdoctoral research at Oak Ridge National Laboratory, the University of Tennessee in Knoxville, and in the Quantum Theory Project at the University of Florida. He joined the Iowa State University faculty in June 1998 to establish a new group devoted to Physics Education Research. He has served as Principal Investigator on three curriculum-related projects funded by the National Science Foundation, and has served on NSF panels to review grant proposals submitted to the Division of Undergraduate Education. He has taught more than two dozen different physics and math courses at the university level, and has been guest instructor in both middle-school and high-school classes. He has given more than 40 presentations on physics and science education to regional, national, and international audiences, and has led several workshops for other university faculty dealing with new teaching methods. He was the lead author of a widely cited feature article on active-learning strategies in **The Physics Teacher** (**34,** 72, 1996), and of the active-learning *Workbook for Introductory Physics*. In Summer 1998 he was an instructor with the Physics Education Group at the University of Washington in Seattle; there he worked both with undergraduate science majors, and with in-service public school teachers. He has published fifteen research papers and edited five books, mostly related to condensed matter physics.

Thomas J. Greenbowe, Professor of Chemistry, received a Ph.D. in chemistry education from Purdue University in 1983. He joined the faculty at Iowa State University in 1990 as coordinator of the general chemistry program. He works collaboratively with high school chemistry teachers, community college chemistry instructors, and university chemistry and education faculty to improve the introductory chemistry experience and curriculum. He has received grants from the National Science Foundation, the U.S. Department of Education, and the Dwight D. Eisenhower Science and Mathematics Improvement Fund. In 1995 he served as Chair of the American Chemical Society General Chemistry Examinations Committee. Dr. Greenbowe's awards include the 1996 Iowa State University, College of Liberal Arts and Sciences Teaching Excellence Award for Introductory Courses, and the 1994 Wilkinson Award for outstanding undergraduate teaching, Department of Chemistry, Iowa State University. He has over 20 publications related to chemistry education research, including several related to a long-term multimedia curriculum development project for electrochemistry (Greenbowe, 1994; Burke, Greenbowe, and Windschitl, 1998; Sanger and Greenbowe, *in press*).

Appendix A

Question Types Incorporated in the Workbook

I. **"Expository" Material** *(Lecture Notes/Text Material designed in highly interactive format to guide students toward development of concepts)*

An inherent weakness of traditional textbook expositions of physics and chemistry concepts is that, for proper utilization, they require an extremely "active" reader. An active reader continuously probes their own understanding of a concept, for instance by posing their own questions to themselves as they read. The look for unstated assumptions implicit in derivations, carefully work through each step of a derivation or argument, examine alternate lines of reasoning, and continually test the generality of stated results. It has been said that, in a sense, they "interrogate" the text. They are sensitive to areas of their own confusion, and they have the confidence to confront those areas directly.

By contrast, the majority of introductory students are unable to do efficient active reading on their own. They don't know "which questions they need to ask." They require considerable prodding by instructors (aided by appropriate curricular materials), and need frequent hints and confidence boosts (Reif, 1995). In recognition of this problem, we believe that a more explicitly "interactive" style of exposition can be extremely helpful as a supplement (or even, in some cases, as a replacement) for much traditional text material. In this type of exposition, the reader is continually probed with questions, and asked to fill in steps both in qualitative reasoning and in algebraic derivation. (An excellent model of this type of exposition is the text "Electric and Magnetic Interactions" by R. Chabay and B. Sherwood [Chabay and Sherwood, 1995].)

This form of interactive exposition perhaps more closely resembles lecture notes than ordinary text. The intention is to induce all students to carefully work through the material, instead of resorting to merely assimilating chapter summaries as is frequently done. (It is likely that many, if not most students do not read their assigned texts with the care desired by their instructors!)

An example of this type of material is included in Appendix D, Questions #3 and #4 (pp. 35-40), and also in Appendix G

II. **Multiple-Choice Questions for Peer Instruction in Large Classes** *(Structured sequences of multiple-choice questions stressing qualitative, conceptual understanding; for use with classroom communications systems [(e.g., "flash cards" or "Classtalk")] in which instantaneous feedback is obtained from the whole class simultaneously.)*

These questions are designed to form the basis for an initial classroom discussion of a new topic, after its introduction with a brief "mini-lecture" and/or use of the interactive expository material described above. After the initial presentation, a series of multiple-choice questions may be presented for the students to work on and discuss with each other. Students' responses may be solicited either through the use of "flash cards," or with an electronic communication system such as Classtalk.

[With the Flash Card system, each student is given six large cards labeled "A," "B," "C," "D," "E," and "F," which can be held up facing the instructor to signal their answer to a question.

Students may be asked to hold up an "upside-down" letter F, if they do not believe they know the answer. More details are in Meltzer and Manivannan (1996).]

We have successfully used multiple-choice questions with the flash-card system [for topics in Electricity and Magnetism] by requiring students to bring to each class the complete *Workbook for Introductory Physics – Part I*, in which hundreds of such questions are printed. The instructor simply directs the class to a particular sequence of questions relevant to that day's discussion. The questions may be asked and answered in the interactive format described above, in which the students signal their answers to the instructor using flash cards. With this instantaneous, simultaneous feedback from the entire class, the instructor is better able to gauge the students' understanding of the material, and so guide the subsequent presentation and discussion. The sets of questions are designed to be asked in the sequence shown; a question should not be asked until the instructor is confident that the students have an adequate understanding of the answer to the previous questions on the list.

The first few questions are usually fairly easy, in order to build students' confidence. They can usually be answered by most students without needing to consult with each other. As much as possible, pictorial, diagrammatic and graphical questions are included. As the sequence progresses, more challenging questions are introduced. Students may give a "preliminary" answer based on their own thinking, and then be asked to consult with their neighbors to see if they are in agreement. (This is essentially the "Peer Instruction" method of Eric Mazur, 1997. A rather similar approach, with many sample questions, is described in Novak et al., 1999.)

An example of a short multiple-choice sequence is given in Appendix E.

III. Material to Elicit Learning Difficulties *(Questions designed to elicit well-known learning difficulties, and to lead students to confront these difficulties directly.)*

This more challenging type of question is modeled after the "Elicit, Confront, Resolve" model of the University of Washington tutorials. Questions are designed to elicit responses based on learning difficulties identified by research. Students are frequently asked to explain the reasoning behind their answers. They are then guided through a sequence of questions that are designed to help them confront inadequacies in their reasoning. This may be done, for instance, by pursuing an alternative line of analysis, and/or by making use of pictorial or diagrammatic representations of the concept.

An example of this type of material is included in Appendix F, Question #4 (p. 46) and the "Study Sheet for Pre-Lab 14" (pp. 48-49). The objective of these questions is to bring out the well-known confusion between "heat" and "temperature." As was demonstrated during our test administration of these questions during Spring 1999, students frequently give mistaken responses to Question #4. These responses may be based, for instance, on the arguments that "the final temperatures will be the same since the original temperatures were the same," or that "the final temperature will be greater in the case of the denser material since it holds more heat." The sequence of questions in the "Study Sheet" is designed to lead the student to confront these mistaken conceptions.

IV. **Material to Deepen Comprehension:** *(Questions designed to deepen students' understanding of a concept, by presenting concepts in a wide variety of contexts using multiple representations [verbal, mathematical, graphical, diagrammatic, pictorial, etc.])*

This type of question grows out of the work of Alan Van Heuvelen (Van Heuvelen, 1991[a,b]), who was among the first to stress the great utility of multiple representations in physics education. A deeper and more sophisticated understanding of concepts is developed by *varying the context* in which problems are presented. A large number of deeply probing questions are posed to students, involving a wide variety of different contexts and representations. One single concept may form the basis of problems posed in several different physical settings. Each problem may then be expressed in a multitude of distinct representational forms, e.g.,

a) with heavy use of mathematical symbols and equations;

b) with use of drawings and diagrams [free-body, vector, etc.];

c) using graphs and bar charts;

d) in "natural language" form, as a story using everyday language without technical terms; etc. (e.g., the "context-rich" problems described by Heller and Hollabaugh, 1992).

Alternatively, the problem may be posed in only one way and the *student* required to produce the additional forms of representation.

Examples of this type of material are interspersed throughout the appendices.

V. **Material to Improve Quantitative Problem Solving Ability** *(Questions designed to improve students' problem-solving abilities, by "conceptually dissecting" quantitative problems and breaking them up into conceptual elements.)*

This type of "conceptual dissection" problem was discussed in the *Physics Teacher* paper by Meltzer and Manivannan (Meltzer and Manivannan, 1996). The objective is both to test and strengthen students' understanding of typical quantitative problems. Often, students will solve such problems with a memorized algorithm. The "conceptual dissection" technique forces them to think through the problem in great detail, to ensure that they grapple with all of the concepts relevant to its solution. In this way, even fairly complicated problems may be made conceptually accessible to students who might otherwise feel compelled to resort to formulaic techniques.

An example of this type of problem is included as Appendix H.

Appendix B

Testing and Improving the Curriculum: An Iterative Process

To illustrate our method for maximizing the effectiveness of the curricular materials, we'll describe the actual process used to produce the preliminary version of the "Chemical Thermodynamics" section included as Appendix D.

