Chemistry 431 - Physical Chemistry I
Course Syllabus
Fall 2020

1. Instructor: Dr. David L. Freeman
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   Office Hours: MWF 10, or by appointment at https://rhody.webex.com/meet/dfreemanuri.edu

2. Scheduling: MWF 9, Online at https://rhody.webex.com/meet/dfreemanuri.edu

3. Text: *Thermodynamics, Statistical Thermodynamics and Kinetics* by Thomas Engel and Philip Reid, Fourth Edition, Prentice Hall, 2019

4. Prerequisites: CHM 192 or CHM 112, MTH 142, PHY 112 or 204. Knowledge of the material in these courses will be assumed.

5. WWW course home page: http://www.chm.uri.edu/courses/?chm431&1

6. Course requirements:

   (a) Attendance (2 Points per Lecture) 66

   (b) Online Hour Exams (Wednesday, September 30; Monday, October 19; Monday, November 9; Friday December 11)
   Lowest numerical score will be dropped 300

   (c) Final exam (Saturday, December 19, 8-11 AM) 200

   (d) Total 566

   Grades will be determined on a curve. Incompletes will be given only for documented medical reasons. Hour exams cannot be made up. In the case of an exam missed for a valid medical reason, discuss options with the instructor. If an exam date is canceled owing to weather or any other reason, the exam will be given on the next date the class meets.

7. Illness: If you are too ill from covid19 or anything else to attend an online class, send me email, and you will be given credit for attending that class.

8. Overview and Course Goals:

   Physical chemistry is the study of the application of the principles of physics to chemical phenomena. In a simple sense, we can think of physical chemistry as subdivided into three topics: thermodynamics, quantum mechanics and kinetics. In reality, these subtopics are interrelated, and it is a goal of both CHM 431 and CHM 432 for you to appreciate the relations.

   Physical chemistry has the reputation of being a hard course. It is my feeling that the difficulties faced by third year students trying to learn physical chemistry arise from the large set of topics that must be mastered. Additionally, many of the topics that are covered are inherently abstract. This abstraction of chemical phenomena is not easy, and a major course goal for this year is to understand how the laws of physics enable us to understand the principles of chemistry in an abstract way.

   Although physical chemistry is difficult, there is a way to be successful in this course. It is imperative that you do homework. Problem sets will be posted about once a week, and the homework problems will be representative of the kinds of questions you will be given on the examinations. Solutions to the problem sets will be posted before each quiz. It is important that the homework be completed before the solutions are posted for you to gain adequate practice with the material. Understanding a solution to a problem is far less difficult than the initiation of a solution to a problem. You will be asked to initiate solutions on examinations.

   This semester we will be concerned with the principles that govern the macroscopic behavior of chemical systems. These principles are contained in the laws of thermodynamics. A major goal for CHM 431 is to understand the three laws of thermodynamics and how to apply the laws to chemical systems.

   The thermodynamic laws we shall learn are only valid for systems at equilibrium. The thermodynamic laws provide the basis for the rationalization of equilibrium phenomena, including both phase and chemical equilibria. Understanding the thermodynamic basis of equilibrium is another course goal.

9. The CHM 431 Web page:

   In this course all problem sets, problem set solutions, quiz solutions and final exam solutions are to be distributed on the course web page. No paper copies of the problem sets are to be distributed. The URL of our course web page is http://www.chm.uri.edu/courses/?chm431&1 . It is strongly suggested that you link to our web page to obtain the first problem set as soon as possible.

   It is expected that for most of you, success in this course will require some level of help beyond classroom instruction. Because some of you may find it difficult to come to the scheduled office hours, we have installed as part of our course web pages, a page that can be used to submit questions. Questions are submitted by anyone in the class by filling out a form on the web page, and answers are distributed either to the entire class or only to the person asking the question. If the entire class is to receive a copy of the question and answer, the question is treated as anonymous; i.e. the person who asks the question is never identified. In fact, it is possible to submit a question so that even the instructor does not know who submitted the question. Anonymous questions and responses by the instructor are distributed automatically using Sakai. With ordinary electronic mail, there is a private correspondence between the student and instructor. By using the web page, the entire class has an opportunity to learn from the questions submitted.

The use of the web page does not preclude personal interaction between any of you and the course instructor. Dr. Freeman has regular office hours, and you are all encouraged to make use of these hours. Alternate meeting times can be arranged by appointment. Additionally, you can contact Dr. Freeman by e-mail or telephone. The e-mail address and phone number for Dr. Freeman is given on the first page of this syllabus.

Any student in CHM 431 can submit questions and comments to Dr. Freeman. Submission of such comments or questions must be made using the WWW home page for this course. The address (URL) of our home page is
http://www.chm.uri.edu/courses/?chm431&1 . To submit a question to the list, you must click on the highlighted text that says "submit a question to the CHM 431 list." As an example of how to use the list, suppose a student in our class, Ms. Benzene Ring, wonders, "Is work a path or a state function?" (If you don't know what this means, don't worry. You will understand the question early in the semester). To obtain an answer to her question, Ms. Ring links her web browser (e.g. Firefox, Safari or Google Chrome) to http://www.chm.uri.edu/courses/?chm431&1, and she then clicks on the text linking her to the page for questions (i.e. the highlighted text that says "submit a question to the CHM 431 list"). Ms. Ring then optionally can enter her e-mail address in the appropriate box and specify (this is not optional) whether she wants her question to be answered to the entire CHM 431 class or to her alone. Ms. Ring then types in the large box

