

Article

Increased Preclass Preparation Underlies Student Outcome Improvement in the Flipped Classroom

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Submitted February 21, 2015; Revised July 20, 2015; Accepted July 28, 2015
Monitoring Editor: Mary Lee Ledbetter

Active-learning environments such as those found in a flipped classroom are known to increase student performance, although how these gains are realized over the course of a semester is less well understood. In an upper-level lecture course designed primarily for biochemistry majors, we examine how students attain improved learning outcomes, as measured by exam scores, when the course is converted to a more active flipped format. The context is a physical chemistry course catering to life science majors in which approximately half of the lecture material is placed online and in-class problem-solving activities are increased, while total class time is reduced. We find that exam performance significantly improves by nearly 12% in the flipped-format course, due in part to students interacting with course material in a more timely and accurate manner. We also find that the positive effects of the flipped class are most pronounced for students with lower grade point averages and for female students.

INTRODUCTION

The flipped college science course provides the majority of standard lecture material online as assigned preclass homework, and thus allows for in-class instruction that is more active and engaging for students (Day and Foley, 2006). An active-learning environment provides benefits that are well-known in science, technology, engineering, and mathematics (STEM) education (President's Council of Advisors on Science and Technology, 2012; Graham *et al.*, 2013;

Freeman *et al.*, 2014), including improved test performance for all students (Haak *et al.*, 2011). For example, a recent meta-analysis of the effect of online instruction blended with in-class instruction suggests that the flipped-class format improves student outcomes by ~13% in STEM classes (Bernard *et al.*, 2014). Jensen *et al.* (2015) have shown that standard and flipped formats of the same class employing active learning do not have significantly different student outcomes, thus pointing toward the active-learning element of the flipped class as the key to improved student outcomes. Other literature also suggests that flipping, or blending, college science classroom instruction benefits student performance, but how this performance gain is attained through students' preparation activities and engagement with course materials is less known (Halverson *et al.*, 2014; Stockwell *et al.*, 2015). In addition, what is known is largely indirect evidence, including self-reported or observational data (Herreid and Schiller, 2012; Eddy and Hogan, 2014; Halverson *et al.*, 2014).

In this paper, we examine what college science students do differently or more intensely in preparing for the more active, flipped-course environment that can be directly linked to better exam performance. The flipped structure prompts students to review material earlier and more often

CBE Life Sci Educ December 1, 2015 14:ar36

DOI:10.1187/cbe.15-02-0040

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than in the standard note-taking, lecture-based course. For example, the structure of the flipped environment may provide students impetus for less crammed, more uniform interaction with the course material throughout the semester. Long-standing cognitive psychology research highlights the benefits of spacing out learning activities over time in contrast to blocked learning, for example, short-term cramming in the lead-up to an exam (Bahrick *et al.*, 1993; Son, 2004). In addition, the weekly preclass assignment, which is necessary to participate in a flipped environment, may provide needed structure to engage with course content more deliberately (Baepler *et al.*, 2014). If so, this increased student persistence in a more timely and accurate manner could account for performance gains in the flipped environment (Preszler *et al.*, 2007; Estrada *et al.*, 2011; Graham *et al.*, 2013).

We hypothesize that the type of preparation structure necessary for the active-learning, flipped-class format is systematically different and leads to better knowledge acquisition and performance when compared with more standard lecture-based formats. For the college science education community, demonstrating how students in science courses attain performance gains in a flipped-classroom environment offers novel and deeper levels of insight into how to structure the college science education experience. Showing that students in a flipped classroom consistently do things differently, earlier, or more often—and in ways that contribute to their higher performance—would make a stronger case that flipping a course is worthwhile and recommended.

Nevertheless, one difficulty in determining how the performance benefits of the flipped classroom are attained is that many STEM education research studies focus on introductory science or distance-education courses (Halverson *et al.*, 2014). While student performance gains in these environments is encouraging, there is inherent variability in beginning college students' interests, motivations, and approaches to studying for and taking exams (Day and Foley, 2006). This makes it challenging to identify precisely what the students are doing differently in their preparation for and interaction with the flipped environment that leads to higher performance. Though there are only a few studies of flipped or blended curriculum innovation that span across introductory and advanced courses or that focus solely on upper-level courses (Preszler *et al.*, 2007), it is in these courses that there is more stability in interest and motivation factors due to students already being committed science majors.

METHODS

Human Subjects Protocol

The Institutional Review Board at the University of Massachusetts–Amherst has approved the work described in this work under protocol number 2013-1714.

Course Structure

The course under study is an upper-level undergraduate one-semester course that covers classical thermodynamics, equilibrium phenomena, reaction kinetics, and statistical and quantum mechanics. The course is required for undergraduate majors in biochemistry and molecular biology, undergraduate BA majors in chemistry, and, for the first 3 yr of the study, for some PhD students in the graduate program in molecular and cellular biology, all at the University of Massachusetts–Amherst. All instances of the course were taught by the same instructor using very similar in-class slide presentations for the standard course and similar activities for the flipped course. Example problems solved in class by the instructor in the standard course were adapted for peer–peer activities in the flipped-format course.

Student outcomes in the course were studied over a period of 5 yr, during which the course was offered in the standard instructor-centered lecture style for the first 3 yr and in the flipped student-centered style for the last 2 yr. All 5 yr had course elements in common. Online homework based in the Online Web Learning (OWL) system (Hart *et al.*, 1999) provided an out-of-class opportunity for students to practice problem solving. An online, interactive textbook, also based in the OWL system (an OWLBook), provided students with background readings, interactive illustrations, and assignable example problems of greater complexity than the online homework. Summative assessments for all years were via three written exams, all of similar format and content. Student populations and class sizes were similar for all 5 yr (Table 1).

The standard-format course met three times per week for 50 min per meeting. Lecture material was presented using a tablet PC that permitted on-screen inking on PowerPoint slides that were projected to the class, and the slide presentation, along with the instructor's verbal comments, were recorded and provided online to students within 24 h of the end of each class. These postlecture recordings, the OWL homework, and the OWLBook, as well as electronic copies of old exams (including solutions) and course handouts, formed the online portion of the standard-format course.

Table 1. Course data for the 5 yr under study^a

AY	Number of students	Number of sections	Number of meetings/week	Number of minutes/week	Active
2007–2008	79	1	3	150	No
2008–2009	88	1	3	150	No
2009–2010	78	1	3	150	No
2011–2012	111	3	1	75	Yes, clickers, peer
2012–2013	133	2	2	100	Yes, TBL

^aAY is the academic year in which the course was offered. Enrollment numbers are for all sections for each AY. The number of meetings per week and the total number of minutes per week spent in class with the instructor are given. The extent and type of active-learning activities in the classroom are shown in the "Active" column. Clickers, use of personal-response hardware in class; peer, student–student interactions facilitated by instructor; TBL, team-based, collaborative student interactions in class.

The flipped-format course met either for one 75-min session per week or for two 50-min sessions per week. This reduced in-class time was supplemented with prerecorded "lectures" available to the students at least a week before class, which increased the online component in the flipped course compared with the standard course. These supplemental lectures were broken into 5- to 20-min chunks on specific topics in the OWLBook. Students were free to view the supplemental lectures or to skip them, as these lectures carried no course credit. The use of less in-class time allowed the instructor to offer more sections of the course, which allowed the class size to remain about constant despite a rapidly increasing total number of students taking the course. All other components of the standard course were present in the flipped course.

Aside from the prerecorded lectures and reduced in-class time for the flipped-format course, a substantial difference between course formats was the increased use of active learning in the flipped classroom. This took the form of peer–peer think–pair–share activities, clicker responses, and example problems for students to work in the once-weekly 75-min sections. In the twice-weekly 50-min sessions, team-based learning (Michaelsen *et al.*, 2004) was used. In this format, teams of five to eight students remained allied throughout the semester. In-class activities included difficult example problems attacked by teams, individual and team readiness assessments on new material, and student explanations of problem solutions on projected whiteboards.

Written exams that were identical in structure and very similar in content form the basis of analysis in this paper. Three exams were used in each iteration of the course, both in the standard and in the flipped format. Exam 1 covered material from the first third of the course and focused mostly on classical thermodynamics. Exam 2 covered material from the middle third of the course and focused on chemical and physical equilibria. Exam 3 covered material from the final third of the course and focused on reaction kinetics and statistical and quantum mechanics. The third exam was not cumulative, and there was no cumulative final exam in the course. The first two exams were given to students over a 90-min time period on an evening during the semester. The third exam was given during the regularly scheduled 120-min final exam period at the conclusion of the semester. Analysis of student access to online material in the weeks before and after each exam was aligned to the day on which each exam was given.

The course exams in this study were all constructed identically, contained assessment questions that probed very similar aspects of course content, and were presented at the same point in the course for each iteration of the course during the 5-yr period being studied and the 2 yr prior to the study. Individual questions on each exam were graded by one person following a grading rubric provided by the instructor, who was the same individual for all iterations of the course. All exams from the three prior years of the course along with the answer keys for each exam were provided to students at the start of each iteration of the course. Given this standardization of exam format and content, we employ the course exams as a measure of student learning outcomes.

Each exam contained five questions. Students were given the option of answering any four or all five of the questions. Most students chose to answer four questions. If four

questions were answered, each one was worth 25 points. If five questions were answered, each one was worth 20 points. Every question was structured with four or five subquestions that, in general, increased in difficulty in progression through the question. Early subquestions typically involved straightforward application of previously described manipulations of data, whereas late subquestions typically involved integration of concepts not explicitly covered in class. Nearly all questions involved mathematical calculations. Students were given formula sheets with the exam and were told not to memorize formulas.

Analyzing Online Material Access

Student usage profiles for online homework (OWL) attempts, correctness, online OWLBook access, and prerecorded lecture video access were examined as a function of time relative to an exam. These data were binned by week, with week 0 including the 7 d before an exam, concluding with the exam date. The 2 wk before (negative values) or following (positive values) the exam week included the seven consecutive days preceding or following the subsequent or prior week. Exams 1 and 2 occurred during the semester at the one-third and two-thirds points of the course, whereas exam 3 occurred during finals week, even though it was not a cumulative exam. Because the third exam terminated the course, the +1- and +2-wk data cover only the first two exams.

Detailed Description of Statistical Analyses

To run the statistical analysis reported in the paper, we used IBM's SPSS software version 19.