1. **Review previous research reported in the literature.** As was discussed in the literature review section in the Project Description, Granville (1985) identified a number of common learning difficulties with chemical thermodynamics. The ones that are most relevant to the topics we treat in this section are (1) a belief that ***system*** entropy must increase during spontaneous reactions, rather than entropy of [system + surroundings]; (2) failure to realize that Gibbs Free Energy decreases during spontaneous processes only for ***isothermal, constant-pressure*** processes.
2. **Determine pedagogical objectives for worksheet.** This particular section is intended for the second semester of the general chemistry course, in which the focus is on entropy, free energy, and the second law of thermodynamics. However, based on instructional experience, we know that students in this course have only a shaky grasp on key concepts from the first semester, such as internal energy, enthalpy, and the first law of thermodynamics. For this reason, we begin this section with review material, and continue to intersperse "review" questions throughout. Our primary targeted concepts are: (1) the relationship between internal energy, work, and heat, (2) the meaning of "state function," (3) the operational definition of enthalpy change (i.e., heat absorbed in a constant-pressure process), (4) the

relation between "spontaneous" reactions and entropy changes, (5) the definition of Gibbs free energy, which simultaneously accounts for entropy changes in ***both*** system ***and*** surroundings under conditions of constant pressure and temperature, and (6) the relation between spontaneity of reactions and changes in Gibbs free energy.

3. **Draft initial version of worksheet.** PI prepares first draft of section.

4. **First revision carried out jointly by Project Directors.** PI and Co-PI work through material line by line, to ascertain points of confusion and ambiguity; many revisions are made. We come to realize that physicists' emphasis tends to be on "internal energy" and chemists' emphasis instead is on "enthalpy." Additional questions are inserted in the worksheets to clarify both of these concepts. A diagram is added to make contact with typical presentations in chemistry textbooks. A previous diagram is modified, and a bar chart question is inserted.

5. **Second revision in consultation with chemistry graduate student.** A review by a graduate student results in further changes to one of the diagrams, improving its clarity.

6. **First test usage with undergraduate students.** Preliminary worksheet is tested by 15 students in chemistry lab section. (Students are paid $10 each for their participation, since it is "after hours.") PI circulates throughout room, asking questions and offering hints and clarifications while the students work through material. Various points of confusion are found, e.g.: many students are uncertain about basic definitions of internal energy, enthalpy, and state function; hints provided in worksheets in several cases were inadequate to catalyze understanding; most students were unable to follow sequence of algebraic steps in derivation of free energy.

7. **Third revision.** Worksheets are rewritten to add more detailed questions on enthalpy, with explicit definitions of enthalpy, state function, and change of entropy; additional detailed steps with explicit hints are added to section on free energy. Question #1 is slightly reworded to make it more thought provoking, since students tended to rush through that section.

8. **Second testing with undergraduate students.** A second group of 15 students (each paid $10) works through material as both Project Directors circulate throughout room, asking and answering questions. Confusion is found due to ambiguities in wording of questions on exothermic and endothermic reactions; the meaning of "initial" and "final" state is not clear to many students; some references to previous subsections of a given question are found to be ambiguous; difficulty in following algebraic steps persists.

9. **Fourth revision.** Worksheets are again rewritten to remove ambiguities, add more explicit hints, and simplify the sequence of algebraic steps. Emphasis is added by bold-facing and underlining of certain key passages.

10. **Third testing with undergraduate students.** A third group of 6 students (each paid $10) works through material as PI again circulates throughout room. Much less confusion is evident when compared with the first two testing sessions; students are able to work through material with less direct assistance than in previous cases. A few more points of unnecessary ambiguity are noted in some of the diagrams, and in some of the wording.

11. **Fifth revision.** Ambiguous wording that was found in third testing session is clarified. Substantial revisions are made to Questions #3 and #4 (which were formerly one single question), including the addition of a series of bar-chart questions, in an attempt to improve the clarity of the conceptual development.

12. **Further testing:** Continued testing and redesign is taking place during the summer session. As much as possible, materials are tested as part of regular class activities, to minimize necessity of paying students to participate in testing.

This account of the actual process undertaken to produce some of the preliminary material included in this proposal illustrates several points that we consider critical in curriculum development:

1. Even very experienced instructors, such as the PI's of this proposal, have sufficiently diverse viewpoints and perspectives to render review of each other's initial drafts highly productive. This is particularly true of interdisciplinary areas, even though thermodynamics represents such a close interface between chemistry and physics.
2. Graduate students can make a valuable contribution to initial revisions of curricular materials. Indeed, as is demonstrated by ongoing work in both of our groups, graduate students (in close collaboration with faculty) can become the ***primary*** authors of curricular material based on their own research.
3. In order to optimize the utility of the materials produced it is ***absolutely essential*** for them to undergo ***repeated*** testing in the hands of the undergraduate students who are the intended end-users.
4. To gain as much as possible from students' test use of the materials, curriculum developers (faculty and graduate students) should maintain the closest possible contact with the undergraduate students as they work through the materials. By asking probing questions and carefully listening to students' responses, we discovered literally dozens of cases of unclear

or ambiguous wording, unexpected gaps in students' knowledge, unintended interpretations of diagrams, etc. Without this close and extended interaction between student users and faculty developers, the shortcomings in our initial drafts might have gone undetected for months or years.

It is our desire and intention to subject each segment of our thermodynamics workbook to this same intense process of testing, redesign and re-testing outlined here. As we have suggested above, this iterative process ***does*** tend to converge. It is found that the number of ambiguous and confusing points brought up during student testing sesssions eventually declines, and students are able to work through the materials with less direct assistance from instructors. As in any iterative procedure, one must choose a cut-off point at which convergence is assumed to be adequate. This we judge to take place at approximately the point when only minor linguistic or stylistic problems arise during testing.

The next step in the process is ***assessment of student learning gains resulting from use of the curricular materials.*** This is described in detail in the following Appendix.

Appendix C

Assessment of Student Learning: Do the Materials Produce Results?

The acid test of the curricular materials we develop is to assess what students have learned as a result of using them. To illustrate our methods for carrying this out, we describe here our ongoing assessment of the preliminary materials included in this proposal.

1. We are examining the performance on the final exam of the chemistry students who tested the "Chemical Thermodynamics" worksheets (Appendix D). We are determining the average grade achieved on ***thermodynamics-related*** questions on the final exam of these students, and comparing this to the average grade on these same questions by students who did not use our worksheet materials. We will examine whether there is any difference in the grades of the two groups of students, specifically on the thermodynamics questions. However, we will also examine the grades on the ***complete final exam*** of the two groups of students. If there is any statistically significant difference between the two groups on the complete exam, then that will have to be taken into account in evaluating any possible differences that may appear on the thermodynamics grades.
2. We are following a similar procedure with the physics students in the lab-recitation sections that used the "Thermal Measurements" worksheets included in this proposal as Appendix F. We are examining their grades on thermodynamics-related questions on the final exam, and comparing those grades to that of students who used the standard version of the Pre-Lab instead. We will also examine the relative grades on

the complete final exam of the two groups, to determine if any normalization is required when judging the grades on the thermodynamics questions.

In the preliminary assessment method described above, there are several weaknesses which we plan to correct in future evaluations of student learning:

1. The physics and chemistry final course exams stress quantitative problem solving and do not necessarily assess students' qualitative conceptual understanding of thermodynamics topics. In the future, we will add one or two qualitative, concept-oriented questions to these exams. In some cases, students will be asked to write explanations of the reasoning they use to obtain their answers. (Both PI's are involved in teaching these courses, and in addition we have obtained agreement in principle from other course instructors to include this type of material on exams.)
2. In the case of the physics material included as Appendix F, we had two distinct groups assigned in the testing procedure: (1) those who used only the preliminary versions of our worksheets (given as a Pre-Lab in four lab sections); (2) those who used only the traditional version of the Pre-Lab, which stressed quantitative problem solving (given to all other lab sections – 14 in all). In this case, the new materials were ***substituted*** for the standard materials in the test sections. As a result, ***no additional study time*** was expended (presumably) by the students using the materials being tested. However, those students involved in testing the chemistry materials took this on as an additional task beyond their other class activities (due to logistical difficulties on our part). In this case, there was indeed additional study time expended by the students. This, of course, may have had an independent effect on their exam performance, beyond any particular

utility of the new materials. In the future, we will try to ensure that student learning is assessed by examining groups of students that have expended comparable amounts of class/study time on the thermodynamics topics, and who differ only on ***which*** materials they have used for study.

Finally, we will describe two additional forms of assessment which we are using in other curriculum development projects, and which we will employ in this project as well.

1) Questions related to topics covered in the curricular materials are given as "pretests," before use of the materials, and then identical or closely related questions are given on course quizzes, midterms, and final exams. Often, students are asked write explanations of the reasoning they use to obtain their answers. We compare pretest-to-posttest gains of students who have used the new materials, to those of students who use only standard textbooks and study guides. In this way we gather information about the pedagogical effectiveness of the new materials, relative to those that are presently being used.

2) Individual interviews with students are carried out, and recorded on videotape. During these interviews, students work through curricular materials as they "think out loud," and the interviewer (faculty member or graduate student) probes them with additional questions when necessary. These interviews give significant additional insight into the utility of the materials, and help uncover ambiguous or confusing language, as well as unanticipated gaps in students' background knowledge.

