

COURSE GUIDE

FOR

PHYSICAL CHEMISTRY II

FCH 361
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State University of New York
College of Environmental Science and Forestry

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Acknowledgments

This course guide is based on the ones I developed for FCH 360, Physical Chemistry I. The inspiration for those course guides came largely from Chuck Spuches of the Instructional Development, Evaluation and Services Office here at SUNY-ESF. Some ideas are derived from Dan Apple of Pacific Crest.

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Homework:

Homework *Problems* will be turned in and graded. Tentative due dates are listed in the course Schedule. The *Exercises* provided towards the end of this document are designed to help you learn the basics, but the answers will not be turned in or graded.

Feedback Exercises:

Feedback Exercises (henceforth labeled "*Feedbacks*") will be posted on Blackboard. Feedbacks are short quizzes; for each one there is a set of the *Exercises* to help you learn the material. You will need to turn in your answers to the *Feedbacks* on the day indicated in the course calendar. Feedbacks are required, but do not count towards your grade; however, each Feedback on which you do not exhibit effort or you skip (that is not excused by the instructor) may result in a 1% subtraction from your course average.

Attitude Check

Physical chemistry has a reputation as a difficult course. Some students arrive in class the first day already convinced they cannot do the work, and therefore they do not see any reason to study hard or to study smart. With this attitude, they create a self-fulfilling prophecy.

DO NOT MAKE THIS MISTAKE!!!

Physical chemistry can be very rewarding. The material is deep; there is much more than just what appears on the surface or in any textbook. Yet the struggle for mastery of physical chemistry can be rewarded with a sense of accomplishment and the power of a new type of knowledge.

Personal Statement

I am in my fifteenth year at ESF, and my eleventh year teaching FCH 361 (Physical Chemistry II). My appreciation for the power and profound insights to be found in physical chemistry led me to choose my undergraduate thermodynamics professor as a research advisor in graduate school. From graduate school on, I have been doing research in most of the topics of this course: thermodynamics, kinetics, quantum chemistry, and spectroscopy.

My goal in this course is for students to gain an understanding of the equations and methods they will encounter in this course, rather than merely memorize a method to solve common types of problems. This goal guides the way I structure homework assignments, classroom time, and exams. Keep this goal in mind when you think about how to prepare for this course.

Moreover, some of the topics in this course and the way they are approached may be rather different from what you are used to. This may present you with a challenge and require effort on your part to meet. If you are aware of the differences, then you can figure out how to rise to the challenges.

Prerequisites - Knowledge, Skills, and Attitudes

To take this course, you must have passed one year of college physics (Mechanics, Electricity and Magnetism) and one year of calculus (Differential and Integral). There are no exceptions without the written permission of the instructor, which may or may not be forthcoming.

The physics we use is primarily Electricity and Magnetism. If your algebra and calculus are rusty, then you need to brush up on those areas. You will need a good scientific calculator for homework assignments and examinations, and you will be using it in class.

There are skills and attitudes required for this course beyond the prerequisites cited in the course catalog. Here I present an incomplete list of skills you should have mastered and attitudes you should have wholeheartedly adopted:

- 1) Graph numerical data and interpret graphical data, by hand and using Excel.
- 2) Extract numerical data from a statement of a problem, identify needed information, and identify the equations necessary to solve the problem.
- 3) Take the initiative to obtain data from reference works like the CRC or other data sources.
- 4) Recall and use basic principles learned in previous chemistry, math, and physics courses.
- 5) Make estimates, such as deciding when a quantity in an equation is negligibly small and can be ignored in calculations; estimating uncertainties.
- 6) Analyze the units and dimensions of quantities or equations.
- 7) Understand the meaning of a derivative or integral.
- 8) Check to see whether your answers on homework or test problems are reasonable physically, chemically, and mathematically.

If you are already skilled in all the above, great! If not, then you will want to further develop these skills this semester. Here are some ways to do that:

- We will be addressing some of these issues in class and on the Problem Sets. So come to class, and work hard.
- See the text or other textbooks for reviews of mathematics and of units analysis.
- Your text books and notes from old classes in high school and college are still valuable sources of explanations and problems!

Background and Purpose of the Course

You may have been exposed to many of the ideas presented in this course in your first college chemistry course or even in high school. Why then, are they presented again? One obvious reason is that there is far more to these ideas than what you saw in previous courses, and many more applications. A knowledge of electrochemistry is obviously crucial to understanding batteries and corrosion, but is also the basis of much of temperature measurement (thermocouples) and understanding the fate and toxicity of metals in the environment. The conductivity of electrolyte solutions is the basis of a several analytical techniques and gives insight into diffusion at the molecular level. Rates of diffusion set limits to the rates of reactions (kinetics) in solution. Kinetics is crucial for understanding the rates of reactions, whether they be in a large scale reactor, the environment, or inside a cell of a living organism. As you may have been taught, thermodynamics dictates that diamond should eventually transform itself to graphite, but kinetic arguments have convinced chemists their diamond jewelry is safe from that hazard. Quantum mechanics allows a description of the behavior of matter at the atomic level,

where our physical intuition (developed from our knowledge of macroscopic objects) fails. Quantum mechanics is also the basis of spectroscopy. Spectroscopy encompasses a broad range of tools used for analysis in different wavelength regions; in this class we will focus on infrared spectroscopy, which arises from molecular vibrations. Quantum mechanics is also the basis for understanding chemical change induced by light absorption (photochemistry).