Description of Exam Analysis

For our main analysis comparing the flipped with the standard classroom, we ran a mixed-model 2 (class type) \times 3 (exam) analysis of covariance (ANCOVA). We controlled for student grade point average (GPA), which significantly predicted students' exam scores, $F(1440) = 420.39$, $p < 0.001$, partial $\eta^2 = 0.489$. We treated exams 1, 2, and 3 as the within-subjects variables and class type as the between-subjects variable. We found a significant effect for both exam, $F(2439) = 25.41$, $p < 0.001$, partial $\eta^2 = 0.055$, and class type (i.e., standard or flipped), $F(1440) = 59.91$, $p < 0.001$, partial $\eta^2 = 0.12$, but no interaction, $F(2439) = 1.45$, $p < 0.24$, partial $\eta^2 = 0.003$, between the two. Exam scores were higher in the flipped classroom than in the standard classroom. Furthermore, using a Sidak adjustment for multiple comparisons, exam 1 scores were lower than exam 2 scores ($p < 0.001$), and exam 3 scores were lower than both exam 1 ($p < 0.001$) and exam 2 ($p < 0.001$) scores.

Description of Attempts of Online Material Analysis

To analyze attempts at answering online material across the two class types, we ran a mixed-model 2 (class type) \times 5 (week) ANCOVA, controlling for GPA, $F(1445) = 0.60$, $p = 0.44$, partial $\eta^2 = 0.001$. We treated the 3 wk before the exam and the 2 wk after the exam as our within-subjects variable and class type as the between-subjects variable. For the 3 wk before the exam, we averaged across exams 1, 2, and 3, and for the 2 wk after the exam, we averaged across exams 1 and 2. Thus, we looked at students' average attempts to answer the online material 2 wk before, the week of, and 2 wk after an exam.

Description of Accuracy of Online Material Analysis

To analyze accuracy at answering the online questions, we ran a mixed-model ANCOVA, controlling for GPA, $F(1249) = 56.94$, $p < 0.001$, partial $\eta^2 = 0.186$. Again, we treated the 3 wk before the exam and the 2 wk after the exam as our within-subjects variable (averaged across exams) and class type as the between-subjects variable.

Description of Moderation by GPA Analyses

To first examine whether GPA moderated our students' attempts on the online problems in the 3 wk before the exam, we treated GPA as a continuous variable and ran a regression equation predicting attempts from class type (with the flipped class as 1, and the standard class as 0), GPA mean centered, and the interaction between the two.

Description of Gender Analysis

We ran a 2 (class type) \times 2 (gender) \times 3 (exam) mixed-model ANCOVA, again controlling for GPA, $F(1438) = 441.68$, $p < 0.001$, partial $\eta^2 = 0.502$. Although, there was not a significant interaction between class type, gender, and exam, $F(2437) = 1.71$, $p = 0.31$, partial $\eta^2 = 0.005$, we still examined whether gender differences emerged across each class type and the three exams. Across exams 1, 2, and 3 in the standard class, male students performed better than female students (all p values < 0.02). In the flipped class, this difference was no longer significant on exam 1 ($p = 0.088$) and exam 3 ($p = 0.32$).

Student Surveys

To analyze student satisfaction with the flipped-course format, we examined student responses to an anonymous, standardized student evaluation instrument (the University of Massachusetts Student Response to Instruction) that was given to students at the end of each of the standard- and flipped-course instances. We analyzed student responses to questions on 1) their perception of how much they learned and 2) how they ranked the physical chemistry course compared with other courses. Students in the flipped-course instances were offered a separate survey opportunity to probe specific aspects of their satisfaction with the course.

RESULTS

The aim of this study is to investigate how higher exam scores result from different preparation activities of declared science majors in a flipped, upper-level, required biochemistry course titled Elementary Physical Chemistry. The student population for this course is relatively uniform year to year and is composed of individuals who not only have already demonstrated success in a science major but also have shown they are highly motivated to persist in science. Thus, the upper-level course context reduces the potential individual differences in student ability often found in introductory courses, whether for nonmajors or majors. Details of course elements across five student cohorts totaling 464 students (36% female) are described in Table 1. Both the standard and flipped physical chemistry course formats we analyze shared common elements, including online homework (Hart *et al.*, 1999), an online textbook, and three

summative assessment exams that had identical formats and very similar or identical questions between course instances (see the Supplemental Material).

To investigate what students in a flipped-course environment do differently in terms of timing, preparation, and accuracy in answering homework questions, we use a time-series design (i.e., standard to flipped) and a mixed-model ANCOVA to control for potential cohort differences. We compare two versions of the same course, one presented in a standard format that contained several online learning elements but used instructor-based lecturing in class (i.e., a blended course; Bliuc *et al.*, 2007) and the other a flipped course with enhanced in-class activities. We also analyze all results, with students' undergraduate GPA included as an additional control for differences in intrinsic ability. Our measure of student learning outcomes uses three summative exam grades. The averages of each of these exam grades are not statistically significantly different from one another for the three offerings of the standard-course version. The same is true for the averages for the two offerings of the flipped-course version.

Similar to results from other interventions involving a more active and engaged classroom experience (Freeman *et al.*, 2014), when compared with the standard-course format for student cohorts in the flipped-course format we found significant improvements in exam scores for each of the three exams ($p < 0.01$). Figure 1 shows the mixed-model ANCOVA controlling for students' undergraduate GPA. Averaging across all three exams, the flipped class shows an average 11.6% improvement when compared with the standard course ($F(1440) = 59.91$, $p < 0.001$, partial $\eta^2 = 0.12$). This difference occurred for all three exams, and thus there was no interaction between exam or class type ($F(2440) = 1.45$, $p < 0.24$, partial $\eta^2 = 0.003$). However, there was a significant difference between exams ($F(2440) = 25.41$, $p < 0.001$, partial $\eta^2 = 0.055$). Exams 1 and 2 were significantly higher than the third exam ($p < 0.001$), and exam 2 was significantly higher than exam 1 ($p < 0.001$). The third exam covered quantum mechanics, a topic on which students historically do not fare as well. Still, regardless of the individual exam, students did better on exam performance in the flipped classroom than they did in the standard classroom.

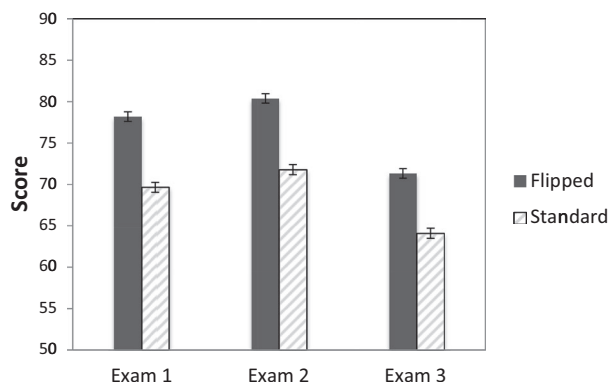


Figure 1. Student exam scores improved significantly in the flipped course as compared with the standard course. We ran a mixed-model ANCOVA while controlling for GPA, and found that students did better in the flipped classroom than the traditional classroom.

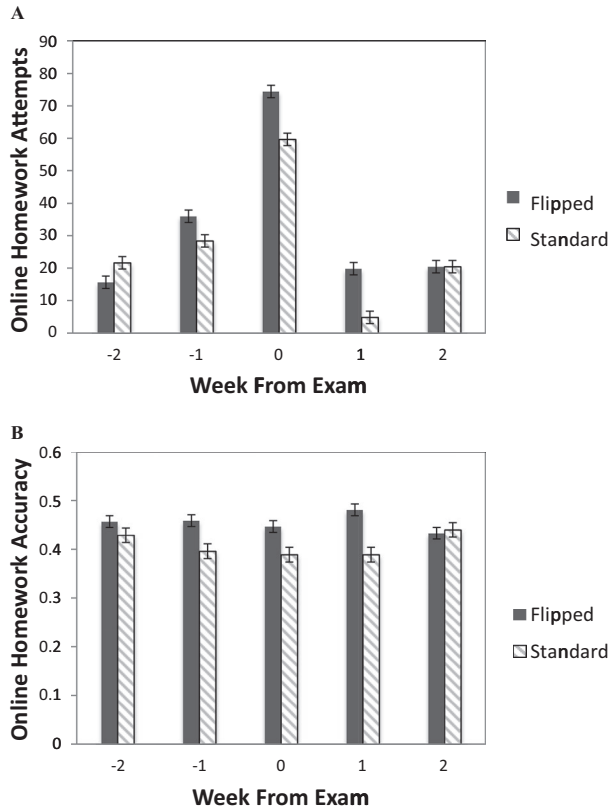


Figure 2. Online homework attempts and accuracy of those attempts as a function of weeks before (negative weeks) or after (positive weeks) an exam. (A) Homework attempts for the two course modes. (B) Accuracy of homework completion for the two course modes.

Exam performance was paired to GPA values binned in six equal size ranges, and these paired data were compared among all course offerings (Supplemental Material Table S1). Comparing years in which the same pedagogy was employed, 28% of the paired scores were significantly different from each other (2-sided *t*-test, $p > 0.05$). In contrast, comparing pairs of years in which one was standard and one was flipped, 43% of the paired exams were statistically significantly different from each other (2-sided *t*-test,

$p > 0.05$), a 50% improvement in student outcomes for the flipped format.

Regarding how this performance increase manifested in the flipped classroom, there are four significant indicators. First, use of the same online material differed substantially between the standard course and the flipped course. Students in the flipped class attempted online homework questions more often, $F(1, 445) = 38.41$, $p < 0.001$, partial $\eta^2 = 0.08$ (Figure 2A). This difference was not evident for homework completed by the end of the semester (Supplemental Material Table S2). Second, although all students were most likely to attempt homework problems during the week of an exam (p values < 0.001) regardless of class mode, students in the flipped class worked through the online homework more steadily, that is, across the span of weeks, than did students in the standard class. The flipped-class students attempted more homework questions 1 wk before, the week of, and the 2 wk following the exam (p values < 0.001) than did the students in the standard class. Third, students in the flipped class more accurately answered homework problems on average than students in the standard class ($F(1, 249) = 5.84$, $p < 0.02$, partial $\eta^2 = 0.023$). Fourth, accurately answering homework questions significantly predicted exam scores ($p < 0.001$), indicating that homework accuracy in the 2 wk before the exam mediated the relationship between class type and exam scores ($p < 0.01$). Thus, participating in the flipped class is associated with students more accurately answering homework questions leading up to the exam, which is then significantly related to higher exam scores (Figure 3). Specifically, accuracy partially mediated the relationship between class type and exam scores. We found evidence of mediation both using a traditional Sobel test (Sobel's $z = 3.24$, $p < 0.01$; Baron and Kenny, 1986) and Hayes' (2013) PROCESS macro with 5000 bootstrap samples to examine the indirect effect. There was a significant indirect effect (i.e., the 95% confidence interval did not cross 0; indirect effect = 1.00, 95% CI = 0.49–1.68). As the figure shows, when we control for accuracy, the relationship between class type and exam scores gets weaker (the β in the parentheses in Figure 3 indicates the effect of class type, controlling for accuracy of OWL problems). However, that relationship is still significant, suggesting that other factors also account for the higher exam scores.