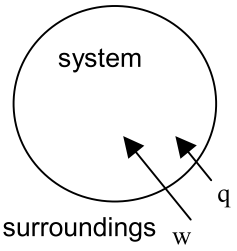
Appendix D

Chemical Thermodynamics

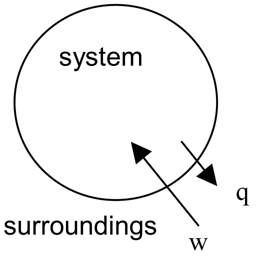
→ ***<u>Note:</u> In this section we use the convention that w (work) is positive for work done <u>on</u> the system***←

1. Rank the following processes in order according to the ***change in internal energy of the system*** (largest increase first, followed by second-largest increase, … largest ***decrease*** in internal energy placed ***last***.) A "*w*" arrow going *in* means that work is being done ***on*** the system ***by*** the surroundings; a "*w"* arrow going *out* means that work is being done ***by*** the system ***on*** the surroundings. The direction on the "*q*" arrow shows the direction of heat flow. Arrow *length* is proportional to the *magnitude* of the quantity it represents.

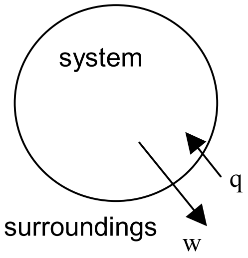
(A)



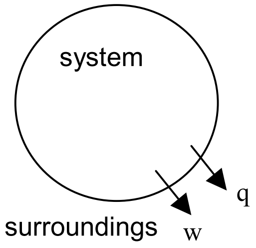
(B)



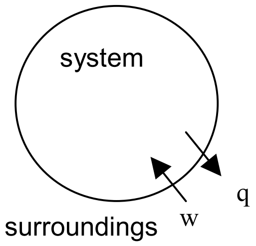
(C)



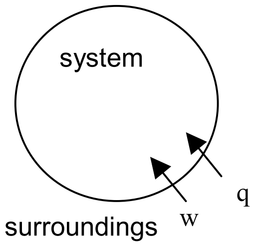
(D)



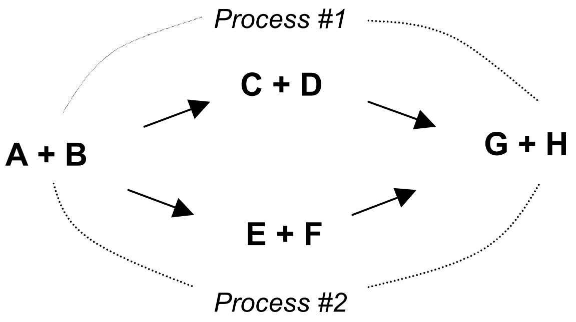
(E)

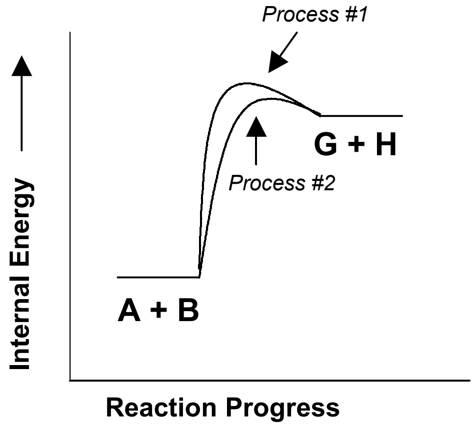


(F)



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





The reactants (**A** and **B**) and the products (**G** and **H**) are ***identical*** in both cases and are in *identical* states. That is, the reactants in Process #1 have all the same properties – P, V, T, etc. – as the reactants in Process #2; the products in Process #1 have all the same properties as the *products* in Process #2. 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.*

a) 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? (Remember that $\Delta E \equiv E_{\text{final}} - E_{\text{initial}}$; here, the "initial" state is the state in which **A** and **B** are combined; the "final" state is the state in which **G** and **H** are formed.)

b) Let's call the initial and final temperatures of the system T_i and T_f, respectively. Then T_i is the temperature of (**A** + **B**); T_f is the temperature of (**G** + **H**).

   i) Is T_f for Process #1 *greater than, less than,* or *equal to* T_f for Process #2?

   ii) Is T_i for Process #1 *greater than, less than,* or *equal to* T_i for Process #2?

   iii) Is the *net change* in temperature of the system ΔT ($= T_f - T_i$) during Process #1 *greater than, less than,* or *equal to* the ΔT during Process #2?

Temperature is an example of a ***state function***, i.e., something that is a property of a system in a given condition at a given moment, which does not depend in any way on *how* the system came to be in its present condition. Are your answers to (b)[i-iii] consistent with this?

c) Is the net change in entropy of the system during Process #1 *greater than, less than,* or *equal to* the net change in entropy during Process #2?

d) Is the net change in enthalpy of the system ΔH during Process #1 *greater than, less than,* or *equal to* the ΔH during Process #2?

e) What can you say about the ***net change*** in any state function during Process #1 as compared to its net change during Process #2? Explain your answer. Are your answers to questions a-d above consistent with your answer to this question? (Note that internal energy, temperature, entropy, and enthalpy are all state functions.)

f) Recall that the ***change*** in the enthalpy (ΔH) may be defined as "the heat absorbed by a system under conditions of constant pressure." If a system starts out with enthalpy $H_{initial}$ and finishes with enthalpy H_{final}, will the final value of the enthalpy be *greater than, less than,* or *equal to* the initial value of the enthalpy:

i) if the system undergoes an ***endothermic*** reaction (i.e., a reaction in which the system absorbs heat from the surroundings) at *constant pressure*?

ii) if it undergoes an ***exothermic*** reaction at *constant pressure*?

If the reaction does ***not*** take place at constant pressure, could you be sure of the answer to this question?

g) The first law of thermodynamics states that the ***change*** in the internal energy of a system (ΔE) equals the heat absorbed by that system (q) plus the work done by the surroundings on that system (w). Write this in the form of an algebraic equation.

h) A system starts out with internal energy $E_{initial}$, undergoes an *endothermic* reaction (i.e., a reaction in which the system absorbs heat from the surroundings), and ends up with a value E_{final}. Will E_{final} be *greater than, less than,* or *equal to* $E_{initial}$ for:

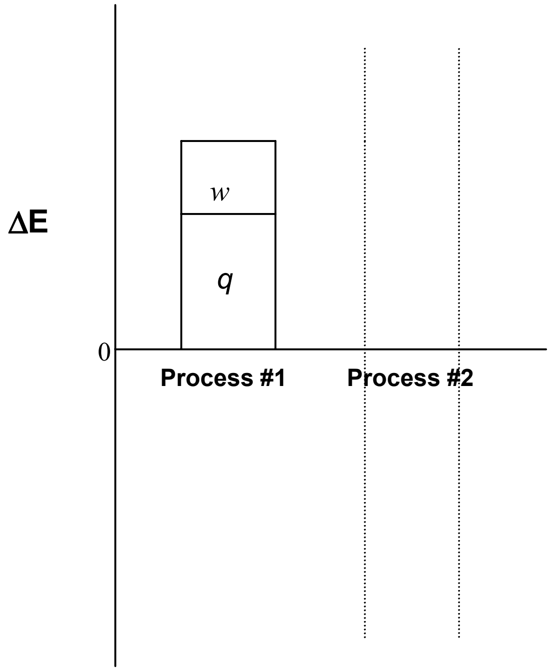
  i) an endothermic reaction during which the surroundings do *no work* on the system?

  ii) an endothermic reaction during which the surroundings *do* work on the system?

  Explain your answers.

  Hint: For each case, consider whether q *and* w *are positive, negative, or zero. What does that tell you about ΔE?*

i) In the bar chart below, the first bar represents the change in internal energy of the system during Process #1; the distribution between heat absorbed by the system, and work done on the system, has been indicated for this process. (Note that ΔE is shown to be *positive* for Process #1.) In the space indicated by the dashed lines, draw in the corresponding bar for Process #2, making sure you have correctly represented the *size* of the bar (and whether it is above or below the horizontal axis), as well as the relative distribution between *q* and *w* for this process. (Refer back to the assumptions we made about these two processes on page 2.)



j) Is the work done ***on the system*** during Process #1 *greater than, less than,* or *equal to* the work done on the system during Process #2? Explain your answer.

k) *[Optional question]* We often express q in terms of specific heat c, as in the equation $q = mc\Delta T$. If you make use of your answer to c(iii), does this equation then imply that q for Processes #1 and 2 must be the *same*, in contradiction to the given information? What is wrong with this interpretation?

> *Hint:* Different substances have *different values* of specific heat. Also, the specific heat at constant *pressure* is different from the specific heat at constant *volume.* Is the *same* substance undergoing the same temperature change *all throughout* Processes #1 and 2? Is either the *pressure* or the *volume* constant?

3. The ***change*** in the enthalpy ΔH may be defined as "the heat absorbed by a system under conditions of constant pressure." (That is, if ΔH > 0, heat is *absorbed* and enthalpy *increases*; if ΔH < 0, heat is *given off* and enthalpy *decreases*.) Let's see how ΔH is related to the internal energy E of a system.

a) As in 2(g), write down the algebraic equation that expresses the first law of thermodynamics, which states that the change in the internal energy of a system equals the heat absorbed by that system (q) plus the work done by the surroundings on that system (w). Write this equation to express q in terms of ΔE and w. That is, write an equation such as: q = [*combination of* ΔE *and* w].