Course Goals/Objectives

Broadly speaking, there are three overarching goals for your technical learning. The first two are to help you master fundamental chemical concepts within a much more rigorous and powerful mathematical framework, and to help you develop an intuition about physical and chemical processes.

These two goals may seem contradictory, but they are not. There are very few researchers who can use the mathematical methods of physical chemistry well without keeping a physical framework in mind. Those who try too often make ridiculous errors without even knowing it. On the occasions when I have forgone physical thinking, I have often blundered. Most of the resulting errors were caught before doing damage, but I know at least one that made it to print. If this is the result when professionals try to do mathematics blindly, you can guess what happens when novices try.

While the physical model is crucial, much of its power lies in how it lends itself to calculation. The attitude of a physical chemist (like that of a physicist) is that the physical and chemical properties of matter are subject to mathematical modeling, leading to the power to make predictions for species and systems not yet studied. If you begin to adopt this attitude, you will be making a large step towards understanding, not only this course, but any physical system you will encounter in the future.

Quantum mechanics is one of the most important scientific and intellectual developments of the 20th century. It provides powerful and very useful ways of thinking about physical phenomena that cannot be understood through classical models. The third goal for your technical learning is that you begin to integrate quantum mechanical thinking into your analyses of molecular-level phenomena.

Course Description and Organization

The course will bounce around in the textbook. Most of the material will be from the text, but significant portions will not.

You already have experience with chemical equilibrium in the P-Chem I. We will extend equilibrium principles to electrochemistry. We will study conductivity and diffusion in electrolyte (and non-electrolyte) solutions out of Chapter 21 of the 8th Edition of the textbook (20 in the 9th Edition).

Chapter 22 (21) is your introduction to kinetics. While thermodynamics tells you what can and cannot occur, kinetics tells you whether something will happen before you blink or some time after your great-grandchildren are born: the world is not at equilibrium! Chapter 24 (22) presents a microscopic view of kinetics.

Chapter 8 (7) is our introduction to quantum mechanics: a field born in the 20th century. We will study the failures of 19th century physics and begin to learn a new language needed for describing matter at the atomic level. In Chapter 9 (8) we will see the bizarre predictions of

quantum mechanics for selected model systems, including a model for understanding infrared (vibrational) spectroscopy.

Academic Dishonesty: A fancy word for Cheating

Full details appear in the Code of Student Conduct, to be found in your Student Handbook. The most relevant passages are excerpted here:

Examples of academic dishonesty include, but are not limited to, actions defined below...

c) Writing, or attempting to write an examination paper, computer work, or other material for another student; allowing someone else to take one's examination.

d) Possession of examinations or other test materials without permission of the instructor.

e) Using ...books; looking at another's paper; or talking to someone other than the instructor or proctor during an examination, without the instructor's permission.

f) Failing to follow the rules of conduct for taking an examination as stipulated by the instructor prior to the examination or as stated by the instructor in a written course syllabus.

The penalties for cheating that will be administered by the instructor include a zero on the particular assignment and possibly also failing the course. The incident will definitely be reported to the ESF Coordinator of Judicial Affairs. Further details, including information about additional penalties that could be handed down by the administration, appear in the ESF Judicial Handbook.

My attitude towards cooperation on *Problems* is described below in the section entitled "How to Get a Good Grade in Physical Chemistry". Also, read point (f) above, substituting the work "homework" for "examination."

How to Get a Good Grade in Physical Chemistry

My goal for you is not that you get a good grade in this course, although I would be delighted if you all earn high marks. Rather, my goal is to have you learn the principles of physical chemistry and how to apply them.

Why then, do you ask, do I give advice on getting a good grade?

The answer is that the graded assignments will be structured so that it is very difficult to do well without understanding the material. I will attempt to set up this course so that studying for the exams is learning physical chemistry rather than an exercise in memorization of facts, formulas, and algorithms for doing problems. Perhaps the most obvious means by which I devalue memorization is that I permit each student to bring to each exam a single 8.5" x 11" piece of paper (the "cheat sheet") with whatever notes the student wants to put there.

This class is not about memorization. If you try to get through this class by memorizing formulas and algorithms for solving certain types of problems, you are likely to fail the class.

Studying for mastery does not take much more time or effort (perhaps less) than memorization, and it leads to better grades, better long-term retention, and a greater ability to apply your knowledge to real problems.

*"You damn sadist," said Mr Cummings,
'you try to make people think.'
Ezra Pound, Canto 89, 1956*

So how should you study?

Come to class and PARTICIPATE

I will be presenting material that is not in the text or in a different manner than the text. I will also try to organize the material and make it more coherent; it is often difficult for students to see this organization in a textbook. Also, the act of writing down formulas I put on the board or things I say in class is a first step towards learning the material. This is particularly true if you can edit what I say and write, either while taking notes or in while studying outside of class. If you can do this, you will have already begun grappling with the material. In the jargon of pedagogy this grappling is called active learning, the opposite of passive learning. Active learning is the way people actually master skills or knowledge.

Ask questions in class. If you have a question, it is likely that half the class also is also wondering about the same topic. Even the best students in the class often learn something from the answer to the question you feel is too "dumb" to ask.

