Chemistry 531 - Advanced Physical Chemistry I
Course Syllabus
Spring 2009

1. Instructor: David L. Freeman
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2. Texts:

   (a) *Chemical Thermodynamics* by Irving M. Klotz and Robert M. Rosenberg, Seventh Edition, (John Wiley, New York, 2008)

   (b) *Statistical Mechanics* by Donald A. McQuarrie, (University Science Books, Sausalito, CA, 2000).

3. Prerequisites: Undergraduate physical chemistry, one year of college level calculus, one year of college level physics.

4. Course requirements:

(a) Two one hour exams at 100 points each	200
(b) Homework	50
(c) Final exam	200
(d) Total	450

   Grades will be determined on a curve with B as the average. All exams will be closed book.

5. The CHM 531 Web page:

   In this course all problem set and exam solutions are to be distributed on the course web page. No paper copies of the solutions are to be distributed. The URL of our course web page is

http://www.chm.uri.edu/courses/?chm531&1. It is strongly suggested that you link to our web page as soon as possible. If you have no web access, please see Dr. Freeman.

It is expected that for most of you, success in this course can be expected to require some level of help beyond classroom instruction. Because this course is offered at Pfizer rather than in Kingston, 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 to everyone who has submitted their e-mail address to the instructor. 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. You can contact Dr. Freeman directly by e-mail or telephone. The e-mail address and phone number for Dr. Freeman are given on the first page of this syllabus. If any of you have no access to electronic mail, please see Dr. Freeman.

To receive copies of the submitted questions and the answers to the questions, you must submit your e-mail address. To submit your e-mail address, go to our home page (http://www.chm.uri.edu/courses/?chm531&1) and click on "Subscribe to the CHM 531 list." On the resulting form, enter your e-mail address, click on the small "subscribe" button and then click on the submit button. You can also use this form to unsubscribe from the list in case you drop CHM 531.

Any student in CHM 531 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/?chm531&1. To submit a question to the list, you must click on the highlighted text that says "submit a question to the CHM 531 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 Microsoft Internet Explorer) to http://www.chm.uri.edu/courses/?chm531&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 531 list"). Ms. Ring then enters her e-mail address in the appropriate box and specifies whether she wants her question to be answered to the entire CHM 531 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:  Is work a path or a state function?
Answer:  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 $\hat{\{\}}$ 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 → is typed `--->`. For example C+O_2 → 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/?chm531&1, clicks on the line that says, "submit a question to the CHM 531 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

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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

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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.
```

Remember, your first task is to send Dr. Freeman your e-mail address to be added to the class list. You can then send questions and comments to Dr. Freeman using your web browser starting at the URL
http://www.chm.uri.edu/courses/?chm531&1.

6. Course outline:

   (a) Review of calculus and mathematical methods needed to study thermodynamics.
   (b) The first law of thermodynamics and thermochemistry
   (c) The second law of thermodynamics
   (d) Free energy functions
   (e) Phase equilibria
   (f) The third law of thermodynamics
   (g) Multiple component systems
   (h) Chemical equilibrium
   (i) Exam Number 1
   (j) A review of quantum energy levels
   (k) An introduction to probability and the random walk
   (l) The canonical ensemble
   (m) The ideal monatomic gas
   (n) Other ensembles and fluctuations
   (o) Exam Number 2
   (p) The ideal diatomic gas
   (q) The statistical thermodynamics of chemical equilibrium
   (r) Classical statistical mechanics
   (s) The statistical thermodynamics of crystals (time permitting)
   (t) Final exam (comprehensive)