GENERAL CHEMISTRY II
CHEM 1120
PACKAGE

Contains: Syllabus
Lecture Notes
Old Practice Exams

Prepared by Dr. Titus V. Albu
Department of Chemistry
University of Tennessee at Chattanooga

Spring 2018
### Periodic Table of the Elements

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General Chemistry II
Spring 2018
CHEM 1120, CRN 20812, 3 credit hours

Instructor: Dr. Titus V. Albu

Phone and Email: 423-425-4143; Titus-Albu@utc.edu

Office Hours and Location: Monday 8:30-11:00 am & Wednesday 8:30-11:00 am or by appointment; Grote 314

Course Meeting Days, Time, and Location: Tuesday & Thursday 9:25-10:40 am; Grote 131

Course Catalog Description: Examines chemical concepts in inorganic, organic, analytical and physical chemistry. Every semester. Lecture 3 hours. Prerequisite: CHEM 1110 and CHEM 1110L with minimum grades of C or department head approval. Corequisite: CHEM 1120L, or Prerequisite: CHEM 1120L with a minimum grade of C, or department head approval.

Course Pre/Co Requisites: Prerequisite: CHEM 1110 and CHEM 1110L with minimum grades of C or department head approval. Corequisite: CHEM 1120L, or Prerequisite: CHEM 1120L with a minimum grade of C, or department head approval.

Course Student Learning Outcomes: Upon completion of the required credit hours in this category, students should be able to: Define and use basic scientific and chemical language and processes; Distinguish between scientific and non-scientific explanations; Identify and describe principles and patterns governing matter; Apply principles and patterns to problems or issues of a chemical nature; Calculate and convert between various chemical and physical quantities; Analyze, evaluate and justify a chemical hypothesis.

General Education Statement: This course (along with CHEM 1120L) is certified as a General Education course fulfilling the Natural Science with Lab general education goal. Please consult with your advisor and check the specific requirements for your major to determine if this course is a good fit for your plan of study. Upon completion of the required credit hours in this category, students will be able to: Explain intellectual foundations, conceptual approaches, and methodologies of the natural sciences, Understand and explain scientific terminology, Discuss historical, social and political issues related to scientific data and advances, Construct graphic and analytical models from a description of a specific natural phenomenon, Formulate a hypothesis based on empirical data, Apply the scientific method to solve problems, Design experiments to test hypotheses, Express conclusions and implications from scientific experiments using a variety of methods, Experience the methods and technology of scientific inquiry, Demonstrate significant concepts of the discipline, Use scientific technology to gather and interpret data, Practice the development of independent thought.
Course Fees: None.

Course Materials/Resources:

Textbook: Chemistry: Structure and Properties, 2nd edition by Nivaldo J. Tro, Pearson, 2018. Although the use of the regular textbook is possible, the customized version containing only the chapters to be covered this semester and an access code to Mastering Chemistry is strongly preferred. ISBNs for this option are: 1323742468/9781323742464. If you don’t have the textbook already, when you go to the University bookstore, make sure that you buy the customized package for CHEM 1120.

Lecture Notes: The material in this class will be presented using Lecture Notes that are available to students as a pdf file on UTC Learn. The entire course package containing the syllabus, the lecture notes and the old/practice exams. The Lecture Notes have to be printed, coil bonded or put in a binder, and brought to class.

MasteringChemistry: MasteringChemistry is the online homework system that will be used in this class, and it also allows you to access the e-book. It is strongly recommended to purchase the access code with your customized textbook, which is probably the cheapest option. You must register for MasteringChemistry through UTC Learn; do not go directly to MasteringChemistry website!
1. Sign into UTC Learn (http://www.utc.edu/learn)
2. Go to our course: “SP18.CHEM.1120.20812: General Chemistry II”.
3. Go to Online Homework content.
4. Click on Pearson’s MyLab and Mastering
5. On Pearson site enter the access code from the customized book (or purchase an access code or choose free trial if available).
6. Go to Mastering Assignments.

Scientific Calculator: You will be allowed to use one, so own one and bring it to class. It must do exponentials and logarithms, but a graphing calculator is not necessary. You should familiarize yourself with how to use scientific notation and other functions on it. Calculators on cell phones and other personal electronic devices are not permitted.

Technology Requirements for Course:

Computer: You need access to a computer with a reliable internet connection for this course. Test your computer set up and browser for compatibility with UTC Learn at http://www.utc.edu/learn/getting-help/system-requirements.php. Although not required, the computer might need to have speakers or headphones. You should also have an updated version of Adobe Acrobat Reader, available free from https://get.adobe.com/reader/.

UTC Learn: Access this class by selecting “SP17.CHEM.1120.20812: General Chemistry II” course on UTC Learn (http://www.utc.edu/learn/). Log in using your utcID and password (the same as for your UTC email). In this class, UTC Learn will be used for: (1) Course announcements; (2) Syllabus; (3) Course Materials: Lecture Notes & Old/Practice exams; (4) Online homework/assignments; and (5) Individual grades.
Technology Skills Required for Course: You will need to have basic computer skills including using the learning management system (UTC Learn), using MOCSNet email, completing online homework, and downloading and printing pdf files.

Technology Support: If you have problems with your UTC email account or with UTC Learn, contact IT Solutions Center at 423-425-4000 or email itsolutions@utc.edu.

Course Assessments and Requirements: Your overall course grade will be computed based on:

- Four in-class exams 60%
- Final exam 25%
- Homework 15%

Exams: There will be four exams during the class period. Each exam will cover 2 or 3 chapters/units. The lowest exam grade can be replaced with the final exam grade, if the final exam grade is higher. A grade of 0 will be assigned for any exam that is not taken. Only one grade of 0 can be replaced by the final exam grade. The typical average exam score is expected to be around 70, and the maximum score is capped to 100. You should bring a working calculator and two pencils to exams. You may not share a calculator during testing. No other paper, notes, books or stored information is to be used except what will be provided to you. After the first person leaves an exam, no one else can come late and start the exam. No cell phone use, texting, or checking phone in class at any time during the exam. The tentative exam dates are listed below. The format of the exam (i.e., number of questions, type of questions, number of points, etc.) will be announced at least one week prior to the exam date. Old exams (of different format) are available on UTC Learn for practice. No makeup exams will be given. Rarely, under extreme situations, an exam can be taken earlier but be sure that you let the instructor know about it as soon as possible so proper arrangements could be made.

Final Exam: The final exam is a two-hour standardized ACS exam that is scheduled for 8:00 - 10:00 am Thursday, April 26 in Grote 131. The final exam has 70 multiple-choice questions (with 4 answers), and it covers material from both CHEM 1110 and CHEM 1120 as well as few questions from lab and sections not covered in the lecture. The final exam grade will be determined by dividing the number of correct answers to 0.58 then adding 20 points. The maximum score is capped to 100. After adjusting, the average on this exam is expected to be around 70. There is NO MAKEUP for the final exam.

Online Homework: Every student will have to acquire an access code to the MasteringChemistry platform that runs the online homework. You will have a homework assignment to do for each unit/chapter we cover. Each assignment is due at 10:00 pm on a due date, and submissions after the due date will not receive any credit. The problems in each assignment are from the end of the chapter and are worth 1 point each. You can submit each problem (or problem part) for correctness individually. There is a maximum of 5 times you can “Submit” your answer. You will not be
penalized for using Hints (if they exist) or the eBook. The grade for an assignment is the sum of points for each problem.

- No make-up assignments will be given/allow under any circumstances after the deadline. I occasionally grant extensions for the homework deadline but only with a reasonable excuse and a timely (i.e., pre-deadline) request.
- If you believe that you answered correctly one question in MasteringChemistry but the program graded it incorrectly, send me an e-mail to let me know about the error, and I will verify it and give you the deserved credit. (I will however do that at the end of the semester.) Send me the email only after the correct answer/solution had been posted. In your e-mail be sure that you include your name, the class you are registered in, the homework number (or unit number), and the question number.
- Overall there will be between 104 and 108 problems, and, if necessary, an adjustment will be done at the end of semester so at least some students will get a score of 100, which is the maximum score for homework.

**Course Grading**

**Course Grading Policy:** Your letter grade in the class is expected to be determined according to the following scale: $F < 54 \leq D < 66 \leq C < 78 \leq B < 90 \leq A$.

**Instructor Grading and Feedback Response Time:** I will try my best to grade all assignments before the next class period, and provide written feedback when necessary.

**Course and Institutional Policies:**

**Late/Missing Work Policy:** Submissions of homework assignments after the due date will not receive any credit. Extensions for the homework deadline can be granted but only with a reasonable excuse and a pre-deadline, timely request. There is no makeup for in-class exams. Rarely, under extreme situations, an exam can be taken earlier but be sure that you let the instructor know about it as soon as possible so proper arrangements could be made. As presented above, the lowest-scored (or a missed) class exam will be replaced with the final exam grade, if the final exam grade is higher. There is no makeup for the final exam.

**Student Conduct Policy:** UTC’s Academic Integrity Policy is stated in the Student Handbook. A violation of the honor code could result in appearing in honor court and receiving a course grade of F. Instructor will not tolerate academic dishonesty. Specifics for this class: (1) Any attempt (successful or unsuccessful) to cheat during any exams will automatically result in an “F” grade in the course; (2) Keying in another student's online homework for them or having another student key in your online homework will result in a grade of 0 for that assignment.

**Honor Code Pledge:** I pledge that I will neither give nor receive unauthorized aid on any test or assignment. I understand that plagiarism constitutes a serious instance of unauthorized aid. I further pledge that I exert every effort to ensure that the Honor Code
is upheld by others and that I will actively support the establishment and continuance of a campus-wide climate of honor and integrity.

Course Attendance Policy: Students are expected to attend every lecture, be punctual, and be respectful of others in the class. Classroom behavior such as talking to your neighbor during lecture, reading, sleeping, or checking cell phone, might interfere with my ability to teach effectively and others ability to learn. I might require you to meet with me before you are allowed to take the next exam so I can explain more clearly why your activities are a problem. I might also ask you to leave the classroom. Laptop computers can be a big distraction in class so no laptops may be used at any time during class. Similarly, there should be no cell phone use of any kind during class. You are responsible for everything covered in lecture. Information missed during unexcused absences cannot be reclaimed from me so check with a fellow student who is able to share notes and go over items you missed. The only acceptable (but not necessarily accepted) excuses are the ones received from The Dean of Students office. During lecture period, there might be some additional assignments, class pop-quizzes, or attendance quizzes that might be used as bonus points for the next exam grade. Points missed during absences, unexcused or excused, cannot be reclaimed. Points will be subtracted for unexcused absences. Class will include lecture and discussions with assumption that you have read and studied textbook and study materials ahead of where we are in class. Always bring your printed Lecture Notes and old Exams/Tests to class as I may refer to examples from these documents. Bring a calculator to ALL class meetings.

Communication: Class announcements will be made through UTC Learn and email. UTC email is the official means of communication between instructor and student at UTC. Please check your UTC email and UTC Learn on a regular basis. (i.e., daily). I will try to answer emails from students with questions/comments/concerns within 24 hours (Monday through Friday) although occasionally it might take longer. I might not answer student emails if they require repeating information already mentioned in a class that the student missed.

Course Participation/Contribution: The course contains several learning objectives that are critical to building a foundation in chemistry. For this reason, several methods will be employed, including (but not limited to): lecture, group study, pre-class reading, and post-class work. To be successful in this course, I recommend that you engage in all methods.

Teaching/Learning Strategies:

Lecture Notes: The material in this class will be presented using Lecture Notes that are available to students as a pdf file on UTC Learn, and that need to be printed and brought to class. The Lecture Notes have some information missing and the student should fill out the missing information during lectures from Power Point presentations that have that information in red. Lecture Notes are organized in Units that resemble closely (but are not necessarily the same as) the chapters from the textbook. Each Unit will have a
number of Sections (denoted by capital letters), each Section will have a number of
Topics (denoted by numerals), and each Topic will have a number of Statements/Ideas
(denoted by lower-case letters) and some additional issues, comments or clarifications.
Lecture Notes contain the same information that, in the past, the instructor used to write
on the board or talked about in the lecture. Lecture Notes are not intended and should not
be used as textbook replacement but rather as textbook summary.

**Lecture Attendance:** Class time will include lecturing, solving problems and discussions
with assumption that you have read and studied textbook and study materials ahead of
where we are in the class. Attendance in class on time is essential. Students are
responsible for all information that is given in class and assigned as reading. I encourage
active participation from students in class to enhance your understanding of problem
solving and concepts. Lecture sessions will not necessarily spend time covering
definitions which are easily understood from reading, but I will discuss important
concepts and distinctions in depth. We might also work problems which may not be on
the practice or in the textbook. Always bring your printed Lecture Notes and old
Exams/Tests to class as I may refer to examples from these documents. Bring a
calculator to ALL class meetings.

**Textbook Reading:** Successful students complete the textbook readings for topics to be
discussed in advance of the lecture. It is important in the learning process that students
participate in class discussion/problem-solving and have a conceptual understanding of
the material, not just algorithmic processes for working problems. It is imperative that
you read the material and are ready to ask questions about it in class. Exams might
contain material/definitions that are not covered in depth in class, but are easily
understood from reading the textbook.

**Unit Objectives:** In Lecture Notes, there are unit objectives for each unit of covered
material. These objectives are intended to make your study focused on aspects and key
concepts that will likely be in exams. However, they are not explicit markers for
individual exam questions, and they should not necessarily be interpreted as the only
material possible on an exam.

**Practice Problems:** In addition to homework assignments that are graded, Lecture Notes
contain some practice problems. Most of these are problems that I asked at examinations
in the past, and are organized based on the unit objective that they relate to. It is in your
best interest to complete the practice problems and try additional end-of-chapter
problems in order to give you sufficient practice at problem-solving methods and
understanding of concepts. The materials they cover are skills needed to score well on
exams, and although they may not be graded themselves, responsible completion of these
problems will likely increase your grades.

**Time Investment:** The general rule of thumb for university courses is that for every hour
spent in class you should be spending two-three hours outside of class studying for that
course. Since this is a 3-credit hour course, that means you should be devoting at least 9
hours per week (minimum) to this class. Typically, students with a time investment of one hour working on assignments outside of class for every one hour spent in class usually earn a grade of C while A students usually spend more time. The time invested is your own studying, and does not include time spent with a tutor working homework problems for you. It does include studying your textbook and posted materials, reviewing your notes, doing homework on your own, and practicing additional problems on a regular basis (not just the night before an exam). If you are taking a full-time student course load and are also working 10 or more hours per week, this course could prove difficult for you due to time commitments.

**Study Groups:** Successful students can found that studying with a fellow student or a group of students is beneficial. The instructor personally encourages students to participate in group study for preparing exams, working homework problems, or just better understanding the material. It is preferred that the groups contain students of similar levels of preparation and similar goals. A student should seek fellow students about studying together.

**Tutoring and Supplemental Instruction:** Typically, there are a number of free options for tutoring and supplemental instruction for this class on campus, as well as some that charge fees. I will update this information on UTC Learn as I get it. It is important for you to get help as soon as, or even before, you think you need it. This course moves quickly and the material builds on previously-covered skills, so you will get behind fast if you are missing important concepts or skills.

**Course Learning Evaluation:** Course evaluations are an important part of our efforts to continuously improve the learning experience at UTC. Toward the end of the semester, you will receive a link to evaluations and are expected to complete them. We value your feedback and appreciate you taking time to complete the anonymous evaluations.

**Syllabus Changes:** Although unlikely, some things on this syllabus are subject to change at the discretion of the instructor. Every attempt will be made to follow this syllabus, however, if changes are made, they will be announced in class, by email, and/or on UTC Learn, and it is the responsibility of the student to keep up with the changes.

**Course Calendar/Schedule:** Material from chapters 9 and 13-20 of the textbook will be covered in this class, although some selected topics might be skipped. The material will be divided into units, and typically one unit is equivalent with a chapter. Each unit will be covered in two-three lectures. The following is a tentative schedule of topics and exams, and it is based on the assumption that no classes will be cancelled (due to weather or other emergencies).
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<tr>
<th>Date</th>
<th>Exams</th>
<th>Tentative Topics</th>
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<td>Syllabus, Introduction to class</td>
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<td>January 11</td>
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<td>Unit I – Thermochemistry (Chapter 9)</td>
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<td>January 16</td>
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<td>Unit V – Acids and Bases (parts of Chapter 16)</td>
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<td>Unit V – Acids and Bases (parts of Chapter 16)</td>
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<td>March 1</td>
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<td>Unit VI – Acid-Base Equilibria (parts of Chapters 16 &amp; 17)</td>
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<td>Unit VI – Acid-Base Equilibria (parts of Chapters 16 &amp; 17)</td>
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<td>Unit VII – Solubility Equilibria (parts of Chapter 17)</td>
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<td>Review</td>
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<td>April 26 8:00 am</td>
<td>Final Exam</td>
<td>Comprehensive ACS exam (70 questions) Grote 131</td>
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Unit I
Thermochemistry

Unit Objectives

O-I.1 Learn terminology: Heat, Internal energy, Enthalpy, State function, Exothermic, Endothermic, Calorimetry, Heat capacity, Specific heat, Standard state, Standard enthalpy of formation, Bond enthalpy, Lattice energy

O-I.2 Define and describe properties of various forms of energy and energy transfer

O-I.3 Carry out calorimetry calculations involving heat capacity and specific heat

O-I.4 Apply properties of thermochemical equations

O-I.5 Apply Hess’s law

O-I.6 Carry out stoichiometry calculations using thermochemical equations

O-I.7 Define and apply enthalpies of formation

O-I.8 Determine enthalpy of reaction using enthalpies of formation

O-I.9 Determine phase-transformation enthalpy using enthalpies of formation

O-I.10 Determine enthalpy of reaction using bond enthalpies

O-I.11 Identify and describe processes involved in Born-Haber cycle
A. Energy and Energy Changes (O-I.2)

1. Introduction
   a. Thermodynamics is the branch of chemistry/physics dealing with the energy associated with any process.
   b. Thermochemistry is the branch of chemistry dealing with the energy associated with chemical reactions.

2. The system and surroundings
   a. Dealing with energy requires a clear way of labeling and describing the quantities that we are discussing.
   b. The universe is divided in two parts:
      □ the system which is the part of the universe that we are interested in (or we are monitoring),
      □ the surrounding which is
   c. Based on the types of interactions that are possible between the system and surroundings, the system can be:
      □ open system – exchanges
      □ closed system – exchanges
      □ isolated system – exchanges
   d. A system is characterized by which is a set of parameters/conditions describing the system:
      □ Energy \( (E) \)
      □ Temperature \( (T) \)
      □ Volume \( (V) \)
      □ Pressure \( (P) \)
      □ Composition (i.e., masses or number of moles of components in the system)
3. Forms of energy
   a. In general, there are two forms of energy:
      □ Kinetic energy \((K \text{ or } KE \text{ or } E_k)\) is the energy associated with the

      □ Potential energy \((V \text{ or } PE \text{ or } E_p)\) is the energy associated with the

   b. Potential energy can sometimes be seen as stored energy like the energy stored in chemical bonds.

   c. Both of these forms of energy (as well as other energies to be discussed later) are relative meaning that they should be defined

   d. The SI unit of energy is joule (J), and another accepted (and highly used) unit of energy is calorie (cal).
      □ 1 cal = 4.184 J exactly

4. Internal energy of the system
   a. Internal energy of the system is denoted by \(U\) and is generally defined as the sum of all kinetic and potential energy associated with all particles in the system.

   b. Internal energy is
      □ depends only on the state of the system and not how the system got in that state.

   c. Defining or determining the absolute value of internal energy is difficult or impossible, however we will focus not on the absolute value of the internal energy but on the relative energy

      □ The change in internal energy is denoted as

      □ \(\Delta U = U_{\text{final state}} - U_{\text{initial state}}\) (same for all other state functions).

      □ for isolated systems.
5. Work, heat and the first law of thermodynamics
   a. The first law of thermodynamics states that energy can be converted from one form to another but cannot be created or destroyed.
      □ It could be seen as
   b. The first law of thermodynamics, for a closed system, is described by \( \Delta U = q + w \).
      □ \( \Delta U \) is the change in internal energy of the system.
      □ \( q \) is
      □ \( w \) is
   c. Heat and work
      □ are forms of
      □ are (not state functions) because they depend on the path of the system (i.e., how the system transformation is taking place),
      □
   d. Heat \((q)\) is an energy exchange between the system and surroundings due to a difference (i.e., is an exchange in thermal energy).
      □ The energy transfers from
   e. Work \((w)\) is typically an energy exchange between the system and surroundings due to a difference and this particular type of work is called
      □ If the pressure inside the system is larger than outside, the system will expand
   f. By convention, \( \Delta U \) is when energy goes into the system, and \( \Delta U \) is when energy is leaving the system.
   g. When \( q \) is positive the process is called and when \( q \) is negative the process is called
6. Enthalpy of the system
   a. Enthalpy is another form of energy characterizing the system, it is denoted by \( H \), and its use is preferred to that of the internal energy because it is directly associated with measurable quantities.
   b. Enthalpy is defined as:
      - PV term is a form of energy, and it is the energy associated with
      - Because PV term is always positive,
   c. Enthalpy is
      - \( \Delta H = \Delta U + \Delta(PV) \)
   d. Enthalpy change is equal to the heat exchanged at constant pressure (i.e., in a transformation carried out at constant pressure):
      - Subscript \( P \) means at constant \( P \).
      - At constant \( P \): \( \Delta H = \Delta U + P\Delta V; \ w = - P\Delta V; \ and \ \Delta U = q_P - P\Delta V \)
   e. Internal energy change is equal to the heat exchanged at constant volume (i.e., in a transformation carried out at constant volume):
   f. The use of enthalpy is preferred over the use of internal energy because it also accounts for the changes in the system’s volume.
   g. When \( \Delta H \) (or \( q_P \)) is positive the process is called and when \( \Delta H \) is negative the process is called
   h. When the transformation occurring in the system is a chemical reaction (so that the initial state = reactants and the final state = products):
   i. Energy (or enthalpy) diagrams are sometimes used to represent the relative energy/enthalpy of reactants and products.

\[ \begin{array}{c|c|c}
E & R & E \\
H & P & H \\
\end{array} \]
j. Properties like $H$ and $U$ can be:

- when they depend on the amount or the size of the system (e.g., volume, mass, enthalpy, etc.)
- when they do not depend on the amount or the size of the system (e.g., density, temperature, etc.)
- intensive property $= \frac{\text{extensive property}}{\text{extensive property}}$

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**O-I.2**

1) The energy associated with a speeding bullet is called

a. potential energy.
b. internal energy.
c. kinetic energy.
d. heat.
e. temperature.

**O-I.2**

2) The energy associated with a motionless rock on the top of Mount Rainier is

a. potential energy.
b. internal energy.
c. kinetic energy.
d. heat.
e. temperature.

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**O-I.2**

3) An insect in flight at the top of a cliff possesses what type(s) of energy?

a. kinetic energy only
b. potential energy only
c. internal energy only
d. kinetic energy and potential energy only
e. kinetic energy, potential energy, and internal energy

**O-I.2**

4) If $q = -1$ kJ for a certain process, that process

a. occurs rapidly.
b. is exothermic.
c. is endothermic.
d. cannot occur.
e. requires a catalyst.
5) Which of the following statements about heat is false?
   a. Heat is a form of energy flow.
   b. If the system and surroundings are in thermal equilibrium, there is no heat flow between them.
   c. A process in which heat flows out of a system is said to be exothermic.
   d. If heat flows into a system, the extra energy of the system appears in the form of internal energy.
   e. A hot object possesses more heat than a cold object.

6) Which of the following statements about enthalpy is false?
   a. Enthalpy is a state function.
   b. At constant pressure, the enthalpy change is equal to the heat absorbed or released.
   c. Enthalpy is an extensive property.
   d. The change in enthalpy of a process cannot be negative.
   e. The SI unit of enthalpy is J.

7) All of the following statements are true for an exothermic reaction except
   a. The temperature of the reaction system increases.
   b. The temperature of the surroundings increases.
   c. Heat passes from the reaction system to the surroundings.
   d. The products have a higher heat content than the reactants.
   e. The enthalpy change for the reaction is negative.

8) For which of the following reactions is \( \Delta H \) equal to \( \Delta U \)?
   a. \( 2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g) \)
   b. \( BaO(s) + SO_3(g) \rightarrow BaSO_4(s) \)
   c. \( 2NO(g) + O_2(g) \rightarrow 2NO_2(g) \)
   d. \( H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \)
   e. \( 2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g) \)

9) Which of the following statements is incorrect?
   a. The value of \( q \) is positive when heat flows into a system from the surroundings.
   b. Heat flows from a system into the surroundings in an endothermic process.
   c. Enthalpy is a state function.
   d. Internal energy is a state function.
   e. The value of \( q \) is positive in an endothermic process.

10) Which of the following statements is true concerning the decomposition of liquid water to form hydrogen gas and oxygen gas?
    \( 2H_2O(l) \rightarrow 2H_2(g) + O_2(g) \)
    a. \( \Delta H \) equals \( \Delta U \) because both are state functions.
    b. \( \Delta H \) is greater than \( \Delta U \) because the pressure is constant.
    c. \( \Delta H \) is greater than \( \Delta U \) because of the pressure–volume work done by the gaseous products.
    d. \( \Delta H \) is less than \( \Delta U \) because of the pressure–volume work done by the gaseous products.
    e. \( \Delta H \) is less than \( \Delta U \) because the atmosphere does pressure–volume work on the gaseous products.
B. Calorimetry (O-I.3)

1. Introduction
   a. Calorimetry is dealing with determining the changes in energy/enthalpy of a system by measuring heat exchanged with the surroundings.
   b. One focus will be on determining heats of reaction.
   c. The heat exchanged between the system and the surroundings is estimated by determining the change in temperature.

2. Heat capacity and specific heat
   a. Heat capacity \( (C) \) is the amount

   \( \square \) It is an extensive property.
   \( \square \) The temperature change can be expressed as 1 K as this is same as 1\(^\circ\)C.
   \( \square \) It has units of \( J/\text{degree} \) (\( J/\degree\C \) or \( J/\degree K \)).

   b. Formulas: \( C = \frac{q}{\Delta T} \) or \( q = C\Delta T \) or \( \Delta T = \frac{q}{C} \)

   c. At constant \( V \), \( q = q_V = \Delta U \) so: \( C = \frac{\Delta U}{\Delta T} \) or \( \Delta U = C\Delta T \) or \( \Delta T = \frac{\Delta U}{C} \)

   d. At constant \( P \), \( q = q_P = \Delta H \) so: \( C = \frac{\Delta H}{\Delta T} \) or \( \Delta H = C\Delta T \) or \( \Delta T = \frac{\Delta H}{C} \)

   \( \square \) This situation is experimentally more convenient so monitoring the changes in enthalpy is preferred.

   e. When \( \Delta T = T_f - T_i \) is (meaning the final \( T \) is larger than initial \( T \)), \( q \) is also because energy is going into the system.

   f. Specific heat \( (s) \) is the amount

   \( \square \) It is an intensive property.
   \( \square \) It has units of \( J/(\text{g} \cdot \degree) \); either \( J/(\text{g} \cdot \degree\C) \) or \( J/(\text{g} \cdot \degree K) \).
\[ s = \frac{C}{\text{mass}} \quad \text{or} \quad s = \frac{C}{m}. \]

- For water, \( s = 4.184 \text{ J/(g} \cdot \text{K}) = 1.00 \text{ cal/(g} \cdot \text{K}) \).
- Typically, for metals, \( s \approx 0.2 \text{ J/(g} \cdot \text{K}) \approx 0.05 \text{ cal/(g} \cdot \text{K}) \).

\[ \text{g. Formulas: } s = \frac{q}{m\Delta T} \quad \text{or} \quad q = ms\Delta T \quad \text{or} \quad \Delta T = \frac{q}{ms} \]

\[ \text{h. At constant } P, \quad s = \frac{\Delta H}{m\Delta T} \quad \text{or} \quad \Delta H = ms\Delta T \quad \text{or} \quad \Delta T = \frac{\Delta H}{ms} \]

i. Heat or \( \Delta T \) can be positive or negative but \( C \) and \( s \) are always positive.

3. Calorimeter

a. Calorimeter is the device that is used to measure heat changes.
   - A simple calorimeter is a Styrofoam cup (with water in it).

b. Calorimeter has a heat capacity of its own, a quantity often called the calorimeter constant.
   - The heat associated with the calorimeter has to be accounted for in problems involving calorimeters.

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O-I.3

11) What is the specific heat of a 5.75 g piece of metal if the addition of 175 joules of heat causes a 27.4 K temperature increase?

- a. 1.11 J/g•degree
- b. 4.18 J/g•degree
- c. 0.73 J/g•degree
- d. 1.54 J/g•degree
- e. 1.36 J/g•degree

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O-I.3

12) The specific heat of aluminum is 0.900 J/g•ºC. How many joules of heat are absorbed by 15.0 g of Al if it is heated from 20.0 ºC to 40.0 ºC?

- a. 270 J
- b. 540 J
- c. 2.40 J
- d. 812 J
- e. \( 1.17 \times 10^4 \) J

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C. Thermochemical Equations (O-I.4 & O-I.5 & O-I.6)

1. Enthalpy of reaction
   - a. Enthalpy of reaction (or heat of reaction) is the difference between the enthalpy of products and the enthalpy of reactants.
b. When $\Delta H_{\text{rxn}}$ is positive, the reaction is endothermic.

c. When $\Delta H_{\text{rxn}}$ is negative, the reaction is exothermic.

d. When $\Delta H_{\text{rxn}}$ is determined using calorimetric measurements, an increase in the temperature of the calorimeter (and/or water) is due to reaction (i.e., the system) releasing energy therefore it is

2. Thermochemical equations

a. A thermochemical equation is a balanced chemical equation that also includes the enthalpy of reaction associated with it.

b. In general an equation can be written as:

$$aA(g) + bB(l) \rightarrow cC(s) + dD(aq) \quad \Delta H = x \frac{\text{kJ}}{\text{mol}}$$

□ A, B, C, and D are the chemical formulas of reaction participants.
□ $a$, $b$, $c$, and $d$ are the stoichiometric coefficients.
□ $\Delta H$ is the same as $\Delta H_{\text{rxn}}$.
□ The physical states of the reactants and products should be specified.

c. The value of $\Delta H$, $x$, can be positive or negative.

d. The unit of $\Delta H$ is kJ/mol (although sometime it appears just as kJ) where mol refers to “a mole of reaction” which is equivalent to the expressing the chemical equation in terms of moles: $a$ moles of $A$ reacts with $b$ moles of $B$ to form $c$ moles of $C$ and $d$ moles of $D$.

3. Properties of thermochemical equations

a. If a thermochemical equation is (or the stoichiometric coefficients in the equation are) multiplied with a number, the enthalpy of reaction have to be

□ $2aA(g) + 2bB(l) \rightarrow 2cC(s) + 2dD(aq) \quad \Delta H =$
b. If a thermochemical equation is (or the stoichiometric coefficients in the equation are) divided by a number, the enthalpy of reaction have to be
c. If a thermochemical equation is reversed (or flipped) such that the products become reactants and the reactants become products, the enthalpy of reaction
\[ cC(s) + dD(aq) \rightarrow aA(g) + bB(l) \quad \Delta H = \]

**O-I.4**
13) From the following data at 25°C,
\[ 2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \quad \Delta H^0 = -484 \text{ kJ} \]
Calculate \( \Delta H^0 \) at 25°C for the following reaction
\[ H_2O(g) \rightarrow H_2(g) + 1/2O_2(g) \]

a. +242 kJ  
b. +484 kJ  
c. +968 kJ  
d. -242 kJ  
e. -484 kJ 

***O-I.2 & O-I.4***
14) At constant pressure, the sign of \( q \) for the process \( H_2O(g) \rightarrow H_2O(l) \) is expected to be

a. negative, and the process is endothermic.  
b. positive, and the process is exothermic.  
c. positive, and the process is endothermic.  
d. negative, and the process is exothermic.  
e. impossible to predict.

4. Hess’s law
   a. Hess law states that the energy associated with a chemical process is independent of the path the process takes.
   
   □ A process can take place in one step or a series of steps.
   b. Hess law is an example of the property of state functions to be
   c. Example of reaction of C with O\(_2\) to form CO\(_2\) either directly or through CO:

\[ \begin{align*}
C + O_2 & \xrightarrow{\text{direct}} CO_2 \\
\text{CO} + \frac{1}{2}O_2 & \xrightarrow{\text{through CO}} CO_2
\end{align*} \]
Applications of Hess law involve determining the enthalpy of reaction for a target reaction based on enthalpies of reactions of other reactions that can combine to give the target equation.

The first step is to determine what to do with each given chemical equation and that can be done by identifying a compound that appear only in that given equation and the target equation and identifying what modifications (multiplication by a number, division by a number, reversing from reactant to product, etc.) needed to be done to that compound.

Once modifications to each given chemical equation is identified, do the same modifications to the enthalpies of reaction.

15) From the following data at 25°C, calculate \( \Delta H^0 \) at 25°C for the following reaction:
\[
4\text{HCl}(g) + \text{O}_2(g) \rightarrow 2\text{Cl}_2(g) + 2\text{H}_2\text{O}(g)
\]
- a. +114 kJ
- b. +299 kJ
- c. -299 kJ
- d. -114 kJ
- e. -86.8 kJ

16) Calculate \( \Delta H^0 \) at 25°C for the following reaction:
\[
4\text{Al}(s) + 3\text{MnO}_2(s) \rightarrow 2\text{Al}_2\text{O}_3(g) + 3\text{Mn}(g)
\]
Based on the data below:
\[
2\text{Al}(s) + 3/2\text{O}_2(g) \rightarrow \text{Al}_2\text{O}_3(s) \quad \Delta H^0 = -1676 \text{ kJ}
\]
\[
\text{Mn}(s) + \text{O}_2(g) \rightarrow \text{MnO}_2(s) \quad \Delta H^0 = -520 \text{ kJ}
\]
- a. +2196 kJ
- b. +1792 kJ
- c. -1792 kJ
- d. -2196 kJ
- e. -2312 kJ

17) Given the following at 25°C and 1.00 atm:
\[
1/2\text{N}_2(g) + \text{O}_2(g) \rightarrow \text{NO}_2(g) \quad \Delta H^0 = 33.2 \text{ kJ}
\]
\[
\text{N}_2(g) + 2\text{O}_2(g) \rightarrow \text{N}_2\text{O}_4(g) \quad \Delta H^0 = 11.1 \text{ kJ}
\]
Calculate the \( \Delta H^0 \) for the reaction below at 25°C:
\[
2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)
\]
- a. +11.0 kJ
- b. +44.3 kJ
- c. +55.3 kJ
- d. -22.1 kJ
- e. -55.3 kJ
5. Stoichiometric calculations using thermochemical equations
   a. A thermochemical equation can be used in stoichiometric calculations to determine relations between masses (or number of moles) used in reaction and the energy/enthalpy involved.
   b. These calculation can be done based on the following equalities:

   ** O-I.6
18) How much heat is released when 75 g of octane is burned completely if the enthalpy of combustion is -5,500 kJ/mol C₈H₁₈?
The reaction is:
   C₈H₁₈ + 25/2 O₂ → 8CO₂ + 9H₂O
   a. 3620 kJ
   b. 7200 kJ
   c. 5500 kJ
   d. 4.1 × 10⁵ kJ
   e. 8360 kJ

   ** O-I.6
19) Calculate the amount of heat released in the complete combustion of 8.17 grams of Al to form Al₂O₃(s) at 25°C and 1 atm.
The reaction is:
   4Al(s) + 3O₂(g) → 2Al₂O₃(s); ΔH = 3352 kJ
   a. 203 kJ
   b. 127 kJ
   c. 254 kJ
   d. 237 kJ
   e. 101 kJ

   ** O-I.6
20) How much would heat of reaction be if 5.00 g of methane are combusted?
   CH₄(g) + 2O₂(g) → 2H₂O(l) + CO₂(g)
   ΔH = -890.3 kJ
   a. -445 kJ
   b. -157 kJ
   c. -14300 kJ
   d. -278 kJ
   e. -714 kJ
D. Enthalpies of Formation (O-I.7 & O-I.8 & O-I.9)

1. Enthalpies of formation
   a. The enthalpy of formation ($\Delta H_f$) is the enthalpy associated with the
      □ The units of $\Delta H_f$ are kJ/mol.
   b. The standard enthalpy of formation ($\Delta H^\circ_f$) is the enthalpy associated
      with the thermodynamic process of formation under standard conditions.
      □ Standard conditions refer to a pressure of 1 atm and a molar
      concentration of 1 mol/L (but not the typical temperature of 25°C).
      □ The standard enthalpies of formation at 25°C are tabulated.
   c. Thermodynamic process of formation is defined as the process of
      forming exactly from
      □ This thermodynamic process of formation is often an imaginary
      process.
   d. Examples:
      □ C(s) + 1/2O$_2$(g) $\rightarrow$ H$_2$SO$_4$(l)
   e. Elements in their standard (or reference) state have, by definition
      □ The need for enthalpies of formation is due to the fact that
      energies/enthalpies are relative quantities.
      □ As the elements in their reference state are defined to have an
      enthalpy of 0 kJ/mol, all other substances can be determined with
      respect to these values.
g. The reference state of an element refers to the lowest energy (or the most stable) state in terms of physical state (solid, liquid, or gas) and in terms of possible allotrope forms.

- An allotrope form is a different form of existence of an element in the same physical state.
- Example: C(graphite) and C(diamond)
- Example: O₂(g), O(g) and O₃(g)

h. Table with the reference state of elements:

<table>
<thead>
<tr>
<th>State</th>
<th>Gas</th>
<th>Liquid</th>
<th>Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diatomic molecules</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyatomic molecules</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

O-I.7
21) Which of the following is not a formation reaction?
   a. Ca(s) + 1/2O₂(g) → CaO(s)
   b. 1/2H₂(g) + 1/2 Br₂(l) → HBr(g)
   c. H₂(g) + 1/2O₂(g) → H₂O(l)
   d. H₂O(l) + SO₃(l) → H₂SO₄(l)
   e. 4Al(s) + 3/2O₂(g) → Al₂O₃(s)

O-I.7
22) For which of the following substances does ΔHᵢ = 0?
   a. C(diamond)
   b. Fe(s)
   c. HCl(aq)
   d. HCl(g)
   e. I₂(g)
2. Using enthalpies of formation to determine the enthalpy of reaction
   a. The enthalpies of formation can be used to determine the enthalpy of reaction.
   b. For the general chemical equation \( aA(g) + bB(l) \rightarrow cC(s) + dD(aq) \):
      \[
      \Delta H_{\text{rxn}} = c\Delta H_f(C) + d\Delta H_f(D) - a\Delta H_f(A) - b\Delta H_f(B)
      \]
      \[ \Delta H_{\text{rxn}} = \]
   c. When learning this formula, remember two important aspects:
      \]
   d. The formula above is an application of Hess’s law using enthalpies of formation.

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**O-I.8**

23) Calculate the standard enthalpy change for the reaction below.

\[
\begin{array}{c|cccc}
\text{C (graphite)} & +4\text{HNO}_3(l) & \rightarrow & \text{CO}_2(g) & +\text{4NO}_2(g) & +2\text{H}_2\text{O}(l) \\
\Delta H_f^\circ & -174.1 & & -393.5 & 33.2 & -285.8 \\
\end{array}
\]

**O-I.8**

24) Evaluate \( \Delta H^0 \) for the reaction below at 25°C.

\[
\begin{array}{c|cccc}
\text{SiO}_2(s) & +4\text{HF}(aq) & \rightarrow & \text{SiF}_4(g) & +2\text{H}_2\text{O}(l) \\
\Delta H_f^\circ & -910.9 & & -320.8 & -1615 & -285.8 \\
\end{array}
\]

**O-I.8**

25) Given the following at 25°C, calculate \( \Delta H_f \) for HCN(g) at 25°C.

\[
2\text{NH}_3(g) + 3\text{O}_2(g) + 2\text{CH}_4(g) \rightarrow 2\text{HCN}(g) + 6\text{H}_2\text{O}(g) \Delta H_{\text{rxn}} = -870.8 \text{ kJ}
\]

\[
\Delta H_f = -80.3 \text{ kJ/mol for NH}_3(g), -74.6 \text{ kJ/mol for CH}_4, \text{ and } -241.8 \text{ kJ/mol for H}_2\text{O}(g).
\]

a. -870.8 kJ/mol
b. -135 kJ/mol
c. -147 kJ/mol
d. +270 kJ/mol
e. +135 kJ/mol
3. Using enthalpies of formation to determine the enthalpy of phase changes
   a. Similarly to determining the enthalpy of reaction, the enthalpies of formation can be used to determine the enthalpy of phase changes.
   b. Remember the possible phase transformations:
      □ Melting (or fusion): S \rightarrow L
      □ Vaporization (or evaporation or boiling): L \rightarrow G
      □ Sublimation: S \rightarrow G
      □ Condensation: G \rightarrow L
      □ Deposition: G \rightarrow S
      □ Freezing: L \rightarrow S
   c. The phase transformation/change can be seen as a “chemical reaction” A(phase 1) \rightarrow A(phase 2).
      □ \Delta H_{pc} = \Delta H_f (phase 2) - \Delta H_f (phase 1)
   d. Example: \Delta H_{vap} =
      □ \Delta H_{vap} is
      □ Condensation, which is the reverse of vaporization, is

26) Calculate the standard heat of vaporization, \Delta H_{vap}, for tin(IV) chloride, SnCl_4, in kJ per mole. \Delta H_f = -511.3 kJ/mol for SnCl_4(l) and -471.5 kJ/mol for SnCl_4(g).
   a. 44.8
   b. 53.2
   c. 26.4
   d. 16.4
   e. 39.8

**O-I.9**
E. Enthalpies/Energies Associated with Chemical Bonds (O-I.10 & O-I.11)

1. Bond energies/enthalpies
   a. Remember that a covalent bond is formed when two atoms share two electrons (one from each atom).
      □ The relative energy of bond atoms is lower than the energy of separated atoms.
   b. The formation of a covalent bond is the breaking of a covalent bond is
   c. For example, the breaking of the first O–H bond in H₂O required different energy than the second O–H bond.
   d. Bond energy/enthalpy (BE) is the average energy necessary to break a particular covalent bond.
      □ It is
      □ It is
      □ It is defined for
   e. Bond energy/enthalpy can be used to estimate (but not exactly determine) the enthalpy of reaction:
      □ \( \Delta H_{\text{rxn}} \approx \sum_{\text{all bonds}} \Delta H_{\text{BE(broken)}} - \sum_{\text{all bonds}} \Delta H_{\text{BE(forming)}} \)
      □ \( \Delta H_{\text{rxn}} \approx \)
   f. Knowing the Lewis structures of reactants and products (i.e., the types of bonds involved) is necessary.
27) Based on the values of bond energies in textbook, what is the enthalpy of reaction for the following reaction?

\[ \text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl} \]

a. –244 kJ  
b. –183 kJ  
c. –114 kJ  
d. +183 kJ  
e. +244 kJ

28) Based on the values of bond energies in textbook, what is the enthalpy of reaction for the following reaction?

\[ \text{CH}_4 + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} \]

a. –1169 kJ  
b. –699 kJ  
c. –338 kJ  
d. +338 kJ  
e. +699 kJ

2. Lattice energy and Born-Haber cycle

a. Remember that an ionic bond (or an ionic interaction) describe the interaction between two ions of opposite charge.

