SYLLABUS
FOR

Atmospheric Chemistry

FCH 511
Fall 2016

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Acknowledgments

Many elements of this course guide are based on the ones I developed for FCH 360 and 361. The inspiration for these course guides come 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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Basic Course Information

Class Time  T Th 12:30-1:50
111 Marshall Hall

Instructor  Dr. Ted Dibble
421 Jahn
470-6596
tsdibble@esf.edu

Office Hours  T Th 10-11 am


Course Grade  determined by:

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<td>Exam I</td>
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<td>Exam II</td>
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<td>Final Exam</td>
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<td>Homework/Class Work/Project</td>
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Grading Scale  85%-100% at least an A-
75%-84% at least a B-
65%-74% at least a C-
55%-64% at least a D

“at least” means the instructor may make the scale easier than the above, but will not make it any harder.

Exams
Exam I  Thursday, Oct. 6  (Structure and Transport, Stratospheric Chemistry)
Part A in class. Part B handed out: due Monday, October 10

Exam II  Thursday November 10 (Tropospheric Chemistry and Aerosols)
Part A in class. Part B handed out: due Monday, November 14

Final Exam  Due Monday, December 19 at 4:00 p.m.
(Climate Change and all previous topics)

Exams I and II are planned as two parts: An in-class part (A) and a take-home part (B). Part A will be short problems and Part B will combine conceptual questions plus more involved numerical problems. The Final Exam will entirely a take-home exam and will be comprehensive.

Homework
Some Exercises are assigned to accompany the reading. These are mostly straightforward questions and computations intended to help you build your understanding of the facts and concepts presented in class and in the text. Answers to these questions will be posted and briefly
discussed in class. While not turned in or graded, these are important building blocks for what I will ask of you in this course.

To build your ability to apply these concepts to new situations you will also be assigned a variety of Problems. These may be calculations or conceptual, but will commonly require you to integrate multiple concepts or pieces of data or apply your knowledge to a new situation. A significant proportion of class time will be spent discussing the Problems. Problems will be turned in for grading. Answers will be posted.

Projects
One project will be assigned. The due date is listed on the Calendar. It centers on numerically calculating photolysis rate constants (J) and analyzing/explaining the trends in J as a function of altitude and solar zenith angle.

Class Work
In addition, I will often have you work in class, alone or in groups, to answer more open-ended questions, or some of the Problems. Both types of assignments may be collected and graded. This work cannot be made up, but I will make accommodations when illness or a family emergency requires you to miss class.

Attendance
The student is responsible for contacting each faculty member in a timely manner to discuss any late assignments/missed work. When possible, students finding it necessary to be absent from class should make arrangements with their instructors prior to being absent.

Background and Purpose of the Course
This course is designed to give you an overview of atmospheric chemistry. This course, together with Environmental Chemistry I (Aquatic Chemistry) and Methods of Environmental Chemical Analysis, constitute the required environmental chemistry courses for both undergraduate and graduate students specializing in Environmental Chemistry at ESF. Despite its broad name, the “Methods” course only covers water analysis; there is no laboratory course here on the analysis of air.

Course Goals and Objectives
While we cannot hope to cover all the topics of significance to atmospheric chemistry or every atmospherically significant pollutant, you will be exposed to the most important issues in atmospheric chemistry. You will also be prepared to understand many topics omitted from the course as well as issues that may arise in the future.

In determining the significance of an a compound, a reaction, or an issue, one might need to know how much of the compound is present, the extent to which the reaction occurs, or the contribution of that reaction or compound to the overall problem. In other words, one needs information. Given our somewhat fragmentary knowledge of atmospheric abundances, reaction rate constants, and problems, there are few areas where we can say, “________ is always/never a concern.” Therefore, the ability to remember or look up information or answers is NOT a sufficient skill.
I believe, instead, that a professional must be able to use data to calculate the best present estimate of the magnitude of the problem (or the magnitude under hypothetical conditions), and that is what I hope to teach you to do. We will make extensive use of kinetics to understand atmospheric issues. This is the training the will enable you to achieve the grandiose goal, stated two paragraphs above, of being “prepared to understand many topics omitted from the course as well as issues that may arise in the future.”