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Is work a path or a state function?
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Ms. Ring then clicks the "send" button. Ms. Ring's question is received by Dr. Freeman. Dr. Freeman then sends an e-mail message to the whole list that might be

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Subject:  work
The question is:  The question is:  Is work a path or a state function?
Answer:  Work is a path function.
```

Now Ms. Ring and the entire class have an answer to her question.

If the answer to the question can be sent to the entire list, the answer will not indicate who asked the question. If Ms Ring wants to ask the question with full anonymity so that even Dr. Freeman has no idea who asked the question, the e-mail portion of the form can be left blank. Of course, if the e-mail section of the form is blank, the answer must be sent to the list and not just to the sender.

Because many questions may contain mathematical formulas, we need a notation to communicate the special symbols used in the course. To avoid confusion, it is most useful if we agree on the same set of symbols. The symbols that follow are taken from a language called LaTeX. LaTeX is a language that is frequently used to prepare scientific documents, and LaTeX can be used to translate special symbols into simple text characters. By learning LaTeX notation, you will learn a widely used method to communicate mathematical symbols via e-mail. The instructor plans to use these symbols in answering your questions, and it is asked that you use the same symbols in posing questions. The most important symbols are the following:

(a) Greek letters are represented by \ followed by the name of the letter. For example α is typed `\alpha`, β is typed `\beta`, and so on. A Greek letter is made upper case by making the first letter of its name upper case. For example, the letter Δ is typed `\Delta`.

(b) Subscripts are represented by _{} where the brackets contain the subscripts. For example, μ_{ij} is typed `\mu_{ij}`.

(c) Superscripts are represented by ^{} where the brackets contain the superscripts. For example, β^{12} is typed `\beta^{12}`.

(d) Infinity (∞), is typed `\infty`.

(e) The integral sign $\int$ is typed `\int`. The limits on a definite integral are included by introducing subscripts and superscripts. As an example $\int_0^\infty e^{-x^2} dx$ is typed `\int_{0}^{\infty} e^{-x^{2}} dx`.

(f) The partial derivative symbol ∂ is typed `\partial`.

(g) The summation sign $\sum$ is typed `\sum`. The lower and upper limits of summation are included as subscripts and superscripts. As an example $\sum_{n=0}^{\infty} 1/n^2$ is typed `\sum_{n=0}^{\infty} 1/n^{2}`.

(h) Square roots $\sqrt{a+b}$ are typed `\sqrt{a+b}`.

(i) The arrow in chemical reactions $\rightarrow$ is typed --->. For example $C + O_2 \rightarrow CO_2$ is typed `C + O_{2} ---> CO_{2}`.

Let us now look at another example of a question submitted using the web. In this case, Ms. Ring has a question requiring an equation. This might be a real question. If you don't understand the context, don't worry. You will understand the details of the question later in the course. Suppose Ms. Ring wants to ask

"In deriving the expression for the phase equilibrium line between solid and liquid, when evaluating the integral expression

$$p_2 - p_1 = \int_{T_1}^{T_2} \frac{\Delta H}{T \Delta V} dT$$

the ratio of ΔH to ΔV is taken outside the integral. What is the justification for this?"

To submit the question, Ms. Ring uses her web browser to attach to http://www.chm.uri.edu/courses/?chm431&1, clicks on the line that says, "submit a question to the CHM 431 list," and then Ms. Ring enters the information requested by the form. If Ms. Ring wishes to remain anonymous, Ms. Ring leaves the e-mail box blank. Ms. Ring then types into the large box

```
In deriving the expression for the phase equilibrium line between solid and
liquid, when evaluating the integral expression
p_{2}-p_{1}=\int_{T_{1}}^{T_{2}} \Delta H/T\Delta V dT the ratio of \Delta H
to \Delta V is taken outside the integral.  What is the justification for
this?
```

and clicks on the submit button. Ms. Ring's question is received by Dr. Freeman. The answer will be sent either to Ms. Ring alone, or preferably to the entire class if the appropriate box is checked. Dr. Freeman might reply

```
Subject:  Phase equilibrium question
The question is:In deriving the expression for the phase equilibrium line
between solid and liquid, when evaluating the integral expression
p_{2}-p_{1}=\int_{T_{1}}^{T_{2}} \Delta H/T\Delta V dT the ratio of \Delta H
to \Delta V is taken outside the integral.  What is the justification for
this?

The answer is:  For solids and liquids the ratio \Delta H/\Delta V is only
weakly dependent on temperature.  The ratio, then, can be taken outside the
integral to a good approximation.
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10. Course outline:

Topic	Book Chapter
1. Energy and Work	
2. Thermodynamic Systems and the Ideal Gas Law	1
3. Heat, Work and the First Law	2
4. State Functions and Some Mathematics for Thermodynamics	3
5. Thermochemistry	4
6. The Second and Third Laws	5 (Skip Sec. 5.11-5.13)
7. The Free Energy Functions and Chemical Equilibrium	6, 5.11, 5.12
8. Real Fluids	7
9. Phase Transitions in One-component Systems	8
10. Ideal and Real Solutions	9
11. Electrolyte Solutions	10
12. Electrochemistry	11
16. Final Exam	Comprehensive