□ The ions are formed from atoms by transfer of electron/electrons.

b. Typically the metals donate electrons to form while non-metals accept electrons to form

□

c. Ionic compounds are typically solids.

d. Lattice energy is defined as the energy required to break 1 mole of ionic compound into constituting ions in gas phase.

□ It is

□ It is

□ It is

e. Lattice energies are known (and tabulated) values that can be determined using Born-Haber cycle.

f. Born-Haber cycle is a cycle of processes in which lattice energy is the only one that cannot be directly determined experimentally but can be determined using Hess’s law.
g. For NaCl, the processes involved in Born-Haber cycle are:

\[
\begin{align*}
\text{Na}(s) + \frac{1}{2}\text{Cl}_2(g) & \xrightarrow{\Delta H_f} \text{NaCl}(s) \\
\Delta H_{\text{sub}} & \downarrow \frac{1}{2}\text{BE} \\
\text{Na}(g) + \text{Cl}(g) & \xrightarrow{\text{IE}_1/E\text{A}} \text{Na}^+(g) + \text{Cl}^-(g) \\
& \uparrow -\Delta H_{\text{lattice}}
\end{align*}
\]

- Formation of NaCl ($\Delta H_f$):
- Sublimation of sodium ($\Delta H_{\text{sub}}$):
- Dissociation of Cl$_2$ gas ($\frac{1}{2}\text{BE}$)
- First ionization energy of sodium ($\text{IE}_1$):
- Electron affinity of chlorine ($E\text{A}$):
- Lattice energy of NaCl ($\Delta H_{\text{lattice}}$):
Unit II
Solutions

Unit Objectives

O-II.1 Learn terminology: Colligative proprieties, Saturated solution, Supersaturated solution, Osmosis, Osmotic pressure
O-II.2 Describe solutions, identify intermolecular interactions & predict miscibility
O-II.5 Describe solubility dependence on temperature
O-II.6 Describe solubility dependence on pressure & apply Henry’s law
O-II.3 Carry out calculations involving concentration expressed as mass percentage, mole fraction, molarity, and molality
O-II.4 Transform concentration of solution from one form of expression to another
O-II.7 Carry out determinations of vapor pressure lowering – Raoult’s law
O-II.8 Carry out calculations of boiling point elevation
O-II.9 Carry out calculations of freezing point depression
O-II.10 Carry out calculations of osmotic pressure
O-II.11 Carry out calculations involving colligative properties of solutions of electrolytes
A. Solution Miscibility (O-II.2)

1. Introduction
   a. A solution is a homogeneous mixture of two or more components.
   b. Components of a solution are named:
      □ Solvent – typically the component in larger amount; denoted by
      □ Solute – typically the component in smaller amount; denoted by
   c. The most common solvent is water, in which case the solution is called
   d. Based on the physical state solutions can be gas, liquid or solid but our
      interest is mainly in liquid solutions.
   e. A solution is typically made by mixing the components, and when
      mixing is desired, two aspects are of interest:
      □ miscibility – Do components mix? Why or Why not?
      □ solubility – How much they can mix? Why?

2. Intermolecular forces
   a. Intermolecular forces are interaction (i.e., forces) between molecules
      and should not be confused with interactions (i.e., bonds) within a
      molecule (or ions) like covalent or ionic or metallic bonds.
   b. There are three types of interactions that can exit between molecules of
      the same type (i.e., homogeneous interactions):
   c. forces/interactions (or forces or forces) are interactions between clouds of electrons.
      □ They are sometimes wrongly defined as induced dipole-induced
      dipole interactions.
      □ They are considered to be interactions.
      □ They become stronger with the
      and they can become very strong for large molecules.
- They exist for all molecules/compounds.

d. Bonds (or \(H-bonds\)) are interaction between the hydrogen atom in one molecule and an atom of another molecule so they can be represented as

- Both \(X\) and \(Y\) should be
- They are considered to be interactions.

e. Forces are interactions between molecules having dipole moments (i.e., polar molecules).

- For a molecule to have a dipole moment it has to have
  (which are pretty much every covalent bond in which the atoms are different) and
- They are considered to be interactions.

f. In addition to homogeneous interactions, in solution, heterogeneous interactions (i.e., between molecules of different type) are possible:

- Ion-dipole interactions – particularly important in dissolving ions in water
- Ion-induced dipole interactions
- Dipole-induced dipole interactions

3. Miscibility

a. To try to understand why some substance mix (like water and ethanol) and why some do not (like water and oil), one should look at the interactions being destroyed and formed during the solution process.

b. Look at a solvent \(A\) being mixed with a solute \(B\):

\[
\Delta H_1 = + \quad \frac{\text{Solvent}}{A \cdots A} \quad \Delta H_2 = + \quad \frac{\text{Solute}}{B \cdots B} \quad \Delta H_3 = -
\]
□ Some solvent-solvent (A⋯A) interactions will vanish, and this is an endothermic process, denoted by \( \Delta H_1 \) in this example.

□ Some (or all) solute-solute (B⋯B) interactions will disappear, and this is an endothermic process, denoted by \( \Delta H_2 \) in this example.

□ New solute-solvent (A⋯B) interactions will appear, and this is an exothermic process, denoted by \( \Delta H_3 \) in this example.

□ The enthalpy (or heat) of solution, \( \Delta H_{\text{solution}} = \Delta H_1 + \Delta H_2 + \Delta H_3 \), can be positive (i.e., \( \Delta H_{\text{solution}} > 0 \)) or negative (i.e., \( \Delta H_{\text{solution}} < 0 \)) depending on the strength of broken and formed interactions.

c. The process of separating apart solute molecules and having them surrounded by solvent molecules is called solvation, in general, and hydration, when the solvent is water.

d. In addition to the energetic factor, the mixing of substances is associated with an increase of entropy (\( \Delta S_{\text{solution}} > 0 \)), which is a driving force toward mixing.

e. Although both energetic and entropic factors should be considered, the energetic factor will be decisive in determining if two substances are miscible.

f. There is a rule meaning that substances with some kind of interactions (H-bond, dipole-dipole and/or dispersion) will be miscible in substances that have the same type of interactions.

□ Water and ethanol are miscible because they have the same types of interactions:

□ Water (with H-bond, dipole-dipole and dispersion) and oil (with dispersion only) are

g. Simplistically, substances with only dispersion forces (e.g., \( \text{CH}_4 = \), \( \text{C}_8\text{H}_{18} = \), benzene, oil, etc.) will not be soluble/miscible in substances having H-bonding (e.g., \( \text{H}_2\text{O} \),
\[ \text{CH}_3\text{COOH} = \text{acetic acid}, \quad \text{CH}_3\text{CH}_2\text{OH} = \text{ethanol}, \quad \text{CH}_3\text{OH} = \text{methanol}, \quad \text{etc.}. \]

O-II.2

1) The dissolution process is exothermic if the amount of energy released in bringing about \(a\) interactions exceeds the sum of the amounts of energy absorbed in overcoming \(b\) and \(c\) interactions.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. solute-solute</td>
<td>crystal lattice</td>
<td>solvent-solvent</td>
<td></td>
</tr>
<tr>
<td>b. solvent-solute</td>
<td>solute-solute</td>
<td>solvent-solvent</td>
<td></td>
</tr>
<tr>
<td>c. solute-solute</td>
<td>solute-solute</td>
<td>solvent-solvent</td>
<td></td>
</tr>
<tr>
<td>d. solvent-solute</td>
<td>solute-solute</td>
<td>crystal lattice</td>
<td></td>
</tr>
<tr>
<td>e. solvent-solvent</td>
<td>solute-solute</td>
<td>solvent-solvent</td>
<td></td>
</tr>
</tbody>
</table>

O-II.2

2) Which of the following solutions would not be expected to exist?

a. NaCl in water
b. CH\(_3\)OH in water
c. NaCl in CCl\(_4\)
d. Benzene, C\(_6\)H\(_6\), in oil
e. Pentane, C\(_5\)H\(_{12}\), in CCl\(_4\)

O-II.2

3) Which of the following pairs are not miscible?

a. hexane, C\(_6\)H\(_{14}\) and water
b. methyl alcohol, CH\(_3\)OH and water
c. pentane, C\(_5\)H\(_{12}\) and hexane, C\(_6\)H\(_{14}\)
d. ethyl alcohol, CH\(_3\)CH\(_2\)OH and water
e. benzene, C\(_6\)H\(_6\) and hexane, C\(_6\)H\(_{14}\)

O-II.2

4) Which of the following compounds is not miscible with water?

a. CH\(_3\)OH
b. CCl\(_4\)
c. CH\(_3\)CN
d. CH\(_3\)COOH
e. H\(_2\)O\(_2\)

B. Solubility (O-II.3 & O-II.4)

1. Types of solutions and solubility

a. Based on the amount of solute that is mixed with solvent, a solution can be classified as:

- \(\square\) – when the maximum amount of solute is dissolved/mixed.
- \(\square\) – when less than the maximum amount of solute is dissolved/mixed.
Suprasaturated solution – when the maximum amount of solute is dissolved/mixed.

b. A suprasaturated solution is an unstable situation that can be achieved by cooling a hot solution fast enough such that the solute does not have time to precipitate.

c. Solubility is generally describing the amount of solute in solution.

d. Solubility can be expressed in g/mL or g/L or as molar concentration (in mol/L).

e. When solubility is expressed as molar concentration, it becomes although, for simplicity, it is still called solubility.

2. Solubility dependence on temperature

a. Solubility of gases (in liquids) as the temperature increases.

b. Solubility of liquids or solids (in liquids) as the temperature increases.

□ When $\Delta H_{sol} < 0$, the solubility as $T$ increases.

□ When $\Delta H_{sol} > 0$, the solubility as $T$ increases.

3. Solubility dependence on pressure

a. Solubility of liquids or solids (in liquids) is not influenced by the pressure.

b. Solubility of gases (in liquids) with the pressure of gas above the liquid.

c. The dependence is given by Henry’s law: $c = k_H \times P$.

□ $c$ is the

□ $k_H$ is Henry’s law constant, and it has the units of concentration/pressure.
d. Henry’s law can be rearranged based on two pressures and two concentrations:

\[
P_1 \cdot c_1 = P_2 \cdot c_2
\]

5) Which of the following statements is false?
   a. Nonpolar solids do not dissolve appreciably in polar solvents.
   b. For solids that dissolve endothermically, solubility increases as temperature increases.
   c. Most gases that are soluble in water are polar or react with water.
   d. Gas solubility decreases with increasing temperature.
   e. Gases are less soluble under high pressure than under low pressure.

6) Which one of the following statements is false?
   a. The solubility of a gas not reacting with the solvent decreases as temperature increases.
   b. Lattice energy and hydration energy have opposite effects in dissolution of solids in liquids.
   c. The solubilities of solids in liquids always increase as temperature increases.
   d. Nonpolar solids do not dissolve appreciably in polar solvents.
   e. The separation of solute particles from a crystal requires energy.

7) If the concentration of CO₂ is 5.80 g of CO₂ per 1.00 L of soft drink when bottled under 4.0 atm of CO₂ pressure, what will be the concentration of the CO₂ in the drink after it has been opened and left to come to equilibrium with the atmosphere which has a CO₂ partial pressure of 3.0 \times 10^{-4} atm?
   a. 2.2 \times 10^{-3} g CO₂/L
   b. 4.4 \times 10^{-4} g CO₂/L
   c. 2.0 \times 10^{-4} g CO₂/L
   d. 1.0 \times 10^{-4} g CO₂/L
   e. 4.6 \times 10^{-2} g CO₂/L

C. Concentration Units (O-II.5 & O-II.6)

1. Types of concentration
   a. Generally, the term of concentration refers to expressing how much solute exists in solution.
   b. There are four common ways to express concentration:
<table>
<thead>
<tr>
<th>Concentration</th>
<th>Formula</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass percentage</td>
<td></td>
<td>for solids and liquids</td>
</tr>
<tr>
<td>Mole fraction</td>
<td></td>
<td>for gases and liquids</td>
</tr>
<tr>
<td>Molarity</td>
<td></td>
<td>for liquids</td>
</tr>
<tr>
<td>Molality</td>
<td></td>
<td>for liquids</td>
</tr>
</tbody>
</table>

c. Some additional comments on the concentration units above:
   - Molarity depend on the volume of solution, which is temperature dependent.
   - Molality is temperature independent.
   - The number of moles depend on the molar mass \( (n_B = \text{mass}_B/M_{M,B}) \)
   - so the equations above can be rewritten depending on the molar mass of solute \( (M_{M,B})\).

8) What is the molarity of 2500. mL of a solution that contains 320. grams of NH\(_4\)NO\(_3\)?
   - a. 0.600 \( M \)
   - b. 0.450 \( M \)
   - c. 1.60 \( M \)
   - d. 0.333 \( M \)
   - e. 0.800 \( M \)

9) How many grams of C\(_{12}\)H\(_{22}\)O\(_{11}\) must be dissolved in 750. g of water to prepare a 0.250 molal solution?
   - a. 85.5 g
   - b. 78.2 g
   - c. 96.4 g
   - d. 64.1 g
   - e. 114 g
2. Expressing concentration in one unit given another unit
   a. A particular type of problem requires calculating the concentration of a solution in a particular unit giving the concentration in a different unit.
   b. Concentration units are intensive properties, which do not depend on the amount of solution.
   c. The easiest approach is to assume a particular amount of solution, and the best amount is the one on the denominator of the given concentration:

   □ Automatically, the amount in the numerator is known.
   d. Additional calculations involving mass-number of moles (and maybe density also) transformations will be necessary.
   □ Volume (of the solution) appears only in the molarity, and it is related to the mass of the solution through density ($D$).
   e. It may be useful to imagine a table with entries for solvent, solvent and solution.

<table>
<thead>
<tr>
<th>Amount</th>
<th>Solvent (A)</th>
<th>Solute (B)</th>
<th>Solution (A + B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>$n_A$</td>
<td>$n_B$</td>
<td>$n_{sol} = n_A + n_B$</td>
</tr>
<tr>
<td>mass</td>
<td>mass$_A$</td>
<td>mass$_B$</td>
<td>mass$_{sol} = mass_A + mass_B$</td>
</tr>
<tr>
<td>$V$</td>
<td></td>
<td></td>
<td>$V_{sol} = mass_{sol}/D$</td>
</tr>
</tbody>
</table>
What is the mole fraction of methanol, CH\(_3\)OH, in an aqueous solution that is 20.0\% methanol by mass?

a. 0.123  
b. 0.101  
c. 0.250  
d. 0.544  
e. 0.308

What is the mole fraction of CH\(_3\)OH in a 3.50 m aqueous solution of CH\(_3\)OH?

a. 0.0630  
b. 0.0592  
c. 0.650  
d. 0.350  
e. 0.0679

Calculate the molality of a 20.0\% H\(_3\)PO\(_4\) solution in water.

a. 0.380 m  
b. 2.55 m  
c. 1.51 m  
d. 0.760 m  
e. 1.13 m

D. Colligative Properties (O-II.7 → O-II.11)

1. General comments
   a. Colligative properties are properties of solutions (compared with those of pure solvent) that depend only on the number (or concentration) of solute particles
   b. There are four properties that are described in the table below:
<table>
<thead>
<tr>
<th>Property</th>
<th>Solution change</th>
<th>Non-electrolyte solution</th>
<th>Electrolyte solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor pressure</td>
<td>lower</td>
<td>$\Delta P = P_A^* - P_A = x_B P_A^*$</td>
<td>even lower</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$P_A = x_A P_A^*$</td>
<td></td>
</tr>
<tr>
<td>Boiling Point</td>
<td>higher</td>
<td>$\Delta T_b = T_b - T_b^* = K_b m$</td>
<td>(\Delta T_b = iK_b m)</td>
</tr>
<tr>
<td>Freezing Point</td>
<td>lower</td>
<td>$\Delta T_f = T_f^* - T_f = K_f m$</td>
<td>(\Delta T_f = iK_f m)</td>
</tr>
<tr>
<td>Osmotic Pressure</td>
<td>exist</td>
<td>$\pi = cRT$</td>
<td>$\pi = icRT$</td>
</tr>
</tbody>
</table>

2. Vapor pressure lowering
   
a. Vapor pressure of a liquid is the pressure of a gas above the liquid, in equilibrium with the liquid, in a closed system.
   
   - Typically, the vapor pressures are small at normal temperature except for volatile compounds.
   
   - Vapor pressure of a liquid as the temperature increases.
   
   - If vapor pressure of a liquid equals the atmospheric pressure, the liquid starts boiling.

b. When the solute is nonvolatile (i.e., does not have any vapor pressure), the vapor pressure of a solution is due to the solvent only and is given by the Raoult’s law: $\Delta P = P_A^* - P_A = x_B P_A^*$
   
   - $P_A^*$ is the vapor pressure of the pure solvent, $P_A$ is the vapor pressure of the solution, and $x_B$ is the solute mole fraction.
   
   - An equivalent expression is

c. Solutions that obey Raoult’s law are called ideal solutions, and these will be the only types of solutions that we are considering in this class.
d. It is possible that the solute is also volatile (i.e., it has a vapor pressure on its own) so the vapor pressure of a solution will be the sum of solvent and solute: 

\[ P_{\text{total}} = \]

\[ P_A + P_B \]

- For solute, \[ P_B = x_B P_B^* \].

e. When both solvent and solute are volatile, the gas phase will have higher concentration in the more volatile component than the solution.

- Multiple evaporations and condensations of solution can lead to pure components in a process called

<table>
<thead>
<tr>
<th>O-II.7</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>13) Calculate the vapor pressure of a solution prepared by dissolving 70.0 g of naphthalene, ( C_{10}H_8 ) (a nonvolatile nonelectrolyte), in 220.0 g of benzene, ( C_6H_6 ), at 20°C. Assume the solution is ideal. The vapor pressure of pure benzene is 74.6 torr at 20°C.</strong></td>
</tr>
<tr>
<td>a. 60.1 torr</td>
</tr>
<tr>
<td>b. 40.8 torr</td>
</tr>
<tr>
<td>c. 14.5 torr</td>
</tr>
<tr>
<td>d. 12.1 torr</td>
</tr>
<tr>
<td>e. 62.5 torr</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>O-II.7</th>
</tr>
</thead>
<tbody>
<tr>
<td><em><strong>14) Which aqueous solution of nonelectrolyte would have the lowest vapor pressure at 25°C?</strong></em></td>
</tr>
<tr>
<td>a. 1 g glucose, ( C_6H_{12}O_6 ), in 100 g water</td>
</tr>
<tr>
<td>b. 1 g ( CH_3CH_2OH ) in 100 g water</td>
</tr>
<tr>
<td>c. 2 g sucrose, ( C_{12}H_{10}O_{11} ), in 100 g water</td>
</tr>
<tr>
<td>d. 1 g ( CH_3OH ) in 100 g water</td>
</tr>
<tr>
<td>e. 1 g sucrose, ( C_{12}H_{10}O_{11} ), in 100 g water</td>
</tr>
</tbody>
</table>

3. **Boiling point elevation and freezing point depression**

a. A solution (of a nonvolatile solute) will boil at higher temperature than the pure solvent.

b. The increase in boiling temperature depends on the molality of solution: 

\[ \Delta T_b = T_b - T_b^* = K_b \cdot m \]

- \( T_b \) is the boiling temperature of the solution, \( T_b^* \) is the boiling temperature of the solvent, and \( m \) is the molality.

- \( K_b \) is the boiling-point elevation constant (or ebullioscopic constant).

c. A solution (of a nonvolatile solute) will freeze at lower temperature than the pure solvent.
The decrease in freezing temperature depends on the molality of solution: 

\[ \Delta T_f = T_f^* - T_f = K_f m \]

- \( T_f \) is the freezing temperature of the solution, \( T_f^* \) is the freezing temperature of the solvent, and \( m \) is the molality.
- \( K_f \) is the freezing-point depression constant (or cryoscopic constant).

e. Pure water freezes at \( 0.0 \) °C and boils at \( 100.0 \) °C.

f. The temperature difference in formulas above can be expressed either in °C or in K.

g. The boiling point elevation and freezing point depression experiments can be used to estimate the molar mass of the solute.

---

15) The boiling point of pure water in Winter Park, CO (elev. 9000 ft) is 94°C. What is the boiling point of a solution containing 11.3 g of \( \text{C}_6\text{H}_{12}\text{O}_6 \) (\( \text{M}_M = 180 \text{ g/mol} \)) in 55 g of water in Winter Park? \( K_b \) for water = 0.512°C/m.

- a. 95.1°C
- b. 98.6°C
- c. 93.4°C
- d. 100°C
- e. 94.6°C

16) When 45.0 g of an unknown nonelectrolyte is dissolved in 330. g of benzene, the solution boils at 83.2°C. Calculate the molecular weight of the unknown nonelectrolyte. The \( K_b \) for benzene = 2.53°C/m. The boiling point of pure benzene is 80.1°C.

- a. 194 g/mol
- b. 20.3 g/mol
- c. 130 g/mol
- d. 183 g/mol
- e. 111 g/mol

17) 3.62 g of a compound with a molecular weight of 78.0 g/mol are dissolved in 100 g of nitrobenzene. What is the freezing point of the solution? For pure nitrobenzene: \( T_f = 5.70°C \) and \( K_f = 7.00°C/m \).

- a. -2.45°C
- b. 2.45°C
- c. 3.25°C
- d. 8.95°C
- e. -3.25°C

18) When 1.150 grams of an unknown nonelectrolyte dissolves in 10.0 grams of water, the solution freezes at -2.16°C. What is the molecular weight of the unknown compound? \( K_f \) for water = 1.86°C/m.

- a. 74.2 g/mol
- b. 132 g/mol
- c. 99.1 g/mol
- d. 88.6 g/mol
- e. 116 g/mol
4. Osmotic pressure
   a. Osmotic pressure is the pressure difference between the two sides of a membrane (i.e., a membrane that allow the solvent to pass through but not the solute).
   b. The osmotic pressure depends on the difference in solute concentration between the two sides of the membrane.
   c. When on a side of the membrane there is pure solvent, the osmotic pressure is given by
      \[ \pi = cRT \]
      where:
      - \( c \) is the molar concentration of solute (in mol/L),
      - \( R \) is the ideal gas law (0.08206 L·atm/mol·K),
      - \( T \) is the temperature in K, and
      - \( \pi \) is the osmotic pressure in atm.
      \[ 1 \text{ atm} = 760 \text{ mmHg} = 760 \text{ torr}. \]
   d. Because \( c = n/V \), the osmotic pressure formula can be rewritten as
      \[ \pi V = nRT, \]
      which is equivalent to ideal-gas law/formula.
   e. Because \( n = \text{mass}/M_M \), the osmotic pressure formula can be used to determine the molar mass of the solute given the osmotic pressure.

O-II.10

19) Calculate the osmotic pressure associated with 62.0 g of an enzyme of molecular weight 85,000 g/mol dissolved in 3250 mL of benzene at 27.0°C.
   a. 0.378 torr
   b. 4.20 torr
   c. 3.71 torr
   d. 3.90 torr
   e. 1.76 torr

20) What is the molecular weight of a biological macromolecule if 2.33 g of it dissolved in 200 mL of water generates osmotic pressure equal to 5.75 torr at 30°C?
   a. 76,600 g/mol
   b. 19,000 g/mol
   c. 38,300 g/mol
   d. 3,790 g/mol
   e. 34,500 g/mol
5. Solutions of electrolytes
   a. Aqueous solutions of electrolytes are solutions that conduct the electric
current because the substance that dissolves also dissociates into ions.
   b. As the colligative properties are properties that depend on the amount
of solute, and electrolyte solutions contains more particles (i.e., ions)
once dissolved, aqueous solutions of electrolytes are described by
formula slightly different than nonelectrolyte solutions (see table
above).
   c. Formulas for electrolyte solutions contain van’t Hoff coefficient $i$
which is the moles of particles in solution per mole of substance.
   □ $i =$
   d. Van’t Hoff coefficient $i = 1$ for
      □ Examples: sugar (or sucrose or $C_{12}H_{22}O_{11}$), $CH_3OH$, $CH_3CH_2OH$,
      etc.
   e. Van’t Hoff coefficient $i = 2$ or 3 for
      □ Strong acids: HCl, HBr, HI, HNO$_3$, etc.
      □ Strong bases: NaOH, KOH, Ca(OH)$_2$, Ba(OH)$_2$, etc.
      □ Soluble salts: NaCl, CaCl$_2$, ZnCl$_2$, etc.
   f. Van’t Hoff coefficient $1 < i < 2$ for
      □ Examples: CH$_3$COOH, HF, HCN, etc.
21) If the van't Hoff factor for NaCl is 1.88, what is the freezing point of a 0.60 molal NaCl solution in water? \( K_f = 1.86 \degree C/m \) for water.

a. -2.10°C  
b. 1.75°C  
c. -1.05°C  
d. 2.10°C  
e. -1.75°C

22) Which of the following statements regarding a 1 M sucrose solution is not correct?

a. The vapor pressure at 100°C is less than 760 torr.  
b. The freezing point is less than 0.0°C.  
c. The boiling point is less than that of a 1 M NaCl solution.  
d. The freezing point is less than that of a 1 M NaCl solution.  
e. The boiling point is greater than 100°C.

23) Which of these aqueous solutions would be expected to have the highest boiling point?

a. 0.20 m Ca(NO\(_3\))\(_2\)  
b. 0.25 m NaOH  
c. 0.20 m CH\(_3\)OH  
d. 0.05 m Al\(_2\)(SO\(_4\))\(_3\)  
e. 0.15 m K\(_2\)SO\(_4\)
Unit III
Chemical Kinetics

Unit Objectives

O-III.1 Learn terminology: Collision theory, Activation energy, Transition state theory, Activated complex, Rate law, Reaction order, Integrated rate law, Half-life, Elementary reaction, Reaction mechanism, Reaction intermediate, Molecularity, Rate-determining step, Catalysis

O-III.2 Describe key aspects of the two theories of chemical reactions: collision theory and transition state theory

O-III.3 Define reaction rate and describe factors that influence it

O-III.4 Define and identify rate laws and reaction orders

O-III.5 Determine the rate law using the method of initial rates

O-III.6 Carry out calculations with the integrated rate laws (first order, second order, zeroth order) and half-lives

O-III.7 Describe linear graphs derived from integrated rate laws

O-III.8 Carry out calculations using the temperature dependence of the rate constant using Arrhenius equation

O-III.9 Describe elementary reactions and molecularity

O-III.10 Describe complex reactions and interpret simple reaction mechanisms and approximations

O-III.11 Describe catalysis and factors that influence it
A. Theories of Chemical Reactions (O-III.2)

1. Introduction
a. Chemical kinetics deals the rates (or speed) of chemical reactions, factors influencing it, and details on how reactions are taking place.

2. Collision theory
a. It explains the reaction taking place in gas phase through collisions between molecules.
b. The rate of reaction is determined by factors including:
   □
   □
   □

3. Transition state theory
a. Transition state theory is a theory of chemical reactivity that focuses on intermediary stages of reaction called transition states or activated complexes.
b. The transition state (TS) or activated complex:
   □ is a transient state between reactants and products,
   □ is higher in energy than both reactants and products,
   □ is characterized by bonds
   □ is denoted by

c. Example: \( \text{Cl}_2 + \text{NO} \rightarrow \text{Cl} + \text{Cl}−\text{NO} \)
d. Transition state theory introduces or uses (potential) energy diagrams and the concept of activation energy which is the energy difference between the transition state and the reactant (or products):
B. Experimental Chemical Kinetics (O-III.3 → O-III.8)

1. Reaction rate
   a. Reaction rate for a reaction in solution can be generally defined as “the change in (molar) concentration in time”, and it measures how fast the molarity changes in time.
   b. There is the “overall” reaction rate defined as \( \frac{[P]_{\text{end}} - [P]_{\text{start}}}{\text{time}} \), where P stands for product, but it is not very useful.
   c. More useful is the “instantaneous” reaction rate defined as the slope of [P] versus time graph for which, by looking at shorter and shorter time intervals, one can get the rate at a specific point in time.
   d. For a general reaction, \( a \ A + b \ B \rightarrow c \ C + d \ D \), reaction rate is defined as
      \[
      \text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = +\frac{1}{c} \frac{\Delta[C]}{\Delta t} = +\frac{1}{d} \frac{\Delta[D]}{\Delta t}
      \]
      \[\square\] [A] represents the molar concentration or molarity of A.
      \[\square\] As the reaction rate is always \( \text{positive} \), and the change of concentration of reactants is \( \text{negative} \), there is
      \[\square\] If \( a = 1 \) and \( b = 2 \), the rate of disappearance (or consumption) of B is twice as large as that for A, but by dividing to the stoichiometric coefficients, the two rates become equal.
   e. The rate of reaction depends on a number of factors:
      \[\square\] concentrations of (some) reactants (A and/or B) and sometimes of products (C and/or D),
      \[\square\]
      \[\square\]
O-III.2
1) For the reaction diagram shown aside, which of the following is not true?

a. the X axis is reaction progress; the Y axis is energy
b. A represents reactants; C represents products
c. B represents the transition state
d. D represents activation energy; E represents $\Delta H$ for the reaction.
e. Reaction is exothermic.

O-III.3
2) For the reaction: $aA + bB \rightarrow cC + dD$, which of the following is NOT a proper expression for the rate of reaction?

a. $\frac{\Delta[D]}{d \Delta t}$
b. $\frac{\Delta[A]}{a \Delta t}$
c. $-\frac{\Delta[B]}{b \Delta t}$
d. $\frac{\Delta[C]}{c \Delta t}$

3) Iodide ion is oxidized by hypochlorite ion in basic solution:
$I^-(aq) + ClO^-(aq) \rightarrow Cl^-(aq) + IO^-(aq)$
In 1.00 M NaOH at 25°C, the iodide concentration is 0.00169 M after 2.00 s and 0.00121 after 7.00 s. What is the average rate of reaction of iodide in this interval?

a. $+ 9.6 \times 10^{-4}$ M/s
b. $+ 9.6 \times 10^{-5}$ M/s
c. $- 9.6 \times 10^{-4}$ M/s
d. $- 9.6 \times 10^{-5}$ M/s

2. Rate law

a. Rate law refers to the expression describing the dependence of the reaction rate to concentrations.
b. The typical expression is: $\text{Rate} = k[A]^m[B]^n[C]^p$
   □ $k$ is the rate constant (because it is independent of concentrations but it is dependent on the temperature).
   □ $m$ is the order of reaction with respect to A, $n$ is the order of reaction with respect to B, and $p$ is the order of reaction with respect to C.
   □ The sum $(m + n + p)$ is called
c. The orders $m$, $n$ and $p$:
   □ are not necessarily the same as the stoichiometric coefficients $a$, $b$, and $c$,
   □ should be experimentally determined (so $m = a$ or $m \neq a$),
   □ could be zero (meaning that the reaction rate is independent of that concentration).

d. “Determining the rate law” means determining the orders ($m$, $n$, and/or $p$) and then determining

| O-III.4 | 4) For the following reaction
|         | $2\text{NO}(g) + \text{Cl}_2(g) \rightarrow 2\text{NOCl}(g)$
|         | the observed rate law is:
|         | Rate = $k[\text{NO}]^2[\text{Cl}_2]$.
|         | What is the reaction order with respect to nitrogen monoxide?
| a. 0    | b. 1
| c. 2    | d. 3

| O-III.4 | 5) For the following reaction
|         | $2\text{NO}(g) + \text{Cl}_2(g) \rightarrow 2\text{NOCl}(g)$
|         | the observed rate law is:
|         | Rate = $k[\text{NO}]^2[\text{Cl}_2]$.
|         | What is the overall order of reaction?
| a. 0    | b. 1
| c. 2    | d. 3

3. The method of initial rates
   a. The method of initial rates is a method of determining the rate law.
   b. The general idea is to carry out a series of experiments under various conditions (i.e., different reactant concentrations) and look on the changes on initial reaction rates.
   c. The preferred case is determining initial reaction rates for two different concentration of B while concentration of A stays the same.
      □ In this case:
      \[
      \begin{align*}
      \text{Rate}_1 &= k[A]_0^n[B]_1^n \\
      \text{Rate}_2 &= k[A]_0^n[B]_2^n
      \end{align*}
      \]
□ Similarly, the order with respect to A can be determined by comparing experiments

d. Once the orders \( m \) and \( n \) are determined, the rate constant \( k \) can be obtained by using any data set and the determined rate law.

6) Consider the tabulated data showing the initial rate of reaction (A \( \rightarrow \) Products) at three concentrations of A. What is the order of reaction?

\[
\begin{array}{|c|c|c|}
\hline
[A] (M) & Initial rate (M/s) \\
\hline
0.100 & 0.053 \\
0.200 & 0.210 \\
0.300 & 0.473 \\
\hline
\end{array}
\]

a. 0
b. 1
c. 2
d. 3

7) The initial rate of reaction for \( D + E \rightarrow P \) was measure with different concentrations of reactants:

\[
\begin{array}{|c|c|c|}
\hline
\text{Exp.} & [D] (M) & [E] (M) & \text{Rate (M/s)} \\
\hline
1 & 0.20 & 0.20 & 2.0 \times 10^{-5} \\
2 & 0.40 & 0.20 & 2.0 \times 10^{-5} \\
3 & 0.20 & 0.40 & 8.0 \times 10^{-5} \\
\hline
\end{array}
\]

The rate law for the reaction is:

a. \( r = k[D][E] \)
b. \( r = k[D]^2 \)
c. \( r = k[E]^2 \)
d. \( r = k[D][E]^2 \)
e. \( r = k[D]^2[E] \)

8) The initial rate of reaction for \( D + E \rightarrow P \) was measure with different concentrations of reactants:

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Exp.} & [D] (M) & [E] (M) & \text{Rate (M/s)} \\
\hline
1 & 0.20 & 0.20 & 2.0 \times 10^{-5} \\
2 & 0.40 & 0.20 & 2.0 \times 10^{-5} \\
3 & 0.20 & 0.40 & 8.0 \times 10^{-5} \\
\hline
\end{array}
\]

The rate law for the reaction is \( r = k[E]^2 \). The rate constant \( k \) is equal to:

a. \( 5.0 \times 10^{-4} \)
b. \( 8.0 \times 10^{-6} \)
c. \( 2.0 \times 10^{-5} \)
d. \( 6.4 \times 10^{-5} \)
e. \( 5.0 \times 10^{-5} \)

4. Integrated rate laws

a. Integrated rate laws are equations involving only concentration and time and not the reaction rate (i.e., the change in concentration).
b. There are few integrated rate law expressions depending on the order of the reaction as well as other associated quantities including half-life, denoted $t_{1/2}$, which is the time to reduce the original concentration to half:

<table>
<thead>
<tr>
<th>Order</th>
<th>Rate law</th>
<th>Unit of $k$</th>
<th>Integrated rate law</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{Rate} = k[A]$</td>
<td>time$^{-1}$</td>
<td>$\ln \left( \frac{[A]_t}{[A]_0} \right) = -kt$</td>
</tr>
<tr>
<td>2</td>
<td>$\text{Rate} = k[A]^2$</td>
<td>M$^{-1}$·time$^{-1}$</td>
<td>$\frac{1}{[A]_0} = kt + \frac{1}{[A]_0}$</td>
</tr>
<tr>
<td>0</td>
<td>$\text{Rate} = k$</td>
<td>M·time$^{-1}$</td>
<td>$[A]_t = -kt + [A]_0$</td>
</tr>
</tbody>
</table>

Reorganized integrated rate law

Linear graph

Math function

<table>
<thead>
<tr>
<th>Half-life</th>
<th>$t_{1/2} = \frac{\ln 2}{k}$</th>
<th>$t_{1/2} = \frac{1}{k[A]_0}$</th>
<th>$t_{1/2} = \frac{[A]_0}{2k}$</th>
</tr>
</thead>
</table>

- Half-life for first-order reactions is independent of concentration.
- For first order reactions, because the integrated rate law involves a ratio of concentrations, this ratio can be replaced by a ratio of masses: $\ln \left( \frac{[A]_t}{[A]_0} \right) = \ln \frac{m_t}{m_0} = -kt$.
- Math notes: $\ln a + \ln b = \ln(a \times b)$ and $\ln a - \ln b = \ln \left( \frac{a}{b} \right)$
9) A chemical reaction A → B + C is first order in A and has a rate constant of $1.2 \times 10^{-3}$ min$^{-1}$. If the initial concentration of A is 0.40 M, how much time must pass in order to reduce the concentration of A to 0.22 M?

a. $5.0 \times 10^2$ min
b. $4.3 \times 10^{-4}$ min
c. $2.2 \times 10^2$ min
d. $3.0 \times 10^2$ min
e. $5.0 \times 10^4$ min

10) Fluorine-18 is commonly used as a source of positrons for use in tumor imaging (PET scanning). The half-life of fluorine-18 is 110 minutes. A vial of a solution containing 5.00 grams of fluorine-18 is standing in the imaging laboratory. After 27 minutes, how much fluorine-18 remains?

a. 1.78 grams
b. 3.54 grams
c. 2.50 grams
d. 4.22 grams
e. 8.44 grams

11) At 300 K the reaction below obeys the rate law $rate = k[NOCl]^2$ where $k= 2.8 \times 10^{-5}$ M$^{-1}$·s$^{-1}$. 2NOCl → 2NO + Cl$\textsubscript{2}$

Suppose 1.0 mole of NOCl is introduced into a 2.0-liter container at 300 K. How much NOCl will remain after 30 minutes?

a. 0.77 mol
b. 0.95 mol
c. 0.87 mol
d. 0.84 mol
e. 0.65 mol

12) At a certain temperature the reaction 2B → C + D obeys the rate-law expression $Rate = (1.14 \times 10^{-3}$ M$^{-1}$ · s$^{-1}$)[B]$^2$.

If 5.00 mol of B is initially present in a 1.00-L container at that temperature, how long would it take for 2.00 mol of B to be consumed at constant temperature?

a. 224 s
b. 73.0 s
c. 58.5 s
d. 46.0 s
e. 117 s

13) Which of the following statements concerning graphical methods for determining reaction order is false?

a. For a first-order reaction the plot of ln [A] vs. time gives a straight line.
b. For a zero-order reaction the plot of [A] vs. time gives a straight line.
c. For a first-order reaction the slope of the straight-line graph equals -k.
d. For a second-order reaction the plot of [A]$^2$ vs. time gives a straight line.
e. For a second-order reaction the plot of 1/[A] vs. time gives a straight line.
5. Rate constant dependence on temperature
   a. The rate constant (and therefore the reaction rate) depends on temperature.
      □ The rate constant (almost) always increases as temperature increases.
      □ An old rule, that might be applicable on a subset of reactions, is that rate constant doubles when temperature increases.
   b. Arrhenius observed that a plot of \( \ln k \) versus \( 1/T \) is linear.
      □ This linear behavior can be written as:
      \[
      \ln k = a - \frac{b}{T} \quad \text{where} \quad b = \frac{E_a}{R}
      \]
   c. Reorganizing the expression gives the Arrhenius equation.
      □ \( k = A e^{-\frac{E_a}{RT}} \) or

      □ \( A \) is the pre-exponential factor,
      □ \( E_a \) is the activation energy,
      □ \( R = 8.3145 \text{ J/mol·K} \) and \( T \) should be in K.
   d. Typical \( E_a \) values are in the range 2-25 kcal/mol (or 10-100 kJ/mol).
   e. Arrhenius equation can be reorganized further by looking at 2 different temperatures and eliminating the pre-exponential factor.
      □ \( \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \) or

      □ This expression can be used to determine \( E_a \) based on rate constants at two different temperatures or to determine rate constant at a different temperature given \( E_a \).
14) Reaction rate increases as temperature increases because:
   a. molecular motion is increased, causing more collisions to occur
   b. more molecules are able to overcome the activation energy barrier
   c. \( \Delta H \) is a smaller value at higher temperatures
   d. all of the above
   e. a and b only

15) As a general rule for reactions near room temperature, for every 10\(^\circ\) C rise in the temperature of a reaction, the rate of the reaction:
   a. is doubled
   b. is halved
   c. remains unchanged
   d. is relative to the observer
   e. is quadrupled

16) A first-order reaction has a rate constant of \( 7.57 \times 10^{-3} \text{ s}^{-1} \) at 105\(^\circ\)C and \( 5.22 \times 10^{-3} \text{ s}^{-1} \) at 95\(^\circ\)C. What is the activation energy for this reaction?
   a. +3.08 kJ/mol
   b. –3.08 kJ/mol
   c. –42.9 kJ/mol
   d. +42.9 kJ/mol
   e. +5.17 kJ/mol

C. Reaction Mechanisms (O-III.9 \( \rightarrow \) O-III.11)

1. Types of reactions
   a. Based on their complexity of the path it takes for reactants to transform into products, chemical reactions can be classified as:
      □ elementary reactions
      □ complex reactions
2. Elementary reactions
   
a. Elementary reactions are simple processes that have some common characteristics.
   
   □ They are one-step processes, characterized by energy profiles in which energy goes up from the reactants, reaches a maximum at the transition state (or activated complex), and then goes lower to the products.
   
   □ A limited number of bonds are broken or formed during the reaction.
   
   □ A limited number of molecules (1, 2, or 3) are participating in the reaction as reactants or products.

b. If a reaction were elementary in the forward direction, it is also elementary in the reverse direction.

c. If the reaction has more than 3 molecules of reactants (or products), it cannot be elementary.

d. For elementary reactions (and elementary reactions only), the rate law is known, and it is based on the number of reactant molecules participating called molecularity.