Course Learning Outcomes

After completing this course the student should be able to:

1. Predict fate of molecules and radicals under typical atmospheric conditions.
2. Qualitatively explain and quantitatively compute trends in photolysis rate constants with altitude, season, and time of day for molecules whose photochemistry is known.
3. Compute rates of heterogeneous and homogeneous oxidation of S(IV).
4. Qualitatively predict effects of chemical perturbations on catalytic cycles producing and destroying ozone.
5. Explain basic principles of greenhouse effect and compute global warming potentials.
6. Predict major atmospheric degradation pathways of natural and anthropogenic trace gases

Program and College Learning Outcomes

This course contributes to meeting the Chemistry Department’s objective that undergraduate students develop a “sound understanding of the fundamental chemical principles, underlying theories, and applications of one of the departmental specialties.”

This course contributes to meeting College Learning Outcomes for undergraduate students to develop skills in Scientific Reasoning, Quantitative Reasoning, and Critical Thinking.

Course Description and Organization

After a basic introduction to atmospheric issues, composition, and structure, we will focus on the stratosphere, that portion of the atmosphere between about 10 and 50 km. We will use the relatively simple chemistry of the stratosphere to introduce concepts of kinetics, photolysis, and catalytic cycles that are broadly important in atmospheric chemistry. We will then turn to the troposphere, the layer of the atmosphere extending from the ground up to the bottom of the stratosphere. The concepts listed above will then be applied to the messier chemistry of the lower atmosphere. The study of aerosols will emphasize thermodynamics as much as kinetics. Near the end we will address global climate change.

Detailed Outline of Topics

I. Introduction
   A. To me and each other
   B. Web Page
   C. Syllabus
   D. Ozone: The Good, the Bad, and the Ugly
II. Composition, Structure, and Transport in the Atmosphere
   A. Composition
      1. Units
      2. Table of Composition
   B. Pressure Structure
      1. Barometric Law for gases at equilibrium
      2. Scale Height for actual atmosphere
   C. Temperature Structure
   D. Vertical Transport mechanisms and timescales
   E. Horizontal Transport mechanisms and timescales

III. Photochemistry
   A. Factors affecting light flux
      1. Factors that are common knowledge
      2. Solar Zenith Angle (SZA) (absorption, Rayleigh scattering)
      3. Graphs illustrating light flux
   B. Quantitative Spectroscopy
   C. Rates of Photolysis
      1. Rate Law
      2. Calculating a photolysis rate constant
      3. NO₂ as example
      4. Spreadsheets to use to calculated
         a) SZA
         b) photolysis rate constant
      5. Getting J from DeMore vs. spreadsheet
      6. O₃ photolysis can make O(¹D) or O(³P)

IV. Kinetics
   A. First Order
   B. Elementary vs. Composite
   C. Second Order
      1. elementary vs. composite
      2. pseudo-first order approximation
   D. Computing the fraction of X lost via reaction Y
   E. Steady State Approximation
   F. Arrhenius
   G. Kinetics of barrierless reactions

V. Stratospheric Ozone
   A. Chapman Cycle
   B. Ozone-Destroying Catalytic Cycles
      1. Sources of Radicals
      2. Propagation
         a. Common cycles
         b. Less common cycles compete
         c. Rate-limiting step
3. Termination
C. Null Cycles
D. Coupling radical families
E. The story of CFCs and their replacements, ODP
F. Effectiveness of Initiation and Termination: Cl versus other halogens
   1. Thermodynamics and kinetics of HX formation (Homework #3)
   2. Photolysis of HOX and XONO₂
G. Night and Day/Summer and Winter
H. Observations of the Ozone Hole
   1. [O₃] vs time and altitude
   2. the polar vortex and competing hypotheses
   3. The smoking gun
I. Meteorology and Chemistry Needed for Ozone Hole
   1. Polar Stratospheric Cloud (PSC) formation
   2. Reactions on PSCs
   3. Gas phase reactions and cycles
   4. Arctic vs. Antarctic
   5. Closing the hole
J. Heterogeneous Chemistry Outside the Polar Vortices
   1. Stratospheric Sulfate (Junge) Layer (SSL)
   2. Reaction of N₂O₅ on SSL
   3. Deducing the effects on Ozone

