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University of Waterloo

CHEM 123 (Winter 2011)

Intermolecular forces, Chemical Kinetics, Equilibrium, and Electrochemistry

Section (class #)	Lecture Time & Room	Instructor (Office, Extension and e-mail address)
001 (#5898)	8:30 am MWF in RCH 101	T. Leung (C2-066A, ext. 35826, *tong@uwaterloo.ca*)
002 (#5899)	9:30 am MWF in DC 1350	R. Marta (C2 273A, ext. 36388, *ramarta@uwaterloo.ca*)
003 (#6002)	10:30 am MWF in AL 116	C. Bissonnette (C2 274, ext. 32434, *cbissonn@uwaterloo.ca*)
004 (#6116)	12:30 pm MWF in DC 1350	D. Gilbert (C2-263, ext. 35047, *d2gilber@uwaterloo.ca*)

Course Coordinator: C. Bissonnette (C2-274, ext. 32434, *cbissonn@ uwaterloo.ca*)

Lab Coordinator: S. Stathopulos (ESC 149, ext. 33868, *sckramer@ uwaterloo.ca*)

Text: R.H. Petrucci, F.G. Herring, J.D. Madura and C. Bissonnette, *General Chemistry (Principles and Modern Applications)*, Prentice Hall, Tenth Edition, 2011. The text comes with a full *Solutions Manual*.(Note: The 9th edition of this text book is also acceptable.) Several copies of the text and the solutions manual have been placed on Reserve in the Davis Centre Library. Use the call numbers **UWD 1532** (for the text) and **UWD 1534** (for the solutions manual).

Chapter	Topic(s)	# of Lectures	Comments
12	Liquids, Solids and Intermolecular Forces	6	You will not be expected to remember or use the equation $n\lambda = 2\,d\sin\theta$.
14	Chemical Kinetics (including supplementary topic #1 on p. 10 of this booklet)	6	The integrated rate laws will always be provided on all tests and exams. Learn how to use them.
15	Chemical Equilibrium (including supplementary topic #2 on p. 10 of this booklet)	4	The Van't Hoff equation will always be provided. Learn how to use this equation.
16	Acids and Bases	4	
17	Acid-Base Equilibria	5	
18	Solubility and Complex Ion Equilibria	4	You are not responsible for section 18-9.
20	Electrochemistry	4	Ignore Gibbs free energy aspects in Chapter 20. You do not have to memorize of the half- reactions in sections 20-5, 20-6, 20-7 or 20-8.

Access to Assistance

Office for Persons with Disabilities (OPD): This office collaborates with all academic departments to arrange appropriate accommodations for students with disabilities without compromising the academic integrity of the curriculum. If you have a documented disability, (i.e. physical, learning, or sensory disabilities or chronic medical conditions), you are encouraged to contact this office to determine eligibility for our services. It is recommended that you register with the OPD at the beginning of each academic term, if you anticipate that you require academic accommodations to lessen the impact of your disability. The office is located in Needles Hall, Room 1132.

Counselling Services: The University of Waterloo can be a challenging environment. A meeting with a friendly and experienced counsellor can help you handle and manage your goals. Counselling Services provides a wide range of strategies to help you do your very best during your time at Waterloo. Counselling Services can help you with Study Skills, Career Planning and Personal Goals. For an appointment, call 519-888-4567, extension 32655 or go to Needles Hall, Room 2080. Their web-site is **www.adm.uwaterloo.ca/infocs/**

Important Dates

Jan.4 Lectures start. No CHEM 123 tutorials during the first week.
Jan. 10 CHEM 123 tutorials and CHEM 123L labs start in the second week.
Jan. 17 Last day to add a course.
Jan. 24 Last day to drop a course.
Feb. 21-25 Reading Week
Mar. 2 Term Test (during your lecture time)
Mar. 14 Last day to withdraw from a course.
Apr. 4 Lectures end
Apr. 8 Exams begin. The exam schedule is normally posted in March.
Apr. 21 Exams end.

Avoidance of Academic Offenses

Students are expected to know what constitutes academic integrity, to avoid committing academic offenses, and to take responsibility for their actions. Students who are unsure whether an action constitutes an offense, or who need help in learning how to avoid offenses (e.g., plagiarism, cheating) or about "rules" for group work/collaboration should seek guidance from the course professor, TA, academic advisor, or the Undergraduate Associate Dean. For information on categories of offenses and types of penalties, refer to Policy #71, Student Academic Discipline, **www.adm.uwaterloo.ca/infosec/Policies/policy71.htm** . Students who believe that they have been wrongly or unjustly penalized have the right to grieve; refer to Policy #70, Student Grievance, **www.adm.uwaterloo.ca/infosec/Policies/policy70.htm** .

Learning Outcomes

By the end of this course, you should be able to apply principles of kinetics and equilibrium to a variety of different chemical reaction types. More specifically, this course is designed so that by the end, you should be able to:

- describe the behaviour and interactions of molecules in gases, liquids and solids and predict the properties of these phases
- describe the interactions of molecules in liquids and solids and rationalize trends in the properties of liquids and solids
- describe and visualize the three-dimensional structures of molecular, ionic, covalent and metallic solids
- determine the rate law for a chemical reaction and explain how the rate of a reaction depends on time, concentration, temperature, and the use of a catalyst
- explain how the rate law for a reaction is related to the reaction mechanism
- determine the equilibrium constant for a chemical reaction and apply equilibrium principles to a variety of chemical reaction types, including gas-phase reactions, acid-base reactions, precipitation reactions, complexation reactions and oxidation-reduction reactions
- explain the basic construction of, uses of, and the differences between galvanic and electrolytic cells

Learning Methods

Lectures: During lectures, your instructor will focus on selected topics. Prepare for each lecture by reading the relevant sections of the text in advance. Your instructor may expect you to learn some of the course material on your own.

Tutorials: The tutorial periods are run by highly-qualified teaching assistants or "Tutors" who have been selected for this course because they have exceptional teaching abilities. During the tutorial periods, the Tutors will review essential concepts and work through some examples. More information about the tutorials is provided on page 3 of this course information booklet.