<table>
<thead>
<tr>
<th>Molecularity</th>
<th>Name</th>
<th>Reaction</th>
<th>Rate Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>unimolecular</td>
<td>A → Products</td>
<td>Rate = k[A]</td>
</tr>
<tr>
<td>2</td>
<td>bimolecular</td>
<td>A + B → Products</td>
<td>Rate = k[A][B]</td>
</tr>
<tr>
<td>3</td>
<td>termolecular</td>
<td>A + B + C → Products</td>
<td>Rate = k[A][B][C]</td>
</tr>
</tbody>
</table>
3. Complex reactions
   a. Complex reactions are reactions that consist of two or more elementary reactions.
   b. The series of elementary reactions making up the complex reactions, written in the order of occurrence, is called
      □ The reaction mechanism involves intermediates
      □ An intermediate is a species that is formed in a step of a complex reaction and is consumed in a consequent step.
   c. There is a correlation (although generally complicated) between the reaction mechanism and the rate law.
      □ Rate law $\iff$ Mechanism
      □ The rate law can contain the concentrations of reactants and/or products but not those
   d. Sometimes a mechanism has a step that is slower than all the other steps.
      □ The rate of the slowest step will determine the rate of the overall process.
      □ This slowest step in the mechanism is called
      □ This slowest step in the mechanism is typically either the first or the second step of the mechanism.
      □ Although the concentrations are also important, the slowest step in the mechanism is typically a step with
      □ One can “apply the rate-determining-step approximation” to determine the rate law of the reaction.
17) For the following elementary reaction, what is the rate law and what is the molecularity?

\[ 2\text{NOCl} \rightarrow 2 \text{NO} + \text{Cl}_2 \]

a. unimolecular, rate = k[NOCl]
b. bimolecular, rate = k[NOCl]^2
c. bimolecular, rate = k[NO][Cl_2]
d. termolecular, rate = k[NO]^2[Cl_2]
e. unimolecular, rate = k[NOCl]^2

18) In regards to reaction mechanisms, the rate of the reaction is determined by the rate of the _____ step in the mechanism.

a. first
b. last
c. slowest
d. fastest
e. baby

19) Ozone, O_3, can be decomposed in the stratosphere by reaction with nitrogen oxide, NO, from high flying jet aircraft. The following mechanism has been proposed:

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_3 + \text{O} \quad \text{(slow)} \\
\text{NO}_3 + \text{O} & \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{(fast)} \\
\text{O}_3 + \text{NO} & \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{(overall)}
\end{align*}
\]

What is the rate law that corresponds to this mechanism?

a. rate = k[NO_3][O]
b. rate = k[NO][O_3]
c. rate = k[NO_2][O_2]
d. rate = k[NO]^2
e. rate = k[O_3]

20) Consider the following proposed mechanism. If this mechanism for the overall reaction were correct, and if \( k_1 \) were much less than \( k_2 \), then the observed rate law would be

\[
\begin{align*}
2\text{A} & \overset{k_1}{\rightarrow} \text{C} + \text{I} \\
\text{I} + \text{B} & \overset{k_2}{\rightarrow} \text{C} + \text{D}
\end{align*}
\]

a. rate = \( k_1[A] \)
b. rate = \( k_2[I][B] \)
c. rate = \( k_1[A]^2 \)
d. rate = \( k_1[A]^2 - k_2[C][D] \)
e. rate = \( k_1 k_2[A]^2[I][B] \)

21) Which statement concerning a possible mechanism for a reaction is false?

a. A possible mechanism must be consistent with the experimental data.
b. Each elementary step is represented by a balanced equation.
c. The elementary steps must add to give the equation for the overall reaction.
d. For all reactions the experimentally determined reaction orders of the reactants indicate the number of molecules of those reactants involved in the slow step of the mechanism.
e. The speed of the slow step limits the rate at which the overall reaction occurs.

4. Catalysis

a. Catalysis refers to chemical transformations that use of a catalyst.
b. A catalyst is a substance that is participating in reaction (without being reactants or products) and speeds up the reaction.

c. A catalyst speeds up the reaction by providing a different, faster reaction pathway, which has

- \( \Delta H \) stays the same for both reactions.

d. Catalysis (or the catalyst) can be:

- homogeneous (when the catalyst is in the same phase as the reactants and products),
- heterogeneous (when the catalyst is in a different phase).

e. Enzymes are a special case of catalysis.

- They are large protein molecules, denoted by E.
- They act on a substrate, denoted by S.
- The catalyzed pathway, going through a substrate-enzyme complex (denoted SE),

O-III.11

22) Catalysts:

- Lower the activation energy of a given reaction
- Provide a different mechanism for a given reaction
- Increase the rate at which reactants are converted to products but are not consumed in the reaction
- All of the above
- None of the above

O-III.11

23) A catalyst (usually a solid) that is not in the same phase with the reactants is:

- homogeneous
- heterogeneous
Unit IV
Chemical Equilibrium

Unit Objectives

O-IV.1  Learn terminology: Reversible process, Chemical equilibrium, Reaction quotient, Le Chatelier’s principle

O-IV.2  Define and explain the concepts of reversible processes and equilibrium

O-IV.3  Write expression and discuss values of equilibrium constant written as a function of molarities

O-IV.4  Write expression of equilibrium constant based on partial pressures and its relation to $K_c$

O-IV.5  Carry out manipulations of equilibrium expressions and values

O-IV.6  Apply the relation between equilibrium constant and rate constants

O-IV.7  Define reaction quotient and compare with value of $K_c$

O-IV.8  Determine $K_c$ value from equilibrium concentrations

O-IV.9  Determining equilibrium concentrations from $K_c$ value

O-IV.10 Discuss factors affecting equilibria and Le Chatelier’s principle

O-IV.11 Choose optimal reaction conditions (high/low pressure/temperature)
A. Chemical Equilibrium and Equilibrium Constant (O-IV.2 $\rightarrow$ O-IV.7)

1. Chemical equilibrium
   a. Consider a reaction taking place in an aqueous solution:
      □ $aA(aq) + bB(aq) \rightarrow cC(aq) + dD(aq)$
   b. Sometimes the reaction does not go to completion, so some A and B remained untransformed.
   c. A situation is reached when “nothing changes” (i.e., the concentrations/amounts of A, B, C, and D are constant).
   d. The direct process ($A + B \rightarrow C + D$) and the reverse process ($C + D \rightarrow A + B$) both happen (with equal speed so that the net change is zero).
   e. This is the case of a reversible reaction being at equilibrium (so concentrations do not change).
   f. A reversible reaction is a reaction that can take place in both directions.
      □ from left to right
      □ from right to left
   g. A reversible reaction is denoted by a double half arrow sign: $\rightleftharpoons$.
      □ $aA(aq) + bB(aq) \rightleftharpoons cC(aq) + dD(aq)$
      □ Double arrow sign ($\rightleftharpoons$) is acceptable.

2. Equilibrium constant
   a. The equilibrium situation (i.e., a reversible reaction that has reached the state in which nothing apparently changes) is characterized by the equilibrium constant $K_c$.
      □ “c” means that $K$ is expressed based on
   b. The equilibrium constant is $K_c = \frac{[C]^{c}_{eq}[D]^{d}_{eq}}{[A]^{a}_{eq}[B]^{b}_{eq}}$ or $K_c = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$
      □ a ratio of
      □ products/reactants
      □ raised to the power of stoichiometric coefficients
the concentrations are at equilibrium

The equilibrium constant is called constant because it is independent on the concentrations/amounts of reactants or products.

It is however dependent on the (as we will see later).

The equilibrium constant for reactions in gas phase is similar to \( K_c \) but used (partial) pressures: 

\[
K_P = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}
\]

Reactions in gas phase at equilibrium can be also characterized by \( K_c \) and there is a relation between \( K_c \) and \( K_P \).

\[
K_P = K_c (RT)^\Delta n
\]

where

For heterogeneous (i.e., reactants participants in multiple phases) reactions at equilibrium, a thermodynamic equilibrium constant (denoted \( K \) or \( K_a \)) can be defined.

use concentrations for solutions
use pressures for gas phase
the solvent, pure liquids or solids

The magnitude of the equilibrium constant indicates what is mostly present when the equilibrium is reached.

\[
K >> 1 \text{ (or } K > 100) \Rightarrow \text{there are mostly at equilibrium}
\]

\[
K << 1 \text{ (or } K < 0.01) \Rightarrow \text{there are mostly at equilibrium}
\]

\[
K \approx 1 \text{ (or } 0.01 < K < 100) \Rightarrow \text{both reactants and products are present (significantly) at equilibrium}
\]
O-IV.2-O-IV.3

1) Which of the statements concerning equilibrium is false?

a. A very large value of equilibrium constant indicates that the reaction favors the reactants.
b. The rate of forward reaction is equal to the rate of reverse reaction.
c. The equilibrium constant is independent of concentrations.
d. Generally, the concentrations of reactants and products are not equal.
e. Equilibrium is dynamic, with two opposing processes balancing one another.

2) Consider the following reaction. What would be the equilibrium constant expression?

\[ \text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g) \]

a. \( [\text{H}_2][\text{CO}]^3 \) \( / \) \( [\text{CH}_4][\text{H}_2\text{O}] \)
b. \( [\text{CH}_4][\text{H}_2\text{O}] \) \( / \) \( [\text{H}_2][\text{CO}]^3 \)
c. \( [\text{H}_2\text{O}] \) \( / \) \( [\text{CO}][\text{H}_2]\text{O} \)
d. \( [\text{CH}_4][\text{H}_2\text{O}] \) \( / \) \( [\text{H}_2][\text{CO}]^3 \)

3. Properties of equilibrium constant

a. If chemical equations are combined (added, subtracted, etc.) to create new chemical equations, expressions and values of equilibrium constants also change.

b. When adding two equations to create a new equation, the new equilibrium constant is the product of the original two.
   \[ (3) = (1) + (2) \Rightarrow \]

c. When an equation is doubled to create a new equation, the new equilibrium constant is the square of the original one.
   \[ (4) = (1) + (1) \Rightarrow \]
d. When an equation is reversed to create a new equation, the new equilibrium constant is the reciprocal of the original one. 
\[ (5) = - (1) \Rightarrow \]

\[ \square \]

e. When two equations are subtracted to create a new equation, the new equilibrium constant is the ratio of the original two. 
\[ (6) = (1) - (2) \Rightarrow \]

\[ \square \]

**O-IV.5**

5) If the equilibrium constant at a certain temperature is $2.1 \times 10^{13}$ for the following reaction,

$4\text{HCl}(g) + \text{O}_2(g) \rightleftharpoons 2\text{Cl}_2(g) + 2\text{H}_2\text{O}(g)$

calculate the value of the equilibrium constant at the same temperature for

$\text{Cl}_2(g) + \text{H}_2\text{O}(g) \rightleftharpoons 2\text{HCl}(g) + \frac{1}{2}\text{O}_2(g)$.

a. $5.3 \times 10^{12}$
b. $3.8 \times 10^3$
c. $1.2 \times 10^{-14}$
d. $4.7 \times 10^{-4}$
e. $2.2 \times 10^{-7}$

**O-IV.5**

6) If $K_c$ at a certain temperature for $\text{A}(g) \rightleftharpoons \text{B}(g)$ reaction is 2.5, and $K_c$ for $\text{B}(g) \rightleftharpoons \text{C}(g) + \text{D}(g)$ reaction is 3.0, what is the $K_c$ for $\text{A}(g) \rightleftharpoons \text{C}(g) + \text{D}(g)$ reaction?

a. 5.5
b. 7.5
c. 2.5
d. 2.75
e. 3.0

4. Equilibrium constant dependence on the rate constants

a. Consider a simple chemical reaction at equilibrium $\text{A} \rightleftharpoons \text{B}$, and assume simple first-order rate laws: Rate$_f$ = $k_f[A]$ and Rate$_r$ = $k_r[B]$.

\[ \square \ f \text{ subscript stands for forward, and } r \text{ subscript stands for reverse.} \]

b. The equilibrium constant is equal to the ratio of forward to reverse rate constants: $K = k_f / k_r$.

\[ \square \ At \ equilibrium, \ forward \ rate \ is \ equal \ to \ reverse \ rate, \ Rate_f = Rate_r. \]

\[ \square \ K = \frac{[B]}{[A]} = \frac{k_f}{k_r} \]

5. Reactant quotient

a. The equilibrium constant describes the reaction/system at equilibrium but a quantity similar to it can be defined for a reaction/system that did not reach equilibrium yet.
b. Reaction quotient (\(Q_c\) or \(Q_P\) or \(Q\) or \(Q_a\)) is a quantity that has the same expression as the equilibrium constant except that the concentrations/pressures are not necessarily the ones at the equilibrium.

\[ Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]

where “i” stands for instantaneous (or current).

\(Q_P\) is similar to \(K_P\).

c. When there are more products than at equilibrium so the reaction will proceed toward equilibrium by consuming some of the

\[ \square \] Actually, both forward and reverse are occurring but the reverse reaction is faster so the net change is the reverse reaction.

d. When there are less products than at equilibrium so the reaction will proceed toward equilibrium by consuming some of the

\[ \square \] Actually, both forward and reverse are occurring but the forward reaction is faster so the net change is the forward reaction.

e. When \(Q = K\), reaction is at equilibrium so

\[ \square \] The relative values of \(Q\) and \(K\) can be used to determine in what direction a reversible reaction is taken place.

**O-IV.6**

7) For a reversible reaction with a one-step mechanism, \(A \rightleftharpoons B\), the rate of the forward reaction is \(\text{rate}_f = 3.2 \times 10^{-6} \text{ s}^{-1} [A]\) and the rate of the reverse reaction is \(\text{rate}_r = 4.6 \times 10^{-4} \text{ s}^{-1} [B]\). What is the value of \(K_c\) for this reaction?

a. \(2.5 \times 10^{-11}\)

b. \(7.0 \times 10^9\)

c. \(1.4 \times 10^2\)

d. \(1.5 \times 10^{-9}\)

e. \(7.0 \times 10^{-3}\)

**O-IV.7**

8) Which of the following statements about the reaction quotient is false?

a. It has the same expression as \(K_c\).

b. If \(Q > K_c\), the reaction must move to equilibrium by forming more products.

c. If \(Q < K_c\), the rate of forward reaction is larger than the rate of reverse reaction.

d. If \(Q = K_c\), the reaction is at equilibrium.

e. The value of \(Q\) is determined by the concentrations of reactants and products.
B. Concentrations at Equilibrium (O-IV.8 → O-IV.9)

1. Determining the equilibrium constant
   a. There is a direct relation between the equilibrium constant and the equilibrium concentrations.
   b. The equilibrium constant can be determined from the equilibrium concentrations by writing the correct expression and carry out the calculations.
   c. Additional simple stoichiometry calculations might be necessary if some initial concentrations are provided instead of equilibrium concentrations.

2. Determining the equilibrium concentrations
   a. The equilibrium constant value is necessary to determine the concentrations at equilibrium.
   b. If the equilibrium constant and the other equilibrium concentrations are given, write the expression of the equilibrium constant and solve for the unknown concentration.
   c. If the equilibrium constant and the initial concentrations are given, the equilibrium concentrations can be determined by following a multi-step procedure.
      □ Set up a table with all R and P (under the chemical equation).
      □ Set up three lines ICE (initial, change, and equilibrium).
      □ Put the initial concentrations of R and P (some could be 0).
      □ Define one change as “$x$” and solve for all other changes based on that choice (getting $-x$, $+2x$, etc.).
      □ Sum I and C entries to get the E entries (depending on $x$).
      □ Write the $K$ expression based on E entries to get an equation in $x$.
      □ Solve for $x$ and therefore for the desired E entry.
There could be multiple possibilities leading to different types of equations.

e. Examples:

<table>
<thead>
<tr>
<th>Example 1:</th>
</tr>
</thead>
<tbody>
<tr>
<td>A \rightleftharpoons C</td>
</tr>
<tr>
<td>Initial</td>
</tr>
<tr>
<td>Change</td>
</tr>
<tr>
<td>Equilibrium</td>
</tr>
<tr>
<td>(K_c = \frac{[C]_0 + x}{[A]_0 - x})</td>
</tr>
<tr>
<td>- This is a first-order equation in (x).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Example 2:</th>
</tr>
</thead>
<tbody>
<tr>
<td>A + B \rightleftharpoons C + D</td>
</tr>
<tr>
<td>Initial</td>
</tr>
<tr>
<td>Change</td>
</tr>
<tr>
<td>Equilibrium</td>
</tr>
<tr>
<td>(K_c = \frac{([C]_0 + x)^2}{([A]_0 - x)^2} \quad \sqrt{K_c} = \frac{[C]_0 + x}{[A]_0 - x})</td>
</tr>
<tr>
<td>- This is a first-order equation in (x).</td>
</tr>
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</table>

<table>
<thead>
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<th>Example 3:</th>
</tr>
</thead>
<tbody>
<tr>
<td>A + B \rightleftharpoons 2C</td>
</tr>
<tr>
<td>Initial</td>
</tr>
<tr>
<td>Change</td>
</tr>
<tr>
<td>Equilibrium</td>
</tr>
<tr>
<td>(K_c = \frac{([C]_0 + 2x)^2}{([A]_0 - x)^2} \quad \sqrt{K_c} = \frac{[C]_0 + 2x}{[A]_0 - x})</td>
</tr>
<tr>
<td>- This is a first-order equation in (x).</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>Example 4:</th>
</tr>
</thead>
<tbody>
<tr>
<td>A + B \rightleftharpoons C + D</td>
</tr>
<tr>
<td>Initial</td>
</tr>
<tr>
<td>Change</td>
</tr>
<tr>
<td>Equilibrium</td>
</tr>
<tr>
<td>(K_c = \frac{([C]_0 + x)([D]_0 + x)}{([A]_0 - x)([B]_0 - x)})</td>
</tr>
<tr>
<td>- This is a second-order equation in (x).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Example 5:</th>
</tr>
</thead>
<tbody>
<tr>
<td>A + B \rightleftharpoons C</td>
</tr>
<tr>
<td>Initial</td>
</tr>
<tr>
<td>Change</td>
</tr>
<tr>
<td>Equilibrium</td>
</tr>
<tr>
<td>(K_c = \frac{([C]_0 + x)}{([A]_0 - x)([B]_0 - x)})</td>
</tr>
<tr>
<td>- This is a second-order equation in (x).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Example 6:</th>
</tr>
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<tbody>
<tr>
<td>A + 4B \rightleftharpoons C</td>
</tr>
<tr>
<td>Initial</td>
</tr>
<tr>
<td>Change</td>
</tr>
<tr>
<td>Equilibrium</td>
</tr>
<tr>
<td>(K_c = \frac{([C]_0 - x)}{(x)(4x)^4})</td>
</tr>
<tr>
<td>- This is a fifth-order equation in (x).</td>
</tr>
</tbody>
</table>
9) What is the value of $K_c$ for the reaction

$$2A(g) + 3B(g) \rightleftharpoons 2C(g) + D(g)$$

if at equilibrium $[A] = 0.60 \ M$, $[B] = 0.30 \ M$, $[C] = 0.10 \ M$ and $[D] = 0.50 \ M$?

a. 0.51  
b. 0.088  
c. 0.15  
d. 2.4  
e. 1.9

10) Consider $A + 2B \rightleftharpoons 2C + D$ reaction in which all reactants and products are gases. 1.00 mol of A and 2.00 mol of B are placed in a 5.0-liter container. After equilibrium has been established, 0.50 mol of D is present in the container. Calculate the equilibrium constant, $K_c$, for the reaction.

a. 0.15  
b. 5.0  
c. 3.0  
d. 1.0  
e. 0.33

11) In a 1.0-liter container there are, at equilibrium, 0.10 mole H$_2$, 0.20 mole N$_2$, and 0.40 mole NH$_3$. What is the value of $K_c$ for this reaction at this temperature?

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

a. 0.0012  
b. 20  
c. $8.0 \times 10^2$  
d. 0.050  
e. 8.0

12) For $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ reaction, the equilibrium constant, $K_c$, is 0.50 at a certain temperature. When a certain reaction mixture reaches equilibrium, the concentration of O$_2$ is found to be 2.0 M, while the concentration of SO$_3$ is found to be 10 M. What is the equilibrium concentration of SO$_2$ in this mixture?

a. 0.10 M  
b. 0.50 M  
c. 5.0 M  
d. 10 M  
e. 1.0 M

13) At a certain temperature, a simple reaction A(g) $\rightleftharpoons$ B(g) has an equilibrium constant of 4.0. If the initial concentration of A in the reaction vessel is 4.0 M and there is no B present, what will be the concentration of A when the system reaches equilibrium?

a. 3.20 M  
b. 2.00 M  
c. 0.16 M  
d. 3.84 M  
e. 0.80 M

14) What is the equilibrium concentration of HI(g) if the reaction starts with 0.500 mol each of H$_2$ and I$_2$ in a 1.00-L vessel?

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

The equilibrium constant is 49.7 at 458°C.

a. 0.17 M  
b. 0.78 M  
c. 1.35 M  
d. 0.49 M  
e. 0.92 M
C. Changing Equilibrium Conditions (O-IV.10 $\rightarrow$ O-IV.11)

1. Le Chatelier’s Principle
   a. Le Chatelier’s principle describe how a system at equilibrium will evolve when

   b. If changes occur for a system at equilibrium, the system will evolve toward a new equilibrium position by

   □ This is the statement of Le Chatelier’s principle.

2. Changes in amounts of reaction participants
   a. At equilibrium, $K = Q$.
   b. When reactants are added or products are removed, the system will shift in the forward direction (i.e., by creating products).
      □
   c. When reactants are removed or products are added, the system will shift in the backward direction (i.e., by creating reactants).
      □

3. Changes in temperature
   a. Changing the temperature changes the value of the equilibrium constant (depending if the reaction is exothermic or endothermic).
   b. There is a formula, named van’t Hoff equation, showing how equilibrium constant varies with the temperature.
      □ $\ln \frac{K_{T_2}}{K_{T_1}} = \frac{\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$
   c. For an endothermic reaction ($\Delta H_{\text{rxn}} > 0$), when temperature is increased, the system will shift in the direction (to use the extra energy).
      □
d. For an endothermic reaction ($\Delta H_{\text{rxn}} > 0$), when temperature is decreased, the system will shift in the \[\square\] direction.

e. For an exothermic reaction ($\Delta H_{\text{rxn}} < 0$), when temperature is increased, the system will shift in the \[\square\] direction (to produce less energy).

f. For an exothermic reaction ($\Delta H_{\text{rxn}} < 0$), when temperature is decreased, the system will shift in the \[\square\] direction (to produce more energy).

4. Changes in pressure
   a. Only the changes in pressure by modifying the volume are discussed here.
      \[\square\] Reducing the volume increases the pressure.
   b. Changing the pressure of a system at equilibrium effect only reactions that involve gases.
   c. Look at the number of moles of gasses on the reactant and the product sides:
      \[\square\] A higher pressure favors the side with number of moles of gases, and the equilibrium will shift toward that side.
      \[\square\] A lower pressure favors the side with number of moles of gases, and the equilibrium will shift toward that side.

5. Other comments
   a. Catalysts do not change the equilibrium (concentrations).
      \[\square\] They speed up reactions.
      \[\square\] They speed up reaching the equilibrium situation.
   b. There is a specific type of problem asking what conditions (i.e., high/low $T$ and high/low $P$) lead to increased product formation at equilibrium.
15) For $A(g) + B(g) \rightleftharpoons C(g) + D(g)$ reaction at equilibrium, a 1.0-liter container was found to contain 0.20 mol of $A$, 0.20 mol of $B$, 0.40 mol of $C$, and 0.40 mol of $D$. If 0.10 mol of $A$ and 0.10 mol of $B$ are added to this system, which of the following statements is true?

a. The system remains in equilibrium.
b. The value of $K_c$ decreases.
c. More reactants are formed to increase the $Q$ value.
d. More products are formed to increase the $Q$ value.
e. $Q > K_c$

16) For $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ at equilibrium, the removal of some of the $H_2O(g)$ would cause (according to LeChatelier's principle)

a. the amount of $CO(g)$ to remain constant while the amount of $H_2O(g)$ increases to the original equilibrium concentration.
b. more $H_2(g)$ to be form.
c. more $CO(g)$ to be form.
d. more $CO_2(g)$ to be form.
e. no change in the amounts of products or reactants.

17) Consider the following reversible reaction at equilibrium.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92.2 \text{ kJ}$

Which response contains all the choices below that refer to changes that would shift the equilibrium to the right, and no other choices?

I. add $H_2$
II. remove $N_2$
III. add an iron catalyst
IV. increase $T$ at constant $P$
V. increase $P$ at constant $T$ by decreasing $V$

a. I and V  b. I, IV and V  c. III and V
d. IV and V  e. I, II and III

18) Consider a reaction for which $K_{298} = 16.3$ and $\Delta H^0 = -116 \text{ kJ/mol}$. Which of the following statements is true?

a. The value of $K$ would be larger at 398 K.
b. A decrease in temperature will cause the forward reaction to be favored more.
c. The reverse reaction is favored at 298 K.
d. An increase in temperature will cause the forward reaction to be favored more.
e. The reaction is endothermic.

19) For the gas phase reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3 \Delta H^0 = -320. \text{ kJ}$ for the forward reaction. In order to increase the yield of $SO_3$, the reaction should be run

a. at high $P$, low $T$.
b. at high $P$, but is independent of $T$.
c. at low $P$, low $T$.
d. at high $P$, high $T$.
e. at low $P$, high $T$.

20) Exactly one mol/L of each of the four gases involved in $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ reaction is placed in a reactor at 200°C and allowed to reach equilibrium. What is the equilibrium concentration of $H_2O$? $K_c = 2.38$ at 200°C.

a. 0.213 $M$
b. 2.38 $M$
c. 1.21 $M$
d. 1.0 $M$
e. 0.787 $M$
Unit V
Acids and Bases

Unit Objectives

O-V.1 Learn terminology: Names for acids, bases & ions, Bronsted acids, Bronsted bases, Conjugate acid-base pair, Lewis acids, Lewis bases, Self-ionization, Ion-product for water

O-V.2 Identify and describe Arrhenius acids and bases, acid-base neutralization reactions, and molecular and ionic equations – (Chapter 8 review)

O-V.3 Identify strong (or weak) acids and bases – (Chapter 8 review)

O-V.4 Apply acid structure-strength relationships

O-V.5 Describe Lewis acids and bases and some of their properties

O-V.6 Identify and describe Bronsted acids and bases & conjugate acid-base pairs

O-V.7 Describe (and carry out calculations involving) autoionization of water, [H₃O⁺] and [OH⁻] in solution, pH and pOH

O-V.8 Carry out calculation for solutions of strong acids ([H₃O⁺], [OH⁻], pH and pOH)

O-V.9 Carry out calculation for solutions of strong bases ([H₃O⁺], [OH⁻], pH and pOH)

O-V.10 Describe acid-base properties of hydroxides and oxides
A. Acids, Bases and Acid-Base Reactions (O-V.2 → O-V.7)

1. Acids and bases
   a. There are three definitions/theories of acids and bases, summarized in the table below:

<table>
<thead>
<tr>
<th>Definition</th>
<th>Acids</th>
<th>Bases</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arrhenius</td>
<td>make H⁺</td>
<td>make OH⁻</td>
<td></td>
</tr>
<tr>
<td>Bronsted-Lowry</td>
<td>give H⁺</td>
<td>accept H⁺</td>
<td></td>
</tr>
<tr>
<td>Lewis</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

b. When present in solution, H⁺ exists actually as H₃O⁺.
   □ H₃O⁺ is called
   □ OH⁻ (sometimes written as HO⁻) is called

c. Acids and bases are classified (just as electrolytes are) as:
   □ strong – when they completely ionize/dissociate in water
   □ weak – when they partially ionize/dissociate in water

d. The strong acids and bases are listed below.

<table>
<thead>
<tr>
<th>Strong acids</th>
<th>Strong bases</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl – hydrochloric acid</td>
<td>LiOH – lithium hydroxide</td>
</tr>
<tr>
<td>HBr – hydrobromic acid</td>
<td>NaOH – sodium hydroxide</td>
</tr>
<tr>
<td>HI – hydroiodic acid</td>
<td>KOH – potassium hydroxide</td>
</tr>
<tr>
<td>HClO₃ – chloric acid</td>
<td>RbOH – rubidium hydroxide</td>
</tr>
<tr>
<td>HClO₄ – perchloric acid</td>
<td>Ca(OH)$_2$ – calcium hydroxide</td>
</tr>
<tr>
<td>HNO₃ – nitric acid</td>
<td>Sr(OH)$_2$ – strontium hydroxide</td>
</tr>
<tr>
<td>H₂SO₄ – sulfuric acid</td>
<td>Ba(OH)$_2$ – barium hydroxide</td>
</tr>
</tbody>
</table>
2. Neutralization reactions and chemical equations
   
a. A neutralization reaction (or an acid-base reaction or a proton-transfer reaction) is a reaction between an acid and a base to give salt and water:
   - Acid + Base → Salt + Water
   - 
   
b. A salt is an ionic compound in which:
   - the cation is
   - the anion is

c. A reaction is described by a chemical equation, and, typically the molecular equation is used, but for reactions in aqueous solutions, a net ionic equation is preferred.
   - A complete (or total) ionic equation is obtained from the molecular equation by writing the strong electrolytes as
   - A net ionic equation is obtained from the complete ionic equation by removing the spectators ions

2. Example: reaction of hydrochloric acid with sodium hydroxide
   - Molecular equation: HCl(aq) + NaOH(aq) → NaCl(aq) + H₂O(l)
   - Complete (or total) ionic equation:
   
   - Net ionic equation:
e. \( \text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l) \) is the net ionic equation for (almost) all reactions of strong acid with strong bases.

**O-V.2**

1) Which of the following reactions is the net ionic equation for the acid-base reaction between \( \text{H}_2\text{CO}_3 \) and \( \text{Sr(OH)}_2 \)?

- a. \( \text{H}_2\text{CO}_3 + \text{Sr}^{2+} + 2 \text{OH}^- \rightarrow \text{SrCO}_3 + 2 \text{H}_2\text{O} \)
- b. \( 2 \text{H}_3\text{O}^+ + \text{Sr}^{2+} + 2 \text{OH}^- \rightarrow \text{Sr}^{2+} + 4 \text{H}_2\text{O} \)
- c. \( \text{H}_2\text{CO}_3 + \text{Sr(OH)}_2 \rightarrow 2\text{H}_2\text{O} + \text{Sr}^{2+} + \text{CO}_3^{2-} \)
- d. \( \text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2 \text{H}_2\text{O} \)
- e. \( 2 \text{H}_3\text{O}^+ + \text{Sr(OH)}_2 \rightarrow 4 \text{H}_2\text{O} + \text{Sr}^{2+} \)

**O-V.2**

3) Which salt is not produced from a strong acid and a strong base?

- a. CsClO
- b. Ca(NO\(_3\))\(_2\)
- c. NaClO\(_4\)
- d. K\(_2\)SO\(_4\)
- e. SrCl\(_2\)

**O-V.2**

4) For which one of the pairs of acid and bases does \( \text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \) represent the correct net ionic equation?

- a. \( \text{CH}_3\text{COOH}, \text{Cu(OH)}_2 \)
- b. \( \text{CH}_3\text{COOH}, \text{Cr(OH)}_3 \)
- c. \( \text{CH}_3\text{COOH}, \text{Ca(OH)}_2 \)
- d. NaOH, HBr
- e. HNO\(_3\), Mg(OH)\(_2\)

**O-V.2**

5) Which pair of acids would each react with barium hydroxide and have the net ionic equation: \( \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \)?

- a. HNO\(_3\) and H\(_2\)CO\(_3\)
- b. HCl and HNO\(_3\)
- c. HBr and HF
- d. HCl and HNO\(_2\)
- e. HClO\(_4\) and H\(_2\)SO\(_4\)
3. Structure-strength relations for acids
   a. The strength of an acid is a measure of how easily an HX acid dissociates into H$^+$ and X$^-$.  
   \[ \text{H} \cdot \text{X} \rightarrow \text{H}^+ + \cdot\text{X}^- \]
   b. How easily this H–X bond (heterolytically) breaks depends on the strength of the bond and the polarity of the bond.  
   \[ \text{The weaker the bond, the easier it breaks, the stronger the acid.} \]
   \[ \text{The more polar the bond, the easier it breaks, the stronger the acid.} \]
   c. The strength of binary acids increases in group from top to bottom:  
   \[ \text{This trend is due to bond strength.} \]
   d. The strength of binary acids increases in period from left to right:  
   \[ \text{This trend is due to bond polarity.} \]
   e. The strength of oxoacids increases with electronegativity of central atom:  
   \[ \text{This trend is due to O–H bond polarity.} \]
   f. The strength of oxoacids increases with number of O in the formula:  
   \[ \text{This trend is due to O–H bond polarity.} \]
   g. The strength of polyprotic acids decreases as:
   h. ClCH$_2$COOH is stronger than CH$_3$COOH.

4. Lewis acids and bases
   a. The most recent and the most comprehensive theory of acids and bases was proposed by Lewis.
   b. A Lewis acid is an electron-pair acceptor and a Lewis base is an electron-pair donor
A + :B → A:B

A–B bond is coordinate covalent.

c. A proton-transfer reaction is a reaction in which H⁺ is the Lewis acceptor and the base is an electron-pair donor so all Bronsted acids and bases are also Lewis acid and bases.

d. Examples:

□ H⁺ + OH⁻ → H₂O

□ BF₃ + NH₃ → F₃B–NH₃ (where BF₃ is the Lewis and NH₃ is the Lewis)

□ Na₂O + SO₃ → Na₂SO₄ (where Na₂O is oxide and SO₃ is oxide – see later)

6) Arrange H₂O, H₂Se, H₂S in order of increasing acid strength:

a. H₂S < H₂Se < H₂O
b. H₂Se < H₂O < H₂S
c. H₂Se < H₂S < H₂O
d. H₂O < H₂Se < H₂S
e. H₂O < H₂S < H₂Se

7) Which one of the following pairs of acids lists the weaker acid first?

a. HNO₃ - HNO₂
b. H₂SO₃ - H₂SeO₃
c. H₂SO₄ - H₂SO₃
d. HClO₄ - HIO₄
e. HClO - HClO₂

8) Which indication of relative acid strength is incorrect?

a. HClO₃ > HBrO₃
b. HI > HF
c. H₃PO₄ > HPO₄²⁻
d. HClO > HClO₄
e. HNO₃ > HNO₂

9) Which statement is not consistent with the Lewis theory of acids and bases?

a. In FeBr₃ + Br⁻ → FeBr₄⁻ reaction, Br⁻ act as a base.
b. H₂O can act as both Lewis acid and Lewis base.
c. An acid is an electron pair acceptor.
d. A base makes available a share in a pair of electrons.
e. In the reaction BF₃ + NH₃ → F₃B:NH₃, the BF₃ functions as a base.
5. Bronsted acids and bases
   a. Reaction of HCl and NH₃: HCl\((aq)\) + NH₃\((aq)\) → NH₄Cl\((aq)\)
      □ This is a proton-transfer reaction that can be written as:
      \[ \text{H}_3\text{O}^+(aq) + \text{NH}_3(aq) \rightarrow \text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \]
      □ H₃O⁺ is a H⁺ donor (i.e., a Bronsted acid) and NH₃ is a H⁺ acceptor (i.e., a Bronsted base).
   b. Reaction of H₂O and NH₃: H₂O\((l)\) + NH₃\((aq)\) ⇌ NH₄⁺\((aq)\) + OH⁻\((aq)\)
      □ This is a reversible proton-transfer reaction where H₂O is the
      and NH₃ is a
      □ For the reverse reaction, OH⁻ is the H⁺ acceptor, i.e., the base.
      □ OH⁻ is the of H₂O.
   c. A conjugate base of a Bronsted acid is the species that is left after H⁺ is
      transferred.
      □ For every Bronsted acid there is one (and only one) conjugate base.
   d. A conjugate acid of a Bronsted base is the species that is created after
      H⁺ is added.
      □ For every Bronsted base there is one conjugate acid.
   e. There are acid-base conjugate pairs.
      □ Example: H₂O – OH⁻
      □ Example: NH₄⁺ – NH₃
      □ Example: H₃O⁺ – H₂O
      □ Example: HNO₃ –
      □ Example: HNO₂ –
   f. There are some species (i.e., molecules or ions) that can act both as an
      acid and as a base and they are called
      □ Examples: H₂O, H₂PO₄⁻, HPO₄²⁻, etc.
   g. The multi-step ionization of H₃PO₄ is interesting.
      □ H₃PO₄ ⇌ H₂PO₄⁻ ⇌ HPO₄²⁻ ⇌ PO₄³⁻
10) Which of the following statements is true?

\[
\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^-
\]
methylamine \hspace{1cm} \text{methylammonium ion}

a. CH₃NH₃⁺ is the conjugate base of CH₃NH₂.
b. There are no conjugate acid-base pairs.
c. H₂O is the conjugate acid of OH⁻.
d. OH⁻ is the conjugate acid of H₂O.
e. CH₃NH₂ is the conjugate base of H₂O.

11) Which of the following does not represent a conjugate acid-base pair?

a. H₂O/OH⁻
b. H₃O⁺/H₂O
c. NH₄⁺/NH₂⁻
d. HCl/Cl⁻
e. HNO₃/NO₃⁻

12) Which one of the following species could not react as a Brønsted-Lowry base?

a. CH₃COO⁻
b. CN⁻
c. NH₄⁺
d. NH₂⁻
e. NH₃

13) Which cannot be both a Brønsted-Lowry acid and a Brønsted-Lowry base?

a. PO₄³⁻
b. HCO₃⁻
c. H₂O
d. H₂PO₄⁻
e. HPO₄²⁻

6. Autoionization of water, pH and pOH

a. Water can act as both acid and base, and it actually ionize by itself (i.e., autoionize).

□ H₂O(l) + H₂O(l) \rightleftharpoons H₃O⁺(aq) + OH⁻(aq)

□ This equilibrium is actually

b. The autoionization of water process is characterized by \( K_w \).

□ \( K_w = \)

□ \( K_w \) is called

□ \( K_w \) expression and value are true only for aqueous solutions.
\( K_w \) is independent of concentrations (i.e., it has the same value for 

pure water or for aqueous solutions of acids or bases) but it is 
dependent on temperature.

c. In pure water,
d. In acidic solutions,
   \( [\text{H}_3\text{O}^+] > 10^{-7} \) and \( [\text{OH}^-] < 10^{-7} \)
e. In basic solutions,
   \( [\text{H}_3\text{O}^+] < 10^{-7} \) and \( [\text{OH}^-] > 10^{-7} \)
f. As the concentrations of \( \text{H}_3\text{O}^+ \) and \( \text{OH}^- \) in solution are typically small, 
it is more convenient to introduce (and use) pH and pOH.
   \( \text{pH} = -\log[\text{H}_3\text{O}^+] \) therefore \( [\text{H}_3\text{O}^+] \)
   \( \text{pOH} = -\log[\text{OH}^-] \) therefore \( [\text{OH}^-] \)
   \( \text{pH} + \text{pOH} = 14.00 \)
g. The number of decimal digits in the value of pH or pOH is equal to the 
number of significant figures in the molar concentration.
h. Examples:

<table>
<thead>
<tr>
<th>pH</th>
<th>[H(_3)O(^+)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0</td>
<td>( 1 \times 10^{-5} )</td>
</tr>
<tr>
<td>4.5</td>
<td>( 2 \times 10^{-12} )</td>
</tr>
<tr>
<td>0.00</td>
<td>2.0</td>
</tr>
</tbody>
</table>

i. For every aqueous solution there are 
relationships between \( [\text{H}_3\text{O}^+] \), \( [\text{OH}^-] \), 
pH, and pOH so giving one quantity, 
one can (and should) be able to 
determine the other three quantities.
14) Calculate the pH of a solution that has the $\text{H}_3\text{O}^+$ concentration of 0.50 $M$.

a. 0.50  
b. -0.30  
c. 7.30  
d. 0.30  
e. 13.70

15) The pH of a solution is 2.80. What is the hydronium ion concentration?

a. $4.2 \times 10^{-3} M$  
b. $6.3 \times 10^{-2} M$  
c. $6.3 \times 10^{-3} M$  
d. $4.2 \times 10^{-2} M$  
e. $1.6 \times 10^{-3} M$

16) What is the pOH of a solution in which $[\text{H}_3\text{O}^+] = 3.60 \times 10^{-10} M$?

a. 4.56  
b. 8.56  
c. 5.44  
d. 4.32  
e. 9.44

17) A solution in which the pOH is 12.8 would be described as __________.

a. slightly acidic  
b. distinctly basic  
c. slightly basic  
d. neutral  
e. distinctly acidic

18) If enough base is added to a solution to cause the pH to increase from 7.0 to 9.0, the __________.

a. $[\text{OH}^-]$ increases by a factor of 100  
b. $[\text{OH}^-]$ increases by a factor of $9/7$  
c. $[\text{OH}^-]$ increases by a factor of 0.010  
d. $[\text{OH}^-]$ increases by a factor of 2  
e. $[\text{OH}^-]$ increases by 2 $M$
B. **Solutions of Strong Acids and Strong Bases (O-V.8 → O-V.9)**

1. **Solutions of strong acids**
   a. Strong acids ionize/dissociate completely in solution.
      □ \( \text{HX} \rightarrow \text{H}^+ + \text{X}^- \)
   b. The concentration of \( \text{H}^+ \) (or \( \text{H}_3\text{O}^+ \)) is the same as the concentration of acid.
      □ Acid concentration is denoted as
   c. The pH of the solution is \( \text{pH} = \)
      □ Example: \( C_{\text{SA}} = 1.0 \text{ M} \Rightarrow \text{pH} = \)
      □ Example: \( C_{\text{SA}} = 0.020 \text{ M} \Rightarrow \text{pH} = \)
      □ Example: \( C_{\text{SA}} = 10. \text{ M} \Rightarrow \text{pH} = \)

2. **Solutions of strong bases**
   a. Strong bases ionize completely in solution.
      □ \( \text{MOH} \rightarrow \text{M}^+ + \text{OH}^- \)
      □ \( \text{M(OH)}_2 \rightarrow \text{M}^{2+} + 2\text{OH}^- \)
   b. The concentration of \( \text{OH}^- \) is either the same as the concentration of base (for \( \text{MOH} \)-type base) or twice the concentration of base (for \( \text{M(OH)}_2 \)-type base).
      □ Base concentration is denoted as
      □ \[ \text{[OH}^-] = \]
   c. The pOH of the solution is \( \text{pOH} = \)
   d. The pH of the solution is \( \text{pH} = \)
19) The pH of a solution of hydrochloric acid is 2.80. What is the molarity of the acid?

a. $4.2 \times 10^{-3}$ M
b. $6.3 \times 10^{-2}$ M
c. $6.3 \times 10^{-3}$ M
d. $4.2 \times 10^{-2}$ M
e. $1.6 \times 10^{-3}$ M

20) What is the concentration of OH$^-$ ions in a 0.25 M HClO$_4$ solution?

a. 0.25 M
b. $1.0 \times 10^{-7}$ M
c. $2.0 \times 10^{-14}$ M
d. $4.0 \times 10^{-14}$ M
e. 4.0 M

21) Calculate the pH of a 1.0 L solution obtained by mixing 500 mL of 0.120 M KOH solution with 500 mL of 0.048 M Ca(OH)$_2$ solution.

a. 14.00
b. 13.23
c. 13.03
d. 13.33
e. 12.92

C. Hydroxides and Oxides (O-V.10)

1. Hydroxides
   a. The hydroxides we are discussing here are the metallic hydroxides, generally described by the formula M(OH)$_x$.
   b. The hydroxides can be classified as
   c. The hydroxides are the strong bases.
      □ Examples: NaOH, KOH, Ca(OH)$_2$, Ba(OH)$_2$, etc.
   d. The hydroxides can be considered as weak bases because not all hydroxides ions end up in solution.
      □ Examples: Fe(OH)$_3$, Cr(OH)$_3$, etc.
e. Some hydroxides can be solubilized in acid solution or basic solution, and they are called
   □ An species is a species (molecule/ion) that can react both as an acid and as a base.
   □ Example: Fe(OH)$_3$ + 3H$^+$ $\rightarrow$ Fe$^{3+}$ + 3H$_2$O
   □ Example: Fe(OH)$_3$ + OH$^-$ $\rightarrow$ [Fe(OH)$_4$]$^-$