Two individual differences, overall GPA and gender, were also predictive of performance. In the flipped classroom,

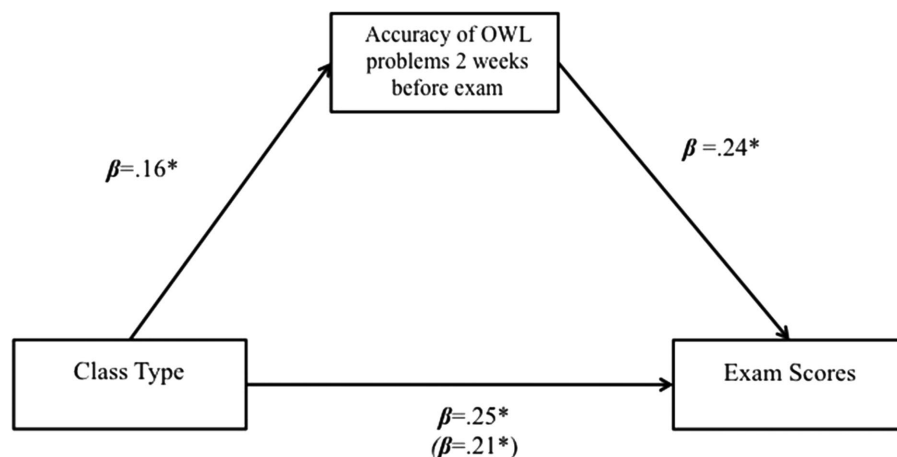


Figure 3. Students in the flipped class answered the online homework problems more accurately in the 2 wk before the exam than students in the standard class. This accuracy in part explains why students in the flipped class had higher exam scores than students in the standard class. Specifically, accuracy partially mediated the relationship between class type and exam scores. β indicates how many SDs the dependent variables (i.e., accuracy, exam score) change per SD increase of the predictor variables (*, $p < 0.05$). β in parentheses indicates the effect of class type, controlling for accuracy of OWL problems.

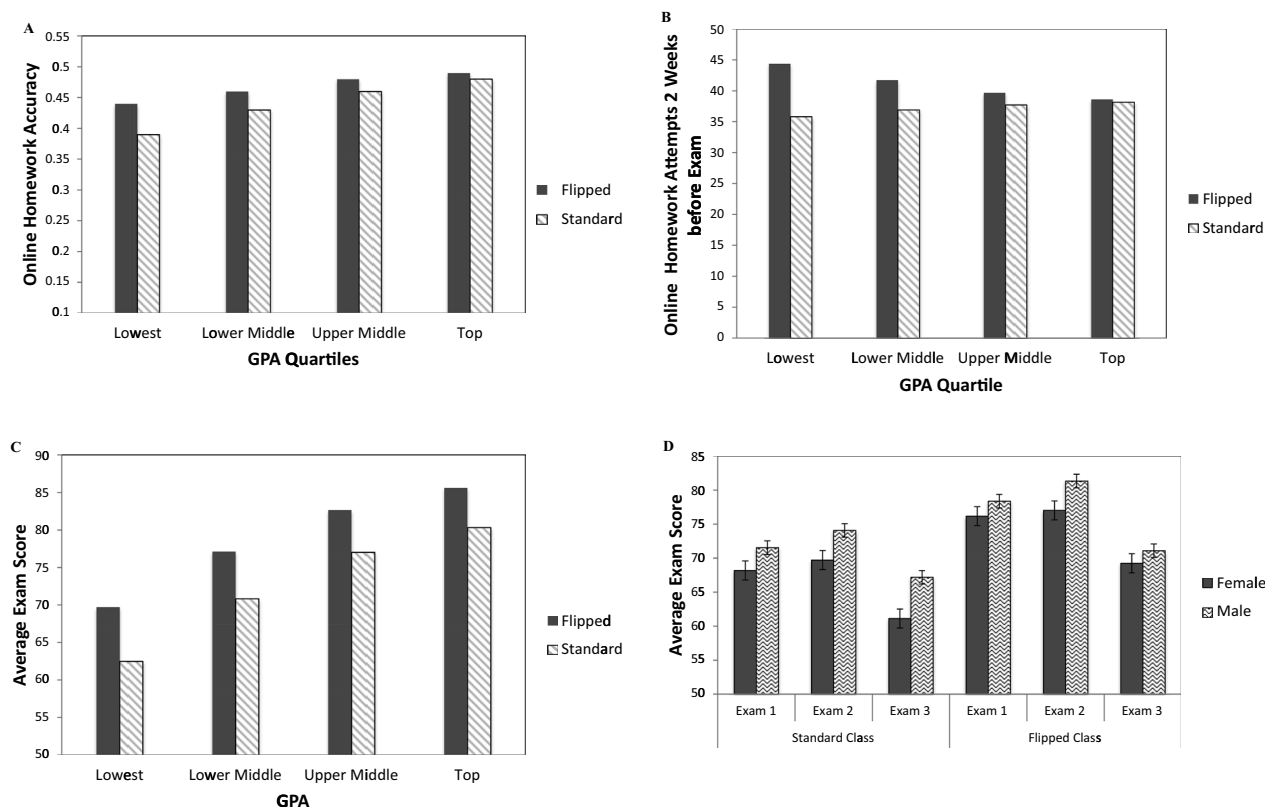


Figure 4. Student GPA correlates with (A) accuracy of completion of online homework 2 wk before an exam, (B) the number of attempts at online homework 2 wk before an exam, and (C) exam score differences between the flipped- and standard-course modes. (D) Female students received significantly lower average exam scores compared with male students in the standard-course format across all three exams, but in the flipped-format course, female and male student scores were not significantly different on exams 1 and 3.

students with lower GPAs showed greater improvement in attempting and accurately answering online homework problems in the weeks immediately before the exam than students with higher GPAs (Figure 4, A and B). Students with lower GPAs also showed greater improvement on exam scores in the flipped- versus standard-course modes (Figure 4C). When examining student attempts and accuracy of answers to online homework problems in the 2 wk leading up to the exam, we saw that students in the lowest GPA quartile in the flipped course showed a larger improvement than students in the highest GPA quartile. This was indicated by a significant interaction between GPA and class type predicting both attempts ($t(444) = -2.68, p < 0.01$) and accuracy ($t(443) = -2.17, p < 0.04$), with students in the lower two GPA quartiles showing the greatest improvement in attempts and accuracy (p values < 0.01).

A gender difference in exam outcomes was also evident. Women demonstrated a greater benefit from the flipped classroom on exam scores than men (Figure 4D). Specifically, there were smaller gender differences on exam scores in the flipped class compared with the standard class. In the standard class across all three exams there was a consistent four to five percentage point difference between female and male students (p values < 0.02). In the flipped class, however, female students did not differ significantly from their male counterparts on exam 1 ($p = 0.09$) and exam 3 ($p = 0.32$). Thus, at least on two out of the three exams, the

flipped-classroom format was alleviating the gender disparity on exam scores.

The flipped-course format relied heavily on online material presented outside of class, including prerecorded lecture videos. Although there was a broad variation in students' access of these videos, there was a significant correlation between average exam score and video access, $r(235) = 0.22, p < 0.001$ (Figure 5A). Students in the flipped-format course with higher exam scores viewed online lecture material more consistently than students with lower exam scores. Students in the top GPA quartile accessed the videos more uniformly across the weeks bordering an exam, in contrast to students in lower GPA quartiles who concentrated their viewing time disproportionately during the week of an exam in a statistically significant manner ($r(235) = 0.24, p < 0.001$; Figure 5B). The relative number of video lecture accesses versus the time in the semester with respect to the three exam dates indicates that the 7 d before an exam are the most likely time for students to access these online materials. There is a significant positive correlation between GPA and video accesses ($r(235) = 0.24, p < 0.001$). Top GPA quartile students opened video lecture files an average of 20.8 times during the semester. Second- through lowest-quartile students opened these files during the semester 13.5, 14.3, and 8.2 times, respectively. (Any set of video accesses by a student that occurred in a time span of < 5 min were counted as a single access for this analysis.)

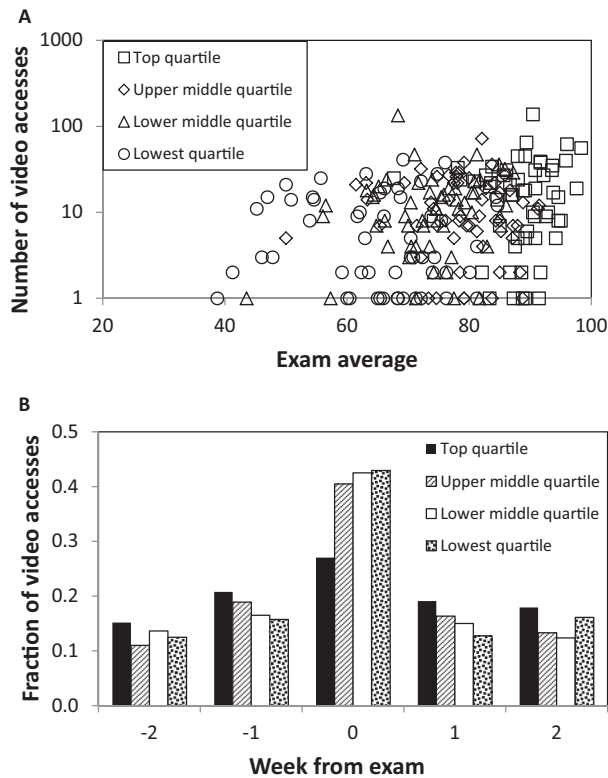


Figure 5. There was substantial correlation between the number of accesses of video recordings and GPA (A) and between the occurrence of those accesses and GPA (B) in the flipped-format course. (A) Note the logarithmic vertical axis. Individual student data are shown. This plot excludes the 14 students who did not access the video lectures. Five of these 14 were GPA fourth-quartile students. The total number of accesses of the online lecture material over the course of the whole semester is plotted vs. the three-exam average for students in the flipped-format course instances.