On-line Assignments: The assignments are provided on-line so that you can obtain frequent and immediate feedback on your understanding of the concepts. Each on-line assignment can be repeated up to four times, so you can correct your mistakes or get help whenever you need it. More information about the assignments is provided on page 4 of this course information booklet.

On-line "mini-lectures": You can find "mini-lectures" on all topics in CHEM 123 in the "Mini-Lectures" folder on our course web-site on UW-ACE. (More information about UW-ACE is provided on page 3 of this course information booklet.) Your lectures and textbook are the primary sources of information for this course, but you can use these mini-lectures whenever you are seeking more information or a different perspective.

Homework Problems: You should be spending a <u>minimum</u> of three hours per week doing problems. For each week of term, we have assigned problems for you to try. (See pages 6-9 of this course information booklet.). You are not required to hand in solutions to these problems; the responsibility to do them is yours. **Make sure you can do all of them.**

Office Hours: Not all learning happens in the classroom. You may find it necessary to meet with your course instructor during his/her office hours to get some one-on-one help. Come prepared with a specific question or questions. (e.g. In reviewing my notes, I understand up to this point, but I get confused here.) It is not a beneficial use of your time, or your instructor's time, to show up and say "I just don't get (insert specific topic)."

CHEM 123L Laboratory: CHEM 123L is a separate course and a separate grade is given for it. Because chemistry is an experimental science, you are encouraged to take CHEM 123L even if you are not required to do so. The experiments in CHEM 123L are designed to reinforce concepts introduced in CHEM 123, while also providing you with the opportunity to learn some of the practical aspects of "doing chemistry". More information about CHEM 123L is given on page 5 of this handout.

Learning Assessment

On-line Assignments (10%): The on-line assignments are accessed via MapleTA. See page 4 of this course information booklet for more information. If you choose not to do the on-line homework assignments, then the 10% weight for the assignments is transferred to the test and exams, with 5% going towards the term test and 5% going towards the final exam.

Term Test (20% or 30%): There will be one 50-minute term test held during your lecture time on **Wed., Mar. 2nd**. Some students will write in the lecture rooms, and the rest will write in other locations. The seating plans for the term test as well as the topics to be covered will be announced in class (and on UW-ACE) one week prior to the test. The test will count for either 20% or 30%, whichever is to your benefit.

Important!! The learning assessment described here applies only if the weighted average of your test and exam is at least 45%. If the weighted average is less than 45%, then that weighted average is also your course grade.

Final Examination (70% or 60%): There will be a 2.5-hour exam held during the exam period (Apr. 8-21). The examination is scheduled by the Registrar. Normally, the examination schedule is posted in early March. Until you know the date of your last examination, **don't make plans to leave campus before April 21.** The exam will count for either 70% or 60%, whichever is to your benefit.

Why do we focus on the weighted average of your test and exam? Our experience, compiled over many years, indicates that low marks on the test and exam are a very strong indicator that a student has not mastered the material and is not yet ready to move on to other courses. Because the assignments will help you prepare for the test and exam, it is in your best interests to do them. Learn from your mistakes on the assignments before writing the test or exam.

Important Policies for CHEM 123

(1) Calculators: You may bring a calculator to all tests and exams. The following calculators have been adopted by the Math Faculty for use in first-year math courses: **Sharp EL-531W, TI 30X II (S or B), and Casio fx-300MS**. If you are also taking MATH courses this term, consider purchasing one of these models.

(2) Absence on the day of a test or exam: A student who misses an examination because of illness must take a completed Verification of Illness Form to the Science Undergraduate Office (ESC 253). The form can be obtained from the Health Services web-site (***http://www.healthservices.uwaterloo.ca/Health_Services/verification.html***). The form must specify the precise period of absence. If a student becomes ill while away from the University and misses an examination as a result of that illness, then he/she may instead supply a Doctor's certificate covering the precise period of absence, provided the certificate includes a classification of the illness as slight, moderate, or severe. In all cases, the letter or form must include contact information of the person who signed the letter or form. **A Verification of Illness Form (VIF) or a doctor's note does not necessarily excuse a student from missing a test or exam!** The instructors and course coordinator will consider the information provided on the VIF or doctor's note when deciding whether a student should be excused. If it is decided that a student had a legitimate excuse for missing the term test, then the weight of the term test is transferred to the final examination. (There is no make-up term test!) If it is decided that a student has a legitimate excuse for missing the final exam, then the student will normally write a make-up exam in August together with students taking CHEM 123 in the Spring term.

CHEM 123 Tutorials

Every student in CHEM 123 is assigned to a tutorial section which meets once every two weeks. **You may attend more than one tutorial session.** During your tutorial periods, the Tutor will review important concepts and work through some examples.

Need extra help? Tutorials are held in DC 1350 on Tuesdays and Thursdays 9:30-11:20 am and 4:30-6:20 pm.

Note: The Tutors are students too! They are working towards M.Sc. or Ph.D. degrees in chemistry. When they are not in the tutorial room, they are working on their own courses or working in their research laboratories. Because they share offices and labs with other graduate students., it is not possible for you to meet with them in their offices or labs. You must seek help from the Tutors in the tutorial rooms during one of the scheduled tutorial periods.

Important Web Sites (Bookmark these sites!)

UW Home Page (*http://www.uwaterloo.ca/*) This is the main UW Home Page. Use the links or search engine to find other important UW web-sites.

Registrar's Office (***http://registrar.uwaterloo.ca/***) The Registrar's Office provides administrative services to all students in a number of areas. The Registrar's Office is where you would go to request a transcript, drop off course override forms and much more. Before going to the Registrar's Office, consult the web-site to obtain important information or forms (e.g. plan modification forms, course override forms, etc.)

Quest (*http://www.quest.uwaterloo.ca/*) Quest is the University of Waterloo's student information system. As a student at UW, you can use Quest to perform a number of important tasks (e.g. update your contact information; view your tuition fees, pay your fees; view your unofficial transcript; enrol in, drop, or swap classes; view your class schedule; etc.)