Finally, do not skip class to study for an exam in a later class. What you miss in my class will probably lower your final grade much more than your cramming will raise your grade in the other class.

The Textbook

Read ahead of the topics being discussed in class. This will help you to get an idea of where I am going in lecture, which will help you take better notes and get more out of the lecture. When studying outside of class, try to see how presentations in the book and in the lecture are linked. Do the example problems in the text while covering up the answer.

You may be able to get oriented to some of the material by reviewing your notes and text from General Chemistry and Analytical Chemistry.

Feedback Exercises and Exercises

I will assign some relatively straightforward questions (*Exercises*) for you to do- these will not be graded. These are mostly intended to be fairly straightforward. You should be able to solve them by reading the book. You are responsible outside of class for making sure you understand the correct answers. The idea of the *Exercises* is to get you familiar with the mechanics of using, one at a time, the many equations which are a part of this course.

To do well in this class you need to not only understand the basics, but be able to apply the individual equations automatically. The analogy is, if you go to bake a cake from scratch, you want to already know a lot about baking first. (If you don't believe me, start writing instructions for your favorite recipe, starting with identifying measuring tools and baking pans, and go on

through to explaining how test for doneness.) If the basics are automatic, then you will likely solve the problem (or bake the cake) efficiently and well.

For the *Exercises* I have usually selected some of the questions that the textbook designates “Exercises.” This is to enable you to check your answers in the *Solutions Manual*. When you finish the assigned *Exercises* you should ask yourself “Can I now solve the same type of problem quickly and get the correct answer?” You definitely should do the other half (a)/(b) of the Exercises to check that you have achieved this level of competency with the material. If you have not, then you need to work harder and/or better!

Feedbacks are small quizzes for you to take outside of class. *Feedbacks* are my chance, and a second chance for you, to get feedback on how you are doing with the basics. If you have trouble assessing how well you know the material, the *Feedbacks* give you a formal way of finding out. Feedbacks are not graded, but they are turned in; tentative due dates are listed in the course calendar.

Homework Problems

I will be collecting and grading homework *Problems*; answers will be posted on Blackboard. Most *Problems* are my own creations. You will not likely do well on the *Problems* unless you have mastered the material in the *Exercises*!

The *Problems* are designed to help you achieve a higher level of understanding of the material. Some *Problems* are conceptual: these are often questions about the assumptions behind an *Exercise* or point out a pattern or oddity in its answer. Other *Problems* are calculations, but often not ones for which the statement of the question allows you to “plug and chug.” You should not expect to answer such *Problems* without thinking for a time about the question: What is being asked? What are the knowns and unknowns? What needs to be done to get from the knowns to the unknowns?

Don't wait until the night before the due date to start doing the *Problems*!

A person can't learn to drive a car just by reading: one needs to actually get in the car and drive. By this analogy, the *Problems* might be the practice drives you take in an empty parking lot before you first get on the road: you learn in a place where no one can get hurt (your performance on the homework does not count a lot towards your grade). Doing problems is usually the only way to begin to learn physical chemistry (and most technical subjects).

You are allowed, nay, encouraged, to cooperate a little bit on the homework. If you are stumped about how to approach a problem, don't stay that way. Ask for a hint (“What equations do I need in order to solve this problem? What error am I making in what I have so far?”). Once you have an answer that seems right, it is appropriate to check with your classmates, and to think together about the way to understand or do a problem, or to point out and explain flaws of logic or math. Giving this type of assistance to a classmate benefits the giver, also, by forcing them to clarify their own thinking about the material. If you compare answers with a fellow student, and disagree, it is appropriate to work together to figure out what errors have been made by either student. Then, however, you should work separately to correct your answer; you may turn in the corrected work!

It is not appropriate to accept help on how to do a problem line by line or to copy someone else's answers.* This is true even when comparing answers with another student. A key

* Your instructor has four surefire ways of catching and penalizing people who make a habit of accepting such “help.” They are: Examination I, Examination II, Examination III, and the Final Exam.

concept here is to work in parallel with other students, and only come together when you are done or stuck. If two students work in parallel, they will likely express things differently, expand equations in different numbers of steps, or do some steps in slightly different order, so that their answers not be identical.

Because *Problems* count little towards your grade, incorrect answers on the homework will not greatly hurt your grade for the course. It also follows that copying answers from somebody else will not raise your grade very much. The goal of the *Problems* is for you to learn the material. If you accept inappropriate help, you defeat the goal of doing homework and lower your chances of getting a good grade.

While we will discuss the answers to *Problems* in class, we will not have time to go over all the questions in detail. Answers will be posted online. Take the time to examine the things you did right and wrong on your homework sets.

It is not sufficient to merely be able to do the problems. You need to think about the answers, whether they make sense physically and mathematically, and why they are what they are. **About 30% of the points on the exams will be for conceptual (qualitative) questions that do not involve use of a calculator. In addition, some of the calculation questions may require a clear understanding of concepts in order to do the right calculation!** If you can do all the numerical problems in the homework, you may just be able to do well enough on the examinations to pass the course. However, if numerical problems are all you try to master, you are only aiming for a D in the course (and risking an F).

Sometimes students spend too much time on homework. They spend half of an hour or more trying to figure out how to start each of a number of problems on the homework, without much success. This results in frustration and wastes a lot of time. Few problems should require that much time just to figure out the way to begin. Time to get help!