Student satisfaction with the course was analyzed based on responses to a standard survey instrument answered anonymously at the conclusion of the course. Aggregate responses from students on 1) their perception of how much they learned and 2) how they ranked the course compared with other university courses were compared between standard- and flipped-course instances. Overall, students did not feel that they learned more in the flipped-course version compared with the standard course (despite having better exam scores); however, flipped-format students did rank their course version better overall than did students in the standard-course version (Supplemental Figure S1A).

Students in the two instances of the flipped course were given a second survey that asked their opinions about the flipped-course format (called “blended” in the survey instrument) and the extent to which the course influenced their ability to be independent learners. Supplemental Figure S1B shows that students had a slightly favorable view of the flipped-course format. Students also felt that the flipped-course format had helped them to become more independent learners.

On this same postcourse survey, when asked to select three things to change to improve the course (out of 13 options), 45% of students from the first flipped-course instance

identified “Increase in-class time” as a desired change. Surprisingly, only 19% of the students from the second flipped offering held this view. This difference may relate to the team-based style of instruction in the second offering of the course, though that conclusion requires further study.

DISCUSSION

Our findings demonstrate that there are substantial, positive differences in how students approach a flipped course as compared with a standard-format course. The flipped course encourages students to become more engaged with course material, persist in their learning through more timely and accurate preparation, and, ultimately, perform better. Specifically, this enhanced interaction induces better student preparation for class meetings in the flipped learning environment. More cycles of timely preparation in a flipped class likely improve in-class interactions, which position students to be more accurate in answering online homework problems. This increased accuracy extends to exams, for which grades improve substantially, particularly for lower-GPA students and female students. Because minority groups and women face many external forces impeding their success in the sciences (e.g., anxiety over confirming a stereotype and a threatening environment in STEM; Spencer *et al.*, 1999; Murphy *et al.*, 2007; Moss-Racusin *et al.*, 2012), employing the flipped-class pedagogy in STEM courses is an encouraging pathway for curricular reform efforts aimed at persistence and retention of all students interested in STEM majors. These gains are found despite the fact that face-to-face instructor time with students is 30–50% less for the flipped class.

The initial impetus to convert the course described here from a standard lecture format to the flipped format was to keep class sizes from growing (due to increasing numbers of student majors) without substantially increasing the in-class time commitment of the instructor. This increase in instructor efficiency is counterbalanced by the need for extensive development of online material on the part of the instructor, although that effort rapidly diminishes after the first offerings of the flipped course. The combination of improved student outcomes, at least in the short term, with improved instructor time and classroom use efficiency, makes course flipping an attractive alternative to the standard lecture course.

A key finding from our data is that successful students interact with the online components of a flipped class in a timely manner as compared with students in a standard-format class. That is, the students in the flipped course prepare for class work and avoid the “cramming” style of study for summative assessments, complete the online work more accurately, and perform better on the summative assessments. An important question surrounding this improvement is the role of the flipped-course environment in these improvements. We think that two aspects of the flipped class lead to this improvement: the increase in active student exercises in the classroom coupled to online course content. There is no doubt that active-learning classrooms improve student outcomes, and it has been argued that, for a flipped course, it is active learning that drives improved student outcomes (Jensen *et al.*, 2015; Stockwell *et al.*, 2015). In our case, we believe that the active flipped classroom leads to a student’s

expectation that attending class will require preparation. Additionally, the active classroom, with point-generating activities included in the class sessions, intrinsically encourages students to attend and participate in the activities. Because the flipped classroom offers a clear and reinforcing online experience in the form of recorded “lectures” aligned with online homework, students are encouraged to prepare before class and well before an exam deadline. The interaction of these two elements of the flipped classroom, we believe, provides the underpinning mechanism that accounts for the improvement in student outcomes for the flipped classroom compared with outcomes for the standard classroom.

Our finding that female students in the standard-format class underperform males while in the flipped-format class they perform equally with males points to a fundamental strength of the flipped classroom: students are exposed to a wider variety of learning tools that allow them to better exploit their learning styles. Similarly, lower-performing students receive additional benefit from the flipped-course format as compared with the standard-course format. This effect may also relate to the availability of the wider variety of available learning tools in the flipped-format course. Having several different ways to interact with course content is more likely to resonate with a larger proportion of students than having only one or two modes of interaction with course content, as is typical in a standard course.

ACKNOWLEDGMENTS

The raw data analyzed in this paper can be obtained from the authors. This work was supported in part by the University of Massachusetts. E.S.P. is supported through the Alfred P. Sloan Foundation. M.J.G. is supported through the Howard Hughes Medical Institute’s Professor Grant to Jo Handelsman and by a National Science Foundation grant (NSF-TUES, 1323258).

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Supplemental Table S1

Supplemental Table S1

SUPPLEMENTAL MATERIAL

A year-by-year comparison of paired exam scores indicates that the standard course offerings were statistically more similar to each other than they were to paired scores from flipped course years. Likewise, paired exam scores from the two flipped years were more similar to each other than they were to paired exam scores from standard course years. Exam scores were binned according to each student's cumulative GPA in equal GPA ranges (4.000-3.667, 3.666-3.333, 3.332-3.000, 2.999-2.667, 2.666-2.333, 2.332-2.000, and below 2.000). A two-sided t-test was employed to compute the probability that each paired set of exam scores was statistically different. The table entries are the probabilities that the paired set of exam scores are statistically significantly different based on a two-sided t-test. Probabilities that suggest statistical difference ($P < 0.05$) are highlighted. Years that employed the same instructional style (standard: 2007-2008, 2008-2009 and 2009-2010), flipped: 2011-2012 and 2012-2013) are indicated by double lines around the respective data ranges. id = insufficient data (not enough students in one of the two years for this GPA range), nd = no data (no students in one of the two years for this GPA range).

Supplemental Table S2.

	GPA quartile	Top	Upper middle	Lower middle	Lowest
OWL homework	Pre	97.8 ± 7.2	94.6 ± 12.4	93.8 ± 13.4	79.5 ± 24.6
	Post	98.5 ± 4.9	97.3 ± 5.5	94.7 ± 9.7	80.7 ± 21.5
OWLBook examples	Pre	86.8 ± 26.4	79.1 ± 27.7	71.6 ± 30.2	55.6 ± 36.4
	Post	97.4 ± 13.0	93.9 ± 19.1	89.6 ± 23.8	76.6 ± 35.0

Students in different GPA quartiles successfully completed similar percentages of online OWL homework problems for the standard (Pre) course format vs. the flipped (Post) format course. In contrast, students were more likely to complete successfully the example problems in the online OWLBook in for the flipped course vs. the standard course. This effect is more pronounced for the lower quartiles than for the upper quartile students. Values are means ± standard deviations. These data are for the end of the course, as opposed to data in Figure 2 which are for timely completion of online homework. Students were told at the start of the course that all online homework and OWLBook example problems were due at the end of the semester.

SUPPLEMENTAL MATERIAL

Supplemental Figure S1

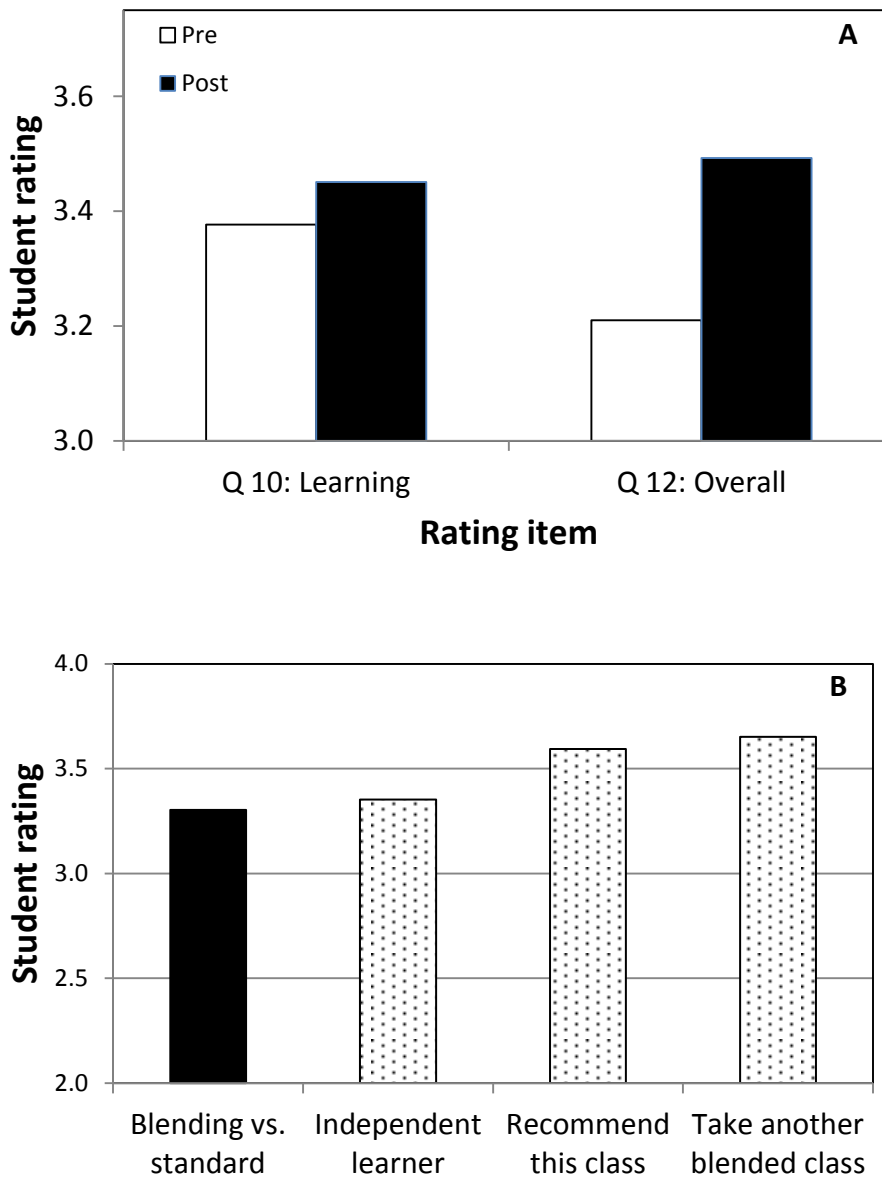


Figure S1. (A) Student responses to two questions on standardized survey instruments demonstrate that students in the flipped course (Post) felt that the course was better than students felt about the standard course (Pre) although students' views on the amount that they learned in the course was equivocal between the two course styles. Students were asked 12 questions on the survey and were allowed to answer on a Likert scale from 1 to 5. Question 10 asked "Overall, how much do you feel you learned in this course? (5=Much more than most, 1=Much less than most)" Question 12 asked "Overall rating of this course. (5=One of the best, 1=One of the worst)". (B) Students in the two instances of the flipped version of the course were asked on an end-of-course survey several questions about the flipped format course: i) Comparing a standard

SUPPLEMENTAL MATERIAL

lecture format with the "BLENDED" format of this course, is the combination of online and face-to-face class time "better" or "worse" for your learning the course material? In your opinion, the blended format is (5=Much better, 4=Better, 3=Equal, 2=Worse, 1=Much worse), ii) Did this experience help you become a more independent/self-reliant LEARNER? (5=Yes, 1=No), iii) Based on this experience, would you recommend this BLENDED LEARNING class? (5=Yes, 1=No), and iv) Would you take another "BLENDED" class at UMass? (5=Yes, 1=No). The averages of the ratings of respondents are shown.