UW-ACE (*http://uwace.uwaterloo.ca/*) ACE stands for "Angel Course Environment", a web-based course management system. When you go to the UW-ACE web-site, you will be prompted for a username and password. Use the same username and password that you use for logging onto Quest. After you log onto UW-ACE, you will see CHEM 123 listed as one of your courses. (Not all of your instructors will be using UW-ACE, so you may not see all of your courses listed!!) We will use UW-ACE for CHEM 123 to post useful information, announcements and important links. You will also find extra problems, sample tests and sample exams. **Make sure you log onto UW-ACE regularly.**

Library Resources

We have placed the following items "on reserve" in the Davis Centre Library. **These resources are for library use only.** You may borrow these items by giving the attendant at the Reserve Desk the appropriate catalogue number. (e.g. Ask for UWD 1532 if you want to borrow the textbook.)

Libray Reserve Item	**Catalogue Number**
Course text (by Petrucci, Harwood, Herring & Medura, 9th edition)	UWD 1532
Solutions manual (for the text above)	UWD 1534

Another useful chemistry resource that can be found in the Reference section of the library is the **CRC Handbook of Chemistry and Physics** (Ref. QD65.H3). This handbook lists, among other things, chemical and physical properties of essentially all organic and inorganic substances that are known. The CRC Handbook of Chemistry and Physics can be accessed on-line, free of charge, from any ".uwaterloo.ca" address. The URL is ***http://www.hbcpnetbase.com/***

On-line Assignments

In this course, we use an on-line homework assessment system, called MapleTA, to deliver on-line assignments. The on-line assignments give you a chance to build your skills gradually and, because they are delivered on-line, you obtain frequent and immediate feedback about your progress.

Your user account on the the MapleTA system will NOT be available until the second week of term. Announcements will be made in class and on UW-ACE to let you know when you will be able to access your user account and the on-line assignments. When it is announced that the user accounts and on-line assignments are available, follow these steps to access them.

(1) Go to ***http://mapleta.uwaterloo.ca*** (You can access this site using the link provided in UW-ACE. When you get to the MapleTA web-site, bookmark it so that you can access the on-line assignments even if UW-ACE is unavailable.)

(2) Log on to the MapleTA system. Use your UW-ACE username as your login name and your UW student number as your password.

(3) Change your password. To change your password, click on the link entitled "My Profile" (in the upper right hand corner of the screen) and then on the link entitled "Password Update". We suggest that you use the same password that you use to log in to UW-ACE, Quest, etc. to minimize the possibility of forgetting your password. The next time you log in, you will have to use your new password.

(4) Find our class (CHEM 123, Winter 2011). The course coordinator (C. Bissonnette) is listed as the instructor of the course. All students in CHEM 123 access the same class (i.e., your instructor does not have his or her own class in MapleTA!!) There are many courses using MapleTA this term, so make sure you have found our class.

If you forget your password, or require assistance with your account, then contact one of the people below. These contacts cannot help you with chemistry-related questions! They can only resolve technical issues related to your MapleTA account.

Paul Kates, Mathematics & Engineering Faculties CTE Liaison (pkates@uwaterloo.ca, ext. 37047)

Carrie Howells, Instructional Support Coordinator, Mathematics Faculty/MFCF (cahowells@math.uwaterloo.ca, ext. 36272)

Guidelines concerning the on-line homework assignments

(1) **Each assignment is available until the end of the exam period, but you must do the assignments by the recommended due dates.** The recommended due dates will be posted on the Announcements on UW-ACE. The assignments are available until the end of the exam period so that you have access to them for review and study purposes. For each assignment, the assignment marks will be downloaded shortly after the recommended due date. If you submit an assignment for grading after the recommended due date, then there is a very good chance that the submission will be ignored. Also, do NOT wait until the last minute to do an assignment because you will not have time to resolve technical difficulties or get help.

(2) **Print off a paper copy of every assignment and work on the problems at home.** When you have finished those problems, return to MapeTA, enter your answers and then submit your assignment for grading. Note carefully: Your instructor or Tutor cannot help you with your assignment if you do not have a paper copy of your assignment!!

(3) **You can attempt each assignment up to four times.** We use only the highest mark you achieved on each assignment when calculating your assignment average at the end of term. Each time you attempt an assignment, you get the same set of questions so that you can correct your mistakes or get help whenever you need it.

(4) **Do not waste attempts by guessing or changing your answers one at a time.** If you cannot figure out why your answers are wrong, or when you are struggling with the assignment problems, take your paper copy of the assignment to a teaching assistant or your instructor to get some help before you use up all of your attempts.

(5) **Do the assignments one at-a-time, in the proper order!** The assignments are designed to be done in order. So, you should complete Assignment #1 before accessing or attempting Assignment #2. Also, if you try to access Assignment #2, for example, before you finish or submit answers for Assignment #1, the system will automatically grade Assignment #1 (even if you have not yet inputted any answers!) and you will use up one of your attempts at Assignment #1.

(6) **Every time you achieve a grade of 80% or higher on an assignment, the mark will be treated as 100%** when calculating your assignment average. Otherwise, we use your actual mark on the assignment when calculating your assignment average.

Some Helpful Tips

- Read the questions carefully and make sure you answer the question that is asked. Some questions ask you to enter your answer in a certain format and, if you want credit for a correct answer, you must use the specified format.
- Use correct symbols for units when submitting your answers. (e.g. The correct symbol for grams is "g", not "G", "gm", "gms", etc.) Make sure you know the proper SI units and prefixes. See Tables 1.1 and 1.2 of Petrucci. If you enter an answer with the wrong symbol for the unit, your answer will be marked wrong even if the numerical part is correct. The numerical part of an answer is meaningless when the unit cannot be interpreted.
- If there is only one answer box, the question is usually asking you to calculate your answer in a specific unit and the answer box is for the numerical part of the answer only (i.e., enter your an answer without units). When units are required, there are two answer boxes, one for the numerical part and the other for the units.

CHEM 123L

CHEM 123L is closely related to the lecture course, CHEM 123, but it is a separate course and a separate grade is given for it. The experiments are designed to explore and expand on the concepts presented in the lecture course. A **tentative** schedule for the term is given below.