$q =$

b) We will assume that the only work being done on the system is mechanical work, or "P-V" work. Then (under conditions of constant pressure), $w = –P\Delta V$; rewrite the equation for q in terms of ΔE, P and ΔV.

$q =$

c) We should now have arrived at the expression $q = \Delta E + P\Delta V$, which holds for constant-pressure conditions. This equation says that ***heat absorbed*** under constant pressure does two things: (1) increases the ***internal energy (E)*** of the system, and (2) allows the system to do mechanical work ***on the surroundings***. (The amount of work done ***by*** the system ***on*** the surroundings equals PΔV. This is the *negative* of the amount of work done ***on*** the system ***by*** the surroundings, which is what we have called w; $w = – P\Delta V$.)

Using the definition that ΔH is *equal* to heat absorbed under constant pressure, write the equation from (b) in terms of ΔH, instead of q. (So now you should have: ΔH = [some combination of ΔE, P, and ΔV])

ΔH =

So now we can see that when the enthalpy of a system ***changes*** by an amount ΔH (under conditions of constant pressure), there are actually ***two*** separate contributions to this change: (1) the change in the *internal energy* of the system (ΔE), and (2) the work done ***by*** the system ***on*** the surroundings (PΔV). An increase in internal energy, ***or*** positive work being done ***by*** the system, will both result in an increase in the enthalpy H of the system.

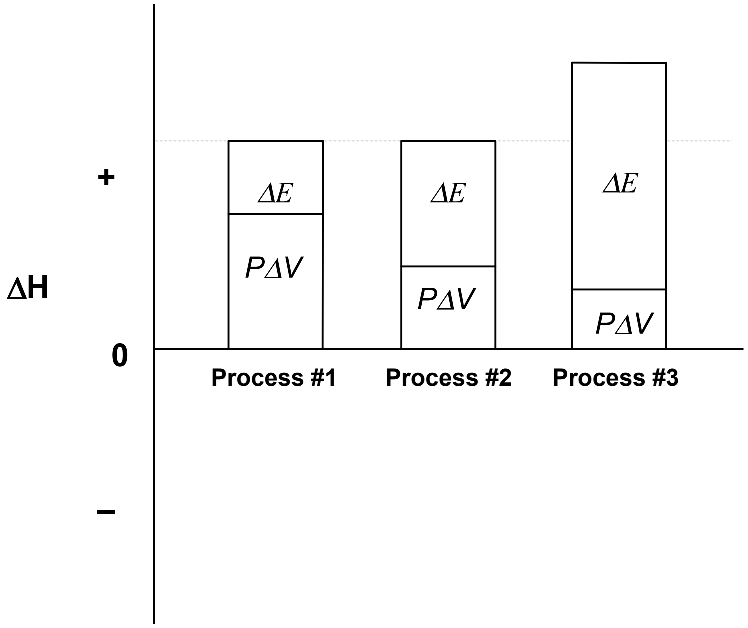
d) On the bar chart below we consider three different processes; all of these processes take place at *constant pressure* and have *positive* values of ΔH. The ΔH for Processes #1 and #2 is the same.

i) Under conditions of constant pressure, is the amount of work done ***by*** the system ***on*** the surroundings during Process #2 *greater than, less than,* or *equal to* the amount of work done ***by*** the system during Process #1?

ii) In all three processes, is the quantity *w* (the amount of work done ***on*** the system) *positive, negative,* or *zero*?

iii) Under conditions of constant pressure, is the amount of heat absorbed by Process #2 *greater than, less than,* or *equal to* the amount of heat absorbed by Process #1?

iv) Under conditions of constant pressure, is the amount of heat absorbed by Process #3 *greater than, less than,* or *equal to* the amount of heat absorbed by Process #1? Explain.



4. It would be very useful to be able to predict whether a reaction will occur ***spontaneously***, that is, whether it will occur on its own with no external influence. We will try to find some property of the system that would allow us to make such a prediction. In order to do this, we will have to make use of the fundamental physical principle that relates to the "spontaneity" of physical processes: the **second law of thermodynamics.** This law deals with the quantity called "entropy" (symbol: S), which is a measure of the "disorder" in a system.

a) According to the second law of thermodynamics, any *spontaneous* reaction (i.e., one that will occur on its own with no external influence) can only occur if $S_{universe}$ (the total entropy of the *universe*) ***increases***. Then will $\Delta S_{universe}$ be *greater than zero, less than zero,* or *equal to zero*? ($\Delta S = S_{final} - S_{initial}$)

b) By definition, $S_{universe} = S_{system} + S_{surroundings}$. Then ***in order for a reaction to proceed spontaneously***, which of these conditions will have to hold?

$\Delta S_{system} + \Delta S_{surroundings} > 0$

$\Delta S_{system} + \Delta S_{surroundings} = 0$

$\Delta S_{system} + \Delta S_{surroundings} < 0$

c) It can be shown that if a *system* absorbs heat q under conditions of constant temperature, the change in the entropy of the *surroundings* will be given by this relationship: $\Delta S_{surroundings} = -q/T$.

Substitute this relationship into the correct expression from (b), to show that the entropy change of the ***system*** must obey the following condition, ***if*** the reaction is to proceed spontaneously at constant temperature:

$\Delta S_{system} + (-q/T) > 0$

If we make use of the fact that the absolute temperature T has to be positive (why is this true?) we can rewrite this relationship in this way:

$T\Delta S_{system} - q > 0$

(Explain why this relationship would ***not*** be true if T could be *negative*.)

You can now answer this question: If a reaction is to occur spontaneously, does the product $T\Delta S_{system}$ have to be *larger than, smaller than,* or *equal to* the heat absorbed by the system?

Suppose that heat is ***given off*** by the system during a process (so now q is *negative*, and the quantity $(-q)$ is ***positive***). Is that the type of process that would ***always*** occur spontaneously? What kind of change in the entropy of the system could prevent that process from occurring spontaneously?

It would be convenient to invent a ***single*** quantity that would be a property of the system only – not its surroundings – that could be used to determine whether a reaction can proceed spontaneously. We can't do this for ***all*** possible conditions. Since in chemistry we are most concerned with *constant pressure*, let's focus on that condition.

d) With pressure constant, what is the relationship between ΔH of a system and the q absorbed by that system? [See 3(c) above.] Use this in the expression found in 4(c) to prove this statement:

If a process occurs spontaneously at constant pressure and temperature, then this condition must be obeyed by the properties of the system:

$$T\Delta S_{system} - \Delta H > 0.$$

WARNING: **Both ΔS_{system} and ΔH may be <u>negative</u> quantities.**

Note that these three quantities – T, ΔS_{system}, and ΔH – are all properties of the ***system*** as it undergoes a process at constant temperature. They do not depend directly on the ***surroundings***. Since T, S_{system}, and H are all state functions, the ***change*** in any of these quantities only depends on the final and initial state of the system, and not on the particular process that links those two states. We can put these quantities together to define a ***new*** state function – "Free Energy" – which would also be a property of the system.

The Gibbs Free Energy G of a system is defined by this relationship:

$$G = H - TS_{system}$$

Under conditions of ***constant temperature***, write down the corresponding relationship for ΔG, the ***change*** in the Gibbs Free Energy:

$$\Delta G =$$

e) In (d) a relationship among temperature, entropy, and enthalpy was found that must be obeyed if a reaction is to proceed spontaneously under constant temperature and pressure. This relationship is $T\Delta S_{\text{system}} - \Delta H > 0$. You should also have found a relationship for the change in the Free Energy: $\boldsymbol{\Delta G = \Delta H - T\Delta S_{\text{system}}}$.

If a process is to occur spontaneously when pressure and temperature are constant, what condition must be obeyed by the ***change*** ΔG in the Gibbs Free Energy of the system? You should end up with *one* of these three equations (which is correct?):

$$\Delta G > 0$$

$$\Delta G = 0$$

$$\Delta G < 0$$

f) With this result, answer this question: **If a reaction is to proceed spontaneously under conditions of constant temperature and pressure,** will the value of G have to *increase, decrease,* or *remain constant*?

g) Let's apply this to a sample case. At standard conditions (298 K, 1 atm), the G of an *element* is set to be equal to zero. So, G for $N_2(g)$ = 0.0 kJ/mol, and G for $H_2(g)$ is also 0.0 kJ/mol. The G for $NH_3(g)$ = –16.66 kJ/mol. (So, G for *two* moles of $NH_3(g)$ = –33.32 kJ.) Which of these reactions would occur spontaneously at 298 K:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \quad \textit{\textbf{or}} \quad 2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$$

Explain your answer.