SUPPLEMENTAL MATERIAL

Exam 1 for each of the five years of the study follow in chronological order.

Name: _____

(Please print clearly on all pages)

Please leave the exam pages stapled together. The formulas are on a separate sheet.

This exam has 5 questions. You must answer at least 4 of the questions. You may answer more questions if you wish.

Answering 5 questions can be an advantage if you are unsure of some of your answers (this will distribute the “risk”). Answering 4 questions is advantageous if you are very sure of your answers.

Each page is worth 20 points. The total exam grade will be normalized so that the maximum number of course points for this exam will be 20. For example, getting 80 points on 4 questions equals 100 points on 5 questions equals 20 points toward the final grade. Getting 80 points on 5 questions would be worth 80% of the maximum grade.

If you leave a page blank, it will not be included in the grading. If you work on a page and then decide that you do not want it to be graded, be sure to mark the “DO NOT GRADE THIS PAGE ☐” box at the bottom of the page. If you work on the page and fail to mark the box, the page will be graded.

Work at least 4 problems (of your choosing) or more, as you prefer.

Answers without explanations (where indicated) are not complete.

Name: _____

(Please print clearly on all pages)

1. It is possible to supercool liquid water to below 0 °C. The heat capacities and latent heats for various forms of water are shown below. You may assume that they are constant under conditions found in this problem and that $P = 1 \text{ atm}$.

$C_p(\text{H}_2\text{O}, s) = 38.07 \text{ J K}^{-1} \text{ mol}^{-1}$; $C_p(\text{H}_2\text{O}, \ell) = 75.4 \text{ J K}^{-1} \text{ mol}^{-1}$; $C_p(\text{H}_2\text{O}, g) = 33.76 \text{ J K}^{-1} \text{ mol}^{-1}$; $L_{\text{melting}} = 6.007 \text{ kJ mol}^{-1}$; $L_{\text{vaporization}} = 40.66 \text{ kJ mol}^{-1}$.

a) Suppose you have 0.5 mol of liquid water at -15 °C. You add heat to the supercooled liquid water to bring it to its normal freezing point temperature. How much heat is needed to accomplish that?

b) What is the entropy change in the warming of supercooled water in part a)?

c) If the amount of heat calculated in part a) is removed from liquid water at its normal freezing point, but this time the water freezes rather than supercools, how much ice is formed?

d) Shaking supercooled liquid water will cause it to spontaneously begin to freeze. That means that the entropy change of the Universe must be positive for this process. If you shake supercooled water in a perfectly insulating container, using your above answers, show that $\Delta S_{\text{Universe}}$ for this process is positive.

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Name: _____

(Please print clearly on all pages)

2. Answer the following about various aspects of thermodynamic parameters.

a) Mark the correct statements about the internal energy content of a system:

- ☐ It is the sum of the heat plus work on the system.
- ☐ It consists of the kinetic and potential energies contained in the molecules of a system plus the energies contained in any fields (electric, magnetic, etc.) in the system.
- ☐ It equals the heat entering the system at constant volume.
- ☐ It is constant when temperature is constant for any system.
- ☐ It equals $H - PV$ where H is the enthalpy content of the system.

b) Which of the following illustrate the First Law of thermodynamics?

- ☐ Hot and cold water, when mixed in an insulated container, come to an intermediate temperature.
- ☐ The work done by a Carnot engine equals the net heat that enters the engine.
- ☐ A sealed bottle containing a gas is placed in an evacuated, insulated container that is then sealed. The bottle is broken and the gas spontaneously fills the container.
- ☐ $\Delta E = q + w$.
- ☐ $PV = nRT$.

c) For the following, X out the words contained in parentheses (~~incorrect~~ | correct) that make the statement incorrect. Any number of the words or phrases may be correct.

At 100 °C the equilibrium vapor pressure of water is 1 atm. Consider the process in which 1 mole of water vapor at 1 atm pressure is reversibly condensed to liquid water at 100 °C by slowly removing heat into the surroundings. The water is the system.

- i. In this process, the entropy of the system will (increase | remain unchanged | decrease).
- ii. In this process, the entropy of the Universe will (increase | remain unchanged | decrease).
- iii. Because the condensation process occurs at constant temperature and pressure, the Gibbs free energy change of the system will be (positive | zero | negative).
- iv. Any real process cannot be carried out reversibly. For the condensation described above, comparing the theoretical reversible process to a real, irreversible process, different values will be obtained for the (entropy change of the system | entropy change of the surroundings | entropy change of the Universe | Gibbs free energy change of the system).

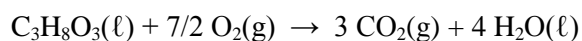
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Name: _____

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3. *E. coli* can transform glycerol(ℓ) ($\text{C}_3\text{H}_8\text{O}_3$) to $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\ell)$ under aerobic conditions. Answer the following using the data provided.

Thermodynamic parameter (25 °C)	ΔH_f°	S_f°	ΔG_f°
$\text{CO}_2(\text{g})$	-393.5 kJ/mol	213.7 J/K·mol	-394.4 kJ/mol
$\text{H}_2\text{O}(\ell)$	-285.8 kJ/mol	69.9 J/K·mol	-237.1 kJ/mol
$\text{O}_2(\text{g})$	0 kJ/mol	205.1 J/K·mol	0 kJ/mol
glycerol(ℓ)	-688.6 kJ/mol	204.5 J/K·mol	-477.1 kJ/mol



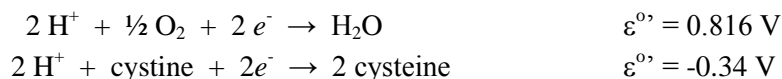
- a) What is the value of ΔG_{rxn}° for the above oxidation of glycerol at 1 atm and 25 °C?
- b) Is the reaction spontaneous in the direction written at 25 °C? Explain.
- c) Suppose the reaction is placed in a chamber so that the pressure can be controlled at 2 atm (with the temperature held constant). Will the reaction be **more** or **less** spontaneous in the direction written at 2 atm pressure as compared to the reaction at standard conditions? Explain using words and/or equations
- d) Will the value of ΔG_{rxn}° that you calculated in part a) above be **less than**, **greater than** or **equal to** $\Delta G_{rxn}^{\circ'}$, the standard state Gibbs free energy change at pH 7? Explain using words and/or equations.

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Name: _____

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4. Consider the oxidation of the amino acid cysteine by oxygen. The reaction involves the crosslinking of the free sulfhydryls of cysteine to form a crosslinked dimer called cystine. The electrochemical potentials for the half-reactions that make up this reaction are



a) Write a balanced chemical equation for the oxidation of cysteine to cystine.

b) Is the oxidation of cysteine to cystine by oxygen favored at standard state conditions and pH 7?

Explain.

c) Calculate the equilibrium constant for the oxidation of cysteine to cystine under biochemical standard state conditions.

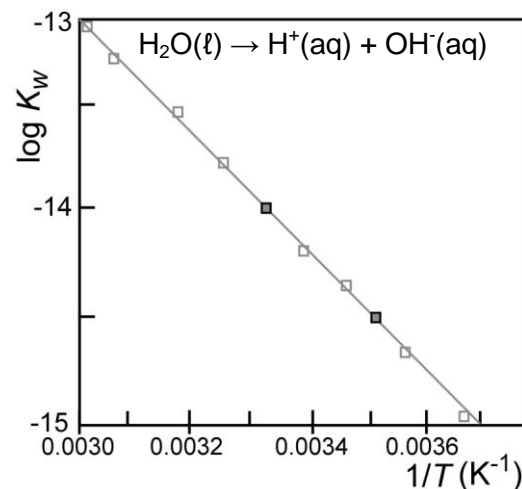
d) Suppose that a protein has a single cysteine exposed on its surface. This cysteine can crosslink to another cysteine on a different protein. From your answers above, determine the ratio of concentrations of monomer protein to dimer protein when a 100 μM solution of pure monomer protein is exposed to atmospheric oxygen (pH 7, 298 K, $p\text{O}_2 = 0.2 \text{ atm}$) and the system comes to equilibrium. (Assume that the driving force for disulfide bond formation of free cysteine is the same as cysteine in the protein and that all species behave ideally). Note: setting up the problem is sufficient. You do not need to compute the final numerical answer.

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Name: _____

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5. The equilibrium constant for the ionization of water, reaction shown as an inset, has been measured at several different temperatures. A plot of $\log(K_w)$ vs. $1/T$ is shown at right. The numerical value of the slope of the line connecting the data points is -2912; it has units of Kelvin.



a) The value of $\log(K_w)$ at $T = 298 \text{ K}$ is -14. What is the value of ΔG° for this reaction at 298 K?

b) What is the value of ΔH° for this reaction at 298 K?

c) What is the value of ΔS° for this reaction at 298 K?

d) Is ΔH° constant between 280 K and 330 K (the range in the plot above)? Explain your answer. If you can't determine the answer, then state what additional information is needed to answer it.