2. Oxides
   a. The oxides refer to the compound of an element with oxygen and they can be oxides (O$^{2-}$) or peroxides (O$_2^{2-}$).
   b. Metal (or metallic) oxides are ionic compounds, and they are called basic oxides because they form solution when dissolved in water.
      □ Example: Na$_2$O + H$_2$O $\rightarrow$ 2NaOH
   c. Nonmetal oxides are molecular (or covalent) compounds, and they are called acidic oxides because they form solution when dissolved in water.
      □ Example: SO$_3$ + H$_2$O $\rightarrow$ H$_2$SO$_4$
   d. The metalloid oxides are amphoteric oxides/compounds.
      □ Example: B$_2$O$_3$ + 3H$_2$O $\rightarrow$ 2B(OH)$_3$ (or 2H$_3$BO$_3$)
   e. The oxides obtained by reaction of group I A metals with oxygen is an interesting issue.
      □ They are Li$_2$O (lithium oxide), Na$_2$O (sodium oxide), Na$_2$O$_2$ and KO$_2$
22) Which response includes all of the following that are insoluble bases, and no others?
LiOH, Cu(OH)₂, Be(OH)₂, Ba(OH)₂, KOH

a. Cu(OH)₂, KOH, Ba(OH)₂
b. Cu(OH)₂, Ba(OH)₂
c. another one or another combination
d. LiOH, Ba(OH)₂
e. LiOH, Be(OH)₂

23) Which one of the following sets of hydroxides contain only amphoteric hydroxydes?
a. Sn(OH)₂, NaOH, Fe(OH)₃
b. Ca(OH)₂, Cr(OH)₃, Fe(OH)₃
c. Al(OH)₃, Cr(OH)₃, Ba(OH)₂
d. Zn(OH)₂, KOH, Al(OH)₃
e. Cr(OH)₃, Zn(OH)₂, Al(OH)₃

24) Which of the following statements is FALSE?
a. Acids react with salts of weaker acids to form the weaker acid and a new salt.
b. The aqueous solutions of strong bases conduct an electric current.
c. Although we often represent hydrogen ions as bare protons (H⁺), they are hydrated in aqueous solutions.
d. Acids and bases change the colors of many indicators.
e. Bases react with metal oxides to form salts and water.
Unit VI
Acid-Base Equilibria

Unit Objectives

O-VI.1 Learn terminology: Acid-ionization constant, Base-ionization constant, Degree of ionization, Common-ion effect, Buffer
O-VI.2 Carry out calculations for solutions of weak acids (relationships of $K_a$, pH, degree of ionization)
O-VI.3 Carry out calculations for solutions of weak bases (relationships of $K_b$, pOH or pH, degree of ionization)
O-VI.4 Define salts (definition and types) & hydrolysis
O-VI.5 Determine the pH of a salt solution
O-VI.6 Carry out calculations of solution pH involving common-ion effect & mixtures of two acids (one weak and one strong)
O-VI.7 Define buffers and describe the needed components
O-VI.8 Carry out calculations of solution pH involving buffers
O-VI.9 Define acid-base titrations and identify various stages
O-VI.10 Carry out calculations of solution pH involving acid-base titrations
A. Solutions of Weak Acids and Weak Bases (O-VI.2 → O-VI.3)

1. Solutions of weak acids
   a. A weak acid is an acid that just partially dissociates or ionizes in water.
   b. The ionization is reversible, and equilibrium is reached fast.
      □ HA(aq) + H₂O(l) ⇌ H₃O⁺(aq) + A⁻(aq)
      □ This equilibrium is (heavily) shifted toward
   c. The equilibrium constant for the ionization process is denoted \( K_a \) and is called acid ionization constant, acid dissociation constant, or acidity constant.
      □ \( K_a = \frac{[H_3O^+]_{eq}[A^-]_{eq}}{[HA]_{eq}} \) or simplistic ally \( K_a = \frac{[H^+][A^-]}{[HA]} \)
      □ Similar to pH, one can define \( pK_a \)
      □ The higher the \( K_a \) value (or the lower the \( pK_a \) value), the more dissociation occurring, the stronger the acid.
   d. An ICE table can be written for discussion here but it is not necessary in problem solving.

   \[
   \begin{array}{ccc}
   \text{HA(aq)} & \text{H}_2\text{O(l)} & \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \\
   \text{I} & C_{WA} & 0 \\
   \text{C} & -x & +x \\
   \text{E} & C_{WA} - x & +x
   \end{array}
   \]
      □ Weak acid concentration is denoted as
      □ \( K_a = \frac{x^2}{C_{WA} - x} \approx \frac{x^2}{C_{WA}} \) because typically \( x \ll C_{WA} \).
      □ \( K_a = \frac{x^2}{C_{WA} - x} \) should be used when \( K_a \) is big (10⁻¹-10⁻²).
   e. Hydronium ion concentration is \( [H^+] = x = \)
   f. The pH of a weak acid solution is \( pH = \)
g. The degree ionization (DI) is defined as
\[ DI = \frac{[A^-]}{[HA]_0} = \frac{[A^-]}{C_{WA}} = \frac{x}{C_{WA}}. \]

- For (pure) weak acid solutions, \[ DI = \frac{[H^+]}{[HA]_0} = \frac{x}{C_{WA}} \approx \frac{[H^+]}{[HA]}. \]

- Useful relationships:
- The percent ionization is

<table>
<thead>
<tr>
<th>O-VI.2</th>
<th>**</th>
<th>O-VI.2</th>
<th>**</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) What is the pH of 0.24 M solution of a acid with ( K_a = 3.0 \times 10^{-8} )?</td>
<td></td>
<td>2) Calculate the pH of a solution of acetic acid that is 3.0% ionized. ( K_a = 1.8 \times 10^{-5} )</td>
<td></td>
</tr>
<tr>
<td>a. 3.76</td>
<td></td>
<td>a. 3.24</td>
<td></td>
</tr>
<tr>
<td>b. 8.14</td>
<td></td>
<td>b. 2.94</td>
<td></td>
</tr>
<tr>
<td>c. 4.07</td>
<td></td>
<td>c. 4.70</td>
<td></td>
</tr>
<tr>
<td>d. 0.62</td>
<td></td>
<td>d. 2.64</td>
<td></td>
</tr>
<tr>
<td>e. 3.45</td>
<td></td>
<td>e. 4.99</td>
<td></td>
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</tbody>
</table>

**O-VI.2**
3) Calculate the \( pK_a \) for a weak acid, HA, that is 2.3\% ionized in 0.080 M solution?
| a. 1.66 |
| b. 3.09 |
| c. 2.33 |
| d. 4.71 |
| e. 4.37 |

h. Polyprotic acids (e.g., \( \text{H}_2\text{SO}_3 \), \( \text{H}_3\text{PO}_4 \), etc.) have two or three ionization steps, each characterized by an acid dissociation constant.

\[
\begin{align*}
\text{H}_3\text{A} & \quad \rightleftharpoons \quad \text{H}^+ + \text{H}_2\text{A}^- & K_{a(1)} \\
\text{H}_2\text{A}^- & \quad \rightleftharpoons \quad \text{H}^+ + \text{HA}^{2-} & K_{a(2)} \\
\text{HA}^{2-} & \quad \rightleftharpoons \quad \text{H}^+ + \text{A}^{3-} & K_{a(3)}
\end{align*}
\]
\[ K_{a(1)} >> K_{a(2)} >> K_{a(3)} \]

- A solution of a polyprotic acid solution should be treated as a weak acid with \( K_{a(1)} \).

### 4) Which of the following statements about polyprotic acids is incorrect?

- a. Polyprotic acids can furnish two or more hydronium ions per molecule.
- b. The ionizations of polyprotic acids occur simultaneously.
- c. Phosphoric acid is a typical polyprotic acid.
- d. It is generally accepted practice to ignore second or third ionizations when calculating the concentration of \( H_3O^+ \).
- e. Successive ionization constants for polyprotic acids generally decrease.

### 5) The hypothetical diprotic weak acid \( H_2A \) ionizes as shown below. Calculate the \([HA^-]\) in 0.20 \( M \) \( H_2A \).

\[
\begin{align*}
H_2A & \rightleftharpoons H^+ + HA^- \\
HA^- & \rightleftharpoons H^+ + A^{2-}
\end{align*}
\]

\[ K_{a1} = 1.0 \times 10^{-7} \]
\[ K_{a2} = 5.0 \times 10^{-11} \]

- a. \( 1.0 \times 10^{-7} M \)
- b. \( 1.4 \times 10^{-4} M \)
- c. \( 2.2 \times 10^{-6} M \)
- d. \( 3.0 \times 10^{-4} M \)
- e. \( 6.3 \times 10^{-5} M \)

### 2. Solutions of weak bases

- a. A weak base partially dissociates or ionizes in water.
- b. The ionization is reversible, and equilibrium is reached fast.
  - :B\( (aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq) \)
  - This equilibrium is (heavily) shifted toward
- c. The equilibrium constant for the ionization process is denoted \( K_b \) and is called base ionization constant, base dissociation constant, or basicity constant.
  - \[ K_b = \frac{[HB^+]_{eq}[OH^-]_{eq}}{[B]_{eq}} \]
  - Simplistically, \( K_b = \frac{[HB^+][OH^-]}{[B]} \)
  - Similar to pH, one can define \( pK_b \)
  - The higher the \( K_b \) value (or the lower the \( pK_b \) value), the more dissociation occurring, the stronger the base.
- d. Hydroxide ion concentration is \([OH^-] = x = \)
  - Weak base concentration is denoted as
e. The pOH of a weak base solution is \( \text{pOH} = \)

f. Examples: \( \text{NH}_3 \) (ammonia), \( \text{CH}_3\text{NH}_2 \) (methyl amine), \( \text{NH}_2\text{NH}_2 \) (hydrazine), etc.

---

6) The \([\text{OH}^-]\) = \(1.3 \times 10^{-6}\) \(M\) for a 0.025 \(M\) solution of a weak base. Calculate the value of \(K_b\) for this weak base.

- a. \(3.1 \times 10^{-7}\)
- b. \(5.2 \times 10^{-5}\)
- c. \(7.7 \times 10^{-9}\)
- d. \(4.0 \times 10^{-8}\)
- e. \(6.8 \times 10^{-11}\)

7) Calculate the pH of a 0.050 \(M\) solution of hydroxylamine, \(\text{NH}_2\text{OH}\), for which \(K_b = 6.6 \times 10^{-9}\).

- a. 8.61
- b. 10.56
- c. 9.48
- d. 9.26
- e. 9.91

8) What is the percent ionization for a 1.0 \(\times\) \(10^{-3}\) \(M\) solution of pyridine? \(K_b = 1.5 \times 10^{-9}\)

- a. 0.67%
- b. 0.12%
- c. 1.6%
- d. 2.8%
- e. 0.045%

9) What is the pH of 0.24 \(M\) solution of a base with \(pK_b = 7.52\)?

- a. 10.23
- b. 8.14
- c. 4.07
- d. 9.93
- e. 10.55

10) What is the pOH of 0.24 \(M\) solution of a base with \(pK_b = 7.52\)?

- a. 3.76
- b. 8.14
- c. 4.07
- d. 0.62
- e. 3.45
B. Solutions of Salts (O-VI.4 → O-VI.5)

1. Salt description
   a. A salt is an ionic compound MX in which:
      - the cation M\(^+\) is
      - the anion X\(^-\) is
   b. A salt can be seen as being the result of a neutralization reaction of the HX acid with MOH base:
      - Example: NH\(_4\)\(^+\) is coming from
      - Example: Na\(^+\) is coming from
      - Example: Cu\(^{2+}\) is coming from
      - Example: Cl\(^-\) is coming from
      - Example: NO\(_3\)\(^-\) is coming from
      - Example: SO\(_3\)^{2-}\) is coming from

2. Hydrolysis of ions
   a. The conjugate base of a weak acid and the conjugate acid of a weak base are ions that do hydrolyze.
      - Hydrolysis is the reaction with water.
   b. The conjugate base of a weak acid
      - HF is a weak acid and F\(^-\) is its conjugate base.
      - NaF is a soluble salt that creates Na\(^+\) and F\(^-\) when dissolved.
      - Fluoride ion (F\(^-\)) hydrolyzes: F\(^-\) + H\(_2\)O ⇌ HF + OH\(^-\)
      - Hydrolysis of F\(^-\) looks like the opposite of HF ionization.
   c. The conjugate base of a strong acid
      - HCl is a strong acid and Cl\(^-\) is its conjugate base.
      - NaCl is a soluble salt that creates Na\(^+\) and Cl\(^-\) when dissolved.
      - Chloride ion (Cl\(^-\)) does not hydrolyze: Cl\(^-\) + H\(_2\)O − no reaction
d. The conjugate acid of a weak base
   □ NH$_3$ is a weak base and NH$_4^+$ is its conjugate acid.
   □ NH$_4$Cl is a soluble salt that creates NH$_4^+$ and Cl$^-$ when dissolved.
   □ Ammonium ion hydrolyzes: NH$_4^+$ + H$_2$O $\rightleftharpoons$ NH$_3$ + H$_3$O$^+$
   □ Hydrolysis of NH$_4^+$ looks like the opposite of NH$_3$ ionization.

e. The cation of a strong base
   □ NaOH is a strong base and Na$^+$ is its cation.
   □ NaCl is a soluble salt that creates Na$^+$ and Cl$^-$ when dissolved.
   □ Sodium ion (Na$^+$) does not hydrolyze: Na$^+$ + H$_2$O – no reaction

3. Strength of acid-base conjugate pair
   a. A stronger acid will have a weaker
   b. A stronger base will have a weaker
   c. Look at HF-F$^-$ conjugate pair:
      □ Ionization of HF: HF + H$_2$O $\rightleftharpoons$ F$^-$ + H$_3$O$^+$
      □ $K_a$(HF) = $\frac{[H^+][F^-]}{[HF]}$
      □ Hydrolysis of F$^-$: F$^-$ + H$_2$O $\rightleftharpoons$ HF + OH$^-$
      □ $K_b$(F$^-$) = $\frac{[HF][OH^-]}{[F^-]}$
      □ $K_a$(HF) $\times$ $K_b$(F$^-$) =
   d. Look at NH$_4^+$- NH$_3$ conjugate pair:
      □ $K_a$(NH$_4^+$) = $\frac{[H^+][NH_3]}{[NH_4^+]}$ and $K_b$(NH$_3$) = $\frac{[NH_4^+][OH^-]}{[NH_3]}$
      □ $K_a$(NH$_4^+$) $\times$ $K_b$(NH$_3$) =
   e. For any weak acid-base conjugate pair, $K_a$(acid) $\times$ $K_b$(base) =
   f. As $K_a$ and $K_b$ for an acid-base conjugate pair are related, only one of them is tabulated.
11) What is the value of the (base) hydrolysis constant for NaNO$_2$, sodium nitrite? $(K_a = 4.5 \times 10^{-4}$ for HNO$_2$)

a. $2.2 \times 10^{-11}$
b. $4.5 \times 10^{10}$
c. $2.1 \times 10^{-9}$
d. $4.5 \times 10^{-4}$
e. $4.5 \times 10^{-18}$

12) The reaction that occurs when NH$_4$Br dissolves in water is __________.

a. NH$_3$ + H$_2$O $\rightleftharpoons$ NH$_4^+$ + OH$^-$
b. Br$^-$ + H$_2$O $\rightleftharpoons$ HBr + OH$^-$
c. NH$_4^+$ + OH$^-$ $\rightleftharpoons$ NH$_4$OH
d. NH$_4^+$ + H$_2$O $\rightleftharpoons$ NH$_3$ + H$_3$O$^+$
e. Br$^-$ + H$_3$O$^+$ $\rightleftharpoons$ HBr + H$_2$O

4. Determining the pH of a salt solution
   a. The salt of a strong acid with a strong base will form
      □ For example, NaCl creates Na$^+$ and Cl$^-$ when dissolved.
      □ Neither Na$^+$ nor Cl$^-$ hydrolyzes so the solution will have pH = 7.
   b. The salt of a strong acid with a weak base will form
      □ For example, NH$_4$Cl creates NH$_4^+$ and Cl$^-$ when dissolved.
      □ NH$_4^+$ hydrolyzes (by acting like a weak acid), and the solution will have pH < 7.
      □ $[H^+] = \sqrt{K_a C_{WA}} = \sqrt{K_a(NH_4^+) C_{SAWB}} = \sqrt{\frac{K_w}{K_b(NH_3)} C_{SAWB}}$
      □ Salt concentration is denoted as $C_{SAWB}$ in these notes (SAWB stands for strong acid-weak base salt).
   c. The salt of a weak acid with a strong base will form
      □ For example, KCN creates K$^+$ and CN$^-$ when dissolved.
      □ CN$^-$ hydrolyzes (by acting like a weak base), and the solution will have pH > 7.
      □ $[OH^-] = \sqrt{K_b C_{WB}} = \sqrt{K_b(CN^-) C_{WASB}} = \sqrt{\frac{K_w}{K_a(HCN)} C_{WASB}}$
      □ Salt concentration is denoted as $C_{WASB}$ in these notes (WASB stands for weak acid-strong base salt).
c. The salt of a weak acid with a weak base will form

□ Both ions (for example, \( \text{NH}_4^+ \) and \( \text{ClO}_2^- \)) will hydrolyze.

13) Which of the following statements is false?

a. For a solution labeled “0.10 M \( \text{H}_2\text{SO}_4(\text{aq}) \)”, the pH is greater than 1.0.

b. Hydrolysis is the reaction of a substance with the water solvent in which it is dissolved.

c. The anion of a weak acid reacts with water to form nonionized acid and \( \text{OH}^- \) ions.

d. If a HF solution is diluted with water, the percent ionization of HF increases.

14) Which one of the following salts produces neutral solutions when it is dissolved in water?

a. \( (\text{NH}_4)^2\text{SO}_4 \)

b. \( \text{NaF} \)

c. \( \text{KNO}_3 \)

d. \( \text{NaCN} \)

e. \( \text{CaSO}_3 \)

15) A 0.10 moles of each of the following substances are used to make 1.0 L solutions. What solution will have the second highest pH value?

a. \( \text{HCl} \)

b. \( \text{NaCl} \)

c. \( \text{CH}_3\text{COOH} \)

d. \( \text{KCN} \)

e. \( \text{NaOH} \)

17) Calculate the pH of 0.15 M NaCN solution. \( (K_a = 4.0 \times 10^{-10} \) for HCN) 

a. 8.08 

b. 10.23 

c. 2.72 

d. 11.29 

e. 7.00
C. Solutions with Multiple Components (O-VI.6 → O-VI.10)

1. Common-ion effect

a. Consider a weak acid: \( HA + H_2O \rightleftharpoons H_3O^+ + A^- \); 
   \[ K_a = \frac{[H^+][A^-]}{[HA]} \]

b. Adding some \( H^+ \) (as a strong acid) or adding some \( A^- \) (as a soluble salt with the cation of a strong base) will shift the equilibrium toward the unionized form of the HX acid, decreasing the degree of ionization.
   □ Adding the strong acid to the weak acid makes a solution of two acids.
   □ Adding the salt to the weak acid makes
   □ These are examples of

c. Common-ion effect refers to modifying an (ionic) equilibrium by adding one ion participant in the equilibrium as a different compound (or from a different source).

2. Solutions of two acids

a. Consider a solution of monoprotic strong acid and weak acid of same (or similar) concentrations.
   □ Assume both concentrations to be 0.10 M and assume \( K_a = 10^{-5} \).
   □ The strong acid is completely ionized but what about the weak acid?
   □ \( K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(C_{SA} + x)x}{(C_{WA} - x) \times (0.10 + x)x \times \frac{1}{0.10 - x}} \)
   □ \( x \) is the molar concentration of \( A^- \) (or how much the weak HA acid ionizes), and it can be determined (or estimated) to be around
   □ Very little of the weak acid ionizes so \( [H^+] \) comes only from the

b. In a mixture of a strong acid and a weak acid, ignore the ionization of the weak acid and take \( [H^+] \) from the strong acid only: \( [H^+] \)
3. **Buffers**
   
   a. A buffer solution is a solution that has the property of changing the pH a little (or much less compared to just water) when either is added.
   
   b. A buffer solution contains two components that result in a weak acid-base conjugate pair and
   
   c. A buffer solution can be a mixture of a weak acid and the salt of the weak acid with a strong base (acting like a weak base).
      - Example:
   
   d. A buffer solution can be a mixture of a weak base and the salt of the weak base with a strong acid (acting like a weak acid).
      - Example:
   
   e. A buffer solution is essentially a mixture of a weak acid and a weak base that can be transformed into each other.
      - Addition of a strong acid will transform (therefore changing the pH much less).
      - Addition of a strong base will transform (therefore changing the pH much less).
   
   f. For example, adding HCl or NaOH to a HF-NaF buffer:
      - HCl + NaF → NaCl + HF (or HCl + F⁻ → HF + Cl⁻)
      - NaOH + HF → NaF + H₂O (or OH⁻ + HF → F⁻ + H₂O)
   
   g. Determination of the pH or [H⁺] for a buffer solution can be done using
   
   \[ K_a = [H^+] \times \frac{[A^-]}{[HA]} = [H^+] \times \frac{[\text{Base}]}{[\text{Acid}]} \]
   
   - [Base] is the concentration of the base in the acid-base pair.
   - [Acid] is the concentration of the acid in the acid-base pair.
h. Another way to determine the pH or $[H^+]$ for a buffer solution is by using Henderson-Hasselbalch equation, which is a reorganization of the formula above.

\[ \text{pH} = pK_a + \log \frac{[\text{Base}]}{[\text{Acid}]} \quad \text{where} \quad pK_a = \]

i. When $[\text{Acid}] = [\text{Base}]$.

j. The ratio of concentrations can be replaced by a ratio of number of moles (because the volume is the same):

\[ \frac{[\text{Base}]}{[\text{Acid}]} = \]

k. Adding some strong acid to the buffer will transform some weak base into weak acid so the ratio changes to

l. Adding some strong base to the buffer will transform some weak acid into weak base so the ratio changes to

---

**O-VI.6&O-VI.7**

19) Which of the following statements is false?

a. A buffer resists changes in pH.

b. A mixture of HCl and CH$_3$COOH is not a buffer.

c. A buffer solution can react with either H$_3$O$^+$ or OH$^-$ ions but not with both of them.

d. A buffer solution contains a conjugate acid-base pair with both the acid and the base in reasonable concentrations.

e. Common ion effect is the alteration of equilibrium in a solution of weak electrolyte by adding one of its ions from another source.

---

**O-VI.7**

20) Which one of the following combinations cannot produce a buffer solution?

a. HCN and NaCN

b. HNO$_3$ and NH$_4$NO$_3$

c. HNO$_2$ and NaNO$_2$

d. NH$_3$ and (NH$_4$)$_2$SO$_4$

e. NH$_3$ and NH$_4$Br
21) Consider a solution which is 0.15 M in HF ($K_a = 7.2 \times 10^{-4}$) and 0.10 M in KF. Which response contains all the true statements, and no others?
I. If NaOH is added, potassium ion reacts with hydroxide ion.
II. If a small amount of NaOH is added, the pH increases very slightly.
III. If HNO$_3$ is added, hydrogen ion reacts with fluoride ion.
IV. If more KF is added, the pH decreases.

a. I, II, and IV  
b. I, III, and IV  
c. II and III  
d. III  
e. II and IV

22) Calculate the pH of a solution that is 0.10 M in acetic acid ($K_a = 1.8 \times 10^{-5}$) and 0.30 M in sodium acetate.

a. 4.74  
b. 5.22  
c. 5.06  
d. 4.87  
e. 4.92

23) What is the [H$_3$O$^+$] of a solution that is 0.0100 M in HOCl ($K_a = 3.5 \times 10^{-8}$) and 0.0300 M in NaOCl?

a. $2.29 \times 10^{-8}$ M  
b. $1.45 \times 10^{-7}$ M  
c. $2.14 \times 10^{-7}$ M  
d. $1.17 \times 10^{-8}$ M  
e. $7.41 \times 10^{-8}$ M

24) Calculate the pH for a buffer solution prepared by mixing 100. mL of 0.60 M NH$_3$ ($K_b = 1.8 \times 10^{-5}$) and 200. mL of 0.45 M NH$_4$Cl.

a. 6.62  
b. 8.65  
c. 9.87  
d. 9.08  
e. 4.90

25) What is the pH of a solution that is 0.30 M in aniline, C$_6$H$_5$NH$_2$, and 0.15 M in anilinium chloride, C$_6$H$_5$NH$_3^+$Cl$^-$?

a. 5.74  
b. 4.32  
c. 4.92  
d. 5.62  
e. 5.95

26) If 0.040 moles of solid NaOH is added to 1.0 liter of a solution that is 0.10 M in NH$_3$ ($K_b = 1.8 \times 10^{-5}$) and 0.20 M in NH$_4$Cl, what will be the pH of the resulting solution? Assume no volume change.

a. 4.80  
b. 8.95  
c. 5.05  
d. 8.65  
e. 9.20
27) If 100. mL of 0.030 $M$ HCl solution is added to 100. mL of buffer solution which is 0.10 $M$ in NH$_3$ ($K_b = 1.8 \times 10^{-5}$) and 0.10 $M$ in NH$_4$Cl, what will be the pH of the new solution?

a. 5.01  
b. 9.52  
c. 4.48  
d. 8.99  
e. 7.88

28) A solution is initially 0.100 $M$ in HOCl ($K_a = 3.5 \times 10^{-8}$) and 0.300 $M$ in NaOCl. What is the pH if 0.030 mol of solid NaOH is added to 1.00 L of this solution? Assume no volume change.

a. 9.06  
b. 8.13  
c. 8.02  
d. 5.24  
e. 5.38

4. Acid-base titrations

a. Titration is a procedure of determining the concentration of a solution (called analyte) by reacting it with a solution of another compound, with known concentration (called titrant).
   □ An acid-base titration is titration based on an
b. The equivalent point (of a titration) is the situation when equivalent amounts of the two reactants (A and B) were reacted.
   □ At that point the reaction (or the titration) “is finished”.
   □ A sudden change in a property (pH value, solution color using an indicator, etc.) is necessary to determine the equivalent point.
   □ is the situation/condition when the indicator changes color, and that can be different than the equivalent point.
   □ Equivalent amounts mean number-of-mole ratio that is equal to the ratio of
   □ For a general reaction $aA + bB \rightarrow$ Products, equivalent amounts mean $n_A/n_B = a/b$ (so $n_A = n_B$ if $a = b$).
   □ Determining the equivalent amounts is done based on molarities and volumes of solutions and stoichiometry calculations using volumes.
c. A titration can be seen as having four stages and the calculations involved in determining the pH of the solution dependent on the type of titration and the stage of titration, as presented in the table below.

<table>
<thead>
<tr>
<th>Stage</th>
<th>SA + SB</th>
<th>WA + SB</th>
<th>WB + SA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>SA</td>
<td>WA</td>
<td>WB</td>
</tr>
<tr>
<td></td>
<td>(pH 7)</td>
<td>(pH 7)</td>
<td>(pH 7)</td>
</tr>
<tr>
<td>Before eq.</td>
<td>SA</td>
<td>WA + Salt&lt;sub&gt;WASB&lt;/sub&gt;</td>
<td>WB + Salt&lt;sub&gt;SAWB&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>(pH 7)</td>
<td>(buffer)</td>
<td>(buffer)</td>
</tr>
<tr>
<td>Equivalence</td>
<td>Salt&lt;sub&gt;SASB&lt;/sub&gt;</td>
<td>Salt&lt;sub&gt;WASB&lt;/sub&gt;</td>
<td>Salt&lt;sub&gt;SAWB&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>(pH 7)</td>
<td>(pH 7)</td>
<td>(pH 7)</td>
</tr>
<tr>
<td>After eq.</td>
<td>SB</td>
<td>SB</td>
<td>SA</td>
</tr>
<tr>
<td></td>
<td>(pH 7)</td>
<td>(pH 7)</td>
<td>(pH 7)</td>
</tr>
</tbody>
</table>

d. For titration problems at “before”, “equivalence” or “after” stages, the concentration of the compound of interest need to be calculated based on independently determining the number of moles and the volume of solution.

e. Titration curves are representations of the pH of the solution versus the volume of titrant (i.e., the solution that is added).

\[
\begin{align*}
\text{SA + SB} & \quad \text{pH} \quad \text{Volume added} \\
\text{WA + SB} & \quad \text{pH} \quad \text{Volume added} \\
\text{WB + SA} & \quad \text{pH} \quad \text{Volume added}
\end{align*}
\]
f. For a WA + SB titration (as well as WB + SA titration), at half-equivalence,
   □ This is one way of determining pKₐ.

**O-VI.9**
29) When a weak base is titrated with a strong acid, the pH at the equivalence point is always ______.
   a. > 4
   b. < 7
   c. 7
   d. > 7
   e. < 1

**O-VI.9**
30) Which titration curve could describe the titration of a solution of HCl by addition of a solution of KOH?
   a. 
   b. 
   c. 
   d. 

**O-VI.9**
31) Which titration curve could describe the titration of a solution of HF by addition of a solution of KOH?
   a. 
   b. 
   c. 
   d. 

**O-VI.9**
32) What is the molarity of the sodium sulfate in the solution resulting from the addition of 100. mL of 0.0500 M H₂SO₄ to 200. mL of 0.0500 M NaOH?
   a. 0.00833 M
   b. 0.0500 M
   c. 0.0333 M
   d. 0.0250 M
   e. 0.0167 M

**O-VI.9**
33) Calculate the molarity of a NaOH solution if 35.42 mL of this NaOH solution is required to titrate 0.7566 g of potassium hydrogen phthalate or KHP, a monoprotic acid with MW =204.2 g/mol.
   a. 0.0105 M
   b. 0.3128 M
   c. 0.2092 M
   d. 0.05278 M
   e. 0.1046 M

**O-VI.9**
34) What volume of 0.0750 M Ba(OH)₂ will completely react with 125 mL of 0.0350 M HCl?
   a. 230. mL
   b. 53.6 mL
   c. 536 mL
   d. 42.0 mL
   e. 29.2 mL
35) What is the pH at the start of the titration of 125. mL of 0.040 M HBr with 0.032 M NaOH solution?

a. 0.63  
b. 2.21  
c. 1.40  
d. 1.67  
e. 1.00  

36) Calculate the pH at the start of the titration of 150 mL of 0.100 M nitrous acid ($K_a = 4.5 \times 10^{-4}$) solution with 0.200 M NaOH.

a. 2.17  
b. 4.17  
c. 1.00  
d. 4.35  
e. 3.35

37) What is the pH of the solution resulting from the addition of 30.0 mL of 0.200 M HClO$_4$ to 20.0 mL of 0.150 M NaOH?

a. 1.36  
b. 1.00  
c. 1.48  
d. 1.22  
e. 1.67

38) If 50.00 mL of 0.1000 M NaOH is titrated with 0.1000 M HCl, what is the pH of the solution after 30.00 mL of HCl solution has been added?

a. 13.00  
b. 12.40  
c. 12.80  
d. 12.60  
e. 12.00

39) During the titration of 40.0 mL of 0.0100 M acetic acid ($K_a = 1.8 \times 10^{-5}$) with 0.0100 M NaOH solution, what is the pH of the solution resulting from the addition of 25.0 mL of NaOH solution?

a. 4.94  
b. 5.17  
c. 4.54  
d. 4.52  
e. 4.97

40) Calculate the pH of a solution resulting from the addition of 60.0 mL of 0.30 M HNO$_3$ to 50.0 mL of 0.30 M NH$_3$ ($K_b = 1.8 \times 10^{-5}$).

a. 1.56  
b. 1.00  
c. 4.62  
d. 8.30  
e. 5.04
O-VI.10

41) What is the pH at the equivalence point in the titration of 50.0 mL of 0.100 M hydrofluoric acid ($K_a = 7.2 \times 10^{-4}$) with 0.100 M NaOH?

a. 8.56  
b. 7.92  
c. 5.88  
d. 6.08  
e. 8.12

***

Review

<table>
<thead>
<tr>
<th>Various Possibilities</th>
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<tbody>
<tr>
<td>Strong acid ($C_{SA}$): $[H_3O^+] = C_{SA}$</td>
</tr>
<tr>
<td>Weak acid ($C_{WA}$): $[H_3O^+] = \sqrt{K_a \cdot C_{WA}}$</td>
</tr>
<tr>
<td>Salt of weak base and strong acid = Weak acid: $[H_3O^+] = \sqrt{K_a \cdot C_{WA}}$ where $K_a = K_w/K_b$</td>
</tr>
<tr>
<td>Strong acid ($C_{SA}$) + Weak acid ($C_{WA}$): $[H_3O^+] = C_{SA}$</td>
</tr>
<tr>
<td>Weak acid ($C_{WA}$) + Salt ($C_{WASB}$) = Buffer: -log[$H_3O^+$] = pH = $pK_a + \log(C_{WASB}/C_{WA})$</td>
</tr>
</tbody>
</table>

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</tbody>
</table>
Unit VII
Solubility Equilibria

Unit Objectives

O-VII.1 Learn terminology: Molar solubility, Fractional precipitation, Complex ion, Ligand, Stability constant
O-VII.2 Identify insoluble compounds
O-VII.3 Define solubility equilibria and relation between $K_{sp}$ and $s$
O-VII.4 Calculate solubility equilibria in presence of common ion (the common-ion effect)
O-VII.5 Define ion product ($Q_{sp}$ or $Q_{c}$) and using criterion for precipitation
O-VII.6 Identify conditions for fractional precipitation
O-VII.7 Discuss the solubility dependence on pH
O-VII.8 Define complex-ion formation and carry out calculations involving $K_f$ or $K_d$
O-VII.9 Define generally qualitative analysis and its principle
A. Solubility (O-VII.2 & O-VII.3)

1. Solubility rules
   a. Compounds with the ions below are always soluble:
      - Cations: Na\(^+\), K\(^+\), Rb\(^+\), Cs\(^+\), NH\(_4\)^+  
      - Anions: NO\(_3\)^-, CH\(_3\)COO\(^-\), ClO\(_3\)^-
   b. Compounds with the ions below are always insoluble (except when they also contain the cations from above):
      - CO\(_3\)^2-, PO\(_4\)^3-, S\(^2-\), CrO\(_4\)^2-
   c. Hydroxides are always insoluble except the strong bases.
   d. The following anions are almost always soluble with some exceptions:
      - CN\(^-\), Cl\(^-\), Br\(^-\), I\(^-\) except for compounds with Ag\(^+\), Hg\(^{2+}\), Pb\(^{2+}\)
      - SO\(_4\)^2- except for compounds with Ag\(^+\), Hg\(^{2+}\), Pb\(^{2+}\), Ca\(^{2+}\), Sr\(^{2+}\), Ba\(^{2+}\)

2. Solubility and solubility product constant
   a. Consider the solubility equilibrium between an ionic solid and a saturated solution containing its ions.
      - \(M_yX_z(s) \rightleftharpoons yM^+(aq) + zX^-(aq)\)
   b. The equilibrium constant for this process is denoted by \(K_{sp}\), and it is called
      - \(K_{sp} = [M^+]_e^y[X^-]_e^z\) or \(K_{sp} = [M^+]^y[X^-]^z\)
      - Solids do not appear in the expression of \(K\).
      - Equilibrium situation means
   c. The value of \(K_{sp}\) generally describes how soluble a compound is.
      - A very small \(K_{sp}\) value means compounds.
      - A higher \(K_{sp}\) value means compounds.
   d. Define molar solubility (or just solubility) as the number of moles of solid solute that dissolve in 1 L solution to make
      - It is denoted by \(s\).
      - It looks like a molar concentration of
e. For the case of an insoluble (or a slightly soluble) compound dissolving in pure water (so no other ions present in solution from a different source), there is a general relationship connecting $K_{sp}$ and $s$.

\[ M_yX_z(s) \rightarrow y M^+(aq) + z X^-(aq) \text{ looks like} \]

\[ K_{sp} = \]

\[ \text{Depending on the type of salt (i.e., the ratio of ions), the general formula will have few alternatives that are listed below.} \]

<table>
<thead>
<tr>
<th>Type of compound</th>
<th>Examples</th>
<th>$K_{sp}$</th>
<th>$s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>AgCl, BaSO$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:2 or 2:1</td>
<td>Mg(OH)$_2$, Ag$_2$S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:3 or 3:1</td>
<td>Cr(OH)$_3$, Ag$_3$PO$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2:3 or 3:2</td>
<td>Ca$_3$(PO$_4$)$_2$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**O-VII.2**

1) If a solution of 0.10 $M$ HCN is mixed with a solution of 0.10 $M$ AgNO$_3$, what possible precipitate may form?

a. Ag$_2$CN
b. NH$_4$NO$_3$
c. NH$_2$OH
d. AgCN
e. None is possible.

**O-VII.3**

2) Which of the following solubility product expressions is **incorrect**?

a. $K_{sp}$ (CaF$_2$) = [Ca$^{2+}$][F]$^2$
b. $K_{sp}$ (Sb$_2$S$_3$) = [Sb$^{3+}$][S$^{3-}$]$^2$
c. $K_{sp}$ (Ag$_2$S) = [Ag$^+$][S$^2$]
d. $K_{sp}$ (Ag$_3$PO$_4$) = [Ag$^{+}$][PO$_{4}^{3-}$]
e. $K_{sp}$ (CuS) = [Cu$^{2+}$][S$^{2-}$]
3) Which of the following solubility product expressions is correct?

a. \( K_{sp}(Ag_3PO_4) = [Ag^+] [PO_4^{3-}]^3 \)
b. \( K_{sp}(MnCO_3) = [Mn^{2+}] [C_4^{3+}] [O_2^{-}]^3 \)
c. \( K_{sp}(Sb_2S_3) = [Sb^{2+}]^2 [S_3^{-}]^3 \)
d. \( K_{sp}(CaCl_2) = [Ca^{2+}] [Cl^-]^2 \)
e. \( K_{sp}(BaF_2) = [Ba^{2+}] [F_2^{2-}] \)

5) At 25°C, 1.4 \times 10^{-5} \text{ mole of Cd(OH)}_2 \text{ dissolves to give 1.0 liter of saturated aqueous solution. What is the solubility product for Cd(OH)}_2? \text{?}

a. 4.1 \times 10^{-12}
b. 1.7 \times 10^{-5}
c. 1.1 \times 10^{-14}
d. 2.9 \times 10^{-10}
e. 5.8 \times 10^{-15}

7) If the solubility of calcium fluoride in water is 2.2 \times 10^{-4} \text{ at 25°C, calculate the solubility product.}

a. 2.1 \times 10^{-14}
b. 1.1 \times 10^{-11}
c. 4.8 \times 10^{-8}
d. 4.3 \times 10^{-11}
e. 2.2 \times 10^{-4}

4) How is the \( K_{sp} \text{ of Ca}_3(PO_4)_2 \) related to \( s \), the molar solubility of \( Ca_3(PO_4)_2 \)?

a. \( K_{sp} = 54s^4 \)
b. \( K_{sp} = 4s^5 \)
c. \( K_{sp} = 27s^3 \)
d. \( K_{sp} = 108s^5 \)
e. \( K_{sp} = 18s^5 \)

6) The value of \( K_{sp} \) for \( SrSO_4 \) is 2.8 \times 10^{-7}. What is the molar solubility of \( SrSO_4 \)?

a. 5.7 \times 10^{-3} \text{ M}
b. 1.3 \times 10^{-8} \text{ M}
c. 5.8 \times 10^{-13} \text{ M}
d. 5.3 \times 10^{-4} \text{ M}
e. 7.6 \times 10^{-7} \text{ M}

8) What mass of \( Zn(OH)_2 \) is contained in 1.0 liter of saturated solution? \( K_{sp} = 4.5 \times 10^{-17} \).

a. 0.00022 g 
b. 0.010 g 
c. 0.00011 g 
d. 0.00044 g 
e. 0.016 g
O-VII.3

9) Calculate the molar solubility of nickel phosphate at 25°C. Its $K_{sp}$ is $5.0 \times 10^{-31}$.

a. $3.4 \times 10^{-7} \text{ M}$
b. $8.7 \times 10^{-7} \text{ M}$
c. $5.0 \times 10^{-11} \text{ M}$
d. $7.1 \times 10^{-16} \text{ M}$
e. $6.1 \times 10^{-7} \text{ M}$

B. Common-Ion Effect and Precipitation (O-VII.4 → O-VII.6)

1. Common-ion effect

a. Common-ion effect occurs when one of the ions of the insoluble (or slightly soluble) compound is present in solution from

b. The solubility in the presence of common ion.

c. For example, look at the case of cation being present from another source (although the final formula will be same if additional anion is present).

\[
\begin{align*}
M_yX_z(s) & \rightleftharpoons y M^+(aq) + z X^-(aq) \\
s & \rightarrow (y s + C_{M^+}) + z s & \text{where } C_{M^+} \text{ is the concentration of } M^+ \\
\text{Normally, } (y s) & \text{ is much smaller than } C_{M^+} \text{ so it can be ignored.} \\
K_{sp} & = (y s + C_{M^+})^y (z s)^z = C_{M^+}^y (z s)^z = C^y (z s)^z \\
s & = \left(\frac{K_{sp}}{C^y z^z}\right)^{1/z} \\
\text{Keep in mind that } C_{X^-} & = z s \text{ or } s = C_{X^-} / z \text{ and that } s = C_{X^-} \text{ only if } z = 1.
\end{align*}
\]
10) $K_{sp}$ for lead fluoride is $3.7 \times 10^{-8}$. What is the molar solubility of PbF$_2$ in 0.10 M NaF?

a. $8.5 \times 10^{-8}$ M
b. $3.7 \times 10^{-7}$ M
c. $1.9 \times 10^{-4}$ M
d. $4.6 \times 10^{-5}$ M
e. $3.7 \times 10^{-6}$ M

11) How many moles of PbSO$_4$ will dissolve in 1.0 liter of 0.010 M K$_2$SO$_4$?

$K_{sp}$ (PbSO$_4$) = $1.8 \times 10^{-8}$.

a. $1.8 \times 10^{-2}$
b. $5.0 \times 10^{7}$
c. $5.0 \times 10^{-3}$
d. $1.8 \times 10^{-6}$
e. $1.8 \times 10^{-4}$

12) $K_{sp}$ for mercury (II) sulfide is $1.6 \times 10^{-52}$. What is the molar solubility of mercury (II) sulfide in 1.00 L of 0.010 M Na$_2$S?

a. $1.6 \times 10^{-54}$ M
b. $1.6 \times 10^{-50}$ M
c. $1.3 \times 10^{-26}$ M
d. $1.3 \times 10^{-25}$ M
e. Impossible to determine based on given information.

13) Calculate the concentration of carbonate ion in a saturated solution of calcium carbonate to which calcium chloride has been added until $[Ca^{2+}] = 0.015$ M at 25° C.