If you ask a your instructor or a classmate for help, try to formulate a specific question. That way, you may get the clues that allow you to solve it yourself. You will learn the material much better this way than if you have someone else show you how to do the problem.

Office Hours and Help Sessions

I have found that there are not any good times for office hours, and students are more likely to come by outside office hours. The best bet is to make an appointment to see me or to talk to me right after class. If you drop by and I am in my office, I will probably be available to help you, but I cannot guarantee that! If you don't feel secure asking questions in class, you **should** be coming to office hours on a regular basis. Conceptual questions can, perhaps, be handled by e-mail.

If you are confused about the homework and care about learning (or your grade), I expect to see you in my office from time to time. If I do not see you or hear from you, I assume that:

- a) you are learning the material pretty well
- or
- b) you do not care about the course (or your grade in the course).

Studying for Examinations

Do not wait until the day before the examination to take your first (or second) look at lecture notes, the textbook, or homework problems. That's how people get D's and F's in my courses. Rather, several days before each exam is the best time to go over things for the *second or third*

time. Review your notes and the textbook to identify ideas that are unclear; then clarify them. Try doing the homework assignments again, and any additional problems that have been suggested or assigned. If you have questions, ask them in the class prior to the exam or come to my office hours. Also, you will benefit enormously by getting together with your fellow students to figure out the difficult points.

As you review this material, start making a draft of your cheat sheet. Once again, the night before the exam is too late. Once you have gone over all the material, you can look back at the draft of the cheat sheet and see how best to pare it down and organize it. If you construct the cheat sheet this way, you may hardly need it during exams! If you make your cheat sheet at the last minute you will not benefit greatly from either making it or its presence during the exam.

Examinations

About 30% of the points on the exams will be for conceptual (qualitative) questions that do not involve use of a calculator. These questions may ask you to briefly explain an observation or predict the result of an experiment. They may ask you to sketch a figure representing the behavior of a system or some phenomenon, or explain phenomena presented in a graph. If you do not learn concepts, you will not be able to answer these questions. If that is the case, you will not do well in the course. **In addition, some of the calculation questions may require a clear understanding of concepts in order to do the right calculation!** The point is: LEARN CONCEPTS!

Standard Advice for Examinations

Look over the entire examination when you first get it. People often gain confidence by answering the easier questions before going on to harder ones, and you may benefit by skipping around (but be sure to come back to the problems you skipped!). Not all problems on the exam are worth the same number of points. If you are pressed for time, you might concentrate on the ones that are worth more.

Non-Standard Advice for Examinations

If you are simply running out of time, then give an outline of the way you would go about answering the question if you did have time. Provide some information about the answer. A numerical estimate is best, but information along the lines of whether the answer will be larger or smaller than the initial value, positive rather than negative, a large number or a small number.

Similarly, if you know an answer is wrong, but don't have time to figure out how you got the wrong answer, you can help yourself by writing something like: "This answer is wrong because _____; a more reasonable answer would be X." If you do this you might not lose as many points as you otherwise would for the error. The blank in the above should be something like "the answer should have been larger than the initial value (positive, a large number) rather than smaller (negative, a small number)." The "X" in the above would be a numerical estimate.

Many students get into trouble by not reading the questions carefully. If you answer the wrong question without realizing it, you will get **zero** credit.

The best use of the cheat sheet during the exam is as a way to double check formulas, results, or ways of approaching a problem. Students who are constantly scanning their cheat sheet to find a formula generally do not find the **right** formula. As is noted in the section on studying for

examinations, the value of a cheat sheet is greatest *before* the exam, when you use it to organize the material.

When you are Struggling

As noted in the ESF Student Handbook, there are offices at both ESF and SU available to **provide academic support, as well as career and personal counseling**. The ESF Office of Career and Counseling Services, 110 Bray Hall, 470-6660, can direct you to the proper source of help. **Confidentiality is assured.**

If you have **family or health emergencies** that will interfere with your ability to succeed in this or other courses, visit or call the ESF Office of Career and Counseling Services (315-470-6660). They can give official endorsement to your need for accommodation. This office will also contact all your class instructors for you, should such an emergency require you to be absent from campus.

Contract

Students can expect that Dr. Dibble will do the following: (to be discussed and possibly modified the first week of classes)

Be on time

Be prepared

Answer questions clearly

Show respect

Provide clear and timely information about assignments or other requirements

Design homework, exercises, and exams fairly

Grade homework, exercises, and exams fairly

Return homework, exercises, and exams quickly

Dr. Dibble can expect that students will do the following: (to be discussed and modified the first week of classes)

Pay attention

Be on time

Study

Agreed upon in class _____, January ____, 2011.

Methodology for Understanding the Physical Meaning of an Equation **(A. P. Chatterjee and T. S. Dibble)**

- 1) Source of Equation: is it empirical, theoretically derived (or justifiable), or, merely a simplifying assumption or hypothesis ?
- 2) Precisely define the physical meaning of each variable.
- 3) Identify the limits to its use and its domain of validity.
- 4) Identify units and dimensions of all variables and constants.
- 5) Identify, if appropriate, which variables are likely to be treated as dependent, and which as independent, in its use.
- 6) Rearrange it to isolate each variable on the L.H.S., where possible.
- 7) Try to express the content of the equation for each variable purely in words, as far as possible.
- 8) Draw graphs, sketch lines, to illustrate key behaviors predicted by the equation; identify relevant turning points, slopes, intercepts, and asymptotes.
- 9) How is the equation likely to be used by a professional in science or engineering?