Remark on notation: *The Gibbs Free Energy of a substance is usually tabulated as $\Delta G_f°$, which is the* ***difference*** *between the Free Energy of that substance, and the Free Energy of the elements composing that substance. Thus the table would show $\Delta G_f°$ of $N_2(g)$ and $H_2(g)$ as 0.0 kJ/mol, and $\Delta G_f°$ of NH_3 as –16.66 kJ/mol. Therefore, when we have written* "ΔG," *we mean "$\Delta G_f°$ (final products) – $\Delta G_f°$ (initial reactants)." Keep in mind that $\Delta G_f°$ (final products) = $n\Delta G_f°$ (product #1) + $m\Delta G_f°$ (product #2) if there are n moles of product #1 and m moles of product #2. Similarly, $\Delta G_f°$ (initial reactants) = $n\Delta G_f°$ (reactant #1) + $m\Delta G_f°$ (reactant #2) if there are n moles of reactant #1 and m moles of reactant #2.*

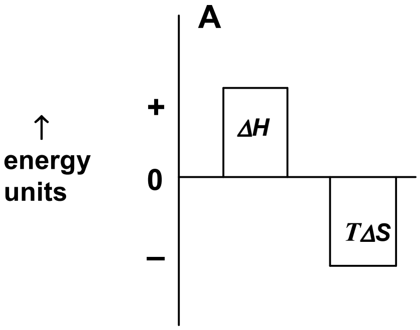
h) These bar charts represent six different processes; in all six, the temperature and the pressure remain *constant*. A bar *above* the horizontal axis indicates a *positive* change (i.e., the quantity *increases* during the process). A bar *below* the horizontal axis indicates a *negative* change (i.e., the quantity *decreases* during the process).

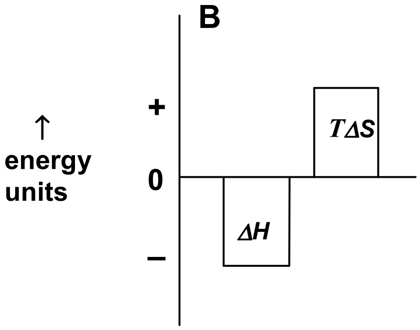
   i) In which of these processes is heat ***lost*** by the system?

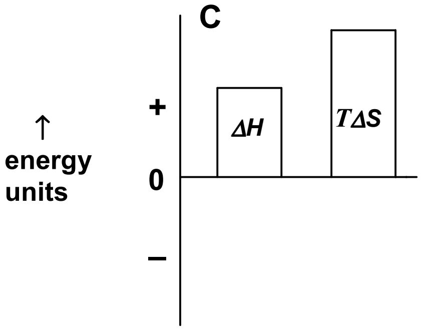
   ii) Which of these processes involves the ***largest absorption*** of heat by the system?

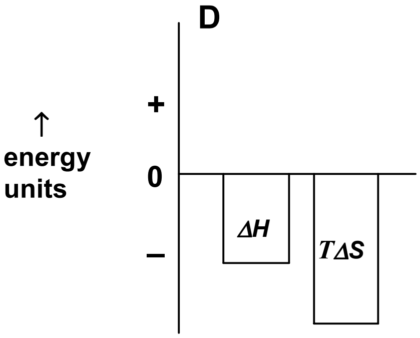
   iii) Which of these processes leads to ***increasing disorder*** of the system?

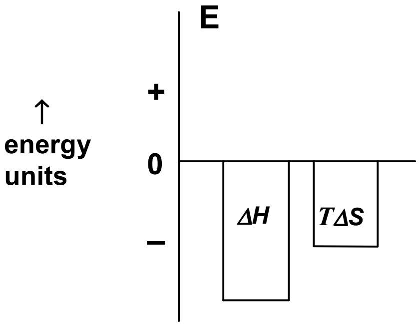
   iv) Which of these processes will occur spontaneously? Explain in each case.

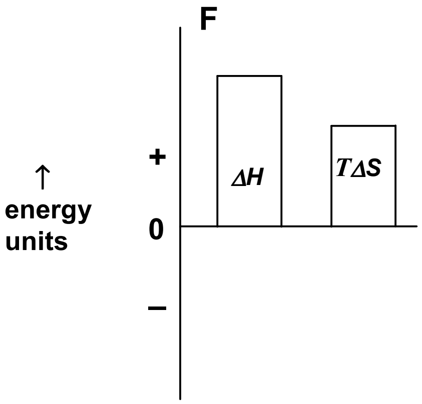












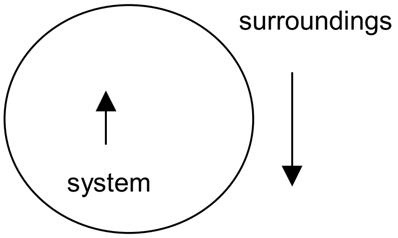
5. The following diagrams represent what happens to the ***entropies*** of a system and its surroundings during several different processes; an "up" arrow means the entropy increases, a "down" arrow means that it decreases. *The length of each arrow is proportional to the absolute value of the entropy change it represents.*

   a) Of these processes, which will occur spontaneously? Explain your answers.

   b) In which of these processes does the Gibbs Free Energy G of the system ***increase?*** Explain.

   c) Which could represent a ***reversible*** process? (That is, a process that could go in *either* direction along the same path.)

(A)



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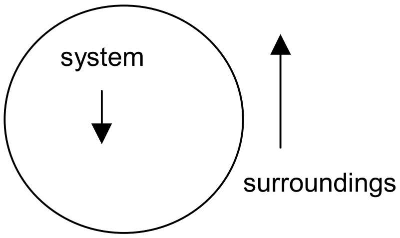
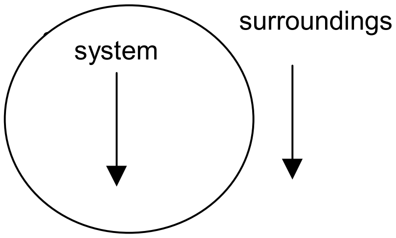
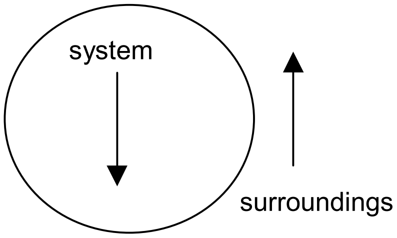


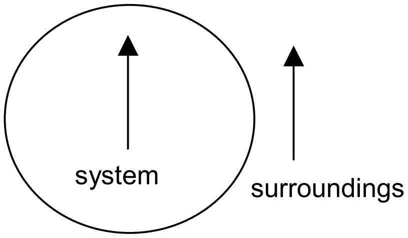
(C)



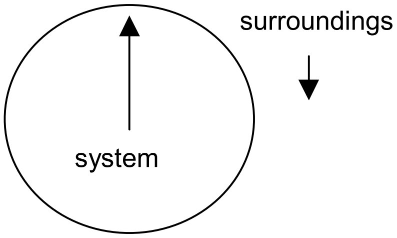
(D)



(E)



(F)



Appendix E: Questions on Entropy and Gibbs Free Energy

1. In any naturally occurring ("spontaneous") process, which of these is true?

   A) The total entropy of the universe increases.

   B) The total entropy of the universe decreases.

   C) The total entropy of the universe remains the same.

   D) The total entropy of the universe may increase or decrease, depending on the particular process.

2. Which of these correctly expresses the relationship between the entropy change of the universe, and the entropy changes of a system and its surroundings during some process?

   A) $\Delta S_{universe} > \Delta S_{system} + \Delta S_{surroundings}$

   B) $\Delta S_{universe} < \Delta S_{system} + \Delta S_{surroundings}$

   C) $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$

   D) $\Delta S_{universe}$ may be greater than or less than $[\Delta S_{system} + \Delta S_{surroundings}]$, depending on the particular process.

3. Consider three different situations:

   I. Gibbs Free Energy of system increases, entropy of system increases.
   II. Gibbs Free Energy of system increases, entropy of system decreases.
   III. Gibbs Free Energy of system decreases, entropy of system increases.

   Which of these cases corresponds to a ***spontaneous*** reaction?

   A) I only

   B) II only

   C) III only

   D) I and II

   E) I and III

4. Which of these situations corresponds to the Gibbs Free Energy G of the system ***increasing***?

A) Entropy of system increases by 5 J/K; entropy of surroundings decreases by 5 J/K.

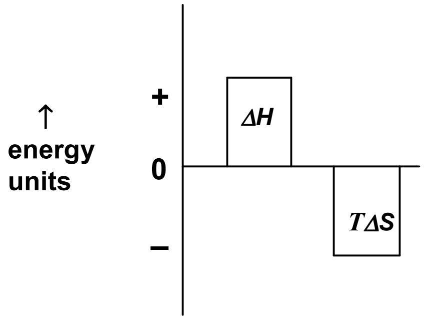
B) Entropy of system increases by 5 J/K; entropy of surroundings decreases by 10 J/K.

C) Entropy of system increases by 10 J/K; entropy of surroundings decreases by 5 J/K.

D) Entropy of system increases by 5 J/K; entropy of surroundings increases by 5 J/K.

E) Entropy of system increases by 5 J/K; entropy of surroundings remains constant.

The next four questions refer to this diagram, which represents a process occurring at ***constant temperature and constant pressure***. Here H, T, and S refer to the ***system***. *(Hint: Recall that* $G \equiv H - TS$*)*



5. In this process:
   - A) heat is absorbed by the system.
   - B) heat is given off by the system.
   - C) heat is neither absorbed nor given off by the system.
   - D) there is not enough information to determine whether heat is absorbed or given off by the system.

6) In this process:
   - A) the disorder of the system is increasing.
   - B) the disorder of the system is decreasing.
   - C) the disorder of the system remains constant.
   - D) there is not enough information to determine whether the disorder of the system is increasing, decreasing, or remaining constant.