$K_{sp}$ for CaCO$_3$ = $2.8 \times 10^{-9}$

a. $4.2 \times 10^{-11}$ M
b. $1.9 \times 10^{-7}$ M
c. $1.2 \times 10^{-5}$ M
d. $6.3 \times 10^{-13}$ M
e. $1.5 \times 10^{-2}$ M

14) Calculate the $[Ca^{2+}]$ required to start the precipitation of calcium fluoride, CaF$_2$, from a solution containing 0.0025 M F$^-$ at 25° C. $K_{sp}$ for CaF$_2$ = $3.9 \times 10^{-11}$.

a. $4.8 \times 10^{-3}$ M
b. $5.2 \times 10^{10}$ M
c. $1.6 \times 10^{-8}$ M
d. $6.4 \times 10^{-7}$ M
e. $6.2 \times 10^{-6}$ M

15) Typical “hard” water contains about $2.0 \times 10^{-3}$ mol of Ca$^{2+}$ per liter. Calculate the maximum concentration of fluoride ion which could be present in hard water. $K_{sp}$(CaF$_2$) = $4.0 \times 10^{-11}$

a. $4.0 \times 10^{-3}$ M
b. $1.4 \times 10^{-4}$ M
c. $7.1 \times 10^{-3}$ M
d. $2.0 \times 10^{-8}$ M
e. $2.0 \times 10^{-3}$ M
16) What is the minimum concentration of iodide ion required to limit the concentration of lead ion in solution to a maximum of $1.0 \times 10^{-6}$ M? $K_{sp}$ for PbI$_2$ is $8.7 \times 10^{-9}$

- a. $1.7 \times 10^{-2}$ M
- b. $1.8 \times 10^{-1}$ M
- c. $7.6 \times 10^{-5}$ M
- d. $8.7 \times 10^{-3}$ M
- e. $9.3 \times 10^{-2}$ M

2. Criterion for precipitation
   a. Precipitation (reaction) is the reaction of two solutions (one containing one ion M$^+$ while the other containing the other ion X$^-$) leading to an insoluble compound MX (which is solid).
   b. One can define $Q$ (or $Q_c$ or $Q_{sp}$) in the case of mixing two solutions (one containing M$^+$ and the other containing X$^-$).
      - $Q = [M^+]^y [X^-]^z$ where the concentrations are determined just by dilution formula (and are not necessarily at equilibrium).
      - When mixing two solutions, the volume changes, so the concentrations in the mixed solution need to be recalculated using dilution law:
   c. Comparing $Q$ to $K_{sp}$ leads to three possibilities:
      - $Q < K_{sp}$: solution is unsaturated so no precipitate form
      - $Q = K_{sp}$: the precipitate starts forming
      - $Q > K_{sp}$: would be the case of a supersaturated solution (which is impossible) so precipitate form

3. Fractional precipitation
   a. Fractional precipitation is a technique of separation of two ions (of the same charge) from a solution by precipitating an ion
b. For example, assume that there are two different metal ions in solution (and called them M\(^+\) and N\(^+\)) and add to that solution a solid having an anion (X\(^-\)) that can make a precipitate with both cations.

\[ y\ M^+(aq) + z\ Y^-(aq) \rightarrow M_yX_z(s) ; K_{sp}(M_yX_z) \]

\[ y\ N^+(aq) + z\ Y^-(aq) \rightarrow N_yX_z(s) ; K_{sp}(N_yX_z) \]

c. One type of problem deals with what compound will precipitate first.

\[ \text{Generally, when concentrations are similar and the charges are the same, the compound with the } K_{sp} \text{ value will start precipitating first (i.e., will precipitate when smaller amount of X}^-\text{ is added).} \]

d. Another type of problem asks what is the concentration of the first metal when the second metal

\[ \text{This is like two common-ion problems, one to determine the concentration of X}^-\text{ when NX start precipitating (assuming that NX precipitate later) then determining the concentration of M}^+\text{ for that concentration of X}^-\text{.} \]

---

**O-VII.2 → O-VII.5**

17) Which of the following statements is false?

- a. Mixing a Pb(NO\(_3\))\(_2\) solution and a H\(_2\)SO\(_4\) solution will probably produce a precipitate.
- b. The solubility product expression is the product of the concentrations of the compound's constituent ions.
- c. \( K_{sp} \) is a constant at a given temperature.
- d. The concentration of the solid is not included in the solubility product expression.
- e. An ion may never be completely precipitated from solution, even when the precipitating reagent is used in large excess.

---

**O-VII.5**

18) \( K_{sp} \) for CaF\(_2\) is \( 3.9 \times 10^{-11} \) and \( K_{sp} \) for PbF\(_2\) is \( 3.7 \times 10^{-8} \). If 200. mL each of \( 5.0 \times 10^{-3} \) M NaF, \( 2.0 \times 10^{-5} \) M Ca(NO\(_3\))\(_2\), and \( 3.0 \times 10^{-3} \) M Pb(NO\(_3\))\(_2\) solutions are mixed,

- a. both CaF\(_2\) and PbF\(_2\) will precipitate, and the precipitate should be visible.
- b. only PbF\(_2\) will precipitate.
- c. only CaF\(_2\) will precipitate.
- d. both CaF\(_2\) and PbF\(_2\) will precipitate, but the precipitate should not be visible.
- e. neither CaF\(_2\) nor PbF\(_2\) will precipitate.
19) A solution contains 0.05 M Au\(^+\), 0.05 M Cu\(^+\), and 0.05 M Ag\(^+\) ions. When solid NaCl is added to the solution, what is the order in which the chloride salts will begin to precipitate?

\[ K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}, \quad K_{sp}(\text{AuCl}) = 2.0 \times 10^{-13}, \quad K_{sp}(\text{CuCl}) = 1.9 \times 10^{-7} \]

- a. AuCl > AgCl > CuCl
- b. AuCl > AgCl > NaCl
- c. AgCl > CuCl > AuCl
- d. CuCl > AgCl > AuCl
- e. NaCl > CuCl > AgCl

20) If solid AgNO\(_3\) is slowly added to a solution that is 0.050 M in NaI and 0.12 M in NaCl, what is the concentration of I\(^-\) when AgCl just begins to precipitate?

\[ K_{sp} \text{ for AgCl} = 1.8 \times 10^{-10}, \quad K_{sp} \text{ for AgI} = 1.5 \times 10^{-16} \]

- a. 1.0 \times 10^{-9} M
- b. 9.2 \times 10^{-9} M
- c. 8.5 \times 10^{-8} M
- d. 1.0 \times 10^{-7} M
- e. 6.7 \times 10^{-7} M

C. Factors Influencing Solubility (O-VII.7 → O-VII.9)

1. pH influence on solubility
   a. This section discusses a situation in which the anion of an insoluble compounds can participate in another reaction (than the solubility equilibrium).
   - Consider that the anion of an insoluble compound is the conjugate base of a weak acid so it will also participate in an acid-base equilibrium.
     - \( X^- + H_3O^+ \rightleftharpoons HA + H_2O \)
   - This is the reverse of the weak acid ionization process.
   c. An insoluble compound in which the anion is the conjugate base of a weak acid will be more soluble at
     - The lower the pH, the higher [H\(^+\)], the more shifted to the right the acid-base equilibrium above (toward HX and away from X\(^-\)), the lower [X\(^-\)], the more shifted toward soluble ions (away from MX solid) is the solubility equilibrium, the higher the solubility is.
   d. If an insoluble compound does not dissolve at pH = 7, it might dissolve
e. Look back at insoluble (or slightly soluble) hydroxides that can be solubilized in acid solution or basic solution, and they are called

□ An species is a species (molecule/ion) that can react both as an acid and as a base.
□ Example: Zn(OH)$_2$ + 2H$^+$ → Zn$^{2+}$ + 2H$_2$O
□ Example: Zn(OH)$_2$ + 2OH$^-$ → [Zn(OH)$_4$]$^{2-}$

2. Complex-ion formation
a. This section discusses a situation in which the cation of an insoluble compounds can participate in another reaction (than the solubility equilibrium).

b. Some metal ions can participate in complex ion formation:
□ M$^+$(aq) + n :L(aq) ⇌ ML$_n^{+/−}$
□ the cation M$^+$ is an electron acceptor in forming a coordinate covalent bond
□ the L is called and it is an electron donor in forming a coordinate covalent bond
□ ML$_n^{+/−}$ is the
□ The ligand can be neutral (e.g., NH$_3$) giving a positively charged complex ion, or negative (e.g., CN$^−$) giving a negatively charged complex ion.

c. The complex ion formation is a reversible process characterized by equilibrium constant $K_f$ called formation constant.
□ $K_f = \frac{[ML_n^{+/−}]}{[M^+][L]^n}$
□ The opposite of the formation process is the dissociation process that is characterized by $K_d = \frac{1}{K_f} = \frac{[M^+][L]^n}{[ML_n^{+/−}]}$
d. An insoluble compound in which the cation can participate in a complex-ion formation will be more soluble at

- The higher the ligand concentration, the more shifted to the right is the formation of complex ion (toward $ML_n$ and away from $L$ and $M^+$), the lower $[M^+]$, the more shifted toward soluble ions (away from MX solid) is the solubility equilibrium, the solubility $s$.

**O-VII.7**

21) Which of the following salts would be expected to be more soluble in acidic solution than in pure water?

a. AgBr
b. Hg$_2$I$_2$
c. CaF$_2$
d. PbCl$_2$
e. BaSO$_4$

**O-VII.8**

22) The cations in many slightly soluble compounds can form complex ions; this results in the ____ of the slightly soluble compound as ____ are formed with molecules and ions such as $NH_3$, CN$^-$, and the halides.

a. precipitation; weak electrolytes
b. dissolution; weak electrolytes
c. dissolution; ions
d. precipitation; coordinate covalent bonds
e. dissolution; coordinate covalent bonds

**O-VII.8**

23) Calculate the concentration of cadmium ions in a 0.10 $M$ [Cd(CN)$_4$]$^{2-}$ solution. The complex ion dissociates:

$$[Cd(CN)_4]^{2-} \rightleftharpoons Cd^{2+} + 4CN^-,$$

and its dissociation constant is $7.8 \times 10^{-18}$.

a. $3.0 \times 10^{-5} M$
b. $5.7 \times 10^{-5} M$
c. $7.9 \times 10^{-5} M$
d. $9.8 \times 10^{-5} M$
e. $2.2 \times 10^{-4} M$

***O-VII.8***

24) Calculate the concentration of Cu$^{2+}$ ions in a 0.010 $M$ [Cu(NH$_3$)$_4$]$^{2+}$ solution at 25°C. $K_d$ for [Cu(NH$_3$)$_4$]$^{2+} = 8.5 \times 10^{-13}$

a. $1.3 \times 10^{-3} M$
b. $5.1 \times 10^{-4} M$
c. $6.3 \times 10^{-5} M$
d. $7.8 \times 10^{-6} M$
e. $1.3 \times 10^{-6} M$
3. Qualitative analysis
   a. Quantitative analysis refers to a multi-step procedure to identify all cations present in an aqueous sample.
   b. An important step in the procedure is to separates (by precipitation) the ions in five different groups (not to be confused with the groups of the periodic table of elements).
   c. The procedure contains multiple precipitation, complex-ion formation, and acid-base reactions including specific reactions to identify particular cations.
Unit VIII
Thermodynamics

Unit Objectives

O-VIII.1 Learn terminology: State function, Path function, Spontaneous process, Entropy, Absolute entropy, Thermodynamics 2nd law, Thermodynamics 3rd law, Criterion of spontaneity, Free energy

O-VIII.2 Apply thermochemistry concepts from unit I: state and path functions, enthalpy, thermochemical equations, Hess law, enthalpies of formation, enthalpy of reaction as a function of enthalpies of formation

O-VIII.3 Describe entropy and properties derived from being a state function

O-VIII.4 Predict qualitatively the sign of $\Delta S$

O-VIII.5 Describe the second and the third law of thermodynamics

O-VIII.6 Describe and apply criteria for spontaneous processes

O-VIII.7 Describe Gibbs free energy and properties derived from being a state function

O-VIII.8 Describe and apply the relation between $\Delta G$, $\Delta H$, and $\Delta S$

O-VIII.9 Predict the sign of $\Delta G$ at various $T$

O-VIII.10 Describing and applying the relations between $\Delta G$, $\Delta G^\circ$ and $K$
A. Thermochemistry (O-VIII.2)

1. Review of concepts
   a. State functions are quantities that depend only on the current state of the system and not how the system got to that state.
      □ For state functions
   b. Enthalpy \( (H = U + PV) \) is a form of energy and its’ change is directly related to heat exchanged under constant-pressure conditions:
   c. Thermochemical equations are balanced chemical equations that include the \( \Delta H \) associated with the reaction (and the physical states of reactants and products).
   d. Hess’s law is a consequence of enthalpies of reaction being additive.
   e. Standard enthalpy of formation \( (\Delta H^\circ_f) \) is the enthalpy change associated with the thermodynamic process of formation of 1 mole of compound from elements in their standard/reference state.
   f. Standard enthalpy of reaction \( (\Delta H^\circ_{rxn} \text{ or } \Delta H^\circ_r) \) can be determined from standard enthalpies of formation.
      □ \( \Delta H_{rxn} = \sum n \Delta H_f \text{ (products)} - \sum m \Delta H_f \text{ (reactants)} \)

2. New state functions
   a. This unit will introduce two new thermodynamic (entropy and Gibbs energy) that have same (or similar) properties as enthalpy and will discuss the conditions for a process to happen (i.e., to be spontaneous).
   b. Entropy \( (S) \) has similar properties to the enthalpy except the entropy of formation is not necessary as the absolute value of entropy can be determined.
      □ \( \Delta S_{rxn} = \sum n S^\circ \text{ (P)} - \sum m S^\circ \text{ (R)} \)
   c. Gibbs free energy \( (G) \) is a form of energy, and it has the same properties as the enthalpy.
      □ \( \Delta G_{rxn} = \sum n \Delta G_f^\circ \text{ (P)} - \sum m \Delta G_f^\circ \text{ (R)} \)
1) Calculate the amount of heat released in the complete combustion of 8.17 grams of Al to form Al$_2$O$_3$(s) at 25°C and 1 atm. The reaction is:

$$4\text{Al}(s) + 3\text{O}_2(g) \rightarrow 2\text{Al}_2\text{O}_3(s); \Delta H = 3352 \text{ kJ}$$

- a. 203 kJ
- b. 127 kJ
- c. 254 kJ
- d. 237 kJ
- e. 101 kJ

2) Which of the following is not a formation reaction?

- a. Ca(s) + 1/2O$_2$(g) \rightarrow CaO(s)
- b. 1/2H$_2$(g) + 1/2 Br$_2$(l) \rightarrow HBr(g)
- c. H$_2$(g) + 1/2O$_2$(g) \rightarrow H$_2$O(l)
- d. H$_2$O(l) + SO$_3$(l) \rightarrow H$_2$SO$_4$(l)
- e. 4Al(s) + 3/2O$_2$(g) \rightarrow Al$_2$O$_3$(s)

3) For which of the following substances does $\Delta H_f^0 = 0$?

- a. C(diamond)
- b. Fe(s)
- c. HCl(aq)
- d. HCl(g)
- e. I$_2$(g)

4) Calculate the standard heat of vaporization, $\Delta H_{vap}$, for tin(IV) chloride, SnCl$_4$, in kJ per mole. $\Delta H_f$ = -511.3 kJ/mol for SnCl$_4$(l) and -471.5 kJ/mol for SnCl$_4$(g).

- a. 44.8
- b. 53.2
- c. 26.4
- d. 16.4
- e. 39.8

5) From the following data at 25°C,

$$\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{HCl}(g); \Delta H^0 = -185 \text{ kJ}$$
$$2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g); \Delta H^0 = -483.7 \text{ kJ}$$

Calculate $\Delta H^0$ at 25°C for the following reaction

$$4\text{HCl}(g) + \text{O}_2(g) \rightarrow 2\text{Cl}_2(g) + 2\text{H}_2\text{O}(g)$$

- a. +114 kJ
- b. +299 kJ
- c. -299 kJ
- d. -114 kJ
- e. -86.8 kJ

B. Entropy (O-VIII.3 → O-VIII.6)

1. Qualitative description of entropy
   a. Entropy is
b. Entropy is not a form of energy but
   - The SI unit of entropy is

   c. Entropy is
   - means that there is not an easy or exact way to calculate the energy dispersion except for Boltzmann formula, which is not very useful \( S = k_B \ln W \) where \( k_B \) is the Boltzmann’s constant.
   - means spreading or distributing the energy over different possible forms/arrangements.
   - An old and incorrect way of defining entropy refers to the entropy as a

   d. Qualitatively (or in general), the entropy is higher when:
   - the energy (or \( U \) or \( H \))
   - the available energy (or \( U \) or \( H \)) is distributed

2. Entropy comparisons
   a. Entropy is higher at temperature because there is more (thermal energy) to disperse.
   b. Entropy is for gasses than the liquids and than for solids (within the same compound at the same temperature).
      - \( S(s) \quad S(l) \quad S(g) \)
      - Solids have less energy states available compared to liquids and much less compared to gasses.
      - A representation of the available energy levels:

\[
\begin{array}{ccc}
\text{less levels} & \text{more levels} \\
\Rightarrow \text{low } S & \Rightarrow \text{high } S \\
\text{s} & \text{l} & \text{g}
\end{array}
\]
c. Entropy is higher at higher volume than at lower volume (for a compound in a gas phase) because more energy levels (as well as space) are available.

\[ \Delta S = RT \ln \frac{V_f}{V_i} \] and \( \Delta S > 0 \) when \( \frac{V_f}{V_i} > 1 \)

d. Given the same temperature, volume and physical state, entropy is higher for compounds with higher molecular mass \( (M_M) \) because more energy levels are available.

e. Given the same temperature, volume, physical state and \( M_M \), entropy is higher for compounds with higher molecular complexity because more energy levels are available.

f. Temperature (and therefore the amount of energy available for dispersion) is the most important factor in determining the entropy so it is important to make comparisons of energy dispersion at the same temperature (and same physical state).

g. Examples above can be represented together like below.

| lower \( S \) | higher \( S \) |
| low \( V \) | high \( V \) |
| low \( M_M \) | high \( M_M \) |
| solid | gas |

3. Third law of thermodynamics

a. The entropy of pure, perfectly crystalline substances is 0 at 0 K.

- Perfectly crystalline substances (or perfect crystals) are crystals with
- At 0 K the substances are in
- At 0 K, there is no energy to distribute so there is

b. Based on the third law of thermodynamics, one can define absolute entropies and not relative ones (like in the case of energy/enthalpy).

- Absolute entropies are sometimes called
c. One can use $S^\circ$ and not needed $\Delta S^\circ_{f}$.

d. Based on entropy of 0 at 0 K and the increase of entropy with temperature, one can graph entropy change versus temperature.

- There is a continuous increase in $S$ with $T$.
- There is a large increase in $S$ going from solid to liquid and an even larger increase going from liquid to gas.
- Typically, $S$(solids) $\approx$ J/K, $S$(liquids) $\approx$ J/K, and $S$(gases) $\approx$ J/K.

**O-VIII.3**

7) Evaluate $\Delta S^0$ for the reaction below at 25°C and 1 atm.

\[ 3\text{NO}_2(g) + \text{H}_2\text{O}(l) \rightarrow 2\text{HNO}_3(aq) + \text{NO}(g) \]

| $S^0$ (J/mol•K) | 240 | 69.91 | 146 | 210.7 |

a. -287.2 J/K  
b. -1370 J/K  
c. +1370 J/K  
d. +287.2 J/K  
e. -531.4 J/K

**O-VIII.3**

8) Which of the following changes represent a decrease in entropy?

a. Freezing water  
b. Diffusion of perfume throughout a room  
c. Sublimation of dry ice, solid CO$_2$  
d. Evaporation of gasoline  
e. Melting snow

**O-VIII.4**

9) Which one of the following reactions has, most likely, a positive entropy change?

a. BF$_3$(g) + NH$_3$(g) → F$_3$BNH$_3$(s)  
b. N$_2$(g) + 3H$_2$(g) → 2NH$_3$(g)  
c. 2SO$_2$(g) + O$_2$(g) → 2SO$_3$(g)  
d. 2NH$_4$NO$_3$(s) → 2N$_2$(g) + 4H$_2$O(g) + O$_2$(g)  
e. H$_2$O(g) → H$_2$O(l)

**O-VIII.4**

10) Which one of the following reactions has, most likely, the most negative entropy change?

a. BF$_3$(g) + NH$_3$(g) → F$_3$BNH$_3$(s)  
b. 2NH$_3$(g) → N$_2$(g) + 3H$_2$(g)  
c. 2SO$_2$(g) + O$_2$(g) → 2SO$_3$(g)  
d. 2NH$_4$NO$_3$(s) → 2N$_2$(g) + 4H$_2$O(g) + O$_2$(g)  
e. H$_2$O(g) → H$_2$O(l)
4. Second law of thermodynamics
   a. The entropy of the universe increases in a spontaneous process.
      □ A spontaneous process is a process that

   b. The entropy of an isolated system (which does not exchange mass or
      energy with the surroundings) increases in a spontaneous process.
      □ $\Delta S_{\text{sys}} > 0$ for

   c. For closed and open systems, as energy can transfer between system
      and surroundings, the entropy of the system can increase or decreases
      in a spontaneous process.
      □ $\Delta S_{\text{universe}} > 0$ for closed (and open) systems.
      □ $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$ for closed (and open) systems.
      □ At constant temperature,
      □ $\Delta S_{\text{sys}} - q/T > 0$ or $\Delta S_{\text{sys}} > q/T$ for a spontaneous process in a closed
      system, at constant $T$.
      □ At constant pressure, $\Delta H_{\text{sys}} = q_P$.
      □ $\Delta S_{\text{sys}} > \Delta H_{\text{sys}} /T$ for a spontaneous process in a closed system, at
      constant $T$ and $P$.

   d. For a spontaneous process in a closed system, at constant $T$ and $P$,
      $\Delta S_{\text{sys}} > \Delta H_{\text{sys}} /T$ or $\Delta H_{\text{sys}} - T\Delta S_{\text{sys}} < 0$.

   e. Look also at the surroundings: $\Delta S_{\text{surr}} = -\Delta H_{\text{sys}} /T$ at constant $T$ and $P$.
      □ In an exothermic process,
      □ In an endothermic process,

   f. A spontaneous process is also referred to as

   g. When no changes happen in the system (i.e., the system is at
      equilibrium) or the changes are so slow that they can be reversible,
For a reversible process (or a process at equilibrium), at constant $T$ and $P$, $\Delta H_{sys} - T\Delta S_{sys} = 0$.

A non-spontaneous process is a process that will not happen as written but it is spontaneous and it can happen in opposite direction.

5. Criteria for spontaneous processes

a. In the table below, there is a review of the criteria for spontaneous processes and the conditions under which they apply.

□ The last line in the table contains approximate criteria, and they involve the standard state ($^\circ$).

<table>
<thead>
<tr>
<th>Condition</th>
<th>Spontaneous (irreversible)</th>
<th>At equilibrium (reversible)</th>
<th>Non-spontaneous (as written)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T = ct.$</td>
<td>$\Delta S_{\text{universe}} &gt; 0$</td>
<td>$\Delta S_{\text{universe}} = 0$</td>
<td>$\Delta S_{\text{universe}} &lt; 0$</td>
</tr>
<tr>
<td>$T, P = ct.$</td>
<td>$\Delta S_{\text{sys}} &gt; \frac{q}{T}$</td>
<td>$\Delta S_{\text{sys}} = \frac{q}{T}$</td>
<td>$\Delta S_{\text{sys}} &lt; \frac{q}{T}$</td>
</tr>
<tr>
<td>$T, P = ct.$</td>
<td>$\Delta H_{\text{sys}} - T\Delta S_{\text{sys}} &lt; 0$</td>
<td>$\Delta H_{\text{sys}} - T\Delta S_{\text{sys}} = 0$</td>
<td>$\Delta H_{\text{sys}} - T\Delta S_{\text{sys}} &gt; 0$</td>
</tr>
<tr>
<td>$T, P = ct.$</td>
<td>$\Delta G_{\text{sys}} &lt; 0$</td>
<td>$\Delta G_{\text{sys}} = 0$</td>
<td>$\Delta G_{\text{sys}} &gt; 0$</td>
</tr>
<tr>
<td>$T, P = ct.$</td>
<td>$\Delta G_{\text{sys}}^\circ &lt; 0$</td>
<td>$\Delta G_{\text{sys}}^\circ = 0$</td>
<td>$\Delta G_{\text{sys}}^\circ &gt; 0$</td>
</tr>
</tbody>
</table>

11) Which of the following statements is correct?
   a. When energy is released by the reacting system, $\Delta E$ is positive.
   b. A positive change in entropy represents a decrease in molecular disorder.
   c. The second law of thermodynamics states that $\Delta H < 0$ and $\Delta S > 0$ for all spontaneous processes.
   d. The absolute $S$ at 298 K can be positive or negative.
   e. The entropy of the universe always increases in spontaneous processes.

12) Which of the following statements is false?
   a. $\Delta S$ is positive for many spontaneous processes.
   b. $\Delta G$ is always negative for spontaneous processes.
   c. $\Delta G$ is always positive for nonspontaneous processes.
   d. $\Delta S$ must be positive for a process to be spontaneous.
   e. If $\Delta S$ is negative then $\Delta H$ must be negative for a spontaneous process.
O-VIII.6

13) Which statement below is false?
   a. Endothermic reactions may be spontaneous.
   b. The entropy of a system decreases when order increases.
   c. If compounds that are stable at low temperature and unstable at high temperature, the decomposition reactions have positive $\Delta H$ and positive $\Delta S$.
   d. If the free energy change of reaction is positive, the reaction cannot occur to give predominantly products under the given conditions.
   e. A process cannot be spontaneous (product-favored) if it is exothermic, and there is a decrease in disorder (or energy dispersion).

C. Gibbs Free Energy (O-VIII.7 $\rightarrow$ O-VIII.10)

1. Qualitative description of Gibbs free energy
   a. Gibbs free energy (or free energy of Gibbs energy) is another form of energy characterizing the system, it is denoted by $G$, and its use is preferred for identifying if a process is spontaneous or not.
   b. Gibbs free energy is defined as:
   c. Gibbs free energy change at constant temperature:
      □ The subscript “sys” is not included but should be understood.
   d. Gibbs free energy is with the appropriate properties.
   e. Similar to enthalpy, Gibbs free energy is relative energy so one uses $\Delta G_f$ on the assumption that elements in reference state has $\Delta G_f = 0$.
      □ $\Delta G_{\text{rxn}} =$
   f. Tabulated values are for standard conditions ($\Delta G^\circ_f$).
      □ $\Delta G^\circ_r =$
   g. Gibbs free energy change at constant temperature and pressure is a criterion for spontaneous reactions/processes.
      □ $\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$.
      □ $\Delta G_{\text{sys}} < 0$ for spontaneous processes at constant $T$ and $P$.
      □ $\Delta G_{\text{sys}} = 0$ for reversible processes at constant $T$ and $P$.
      □ $\Delta G_{\text{sys}} > 0$ for non-spontaneous processes at constant $T$ and $P$.
h. Standard Gibbs free energy change ($\Delta G^\circ_{\text{sys}}$) at constant temperature and pressure can be used as an approximate criterion for spontaneous reactions/processes.

□ Typically, $\Delta G^\circ_{\text{sys}} < 0$ at constant $T$ and $P$ for spontaneous processes.

□ There is a relation between Gibbs free energy change, $\Delta G$, and standard Gibbs free energy change, $\Delta G^\circ$, that will be explained later.

□

i. The meaning of $\Delta G$ is that of the maximum work that can be done by the (reaction in the) system.

2. Predicting the sign of $\Delta G$

a. Based on the values of $\Delta H$ and $\Delta S$, $\Delta G$ can be positive or negative at various temperatures as presented in the table below.

□ The assumption is that $\Delta H$ and $\Delta S$ are not depending on $T$.

<table>
<thead>
<tr>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
<th>$\Delta G = \Delta H - T\Delta S$</th>
<th>Spontaneous at</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-$</td>
<td>$+$</td>
<td>$\Delta G = \Delta H - T\Delta S$</td>
<td>$-$ at high $T$</td>
</tr>
<tr>
<td>$+$</td>
<td>$-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$+$</td>
<td>$+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$-$</td>
<td>$-$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
b. Aspects that help a process being spontaneous ($\Delta G < 0$):
   □ being
   □ being accompanied by an which is equivalent to increase in energy dispersion.

3. Reversible processes and systems at equilibrium
   a. For a reversible process or a system at equilibrium,
      □ $\Delta H = T\Delta S$ or $\Delta S = \Delta H / T$ or $T = \Delta H / \Delta S$.
   b. Examples of reversible processes are the phase transformations at equilibrium.
      □ One can determine $\Delta H_{tr}$ given $T$ and $\Delta S_{tr}$ ($\Delta H_{tr} = T\Delta S_{tr}$).
      □ One can determine $\Delta S_{tr}$ given $T$ and $\Delta H_{tr}$ ($\Delta S_{tr} = \Delta H_{tr}/T$).
      □ One can determine $T$ given $\Delta S_{tr}$ and $\Delta H_{tr}$ ($T = \Delta H_{tr}/\Delta S_{tr}$).

---

**O-VIII.7&O-VIII.8**

14) Evaluate $\Delta G^{\circ}_{298}$ for the following reaction at 25°C.

<table>
<thead>
<tr>
<th>$\Delta H_f^\circ$ (kJ/mol)</th>
<th>$S^\circ$ (J/mol•K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2ZnS(s) + 3O$_2$(g) → 2ZnO(s) + 2SO$_2$(g)</td>
<td></td>
</tr>
<tr>
<td>-205.6</td>
<td>57.7</td>
</tr>
<tr>
<td>0</td>
<td>205.0</td>
</tr>
<tr>
<td>-348.3</td>
<td>43.64</td>
</tr>
<tr>
<td>-296.8</td>
<td>248.1</td>
</tr>
</tbody>
</table>

a. -704.2 kJ
b. -922.6 kJ
c. -1902 kJ
d. -835.2 kJ
e. -951.1 kJ

---

**O-VIII.7&O-VIII.8**

15) Evaluate $\Delta H^{\circ}_{298}$ for the following reaction at 25°C.

<table>
<thead>
<tr>
<th>$\Delta H_f^\circ$ (kJ/mol)</th>
<th>$S^\circ$ (J/mol•K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2ZnS(s) + 3O$_2$(g) → 2ZnO(s) + 2SO$_2$(g)</td>
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<td>-205.6</td>
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</tr>
<tr>
<td>-348.3</td>
<td>43.64</td>
</tr>
<tr>
<td>-296.8</td>
<td>248.1</td>
</tr>
</tbody>
</table>

a. -879.0 kJ
b. -339.5 kJ
c. +879.0 kJ
d. -339.5 kJ
e. -147.0 kJ

---

*O-VIII.7&O-VIII.8*
16) Evaluate $\Delta S_{298}$ for the following reaction at 25°C.

$2\text{ZnS(s)} + 3\text{O}_2(g) \rightarrow 2\text{ZnO(s)} + 2\text{SO}_2(g)$

<table>
<thead>
<tr>
<th>$\Delta H_f^\circ$ (kJ/mol)</th>
<th>205.6</th>
<th>0</th>
<th>-348.3</th>
<th>-296.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S^\circ$ (J/mol•K)</td>
<td>57.7</td>
<td>205.0</td>
<td>43.64</td>
<td>248.1</td>
</tr>
</tbody>
</table>

a. -879.0 J/K  
b. +29.0 J/K  
c. -147.0 J/K  
d. -29.0 J/K  
e. +147.1 J/K

17) Evaluate $\Delta G^\circ$ for the following reaction at 25°C given $\Delta H^\circ = -879$ kJ and $\Delta S^\circ = -147$ J/K.

$2\text{ZnS(s)} + 3\text{O}_2(g) \rightarrow 2\text{ZnO(s)} + 2\text{SO}_2(g)$

<table>
<thead>
<tr>
<th>$\Delta H_f^\circ$ (kJ/mol)</th>
<th>205.6</th>
<th>0</th>
<th>-348.3</th>
<th>-296.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S^\circ$ (J/mol•K)</td>
<td>57.7</td>
<td>205.0</td>
<td>43.64</td>
<td>248.1</td>
</tr>
</tbody>
</table>

a. +871 kJ  
b. -883 kJ  
c. -835 kJ  
d. -871 kJ  
e. +835 kJ

18) Estimate the temperature at which $\Delta G = 0$ for the following reaction.

$\text{NH}_3(g) + \text{HCl(g)} \rightarrow \text{NH}_4\text{Cl(s)}$

$\Delta H = -176$ kJ; $\Delta S = -284.5$ J/K

a. 680 K  
b. 582 K  
c. 619 K  
d. 634 K  
e. 467 K

19) Calculate the standard entropy of vaporization, $\Delta S_{\text{vap}}^\circ$, for water, in J/mole•K.

$\Delta H_f^\circ = -285.8$ kJ/mol for $\text{H}_2\text{O(l)}$ and $\Delta H_f^\circ = -241.8$ kJ/mol for $\text{H}_2\text{O(g)}$.

a. -44  
b. +118  
c. +440  
d. +44  
e. -118
4. Equilibrium and Gibbs free energy
   a. There is a relationship between the equilibrium and the Gibbs free energy change.
   b. There is a relationship between Gibbs energy change for standard and nonstandard conditions:
      □ $Q$ is the reaction quotient, $R$ is the ideal gas law constant (8.3145 J/mol-K), and $T$ is the absolute temperature.
   c. At equilibrium, $\Delta G = 0$, $Q = K$ so
      $K = \exp(-\Delta G^\circ / RT) = e^{\Delta G^\circ / RT}$
   d. As mentioned earlier, the magnitude of the equilibrium constant indicates what is mostly present when the equilibrium is reached.
      □ $K >> 1 \Rightarrow$ mostly at equilibrium (or product-favored) is equivalent to $\Delta G^\circ$ being negative.
      □ $K << 1 \Rightarrow$ mostly at equilibrium (or reactant-favored) is equivalent to $\Delta G^\circ$ being positive.
   e. Combining the two expressions above,
   f. When $Q > K$, reverse reaction is occurring.
      □ $\Delta G > 0$ for forward reaction ($R \rightarrow P$)
      □ $\Delta G < 0$ for reverse reaction ($R \leftarrow P$)
   g. When $Q < K$, forward reaction is occurring.
      □ $\Delta G < 0$ for forward reaction ($R \rightarrow P$)
      □ $\Delta G > 0$ for reverse reaction ($R \leftarrow P$)
   h. The Gibbs energy of a system at equilibrium is lower than the Gibbs energy of reactants or products.
   i. In biological systems, processes with $\Delta G(1) > 0$ are possible
22) Which of the following statements about $\Delta G^0$ and the thermodynamic equilibrium constant is false?

a. When $\Delta G^0 > 0$, $K < 1$.
b. There is a mathematical relationship between $\Delta G^0$ and $K$.
c. When $K > 1$, the reverse reaction is favored.
d. When $\Delta G^0 < 0$, the forward reaction is favored.
e. $\Delta G^0$ and $K$ are both indicators of the direction of a spontaneous reaction.

23) Calculate the thermodynamic equilibrium constant at 25°C for a reaction for which $\Delta G^0 = -25.60$ kJ per mol of reaction. $R = 8.314$ J/mol•K

a. $5.14 \times 10^1$
b. $6.12 \times 10^2$
c. $4.32 \times 10^6$
d. $3.07 \times 10^4$
e. 11.2
Unit IX

Electrochemistry

Unit Objectives

O-IX.1 Learn terminology: Voltaic cell, Electrolytic cell, Anode & Cathode, Salt bridge, Cell potential, Electrode potential, Fuel cell, Electrolysis
O-IX.2 Determine oxidation numbers (or oxidation state) - review
O-IX.3 Define and identify oxidation-reduction (redox) reactions, half-reactions, oxidizing and reducing agents - review
O-IX.4 Balance half reactions and redox reactions in acids or bases
O-IX.5 Describe and identify galvanic (or voltaic) cell: components, notation, and reaction
O-IX.6 Define the electrode potential and apply it to understand the strength of oxidation or reduction agents
O-IX.7 Define and calculate cell potentials $E_{\text{cell}}$ and/or standard cell potentials $E_{\text{cell}}^\circ$
O-IX.8 Apply the relation between cell potential and $\Delta G$ (as well as $K$, $\Delta H$, and $\Delta S$)
O-IX.9 Apply the relation between $E_{\text{cell}}$ and $E_{\text{cell}}^\circ$ (Nernst equation)
O-IX.10 Describe and identify electrolytic cells: components and reactions in electrolysis of molten salts or aqueous solutions
O-IX.11 Carry out quantitative applications of electrolysis
A. Redox Reactions (O-IX.2 → O-IX.4)

1. Oxidation numbers
   a. Oxidation numbers or oxidation states are either the real charge if
      monoatomic ion or the “apparent” (or assigned) charge of an atom in a
      molecule or polyatomic ion.
   b. The “apparent” (or assigned) charge is determined by considering the
      shared electrons of a covalent bond being assigned to the more
      electronegative atom of the covalent bond.

2. Determining oxidation numbers
   a. The oxidation number of an element (in its elemental form) is zero.
      □ Example: O in O₂ or O₃ has O.N. =
   b. The oxidation number of an element in a monoatomic ion is equal to
      the charge of the ion.
      □ Example: Na in NaNO₃ has O.N. =
   c. The sum of the oxidation numbers of all atoms in a species (molecule
      or polyatomic ion) is equal to the charge of the species.
   d. The oxidation number of fluorine is always –1.
   e. The oxidation number of hydrogen is always +1 except in hydrides.
      □ A hydride is an ionic compound in which hydrogen appear as
         anion, H⁻, typically in binary compounds with metals.
      □ Example: NaH (sodium hydride)
   f. The oxidation number of oxygen is –2 except
      □ in peroxides (example H₂O₂) in which it has O.N. =
      □ in superoxides (example KO₂) in which it has O.N. =
   g. Examples:
      □ NH₄⁺: O.N. (H) = ; O.N. (N) =
      □ H₂SO₄: O.N. (H) = ; O.N. (O) = ; O.N. (S) =
      □ K₂Cr₂O₇: O.N. (K) = ; O.N. (O) = ; O.N. (Cr) =
1) What is the oxidation number of chlorine in the KClO\textsubscript{3}?

a. +3  
b. +5  
c. +1  
d. −1  
e. +7

2) What is the oxidation number of phosphorus in Mg\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}?

a. +5  
b. +6  
c. +4  
d. +3  
e. +7

3. Redox reactions
   
a. An oxidation-reduction reaction (or redox reaction) is an electron-transfer reaction.
   
b. Oxidation is a half-reaction and is the process of giving electrons leading to an increase of the oxidation number.
   
c. Reduction is a half-reaction and is the process of accepting electrons leading to a decrease of the oxidation number.
   
d. The species (ion or molecule) containing the atom that gets reduced is called oxidizing agent because it oxidizes another species.
   
e. The species (ion or molecule) containing the atom that gets oxidized is called reducing agent because it reduces another species.
   
f. Some examples of redox reactions include displacement reactions, decomposition reactions, combination reaction, combustion reactions, etc.
3) Which of the following statements is **FALSE**?
   a. In \( \text{K}_2\text{Cr}_2\text{O}_7 \), chromium has higher oxidation number than both potassium and oxygen.
   b. \( \text{KMnO}_4 \) is a common oxidizing agent.
   c. The oxidation number of hydrogen in water is +1.
   d. Oxidation is a process in which electrons are gained.
   e. Reduction is a process in which the oxidation number decreases.

4) Below is the unbalanced equation of a reaction taking place in basic solution:
\[
\text{NO}_2^-(aq) + \text{Al}(s) + \text{H}_2\text{O}(l) + \text{HO}^-(aq) \rightarrow \text{NH}_3(g) + \text{AlO}_2^-(aq)
\]
Which of the following is the oxidizing agent in the reaction above?
   a. \( \text{AlO}_2^-
   
   b. \( \text{Al}
   
   c. \( \text{HO}^-
   
   d. \( \text{NH}_3
   
   e. \( \text{NO}_2^-

4. Balancing redox reactions
   a. The procedure for balancing each half-reaction and the overall redox reaction in acidic media contains the following steps.
     □ Identify the (two) elements that change oxidation numbers.
     □ For these elements, write the species containing the element (ion or molecule) on both reactant and product side of the reaction and include an arrow between them creating therefore an unbalanced half-reaction.
     □ Balance the element (in this unbalanced half-reaction) by adding the proper stoichiometric coefficients (on either R or P side).
     □ If O in unbalanced after previous step, balance the O by adding the appropriate number of \( \text{H}_2\text{O} \) molecules on the side with less O atoms.
     □ If H in unbalanced after previous step, balance the H by adding the appropriate number of \( \text{H}^+ \) ions on the side with less H atoms.
     □ Balance the charges (and therefore the whole half-reaction) by adding the appropriate number of electrons (\( \text{e}^- \)) on the side with more positive charges.
a. Add the two half-reactions multiplied by numbers in such a way that the electrons in each half-reaction will cancel out, to get the overall redox reaction (most likely in a net-ionic-equation form).

b. The procedure for balancing each half-reaction and the overall redox reaction in basic media contains the following steps.

□ First six steps are the same as above.
□ Add on both sides of the half-reaction OH\(^{-}\) ions, equal in number to H\(^{+}\) ions.
□ Write H\(^{+}\) + OH\(^{-}\) as H\(_2\)O, and cancel excess H\(_2\)O molecules (if exist) on both sides of the half-reaction.
□ Add the two half-reactions multiplied by numbers in such a way that the electrons in each half-reaction will cancel out, to get the overall redox reaction (most likely in a net-ionic-equation form).

c. The number of electrons in a half reaction is equal to the change in the oxidation number (multiplied by the number of atoms).

5. Examples:
   a. ... Cu + ... HNO\(_3\) → ... Cu(NO\(_3\))\(_2\) + ... NO + ... H\(_2\)O

   □

   □

   b. ... H\(_2\)S + ... NO\(_3\)\(^{-}\) + ... H\(^{+}\) → ... S + ... NO + ... H\(_2\)O

   □

   □

   c. ... Cl\(_2\) + ... KOH → ... KCl + ... KClO\(_3\) + ... H\(_2\)O

   □

   □

   d. ... K\(_2\)Cr\(_2\)O\(_7\) + ... NH\(_3\) + ... HCl → ... KCl + ... NO + ... CrCl\(_3\) + ... H\(_2\)O

   □

   □
5) Write the balanced net ionic half-reaction for the oxidation of H\textsubscript{2}O to O\textsubscript{2} in acidic solution. What is the sum of the coefficients (including the electrons.)

- a. 5
- b. 9
- c. 15
- d. 11
- e. 7

6) Balance the following net ionic equation. What is the coefficient of S?

\[ \text{H}_2\text{S} + \text{NO}_3^- + \text{H}^+ \rightarrow \text{S} + \text{NO} + \text{H}_2\text{O} \]

- a. 2
- b. 1
- c. 3
- d. 4
- e. 5

7) Balance this equation for a reaction in basic solution. What is the coefficient of H\textsubscript{2}O?

\[ \text{KOH} + \text{Cl}_2 \rightarrow \text{KClO}_3 + \text{KCl} + \text{H}_2\text{O} \]

- a. 2
- b. 8
- c. 3
- d. 4
- e. 6

8) Balance the following equation. How many HCl are there on the left side of the balanced equation?

\[ \text{K}_2\text{Cr}_2\text{O}_7 + \text{NH}_3 + \text{HCl} \rightarrow \text{KCl} + \text{NO} + \text{CrCl}_3 + \text{H}_2\text{O} \]

- a. 4
- b. 8
- c. 16
- d. 20
- e. 40

B. Voltaic Cells (O-IX.5 \rightarrow O-IX.9)

1. Voltaic/galvanic cells description
   
   a. There are two types of electrochemical cells:
      
      - in which a spontaneous redox reaction is taking place creating electricity
      - in which a nonspontaneous reaction is driven by external electric current
   
   b. A voltaic (or galvanic) cell is a device (i.e., an electrochemical cell) in which a spontaneous redox reaction in taken place producing electricity.
c. The two half reactions (reduction and oxidation) are taken place in different locations and electrons are allowed to flow, through an outside circuit, from the location where they are produced to the location where they are used.