Methodology for Checking the Reasonableness of a Calculation **(T. S. Dibble and A. P. Chatterjee)**

- 1) Identify the quantity to be determined and its units
- 2) Determine the sign of the quantity, or if it should be zero.
- 3) Estimate the magnitude of the quantity to be determined (or of the change from the initial value).
- 4) Compare your responses from items (1) - (3) to the answer you are checking and identify discrepancies.
- 5) Review the calculation to find sources of any discrepancies; your initial analysis could be in error!
- 6) List things done correctly and incorrectly during the calculation.
- 7) Identify key error(s), if any.
- 8) Generate insight (about this problem type, or the author of the calculation, etc.).
- 9) Prepare an assessment of the at least one strength, one area for improvement, and one insight.
- 10) Deliver the assessment to the author. If this is your own work, rework the calculation.

On an exam, you may not have time to redo the calculation, but if you correctly identify the key error(s) and/or write down the answer to (1)-(3), you will probably have earned significant partial credit.

On an exam, steps (8) and (9) may need to be postponed until after the exam, but don't forget to do them!

Exercises to prepare for Feedback #1

The numbers refer to the Exercises (not Problems) in *Physical Chemistry*, **8th Edition**, by Peter Atkins and Julio De Paula. Numerical answers for the (b) exercises these are available in the back of the textbook, and more complete answers are in the Student Solutions Manual.

A) The standard Gibbs Free Energy change for isomerization of 5-hydroxy-2-pentanone to 4,5-dihydro-2-hydroxy-2-methylfuran is -4.0 Kcal/mole at 25 °C. Calculate K at 25 °C.

7.1

7.3

7.5

7.7 Also, for 7.7a, Will the reaction shift to make more borneal or isoborneal, or is it already at equilibrium?

7.9

7.11

Answers

A) 860

7.7 (a) +12.3 kJ/mole Needs to make more borneal to reach equilibrium

The numbers refer to the Exercises (not Problems) in *Physical Chemistry*, **9th Edition**, by Peter Atkins and Julio De Paula. Numerical answers for the (a) exercises these are available in the back of the textbook, and more complete answers are in the Student Solutions Manual.

6.3 Also, at $Q=0.010$, determine whether the reaction needs to shift towards reactants or products in order to reach equilibrium.

6.6 6.9 6.13 6.15 6.17

Answers:

6.3 At $Q = 0.01$ ΔG_r is -44.3 KJ/mole, so the reaction must shift to the products to reach equilibrium)

6.13 $Q = 2$ which is more than K (K is less than 1.0) so shift to borneal (reactant) to reach equilibrium

Exercises to prepare for Feedback #2

- A) Compute the ionic strength and mean ionic activity coefficient these aqueous solutions:
i) 10^{-3} molal KBr ii) 10^{-4} molal CuSO_4 iii) 10^{-4} molal $(\text{Cu})_3(\text{PO}_4)_2$

NOTE: If you get the wrong ionic strength, you may not be understanding molality!

- B) What is standard reduction potential for the half-reaction $\text{Ag}^{2+} + 2 \text{e}^- \rightarrow \text{Ag}_{(s)}$?

Note: you cannot add standard reduction potentials, only the corresponding ΔG° values!

ANSWERS TO (A) and (B) are at the bottom of the page

The numbers refer to the Exercises (not Problems) in *Physical Chemistry*, **8th Edition**, by Peter Atkins and Julio De Paula. Numerical answers for the (b) exercises these are available in the back of the textbook, and more complete answers are in the Student Solutions Manual.

5.18 and 5.19

7.14* Also, compute ΔG°_r for each reaction

7.15

7.17 Be sure to solve this from the standard reduction potentials, NOT from standard Gibbs Free Energies of formation!

7.18

* Note that the Solutions Manual has an error in part (c) of this problem: in the half-reaction on the Right it reads $\text{Fe}^{3+}_{(aq)}$ where it should be $\text{H}_2\text{O}_{(l)}$.

Answers to 7.14) ΔG°_r = a) +175 kJ/mole
= b) +120 kJ/mole
= c) -172 kJ/mole

The numbers refer to the Exercises (not Problems) in *Physical Chemistry*, **9th Edition**, by Peter Atkins and Julio De Paula. Numerical answers for the (a) exercises these are available in the back of the textbook, and more complete answers are in the Student Solutions Manual.

5.18, 5.19

6.20, 6.21 Be sure to solve this from the standard reduction potentials, NOT from standard Gibbs Free Energies of formation!

6.23

6.24

Answers

- A) (i) $I = 0.001$ $\gamma_{\pm} = 0.96$
(ii) $I = 4 \times 10^{-4}$ $\gamma_{\pm} = 0.91$
(iii) $I = 1.5 \times 10^{-3}$ $\gamma_{\pm} = 0.76$
B) +1.39 V

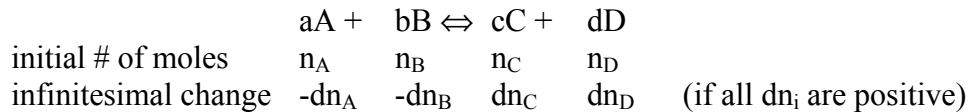
Relationship between $\Delta_r G^\circ$, $\Delta_r G$, Q, and K

Fill in the blanks and boxes!!