Before you arrive for your scheduled laboratory period it is expected that you will have reviewed all relevant sections of the lab manual in preparation for the upcoming experiment.

For your first laboratory period you will need to purchase:

- Laboratory Manual – Available from Chem Stores, ESC-109
- Safety Goggles – EVERYONE must wear them!
- A Sharpie™ glassware marker – not mandatory, but very useful.

Week	Sections	Exp. #	Experiment
Jan 10 - 14	1,3,5,7,9,11	1	Laboratory Check-In **and** A *cis* to *trans* Conversion
Jan 17 - 21	2,4,6,8,10,12		
Jan 24 - 28	1,3,5,7,9,11	2	The Iodide Persulphate Reaction: The Effect of Concentration on Reaction Rate
Jan 31 - Feb 4	2,4,6,8,10,12		
Feb 7 - Feb 11	1,3,5,7,9,11	3	Weak Acid - Strong Base and Weak Base - Strong Acid Titrations
Feb 14 - Feb 18	2,4,6,8,10,12		
Feb 21 - Feb 25	All		**Reading Week - No Labs**
Feb 28 - Mar 4	1,3,5,7,9,11	4	Buffer Solutions
Mar 7 - Mar 11	2,4,6,8,10,12		
Mar 14 - Mar 18	1,3,5,7,9,11	5	Electrochemical Cells **and** Laboratory Check-Out
Mar 21 - Mar 25	2,4,6,8,10,12		
Mar 31 - Apr 6	All		Pick up marked reports #4 and #5 in ESC-148
TBA	All	Exam	The final exam for CHEM 123L will be scheduled by the Registrar; the date, time and location will be announced during the term.

Instructor: **Sue Stathopulos**
Phone: Ext. 33868
Office: ESC-148, at the back of the Labs, ESC-149 and ESC-146
Email: sckramer@sciborg.uwaterloo.ca

CHEM 123 Practice Problems

Work (and learn) from your text book and stay ahead of your instructor throughout the term. This will help you get the most out of the lectures. By working ahead, you can identify topics you find difficult **before** they come up in lectures. (See if your instructor's discussion helps you understand these difficult concepts. If not, ask for clarification during lectures.)

The week-by-week schedule outlined on the next few pages encourages you to build your problem-solving skills gradually. When working through the problems, write down all steps as if you were going to hand in your solutions for marking. A clear, organized approach will help you think through a problem. **Hints to help you with the Part b problems are available on UW-ACE.**

Note: CHEM 123 is the continuation of CHEM 120. There are a number of concepts from CHEM 120 which you must know (and should review, if necessary). These include: SI base units and SI prefixes; reaction and solution stoichiometry (e.g. mass-to-moles conversions, molarity calculations, using the ideal gas equation and partial pressures); thermochemistry and Hess' Law; basic organization of the periodic table and periodic trends; drawing Lewis structures and predicting molecular geometry; assigning formal charges (**always show non-zero formal charges in any structure you draw!**); bonding concepts (e.g. ionic vs. covalent bonding, polar covalent bonds, electronegativity); oxidation-reduction (redox) concepts (e.g. oxidation numbers, balancing redox reactions)

Textbook Exercises: Many of the end-of-chapter exercises from the text emphasize concepts from specific sections. Use these exercises, together with the self-assessment exercises, to help you decide if you are ready to move on to the next section or chapter or if you should spend more time working with concepts in the current section or chapter. The Integrative and Advanced Exercises are multi-concept problems that integrate material from different sections or earlier chapters. Use these exercises to help assess your ability to connect and integrate important concepts.

Extra Problems: These problems are numbered B1 through B33 and are given on pages 7 to 9 of this booklet. Use them to gain additional practice working with concepts many students find challenging.

	Representative Problems (from Petrucci, 10th Edition)	Extra problems (see pages 7-9)
Week 1, Jan. 4-7	Chapter 12: 1, 3, 34, 40, 41, 42, 51, 56, 65, 73	B1-B4
Week 2, Jan. 10-14	Chapter 12: 81, 83, 86, 88, 108, 116	B5-B9
Week 3, Jan. 17-21	Chapter 14: 4, 10, 11, 20, 21, 26, 33, 34, 36, 40	B10, B11
Week 4, Jan. 24-28	Chapter 14: 47, 49, 50, 55, 71, 79, 94	B12, B13
Week 5, Jan. 31-Feb. 4	Chapter 15: 3, 12, 13, 18, 26, 33, 34, 40, 43, 49, 57, 63, 76, 81, 86, 100	B14-B17
Week 6, Feb. 7-11	Chapter 16: 6, 9, 10, 12, 20, 24, 29, 30, 32, 44, 49	
Week 7, Feb. 14-18	Chapter 16: 57, 58, 59, 60, 62, 63, 65, 68, 69, 112, 114	B18, B19
Reading Week, Feb. 21-25 (no classes)		
Week 8, Feb. 28- Mar. 4 **Term Test on Mar. 2**	Chapter 17: 10, 11, 15, 23, 31, 38, 43, 44, 53, 54	B20-B23
Week 9, Mar. 7-11	Chapter 17: 64, 71, 73, 98, 110 Chapter 18: 1, 4, 9, 19, 29, 34, 35	B24-B27
Week 10, Mar. 14-18	Chapter 18: 41, 42, 53, 54, 56, 69, 94, 95, 98	B28, B29
Week 11, Mar. 21-25	Chapter 20: 8, 11, 13, 19, 35, 37	B30, B31
Week 12, Mar. 28-Apr. 1 **Lectures end Apr. 4.** **Exams start Apr. 8.**	Chapter 20: 43, 45, 46, 47, 48, 65, 70, 108, 111, 121 Catch-up and review.	B32, B33

Extra Problems for CHEM 123

B1. Consider a simple cubic lattice of identical hard spheres of radius R.

a) How many spheres are contained *within* one unit cell? What is the coordination number of each sphere?

b) Show that the edge length a of the unit cell is $a = 2\,R$.

c) Calculate the packing efficiency ($V_{spheres}$ / V_{cell}) for the simple cubic lattice. (i.e. What fraction of unit cell volume is occupied by the spheres?