2. Voltaic/galvanic cells components
   a. In general, a voltaic cell (as well as the other electrochemical cells) contains
   b. A half-cell contains an electrode (typically a metal) in contact with a solution (containing the ions of the metal).
      □ Example:
   c. The salt bridge makes electrical contact between the two electrolyte solutions without allowing them
   d. The electrode (or half-cell) in which oxidation takes place is called
      □ For a voltaic cell, this is the electrode.
   e. The electrode (or half-cell) in which reduction takes place is called
      □ For a voltaic cell, this is the electrode.

   f. Example:

3. Voltaic/galvanic cell reaction
   a. The cell reaction is the sum of the oxidation and reduction reactions (sometimes multiplied by coefficients to cancel the electrons).
   b. Example 1: Zn(s) → Zn^{2+}(aq) + 2e^- & Cu^{2+}(aq) +2e^- → Cu(s) give
c. Example 2: \( \text{Cd(s)} \rightarrow \text{Cd}^{2+}(\text{aq}) + 2e^- \) & \( \text{Ag}^+(\text{aq}) + e^- \rightarrow \text{Ag(s)} \) give

4. Voltaic/galvanic cell notation
   a. A voltaic cell is typically denoted as:
      \[ \text{Anode(s)} | \text{anode solution (aq)} || \text{cathode solution (aq)} | \text{Cathode(s)} \]
      □ A vertical bar, |, represents
      □ Two vertical bars, ||, represent
      □ Anode has to be on the left while the cathode has to be on the right.
   b. Example 1:
      \[ \text{Zn(s)} | \text{Zn}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu(s)} \]
   c. Example 2:
      \[ (\text{–}) \text{Cd(s)} | \text{Cd}^{2+}(\text{aq}) || \text{Ag}^+(\text{aq}) | \text{Ag(s)} (+) \]

9) In any electrochemical cell, the cathode is always __________.
   a. the negative electrode
   b. the positive electrode
   c. the electrode at which some species loses electrons
   d. the electrode at which oxidation occurs
   e. the electrode at which some species gains electrons

10) Which of the following statements is TRUE?
   a. The cathode is always the positive electrode.
   b. The anode is always the electrode at which some species gains electrons.
   c. In galvanic cells the flow of electrons is spontaneous.
   d. Oxidation process always takes place at the cathode.
   e. Corrosion is the reduction of a metal due to exposure to air and moisture.

11) Which of the following describes the net reaction that occurs in the cell,
    \( \text{Cd}|\text{Cd}^{2+}(1 \text{ M})||\text{Cu}^{2+}(1 \text{ M})|\text{Cu}\)?
    a. \( \text{Cu} + \text{Cd}^{2+} \rightarrow \text{Cu}^{2+} + \text{Cd} \)
    b. \( \text{Cu}^{2+} + \text{Cd} \rightarrow \text{Cu} + \text{Cd}^{2+} \)
    c. \( 2\text{Cu} + \text{Cd}^{2+} \rightarrow 2\text{Cu}^{+} + \text{Cd} \)
    d. \( \text{Cu} + \text{Cd} \rightarrow \text{Cu}^{2+} + \text{Cd}^{2+} \)
    e. \( \text{Cu}^{2+} + \text{Cd}^{2+} \rightarrow \text{Cu} + \text{Cd} \)

12) In the lead storage battery, the overall cell reaction is
    \( \text{Pb(s)} + \text{PbO}_2(s) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow 2 \text{PbSO}_4(s) + 2 \text{H}_2\text{O(l)} \)
    Which of the following reactions is taking place at the cathode?
    a. \( \text{PbSO}_4(s) + 2e^- \rightarrow \text{Pb}(s) + \text{SO}_4^{2-}(\text{aq}) \)
    b. \( \text{Pb}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Pb}(s) \)
    c. \( \text{PbSO}_4(s) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})^- + 2e^- \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O(l)} \)
    d. \( \text{PbO}_2(s) + 4\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{Pb}^{2+}(\text{aq}) + 2\text{H}_2\text{O(l)} \)
    e. \( \text{Pb(s)} + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(s) + 2\text{e}^- \)
5. Cell potential
   a. Cell potential (or electromotive force) is the voltage (i.e., a measure of the power or energy) of the electrons produced by the voltaic cell.
      □ Cell potential is denoted by
      □ Cell potential is an intensive property, measured in volts, and it is always positive.
   b. When the cell operates under standard conditions \((C = 1 \text{ mol/L}, P = 1 \text{ bar})\), the cell potential becomes standard cell potential, denoted by
   c. The cell potential is dependent on both the reduction and the oxidation, and it can be defined as
      □ \(E_\text{red}\) is the reduction potential for the reduction occurring at the cathode and \(E_\text{oxi}\) is the oxidation potential for the oxidation occurring at the anode.
      □ \(E_\text{red}\) and \(E_\text{oxi}\) are electrode potentials as they depend only on the half-reactions occurring at an electrode.
      □ So \(E_{\text{cell}}\) can be written only as a function of one type of electrode potential.
      □ By convention, the reduction potentials were chosen.
   d. The cell potential is given by
      □ Simplistically,
      □ \(E_s\) represent reduction electrode potentials.
      □ Simplistically, the cell potential is determined by identifying the two electrode potentials and subtracting the smaller value from the larger value.
6. Electrode potentials
   a. The (reduction) electrode potentials, under standard conditions, have tabulated values that are reported with respect to the standard hydrogen electrode.
      □ The standard hydrogen electrode has, by convention, an electrode potential of
   b. The standard hydrogen electrode is obtained by inserting a Pt electrode in a 1.0 M H\(^+\) solution, though which H\(_2\)(g) at 1.0 atm is bobbled through.
      □ It is denoted by Pt(s) \| H\(_2\)(1 atm) \| H\(^+\)(1 M) as anode.
      □ It is denoted by H\(^+\)(1 M) \| H\(_2\)(1 atm) \| Pt(s) as cathode.
   c. An electrode potential can be determined as the cell potential in a voltaic cell in which standard hydrogen electrode is the and the desired electrode is the
   d. The reduction potentials are associated with the following reaction:
      □ Ox represents the oxidized form of the Ox/Red couple or the species that can act as oxidizing agent.
      □ Red represents the reduced form of the Ox/Red couple or the species that can act as reducing agent.
   e. A very high positive value of the (reduction) electrode potential means that reduction is very likely therefore Ox is
   f. A very negative value of the (reduction) electrode potential means that reduction is very unlikely (therefore the reverse reaction is likely) so Red is
13) Which of the following is the best oxidizing agent in 1 M solutions?
   a. Zn$^{2+}$(aq)
   b. Li$^+$ (aq)
   c. Cu$^{2+}$(aq)
   d. Ca$^{2+}$(aq)
   e. Ag$^+$ (aq)

14) Which of the following metals is most easily oxidized?
   a. Fe
   b. Ni
   c. Cu
   d. Zn
   e. Cd

15) Calculate the standard cell potential for the cell: Ni|Ni$^{2+}$(1 M)||Cu$^{2+}$(1 M)|Cu.
   a. +0.11 V
   b. -0.57 V
   c. -0.11 V
   d. +0.25 V
   e. +0.57 V

16) Calculate the standard cell potential for the cell: Cd|Cd$^{2+}$(1 M)||Cu$^+$ (1 M)|Cu.
   a. +0.56 V
   b. -0.56 V
   c. +1.44 V
   d. +0.74 V
   e. +0.92 V

17) What is the cell potential for a cell constructed by immersing a strip of silver in a 1.0 M AgNO$_3$ solution and a strip of nickel in a 1.0 M NiSO$_4$ solution and completing the circuit by a wire and a salt bridge?
   a. +0.53 V
   b. +1.30 V
   c. +0.30 V
   d. +1.83 V
   e. +1.03 V
7. Relation between cell potential and Gibbs free energy
   a. There is a relation between cell potential (as a measure of electrical work that a voltaic cell can produce) and the Gibbs free energy change for the cell reaction:
      □ \( F = 96500 \text{ C} \) is the Faraday constant (and is the charge of 1 mole of electrons).
      □ \( n \) is the number of electrons exchanges in the cell reaction.
   b. A positive value for \( E_{\text{cell}} \) is equivalent to a negative value for \( \Delta G \) therefore
   c. Remember the meaning of \( \Delta G \) (in Thermodynamics unit) as the maximum work that can be done by the (reaction in the) system.
   d. A similar expression is obtained for voltaic cell under standard conditions.
      □ \( n \times F \times E^\circ_{\text{cell}} = -\Delta G^\circ = -(\Delta H^\circ - T\Delta S^\circ) = RT \ln K \)
      □ \( K \) is the equilibrium constant for the cell reaction.

8. Nernst equation
   a. There is a relation between cell potential and the standard cell potential called Nernst equation.
      □ \( E_{\text{cell}} = \)
      □ \( Q \) is the for the cell reaction.
   b. At \( 25^\circ\text{C} \): \( E_{\text{cell}} = \)

9. Voltaic/galvanic cell examples
   a. Batteries and fuel cells are examples of voltaic (or galvanic) cells.
   b. A battery is a voltaic cell that can be used as a portable source of electric current.
   c. A fuel cell is a voltaic cell in which the reactants are continuously supplied to keep the cell functioning.
The cell reaction is typically a combustion reaction of $H_2$ or $CH_3OH$.

**O-IX.7&O-IX.8**

18) Which response lists all of the following reactions that are spontaneous under standard conditions?
I. $Cu^{2+} + Fe \rightarrow Cu + Fe^{2+}$
II. $2Al^{3+} + 3Cd \rightarrow 2Al + 3Cd^{2+}$
III. $Hg^{2+} + Ni \rightarrow Hg + Ni^{2+}$
   a. I and III
   b. II
   c. I
   d. III
   e. II and III

**O-IX.8**

19) A spontaneous redox reaction in which three electrons are transferred has $\Delta G = -245$ kJ/mol. If a galvanic cell is constructed based on this reaction, what would be the cell potential?
   a. 0.846 V
   b. 3.45 V
   c. 0.423 V
   d. 2.54 V
   e. 2.45 V

20) What is $\Delta G^0$ at 25°C for the reaction below? ($F = 96,500$ J/V•mol e⁻)
   $Cu^{2+} + Cd \rightarrow Cu + Cd^{2+}$
   a. -71.1 kJ
   b. -143 kJ
   c. 177 kJ
   d. -177 kJ
   e. +143 kJ

21) Given the standard electrode potentials in the table, calculate $K_c$ at 25°C for the following reaction. ($F = 96,500$ J/V•mol e⁻ and $R = 8.314$ J/mol•K)
   $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(s)$
   a. $2 \times 10^{12}$
   b. $1 \times 10^{-8}$
   c. $1 \times 10^{-4}$
   d. $6 \times 10^{7}$
   e. $1 \times 10^{4}$

22) Consider the following reaction:
   $Cu^{2+}(aq) + Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + Cu(s)$
   If a galvanic cell utilizes this reaction and the initial concentrations are $[Cu^{2+}] = 0.10 \ M$, $[Sn^{2+}] = 0.30 \ M$, and $[Sn^{4+}] = 0.30 \ M$, what will be $E_{cell}$ under these conditions?
   a. 0.58 V
   b. 0.37 V
   c. 0.52 V
   d. 0.41 V
   e. 0.46 V
C. Electrolytic Cells (O-IX.10 → O-IX.11)

1. Electrolysis and electrolytic cells
   a. Electrolysis is the process of using electric current (or energy) to drive a non-spontaneous reaction.
   b. Electrolytic cells are electrochemical cells used to carry out electrolysis.
   c. In electrolytic cells, the anode is the positive electrode and the cathode is the negative electrode, which is opposite then voltaic cells.
   d. In the electrolysis of molten sodium chloride, in which only Na\(^+\) and Cl\(^-\) are present, the electrode processes are:
      □ At anode (+):
      □ At cathode (–):
      □ The overall process is: \(2\text{Na}^+(l) + 2\text{Cl}^-(l) \rightarrow 2\text{Na}(s) + \text{Cl}_2(g)\)
   e. In the electrolysis of water, in which only H\(^+\) and OH\(^-\) are present (or electrolysis participant), the electrode processes are:
      □ At anode (+):
      □ At cathode (–):
      □ The overall process is:
   f. In the electrolysis of aqueous sodium chloride solution, in which two cations (Na\(^+\) and H\(^+\)) and two anions (Cl\(^-\) and OH\(^-\)) are present (or electrolysis participant), the electrode processes are:
      □ At anode (+):
      □ At cathode (–):
      □ The overall process is: \(2\text{Cl}^-(l) + 2\text{H}^+(aq) \rightarrow \text{Cl}_2(g) + \text{H}_2(g)\)
      □ The byproduct of the reaction is
O-IX.10
23) The half-reaction that occurs at the anode during the electrolysis of molten sodium bromide is __________.
   a. $2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$
   b. $\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$
   c. $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$
   d. $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2$
   e. $\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$

O-IX.10
24) Which of the following statements is FALSE?
   a. The electrolysis of molten sodium bromide produces Na metal and Br$_2$.
   b. Electrodes are surfaces on which oxidation or reduction half-reactions occur.
   c. In a voltaic cell a non-spontaneous reaction is taken place due to the exterior electric current.
   d. A spontaneous reaction in a galvanic cell produces a positive cell potential.
   e. The anode can be either positive or negative.

2. Quantitative Applications of Electrolysis
   a. The relationship relating the electric current, the time and the mass produced at the electrode (i.e., Faraday’s law) for a reaction of type $\text{Ox} + x \text{e}^- \rightarrow \text{Red}$ (example: $\text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu}$) is:

   - $I$ is the current intensity, measured in ampere, $1 \text{ A} = 1 \text{ C/s}$.
   - $t$ is the time of electrolysis (in seconds).
   - $F$ is the Faraday constant ($96500 \text{ C}$).
   - $x$ is the number of electrons participating in the half reaction.
   - $m$ is the mass produced at the electrode.
   - $M_M$ is the molar mass of the substance produced at the electrode.
   - $n$ is the number of moles produced at the electrode.
25) How many faradays \((F)\) are passed through a cell if 6.25 amperes of current are passed through the cell for 1.50 hours?

a. 4.19 \(F\)
b. \(5.83 \times 10^{-3} F\)
c. 2.86 \(F\)
d. 0.350 \(F\)
e. 251 \(F\)

26) A current of 10.0 ampere is run through an electrolytic cell for 550 seconds. How many grams of copper metal will be plated out of a \(\text{Cu(II)}\) nitrate solution?

a. 1.81 g
b. 3.62 g
c. 36.2 g
d. 0.955 g
e. 18.1 g

27) How many seconds would a 100 A electric current have to be applied to plate out 10.79 grams of silver metal from aqueous \(\text{AgNO}_3\) solution?

a. 193 s
b. 108 s
c. 965 s
d. 96.5 s
e. 10.8 s

28) An aqueous solution of nickel (II) acetate is electrolyzed for 3 hours with a 1.8 ampere current. What mass of nickel is produced?

a. 5.91 g
b. 0.099 g
c. 7.30 g
d. 3.28 g
e. 11.8 g

29) How long would a constant current of 4.5 amperes be required to flow in order to plate out 15 g of chromium from a chromium(III) sulfate solution?

a. 1.72 hr
b. 268 hr
c. 5.15 hr
d. 23.2 hr
e. 309 hr
Unit X
Nuclear Chemistry

Unit Objectives

O-X.1 Learn terminology: Radioactive decay, Nuclear equation, Positron, Alpha, beta, and Gamma rays, Mass defect, Binding energy, Band of stability, Radioactive decay series, Transmutation, Fusion, Fission
O-X.2 Define and use atomic numbers, mass numbers and isotopes - review
O-X.3 Define and identify types of nuclear reactions and subatomic particles
O-X.4 Balance nuclear equations
O-X.5 Define, identify and calculate nuclear binding energy and the mass defect
O-X.6 Define and identify nuclear stability: band of stability and types of decays
O-X.7 Carry out calculations involving kinetics of radioactive decay, half-life, and dating
O-X.8 Define and identify nuclear fission and nuclear chain reactions
O-X.9 Define and identify nuclear fusion
A. Atomic Structure (O-X.2)

1. Atomic particles
   a. Atoms typically contain three particles.
      □ electron – negative charge, mass of $5.4858 \times 10^{-4}$ amu
      □ proton – positive charge, mass of 1.0073 amu
      □ neutron – neutral charge, mass of 1.0086 amu
   b. Protons and neutron are heavier particles and are located in the atomic nucleus, which contains the large majority of the atom weight.
      □ Protons and neutrons are called

2. Atomic and mass numbers
   a. Atomic number (denoted $Z$) is equal to the number of protons in an atom.
      □ It is an integer.
      □ Atomic number is also equal to the number of electrons in an atom but not equal in an ion.
   b. Mass number (denoted $A$) is equal to the number of protons and neutrons in an atom (i.e., the number of heavy particles in an atom).
      □ It is an integer.
      □ Mass number is equal to the number of
   c. are different forms of an atom having same $Z$ but different $A$ (i.e., same number of protons but different number of neutrons).
   d. refers to a particular isotope (or a particular nucleus) namely an atom/element with a particular mass number.
   e. is denoted by the chemical symbol with the mass number on the top left corner (and sometimes with the atomic number on the bottom left corner) or by name-$A$.
      □ Example: $^{64}_{29}$Cu or $^{64}$Cu or copper - 64
1) Which of the following nuclides have 18 nucleons?
   a. $^{18}\text{O}$
   b. $^{32}\text{S}$
   c. $^{34}\text{S}$
   d. $^{31}\text{P}$
   e. $^{32}\text{P}$

2) Which of the following nuclides have 18 neutrons?
   a. $^{18}\text{O}$
   b. $^{32}\text{S}$
   c. $^{34}\text{S}$
   d. $^{31}\text{P}$
   e. $^{32}\text{P}$

3) Give the number of protons, neutrons, and electrons in the $^{34}_{16}\text{S}^+$ ion.
   a. 16 p, 18 n, 15 e
   b. 16 p, 18 n, 16 e
   c. 16 p, 16 n, 19 e
   d. 16 p, 18 n, 18 e
   e. 34 p, 16 n, 18 e

4) What is the symbol for a species composed of 19 protons, 20 neutrons, and 18 electrons?
   a. $^{40}\text{Ar}$
   b. $^{40}\text{Ca}$
   c. $^{34}\text{S}^2-$
   d. $^{39}\text{K}^+$
   e. $^{40}\text{Ca}^{2+}$

B. Nuclear processes (O-X.3 & O-X.4)

1. Nuclear reactions
   a. Chemical reactions are transformations that are characterized by conservation of mass and energy and by maintaining the identity of atoms.
   b. Nuclear “reactions” are processes that are totally different than the chemical reactions.
      - Nuclear processes involve breaking and forming of new nuclei (i.e., the original identity of atoms is not maintained).
      - The mass and the energy are
- The energy associated with nuclear processes is much greater than that associated with chemical reactions.
- Nuclear processes are typically
  c. Nuclear processes can be classified in two categories.
     - Radioactive decay or radioactivity, in which a nucleus breaks apart on its own (similar to an unimolecular reaction).
     - Nuclear transmutation reactions or nuclear bombardment reactions, in which a nucleus interacts with another nucleus or particle (similar to a bimolecular reaction).

2. Subatomic particles
   a. Nuclear processes can involve, besides atomic nuclei, a number of smaller, subatomic particles.
      - neutron – denoted $^1_0 n$
      - proton – denoted $^1_1 p$ or $^1_1 H$
      - electron or $\beta$ rays – denoted $^0_1 e$ or $^0_1 \beta$
      - positron – denoted
      - $\alpha$ particles – denoted $^4_2 \alpha$ or $^4_2 H e$
      - deuteron – denoted
      - $\gamma$ rays – denoted

3. Nuclear equations
   a. Nuclear processes are denoted by nuclear equations which include all nuclei and subatomic particles involved, and are similar to chemical equations.
   b. Balancing nuclear equations involves balancing
5) Which one of the following statements about nuclear reactions does not correctly distinguish nuclear reactions from ordinary chemical reactions?
   a. Rate of reaction is independent of temperature.
   b. They are often accompanied by the release of enormous amounts of energy.
   c. Particles within the nucleus are involved.
   d. Rate of reaction is independent of the presence of a catalyst.
   e. No new elements can be produced.

6) A positron has a mass number of ____., a charge of ____., and a mass equal to that of a(an) ____.
   a. 0, 1+, proton
   b. 1, 2+, proton
   c. 0, 1+, electron
   d. 1, 2+, electron
   e. 0, 0, proton

7) The conversion of $^{222}\text{Rn}$ to $^{218}\text{Po}$ occurs via ____.
   a. beta emission
   b. K capture
   c. alpha emission
   d. positron emission
   e. fission

8) Complete and balance the following equation. The missing term is:
   $^{85}\text{Kr} \rightarrow ____ + \text{ }^{0}_1\beta$
   a. $^{84}\text{Kr}$
   b. $^{85}\text{Rb}$
   c. $^{86}\text{Rb}$
   d. $^{85}\text{Kr}$
   e. $^{85}\text{Br}$

9) Complete and balance the following equation. The missing term is:
   $^{55}\text{Cu} \rightarrow ____ + \text{ }^{0}_1\beta$
   a. $^{55}\text{Zn}$
   b. $^{56}\text{Cu}$
   c. $^{55}\text{Ni}$
   d. $^{55}\text{Cu}$
   e. $^{55}\text{Cs}$

10) The alpha emission by lead-204 results in the product isotope ____.
    a. $^{200}\text{Pb}$
    b. $^{203}\text{Th}$
    c. $^{204}\text{Hg}$
    d. $^{204}\text{Bi}$
    e. $^{200}\text{Hg}$
**O-X.4**

11) Complete and balance the following equation. The missing term is:

\[
\frac{44}{21}\text{Sc} + \frac{2}{1}\text{H} \rightarrow \boxed{\text{_____}} + \frac{1}{0}\text{n}
\]

a. \(^{45}\text{Sc}\)
b. \(^{45}\text{Ti}\)
c. \(^{42}\text{Ca}\)
d. \(^{46}\text{Sc}\)
e. \(^{46}\text{Ti}\)

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C. **Radioactive Decay (O-X.5 → O-X.7)**

1. **Nuclear stability**
   
   a. The interactions between the particles in nucleus are very strong as the nucleus is very dense and the particles are very close to each other.
   
   □ Coulombic forces are repulsive forces (because the charges are all positive).
   
   □ Nuclear forces are attractive forces.

   b. Some nuclei/nuclide/isotopes are unstable and they decay naturally.

   c. Nuclear stability can be described by some trends or patterns.
   
   □ On stable nuclei, the neutron/proton ratio is approximately 1

   □ Some special stability exists for nuclei with “magic number” of nuclear particles:

   □ Nuclei with number of nucleons (both protons and neutrons) are more numerous than number of nucleons.

   □ have only unstable isotopes.

   □ Elements with Z \(\geq 93\) have only unstable isotopes.

   □ The stable nuclei form (or can be represented on) a band of stability.
d. The band (or valley) of stability is a representation showing the stable and unstable nuclei in a # neutron vs. # protons representation.
e. Certain types of emissions lead to changes toward the band of stability.
  □ β emission: \( ^1_0n \rightarrow ^1_1p + ^0_1e \)
  □ positron emission: \( ^1_1p \rightarrow ^1_0n + ^0_{+1}e \)
  □ electron capture: \( ^1_1p + ^0_{-1}e \rightarrow ^1_0n \)
  □ α emission (followed by γ emission)

2. Nuclear binding energy
   a. Nuclear binding energy (\( \Delta E \)) is defined as the energy required to break a nucleus into its constituting protons and neutrons.
      □ It is a number.
   b. Mass defect (\( \Delta m \)) is the difference between the mass of the nucleus (or an atom) and the sum of masses of its constituents.
      □ It is a number.
   c. There is a mass-energy equivalence (a relation between the binding energy and the mass defect).
\[ \Delta E = -(\Delta m)\ c^2 \text{ where } c \text{ is the speed of light.} \]
\[ \Delta E = (\Delta m)\ c^2 \]
\[ \text{Forming a nucleus from protons and neutrons is exothermic.} \]
d. A better quantity that measures the relative stability of a nucleus is the binding energy per nucleon.

A graph of binding energy per nucleon versus the mass number shows that the maximum is obtained for midsize nuclei of \( A \approx \)

**O-X.6**

14) Calculate the mass deficiency of \(^{17}\text{O}\). The actual mass of an \(^{17}\text{O}\) atom is 16.9991 amu. (Masses of subatomic particles: electron = 0.00055 amu, proton = 1.0073 amu, neutron = 1.0087 amu)

a. 0.147 amu  
b. 0.152 amu  
c. 0.142 amu  
d. 0.153 amu  
e. 0.148 amu

***O-X.6***

16) The mass deficiency of \(^{30}\text{Si}\) is 0.2755 amu/atom. Calculate the binding energy in J/mol of atoms.

a. \(2.48 \times 10^{13}\) J/mol  
b. \(1.79 \times 10^{27}\) J/mol  
c. \(1.06 \times 10^{14}\) J/mol  
d. \(6.19 \times 10^{10}\) J/mol  
e. \(5.93 \times 10^{9}\) J/mol

**O-X.6**

15) Which isotope below has the highest nuclear binding energy per gram? (No calculations are necessary.)

a. \(^{55}\text{Mn}\)  
b. \(^{4}\text{He}\)  
c. \(^{16}\text{O}\)  
d. \(^{32}\text{S}\)  
e. \(^{238}\text{U}\)

***O-X.6***

17) The actual mass of a manganese-55 atom is 54.9381 amu. Calculate its mass deficiency. (Masses of subatomic particles: electron = 0.00055 amu, proton = 1.0073 amu, neutron = 1.0087 amu)

a. 0.436 amu/atom  
b. 0.488 amu/atom  
c. 0.519 amu/atom  
d. 0.533 amu/atom  
e. 0.537 amu/atom
18) Calculate the nuclear binding energy in kJ/g of an isotope that has a mass deficiency of 0.6050 amu/atom. The isotope has a mass of 63.9280 amu.

a. $5.44 \times 10^{10}$ kJ/g
b. $1.89 \times 10^{10}$ kJ/g
c. $2.97 \times 10^{8}$ kJ/g
d. $3.48 \times 10^{12}$ kJ/g
e. $8.52 \times 10^{8}$ kJ/g

3. Natural radioactivity
   a. Unstable nuclei decay by one of the following processes: alpha emission, beta emission, gamma emission, positron emission, or electron capture.
   b. Radioactive decay series is a series of nuclear reactions by which a heavy nuclei decay into smaller nuclei.
      □ It involves multiple steps.
      □ For any radioactive decay step, the starting isotope is called parent while the resulting isotope is called daughter.

4. Kinetics of radioactive decay
   a. Radioactive decay follows kinetics that is similar to 1\textsuperscript{st} order kinetics except that the rate is not typically defined with respect to change in concentration but with respect to change in number of nuclei.
      □ Rate = where $N_t$ is number of radioactive nuclei at time $t$.
      □ Half-life:
      □ “Integrated” rate law: $\ln \frac{N_t}{N_0} = -kt$
   b. The activity of a radioactive source is sometimes described using curie:
      1 curie (Ci) = $3.700 \times 10^{10}$ disintegrations per second.
c.  The kinetics of radioactive decay can be used for dating (using $^{14}$C or other isotopes).

19) A 2.5-µg sample of technetium-99m, an metastable nucleus used in medical diagnosis, has an activity of 13 Ci. What is the decay constant?
   a. 3.2 × 10$^{-4}$ s$^{-1}$
   b. 3.2 × 10$^{-6}$ s$^{-1}$
   c. 3.2 × 10$^{-2}$ s$^{-1}$
   d. 3.2 × 10$^{-5}$ s$^{-1}$
   e. 3.2 × 10$^{-8}$ s$^{-1}$

20) The specific rate constant for the decay of Bi-210 is 0.138 d$^{-1}$. What is its half-life?
   a. 0.20 d
   b. 2.18 d
   c. 5.02 d
   d. 0.096 d
   e. 3.84 d

21) The half-life of $^{33}$P is 25.3 days. How long will it take for 64.0 g to decay to 1.0 g?
   a. 100 d
   b. 150 d
   c. 350 d
   d. 120 d
   e. 210 d

22) Nitrogen-13 has a half-life of 9.97 minutes. How much of a 10.0-g sample remains after 60.0 minutes?
   a. 9.2 g
   b. 0.15 g
   c. 2.5 g
   d. 0.35 g
   e. 1.2 g

23) Fluorine-18 is commonly used as a source of positrons for use in tumor imaging (PET scanning). The half-life of fluorine-18 is 110 minutes. A vial of a solution containing 5.00 grams of fluorine-18 is standing in the imaging laboratory. After 27 minutes, how much fluorine-18 remains?
   a. 1.78 grams
   b. 3.54 grams
   c. 2.50 grams
   d. 4.22 grams
   e. 3.76 grams

24) Cobalt-60 is commonly used as a source of beta particles for treating cancer tumors. The half-life of cobalt-60 is 5.26 years. If you have a 100 g sample, how much time will it take for 69 g of a sample of cobalt-60 to decay?
   a. 2.8 years
   b. 8.9 years
   c. 5.6 years
   d. 6.7 years
   e. 17.8 years
D. **Nuclear Bombardment Reactions (O-X.8 & O-X.9)**

1. **Nuclear transmutation reactions**
   a. Nuclear transmutation reactions (also called nuclear bombardment reactions) are reactions in which two nuclei or a nucleus and another subatomic particle are forced into each other.
   b. Certain nuclear transmutation reactions can be represented using a shorthand notation.
   \[
   ^{14}_7\text{N} + ^{4}_2\alpha \rightarrow ^{17}_8\text{O} + ^{1}_1\text{p}
   \]
   c. Nuclear transmutation reactions are/were used to create transuranium elements.

2. **Nuclear fission**
   a. Nuclear fissions are processes in which a large nucleus is transformed in
   \[
   \text{Example: } ^{235}_{92}\text{U} + ^{1}_0\text{n} \rightarrow ^{90}_{38}\text{Sr} + ^{143}_{54}\text{Xe} + 3^{1}_0\text{n}
   \]
   b. Nuclear fissions can be carried out such that they became
   \[
   \text{Example: } ^{2}_{1}\text{H} + ^{2}_{1}\text{H} \rightarrow ^{3}_{2}\text{He}
   \]
   \[
   \text{Example: } ^{3}_{2}\text{He} + ^{3}_{2}\text{He} \rightarrow ^{4}_{2}\text{He} + 2^{1}_1\text{H}
   \]

   □ A chain reaction is one in which one reactant (the neutron is the example above) is recreated as a product so it will continue the reaction.
   □ A controlled chain reaction occurs in a while an uncontrolled chain reaction occurs in an
   □ A certain amount of uranium is necessary (called critical mass) and the neutrons produced need to be slowed down (using moderators).

3. **Nuclear fusion**
   a. Nuclear fusions are processes in which small nuclei are combined into
   \[
   \text{Example: } ^{1}_{1}\text{H} + ^{1}_{1}\text{H} \rightarrow ^{3}_{2}\text{He}
   \]
   \[
   \text{Example: } ^{3}_{2}\text{He} + ^{3}_{2}\text{He} \rightarrow ^{4}_{2}\text{He} + 2^{1}_1\text{H}
   \]
b. Large amounts of energy are released, and typically, large amounts of energy are necessary to start the reaction.

\[\square\text{ Nuclear fusion reactions are often called thermonuclear reactions.}\]

### O-X.8

25) Which one of the following reactions represents fission?

- a. \(\frac{238}{92}\text{U} + \frac{12}{6}\text{C} \rightarrow \frac{246}{98}\text{Cf} + 4\ \frac{1}{0}\text{n}\)
- b. \(\frac{11}{5}\text{B} + \frac{4}{2}\text{He} \rightarrow \frac{12}{6}\text{C} +\frac{3}{1}\text{H}\)
- c. \(\frac{233}{90}\text{Th} \rightarrow \frac{233}{91}\text{Pa} +\frac{0}{1}\text{e}\)
- d. \(\frac{235}{92}\text{U} + \frac{1}{0}\text{n} \rightarrow \frac{146}{57}\text{La} + \frac{87}{35}\text{Ba} + 3\ \frac{1}{0}\text{n}\)
- e. \(\frac{3}{1}\text{H} + \frac{3}{1}\text{H} \rightarrow \frac{4}{2}\text{He} + \frac{1}{0}\text{n}\)

### O-X.9

26) Which one of the following reactions represents fusion?

- a. \(\frac{238}{92}\text{U} + \frac{12}{6}\text{C} \rightarrow \frac{246}{98}\text{Cf} + 4\ \frac{1}{0}\text{n}\)
- b. \(\frac{11}{5}\text{B} + \frac{4}{2}\text{He} \rightarrow \frac{12}{6}\text{C} +\frac{3}{1}\text{H}\)
- c. \(\frac{233}{90}\text{Th} \rightarrow \frac{233}{91}\text{Pa} +\frac{0}{1}\text{e}\)
- d. \(\frac{235}{92}\text{U} + \frac{1}{0}\text{n} \rightarrow \frac{146}{57}\text{La} + \frac{87}{35}\text{Ba} + 3\ \frac{1}{0}\text{n}\)
- e. \(\frac{3}{1}\text{H} + \frac{3}{1}\text{H} \rightarrow \frac{4}{2}\text{He} + \frac{1}{0}\text{n}\)
Appendix

On the following pages, you can find the exams used in my CHEM 1120 class during Spring 2013 and Spring 2014 semesters. As these exams were created based on the first edition of Chemistry: Atoms First by Burdge and Overby, some questions might not fit the material in the current units of lecture notes.

The keys for these exams are below.

## Spring 2013

<table>
<thead>
<tr>
<th>Exam 1</th>
<th>1. a; 2. A: decrease, B: decrease or increase; 3. 39.1 atm; 4. A: miscible, B: immiscible, C: immiscible, D: immiscible, E: miscible, F: miscible; 5. T, T, F, F, F, T; 6. c; 7. A: 1.69 kJ/K, B: 7.49 J·K; 8. d; 9. 62.1 g/mol; 10. e; 11. e; 12. b; 16. B: Na (s) + 1/2N_2(g) +3/2O_2(g) → NaNO_3(s); 17. a; 18. –1.06°C; 19. A: 101.536°C, B: –5.574°C, C: 100.512°C, D: –1.858°C; 20. a; 21. A: 5.32 m, B: 19.7%; 22. c; 23. 3.078 M; 24. e; 25. –298.5 kJ/mol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exam 2</td>
<td>1. $-\frac{1}{2} \frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\Delta t} = \frac{1}{3} \frac{\Delta[C]}{\Delta t} = \frac{\Delta[D]}{\Delta t}$; 2. $K_P = \frac{P_{CH_4}}{P_{CH_2O}} \cdot \frac{P_{H_2}}{3}$; 3. A: reactants, B: products, C: reactants, D: products; 4. A: 3, B: 0, C: 2, D: 1; 5. A: high, high, B: low, any; 6. c; 7. e; 8. T, F, F, T, T, F; 9. A: [A], negative, B: ln [A], negative; 10. 0.804; 11. F, T, T, F, F, T; 12. b; 13. A: M/s, B: s⁻¹, C: s⁻¹M⁻¹, D: s⁻¹M⁻²; 14. A: 564 s⁻¹, B: 4.07 × 10⁻⁴ s⁻¹M⁻¹; 15. Rate = $k[A]^2[B]^2$ where $k = 0.024$ min⁻¹M⁻²; 17. 1.82 × 10⁻⁷; 18. A: number of collisions, energy of collision, orientation, B: lower, same; 19. $K_c = \frac{([C]_0 + 3x)^3}{([A]_0 - 2x)^2 \cdot ([B]_0 - x)}$; 21. 57.7%; 22. d; 23. 1390 s = 23.2 min; 24. c; 25. 1.75 M.</td>
</tr>
</tbody>
</table>
---|---
---|---
---|---
---|---
---|---
Test 6 | 1. HF = hydrofluoric acid, HNO$_2$ = nitrous acid, B: AgOH = silver hydroxide, NH$_2$OH = ammonium hydroxide; 2. 11.08; 3. 4.53; 4. d; 5. b; 6. A: ammonium chloride – acidic, B: sodium hypochlorite – basic, C: calcium nitrate – neutral; 7. 8.51; 8. 5.33; 9. 7.00; 10. 8.56; 11. 5.11; 12. a; 13. 11.26
---|---
Test 7 | 1. A: $K_{sp} = [\text{Fe}^{3+}][\text{OH}^-]^3$, B: $K_{sp} = [\text{Ag}^+]^3[\text{PO}_4^{3-}]$; 2. d; 3. A: $K_d = \frac{[\text{Zn}^{2+}][\text{OH}^-]^4}{[\text{Zn(OH)}_4^{2-}]}$, B: $K_f = \frac{[\text{Cd(NH}_3)_4^{2+}]}{[\text{Cd}^{2+}][\text{NH}_3]^4}$ covalent; 6. 7.9 × 10$^{-6}$ M; 7. a; 8. A: 1.4 × 10$^{-5}$ M, B: 8.6 × 10$^{-11}$; 9. 9.50; 10. b; 11. 0.203 g; 12. 1.51 × 10$^{-7}$ M
---|---
---|---
Test 9 | 1. A: +4, B: +5, C: −1; 2. A: Zn = anode, Cu = cathode, B: Zn(s)|Zn$^{2+}$(aq)||Cu$^{2+}$(aq)|Cu(s); 3. A: Zn → Zn$^{2+}$ + 2e$^-$ and Cu$^{2+}$ + 2e$^-$ → Cu, B: Zn + Cu$^{2+}$ → Zn$^{2+}$ + Cu; 4. A: −0.25 V, B: 0.80 V, C: 1.05 V; 5. −41.5 kJ/mol; 7. A: 2Cl$^-$ → Cl$_2$ + 2e$^-$, B: Na$^+$ + e$^-$ → Na; 8. 15.6 h; 9. 1.04 V; 10. A: Cr$_2$O$_7^{2+}$ + 14H$^+$ + 6e$^-$ → 2Cr$^{3+}$ + 7H$_2$O, B: NO + 4OH$^-$ → NO$_3^-$ + 2H$_2$O + 3e$^-$; 11. 4, 5, 12, 4, 4, 5, 6; Bonus: F, T, F, F, F, T, T, F, T
Level 1 – “Do or Die Fail!”: 5 Questions (20 points)

1. An endothermic process is one process in which heat is ................. the system and therefore it has a ............ value.
   a. received by; positive
   b. received by; negative
   c. received by; positive or negative
   d. released from; positive
   e. released from; negative
   f. released from; positive or negative

2. A. The solubility of gases in water increases as the temperature ..................
   B. The solubility of ionic compounds in water increases as the temperature
      ..................

3. The solubility of carbon dioxide in water is 0.372 g CO₂ in 100 mL of water at
   20°C and 2.31 atm. The solubility of CO₂ is 6.29 g/100 mL at .............. atm.

4. Circle the best description for the following pairs of liquids:
   A. methanol – acetic acid    miscible    immiscible
   B. mercury – ethanol        miscible    immiscible
   C. octane – water           miscible    immiscible
   D. ethanol – octane         miscible    immiscible
   E. heptane – octane         miscible    immiscible
   F. hydrogen peroxide – water miscible    immiscible

5. Circle T if the statement is true and F if the statement is false:
   T or F Internal energy is an extensive property.
   T or F For a system, H is always greater than U.
   T or F The energy associated with the speeding bullet is the potential energy.
   T or F The SI unit for the enthalpy is pascal.
   T or F ΔH is always positive for a chemical reaction.
   T or F Work is a path function.
6. Calculate the amount of heat released in the complete combustion of 8.17 grams of Al to form Al₂O₃(s) at 25°C and 1 atm.
   \[4\text{Al(s) + 3O}_2\text{(g) \to 2Al}_2\text{O}_3\text{(s); } \Delta H = -3352 \text{ kJ/mol}\]
   a. 203 kJ  b. 127 kJ  c. 254 kJ  
   d. 237 kJ  e. 101 kJ  f. 63.4 kJ

7. When 26.3 kJ of heat are absorbed by a 225-grams sample, the temperature of the sample increases by 15.6 K.
   A. The heat capacity \((C)\) of the sample is .................
   B. The specific heat capacity \((s)\) of the sample is .................

8. \[3\text{H}_2\text{(g) + N}_2\text{(g) \to 2NH}_3\text{(g); } \Delta H^0 = -46 \text{ kJ/mol}\]
   Given the thermochemical equation above, what is \(\Delta H^0\) for the equation below?
   \[\text{NH}_3\text{(g) \to 3/2H}_2\text{(g) + 1/2N}_2\text{(g); } \Delta H^0 = ?\]
   a. –23 kJ  b. –46 kJ  c. –92 kJ  
   d. +23 kJ  e. +46 kJ  f. +92 kJ

9. A mass of 26.1 g of a molecular compound A is dissolved in 300 g of water to form a solution that is 1.40 molal. What is the molar mass of compound A?
   SHOW YOUR WORK for partial credit.
   Molar mass:

10. Two metals of equal mass with different heat capacities are subjected to the same amount of heat. Which undergoes the smallest change in temperature?
    a. Both undergo the same change in temperature.
    b. You need to know the initial temperatures of the metals.
    c. The metal with the lower heat capacity.
    d. You need to know which metals you have.
    e. The metal with the higher heat capacity.
    f. You need to know the final temperatures of the metals.
11. The vapor pressure of pure water at 20°C is 18.0 mmHg. What is the vapor pressure of water obtained by mixing 3.20 g methanol, CH$_3$OH, with 34.2 g of water at 20°C?
   a. 16.2 mmHg  b. 20.0 mmHg  
   c. 17.5 mmHg  d. 18.5 mmHg  
   e. 17.1 mmHg  f. 18.9 mmHg

12. What is the osmotic pressure at 50.0°C for the solution obtained by dissolving 34.6 g of a compound with a molar mass of 25,300 g/mol in 1860 mL of water? For water, $K_f = 1.858 ^\circ$C/m and $K_b = 0.512 ^\circ$C/m.
   a. 2.29 mmHg  b. 14.8 mmHg  
   c. $3.02 \times 10^{-3}$ mmHg  d. $1.95 \times 10^{-2}$ mmHg  
   e. $2.29 \times 10^{-3}$ mmHg  f. $1.84 \times 10^{-3}$ mmHg

13. Provide definitions (or descriptions) for the following terms:
   A. Standard enthalpy of formation
   B. Saturated solution

14. Provide definitions (or descriptions) for the following terms:
   A. Specific heat
   B. Enthalpy

15. Provide definitions (or descriptions) for the following terms:
   A. Lattice energy
   B. Colloids
16. A. Write chemical equations for two reactions/processes that are part of Born-Haber cycle for NaCl:

B. Write the chemical equation associated with the enthalpy of formation of solid NaNO₃.

17. Based on the information given, what is the enthalpy of reaction for the reaction below at 25°C?

\[ 2\text{Fe}_2\text{O}_3(s) + 13\text{CO}(g) \rightarrow 2\text{Fe}(	ext{CO})_5(s) + 3\text{CO}_2(g) \]

\[ \Delta H_f \text{ (kJ/mol)} \]

-824.2 \quad -110.5 \quad -733.8 \quad -393.5

a. +436.8 kJ  
b. +192.6 kJ  
c. +88.2 kJ  
d. -192.6 kJ  
e. -436.8 kJ  
f. -88.2 kJ

18. What is freezing point of a solution obtained by dissolving 3.64 g of HCl in 350 g water? For water, \( K_f = 1.858^\circ\text{C}/m \) and \( K_b = 0.512^\circ\text{C}/m \). SHOW YOUR WORK for partial credit.