At constant P and T and $w_e=0$, dG is a criterion of spontaneity and $dG = \sum_{i=1}^N \mu_i dn_i$ (**Eqn 1**)

and for calculating ΔG or dG , we take $G = \sum_{i=1}^N \mu_i n_i$.

Consider the balanced chemical reaction at some arbitrary composition



$$d\xi = \frac{dn_A}{a} = \frac{dn_B}{b} = \frac{dn_C}{c} = \boxed{}$$

From **Eqn 1**, initial $G = G_i =$

Final $G = G_f = \mu_A(n_A - ad\xi) + \mu_B(n_B - bd\xi) + \mu_C(n_C + cd\xi) + \mu_D(n_D + dd\xi)$

From the previous two equations

$$dG = G_f - G_i = \boxed{}$$

$$= d\xi (-a\mu_A - b\mu_B + c\mu_C + d\mu_D)$$

We can rewrite the equation above as $\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{T,P} = (-a\mu_A - b\mu_B + c\mu_C + d\mu_D)$
 $= (c\mu_C + d\mu_D - a\mu_A - b\mu_B)$

but μ_i of a species in solution is related to activity via $\mu_i = \mu_i^\circ +$

So, $\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{T,P} = (c\mu_C^\circ + d\mu_D^\circ - a\mu_A^\circ - b\mu_B^\circ) + RT [c \ln(a_C) + d \ln(a_D) - a \ln(a_A) - b \ln(a_B)]$

We can rewrite the expression above in more familiar form as:

$$\Delta_r G = \Delta_r G^\circ + RT \ln \left[\right], \text{ where the quantity in square brackets is } Q.$$

Since Q depends on the activity of each species A-D, this equation applies to any arbitrary concentration, and Q is NOT a constant (and not generally equal to K_{eq}).

Study Questions for the Relationship between $\Delta_r G^\circ$, $\Delta_r G$, Q, and K

- 1) For a particular reaction at a particular temperature, how many values can $\Delta_r G^\circ$ have?
Then how many values can K have for the same reaction?
- 2) Is the value of $\Delta_r G^\circ$ a function of the concentrations (activities) or pressures (fugacities) of reactants or products?
Then can the value of K a function of these quantities?
- 3) How does Q differ from K?
- 4) The value of Q can range from _____ (no reactants present) to _____ (no products).
- 5) The units of Q are _____. The units of K are _____.
- 6) Given a value of K and Q, we can determine which way a reaction needs to shift to reach equilibrium (Circle one):
 $Q < K$ reaction needs to shift to (reactants / products) to reach equilibrium.
 $Q > K$ reaction needs to shift to (reactants / products) to reach equilibrium.
- 7) What is the meaning of ξ in the first definition of $\Delta_r G$ on the previous page?
- 8) The value of ξ can range from _____ (all reactants) to _____ (all products).
The units of ξ are _____.
- 9) What is the relationship between $(\partial G / \partial \xi)$ and the slope of a plot of Gibbs Free Energy versus ξ ? _____
What is the relationship between $\Delta_r G$ and the slope? _____
- 10) By definition, the first derivative of a function equals its slope. If one plots Gibbs Free Energy versus ξ for a reaction (at constant T and P), what is the sign of $(\partial G / \partial \xi)$ when:
 $Q > K$? _____
 $Q < K$? _____
the reaction is consuming “reactants” and producing “products”? _____
the reaction is consuming “products” and producing “reactants”? _____
- 11) What is the relationship between $\Delta_r G^\circ$ and the endpoints of a plot of Gibbs Free Energy versus ξ ? _____

Exercises to prepare for Feedback #3

A) Given the data in Table 21.8 and 21.4 (Table 20.4 and 20.7 of the 9th Edition) compute the viscosity of hexane. Assume the effective radius of I₂ is independent of solvent.

Unless otherwise specified, the numbers refer to the Exercises (not Problems) in *Physical Chemistry*, 8th Edition, by Peter Atkins and Julio De Paula. Numerical answers for the (b) exercises these are available in the back of the textbook, and more complete answers are in the Student Solutions Manual.

21.22, 21.23, 21.25-27

21.28 Note that in 3 dimensions, the displacement is $\langle r^2 \rangle^{1/2} = (3\langle x^2 \rangle)^{1/2}$
21.29-31

Problem 21.16 (but only calculate D and a , not the number of water molecules).

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20.23-20.27

20.30 - 20.33

For 20.30 and 20.33, note that in 3 dimensions, the displacement is $\langle r^2 \rangle^{1/2} = (3\langle x^2 \rangle)^{1/2}$

Problem 24.13 (but only calculate D and a , not the number of water molecules).