B2.Consider a body-centred cubic lattice of identical hard spheres of radius R.

a) How many spheres are contained *within* one unit cell? What is the coordination number of each sphere?

b) Show that the edge length a of the unit cell is $a = 4\,R/\sqrt{3}$.

c) Calculate the packing efficiency for the body-centred cubic lattice.

B3.Consider a face-centred cubic lattice of identical hard spheres of radius R.

a) How many spheres are contained *within* one unit cell? What is the coordination number of each sphere?

b) Show that the edge length a of the unit cell is $a = 2\sqrt{2}\,R$.

c) Calculate the packing efficiency for the face-centred cubic lattice.

B4. Calcium crystallizes in a face-centred cubic lattice. The edge length of one unit cell is 557 pm. Calculate the radius of a calcium atom and the density of solid calcium.

B5. Show that the following data are consistent with the fact that silver metal crystallizes in a face-centred cubic lattice:

Edge length of unit cell, a = 408 pm — Density of silver, 10.6 g cm^{-3}

Atomic weight of silver, 107.9 g mol^{-1}, — Avogadro's number, $N_A = 6.022 \times 10^{23}$

(Use any three quantities to calculate the fourth. Compare the calculated value with the given value.)

B6. Let r_o be the radius of the sphere that just fits into an octahedral hole formed by six identical hard spheres of radius R. Show that $r_o = \left(\sqrt{2}-1\right)R$. See Figure 12-47 of the text for a diagram that will help you get started. (Note: The size of the hole depends upon R because the larger the spheres, the larger the octahedral hole.)

B7. A tetrahedral site can be generated by placing four spheres of radius R at alternate corners of a cube. Let r_t be the radius of the sphere that just fits into the tetrahedral site. Show that $r_t = \frac{1}{2}\left(\sqrt{6}-2\right)R$. (Hint: Since the spheres are in contact at the centre of each cube face, the length of the face diagonal of this cube is equal to 2R. What is the length of the body diagonal (BD) of the cube? Since the centre of the tetrahedral site is located at the centre of the cube, the sum of r_t and R must equal to one-half the length of the body diagonal.)

B8. Describe where the octahedral holes are located within the face-centred cubic unit cell. How many octahedral holes lie entirely *within* one unit cell? (Hint: In Figure 12-48 of the text, the sodium ions occupy octahedral sites in the face-centred cubic lattice of chloride ions.)

B9. Describe where the tetrahedral holes are located within the face-centred cubic unit cell. How many tetrahedral holes lie entirely within one unit cell? (Hint: See Figure 12-46 of the text.)

B10. The partial pressure of a compound A changes as follows:

time	0	10	20	30	40	50 min
P_A	4.00	2.94	2.32	1.92	1.64	1.42 Pa

Make a graph of P_A versus *time*. Use your graph to evaluate (i) the average reaction rate (in Pa min^{-1}) over the first 40 minutes, and (ii) the instantaneous reaction rate (in Pa min^{-1}) at *time* = 40 min.

B11. Define and distinguish between the terms *rate* and *rate constant*. Give the units of k for 1st order, 2nd order, 1.5 order, and zeroth order reactions.

B12. From the following initial rate data for the reaction, A + B + C $\rightarrow$ products,

	Expt 1	Expt 2	Expt 3	Expt 4
$[A]_o$	0.0184 M	0.0368 M	0.0184 M	0.0184 M
$[B]_o$	0.0225 M	0.0225 M	0.0384 M	0.0225 M
$[C]_o$	0.0141 M	0.0141 M	0.0141 M	0.0365 M
Initial rate:	0.000145 M s^{-1}	0.000205 M s^{-1}	0.000145 M s^{-1}	0.000375 M s^{-1}

(a) Deduce the differential rate law.
(b) Calculate the value of the rate constant (include units).
(c) Calculate the initial rate for the conditions, $[A]_o = 0.0307$ M, $[B]_o = 0.0228$ M, $[C]_o = 0.0183$ M.

B13. The concentration of a compound A varies with time as follows:

time	0	5	10	15	20 min
[A]	1.82	1.65	1.49	1.35	1.22 mol L^{-1}

(a) Plot [A], ln [A], and $[A]^{-1}$ versus *time*, and determine the order of the reaction with respect to [A].
(b) Calculate the rate constant.

B14. In the following cases, you are given equilibrium constants for the two indicated reactions at 25°C, using atm for partial pressures of the gases. Use the data to calculate K_p for the third reaction.

$N_2(g) + {}^1/_2\,O_2(g) \rightleftharpoons N_2O(g)$ $\quad K_{p,} = 7.1 \times 10^{-19}$

$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$ $\quad K_p = 4.23 \times 10^{-31}$

$2\,N_2O(g) + O_2(g) \rightleftharpoons 4\,NO(g)$ $\quad K_p = ?$

B15. An equilibrium mixture of CO(g), H_2O(g), H_2(g) and CO_2(g) is kept at constant temperature in a cylinder capped by a piston. These gases react as follows: $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$. Show that if the piston is raised so that the volume of the mixture is now three times its original value, the equilibrium is not affected by this change; that is the equilibrium does not shift, even though the total pressure drops to one third of its original value.

B16. For the reaction $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$, $\Delta H = -90.2$ kJ (per mole of CO) and $K_p = 2.2\times10^4$ at 298 K (when the pressures are expressed in atmospheres). What is K_p at 500 K?

B17. For the reaction $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$, K_p is 2.15×10^{11} at 200°C and 4.56×10^8 at 260°C. What is ΔH for the reaction?

B18. What are the concentrations of H^+, OH^-, benzoic acid and the benzoate ion in:
(a) 0.12 M benzoic acid, C_6H_5COOH, $K_a = 6.3\times10^{-5}$?
(b) 1.2×10^{-3} M benzoic acid?
For each case calculate the degree of ionization, α. What do your answers for α in (a) and (b) suggest about the relationship between α and the stoichiometric (or label) concentration?