7) In this process:
   - A) the disorder of the surroundings is increasing.
   - B) the disorder of the surroundings is decreasing.
   - C) the disorder of the surroundings remains constant.
   - D) there is not enough information to determine whether the disorder of the surroundings is increasing, decreasing, or remaining constant.

8) Which of these is true:
   - A) This process will always occur spontaneously.
   - B) This process will never occur spontaneously.
   - C) This process may or may not occur spontaneously, depending on the temperature.
   - D) There is not enough information in the diagram to determine whether or not this process will occur spontaneously.

Appendix F

[Revised Pre-Lab No. 14 on Thermal Measurements for Physics 222]

The heat of fusion of water is 80 cal/g. The specific heats of ice and water are 0.50 and 1.00 cal/g•°C, respectively. (Note: 1 cal = 4.184 J)

1. A block of ice is placed on a table in a room at "room temperature." Several thermometers embedded in the block of ice are visible. A puddle of water begins to form under the ice, but the thermometers in the ice are observed to show no change in temperature occurring during this time. During this time, is there any heat flow occurring between the ice and its surroundings? If yes, which direction is the flow of heat? If no, explain how you know that there is no heat flow.

2. An insulated metal container and the water it contains are both at room temperature of 22°C. A piece of ice with a temperature of 0°C is placed into the container of water.

   In the moments ***immediately after*** the ice is put into the water:

   a) does heat flow *from the water to the ice, from the ice to the water,* in ***both directions** simultaneously,* or is there *no heat flow at all*?

   b) will the temperature of the water *increase, decrease,* or *remain constant*?

   c) will the temperature of the ice *increase, decrease,* or *remain constant*?

   At a certain moment, the last bit of ice is observed to melt.

   d) At this moment, was the temperature of the ice *greater than 0*°C, *equal to 0*°C, or *less than 0*°C?

   e) At this moment, is the temperature of the water *greater than 22*°C, *equal to 22*°C, or *less than 22*°C?

3. If you have 10 g of ice at a temperature of –1°C:

a) How much energy is required to cause the ice to ***just begin*** to melt? What is the temperature of the ice at this point?

b) Starting from the point when the ice begins to melt, how much energy is now required to ***melt all of the ice to water?*** What is the temperature of the water at the completion of this process?

c) Starting from the point when the last bit of ice has melted, how much energy is required to increase the temperature of the water by one degree Celsius?

d)

i) How many joules of energy are required to raise the temperature of 10 g of water by one degree Celsius?

ii) If energy is supplied to 10 g of water at 5 J per second, how many seconds are required to raise the temperature of that water by one degree Celsius?

In #4 below, Substance A has a specific heat of 0.3 cal/g•°C and a density of 1.8 g/cm^3. Substance B has a specific heat of 0.8 cal/g•°C, and a density of 1.3 g/cm^3.

There are two 250-g aluminum containers (#1 and #2); each contains 150 g of water, and (along with their water contents) are both at a room temperature of 22°C.

4.

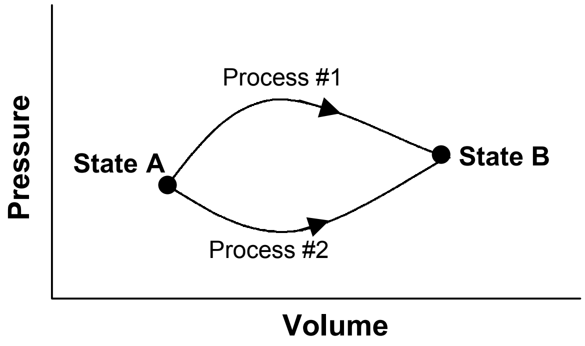
a) Assume 40 g of substance A at a temperature of 80°C is submerged in Container #1, and 80 g of substance A, also at 80°C, is submerged in Container #2. After each container and its contents reaches its final temperature, will the final temperature in Container #2 be *higher, lower,* or *equal to* the final temperature in Container #1?

b) Now assume that 90 g of substance A at a temperature of 80°C is submerged in Container #1, and 90 g of substance B, also at 80°C, is submerged in Container #2. After each container and its contents reaches its final temperature, will the final temperature in Container #2 be *higher, lower,* or *equal to* the final temperature in Container #1? Explain your answer.

c) This time, 50 g of substance A and 50 g of substance B, both at 80°C, are simultaneously submerged in one of the containers. When the final temperature is reached, will the 50 g of substance B have lost *more energy than*, *less energy than,* or *the same amount of energy as* the 50 g of substance A? Explain your answer.

5.

This PV diagram represents a system consisting of a fixed amount of gas undergoing two different processes in going from state A to state B; w is work done *by* the system during a process; q is heat *absorbed* by the system during a process. E_{int} is the internal energy of the system.



a) Is ΔE_{int} for Process #1 *greater than, less than,* or *equal to* that for Process #2?

b) If you can, draw on the diagram another process going from state A to state B that corresponds to a *larger* ΔE_{int} for the system than either Process #1 or Process #2; label it (b). If you can not, explain why you can not.

c) Is w for Process #1 *greater than, less than,* or *equal to* that for Process #2?

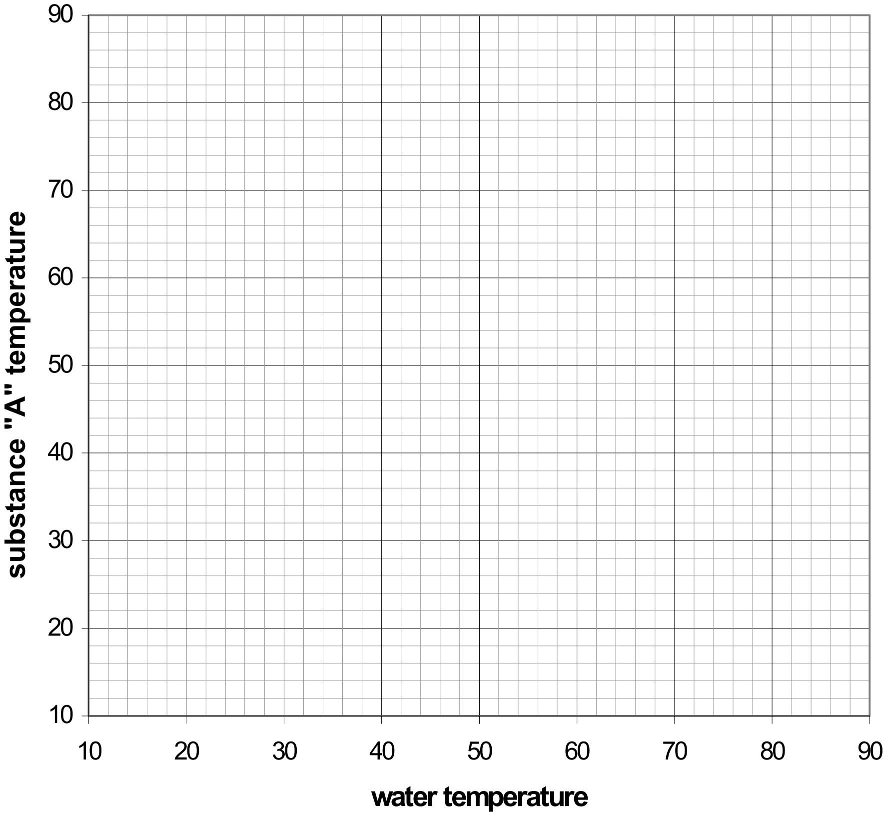
d) Is q for Process #1 *greater than, less than,* or *equal to* that for Process #2?

e) If you can, draw on the diagram another process going from state A to state B that corresponds to a *larger* ***q*** than either Process #1 or Process #2; label it (e). If you can not, explain why you can not.

f) ***Explain*** your answers to (a), (c), and (d) above. (Continue your answer on the back side of this sheet if necessary.)

Study Sheet for Pre-Lab 14

Containers #1 and #2 are identical, and both contain 100 g of water in equilibrium at a temperature of 20°C. Let's start by submerging *x* grams of substance A, initially at 80°C, into Container #1. Each point on the graph below will represent a particular moment in time, where the x-coordinate represents the temperature of the water at that time, and the y-coordinate represents the temperature of substance A at that time.



(1) When equilibrium is reached, is the temperature of substance A *greater than, less than,* or *equal to* the temperature of the water? On the graph above, plot a straight line through all points that might correspond to an equilibrium situation.

(2) Consider the situation in Container #1: When the *x* grams of substance A cools down by 10°C, the water temperature will increase; why is this so?

(3) Let us refer to the heat lost by substance A, as it cools by 10°C, as "q_{10}." Is the amount of heat gained by the water *greater than, less than,* or *equal to* q_{10}?

(4) Let's assume that when the *x* grams of substance A cools down by 10°C , the change in the water temperature is 5°C. Use the relationship $q = C\Delta T$, where "C" represents heat capacity [$C \equiv mc$, where c is the specific heat of a substance, and m is its mass] to find the relationship between C_{water} and C_A .

$C_{water} = (?) \times C_A$

(Find the appropriate numerical factor.)

(5) When the temperature of the *x* grams of substance A cools down by ***another*** 10°C, will the temperature change of the water be *greater than, less than,* or *equal to* 5°C? (Assume that there is no heat flow to or from the surrounding environment, and that heat capacity does not change with temperture.) ***Explain your answer*** by referring to the answer to #4.