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Name: _____

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Please leave the exam pages stapled together. The formulas are on a separate sheet.

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Work at least 4 problems (of your choosing) or more, as you prefer.

Answers without explanations (where indicated) are not complete.

Name: _____

(Please print clearly on all pages)

1. Answer the following about various aspects of thermodynamic parameters.

a) Mark the correct statements about the change in the internal energy content of a system when the system changes states:

- ☐ It is the sum of the heat into the system plus work done on the system.
- ☐ It consists of the kinetic and potential energies contained in the molecules of a system plus the energies contained in any fields (electric, magnetic, etc.) in the system.
- ☐ When the system is an ideal gas, it equals the heat entering the system at constant volume.
- ☐ It is zero when temperature is constant for any system.
- ☐ It equals $\Delta H - \Delta(PV)$ where H is the enthalpy content of the system.

b) Which of the following illustrate the Second Law of thermodynamics?

- ☐ Hot and cold water, when mixed in an insulated container, come to an intermediate temperature.
- ☐ The net work done by a Carnot engine equals the net heat that enters the engine.
- ☐ A sealed bottle containing a gas is placed in an evacuated, insulated container that is then sealed. The bottle is broken and the gas spontaneously fills the container.
- ☐ $\Delta E = q + w$.
- ☐ The entropy of a system at zero Kelvin is equal to zero.

c) Samples of *hot water and cold water* are mixed together in a thermally insulated, closed container of fixed volume. Determine whether each of the following thermodynamic quantities is greater than, equal to, or less than zero for the system, which is shown in italics above. State your reasoning.

>0, =0, <0?	Reason
<i>q</i>	_____
<i>w</i>	_____
ΔE	_____
ΔH	_____
ΔS	_____

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Name: _____

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2. A bartender puts a 50 g ice cube at $-15\text{ }^{\circ}\text{C}$ into a glass with 45 mL of bourbon at $25\text{ }^{\circ}\text{C}$. The bourbon is 80% ethanol and 20% water by volume (plus impurities that can be discounted). The following table gives specific heat capacities and latent heats for ethanol and water. The density of liquid water is 1.00 g/mL and of liquid ethanol is 0.789 g/mL . Ethanol freezes at $-114\text{ }^{\circ}\text{C}$ and vaporizes at $78.4\text{ }^{\circ}\text{C}$.

	$\bar{C}_{P,vapor} (\text{J K}^{-1}\text{g}^{-1})$	$\bar{C}_{P,liquid} (\text{J K}^{-1}\text{g}^{-1})$	$\bar{C}_{P,solid} (\text{J K}^{-1}\text{g}^{-1})$	$L_{vaporization} (\text{J g}^{-1})$	$L_{melting} (\text{J g}^{-1})$
ethanol	1.63	2.44		837	106
water	2.08	4.18	2.05	2260	333

- a) How much heat is required to warm the ice cube to its melting temperature?
- b) What is the entropy change for the ice cube in the process of part a?
- c) If the amount of heat calculated in part a is removed from the bourbon in the glass, what will the temperature of the bourbon be?
- d) If a thermometer is monitoring the temperature of the liquid in the glass, will the thermometer reading be less than, equal to, or greater than the answer in part c? Explain (note: you don't need to compute numbers here, you just need to explain your reasoning)

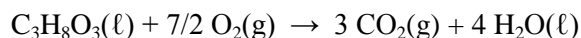
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Name: _____

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3. *E. coli* can transform glycerol(l) ($\text{C}_3\text{H}_8\text{O}_3$) to $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ under aerobic conditions. Answer the following using the data provided.

Thermodynamic parameter (25 °C)	ΔH_f°	S°	ΔG_f°
$\text{CO}_2(\text{g})$	-393.5 kJ/mol	213.7 J/K·mol	-394.4 kJ/mol
$\text{H}_2\text{O}(\text{l})$	-285.8 kJ/mol	69.9 J/K·mol	-237.1 kJ/mol
$\text{O}_2(\text{g})$	0 kJ/mol	205.1 J/K·mol	0 kJ/mol
glycerol(l)	-688.6 kJ/mol	204.5 J/K·mol	-477.1 kJ/mol



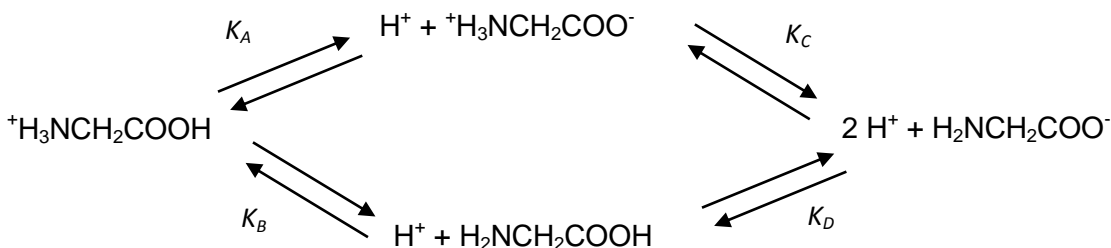
- a) What is the value of $\Delta G_{\text{rxn}}^\circ$ for the above oxidation of glycerol at 1 atm and 25 °C?
- b) What is the value of ΔG_{rxn} at 1 atm and 25 °C when the partial pressure of oxygen and carbon dioxide are those found in the atmosphere? (Oxygen is 0.21 atm and CO_2 is 3.8×10^{-4} atm.)
- c) Is the oxidation of glycerol more favored, equally favored, or less favored under atmospheric conditions compared to standard state conditions? Explain
- d) Is the oxidation of glycerol more favored, equally favored, or less favored when the temperature of the reaction is increased from the standard state temperature? Explain

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Name: _____

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4. The amino acid glycine can convert from the fully protonated form to the fully deprotonated form along two different pathways (see reaction scheme below). The values for three of the equilibrium constants are $K_A = 4.5 \times 10^{-3}$, $K_C = 1.7 \times 10^{-10}$ and $K_D = 1.5 \times 10^{-4}$ when the reactions run from left to right (i.e. products are on the right sides of the arrows) at standard T and P . You may assume that the solutions are ideal.



- What is the value of ΔG^0 for the top left reaction (reaction A)?
- If the concentration of ${}^+\text{H}_3\text{NCH}_2\text{COO}^-$ is 100 mM and the pH is 5.0, what is the concentration of ${}^+\text{H}_3\text{NCH}_2\text{COOH}$ if all reactions are at equilibrium?
- What is the value of ΔG for the top left reaction (reaction A) under the concentration conditions of part b?
- What is the value of K_B ?

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Name: _____

(Please print clearly on all pages)

5. A sample of agar gel is contained in a sealed syringe. The gel can be manipulated by moving the syringe plunger up and down. The amount of heat flowing into or out of the gel can also be controlled. Answer the following about the properties of the gel

a) The gel is held at 27 °C as its volume is changed from 50 mL to 52 mL by pulling the plunger out 5 mm from its original position. A constant force of 100 N is required to pull the plunger out. This process is done reversibly. What is the amount of work done on the gel in this process?

b) To keep the temperature of the gel constant in part a, 50 J of heat was added to the gel. What is the change in the gel's internal energy during the expansion process described in part a?

c) What is the entropy change of the gel in the process described above?

d) Is the process above spontaneous or not spontaneous? Explain

- ☐ Spontaneous
- ☐ Not Spontaneous
- ☐ Can't tell from the information given

e) If the syringe was filled with an ideal gas rather than the gel and the amount of work done on the gas was the same as in part a, what would be the amount of heat that flowed into the gas?

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Name: _____

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Scratch pad:

For grading purposes:

question	1	2	3	4	5		Tot
score							

Name: _____

(Please print clearly on all pages)

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This exam has 5 questions. You must answer at least 4 of the questions. You may answer more questions if you wish.

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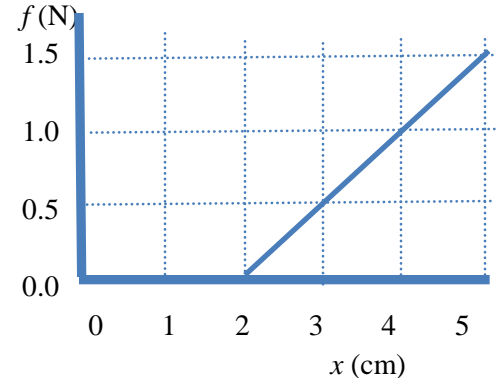
Work at least 4 problems (of your choosing) or more, as you prefer.

Answers without explanations (where indicated) are not complete.

Name: _____

(Please print clearly on all pages)

1. Consider a strip of rubber that is 2 cm long. The rubber band, so long as it is not stretched too much, acts like a spring. Recall that the force vs. length relationship for a spring is $f = k(x - x_0)$ where k is the spring constant, x is the length of the spring and x_0 is the spring length at which no force is applied to the spring. The force vs. length relationship for the strip of rubber is shown at right.



a) When the rubber band is stretched to 3 cm, you find that a force of 0.5 N is required to hold the rubber band at this length. What is the value of the spring constant k ?

b) How much work is done on the rubber band when it is stretched from 2 cm to 3 cm in a slow, reversible way? (Hint: the area of a triangle is width times height divided by two.)

c) Suppose the rubber band stretching in part b was done under conditions in which the rubber band was insulated from the outside world (the process was adiabatic). What is the value of ΔE for the stretching of the rubber band from 2 to 3 cm?

d) Rubber is a crosslinked, long-chain polymer. When rubber is stretched, the rubber polymer molecules go from being randomly distributed to being mostly aligned with each other. In stretching the rubber band from 2 cm length to 3 cm length, will the entropy of the rubber band increase, decrease, or remain constant?

Explain.

e) Will the temperature of the rubber band change if the band is stretched adiabatically as in part c?

Explain.

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2. The latent heat of vaporization of propane is 425 J/g. The specific heat capacity at constant pressure of gaseous propane is $75 \text{ J K}^{-1} \text{ mol}^{-1}$ and the specific heat capacity at constant volume of gaseous propane is $66 \text{ J K}^{-1} \text{ mol}^{-1}$. The molar mass of propane is 44.1 g/mol. At 1 atm pressure propane boils at a temperature of -42°C .

a) Suppose you have 44.1 g of liquid propane at -42°C and 1 atm pressure. How much heat needs to be added to the propane to convert half of it to gaseous propane?

b) How much heat is required to raise the temperature of the gaseous propane at 1 atm pressure in part a to 0°C and 1 atm pressure?

c) What is the change in the total enthalpy of the gaseous propane when it is warmed in part b?

d) Does the total enthalpy of the liquid propane increase, decrease or not change in part a? Explain.