Important!
For an acid-base reaction, most chemists draw an arrow pointing **from the lone pair to the proton** (i.e. from the lone pair of electrons on the base to the proton of the acid). This is the convention we prefer you to follow.

B19. Trimethylamine, $(CH_3)_3N$, is a weak base that ionizes in aqueous solution:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq)$$

A 0.120 M solution of $(CH_3)_3N$ is 2.29% ionized at 25°C.
(a) Calculate $[OH^-]$, $[(CH_3)_3NH^+]$, $[(CH_3)_3N]$, $[H_3O^+]$, and the pH for 0.120 M $(CH_3)_3N$ solution at 25°C.
(b) Calculate K_b for $(CH_3)_3N$ at 25°C.
(c) Calculate the degree of ionization, α, of $(CH_3)_3N$ in 0.0960 M $(CH_3)_3N$(aq). Does the degree of ionization increase, decrease, or remain unchanged as the initial concentration of $(CH_3)_3N$ decreases? Give the reasons for your answer.

B20. Write down material balance equations and charge balance (i.e. electroneutrality) equations for each of the following solutions. (a) 0.100 mol L^{-1} $H_2C_2O_4(aq)$ (b) 0.100 mol L^{-1} $Na_2C_2O_4(aq)$

B21. Calculate $[H_3O^+]$, $[OH^-]$, $[H_2C_2O_4]$, $[HC_2O_4^-]$ and $[C_2O_4^{2-}]$ in 0.0117 mol L^{-1} $H_2C_2O_4(aq)$. What is the pH of the solution? **State** and **justify** your approximations. Look up the K_a values in Appendix D of the text.

B22. Use the K_a values of oxalic acid, $H_2C_2O_4$, to decide whether an aqueous solution of $NaHC_2O_4$ will be acidic, basic or neutral. Look up the K_a values in Appendix D of the text. Note: It is not necessary to do any pH calculations.

B23. Calculate the equilibrium concentrations of all species, except water, in a solution prepared by dissolving 0.0125 mol $Al(NO_3)_3(aq)$ in water to make 1.0 L of solution. (Hint: In aqueous solution, the aluminum ion exists as $Al(H_2O)_6^{3+}$ which behaves as a monoprotic acid with $pK_a = 4.85$. See page 696 of the text.)

B24. How many grams of sodium acetate, $NaC_2H_3O_2$, must be added to 250 mL of 0.100 M acetic acid, $HC_2H_3O_2$, to give a solution with a pH of 6.50? Look up the K_a value in Appendix D of the text.

B25. (a) How many grams of NH_4Cl (a solid) must be added to 500 mL of 0.137 M NH_3 to give a buffer of pH 10.34 ? Assume no change in volume. Take $K_b(NH_3) = 1.76\times10^{-5}$.

(b) By how much would this pH change if 1 mL of 0.1 M HCl were added to 10 mL of the buffer?

(c) By how much would the pH change if 1 mL of 0.1 M HCl were added to 10 mL of pure water?

(d) By how much would the pH of the solution in part (a) change if 500 mL of water were added to it? Explain.

B26. Piperidine, $C_5H_{11}N$, is an organic base with $K_b = 1.30\times10^{-3}$. A 50.0 mL sample of 0.0800 M piperidine is titrated with 0.1000 M HCl. Calculate the pH of the solution

(a) at the start of the titration,

(b) when 35.0 mL of HCl have been added,

(c) when the titration is at the equivalence point.

Select a suitable indicator for this titration. Justify your choice.

B27. Consider the titration of 25.0 mL of 0.120 M $(CH_3)_3N$ with 0.100 M HCl. Trimethylamine, $(CH_3)_3N$, is a weak base in water ($K_b = 6.3\times10^{-5}$ at 25°C).

(a) Calculate the pH of the $(CH_3)_3N$ solution. **State** and **justify** any approximations.

(b) Calculate the pH after adding 5.00 mL of HCl solution. **State** and **justify** any approximations.

(c) Calculate the pH at the half neutralization point.

(d) Calculate the pH at the equivalence point. **State** and **justify** any approximations.

(e) Use the results from parts (a) through (d) to sketch the titration curve. (i.e. Plot pH vs. the volume of HCl added.)

(f) Choose an indicator and explain why it would be suitable.

B28. What is the molar solubility of silver sulfate, Ag_2SO_4, in a 0.40 M $AgNO_3$ solution? Justify any approximations that you use. Note: $K_{sp}(Ag_2SO_4) = 1.7\text{x}10^{-5}$

B29. Soluble lead nitrate, $Pb(NO_3)_2$, solid is slowly dissolved in a solution which is 0.10 M with respect to each of iodide ion, I^-, and carbonate ion, CO_3^{2-}. (Assume that the solution volume does not change throughout the experiment.)

(a) Which substance begins to precipitate first, $PbCO_3$ ($K_{sp} = 1.5\times10^{-13}$) or PbI_2 ($K_{sp} = 1.0\times10^{-9}$) ?

(b) What is the concentration of iodide ion in the solution when $PbCO_3$ just begins to precipitate?

(c) What is the concentration of carbonate ion in the solution when PbI_2 just begins to precipitate?

B30. When 125 mL of 0.014 M $Ca(NO_3)_2$ is added to 195 mL of 0.038 M Na_3PO_4, a precipitate is formed. What is the precipitate, and what are the concentrations of the ions from these salts in the supernatant solution (i.e., the solution above the precipitate) at equilibrium? Find the K_{sp} value in Appendix D of your text.

B31. Given that $E^o = +0.04$ V for the reaction: $Cd^{2+} + Fe(s) \rightarrow Fe^{2+} + Cd(s)$, what is the standard reduction potential for $Cd^{2+} + 2e^- \rightarrow Cd(s)$? (Find E^o for the Fe^{2+}/Fe half-reaction in Appendix D.)