(6) Now plot a line that represents the situation in the container, starting from when substance A (at a temperature of 80°C) is first submerged in the container, to the point at which no further changes in temperature take place. Label this line "*#1*"

(7) Let us now start again with Container #2. This time we submerge *2x* grams of substance A (twice as much as before), also with an initial temperature of 80°C, into the water which also is initially at 20°C.

(a) How does $C_A(II)$ [heat capacity of substance A in container #2] compare to C_A [heat capacity of substance A in container #1]?

$C_A(II) = (?)C_A$ *(Find the appropriate factor)*

(b) $C_w = (?)C_A(II)$ *(Find the appropriate factor; remember that both containers have 100 g of water.)*

(8) If the *2x* grams of substance A cools down by 10°C, by how much will the water temperature change in Container #2? Explain your answer based on the answers to #7.

(9) Now plot a line that represents the situation in Container #2, starting from when substance A is first submerged in the container, to the point at which no further changes in temperature take place. Label this line "*#2*"

(10) Based on your graphs, answer this question: After each container and its contents reaches its final temperature, will the final temperature in Container #2 be *higher than, lower than,* or *equal to* the final temperature in Container #1?

(11) Explain how this line of reasoning can provide the answer to Question #4(a & b) on the Pre-lab.

Appendix G: Efficiency of Heat Engines and the Second Law of Thermodynamics

Note: The purpose of this section is to guide students to show that $|Q_{high}/Q_{low}| = (T_{high}/T_{low})$ for <u>any</u> Carnot cycle, not just one utilizing an ideal gas.

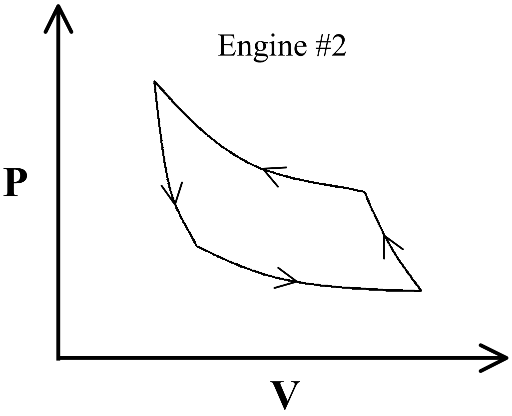
We have used the term "heat" to describe the flow of energy at the microscopic level, mediated by the motion and interaction of atoms and molecules. This is a flow of energy *into* or *out of* some system, where the system is composed of a specific amount of some substance. We have learned that the "state" of a substance at a given moment – i.e., the complete collection of properties that uniquely specify a quantity of the substance at a given moment – includes a property called "internal energy." The internal energy is equal to the sum of kinetic and potential energy possessed by all the atoms and molecules comprising the substance. Heat is related to *changes* in the state of a system, but is not itself a property of a system at a specific time.

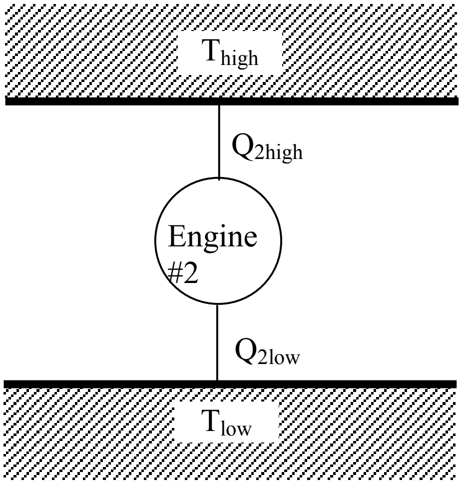
When a system changes from one state to another state, the amount of its internal energy may change from one particular value to another value. At any given moment, the system must have some specific amount of internal energy. However, the amount of *heat* that accompanies a transformation from one state to another may vary greatly, depending on the specific process that is used to carry out the transformation. (For instance, in one process the pressure may first be kept constant while the volume varies, followed by a pressure change at constant volume. In another process, exactly the opposite sequence of variations could be carried out.) If we are given a system in two different states, we have no way of knowing how much heat was absorbed or released during the transformation between those states (unless the exact transformation process used is specified.)

Even if we always start from some specific "reference" state (with specific values of internal energy, pressure, volume, temperature, etc.), the amount of heat (symbolized by "Q") required to transform to some other given state can never be precisely specified. An infinite number of different values is possible, depending on the specific transformation process that is carried out. So there does not exist a specific value of Q for a given state of a system, and therefore it is not meaningful to speak of the "difference in Q" between one state and another. Since heat has such fundamental importance for thermodynamic and chemical transformations, and is so frequently the object of measurement and prediction, it would certainly be useful to find a relationship involving Q that may be used to characterize the state of a system. In this section, we will try to find a general relationship involving Q that is true for any ***cyclic*** process.

We have found that when an ideal gas goes through the reversible cycle known as the "Carnot" cycle, the heat absorbed at the high temperature (Q_{high}), and the heat given off at the low temperature (Q_{low}) are related to the absolute temperatures as follows: $|Q_{high}/Q_{low}| = (T_{high}/T_{low})$. Could it be that some other substance – not an ideal gas – would yield a different relationship among the Q's and T's, if it carried out a reversible cycle between the same two temperatures? For instance, might another substance be characterized by the *inequality* $|Q_{high}/Q_{low}| < (T_{high}/T_{low})$, or perhaps the reverse? ***In this section we will investigate whether or not the relationship $|Q_{high}/Q_{low}| = (T_{high}/T_{low})$ holds for <u>any</u> Carnot cycle, not simply one using an ideal gas.***

Let's suppose that there was in fact a substance which, when taken through a reversible cycle between two different temperatures, was characterized by $|Q_{2high}/Q_{2low}| < (T_{high}/T_{low})$ ***[i.e., a <u>different</u> relationship from the ideal gas case].*** Here "Q_{2high}" and "Q_{2low}" refer to the heat transferred at the high and low temperatures, respectively, for this "second" system (labeled "Engine #2). (We're again assuming a Carnot cycle, with isothermal volume changes linked together by adiabatic processes that take the system from one temperature to the other.) ***We will investigate whether this condition is permitted by the laws of thermodynamics.***





1. Since this is a reversible cycle, let us run it in reverse. (For a gaseous substance, this would mean that instead of *expanding* at the higher temperature, it is *compressed;* this is indicated by arrows on the diagram showing the direction in which the process occurs.)

   If we do that, will heat be *absorbed*, *given off,* or *neither* absorbed *nor* given off at the ***low*** temperature (T_{low})? *(Indicate this on the low-temperature curve on the diagram with an appropriate arrow: pointing **<u>in</u>** toward the center for heat absorbed; pointing **<u>out</u>** for heat given off; **<u>no arrow</u>** for no heat flow.)* [Whether it is absorbed, given off, or equal to zero, we will still refer to this heat as "Q_{2low}."]

2. Will heat be *absorbed*, *given off,* or *neither* absorbed *nor* given off at the ***high*** temperature (T_{high})? *(Indicate this on the diagram with an appropriate arrow.)* [Whether it is absorbed, given off, or equal to zero, we will still refer to this heat as "Q_{2high}."]

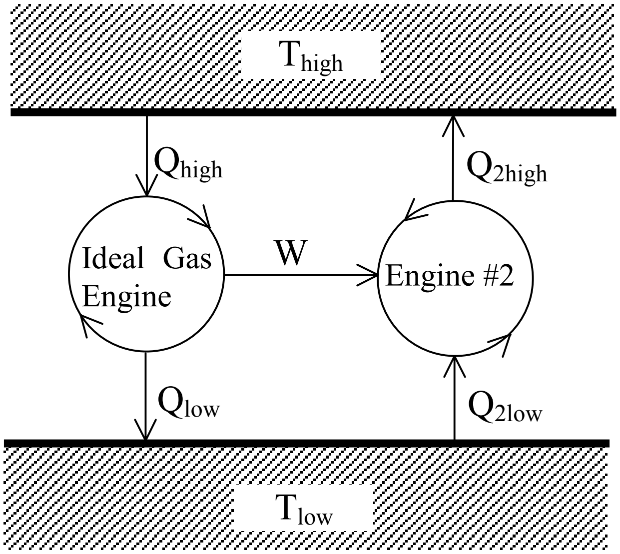
3. For the complete cycle, is the net change in the internal energy of the substance *positive, negative,* or *zero*? Is the net heat absorbed by the system *greater than, less than,* or *equal to* the net work done by the system?

4. Will net work be done *by* the substance, or will net positive work have to be done *on* it to carry out this cycle, *or* is the net work *zero* in this case? Explain your answer.

5. Express the absolute value of the net work, referred to in #4, in terms of Q_{2high} and Q_{2low}. (Use absolute value signs.)

$|W|$ = ______________________ (Use absolute value signs.)

Now suppose that we use the work produced by the *first* engine (the "ideal gas" engine) to run the *second* engine (the one we have described in #1-5 above). That is, we arrange it so that the absolute value of the net work in the two cases is the same. Call this value "$|W_{ideal}|$." Then we have that $|W| = |W_{ideal}|$.



6. Is $|W_{ideal}|$ greater than, less than, or equal to $|Q_{high} - Q_{low}|$?

7. Given the assumption that $|W| = |W_{ideal}|$, is $|W_{ideal}|$ greater than, less than, or equal to $|Q_{2high} - Q_{2low}|$?