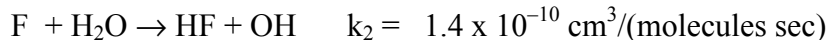
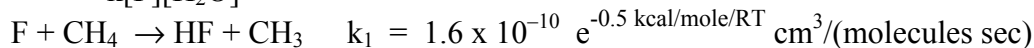
Answer to A:

A) Using the diffusion coefficient, D , for I₂ in benzene, compute effective radius, a , for I₂. Then solve for viscosity of hexane = $0.316 \times 10^{-3} \text{ kg / (meter second)} = 3.16 \times 10^{-4} \text{ kg / (meter second)}$

Exercises to prepare for Feedback #4

A) A fast flash of light creates an initial concentration of electronically excited X ($X^\#$), of 3.5×10^{-6} Molar. The rate constant for $X^\# \rightarrow X + h\nu$ is $1 \times 10^8 \text{ s}^{-1}$. What is the concentration of $X^\#$ after 2.5×10^{-8} seconds?

B) Calculate the rate of reactions (1) and (2) at 298 K, assuming $v_1 = k[F][CH_4]$ and $v_2 = k[F][H_2O]$



$$[CH_4] = 5 \times 10^{13} \text{ molecules/cm}^3$$

$$[H_2O] = 6 \times 10^{17} \text{ molecules/cm}^3$$

$$[F] = 1 \times 10^5 \text{ molecules/cm}^3$$

Note $1 \text{ kcal/mole} = 4184 \text{ J/mole}$

C) A unimolecular reaction has a rate constant $k(T) = A e^{-25 \text{ kcal/mole/RT}} \text{ sec}^{-1}$ which equals 0.01 sec^{-1} at 298 K. What is the rate constant at 500 K?

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22.1 22.3 22.5
 22.7 Note the "2" in front of the N_2O_5 when computing the rate constant !
 22.8 22.11 22.14

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21.2 21.4 21.79
 25.9 Note the "2" in front of the N_2O_5 when computing the rate constant !
 25.10 20.12 20.14

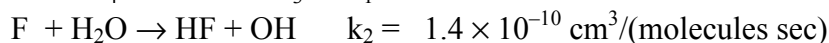
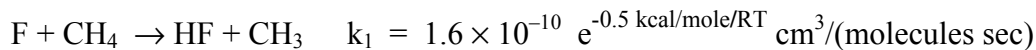
Numerical answers to questions A -B are:

A) $[X^\#] = [X^\#]_0 \exp(-1 \times 10^8 \text{ sec}^{-1} \times 2.5 \times 10^{-8} \text{ seconds}) = 2.9 \times 10^{-7} \text{ molar}$

B) $k_1(298 \text{ K}) = 6.9 \times 10^{-11} \text{ cm}^3/(\text{molecules sec})$
 $v_1 = 3.4 \times 10^8 \text{ molecules/ (cm}^3 \text{ sec)}$
 $v_2 = 8.4 \times 10^{12} \text{ molecules/ (cm}^3 \text{ sec)}$

Additional Kinetics Questions to Prepare You for Problem Set #3

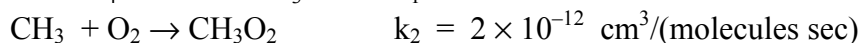
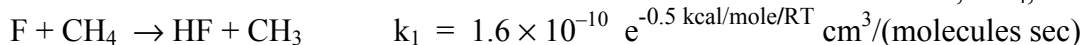
- A) Calculate the pseudo-first order rate constants for loss of F (assume $[\text{CH}_4]$ and $[\text{H}_2\text{O}]$ are constant) in the two following reactions at 298 K, assuming $v_1 = k[\text{F}][\text{CH}_4]$ and $v_2 = k[\text{F}][\text{H}_2\text{O}]$.



$$[\text{CH}_4] = 5.0 \times 10^{13} \text{ molecules/cm}^3$$

$$[\text{H}_2\text{O}] = 5.0 \times 10^{17} \text{ molecules/cm}^3$$

- B) What is the lifetime of F in reaction (1) in Question A? In reaction (2)?
- C) Use the pseudo-first approximation to determine the time at which reaction (1) has decreased $[\text{F}]$ by a factor of 100 from its original concentration in Question A.
- D) Rewrite the expression for the temperature dependence of k_1 in Question A without R (the gas constant) or kcal/mole (or other units of energy).
- E) Consider the mechanism below at **350 K** and the constant concentrations of F, CH_4 , and O_2 .



$$[\text{CH}_4] = 5.0 \times 10^{13} \text{ molecules/cm}^3$$

$$[\text{F}] = 2.0 \times 10^{10} \text{ molecules/cm}^3$$

$$[\text{O}_2] = 5.0 \times 10^{17} \text{ molecules/cm}^3$$

What is the steady state concentration of CH_3 ?