Freezing point:

19. For water, \( K_f = 1.858^\circ\text{C}/m \) and \( K_b = 0.512^\circ\text{C}/m \).

A. The boiling point of a 1.00 m Ca(OH)₂ solution in water is .................

B. The freezing point of a 1.00 m Ca(OH)₂ solution in water is .................

C. The boiling point of a 1.00 m sucrose solution in water is .................

D. The freezing point of a 1.00 m sucrose solution in water is .................

20. If 0.455 g of a substance A is dissolved in 10.0 g of benzene, the freezing point of the solution could be measured as 5.144°C. Pure benzene freezes at 5.444°C and has a value for \( K_f \) of 5.12°C/m. What is the approximate molar mass of A?

a. 777 g/mol  
b. 42.8 g/mol  
c. 7.77 g/mol  
d. 296 g/mol  
e. 7.77 \times 10^5 g/mol  
f. 11.3 g/mol
Level 5 – “Show me what you’ve got!”: 5 Questions (20 points)

21. The mole fraction of ethanol (CH\(_3\)CH\(_2\)OH) in an aqueous solution is 0.0875.
   A. The molality of this solution is ......................
   B. The mass percentage of ethanol in this solution is ......................

22. \[ \text{CH}_3\text{COOH}(l) + 2\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 2\text{H}_2\text{O}(l) \quad \Delta H = -874 \text{ kJ} \]
   \[ \text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta H = -394 \text{ kJ} \]
   \[ \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H = -286 \text{ kJ} \]

Given the thermochemical equations above, what is \( \Delta H \) for the equation below?
\[ \text{CH}_3\text{COOH}(l) \rightarrow 2\text{C}(s) + \text{O}_2(g) + 2\text{H}_2(g) \quad \Delta H = ? \]
   a. -194 kJ   b. -1554 kJ   c. +486 kJ
   d. +194 kJ   e. -486 kJ   f. +2234 kJ

23. A molecular compound with a molar mass of 72.0 g/mol in dissolved in water to form a 3.415 molal solution that has a density of 1.123 g/mL. What is the molarity of this solution? SHOW YOUR WORK for partial credit.

   Molarity:

24. The \( \Delta H^\circ \) value for the vaporization of nitric acid is +39.8 kJ/mol. Giving that \( \Delta H^\circ_f \) = \(-174.1 \text{ kJ/mol} \) for liquid nitric acid, what is the value of \( \Delta H^\circ_f \) for gas nitric acid?
   a. +174.1 kJ/mol   b. +134.3 kJ/mol   c. +213.9 kJ/mol
   d. -174.1 kJ/mol   e. -134.3 kJ/mol   f. -213.9 kJ/mol

25. Using the table of bond energies on the next page, approximate the enthalpy of reaction for the reaction below. SHOW YOUR WORK for partial credit.
\[ \text{H} - \text{C} = \text{O} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]
   \[ \text{O} - \text{H} \]

\[ \Delta H = \]
Useful information:

\[ R = 0.08206 \text{ L} \cdot \text{atm}/(\text{mol} \cdot \text{K}) \]
\[ R = 8.3145 \text{ J}/(\text{mol} \cdot \text{K}) \]

1 atm = 760 torr = 760 mmHg

<table>
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<tr>
<th>Bond</th>
<th>Bond enthalpy (kJ/mol)</th>
<th>Bond</th>
<th>Bond enthalpy (kJ/mol)</th>
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*Bond enthalpies shown in red are for diatomic molecules.

The C=O bond enthalpy in CO₂ is 799 kJ/mol.
Level 1 – “Do or Die Fail!”: 5 Questions (20 points)

1. For $2A + B \rightarrow 3C + D$ reaction, write below the expression for the reaction rate with respect to concentration changes for all reactant and products:

   Rate =

2. For $\text{CH}_2\text{O}(g) + 3\text{H}_2(g) \rightleftharpoons \text{CH}_4(g) + 2\text{H}_2\text{O}(l)$ reaction, the expression of the equilibrium constant $K_p$ is:

   $K_p =$

3. A. If a reaction has an equilibrium constant of $4.33 \times 10^{-4}$, the equilibrium mixture will be mostly ......................
   B. If a reaction has an equilibrium constant of $1.24 \times 10^6$, the equilibrium mixture will be mostly ......................
   C. If $Q_c > K_c$, the equilibrium will be reached by forming more ......................
   D. If $Q_c < K_c$, the equilibrium will be reached by forming more ......................

4. For $A + B + 2C \rightarrow D + E$ reaction, if the rate law is $\text{Rate} = k[B]^2[C]$ then
   A. the overall order of the reaction is ............
   B. the order with respect to $A$ is ............
   C. the order with respect to $B$ is ............
   D. the order with respect to $C$ is ............

5. A. $\text{H}_2\text{O}(g) + 1/2\text{O}_2(g) \rightleftharpoons \text{H}_2\text{O}_2(g)$ is an endothermic reaction that, when at equilibrium, will yield more product at ................. temperature and ................. pressure.
   
   B. $2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$ is an exothermic reaction that, when at equilibrium, will yield more products at ................. temperature and ................. pressure.
6. \( \text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g}) \) has an equilibrium constant \( K_c = 49.7 \) at 458°C. If 3.00 moles of HI and some I\(_2\) are introduced in a 1.00-L container and there are 2.68 moles HI left at equilibrium, what is the equilibrium concentration of \( \text{H}_2? \)
   a. 0.32 M  
   b. 0.64 M  
   c. 0.16 M  
   d. 2.63 M  
   e. 0.08 M  
   f. 1.32 M

7. Consider the hypothetical reaction: \( 3\text{A} + \text{C}_2 \rightleftharpoons \text{A}_2\text{C} + \text{AC} \) and assume that the following proposed mechanism is consistent with the rate data:
   \[
   \begin{align*}
   2\text{A} + \text{C}_2 & \rightarrow \text{A}_2\text{C} + \text{C} \quad \text{slow} \\
   \text{A} + \text{C} & \rightarrow \text{AC} \quad \text{fast} \\
   3\text{A} + \text{C}_2 & \rightarrow \text{A}_2\text{C} + \text{AC} \quad \text{overall}
   \end{align*}
   \]
Based on this information, the reaction law is
   a. Rate = \([\text{A}_2\text{C}][\text{AC}]\)  
   b. Rate = \([\text{A}][\text{C}_2]^2\)  
   c. Rate = \([\text{A}_2\text{C}][\text{C}]\)  
   d. Rate = \([\text{A}]^3[\text{C}_2]\)  
   e. Rate = \([\text{A}]^2[\text{C}_2]\)  
   f. Rate = \([\text{A}][\text{C}_2]\)

8. For \( 2\text{N}_2\text{O}_5(\text{g}) \rightleftharpoons 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \); \( \Delta H = 76 \text{ kJ} \) reaction at equilibrium which of the following will yield more \( \text{N}_2\text{O}_5? \) Circle T if true and F if false!
   T or F decreasing the temperature of the system  
   T or F adding a catalyst  
   T or F adding an inert gas like He  
   T or F decreasing the volume of the system  
   T or F adding more \( \text{O}_2 \)  
   T or F removing some \( \text{NO}_2 \)

9. A. For a zero-order reaction, a representation of …………… vs time is linear, and the slope of this representation is …………… (Choose positive/negative!)
   B. For a first-order reaction, a representation of …………… vs time is linear, and the slope of this representation is …………… (Choose positive/negative!)

10. When \( 2\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons 2\text{C}(\text{g}) \) reaction reaches equilibrium at a certain temperature, the equilibrium concentrations were found to be 0.427 M for A, 0.725 M for B, and 0.326 M for C. At that temperature, the equilibrium constant for this reaction is \( K_c = …………… \)
11. Circle T if the statement is true and F if the statement is false:
   T or F  A first-order reaction is a unimolecular reaction.
   T or F  A unimolecular reaction is a first-order reaction.
   T or F  For an exothermic reaction, the activation energy for the forward reaction is smaller than the activation energy for the reverse reaction.
   T or F  An elementary reaction can have more than one possible mechanisms.
   T or F  The rate constant for a elementary reaction is independent of $T$.
   T or F  The existence of a rate-determining step in a reaction mechanism is not required.

12. The gas phase system $A(g) + B(g) \rightleftharpoons C(g) + D(g)$ has an equilibrium constant $K_p = 0.0169$ at 500 K. If the reaction started from 1.00 atm of $A$ and 1.00 atm of $B$ in a 5.00-L vessel, what will be the partial pressure of $C$ at equilibrium at 500 K?
   a. 0.058 atm  
   b. 0.115 atm  
   c. 0.230 atm  
   d. 0.770 atm  
   e. 0.885 atm  
   f. 0.130 atm

13. A. For a zero-order reaction, the unit of the rate constant is ....................
   B. For a first-order reaction, the unit of the rate constant is ....................
   C. For a second-order reaction, the unit of the rate constant is ....................
   D. For a third-order reaction, the unit of the rate constant is ....................

14. A. For a first-order reaction in which the initial concentration of reactant is 2.00 $M$ and the half-life is $1.23 \times 10^{-3}$ s, the rate constant is ....................
   B. For a second-order reaction in which the initial concentration of reactant is 2.00 $M$ and the half-life is $1.23 \times 10^{-3}$ s, the rate constant is ....................

15. Rate data have been determined at a particular temperature for the overall reaction $2A + 3B \rightarrow \text{Products}$ in which all reactants and products are gases.

<table>
<thead>
<tr>
<th>Trial Run</th>
<th>Initial [A]</th>
<th>Initial [B]</th>
<th>Initial Rate (M-min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.30 $M$</td>
<td>0.10 $M$</td>
<td>$7.20 \times 10^{-5}$</td>
</tr>
<tr>
<td>2</td>
<td>0.60 $M$</td>
<td>0.10 $M$</td>
<td>$1.44 \times 10^{-4}$</td>
</tr>
<tr>
<td>3</td>
<td>0.90 $M$</td>
<td>0.20 $M$</td>
<td>$8.64 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Based on this information, the rate law is .....................
Level 4 – “Now we’re talking!”: 5 Questions (20 points)

16. Provide definitions (or descriptions) for the following terms:
   A. Le Chatelier’s principle
   B. Activated complex

17. Consider the A $\rightleftharpoons$ B elementary reaction at 500 K. If the rate constant for the A $\rightarrow$ B reaction is $3.57 \times 10^{-3}$ s$^{-1}$, and the rate constant for the B $\rightarrow$ A reaction is $1.96 \times 10^{4}$ s$^{-1}$, then $K_c =$ ……………………………

18. A. According to the collision theory, two of the determining factors in the expression of the rate constant are:
   
   B. For a catalyzed reaction, the activation energy is …………………………… and the energy of reaction is ………………………….. compared to the values for uncatalyzed reaction.

19. A reaction $2A(g) + B(g) \rightleftharpoons 3C(g)$ starts from $[A]_0$, $[B]_0$, and $[C]_0$ initial concentrations. Without calculating, set up a correct equation in $x$ and $K_c$ that would allow the determination of equilibrium concentrations. Be sure to define $x$! SHOW YOUR WORK for partial credit.

   \[ K_c = \]

20. Sketch aside a potential energy curve (or diagram) for an elementary endothermic reaction, label the axis and define the important energy parameters associated with it.
Level 5 – “Show me what you’ve got!”: 5 Questions (20 points)

21. For a certain first-order reaction, it takes 32.6 minutes to consume 35.0% of the original concentration of reactant. How much of the original concentration will be consumed after 65.2 minutes? SHOW YOUR WORK for partial credit.

22. At 500 K, $K_c = 89.0$ is for $A \longrightarrow 2B$ reaction, and $K_c = 3.21$ is for $C \longrightarrow B$ reaction. What is the $K_c$ value at 500 K for $A \longrightarrow 2C$ reaction?
   a. 286  
   b. 82.6  
   c. 917  
   d. 8.64  
   e. 95.4  
   f. 27.7

23. A reaction follows a second-order rate law in reactant A with a rate constant of $3.95 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$. If the original concentration of A was 1.32 M, how long will it take for the concentration of A to be reduced to 0.160 M? SHOW YOUR WORK for partial credit.

24. Calculate the activation energy of a reaction if the rate constant is 0.75 s$^{-1}$ at 25°C and 11.5 s$^{-1}$ at 75°C.
   a. 15.8 kJ/mol  
   b. 681 kJ/mol  
   c. 47.1 kJ/mol  
   d. 20.4 kJ/mol  
   e. 31.4 kJ/mol  
   f. 0.465 kJ/mol

25. PCl$_5$ decomposes according to: PCl$_5$(g) $\rightleftharpoons$ PCl$_3$(g) + Cl$_2$(g). If the initial concentrations of PCl$_3$ and Cl$_2$ are 2.00 mol/L and $K_c = 0.0358$, what is the equilibrium composition of PCl$_5$? SHOW YOUR WORK for partial credit.
Level 1 (out of 20):

Level 2 (out of 20):

Level 3 (out of 20):

Level 4 (out of 20):

Level 5 (out of 20):

Class Participation:

Score (out of 100):
Possible useful information: \( R = 0.08206 \text{ L·atm/(mol·K)}; \quad R = 8.3145 \text{ J/(mol·K)} \)

Multiple Choice: Identify the letter of the choice that best completes the statement or answers the question.

____ 1. What is the pH of a 0.0077 \text{ M} \text{ KOH} solution?
   a. 11.89  
   b. 16.11  
   c. 2.11   
   d. 4.87   
   e. 9.13

____ 2. A solution in which the pOH is 12.5 would be described as
   a. slightly basic.          
   c. slightly acidic.        
   e. very acidic.            
   b. neutral.               
   d. very basic.

____ 3. The ionization constant of water at a temperature above 25°C is \( 3.4 \times 10^{-14} \). What is the pH of pure water at this temperature?
   \[
   2\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)
   \]
   a. 5.53  
   b. 7.00   
   c. 7.73   
   d. 6.73   
   e. 13.51

____ 4. Which solution has the highest pH?
   a. 0.10 \text{ M} \text{ HCl}(aq)  
   c. 0.10 \text{ M} \text{ HF}(aq)  
   e. 0.10 \text{ M} \text{ HBr}(aq)  
   b. 0.10 \text{ M} \text{ HClO}_4(aq)  
   d. 0.10 \text{ M} \text{ H}_2\text{SO}_4(aq)

____ 5. What is the pH of a 0.051 \text{ M} \text{ HClO}_4 solution?
   a. 11.02  
   b. 15.29  
   c. 2.98   
   d. 12.71  
   e. 1.29

____ 6. Which are the Brønsted–Lowry bases in the following equilibrium?
   \[
   \text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{OH}^-(aq)
   \]
   a. \text{H}_2\text{O}, \text{HCO}_3^-, \text{and OH}^-  
   c. \text{CO}_3^{2-} \text{and HCO}_3^-  
   e. \text{H}_2\text{O} \text{and HCO}_3^-  
   b. \text{CO}_3^{2-} \text{and OH}^-  
   d. \text{H}_2\text{O} \text{and OH}^-

____ 7. In the reaction \text{CaO(s)} + \text{CO}_2(g) \rightarrow \text{CaCO}_3(s),
   a. O\(^2-\) acts as a Lewis base and \text{CO}_2 acts as a Lewis acid.
   b. O\(^2-\) acts as a Lewis base and \text{Ca}^{2+} acts as a Lewis acid.
   c. \text{CaO} is the Lewis acid and \text{CaCO}_3 is its conjugate base.
   d. \text{Ca}^{2+} acts as a Lewis acid and \text{CO}_3^{2-} acts as a Lewis base.
   e. \text{CO}_2 is the Lewis acid and \text{CaCO}_3 is its conjugate base.

____ 8. Which ranking of acid strength below is correct?
   a. \text{H}_2\text{SO}_3 < \text{HSO}_3^-  
   c. \text{HBrO}_3 < \text{HIO}_3  
   e. \text{H}_2\text{O} < \text{NH}_3  
   b. \text{H}_2\text{SO}_4 < \text{H}_2\text{SO}_3  
   d. \text{HCl} < \text{HBr}

____ 9. The pH of a solution of a strong base is 10.26 at 25°C. What is its \text{H}_3\text{O}^+ concentration?
   a. \( 2.8 \times 10^{-3} \text{ M} \)  
   c. \( 5.5 \times 10^{-11} \text{ M} \)  
   e. \( 1.3 \times 10^{-4} \text{ M} \)  
   b. \( 1.8 \times 10^{-4} \text{ M} \)  
   d. \( 1.4 \times 10^{-2} \text{ M} \)

____ 10. Which of the following pairs of species is not a conjugate acid–base pair?
   a. O\(^2-\), OH\(^-\)  
   c. \text{H}_2\text{CO}_3, \text{HCO}_3^-  
   e. \text{HSO}_4^-, \text{SO}_4^{2-}  
   b. \text{HNO}_2, \text{NO}_3^-  
   d. \text{HOCl}, \text{OCl}^-
11. What is the pH of a 0.24 M solution of pyridine ($K_b = 1.4 \times 10^{-9}$) at 25°C?
   a. 1.24  b. 10.91  c. 8.85  d. 4.74  e. 4.12

12. What is the $H_3O^+$ concentration of a solution formed by combining 400. mL of 0.28 M HNO$_3$ with 600. mL of 0.12 M NaOH at 25°C?
   a. 0.28 M  c. 0.040 M  e. 0.112 M
   b. $2.5 \times 10^{-13}$ M  d. 0.0080 M

13. What is the pH of the solution if 0.094 g of NaF is added to 115.0 mL of a 0.063 M HF solution? $K_a$ for HF is $6.8 \times 10^{-4}$. Assume no volume change.
   a. 2.21  b. 2.66  c. 5.08  d. 6.25  e. 2.48

14. A 0.0529 M solution of a weak base has a pH of 11.68. What is the identity of the weak base?

<table>
<thead>
<tr>
<th>Weak Base</th>
<th>$K_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylamine (CH$_3$CH$_2$NH$_2$)</td>
<td>$4.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>Hydrazine (N$_2$H$_4$)</td>
<td>$1.7 \times 10^{-6}$</td>
</tr>
<tr>
<td>Hydroxylamine (NH$_2$OH)</td>
<td>$1.1 \times 10^{-8}$</td>
</tr>
<tr>
<td>Pyridine (C$_5$H$_5$N)</td>
<td>$1.4 \times 10^{-9}$</td>
</tr>
<tr>
<td>Aniline (C$_6$H$_5$NH$_2$)</td>
<td>$4.2 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

   a. pyridine  c. hydrazine  e. aniline
   b. hydroxylamine  d. ethylamine

15. What is the $H_3O^+$ concentration in a 0.033 M solution of carbonic acid, H$_2$CO$_3$? For carbonic acid, $K_{a1} = 4.2 \times 10^{-7}$ and $K_{a2} = 4.8 \times 10^{-11}$.
   a. $4.8 \times 10^{-11}$ M  c. $4.2 \times 10^{-7}$ M  e. $1.2 \times 10^{-4}$ M
   b. $3.3 \times 10^{-2}$ M  d. $5.9 \times 10^{-5}$ M

16. Which of the following equilibria best represents the hydrolysis reaction that occurs in an aqueous solution of KNO$_2$?
   a. NO$_2^-$ (aq) + H$_3$O$^+$ (aq) $\rightleftharpoons$ HNO$_2$ (aq) + H$_2$O(l)
   b. NO$_2^-$ (aq) + H$_2$O(l) $\rightleftharpoons$ HNO$_3$ (aq) + 2H$^+$ (aq)
   c. NO$_2$ (aq) + H$_2$O(l) $\rightleftharpoons$ HNO$_2$ (aq) + OH$^-$ (aq)
   d. K$^+$ (aq) + NO$_2^-$ (aq) + H$_2$O(l) $\rightleftharpoons$ KOH (aq) + HNO$_2$ (aq)
   e. K$^+$ (aq) + H$_2$O(l) $\rightleftharpoons$ KOH (aq) + H$^+$ (aq)

17. A 0.10 M solution of a weak monoprotic acid has a $H_3O^+$ concentration of $5.0 \times 10^{-4}$ M. What is the acid-ionization constant, $K_a$, for this acid?
   a. $2.5 \times 10^{-6}$  b. $6.0 \times 10^{-5}$  c. $2.2 \times 10^{-2}$  d. $5.0 \times 10^{-4}$  e. $3.6 \times 10^{-3}$

18. A 0.20 M solution of a weak monoprotic acid is 0.21% ionized. What is the acid-ionization constant, $K_a$, for this acid?
   a. $2.2 \times 10^{-5}$  b. $8.8 \times 10^{-3}$  c. $2.1 \times 10^{-6}$  d. $1.1 \times 10^{-4}$  e. $8.8 \times 10^{-7}$

19. What is the $H_3O^+$ concentration in a solution resulting from mixing 111 mL of 0.100 M HCN and 73 mL of 0.100 M KOH at 25°C? $K_a$ for HCN = $4.9 \times 10^{-10}$ at 25°C.
   a. $1.0 \times 10^{-13}$ M  c. $7.0 \times 10^{-6}$ M  e. $3.2 \times 10^{-6}$ M
   b. $2.6 \times 10^{-10}$ M  d. $2.5 \times 10^{-13}$ M

20. What is the pH of a solution prepared by adding 0.622 g of ammonium bromide to 115 mL of water? $K_b$ of NH$_3$ is $1.8 \times 10^{-5}$.
   a. 5.26  b. 8.74  c. 3.01  d. 4.74  e. 10.99
21. For which of the following salts would the addition of nitric acid increase its solubility?
   a. AgNO₃    b. Ag₂S    c. AgBr    d. AgCl    e. AgI

22. \(K_{sp}\) for PbF₂ is 4.0 \(\times 10^{-8}\). If a 0.028 \(M\) NaF solution is saturated with PbF₂, what is [Pb²⁺] in solution?
   a. 1.1 \(\times 10^{-9}\) \(M\)    c. 1.8 \(\times 10^{-3}\) \(M\)    e. 5.1 \(\times 10^{-5}\) \(M\)
   b. 3.1 \(\times 10^{-11}\) \(M\)    d. 1.4 \(\times 10^{-6}\) \(M\)

23. What is the pH of a saturated solution of Ni(OH)₂? For Ni(OH)₂, \(K_{sp}\) = 2.0 \(\times 10^{-15}\).
   a. 7.00    b. 8.90    c. 4.80    d. 5.10    e. 9.20

24. To a 1.0 L solution containing 0.012 moles of Cd(NO₃)₂, 1.0 moles of NH₃ are added. What is the concentration of uncomplexed Cd²⁺ ion? For Cd(NH₃)₄²⁺, \(K_f\) = 1.0 \(\times 10^7\).
   a. 1.2 \(\times 10^{-2}\) \(M\)    c. 3.5 \(\times 10^{-5}\) \(M\)    e. 3.2 \(\times 10^{-4}\) \(M\)
   b. 1.3 \(\times 10^{-11}\) \(M\)    d. 1.5 \(\times 10^{-9}\) \(M\)

25. What is the solubility product expression for Th(IO₃)₄?
   a. \(K_{sp}\) = [Th⁺][IO₃]⁴    c. \(K_{sp}\) = [Th⁺][IO₃]    e. \(K_{sp}\) = [Th⁺][IO₃]⁴
   b. \(K_{sp}\) = [Th⁺] + 4[IO₃]    d. \(K_{sp}\) = [Th⁺][4IO₃]⁴

26. Which of the following hydroxides is amphoteric?
   a. KOH    b. Ca(OH)₂    c. Zn(OH)₂    d. NaOH    e. Sr(OH)₂

27. What is the minimum mass of Na₂CO₃ that must be added to 67.5 mL of a 9.4 \(\times 10^{-4}\) \(M\) AgNO₃ solution in order for precipitation to occur? For Ag₂CO₃, \(K_{sp}\) = 8.6 \(\times 10^{-12}\).
   a. 3.1 \(\times 10^{-4}\) g    c. 7.0 \(\times 10^{-5}\) g    e. 3.4 \(\times 10^{-3}\) g
   b. 6.5 \(\times 10^{-8}\) g    d. 6.7 \(\times 10^{-3}\) g

28. It is found that the concentration of Pb²⁺ in a saturated solution of lead(II) bromide is 1.2 \(\times 10^{-2}\) \(M\). What is \(K_{sp}\) for PbBr₂?
   a. 3.5 \(\times 10^{-2}\)    b. 6.9 \(\times 10^{-6}\)    c. 1.7 \(\times 10^{-6}\)    d. 1.4 \(\times 10^{-4}\)    e. 3.1 \(\times 10^{-7}\)

29. What is the correct mathematical expression for finding the molar solubility (s) of chromium(III) hydroxide?
   a. \(27s^4 = K_{sp}\)    b. \(8s^3 = K_{sp}\)    c. \(108s^5 = K_{sp}\)    d. \(4s^3 = K_{sp}\)    e. \(2s^2 = K_{sp}\)

30. To 1.0 L of water, 1.0 \(\times 10^{-6}\) mol of Pb(NO₃)₂, 6.0 \(\times 10^{-6}\) mol of K₂CrO₄, and 1.0 mol of NaCl are added. What will happen? \(K_{sp}\) for PbCrO₄ = 1.8 \(\times 10^{-14}\) and \(K_{sp}\) for PbCl₂ = 1.6 \(\times 10^{-5}\).
   a. No precipitate will form.
   b. A precipitate of PbCl₂ will form.
   c. Both a precipitate of PbCl₂ and a precipitate of PbCrO₄ will form.
   d. A precipitate of PbCrO₄ will form.
   e. A precipitate of KCl will form.
Extra Credit Definitions (1 point each). Give the textbook (or an equivalent) definition for the following terms:

Lewis base

Complex ion

Ligand

Extra Credit Reaction (1 point). The net ionic equation of the reaction between ammonium hydroxide and hydrochloric acid is:

Extra Credit Fill-Ins (0.5 points each). Fill in the following statements:

The $\text{H}_3\text{O}^+$ ion is called ………………………………

The $\text{OH}^-$ ion is called ……………………

The $\text{HClO}_2$ is called ……………………………

The formula for perbromic acid is ……………………

The conjugate base of $\text{H}_2\text{SO}_3$ is …………………

In $\text{BF}_3 + \text{NH}_3 \rightarrow \text{F}_3\text{B}–\text{NH}_3$ reaction, $\text{BF}_3$ is ……………………………

………………………… is a salt that, when dissolve in water at 25°C, will form a basic solution.

The name of the salt above is ………………………………………………………

Correct multiple-choice answers:  
Extra credit:  
Lecture participation:  
Exam 3 Grade:
Multiple Choice: Identify the letter of the choice that best completes the statement or answers the question.

____ 1. What is \( \Delta G^\circ \) at 298 K for the following equilibrium?
\[
\text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+(aq); \quad K_f = 1.7 \times 10^7 \text{ at 298 K}
\]
 a. 0 b. –18 kJ c. 41 kJ d. –41 kJ e. 18 kJ

____ 2. What is the change in entropy when 0.265 g of silicon is burned in excess oxygen to yield silicon dioxide at 298 K?
\[
\text{Si(s)} + \text{O}_2(g) \rightarrow \text{SiO}_2(s); \quad \Delta S^\circ = -182.4 \text{ J/K at 298 K}
\]
 a. –1.93 × 10^4 J/K b. –1.72 J/K c. –48.3 J/K b. –5.78 × 10^{-3} J/K d. –182 J/K e. –48.3 J/K

____ 3. At the normal boiling point of o-xylene, \( \Delta H^\circ_{\text{vap}} = 36.2 \text{ kJ/mol} \) and \( \Delta S^\circ_{\text{vap}} = 86.7 \text{ J/(mol · K)} \). What is the normal boiling point of o-xylene?
 a. 314 K b. 373 K c. 867 K d. 418 K e. 115 K

____ 4. Which of the following is not a spontaneous process at 25°C and 1 atm pressure?
 a. salt dissolving b. steam condensing c. iron rusting d. ice melting e. water boiling

____ 5. The free-energy change of a reaction is a measure of
 a. the energy given off to the surroundings. b. the excess entropy given off to the surroundings. c. the direction in which a net reaction occurs. d. the increased molecular disorder that occurs in the system. e. the excess entropy given off to the reaction system.

____ 6. What is \( \Delta S^\circ \) at 298 K for the following reaction?
\[
\text{CH}_4(g) + \text{N}_2(g) \rightarrow \text{HCN(g)} + \text{NH}_3(g); \quad \Delta H^\circ = 164.1 \text{ kJ; } \Delta G^\circ = 159.1 \text{ kJ at 298 K}
\]
 a. \( 5.3 \times 10^3 \text{ J/K} \) b. \( 17 \text{ J/K} \) c. \( 5.5 \times 10^3 \text{ J/K} \) e. \( 1.1 \times 10^3 \text{ J/K} \) d. \( 2.0 \text{ J/K} \)

____ 7. The reaction \( \text{Br}_2(g) \rightarrow 2\text{Br}(g) \) is spontaneous only at temperatures in excess of 1600°C. We can conclude that
 a. \( \Delta H \) is – and \( \Delta S \) is + for the reaction. b. \( \Delta H \) is – and \( \Delta S \) is – for the reaction. c. \( \Delta H \) is – and \( \Delta S \) is + for the reaction. d. \( \Delta H \) is + and \( \Delta S \) is – for the reaction. e. \( \Delta G \) is + for all temperatures.

____ 8. The third law of thermodynamics states that
 a. the entropy is zero at 0 K for a perfect crystal. b. the entropy of the universe is constant. c. the entropy of the universe is increasing. d. the entropy of the universe equals the sum of the entropy of system and that of the surroundings. e. the absolute entropy of a substance decreases with increasing temperature.

____ 9. What is \( \Delta G^\circ \) at 298 K for the following reaction: \( \text{Pb(s)} + \text{PbO}_2(s) \rightarrow 2\text{PbO(s)} \)
\[
\begin{array}{|c|c|}
\hline
\text{Substance} & \Delta G^\circ_{\text{f}}(\text{kJ/mol}) \text{ at 298 K} \\
\hline
\text{PbO(s)} & -187.9 \\
\text{PbO}_2(s) & -217.3 \\
\hline
\end{array}
\]
 a. –405.2 kJ b. 158.5 kJ c. –158.5 kJ d. 29.4 kJ e. –29.4 kJ
10. From these two reactions at 298 K,
\[ \text{V}_2\text{O}_5(s) + 3\text{CO}(g) \rightarrow 2\text{V}(s) + 3\text{CO}_2(g); \Delta H^\circ = 369.8 \text{ kJ}; \Delta S^\circ = 8.3 \text{ J/K} \]
\[ \text{V}_2\text{O}_5(s) + 2\text{CO}(g) \rightarrow 2\text{V}_2\text{O}_3(s) + 2\text{CO}_2(g); \Delta H^\circ = -234.2 \text{ kJ}; \Delta S^\circ = 0.2 \text{ J/K} \]
calculate \( \Delta G^\circ \) for the following at 298 K:
\[ 2\text{V}(s) + 5\text{CO}_2(g) \rightarrow 2\text{V}_2\text{O}_5(s) + 5\text{CO}(g) \]
a. +133.1 kJ  
b. -133.1 kJ  
c. +601.6 kJ  
d. -601.6 kJ  
e. +1.6 kJ

11. For which of the following reactions is \( \Delta S^\circ \) < 0 at 25°C?
a. \( \text{P}_4(s) + 5\text{O}_2(g) \rightarrow \text{P}_4\text{O}_{10}(s) \)
b. \( 2\text{HgO}(s) \rightarrow 2\text{Hg}(l) + \text{O}_2(g) \)
c. \( 2\text{KClO}_3(s) \rightarrow 2\text{KCl}(s) + 3\text{O}_2(g) \)
d. \( (\text{NH}_4)_2\text{Cr}_2\text{O}_7(s) \rightarrow \text{N}_2(g) + 4\text{H}_2\text{O}(l) + \text{Cr}_2\text{O}_3(s) \)
e. \( \text{Br}_2(l) \rightarrow \text{Br}_2(g) \)

12. When the following oxidation–reduction reaction in acidic solution is balanced, what is the lowest whole-number coefficient for \( \text{H}^+ \), and on which side of the balanced equation should it appear?
\[ \text{Cr}_2\text{O}_7^{2-}(aq) + \text{CO}(aq) \rightarrow \text{Cr}^{3+}(aq) + \text{CO}_2(aq) \]
a. 8, reactant side  
b. 2, product side  
c. 14, reactant side  
d. 6, product side  
e. 1, reactant side

13. What half-reaction occurs at the anode during the electrolysis of molten potassium bromide?
a. \( \text{Br}_2(l) + 2e^- \rightarrow 2\text{Br}^-(l) \)
b. \( \text{K}^+(l) + e^- \rightarrow \text{K}(s) \)
c. \( 2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(l) \)

d. \( \text{Br}^-(l) \rightarrow \text{Br}_2(l) + 2e^- \)

e. Reduction occurs here.

14. What mass of chromium could be deposited by electrolysis of an aqueous solution of \( \text{Cr}_2(\text{SO}_4)_3 \) for 155 min using a constant current of 12.0 A?
a. 30.1 g  
b. 180.4 g  
c. 0.187 g  
d. 20.0 g  
e. 0.334 g

15. Which statement is always true of the cathode in an electrochemical cell?
a. Negative ions flow toward the cathode.  
b. It is considered the “positive” electrode.  
c. Metal is plated out here.  
d. It is considered the “negative” electrode.  
e. Reduction occurs here.

16. What is the cell reaction for the following electrochemical cell?
\[ \text{Ca} || \text{Ca}^{2+}(aq) \] || \[ \text{Mn} || \text{Mn}^{2+}(aq) \] \[ \text{Mn} \]
a. \( \text{Ca}(s) + \text{Mn}^{2+}(aq) \rightarrow \text{Mn}(s) + \text{Ca}^{2+}(aq) \)
b. \( \text{Ca}(s) + \text{Ca}^{2+}(aq) \rightarrow \text{Mn}(s) + \text{Mn}^{2+}(aq) \)
c. \( 2\text{Mn}(s) + \text{Ca}^{2+}(aq) \rightarrow \text{Ca}(s) + 2\text{Mn}^{2+}(aq) \)
d. \( 2\text{Ca}(s) + \text{Mn}^{2+}(aq) \rightarrow \text{Mn}(s) + 2\text{Ca}^{2+}(aq) \)
e. \( \text{Mn}(s) + \text{Ca}^{2+}(aq) \rightarrow \text{Ca}(s) + \text{Mn}^{2+}(aq) \)

17. \( E^\circ_{\text{cell}} = 1.66 \text{ V} \) for the following cell reaction:
\[ \text{P}_4(s) + 3\text{OH}^-(aq) + 3\text{H}_2\text{O}(l) \rightarrow \text{PH}_3(g) + 3\text{H}_3\text{PO}_4^-(aq) \]
The oxidizing and reducing agents are, respectively,
a. \( \text{P}_4 \) and \( \text{H}_3\text{O}^- \)  
b. \( \text{OH}^- \) and \( \text{P}_4 \)  
c. \( \text{H}_2\text{O} \) and \( \text{P}_4 \)  
d. \( \text{P}_4 \) and \( \text{OH}^- \)  
e. \( \text{P}_4 \) and \( \text{OH}^- \)

18. Given: \( \text{Cr}^{3+}(aq) + 3e^- \rightarrow \text{Cr}(s); E^\circ = -0.74 \text{ V} \)
\( \text{Pb}^{2+}(aq) + 2e^- \rightarrow \text{Pb}(s); E^\circ = -0.13 \text{ V} \)
What is the standard cell potential for the following reaction?
\[ 2\text{Cr}(s) + 3\text{Pb}^{2+}(aq) \rightarrow 3\text{Pb}(s) + 2\text{Cr}^{3+}(aq) \]
a. -0.87 V  
b. 0.61 V  
c. 1.83 V  
d. 0.87 V  
e. -0.61 V
19. What is the copper(II)-ion concentration at 25°C in the cell \( \text{Zn(s)} | \text{Zn}^{2+}(1.0 \text{ M}) \ || \text{Cu}^{2+}(aq) | \text{Cu(s)} \) if the measured cell potential is 1.04 V? The standard cell potential is 1.10 V.
   a. 99.6 M  b. 0.992 M  c. 0.0969 M  d. 1.00 M  e. 0.00940 M

20. In a table of standard reduction potentials, the strongest oxidizing agents are the _______ species in the half-reactions with the _______ \( E^0 \) values.
   a. oxidized, most positive  d. oxidized, most negative
   b. reduced, most positive  e. none of these
   c. reduced, most negative

21. The oxidation numbers of nitrogen in \( \text{NO}_3^- \) ions to \( \text{NH}_4^+ \) ions are, respectively,
   a. +7 and −3  b. +5 and −3  c. −6 and +4  d. +7 and +3  e. +5 and +3.

22. For a certain reaction, \( \Delta H^\circ = -71.0 \text{ kJ} \) and \( \Delta S^\circ = -216 \text{ J/K} \). If \( n = 3 \), calculate \( E^\circ \)cell for the reaction at 25°C.
   a. 0.468 V  b. 0.0961 V  c. 0.0654 V  d. 0.227 V  e. 0.0229 V

23. The first nuclear reaction that was ever observed occurred when nitrogen-14 was bombarded with alpha particles. One product was a proton, and the other was
   a. \( ^7_8\text{O} \)  b. \( ^7_9\text{F} \)  c. \( ^8_9\text{F} \)  d. \( ^7_7\text{N} \)  e. \( ^6_8\text{O} \).

24. What is the mass defect of \( ^{11}_{4}\text{Be} \)?

<table>
<thead>
<tr>
<th>Particle</th>
<th>( ^{11}_{4}\text{Be} )</th>
<th>( ^{1}_{1}\text{p} )</th>
<th>( ^{1}_{0}\text{n} )</th>
<th>( ^{0}_{1}\text{e} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (amu)</td>
<td>11.0216</td>
<td>1.00728</td>
<td>1.00867</td>
<td>0.00055</td>
</tr>
</tbody>
</table>
   a. −0.1707 amu  c. −4.1051 amu  e. −1.685 amu
   b. −0.1055 amu  d. −0.0704 amu

25. The mass deficiency for an isotope was found to be 0.410 amu/atom. Calculate the binding energy in J/mol of atoms. (\( c = 3.00 \times 10^8 \text{ m/s} \), 1 amu = 1.66054 \times 10^{-27} \text{ kg})
   a. 1.23 \times 10^{23} \text{ J/mol}  c. 1.23 \times 10^{3} \text{ J/mol}
   b. 3.69 \times 10^{13} \text{ J/mol}  d. 1.23 \times 10^{20} \text{ J/mol}

26. Which particle does the nuclide symbol \( ^{5}_{3}\text{e} \) represent?
   a. gamma photon  c. positron  e. proton
   b. beta particle  d. neutron

27. The half-life of the radioisotope \( ^{158}_{78}\text{Eu} \) is 0.77 h. How much time is required for a 160.0-g sample of \( ^{158}_{78}\text{Eu} \) to decay to 2.91 g?
   a. 1.9 h  b. 4.0 h  c. 3.0 h  d. 6.0 h  e. 4.5 h

28. It is possible that the world's energy problem could be solved by making use of the fusion reaction of deuterium and tritium. Which of the following reaction equations corresponds to that process?
   a. \( ^{2}_{1}\text{H} + ^{1}_{1}\text{H} \rightarrow ^{2}_{1}\text{He} + ^{1}_{0}\text{n} \)  d. \( ^{2}_{1}\text{H} + ^{1}_{1}\text{H} \rightarrow ^{2}_{1}\text{He} + ^{0}_{1}\text{n} \)
   b. \( ^{3}_{1}\text{H} + ^{2}_{1}\text{H} \rightarrow ^{4}_{1}\text{He} + ^{1}_{0}\text{n} \)  e. \( ^{3}_{1}\text{H} + ^{1}_{1}\text{n} \rightarrow 2 \times ^{2}_{1}\text{H} \)
   c. \( ^{2}_{1}\text{H} + ^{1}_{1}\text{H} \rightarrow 2 \times ^{1}_{0}\text{H} + 3 \times ^{1}_{0}\text{H} \)

29. Which of the following types of nuclear decay results in an increase in the nuclear charge?
   a. electron capture  c. positron emission  e. fission
   b. alpha emission  d. beta emission

30. Which of the following nuclides will produce \( ^{233}_{92}\text{Pa} \) upon undergoing alpha decay?
   a. \( ^{229}_{90}\text{Ra} \)  b. \( ^{233}_{93}\text{U} \)  c. \( ^{237}_{93}\text{Np} \)  d. \( ^{233}_{90}\text{Th} \)  e. \( ^{234}_{92}\text{Pa} \)
Extra Credit Definitions (1 point each). Give the textbook (or an equivalent) definition for any six terms from the following list: State function, Path function, Entropy, Thermodynamics 2nd law, Thermodynamics 3rd law, Voltaic cell, Electrolytic cell, Salt bridge, Fuel cell, Radioactive decay, Band of stability, and Fission.

Term 1:

Term 2:

Term 3:

Term 4:

Term 5:

Term 6:

Extra Credit Problems (1 points each). Balance the following chemical reactions:

...... KOH + ......Cl₂ → ...... KCl + ...... KClO₃ + ......H₂O

...... K₂Cr₂O₇ + ...... NH₃ + ...... HCl → ...... KCl + ...... NO + ...... CrCl₃ + ...... H₂O

Correct multiple-choice answers: Extra credit: Lecture participation: Exam 4 Grade:
Multiple Choice: Identify the letter of the choice that best completes the statement or answers the question.