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3. Consider the conversion of glucose to ethanol and carbon dioxide at a constant pressure of 1 atm and $T = 25\text{ }^{\circ}\text{C}$: Thermodynamic parameter values are given in the table.



Thermodynamic parameter	ΔH_f^0 (kJ/mol)	S_f^0 (J/ K·mol)	ΔG_f^0 (kJ/mol)
glucose (s)	-1274.4	212.1	-910.5
ethanol (ℓ)	-277.0	160.7	-174.1
carbon dioxide (g)	-393.5	213.7	-394.4

a) What is the Gibbs free energy change ΔG^0 for the conversion of glucose to ethanol and CO_2 at $25\text{ }^{\circ}\text{C}$?

b) Suppose 0.5 mole of glucose is completely converted to ethanol and carbon dioxide at $25\text{ }^{\circ}\text{C}$. What is the amount of heat q evolved in this process?

c) If this reaction is performed at a pressure of 4 atm and $25\text{ }^{\circ}\text{C}$, will the reaction be more favorable, less favorable or the same as the reaction performed at a pressure of 1 atm and $25\text{ }^{\circ}\text{C}$? Explain.

d) If this reaction is performed at a pressure of 1 atm and $0\text{ }^{\circ}\text{C}$, will the reaction be more favorable, less favorable or the same as the reaction performed at a pressure of 1 atm and $25\text{ }^{\circ}\text{C}$? Explain.

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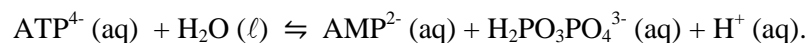
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4 ATP hydrolyzes to AMP and pyrophosphate according to the following reaction:



The standard state Gibbs free energy change for this reaction at pH 7 is -35.2 kJ/mol.

- a) What is the value of the equilibrium constant for this reaction at pH 7, 25 °C and 1 atm pressure?
- b) If the concentration of pyrophosphate decreases to 0.1 M, by what amount will the chemical potential for pyrophosphate change from its standard state value? (You may assume that the solution is ideal.)
- c) If the concentrations of ATP, AMP and pyrophosphate are all 0.1 M, is the reaction at equilibrium at pH 7, 25 °C and 1 atm? (The solution is ideal.) Explain.
- d) Suppose 1 mM ATP is added to water and the above reaction achieves equilibrium. What will be the value of ΔG for the reaction at 25 °C and 1 atm pressure?

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5. Astronauts in the space station have one mole of an ideal gas at 300 K contained in a 2 L cylinder fitted with a piston. The piston is depressed so that the gas occupies half of the volume of the cylinder. The astronauts carry the cylinder out to the vacuum of space, being careful to keep the temperature constant.

a) An astronaut allows the piston to move very slowly so that the gas fills the full volume of the cylinder without changing temperature. How much work did the astronaut do on the gas?

b) How much heat flowed into the gas during the expansion of part a?

c) What is the entropy change of the gas when it transitions from its compressed state to its expanded state in part a?

d) The astronaut slowly (reversibly) returns the piston to its original position, keeping temperature constant. Now she releases the piston and the gas rapidly expands to fill the cylinder. The final temperature of the gas is 300 K. How much work is done on the gas for this expansion process?

e) What is the entropy change for the gas in process d?

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For grading purposes:

question	1	2	3	4	5		Tot
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Work at least 4 problems (of your choosing) or more, as you prefer.

Answers without explanations (where indicated) are not complete.

Name: _____

(Please print clearly on all pages)

1. The heat capacities and latent heats for various forms of water are shown below. You may assume that they are constant under conditions found in this problem and that $P = 1$ atm throughout.

Data: $C_p(\text{H}_2\text{O}, s) = 38.07 \text{ J K}^{-1} \text{ mol}^{-1}$; $C_p(\text{H}_2\text{O}, \ell) = 75.4 \text{ J K}^{-1} \text{ mol}^{-1}$; $C_p(\text{H}_2\text{O}, g) = 33.76 \text{ J K}^{-1} \text{ mol}^{-1}$;
 $L_{\text{melting}} = 6.007 \text{ kJ mol}^{-1}$; $L_{\text{vaporization}} = 40.66 \text{ kJ mol}^{-1}$; $M_{\text{H}_2\text{O}} = 18.0 \text{ g mol}^{-1}$.

a) It is possible to supercool liquid water to below 0°C . Suppose you have 0.75 moles of liquid water at -20°C . You add heat to the supercooled liquid water to bring it to its normal freezing point temperature. How much heat is needed to accomplish this?

b) What is the entropy change in the warming of supercooled water in part a)?

c) If the amount of heat calculated in part a) is removed from liquid water at its normal freezing point, but this time the water freezes rather than supercools, how much ice is formed?

d) Shaking supercooled liquid water will cause it to spontaneously begin to freeze. That means that the entropy change of the Universe must be positive for this process. If you shake the supercooled water of part a) in a perfectly insulating container, calculate $\Delta S_{\text{Universe}}$ for this process.

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2. For the following two processes, state whether each of the four thermodynamic quantities q , w , ΔE , ΔH and ΔS is greater than, equal to, or less than zero *for the system specified in italics*. State explicitly any assumptions that you may need to make and the reason behind your answer.

a) An *ionic compound is mixed with water* in a thermally insulated container (a calorimeter). A thermometer in the calorimeter indicates that the temperature of the water has decreased.

$>0, =0, <0?$	Reason
q	
w	
ΔE	
ΔH	
ΔS	

b) A *sample of He gas* is mixed with an *equimolar amount of Ne gas* at the same T and P under conditions where no chemical reaction occurs. The gases may be assumed to be ideal.

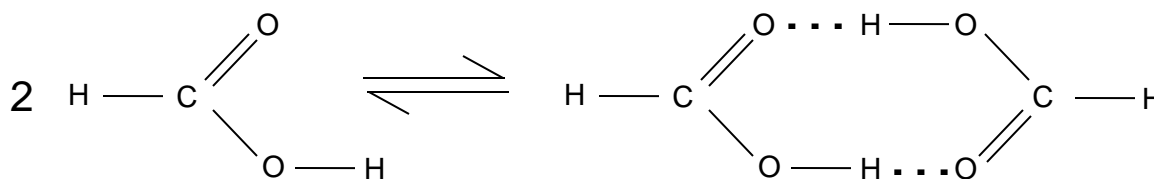
$>0, =0, <0?$	Reason
q	
w	
ΔE	
ΔH	
ΔS	

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3. Consider the gas phase reaction shown below in which two formic acid molecules dimerize. The bonding interaction is via hydrogen bonds (dotted lines).



a) Some thermodynamic values for these components are given in the table to the right. Calculate ΔH° and ΔS° for the gas-phase dimerization of formic acid at $T = 25^\circ\text{C}$ and $P = 1\text{ atm}$. Be sure to include units.

	ΔH_f° (kJ mol ⁻¹)	S (J K ⁻¹ mol ⁻¹)
HCOOH (g)	-362.63	251.0
(HCOOH) ₂ (g)	-785.34	347.7

 $\Delta H^\circ =$ $\Delta S^\circ =$

b) Calculate the heat that is produced by this reaction when 1 mole of HCOOH dimerizes.

c) Calculate the enthalpy change due to one hydrogen bond formation for this reaction. (Note: If you cannot calculate a value, explain why.)

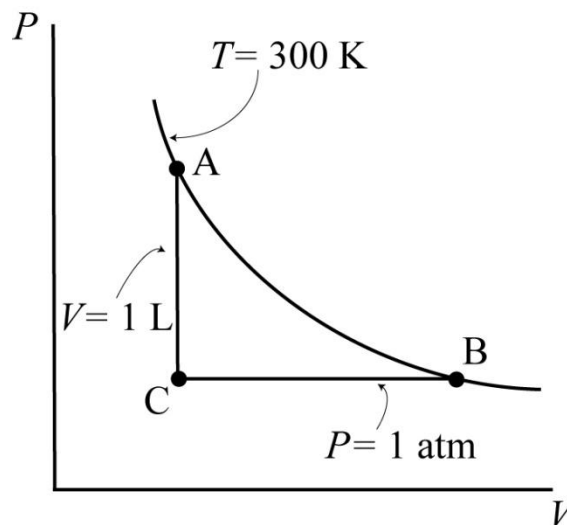
d) Calculate the entropy change due to one hydrogen bond formation for this reaction. (Note: If you cannot calculate a value, explain why.)

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4. The plot at right shows a set of three reversible processes in which 0.5 mole of an ideal gas moves from state A to state B, from state B to state C, and from state C to state A. The first process occurs at constant T , the second at constant P , and the third at constant V .



a) What is the volume of the gas in state B?

b) How much work is done on the gas when it moves from state A to state B along the isothermal?

c) How much heat flows into the gas when it moves from state A to state B along the isothermal?

d) How much work is done on the gas as it moves $A \rightarrow B \rightarrow C \rightarrow A$ around a full cycle?