B32. Consider the following reactions:

(1) $Pb(s) + Co^{2+}(aq) \rightarrow Pb^{2+}(aq) + Co(s)$

(2) $PbSO_4(s) + Ni(s) \rightarrow Ni^{2+}(aq) + Pb(s) + SO_4^{2-}(aq)$

(3) $IO_3^-(aq) + 6H^+(aq) + 5Ag(s) \rightarrow \frac{1}{2} I_2(s) + 3H_2O(l) + 5Ag^+(aq)$

(a) What is E^o for each of the reactions? Look up standard reduction potentials in Appendix D.

(b) In which direction does each reaction proceed spontaneously at standard state conditions?

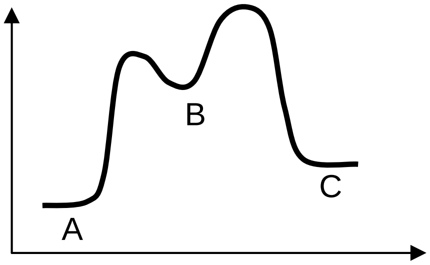
(c) What is the equilibrium constant in each case?

B33. (a) Calculate E^o for the reaction $Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$. Look up standard reduction potentials in Appendix D.

(b) Consider the galvanic cell $Cu(s) \mid Cu^{2+}$ (aq, 0.50 M) $\parallel Ag^+$ (aq, 1.0×10^{-6} M) $\mid Ag(s)$. What is the equation for the spontaneous cell reaction? What is E for this cell?

Supplementary Topic #1: The Rate-determining Step

The step with the greatest activation energy is not necessarily the rate-determining step!! Consider the following reaction profile:



$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

$$B \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C$$

The conversion of A into B has the greatest activation energy and thus, this step has the smallest rate constant (i.e. k_1 is small). Although the conversion of A into B is slow, it is not the rate-determining step. Let's consider why this is the case.

Once B is formed, it will be converted back into A more rapidly than it'll be converted into C. (Compare the activation energies for B $\rightarrow$ C and B $\rightarrow$ A.) As a result, the concentration of B is always going to be very, very small and the rate of conversion of B into C will be very, very slow. Therefore, the rate of production of C is ultimately determined by the rate of conversion of B into C!! So, for the reaction profile given above, the rate-determining step is actually the second step, even though the first step has the smallest rate constant.

In a multi-step reaction, the **rate-determining step is the elementary step that has the transition state of highest energy**. To identify the step which has the transition state of highest energy, simply locate the highest point on the reaction profile.

Supplementary Topic #2: The Van't Hoff Equation

(Background material can be found in Chapters 14 and 15.)

The equilibrium constant (K_c or K_p) for a reaction is essentially constant provided the temperature is held constant. (In reality, the equilibrium constant does vary slightly with pressure and composition, but the variation with temperature is much greater.) The temperature dependence of the equilibrium constant is modelled reasonably well by the Van't Hoff equation:

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^{\circ}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

In the equation above, K_1 is the value of K at T_1, K_2 is the value of K at T_2 and ΔH° is the enthalpy change for the reaction. Please note carefully:

- **Always use ΔH° in joules and R = 8.3145 J K^{-1} mol^{-1}.**
- **When applying the Van't Hoff equation to a gas-phase reaction, K_1 and K_2 represent K_p values. When dealing with a reaction in solution, K_1 and K_2 represent K_c values.**

There are different ways to justify the Van't Hoff equation but we will focus on a simple kinetic explanation.

Consider the elementary reaction $2\ A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 3\ C$ for which

$$K_c = \frac{[C]^3}{[A]^2[B]} = \frac{k_1}{k_{-1}}\ .$$

If the rate constants each obey the Arrhenius form, $k = A \exp(-E_a/RT)$, then the equilibrium constant K_c satisfies

$$K_c = \left(\frac{A_1}{A_{-1}}\right)\exp\left(-\frac{E_{a,for} - E_{a,rev}}{RT}\right) \quad = \quad B\,e^{-\Delta H^{\circ}/RT} \quad \text{(where } B \text{ is a constant).}$$

Using the equation above to construct the ratio K_2 / K_1 (and taking the logarithm), we obtain the Van't Hoff equation.

Note:

1. Recall from chapter 14 that $E_{a,for} - E_{a,rev} = \Delta H$.
2. In justifying the Van't Hoff equation, we assumed that the reaction occurred in a single step for convenience only. If the reaction occurs via an n-step mechanism, then we have $K_c = (k_1 / k_{-1})\,(k_2 / k_{-2}) \ldots (k_n / k_{-n})$. Assuming each rate constant obeys the Arrhenius form, we obtain the same final result.

CHEM 123 DATA SHEET

1 1A																	18 8A
H 1.008	**2** **2A**											**13** **3A**	**14** **4A**	**15** **5A**	**16** **6A**	**17** **7A**	**He** 4.003
Li 6.941	**Be** 9.012											**B** 10.81	**C** 12.01	**N** 14.01	**O** 16.00	**F** 19.00	**Ne** 20.18
Na 22.99	**Mg** 24.31	**3** **3B**	**4** **4B**	**5** **5B**	**6** **6B**	**7** **7B**	**8** ←	**9** **8B**	**10** →	**11** **1B**	**12** **2B**	**Al** 26.98	**Si** 28.09	**P** 30.97	**S** 32.07	**Cl** 35.45	**Ar** 39.95
K 39.10	**Ca** 40.08	**Sc** 44.96	**Ti** 47.88	**V** 50.94	**Cr** 52.00	**Mn** 54.94	**Fe** 55.85	**Co** 58.93	**Ni** 58.69	**Cu** 63.55	**Zn** 65.38	**Ga** 69.72	**Ge** 72.59	**As** 74.92	**Se** 78.96	**Br** 79.90	**Kr** 83.80
Rb 85.47	**Sr** 87.62	**Y** 88.91	**Zr** 91.22	**Nb** 92.91	**Mo** 95.94	**Tc** (98)	**Ru** 101.1	**Rh** 102.9	**Pd** 106.4	**Ag** 107.9	**Cd** 112.4	**In** 114.8	**Sn** 118.7	**Sb** 121.8	**Te** 127.6	**I** 126.9	**Xe** 131.3
Cs 132.9	**Ba** 137.3	(57-71) **La-Lu**	**Hf** 178.5	**Ta** 180.9	**W** 183.9	**Re** 186.2	**Os** 190.2	**Ir** 192.2	**Pt** 195.1	**Au** 197.0	**Hg** 200.6	**Tl** 204.4	**Pb** 207.2	**Bi** 209.0	**Po** (209)	**At** (210)	**Rn** (222)
Fr (223)	**Ra** 226	(89-103) **Ac-Lr**	104 **Rf**	105 **Db**	106 **Sg**	107 **Bh**	108 **Hs**	109 **Mt**	110 **Uun**	111 **Uuu**	112 **Uub**	113 **Uut**					