8. Is $|Q_{high} - Q_{low}|$ greater than, less than, or equal to $|Q_{2high} - Q_{2low}|$?

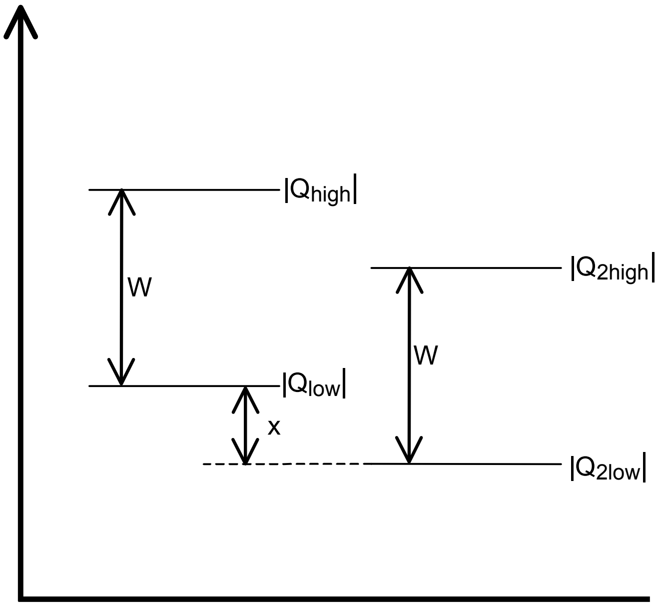
9. For the ideal gas engine, we know that $|Q_{high}| = (T_{high}/T_{low})\ |Q_{low}|$. For the second engine, we have assumed that $|Q_{2high}| < (T_{high}/T_{low})\ |Q_{2low}|$.

   Given what you found in #8, is it possible that $|Q_{2low}| = |Q_{low}|$?

   Could $|Q_{2high}|$ be equal to $|Q_{high}|$? Explain your answer.

Now we will test to see whether $|Q_{2low}|$ is <u>greater than</u> or <u>less than</u> $|Q_{low}|$:

10. Suppose that $|Q_{2low}|$ is ***<u>less than</u>*** $|Q_{low}|$.



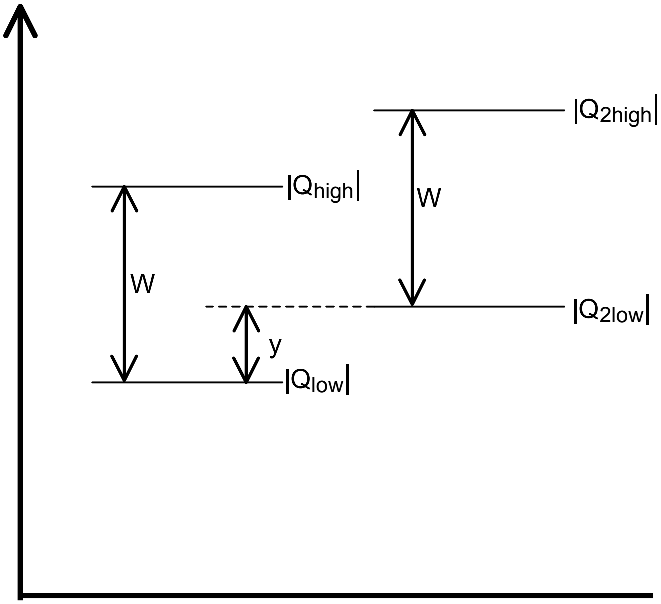
a) Will $|Q_{2high}|$ be greater than, less than, or equal to $|Q_{high}|$? *(Hint: Refer to the answer to #8.)*

b) If $|Q_{low}| - |Q_{2low}| = x$, is $|Q_{high}| - |Q_{2high}|$ greater than, less than, or equal to x?

c) Suppose that $|Q_{high}|$ = 100 J, $|Q_{low}|$ = 40 J, and x = 20 J. In this case, will $|Q_{2high}/Q_{2low}|$ be less than (T_{high}/T_{low})? Is this compatible with our original assumption that $|Q_{2high}/Q_{2low}| < T_{high}/T_{low}$?

d) Would the answer to (c) change if we chose a different set of values for the Q's, as long as $|Q_{high}| > |Q_{low}|$? Explain why or why not.

11. Suppose that $|Q_{2low}|$ is ***<u>greater than</u>*** $|Q_{low}|$.



a) Will $|Q_{2high}|$ be greater than, less than, or equal to $|Q_{high}|$? *(Hint: Refer to the answer to #8.)*

b) If $|Q_{2low}| - |Q_{low}| = y$, is $|Q_{2high}| - |Q_{high}|$ greater than, less than, or equal to y?

c) Suppose that $|Q_{high}|$ = 100 J, $|Q_{low}|$ = 40 J, and y = 20 J. In this case, will $|Q_{2high}/Q_{2low}|$ be less than (T_{high}/T_{low})? Is this compatible with our original assumption that $|Q_{2high}/Q_{2low}| < T_{high}/T_{low}$?

d) Would the answer to (c) change if we chose a different set of values for the Q's, as long as $|Q_{high}| > |Q_{low}|$? Explain why or why not.

12. Based on your answers to #9-11, do you conclude that $|Q_{2low}|$ is *greater than, less than,* or *equal to* $|Q_{low}|$?

13. If both engines are being run simultaneously, they can be considered a single, composite system undergoing a cyclic process. For this composite process, is the net overall work positive, negative, or zero? (The net overall work is the net sum of all positive and negative work)

14. For this composite system, at the lower temperature, is there net heat *absorbed* or *given off*? *Hint: Consider the relative magnitudes of* $|Q_{low}|$ and $|Q_{2low}|$ *and which of these represents heat* *<u>absorbed</u>, and which represents heat <u>given off</u>.*

15. For this composite system, at the higher temperature, is there net heat *absorbed* or *given off*? *Hint: Consider the relative magnitudes of* $|Q_{high}|$ and $|Q_{2high}|$, *and which of these represents heat* *<u>absorbed</u>, and which represents heat <u>given off</u>.*

16. Is the result you found compatible with the Second Law of Thermodynamics, in the form stated by Clausius? ["*It is impossible for an engine operating in a cycle to have as its* ***only*** *effect the transfer of a quantity of heat from a reservoir of low temperature to a reservoir at a higher temperature.*"] Explain your answer.

17. If your answer to #16 is no, suppose you had assumed that $|Q_{2high}/Q_{2low}| > (T_{high}/T_{low})$, and had repeated all of the above steps with each engine operating in the *opposite* direction to that assumed above. Would your answer to #16 change?

Appendix H: Problem "Dissection"

A thin plastic sheet divides an insulated six-liter container in half. Four moles of an ideal gas are confined to one half of the container, at a temperature of 300 K. The plastic divider is suddenly removed and the gas expands to fill the container. What is the change in the entropy of the gas? (This is known as a *free expansion*.)

a) Is Q for this process *greater than zero, less than zero* or *equal to zero*?

b) Is W for this process *greater than zero, less than zero* or *equal to zero*? ***Hint:*** *As the gas expands, does it exert a force on an* ***external*** *body?*

c) Is ΔE for this process *greater than zero, less than zero* or *equal to zero*?

d) Based on your answer for (c), would you say that ΔT for this process will be *greater than zero, less than zero* or *equal to zero*? ***Hint:*** Remember that this is an *ideal gas*, and for a (monatomic) ideal gas, $E=3/2\ nRT$.

e) The change in entropy for a quasi-static, reversible process is given by $\Delta S = \int dQ/T$; however, this free expansion process is not reversible (Why?). Suppose we decide to find ΔS_{rev} for a ***reversible*** process, but one that has the ***same*** initial and final states as the free expansion described here. Then is ΔS_{rev} *greater than, less than* or *equal to* ΔS_{free}? Explain.

f) In order to find ΔS_{rev} for the reversible process, we need to find Q_{rev}, the heat absorbed in this process. From the first law of thermodynamics, what is the relationship between Q_{rev}, E_{rev} and W_{rev}?

$Q_{rev} =$

g) Again, consider a reversible process that has the ***same initial and final states*** as this free expansion process. Then is ΔE_{rev} *greater than, less than* or *equal to* ΔE_{free}? Explain.

h) Based on your answers to (c), (f) and (g), is Q_{rev} *greater than, less than* or *equal to* W_{rev}? Explain.

i) On this P-V graph, sketch a possible path for the reversible process that connects the initial and final states of the free expansion. (Draw an arrow to indicate the direction of the process.) *For simplicity, choose an* ***isothermal*** *path (why is this a permissible choice?)* Would W_{rev}, the work done by the gas, be *positive, negative,* or *zero?*

j) The general expression for mechanical work is $W = \int PdV$. This integral could be carried out if we knew the functional relationship between P and V. What is the algebraic relation among P, V, and T for an ideal gas? Use this to show that $W = nRT\ln V$ for an *isothermal* ideal gas process.

k) For an isothermal process, the change in entropy is given by $\Delta S = \int dQ/T = Q/T$. From your results in (e), (h) and (j), find the change in entropy for the free expansion described above.

l) If the free expansion occurred at a temperature of 600 K, would ΔS be *greater than, less than,* or *the same as* the ΔS found for the 300 K process? Explain.