VI. **Tropospheric Ozone**
A. Catalytic Cycles Producing Ozone
   1. Photostationary State
   2. Cycles consuming CO
   3. Cycles consuming hydrocarbons
B. Propagation vs. Termination
C. Radical Sources and Concentrations
D. Fate of Alkanes
   1. Kinetic overview
   2. Reactions initiated by OH
E. Fate of Alkenes
   1. Kinetic overview
   2. Reactions initiated by OH
   3. Reactions initiated by NO₃
   4. Reactions initiated by O₃
   5. Night versus Day
F. Fate of Aromatic Hydrocarbons
G. Oxygenates
   1. Alcohols
   2. Aldehydes
H. Photochemistry
I. Meteorology of Ozone
J. NOₓ- vs. VOC-limited Ozone Formation
K. Modeling
L. Dry Deposition

VII. Aqueous Aerosols in the Troposphere
A. Liquid Water in the Atmosphere
B. Henry’s Law (Equilibrium between Aqueous and Vapor Phases)
   1. Introduction
   2. Monoprotic acids
   3. Aldehydes
C. SO₂ Oxidation
   1. Motivation
   2. S(IV) equilibria
   3. HSO₄⁻ oxidation by HOOH
   4. S(IV) oxidation by ozone
D. Kinetics of Gas-Surface Interactions

VII. Aerosol Size Distributions
A. Size Classes
B. Discrete
C. Continuous
   1. Normal
   2. Semi-log
   3. Log-log

VIII. Global Climate Change
A. Black Body Model of Earth’s temperature
B. Greenhouse Effect
C. Clouds
D. Temperature Record
E. Radiative Forcing and Absolute and Relative Global Warming Potential
F. Feedbacks
G. Aerosol Effects
H. Where is the heat energy going and what is it doing?

Prerequisites - Knowledge, Skills, and Attitudes

The official prerequisite is a year of Physical Chemistry. Unofficially, we will review (or you need to remember or brush up on) a lot of chemistry and math:

Chemical and Mathematical Concepts
   ideal gas law
   octet rule
   homolytic versus heterolytic bond cleavage
   competition between thermodynamics and kinetics
kinetics (lifetimes, pseudo-first order, steady state approximation, pressure dependent rate constants, Arrhenius/reaction coordinate diagrams)
stability of organic radicals
chemical equilibria
liquid-vapor equilibria
conservation of energy
conservation of spin angular momentum
adiabatic expansions and compressions
Beer-Lambert law
Fundamental meaning of integration and differentiation
Uncertainty

There are skills and attitudes required for gaining the maximum benefit from this course beyond the prerequisites cited in the course catalog. Here I present an incomplete list of these skills and habits:

1) Graph numerical data and interpret graphical data.
2) Present logical arguments about the how the interactions of various processes affect an issue or the value of some quantity.
3) Extract numerical data from a statement of a problem, identify needed information, and identify the equations necessary to solve the problem.
4) Take the initiative to obtain data from appendices of the text and the assigned references.
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) Check to see whether you answers on homework or test problems are reasonable physically, chemically, and mathematically.

Academic Integrity

Academic dishonesty (a fancy word for cheating) is a breach of trust between a student, one’s fellow students, and/or the instructor(s). By registering for courses at ESF you acknowledge your awareness of the ESF Code of Student Conduct (http://www.esf.edu/students/handbook/StudentHB.05.pdf). In particular academic dishonesty (http://www.esf.edu/students/handbook/integrity/) includes but is not limited to plagiarism and cheating. The penalties for cheating that will be administered by this instructor will include a zero on the particular assignment and, possibly, failing the course. The incident will be reported to the administration per ESF guidelines (see the ESF Grading Policy (http://www.esf.edu/provost/policies/documents/GradingPolicy.11.12.2013.pdf).