K_a and K_b for some Acids and Bases

Acid	K_a
Acetic, CH_3COOH	1.7 x 10^{-5}
Chloroacetic, $CH_2ClCOOH$	1.41 x 10^{-3}
Ascorbic, $H_2C_6H_6O_6$	7.9 x 10^{-5} (K_{a1})
$HC_6H_6O_6^-$	1.6 x 10^{-12} (K_{a2})
Benzoic, $HC_7H_5O_2$	6.46 x 10^{-5}
Formic, HCOOH	1.8 x 10^{-4}
Hypobromous, HOBr	2.06 x 10^{-9}
Hypochlorous, HOCl	3.5 x 10^{-8}
Hydrofluoric, HF	6.6 x 10^{-4}
Hydrocyanic,HCN	4.93 x 10^{-10}
Hydrogen sulfide, H_2S	1.0 x 10^{-7} (K_{a1})
HS^-	1.2 x 10^{-13} (K_{a2})
Nitrous, HNO_2	4.5 x 10^{-4}
Phosphoric, H_3PO_4	7.1 x 10^{-3} (K_{a1})
$H_2PO_4^-$	6.3 x 10^{-8} (K_{a2})
HPO_4^{2-}	4.2 x 10^{-13} (K_{a3})
Sulfuric, H_2SO_4	strong
HSO_4^-	1.20 x 10^{-2} (K_{a2})
Base	K_b
Ammonia, NH_3	1.8 x 10^{-5}
Aniline, $C_6H_5NH_2$	4.3 x 10^{-10}
Trimethylamine $N(CH_3)_3$	6.3 x 10^{-5}

Physical constants

Avogadro constant, $N_A = 6.0221\times10^{23}$
Electron charge, $e = 1.6022\times10^{-19}$ C
Faraday constant, F = 96485 C mol^{-1}
Gas constant, R = 0.082058 atm L K^{-1} mol^{-1}
= 8.3145 J K^{-1} mol^{-1}
= 8.3145 kPa L K^{-1} mol^{-1}
Ion product for water, $K_w = 1.0\times10^{-14}$

Conversion factors

0^{o}C ≡ 273.15 K
1 atm = 101.325 kPa
= 760 torr
1 pm = 1×10^{-12} m
1 A = 1 ampere = 1 C s^{-1}

K_{sp} for Some Salts

AgCl	1.8×10^{-10}	$Ag_3(PO_4)$	1.8×10^{-18}	MnS	3.0×10^{-13}
AgBr	5.0×10^{-13}	$Al(PO_4)$	9.8×10^{-21}	ZnS	2.5×10^{-21}
AgI	8.3×10^{-17}	$Ca_3(PO_4)_2$	1.3×10^{-32}	CdS	1.0×10^{-27}
$PbCl_2$	1.7×10^{-5}	$Ni_3(PO_4)_2$	4.7×10^{-32}	Ag_2S	1.6×10^{-49}
AgOH	1.5×10^{-5}	$Ag_2(CrO_4)$	1.2×10^{-12}	$BaCO_3$	2.6×10^{-9}
$Sr(OH)_2$	3.2×10^{-4}	$Sr(CrO_4)$	3.6×10^{-5}	Li_2CO_3	1.7×10^{-3}
$Ca(OH)_2$	6.5×10^{-6}	$Ba(CrO_4)$	1.2×10^{-10}	$MnCO_3$	2.2×10^{-11}
$Mg(OH)_2$	7.1×10^{-12}				
$Mn(OH)_2$	6.0×10^{-14}	$Al(OH)_3$	1.3×10^{-33}		
$Fe(OH)_2$	7.9×10^{-16}	$Cr(OH)_3$	6.3×10^{-31}		
$Zn(OH)_2$	4.5×10^{-17}	$Fe(OH)_3$	1.6×10^{-39}		

K_f for Some Complexes

$Ag(NH_3)_2^+$	1.6×10^{7}
$Ag(CN)_2^-$	5.6×10^{18}
$Zn(NH_3)_4^{2+}$	4.1×10^{8}

Some Standard Reduction Potentials

Half-reaction	E^o	Half-reaction	E^o
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	2.889 V	$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$	–0.04
$Au^+(aq) + e^- \rightarrow Au(s)$	1.691	$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	–0.127
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	1.229	$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	–0.236
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	1.078	$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$	–0.282
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.799	$Tl^+(aq) + e^- \rightarrow Tl(s)$	–0.336
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	0.77	$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	–0.402
$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$	0.401	$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	–0.41
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.339	$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	–0.74
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	0.22	$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	–0.762
$AgBr(s) + e^- \rightarrow Ag(s) + Br^-(aq)$	0.0732	$Li^+(aq) + e^- \rightarrow Li(s)$	–3.00
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.0		

Some formulae

$$[A] = [A]_o - kt \qquad [A] = [A]_o e^{-kt}$$

$$[A]^{-1} = [A]_o^{-1} + kt \qquad k = Ae^{-\left(\frac{E_a}{RT}\right)}$$

$$\ln\left(K_2 / K_1\right) = -\frac{\Delta H^o}{R}\left(T_2^{-1} - T_1^{-1}\right)$$

$$K_p = K_c (RT)^{\Delta n} \qquad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$K_a K_b = K_w \qquad \mathrm{pH} = \mathrm{pK}_a + \log\frac{[\text{base}]}{[\text{acid}]}$$

$$E = E^o - \left(\frac{0.0592}{n}\right)\log Q \quad \text{(at 298 K)}$$