Answers

- A) $k' = k[\text{CH}_4]$
 For CH_4 , $3.4 \times 10^3 \text{ sec}^{-1}$
 For H_2O , $8.4 \times 10^7 \text{ sec}^{-1}$
- B) lifetime, $\tau = 1/k'$
 For CH_4 , $2.9 \times 10^{-4} \text{ sec}$
 For H_2O , $1.2 \times 10^{-8} \text{ sec}$
- C) $\ln([\text{F}] / [\text{F}]_0) = -k' \times t$ Solve for $t = 1.35 \times 10^{-3} \text{ sec}$
- D) $E_a/R = (500 \text{ cal/mole}) / (1.987 \text{ cal /mole K}) = 250 \text{ K}$
 $k_1 = 1.6 \times 10^{-10} e^{-250/T} \text{ cm}^3/(\text{molecules sec})$
- E) $9.0 \times 10^7 \text{ molecules / cm}^3$

Exercises to prepare for Feedback #5

- A) A mole of molecules absorbed a mole of photons, for a total energy increase of 400 kJ. Each photon had the same frequency. What was the frequency and wavelength of the photons?
- B) Problem 8.4 (8th Ed.) or 7.4 (9th Ed.), do parts (a) and (d), only.
For a, use the approximation that ψ is constant over the range of x considered.
For d, use logic.
- C) The value of a wavefunction is constant ($\psi(x) = c$) for $0 \leq x \leq 2 \times 10^{-10}$ meters. If the probability of finding the particle between 0 and 2×10^{-10} (2 nm) meters is 0.01, what is the value and units of c ?

The numbers refer to the Exercises (not Problems) in *Physical Chemistry*, **8th Edition**, by Peter Atkins and Julio De Paula. Numerical answers for the (b) exercises these are available in the back of the textbook, and more complete answers are in the Student Solutions Manual.

8.1 8.3-4
8.7 8.8
8.10, 8.12

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7.1 7.3-4
7.7 7.8
7.10 7.15

Answers to (A-C)

A) $E_{\text{total}} = N_A h \nu$ so $\nu = E_{\text{total}} / N_A h = 1.0 \times 10^{15} \text{ s}^{-1}$ $\lambda = c/\nu = 3 \times 10^{-7} \text{ meters} = 300 \text{ nm}$

B) part a) NOTE that $\sin^2\left(\frac{\pi 4.95 \text{ nm}}{10 \text{ nm}}\right) = \sin^2\left(\frac{\pi 5.05 \text{ nm}}{10 \text{ nm}}\right) = 0.9999 = 1.00$

$$\text{Probability} = \left(\frac{2}{10 \text{ nm}}\right) \int_{4.95 \text{ nm}}^{5.05 \text{ nm}} \sin^2\left(\frac{\pi x}{10 \text{ nm}}\right) dx = \left(\frac{2}{10 \text{ nm}}\right) 1.00 \int_{4.95 \text{ nm}}^{5.05 \text{ nm}} dx = \left(\frac{2}{10 \text{ nm}}\right) (5.05 \text{ nm} - 4.95 \text{ nm})$$

$$= \mathbf{0.020}$$

part d) The box is symmetric, so Probability(Right) = Probability(Left) = **0.50**

C) Probability is given as $0.01 = \int_0^{2 \text{ nm}} c^2 dx = c^2 (2 \times 10^{-10} \text{ meters} - 0)$ so
 $c^2 = 0.01 / (2 \times 10^{-10} \text{ meters})$ and $c = \mathbf{7.07 \times 10^3 \text{ meters}^{-1/2}}$

Exercises to prepare for Feedback #6

- A) For an electron ($m = 9.1 \times 10^{-34}$ kg) in a box with $L_1 = 10$ nm, $L_2 = 20$ nm, and $L_3 = 30$ nm:
What is the energy of the lowest energy state?
What is the energy difference ΔE between the (1, 2, 3) state and the (3, 2, 1) state?
Which state is higher in energy?
What are the frequency and wavelength of the photon absorbed or emitted in exciting the electron between the two states?
What state is degenerate with the (4, 2, 3) state?
- B) Calculate the reduced mass of $^{19}\text{F}^{35}\text{Cl}$
-

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9.1 9.5 9.7

9.8 -10

9.15 Also, what is the vibrational frequency, ν , of Cl_2 , and the energy separation of adjacent energy levels?

Problem 9.2

Answer to 9.15 $\nu = 1.7 \times 10^{13} \text{ sec}^{-1}$ and $\Delta E = 1.12 \times 10^{-20}$ Joules

The numbers refer to the Exercises (not Problems) in *Physical Chemistry*, **9th Edition**, by Peter Atkins and Julio De Paula. Numerical answers for the (a) exercises these are available in the back of the textbook, and more complete answers are in the Student Solutions Manual.

8.1 8.6 -7

8.9-11

8.17 Also, what is the vibrational frequency, ν , of N_2 , and the energy separation of adjacent energy levels?

Problem 8.2

Answer to 8.17 $\nu = 7.1 \times 10^{13} \text{ sec}^{-1}$ and $\Delta E = 4.68 \times 10^{-20}$ Joules

Answers

A) $E(1, 1, 1) = (1 + 1/4 + 1/9) h^2 / (8mL_1^2) = 8.21 \times 10^{-22}$ Joules
 $\Delta E = [(9 + 4/4 + 1/9) - (1 + 4/4 + 9/9)] h^2 / (8mL_1^2) = 4.28 \times 10^{-21}$ Joules
The (3, 2, 1) state is higher in energy
 $\nu = \Delta E / h = 6.45 \times 10^{12} \text{ sec}^{-1}$ and $\lambda = 4.64 \times 10^{-5}$ meters (46.5 μm)
The (1, 8, 3) state

B) $\mu = m_{\text{F}} \times m_{\text{Cl}} / (m_{\text{F}} + m_{\text{Cl}}) = .019 \times .035 / (.019 + .035) / (6.022 \times 10^{23}) = 2.04 \times 10^{-26}$ kg