An older version of the academic integrity policy read:
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.

Cooperation on exams is not allowed.

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

Inclusive Excellence Statement

As an institution, we embrace inclusive excellence and the strengths of a diverse and inclusive community. During classroom discussions, we may be challenged by ideas different from our lived experiences and cultures. Understanding individual differences and broader social differences will deepen our understanding of each other and the world around us. In this course, all people (including but not limited to, people of all races, ethnicities, sexual orientation, gender, gender identity and expression, students undergoing transition, religions, ages, abilities, socioeconomic backgrounds, veteran status, regions and nationalities, intellectual perspectives and political persuasion) are strongly encouraged to respectfully share their unique perspectives and experiences. This statement is intended to help cultivate a respectful environment, and it should not be used in a way that limits expression or restricts academic freedom at ESF.

How to Get a Good Grade in This Course

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 atmospheric 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 homework, projects, and exams 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 atmospheric chemistry rather than an exercise in memorization of facts, formulas, and algorithms for doing problems. 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

Despite this grand claim, I must acknowledge that you will need to learn facts to do well in the course. Atmospheric chemistry is not a unified body of knowledge, and without facts as a guide (O₂ constitutes 21% of the atmosphere by mole fraction) you can get far off track.

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, and integrating material from other texts, reviews, or papers. I will also try to organize the material and make it more coherent; it is often difficult for students to see the organization of material by reading a textbook. Also, the act of copying 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 academic subjects.

We will be discussing answers to homework Problems in class. Questions based on the same logic as the Problems will appear on the exams. We may use class time to address problems that are not part of the homework, but do address important concepts (i.e., ones worthy of a test question).

Much of the learning will take place in class discussing answers to the problems. Also, you may find yourself curious about issues other than those which are the focus of a lecture or homework. Your questions on those issues and the quality of your participation in class discussions can raise your class grade. Ask questions in class. If you have a question, it is likely that half the class is also wondering about the same topic. Even the best students in the class may learn something from the answer to the question you worry is too "dumb" to ask.

The Textbook and Other Assigned Readings
Do the assigned reading - before the topic is discussed in class. This will be necessary to do the Exercises and prepare for in-class assignments. It will also 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 readings and in the lecture are linked.

Homework
I will assign some relatively straightforward problems (Exercises) for you to do. These will generally be tied to the assigned reading or lecture; my answers will be posted to Blackboard. You are responsible outside of class for making sure you understand the correct answers. Exercises are often the basis for Problems and for graded in-class assignments. Therefore, you need to make sure you understand the answers to the Exercises. Exercises will not be graded so you are allowed to give or accept help on the Exercises that would constitute cheating if done for graded assignments (like the Problems).
As mentioned above, I will also provide you with less straightforward questions, the *Problems*, which will be collected and graded. A person can't learn to drive a car just by reading the textbook in their Drivers Education class or watching someone else drive: one needs to actually get in the car and drive. By this analogy, the *Problems* for this class 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 badly hurt (your performance on the *Problems* does not count towards a huge part of your grade). Doing problems and answering questions is the best, for some the only way, to begin to learn 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 facts, relationships, or equations do I need in order to solve this problem? What error am I making in what I have done 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. This cooperation is particularly appropriate to the *Problems* we will be discussing in class.

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 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 will not be identical.

The goal of the Homework is for you to begin to learn the material. *Exercises* will help you learn the facts and basic skills you need to answer *Problems*. The higher-level skills and logic patterns you need to answer *Problems* are the same skills and logic you will need to answer exam questions. If you cheat, you defeat the goal of doing the homework and lower your chances of getting a good grade in the course.

While we will discuss some of the homework *Problems* in class, you will need to do further study on your own to succeed. Take the time to examine the things you did right and wrong on the homework. However, it is not sufficient to merely be able to do the problems. You need to think about the answers, whether they make sense chemically, physically, mathematically, and atmospherically, and why they are what they are. On the examinations you will often be asked to explain things, instead of, or in addition to, providing numerical answers.