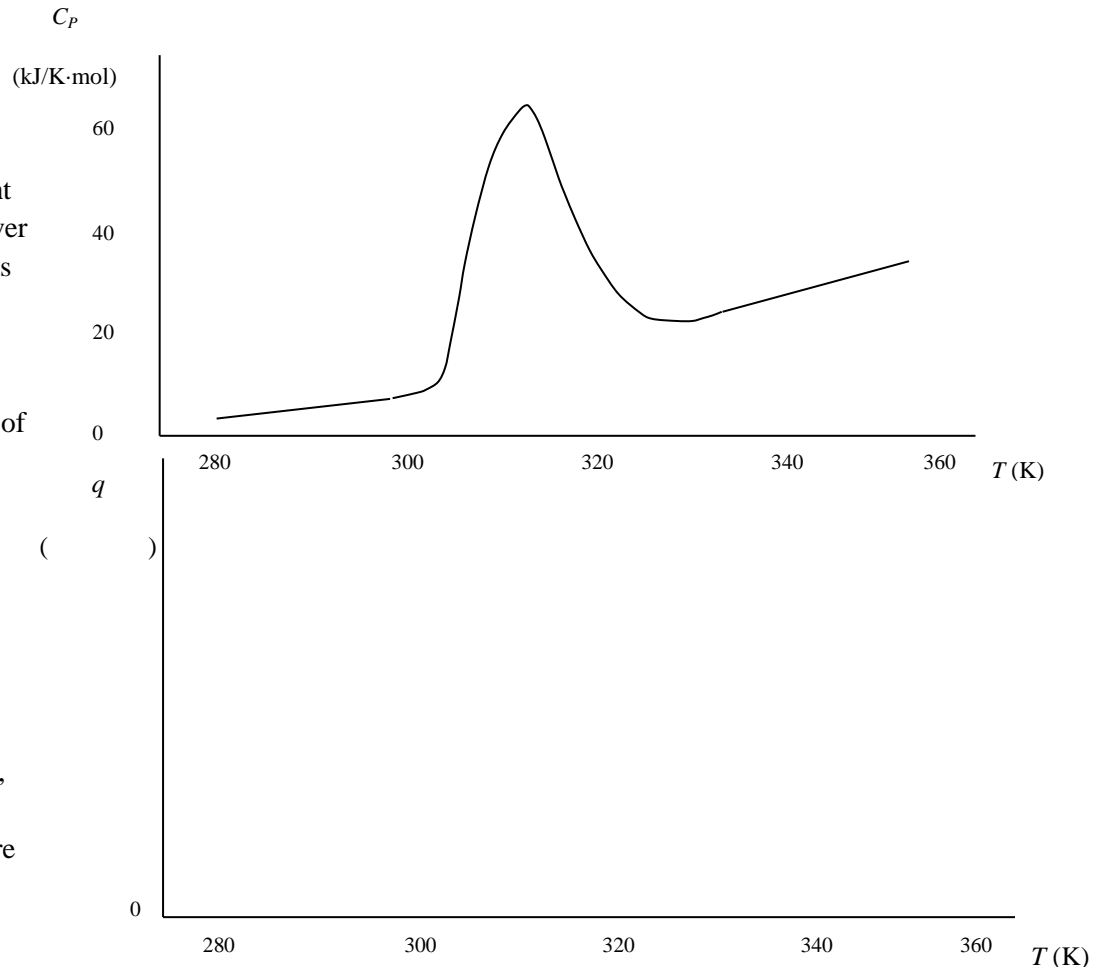
e) How much heat flows into the gas as it moves $A \rightarrow B \rightarrow C \rightarrow A$ around a full cycle?

f) What is the entropy change of the gas along the path $C \rightarrow A$?

Name: _____

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5. Heat is added at constant pressure to a protein in solution. The heat absorbed versus the temperature of the sample is measured as is the heat absorbed by protein-free solution. The latter is subtracted from that for the protein solution, leaving only the heat absorbed by the protein. From this the heat capacity at constant pressure is evaluated over the temperature range as shown at right.



a) Draw on the graph below the total amount of heat added to the protein from 280 to 360 K. **You do not** need to include axis scales. **You do** need to include the units on the vertical axis.

b) On the C_p vs. T plot, the hump occurs in the temperature range where the protein becomes denatured. What is the enthalpy change for the denaturation process?

You may show the value graphically on the plot or estimate the numerical value. The first method is recommended.

c) Is ΔS of the protein positive, negative or zero during the denaturation process? Explain.

d) Why does the C_p vs. T plot have a broad hump instead of a sharp spike at the denaturation point?

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For grading purposes:

question	1	2	3	4	5	Total	Adjusted
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Work at least 4 problems (of your choosing) or more, as you prefer.

Answers without explanations (where indicated) are not complete.

Name: _____

(Please print clearly on all pages)

1. Some data are shown below. You may assume that all heat capacities are constant under conditions found in this problem and that $P = 1$ atm throughout.

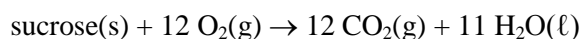
Data: $\overline{C_p}(\text{H}_2\text{O}, s) = 38.07 \text{ J K}^{-1} \text{ mol}^{-1}$; $\overline{C_p}(\text{H}_2\text{O}, \ell) = 75.4 \text{ J K}^{-1} \text{ mol}^{-1}$; $\overline{C_p}(\text{H}_2\text{O}, g) = 33.76 \text{ J K}^{-1} \text{ mol}^{-1}$;
 $L_{\text{melting}, \text{H}_2\text{O}} = 6.007 \text{ kJ mol}^{-1}$; $L_{\text{vaporization}, \text{H}_2\text{O}} = 40.66 \text{ kJ mol}^{-1}$; $M_{\text{H}_2\text{O}} = 18.0 \text{ g mol}^{-1}$,
 $\Delta H_{f, \text{sucrose}, s} = -2222 \text{ kJ mol}^{-1}$, $\Delta H_{f, \text{H}_2\text{O}, \ell} = -241.8 \text{ kJ mol}^{-1}$, $\Delta H_{f, \text{CO}_2, g} = -393.5 \text{ kJ mol}^{-1}$.

a) A hiker drinks 1 L of water at 25 °C. The hiker's body temperature is 37 °C. When the water reaches the hiker's body temperature, how much heat will the water have absorbed? (The density of water is 1 g/mL.)

b) The hiker weighs 60 kg. How much will the temperature of the hiker drop if the amount of heat in part a is removed from the hiker? You may assume that the hiker's heat capacity is the same as that of water.

c) The hiker is sweating. How much water in the form of sweat would the hiker need to evaporate in order to receive as much cooling as was found in part a? You may assume that the air temperature is 37 °C.

d) The hiker eats a candy bar that is mostly sucrose. Assume the sucrose is fully oxidized in the body. How many moles of sucrose does the hiker need to eat to recover the heat lost to the water in part a or the sweat evaporation in part c? (You may assume that the sucrose reaction happens at standard temperature rather than body temperature.)



Name: _____

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2. For the following two processes, state whether each of the listed thermodynamic quantities is greater than, equal to, or less than zero *for the system specified in italics*. State explicitly any assumptions that you may need to make and the reason behind your answer.

a) A sample of *ideal gas* is carried through a complete Carnot cycle (isothermal expansion, adiabatic expansion, isothermal compression, adiabatic compression, all of which are reversible).

>0, =0, <0?	Reason
q	
w	
ΔE	
ΔH	
ΔS	

b) Samples of *hot water and cold water* are mixed together in a thermally insulated, closed container of fixed volume.

>0, =0, <0?	Reason
q	
w	
ΔE	
ΔH	
ΔS	

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3. Consider the reaction of ethanol to ethane and oxygen shown below. Answer the following using the data provided. You may assume the gases to be ideal and ethanol has negligible volume change with temperature change. The volume of 1 mole of ethanol is 58.4 mL.

Thermodynamic parameter (25 °C)	ΔH_f^0	S_f^0	ΔG_f^0
ethanol (ℓ)	-277.0 kJ/mol	160.7 J/K·mol	-174.1 kJ/mol
ethane (g)	-84.7 kJ/mol	229.6 J/K·mol	-32.8 kJ/mol
O ₂ (g)	0 kJ/mol	205.1 J/K·mol	0 kJ/mol



a) What is ΔG^0 for this reaction?

b) What is the amount of heat that is evolved during this reaction?

c) What is ΔE^0 for this reaction?

d) Will ΔG for this reaction at $P = 5$ atm be larger or smaller than ΔG^0 ? Explain.

Name: _____

(Please print clearly on all pages)

4. For the statements below, determine which word or words inside the parentheses serve to make the statement correct. ~~Strikethrough~~ the word or words that are not correct. More than one word or words may be correct in each statement. (Explain your answers for possible partial credit.)

a) For a sample of an ideal gas, the product PV remains constant as long as the (temperature, pressure, volume, internal energy) is held constant.

b) The second law of thermodynamics states that the entropy of an isolated system always (increases, remains constant, decreases) during a spontaneous process.

c) When a sample of liquid is converted reversibly to its vapor at its normal boiling point, (q , ΔP , ΔV , ΔT , ΔH , ΔS , ΔG) is equal to zero for the system.

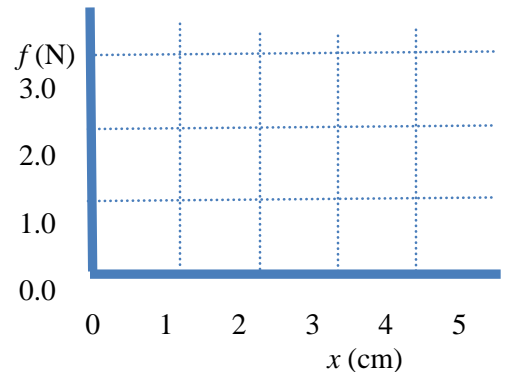
d) For the reaction $\text{methane(g)} + 2 \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2 \text{H}_2\text{O(g)}$, a considerable amount of heat is produced when the reaction occurs at 25 °C and 1 atm pressure. You may consider the species to act like ideal gases. When the reaction occurs at 50 °C and 1 atm pressure, the reaction will be spontaneous in the direction written (more than, less than, the same as) the reaction at 25 °C and 1 atm pressure. When the reaction occurs at 25 °C and 5 atm pressure, the reaction will be spontaneous in the direction written (more than, less than, the same as) the reaction at 25 °C and 1 atm pressure.

Name: _____

(Please print clearly on all pages)

5. Consider a strip of rubber that is 2 cm long. The rubber band, so long as it is not stretched too much, acts like a spring. Recall that the force vs. length relationship for a spring is $f = k(x - x_0)$ where k is the spring constant, x is the length of the spring and x_0 is the spring length at which no force is applied to the spring.

a) The value of the spring constant k of the rubber band is 100 N/m. Plot on the graph the length of the rubber band over the force range of 0 to 3 N.



b) How much work is done on the rubber band when it is stretched from 2 cm to 3 cm in a slow, reversible way? (Hint: the area of a triangle is width times height divided by two.)

c) Suppose the rubber band stretching in part b was done under conditions in which the rubber band was insulated from the outside world (the process was adiabatic). What is the value of ΔE for the stretching of the rubber band from 2 to 3 cm?

d) Rubber is a crosslinked, long-chain polymer. When rubber is stretched, the rubber polymer molecules go from being randomly distributed to being mostly aligned with each other. In stretching the rubber band from 2 cm length to 3 cm length, will the entropy of the rubber band increase, decrease, or remain constant? Explain.

e) Will the temperature of the rubber band increase, decrease, or remain constant if the band is stretched adiabatically as in part c? Explain.

Name: _____

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