If you can’t do a homework problem, and ask me 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. The gain in your understanding and the satisfaction of figuring it out for yourself will help you much more than having someone else show you how to do the problem.

**Project**

The project involves a spreadsheet calculation that is too long to be appropriate for a homework Problem. It is designed to help you understand (and test your understanding of) calculations of photolysis rate constants and the qualitative factors that affect photolysis rate constants. The Project counts directly towards your grade, and questions relevant to the projects may appear on the exams.

**Office Hours and Help Sessions**
E-mail me or stop by my office when you have questions. Set up an appointment in advance if you have trouble finding me.

Examinations

The Final Exam and Part B of Exams I and II are planned as take-home exams: you will be able to use your textbook, your notes, my answers to homework, and some other resources to be specified later. Several days before an exam, review your notes and the textbook to identify ideas that are unclear; then clarify them. Try doing the homework assignments again (without looking at the answers). If you have questions, get them answered. Also, you can benefit by getting together with your fellow students to figure out the difficult points (before the exams, only!).

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

However, if you realize that you don't know how to answer the question, then you might try to provide some information about the answer. On quantitative questions a numerical estimate is best, but it is helpful to provide information along the lines of whether the answer will be a large number or a small number, or larger or smaller than some value. Similarly, if you know an answer is wrong, but can't figure out how you got the wrong answer, you can help yourself by writing something like: "This answer is wrong because X; I don't know how I got it wrong." If you do this you might not lose as many points as you otherwise would for the error. The X in the above should be something like "the answer should have been larger/positive rather than smaller/negative."

When you are Struggling

As noted in the ESF Student Handbook, there are offices at ESF available to provide academic support, as well as career and mental health counseling. The Division of Student Affairs (110 Bray Hall, 470-6660) can provide help and guide you to resources. The Counseling Services Office (105 Bray Hall, 470-4716) can also assist and confidentiality is assured.

If you are absent for several days due to hospitalization, emergency, or other critical incident, the Division of Student Affairs can assist in these instances to coordinate notification to instructors.

Students with Learning and Physical Disabilities

SUNY-ESF works with the Office of Disability Services (ODS) at Syracuse University, which is responsible for coordinating disability-related accommodations. Students can contact ODS at 804 University Avenue- Room 309, 315-443-4498 to schedule an appointment and discuss their needs and the process for requesting accommodations. Students may also contact the ESF Office of Student Affairs, 110 Bray Hall, 315-470-6660 for assistance with the process. To learn more about ODS, visit http://disabilityservices.syr.edu. Authorized accommodation forms must be in the instructor's possession one week prior to any anticipated accommodation. Since accommodations may require early planning and generally are not provided retroactively, please contact ODS as soon as possible.

My Favorite Readings and References

Ahrens, C. D. Meteorology Today Moon QC 861.2 .A3

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SOME REQUIRED READINGS HERE

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Other Useful Readings


Faraday Discussions #130, 2005. (my office)

Atmospheric Sciences: Entering the twenty-first century (National Research Council) *Sci-Tech QC 861.2 .A88*


Arya, S. P. *Air Pollution Meteorology and Dispersion* *Sci-Tech QC 882 .A856*


Chameides, W. L. *Biogeochemical Cycles* *Sci-Tech QH 344 .C45*


Jacob, D. *Introduction to Atmospheric Chemistry* *Sci-Tech QC 879.6 J33*

Jepna, C. J. *Climate Change Policy*. *Sci Tech QC 981.8 C5 J47*

Lave, L. B. *Air Pollution and Health* *Sci-Tech RA 576 .L28*


Price, J. J. *Environmental Pollution and Control* *Sci-Tech TD 145 V43*

Somerville, R. *Forgiving Air: Understanding Environmental Change* *Sci-Tech QC 879.7 .S66*

Warneck, P. *Chemistry of the Natural Atmosphere* *Moon QC 879.6 .W37*

Watts, R. G. *Engineering Response to Global Climate Change* *Sci-Tech QC 981.8 C5 E56*
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!