1. Given: \( \text{Fe}_2\text{O}_3(s) + 3\text{CO}(g) \rightarrow 2\text{Fe}(s) + 3\text{CO}_2(g); \Delta H = -26.8 \text{ kJ} \)
   
   \( \text{FeO}(s) + \text{CO}(g) \rightarrow \text{Fe}(s) + \text{CO}_2(g); \Delta H = -16.5 \text{ kJ} \)

   determine \( \Delta H \) for the following thermochemical equation.
   \( \text{Fe}_2\text{O}_3(s) + \text{CO}(g) \rightarrow 2\text{FeO}(s) + \text{CO}_2(g) \)
   
   a. 10.3 kJ  b. 22.7 kJ  c. -10.3 kJ  d. -43.3 kJ  e. 6.2 kJ

2. How much heat is gained by iron when 10.2 g of iron is warmed from 25.9°C to 76.1°C? The specific heat of iron is 0.449 J/(g \cdot ^\circ\text{C}).
   
   a. \( 2.30 \times 10^2 \text{ J} \)  c. \( 34.2 \text{ J} \)  e. \( 3.49 \times 10^2 \text{ J} \)
   
   b. \( 1.19 \times 10^2 \text{ J} \)  d. \( 22.5 \text{ J} \)

3. At constant pressure, the sign of \( q \) for the process \( \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s) \) is expected to be
   a. positive, and the process is exothermic.
   b. negative, and the process is exothermic.
   c. positive, and the process is endothermic.
   d. negative, and the process is endothermic.
   e. impossible to predict.

4. According to the following thermochemical equation, if 328.9 g of NO\(_2\) is produced, how much heat is released at constant pressure?
   \( 2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g); \Delta H^\circ = -114.4 \text{ kJ} \)
   
   a. \( 8.179 \times 10^2 \text{ kJ} \)  c. \( 4.089 \times 10^2 \text{ kJ} \)  e. \( 114.4 \text{ kJ} \)
   
   b. \( 3.763 \times 10^4 \text{ kJ} \)  d. \( 16.00 \text{ kJ} \)

5. Which of the following statements is incorrect?
   a. Enthalpy is a state function.
   b. The value of \( q \) is positive in an exothermic process.
   c. Internal energy is a state function.
   d. Heat flows from a system into the surroundings in an endothermic process.
   e. The value of \( q \) is positive when heat flows into a system from the surroundings.

6. Given the thermochemical equation \( 2\text{Al}(s) + \frac{3}{2} \text{O}_2(g) \rightarrow \text{Al}_2\text{O}_3(s); \Delta H = -1676 \text{ kJ} \)
   find \( \Delta H \) for the following reaction: \( 2\text{Al}_2\text{O}_3(s) \rightarrow 4\text{Al}(s) + 3\text{O}_2(g) \)
   
   a. 838 kJ  b. -838 kJ  c. 1676 kJ  d. -1676 kJ  e. 3352 kJ

7. What is \( \Delta H^\circ \) for the following reaction?
   \( 2\text{C}_2\text{H}_2(g) + 5\text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 2\text{H}_2\text{O}(l) \)
   
   \[
   \begin{array}{c|c}
   \text{Substance} & \Delta H^\circ \text{(kJ/mol)} \\
   \hline
   \text{C}_2\text{H}_2(g) & +226.7 \\
   \text{CO}_2(g) & -393.5 \\
   \text{H}_2\text{O}(l) & -285.8 \\
   \end{array}
   \]
   
   a. +2599.0 kJ  b. -2599.0 kJ  c. -1692.2 kJ  d. +1692.2 kJ  e. -452.6 kJ

8. The enthalpy change at 1 atm of which reaction corresponds to the standard enthalpy of formation of solid magnesium nitrate, \( \text{Mg(NO}_3)_2(s) \)?
   a. \( \text{Mg}(s) + \text{N}_2(g) + 3\text{O}_2(g) \rightarrow \text{Mg(NO}_3)_2(s), \Delta H \)
   
   b. \( \text{Mg}^{2+}(aq) + 2\text{NO}_3^-(aq) \rightarrow \text{Mg(NO}_3)_2(s), \Delta H \)
   
   c. \( \text{Mg}^{2+}(g) + 2\text{NO}_3^-(g) \rightarrow \text{Mg(NO}_3)_2(s), \Delta H \)

9. For which of the following reactions is \( \Delta H \) not equal to \( \Delta U \)?
   a. \( \text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) \)
   
   b. \( \text{Hg}(s) \rightarrow \text{Hg}(l) \)
   
   c. \( 2\text{HF}(g) \rightarrow \text{H}_2(g) + \text{F}_2(g) \)
   
   d. \( \text{I}_2(s) \rightarrow \text{I}_2(g) \)
   
   e. \( \text{CH}_4(g) + \text{C}_2\text{H}_4(g) \rightarrow 2\text{C}_2\text{H}_6(g) \)
10. Using bond-energy data, what is $\Delta H^\circ$ for the following reaction? \( \text{CH}_4(\text{g}) + 2\text{Cl}_2(\text{g}) \rightarrow \text{CCl}_4(\text{g}) + 2\text{H}_2(\text{g}) \)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>411</td>
</tr>
<tr>
<td>H-H</td>
<td>432</td>
</tr>
<tr>
<td>Cl-Cl</td>
<td>240</td>
</tr>
<tr>
<td>C-Cl</td>
<td>327</td>
</tr>
</tbody>
</table>

a. –144 kJ  
b. 1410 kJ  
c. –48 kJ  
d. 48 kJ  
e. 144 kJ

**Bonus questions (1 points each).**

*Give the names and the chemical equations for two processes that are part of Born-Haber cycle:*

Name: 
Chemical equation:

Name: 
Chemical equation:

**Multiple-choice questions:**  
**Bonus questions:**  
**Pre-lecture assignments:**  
**Test 1 Grade:**
Multiple Choice: Identify the letter of the choice that best completes the statement or answers the question.

___ 1. The Henry’s law constant for the solubility of carbon dioxide in water is 0.0769 M/atm at 0.00°C. If the pressure of CO$_2$ is 0.550 atm, what concentration of carbon dioxide can be dissolved in water at 0.00°C?
   a. 0.00715 M   b. 0.0118 M   c. 0.140 M   d. 0.0236 M   e. 0.0423 M

___ 2. A solution consisting of 0.266 mol of methylbenzene, C$_6$H$_5$CH$_3$, in 257 g of nitrobenzene, C$_6$H$_5$NO$_2$, freezes at –1.2°C. Pure nitrobenzene freezes at 6.0°C. What is the freezing-point depression constant of nitrobenzene?
   a. 14.0°C/m   b. 4.7°C/m   c. 3.5°C/m   d. 7.0°C/m   e. 27°C/m

___ 3. What mass of water must be used to dissolve 20.0 grams of ethanol, C$_2$H$_5$OH, to prepare a 0.0500 molal solution of ethanol?
   a. 3.76 kg   b. 4.00 kg   c. 8.70 kg   d. 7.18 kg   e. 6.35 kg

___ 4. Which of the following statements is incorrect?
   a. The solubility of a gas in water increases as the temperature rises.
   b. The smaller the lattice energy of an ionic compound, the greater its solubility in water.
   c. Pressure has almost no effect on the solubility of solids in liquids.
   d. If the heat of solution of a salt is negative, the solubility decreases as the temperature increases.
   e. Pressure has a strong effect on the solubility of gases in liquids.

___ 5. Calculate the molecular weight of a small protein if a 0.25-g sample dissolved in 168 mL of water has an osmotic pressure of 9.9 mmHg at 23°C. (1 atm = 760 mmHg)
   a. 2.2 × 10$^2$ g/mol   c. 2.8 × 10$^3$ g/mol   e. 3.7 g/mol
   b. 2.7 × 10$^2$ g/mol   d. 3.7 × 10$^{-3}$ g/mol

___ 6. Which of the following pairs has compounds with same types of intermolecular interactions?
   a. CH$_3$F and PH$_3$   c. CH$_3$CH$_2$CH$_3$ and H$_2$O   e. CH$_3$OH and H$_2$S
   b. HCl and CH$_3$CH$_3$   d. CH$_3$CH$_2$OH and CCl$_4$

___ 7. What is the freezing point of a 0.48 m solution of CaCl$_2$ in water at 1 atm? ($K_b = 0.512°C/m$ for water.)
   a. 99.75°C   b. 100.74°C   c. 100.25°C   d. 100.50°C   e. 99.26°C

___ 8. What is the mass percent of an aqueous sodium hydroxide solution in which the mole fraction of NaOH is 0.231? The density of the solution is 1.4339 g/mL.
   a. 33.1%   b. 68.9%   c. 6.21%   d. 40.0%   e. 6.44%

___ 9. What is the vapor pressure at 20°C of an ideal solution prepared by the addition of 2.83 g of the nonvolatile solute urea, CO(NH$_2$)$_2$, to 51.6 g of methanol, CH$_3$OH? The vapor pressure of pure methanol at 20°C is 89.0 mmHg.
   a. 84.4 mmHg   c. 8.30 mmHg   e. 2.53 mmHg
   b. 86.5 mmHg   d. 80.7 mmHg

___ 10. What is the molarity of 2500. mL of a solution that contains 160. grams of NH$_4$NO$_3$?
   a. 1.00 M   b. 0.600 M   c. 0.450 M   d. 0.333 M   e. 0.800 M
**Bonus questions (2 points each).** *Give the textbook (or an equivalent) definition for the following terms:*

Saturated solution

Colligative properties

Colloid

Tyndall effect
Multiple Choice: Identify the letter of the choice that best completes the statement or answers the question.

1. The compound A decomposes by a first-order process with a rate constant of $2.96 \times 10^{-2}$ h$^{-1}$. How long will it take for 13.0% of the initial concentration of A to be achieved?
   a. 29.4 h  
   b. 4.70 h  
   c. 68.9 h  
   d. 4.39 h  
   e. 33.8 h

2. The reaction $2\text{H}_2(\text{g}) + 2\text{NO}(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g})$ is first-order in H$_2$ and second-order in NO at a particular temperature. What is the rate law?
   a. Rate $= k[\text{H}_2][\text{NO}]$  
   b. Rate $= k[\text{H}_2][\text{NO}]^2$  
   c. Rate $= k[\text{H}_2][\text{NO}]$  
   d. Rate $= [\text{H}_2][\text{N}_2]$  
   e. Rate $= [\text{H}_2][\text{N}_2]$  

3. The reaction rate of CO and NO$_2$ in the reaction $\text{CO}(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{NO}(\text{g})$ is measured using the initial rates method, and the results are tabulated below. Which of the following is the rate expression for the reaction?

<table>
<thead>
<tr>
<th>[CO] (mol/L)</th>
<th>NO$_2$ (mol/L)</th>
<th>$-\dfrac{\Delta[\text{CO}]}{\Delta t}$ (mol/L·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8.00 \times 10^{-4}$</td>
<td>$5.50 \times 10^{-4}$</td>
<td>$8.40 \times 10^{-8}$</td>
</tr>
<tr>
<td>$8.00 \times 10^{-4}$</td>
<td>$11.0 \times 10^{-3}$</td>
<td>$1.68 \times 10^{-7}$</td>
</tr>
<tr>
<td>$1.60 \times 10^{-3}$</td>
<td>$5.50 \times 10^{-4}$</td>
<td>$1.68 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

   a. Rate $= k[\text{CO}]^2 \times [\text{NO}_2]$  
   b. Rate $= k[\text{CO}]$  
   c. Rate $= k[\text{CO}]$  
   d. Rate $= k[\text{CO}] \times [\text{NO}_2]$  
   e. Rate $= k[\text{CO}] \times [\text{NO}_2]^2$

4. At 100 K the reaction $\text{AB}_2 \rightarrow \text{A} + \text{B}_2$ obeys the rate law rate $= k[\text{AB}_2]^2$ where $k = 5.7 \text{ M}^{-1}\text{s}^{-1}$. What would the concentration of AB$_2$ be after 60 minutes if the initial concentration was 1.45 mol/L?
   a. $2.4 \times 10^{-5} \text{ M}$  
   b. $2.0 \times 10^{-5} \text{ M}$  
   c. $1.2 \times 10^{-2} \text{ M}$  
   d. $2.9 \times 10^{-3} \text{ M}$  
   e. $4.9 \times 10^{-5} \text{ M}$

5. For the reaction $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$, which of the following expressions is equal to the rate of the reaction?
   a. $\Delta[\text{N}_2\text{O}_5] \over \Delta t$  
   b. $\Delta[\text{N}_2\text{O}_5] \over 2 \Delta t$  
   c. $\Delta[\text{NO}_2] \over \Delta t$  
   d. $\Delta[\text{NO}_2] \over 4 \Delta t$  
   e. $-2 \times \Delta[\text{N}_2\text{O}_5] \over \Delta t$

6. For the first-order reaction below the rate constant is $k = 4.24 \times 10^5$ s$^{-1}$ at $-4^\circ\text{C}$, and the activation energy is 53.7 kJ/mol. What is the rate constant at 16°C?
   \[ \frac{1}{2}\text{N}_2\text{O}_5(\text{g}) \rightarrow \text{NO}_2(\text{g}) \]
   a. $4.24 \times 10^5$ s$^{-1}$  
   b. $5.63 \times 10^4$ s$^{-1}$  
   c. $2.24 \times 10^6$ s$^{-1}$  
   d. $4.56 \times 10^5$ s$^{-1}$  
   e. $7.97 \times 10^3$ s$^{-1}$

7. Which of the following statements is not always true?
   a. The rates of most chemical reactions change with time.
   b. A catalyst provides an alternative reaction mechanism with lower activation energy.
   c. The rate constant for a reaction can be changed by changing the temperature.
   d. The rate-determining step in a mechanism is a bimolecular process.
   e. The rate of a catalyzed reaction is dependent on the concentration of the catalyst.

8. For a zero-order reaction, the half-life is 0.14 min when the initial concentration of the reactant is 2.0 M. What is the rate constant for this reaction?
   a. $7.1 \text{ M min}^{-1}$  
   b. $14 \text{ M min}^{-1}$  
   c. $28 \text{ M min}^{-1}$  
   d. $57 \text{ M min}^{-1}$  
   e. $3.6 \text{ M min}^{-1}$
Consider the hypothetical reaction $2A + C_2 \rightarrow A_2C + C$ with the proposed mechanism below. Which one of the following statements must be true? The reaction is ____.

\[
\begin{align*}
A & \quad + \quad C_2 \quad \rightarrow \quad AC + C \quad \text{slow} \\
AC & \quad + \quad A \quad \rightarrow \quad A_2C \quad \text{fast} \\
2A & \quad + \quad C_2 \quad \rightarrow \quad A_2C + C \quad \text{overall}
\end{align*}
\]

a. first order in A and first order in $C_2$

b. second order in $C_2$ and second order overall

c. second order in A and second order overall

d. first order in A, first order in $C_2$, and third order overall

e. second order in $C_2$, zero order in A, and third order overall

10. Given the following potential energy diagram for the one-step reaction $X + Y \rightarrow Z + R$. The arrow "a" represents the ____.

\[
\begin{align*}
\text{Potential energy} \\
\text{Reaction:} \quad X + Y \rightarrow Z + R
\end{align*}
\]

a. energy content of products

b. energy content of reactants

c. activation energy for the reverse reaction

d. the net change in energy for the reaction

e. activation energy for the forward reaction

**Bonus questions (2 points each).** Give the textbook (or an equivalent) definition for the following terms:

An activated complex (also known as a transition state) is ____________

The molecularity is ____________

**Bonus Fill-Ins (1 points each).** Fill in the following statements with the appropriate numbers or words:

For a __________________reaction, the graph of $1/[A]$ versus time is linear.

An elementary reaction $A + B + C \rightarrow \text{Products}$ is called ____________________________

The expression for the half-life for a second-order reaction is $t_{1/2} =$ __________

A catalyst that is in the same phase as the reacting species is called ________________________
CHEM 1120 - Test 4  

Spring 2014  

Multiple Choice: Identify the letter of the choice that best completes the statement or answers the question.

___ 1. Consider the following equilibrium: 2NO(g) + 3F_2(g) \rightleftharpoons 2NOF_3(g)
Suppose 0.20 mol of NO and 0.30 mol of F_2 are added to a 5.0-L container. If x mol of NOF_3 is present at equilibrium, what is the equilibrium concentration of NO?
   a. 0.05 – 0.50x   b. 0.20 – x   c. 0.20 – 2x   d. 0.04 – 0.20x   e. 0.04 – x

___ 2. Consider the following reaction: 2HF(g) \rightleftharpoons H_2(g) + F_2(g) \quad (K = 1.00 \times 10^2)
Given that 1.00 mol of HF(g), 0.234 mol of H_2(g), and 0.750 mol of F_2(g) are mixed in a 5.00-L flask, determine the reaction quotient, Q.
   a. Q = 0.0351   b. Q = 0.176   c. Q = 0.439   d. Q = 1.98   e. Q = 0.0439

___ 3. For a reversible reaction with a one-step mechanism, A \rightleftharpoons B, the rate of the forward reaction is rate_f = 4.6 \times 10^{-4} \text{ s}^{-1} \text{[A]} \quad \text{and} \quad \text{the rate of the reverse reaction is rate_r = 3.2 \times 10^{-6} \text{ s}^{-1} \text{[B]}}.\text{ What is the value of } K_c \text{ for this reaction?}
   a. 1.5 \times 10^9   b. 7.0 \times 10^{-3}   c. 1.4 \times 10^2   d. 7.0 \times 10^9   e. 2.5 \times 10^{-11}

___ 4. For the following reaction system at equilibrium, which one of the changes below would cause the equilibrium to shift to the right?
   Br_2(g) + 2NO(g) \rightleftharpoons 2NOBr(g); \Delta H^\circ = -30 \text{ kJ}
   a. Increase the volume of the reaction vessel.
   b. Remove some NO.
   c. Add some NOBr.
   d. Remove some Br_2.
   e. Decrease the temperature.

___ 5. If } K_C = 0.142 \text{ for } A_2 + 2B \rightleftharpoons 2AB, \text{ what is the value of } K_C \text{ for the reaction } 4AB \rightleftharpoons 2A_2 + 4B?
   a. 49.6   b. 0.142   c. 2.65   d. 0.284   e. 3.52

___ 6. For which of the following equilibria does } K_C = K_P?\text{ }
   a. CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)   \quad d. N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)
   b. CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)   \quad e. CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)
   c. HBr(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}Br_2(l)

___ 7. For which of the following reactions will the reactant experience the largest degree of decomposition upon reaching equilibrium at 500 K?
   a. 2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g); K_p = 1.7 \times 10^{-2}
   b. 2NOF(g) \rightleftharpoons 2NO(g) + F_2(g); K_p = 1.2 \times 10^{-26}
   c. 2SO_2(g) \rightleftharpoons 2SO_3(g) + O_2(g); K_p = 1.3 \times 10^{-5}
   d. 2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g); K_p = 6.6 \times 10^{-22}
   e. 2NO(g) \rightleftharpoons 2NO(g) + O_2(g); K_p = 5.9 \times 10^{-5}

___ 8. At 550 K, } K_C = 7.7 \times 10^2 \text{ for the following equilibrium: SO}_3(g) + NO(g) \rightleftharpoons \text{ SO}_2(g) + \text{ NO}(g)
If 0.133 mol each of SO_3 and NO are placed in a 5.00-L container at 550 K, what is the concentration of SO_3 at equilibrium?
   a. 0.022 M   b. 0.0067 M   c. 0.017 M   d. 0.052 M   e. 0.026 M

___ 9. Consider the following equilibrium: 2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g); \Delta H = 92 \text{ kJ}
What change should be made in order to increase the value of } K_p \text{ for this reaction?
   a. Decrease the temperature.   d. Decrease the pressure.
   b. Nothing; } K_p \text{ cannot be changed.   e. Increase the pressure.
   c. Increase the temperature.
10. Which expression correctly describes the equilibrium constant $K_c$ for the following reaction?

$$4\text{NH}_3(g) + 5\text{O}_2(g) \rightleftharpoons 4\text{NO}(g) + 6\text{H}_2\text{O}(g)$$

a. $K_c = \frac{[\text{NO}][\text{H}_2\text{O}]}{[\text{NH}_3][\text{O}_2]}$

b. $K_c = \frac{4[\text{NO}][\text{O}_2]}{4[\text{NH}_3][\text{H}_2\text{O}]}$

c. $K_c = \frac{[\text{N}\text{H}_3]^4[\text{O}_2]^5}{[\text{NO}]^4[\text{H}_2\text{O}]^6}$

d. $K_c = \frac{[\text{NO}]^4[\text{H}_2\text{O}]^6}{[\text{N}\text{H}_3]^4[\text{O}_2]^5}$

e. $K_c = \frac{4[\text{NO}]+6[\text{H}_2\text{O}]}{4[\text{NH}_3]+5[\text{O}_2]}$

**Bonus questions (2 points each).** *Give the textbook (or an equivalent) definition for the following terms:*

Reversible process

Le Chatelier’s principle

**Bonus Fill-Ins (1 points each).** *Fill in the following statements with the appropriate numbers or words:*

If $Q_c$ .................., the reaction will go to the left.

If $P$ is increased by decreasing $V$, the equilibrium will shift in the direction of ..........................
1. For a solution at 25°C, $[\text{H}_3\text{O}^+] = 4.0 \times 10^{-4}$.
   A. For this solution, $[\text{OH}^-] =$ ........................
   B. For this solution, pH = .............
   C. For this solution, pOH = ...........
   D. This solution is ........................ (choose acidic/basic/neutral)

2. A. Write below the formulas and the correct names for two strong acids:

   B. Write below the formulas and the correct names for two strong bases:

3. For a solution at 25°C, $[\text{OH}^-] = 3.5 \times 10^{-5}$.
   A. For this solution, $[\text{H}_3\text{O}^+] =$ ........................
   B. For this solution, pH = .............
   C. For this solution, pOH = ...........
   D. This solution is ........................ (choose acidic/basic/neutral)

4. A. The conjugate base of HClO$_4$ is ........................
   B. The conjugate base of H$_2$PO$_4^-$ is ........................
   C. The conjugate base of HO$_2$CN is ........................
   D. The conjugate acid of ClO$_-$ is ........................
   E. The conjugate acid of H$_2$PO$_4^-$ is ........................

5. A. The pH of an HCl solution is 4.24. The molarity of this solution is ........
   B. The pH of a KOH solution is 13.15. The molarity of this solution is ........

6. For the following pairs, circle the acid that is stronger:
   A. H$_2$PO$_4^-$ or HPO$_4^{2-}$   D. H$_2$S or HCl
   B. HClO$_3$ or HIO$_3$     E. HClO$_4$ or HClO$_3$
   C. HI or HBr  F. HNO$_3$ or H$_2$SO$_3$

7. A. The pH value for a 1.0 L solution that is 0.35 M HBr and 0.15 M HI is ........
   B. The pH value for a 0.065 M Ba(OH)$_2$ solution is ...........
8. For the compounds below, circle the appropriate description:
   A. \( \text{H}_3\text{PO}_4 \)  acid  base  weak  strong
   B. \( \text{RbOH} \)  acid  base  weak  strong
   C. \( \text{Fe(OH)}_2 \)  acid  base  weak  strong
   D. \( \text{H}_2\text{O} \)  acid  base  weak  strong
   E. \( \text{HCl} \)  acid  base  weak  strong

9. For the oxides below, circle the appropriate class:
   A. \( \text{CuO} \)  acidic  basic  amphoteric
   B. \( \text{P}_4\text{O}_6 \)  acidic  basic  amphoteric
   C. \( \text{Sb}_2\text{O}_5 \)  acidic  basic  amphoteric
   D. \( \text{Na}_2\text{O}_2 \)  acidic  basic  amphoteric
   E. \( \text{NO}_2 \)  acidic  basic  amphoteric

10. A. Write the **net ionic equation** for the reaction between sodium hydroxide and hydrofluoric acid:

    B. Write the **net ionic equation** for the reaction between chloric acid and potassium hydroxide:

**Bonus** (2 points each) - Provide short but complete definitions for the following terms:

  Bronsted-Lowry acid:

  Bronsted-Lowry base:

  Lewis acid:

  Lewis base:

**Bonus** (1 points each) - Provide the names for the following ions:

  \( \text{H}_3\text{O}^+ \) is called …………………………; \( \text{OH}^- \) is called ………………………….
Instructions: On the eight free-response problems requiring to calculate the pH of the solution, you can choose to answer, for 2 points, with one of the three options: > 7, < 7 or =7. For full credit, you need to give the actual value of pH, with 2 decimal digits, and you need to show your work.

1. A. Write below the formulas and the correct names for two weak acids:
   
   B. Write below the formulas and the correct names for two weak bases:

2. Calculate the pH value for a 0.85 M N\textsubscript{2}H\textsubscript{4} solution. \((K_b = 1.7 \times 10^{-6} \text{ for } N_2H_4)\)
   \[
   \text{pH} = 
   \]

3. Calculate the pH value for a 0.025 M HClO solution. \((K_a = 3.5 \times 10^{-8} \text{ for } HClO)\)
   \[
   \text{pH} = 
   \]

4. \(K_a = 1.7 \times 10^{-7} \text{ for an acid } HX \text{ and } K_a = 1.3 \times 10^{-5} \text{ for an acid } HY. \) Which of the following solutions will have the highest pH value?
   a. \(1.0 \times 10^{-3} \text{ M HY}\)
   b. \(1.0 \times 10^{-2} \text{ M HY}\)
   c. \(1.0 \times 10^{-1} \text{ M HY}\)
   d. \(1.0 \times 10^{-3} \text{ M HX}\)
   e. \(1.0 \times 10^{-2} \text{ M HX}\)
   f. \(1.0 \times 10^{-1} \text{ M HX}\)

5. A 0.0400 \(M\) weak base solution is 0.35% ionized at 25°C? What is the \(K_b\) value for the weak base?
   a. \(4.9 \times 10^{-5}\)
   b. \(4.9 \times 10^{-7}\)
   c. \(4.9 \times 10^{-3}\)
   d. \(1.4 \times 10^{-4}\)
   e. \(1.4 \times 10^{-2}\)
   f. \(3.5 \times 10^{-3}\)

6. For each of the 3 salts below, give the correct name and specify if it produces an \textit{acidic, basic or neutral} solution when dissolved in water to form a 1.0 M solution:
   
   A. \(\text{NH}_4\text{Cl}:\)
   
   B. \(\text{NaClO}:\)
   
   C. \(\text{Ca(NO}_3\text{)}_2:\)
7. Calculate the pH value for a 0.70 M NaF solution. \(K_a = 6.8 \times 10^{-4}\) for HF

\[ \text{pH} = \] 

8. Calculate the pH value for a 0.040 M \(\text{NH}_4\text{Br}\) solution. \(K_b = 1.8 \times 10^{-5}\) for \(\text{NH}_3\)

\[ \text{pH} = \] 

9. Calculate the pH value for a \(2.5 \times 10^{-4}\) M \(\text{RbNO}_3\) solution.

\[ \text{pH} = \] 

10. What is the pH of a solution that is 0.15 M ammonia and 0.75 M ammonium chloride? \(K_b = 1.8 \times 10^{-5}\) for ammonia

\[ \text{pH} = \] 

11. If 100. mL of 0.040 M NaOH solution is added to 100. mL of solution which is 0.10 M in acetic acid and 0.10 M in sodium acetate, what will the pH of the new solution be? \(K_a = 1.8 \times 10^{-5}\) for acetic acid

\[ \text{pH} = \] 

12. A volume of 12.47 mL HCl solution will completely react with 225. mL of 0.0120 M NaOH. What is the molarity of the HCl solution?

a. 0.217 \(M\)  
   b. 0.108 \(M\)  
   c. 0.433 \(M\)  
   d. 6.65 \(\times 10^{-4}\) \(M\)  
   e. 1.33 \(\times 10^{-3}\) \(M\)  
   f. 3.33 \(\times 10^{-4}\) \(M\)

13. 50.0 mL of 0.20 M HCN \((K_a = 4.0 \times 10^{-10})\) solution is titrated with a 0.40 M NaOH solution. What is the pH at the equivalence point of this titration?

\[ \text{pH} = \]
1. A. The $K_{sp}$ expression for iron(III) hydroxide is $K_{sp} =$

B. The $K_{sp}$ expression for $\text{Ag}_3\text{PO}_4$ is $K_{sp} =$

2. A solution contains equal concentrations of $\text{Pb}^{2+}$, $\text{Sr}^{2+}$, and $\text{Ba}^{2+}$ ions. When a dilute solution of $\text{K}_2\text{CrO}_4$ is added to the solution, what is the order in which the chromate salts will begin to precipitate? $K_{sp}(\text{PbCrO}_4) = 1.8 \times 10^{-14}$, $K_{sp}(\text{SrCrO}_4) = 3.5 \times 10^{-5}$, and $K_{sp}(\text{BaCrO}_4) = 1.2 \times 10^{-10}$
   a. $\text{PbCrO}_4$ then $\text{SrCrO}_4$ then $\text{BaCrO}_4$
   b. $\text{SrCrO}_4$ then $\text{BaCrO}_4$ then $\text{PbCrO}_4$
   c. $\text{BaCrO}_4$ then $\text{SrCrO}_4$ then $\text{PbCrO}_4$
   d. $\text{PbCrO}_4$ then $\text{BaCrO}_4$ then $\text{SrCrO}_4$
   e. $\text{BaCrO}_4$ then $\text{PbCrO}_4$ then $\text{SrCrO}_4$
   f. $\text{SrCrO}_4$ then $\text{PbCrO}_4$ then $\text{BaCrO}_4$

3. A. The dissociation constant ($K_d$) expression for $[\text{Zn(OH)}_4]^{2-}$ is:

   $$K_d =$$

B. The formation constant ($K_f$) expression for $[\text{Cd(NH}_3)_4]^{2+}$ is:

   $$K_f =$$

4. The molar solubility of $\text{BaCO}_3$ is $9.0 \times 10^{-4}$ M at 25°C. What is the solubility product constant for $\text{BaCO}_3$?
   a. $6.7 \times 10^{-11}$
   b. $4.0 \times 10^{-15}$
   c. $1.2 \times 10^{-8}$
   d. $5.3 \times 10^{-12}$
   e. $8.1 \times 10^{-7}$
   f. $9.0 \times 10^{-4}$

5. Consider the following reaction: $\text{Cu}^+(aq) + 2\text{CN}^-(aq) \rightarrow [\text{Cu(CN)}_2]^- (aq)$
   A. The complex ion is …………………
   B. The ligand is …………………
   C. The Lewis acid is …………………
   D. The bonds formed in this reaction are ………………………

6. $K_{sp} = 2.0 \times 10^{-15}$ for $\text{Ni(OH)}_2$. What is the molar solubility for a saturated $\text{Ni(OH)}_2$ solution? SHOW YOUR WORK for full credit.

   $$s =$$
7. The $K_{sp}$ for CaF$_2$ is $K_{sp} = 3.9 \times 10^{-11}$. When 100 mL of $4.0 \times 10^{-4}$ M CaCl$_2$ is mixed with 50 mL of $6.0 \times 10^{-4}$ M NaF, which of the following statements is true?
   a. No precipitate forms, because $Q_{sp} < K_{sp}$.
   b. A precipitate forms, because $Q_{sp} < K_{sp}$.
   c. No precipitate forms, because $Q_{sp} > K_{sp}$.
   d. A precipitate forms, because $Q_{sp} > K_{sp}$.
   e. No precipitate forms, because $Q_{sp} = K_{sp}$.
   f. A precipitate forms, because $Q_{sp} = K_{sp}$.

8. $K_{sp} = 3.4 \times 10^{-11}$ for CaF$_2$.
   A. The molar solubility of CaF$_2$ in 0.045 M CaCl$_2$ solution is …………………
   B. The molar solubility of CaF$_2$ in 0.63 M NaF solution is …………………

9. The $K_{sp}$ value for Fe(OH)$_2$ is $K_{sp} = 1.6 \times 10^{-14}$. What is the pH of a 1.00 L saturated solution of Fe(OH)$_2$? SHOW YOUR WORK for full credit.

$$\text{pH} =$$

10. If solid AgNO$_3$ is slowly added to a solution that is 0.67 M in NaBr and 0.043 M in NaCl, what is the concentration of Br$^-$ when AgCl just begins to precipitate?
    $K_{sp} = 5.0 \times 10^{-13}$ for AgBr and $K_{sp} = 1.8 \times 10^{-10}$ for AgCl.
    a. $1.9 \times 10^{-3} \text{ M}$
    b. $1.2 \times 10^{-4} \text{ M}$
    c. $2.4 \times 10^{-4} \text{ M}$
    d. $1.5 \times 10^{-5} \text{ M}$
    e. $7.1 \times 10^{-7} \text{ M}$
    f. $1.3 \times 10^{-5} \text{ M}$

11. A 500. mL saturated solution of MgCO$_3$ ($M_M = 84.3$ g/mol) is reduced to 120. mL by evaporation. What mass of solid MgCO$_3$ is formed? $K_{sp} = 4.0 \times 10^{-5}$ for MgCO$_3$. SHOW YOUR WORK for full credit.

$$\text{mass} =$$

12. Calculate the concentration of Ni$^{2+}$ ions in a 0.20 M K$_2$[Ni(CN)$_4$] solution at 25°C. $K_f$ for [Ni(CN)$_4$]$^{2-} = 1.0 \times 10^{+31}$. SHOW YOUR WORK for full credit.

$$[\text{Ni}^{2+}] =$$
CheM 1120 Test 8A Spring 2014

April 10, 2014

Name: _________________________________  
This exam covers unit VIII.

At 25°C:  

\[
\begin{align*}
\text{CO}(g) + 2 \text{H}_2(g) & \rightarrow \text{CH}_3\text{OH}(g) \\
\Delta H^\circ_f \text{ (kJ/mol)} & = -110.5 \quad 0 \quad -200.7 \\
S^\circ \text{ (J/mol-K)} & = 197.5 \quad 130.6 \quad 239.7
\end{align*}
\]

1. A. Based on the information above, the standard enthalpy of reaction for this reaction at 25°C is ..........................  
B. Based on the information above, the standard entropy of reaction for this reaction at 25°C is ..........................  

2. A. Based on the information above, the standard free energy of reaction for this reaction at 25°C is ..........................  
B. Based on the information above, the standard free energy of reaction for this reaction is zero at ..........................  

3. What is the change in entropy when 0.490 g of water decomposes to form hydrogen gas and oxygen gas at 298 K?  
\[
2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2; \quad \Delta S^\circ = 326.3 \text{ J/mol-K}
\]
  a. 2.22 J/K  
  b. 159.9 J/K  
  c. 4.44 J/K  
  d. 17.8 J/K  
  e. 8.88 J/K  
  f. 1.11 J/K

4. For the statements below, choose among low, high, all or no:  
A. When \(\Delta H < 0\) and \(\Delta S > 0\), a reaction is spontaneous at .......... temperature(s).  
B. When \(\Delta H > 0\) and \(\Delta S > 0\), a reaction is spontaneous at .......... temperature(s).  
C. When \(\Delta H < 0\) and \(\Delta S < 0\), a reaction is spontaneous at .......... temperature(s).  
D. When \(\Delta H > 0\) and \(\Delta S < 0\), a reaction is spontaneous at .......... temperature(s).  

5. For HCN(l): \(\Delta H^\circ_f = 108.9 \text{ kJ/mol}\) and \(S^\circ = 112.8 \text{ J/mol-K}\).  
For HCN(g): \(\Delta H^\circ_f = 135.1 \text{ kJ/mol}\) and \(S^\circ = 201.7 \text{ J/mol-K}\).  
A. The entropy of condensation of HCN is \(\Delta S^\circ_{\text{con}} = \) ......................  
B. The enthalpy of condensation of HCN is \(\Delta H^\circ_{\text{con}} = \) ......................  
C. Based on the above information, the boiling temperature is ..........................  

6. Circle T if the statement is true and F if the statement is false:  
T or F  The free energy change in a chemical reaction is the maximum energy available to do useful work.  
T or F  \(\Delta S\) is positive for an endothermic process.  
T or F  \(\Delta S\) can be negative in a spontaneous chemical reaction.  
T or F  Heat is a state function.  
T or F  The entropy of a system increases when the energy is less dispersed.  
T or F  When \(\Delta G^\circ\) is negative, products are favored compared to reactants.
7. For each of the following reactions, circle + if $\Delta S^\circ$ is positive, circle – if $\Delta S^\circ$ is negative, and circle 0 if $\Delta S^\circ$ is close to zero (i.e., slightly positive or negative):
   A. $-0$ + $\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(s)}$
   B. $-0$ + $\text{N}_2\text{O}_5(g) \rightarrow 2\text{NO(g)} + 3/2\text{O}_2(g)$
   C. $-0$ + $\text{BF}_3(g) + \text{NH}_3(g) \rightarrow \text{F}_3\text{BNH}_3(s)$
   D. $-0$ + $\text{CH}_4(g) + \text{Cl}_2(g) \rightarrow \text{CH}_3\text{Cl(g)} + \text{HCl(g)}$

8. For a chemical reaction, $\Delta S^\circ = +376 \text{ J/mol} \cdot \text{K}$. If this reaction is spontaneous at all temperatures above 500°C, what is the value of $\Delta H^\circ$? SHOW YOUR WORK for credit.

$$\Delta H^\circ =$$

9. For a chemical reaction, the equilibrium constant $K$ is $1.70 \times 10^{-5}$ at 25°C. What is the $\Delta G^\circ$ value for this reaction at 25°C? ($R = 8.314 \text{ J/mol} \cdot \text{K}$)
   a. $-11.8 \text{ kJ}$
   b. $-2.28 \text{ kJ}$
   c. $-27.2 \text{ kJ}$
   d. $+11.8 \text{ kJ}$
   e. $+2.28 \text{ kJ}$
   f. $+27.2 \text{ kJ}$

10. A. Give two criteria (specifying the conditions) for a spontaneous process:
    B. Give two criteria (specifying the conditions) for a non-spontaneous process:

11. Provide definitions (or descriptions) for the following terms:
   A. Second law of thermodynamics
   B. Third law of thermodynamics

12. For $\text{A(g)} \rightleftharpoons \text{B(g)} + \text{C(g)}$ reaction, $\Delta G^\circ = -17.2 \text{ kJ}$ at 325 K. What is the value of $\Delta G$ at 325 K when $P_A = 0.121 \text{ atm}$ and $P_B = P_C = 93.6 \text{ atm}$. ($R = 8.314 \text{ J/mol} \cdot \text{K}$)

$$\Delta G =$$

SHOW YOUR WORK for credit.
1. A. The oxidation number of S in H$_2$SO$_3$ is ………
   B. The oxidation number of N in Ca(NO$_3$)$_2$ is ………
   C. The oxidation number of O in H$_2$O$_2$ is ………

2. A voltaic cell has a Cu electrode (Cu metal in Cu$^{2+}$ solution) and a Zn electrode (Zn metal in Zn$^{2+}$ solution).
   A. The anode is the ……… electrode and the cathode is the ……… electrode.
   B. The notation for this voltaic cell:

3. A voltaic cell has a Cu electrode (Cu metal in Cu$^{2+}$ solution) and a Zn electrode (Zn metal in Zn$^{2+}$ solution).
   A. The two half reactions are:
   B. The cell reaction is:

4. A voltaic cell has a Ni electrode (Ni metal in Ni$^{2+}$ solution) and an Ag electrode (Ag metal in Ag$^{+}$ solution).
   A. The standard electrode potential at 25°C for Ni electrode is …………
   B. The standard electrode potential at 25°C for Ag electrode is …………
   C. The standard cell potential at 25°C for this voltaic cell is …………

5. The standard cell potential for a voltaic cell is 0.43 V at 25°C when $n = 1$. Calculate the standard change is Gibbs energy for the cell reaction.
   \[ \Delta G^\circ = \]
6. Provide definitions (or descriptions) for the following terms:
   A. Galvanic cell
   
   B. Electrolytic cell

7. Write the half-reaction occurring during electrolysis of molten sodium chloride.
   A. At anode:
   
   B. At cathode:

8. When molten LiCl is electrolyzed, lithium metal is produced at the cathode. How long a 2.46 A current has to be passed through the cell to produce 10.0 g of Li metal? SHOW YOUR WORK for partial credit.

   \[ t = \] 

9. Calculate the cell potential at 25°C for a voltaic cell in which one electrode is Zn metal inserted in a 2.0 M Zn²⁺ solution and the other electrode in Cu metal inserted in a 0.020 M Cu²⁺ solution. SHOW YOUR WORK for partial credit.

   \[ E_{\text{cell}} = \] 

10. Write and balance the following half reactions:
    A. Reduction of \( \text{Cr}_2\text{O}_7^{2-} \) to \( \text{Cr}^{3+} \) in acidic medium:
    
    B. Oxidation of NO to \( \text{NO}_3^- \) in basic medium:

11. Balance the following reaction. SHOW YOUR WORK for partial credit.
    \[ \text{....KMnO}_4 + \text{.... HClO} + \text{.... HCl} \rightarrow \text{.... MnCl}_2 + \text{.... KCl} + \text{.... HClO}_3 + \text{.... H}_2\text{O} \]
**Bonus** (1 point each): Circle T for true statement and F for false statement:

T or F  Transforming NH$_3$ in HNO$_3$ is a reduction reaction.

T or F  The cathode is the positive electrode in a voltaic cell.

T or F  The oxidation number of H in hydrogen peroxide is +2.

T or F  Reduction is the reaction in which electrons are lost.

T or F  Zn$^{2+}$ is a better oxidizing agent than Cu$^{2+}$.

T or F  Nitric acid is the reducing agent in the reaction below

\[ 2\text{HNO}_3 + 3\text{HClO} \rightarrow 2\text{NO} + 3\text{HClO}_2 + \text{H}_2\text{O} \]

T or F  The anode is the electrode where oxidation takes place.

T or F  The anode is the positive electrode in an electrolytic cell.

T or F  Cu$^{2+}$ + Fe $\rightarrow$ Cu + Fe$^{2+}$ reaction is spontaneous under standard conditions.

T or F  \(2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-\) is the reaction that is taken place at the anode during the electrolysis of molten sodium bromide.
**BLE 19.1 Standard Reduction Potentials at 25°C**

<table>
<thead>
<tr>
<th>Half-Reaction</th>
<th>( E^\circ ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{F}_2(g) + 2e^- \rightarrow 2\text{F}^-(aq) )</td>
<td>+2.87</td>
</tr>
<tr>
<td>( \text{O}_2(g) + 2\text{H}^+(aq) + 2e^- \rightarrow \text{O}_2(g) + \text{H}_2\text{O}(l) )</td>
<td>+2.07</td>
</tr>
<tr>
<td>( \text{Co}^{3+}(aq) + e^- \rightarrow \text{Co}^{2+}(aq) )</td>
<td>+1.82</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2(aq) + 2\text{H}^+(aq) + 2e^- \rightarrow 2\text{H}_2\text{O}(l) )</td>
<td>+1.77</td>
</tr>
<tr>
<td>( \text{PbO}_4^{2-}(s) + 4\text{H}^+(aq) + \text{SO}_4^{2-}(aq) + 2e^- \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}(l) )</td>
<td>+1.70</td>
</tr>
<tr>
<td>( \text{Ce}^{4+}(aq) + e^- \rightarrow \text{Ce}^{3+}(aq) )</td>
<td>+1.61</td>
</tr>
<tr>
<td>( \text{MnO}_4^{2-}(aq) + 8\text{H}^+(aq) + 5e^- \rightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l) )</td>
<td>+1.51</td>
</tr>
<tr>
<td>( \text{Au}^{3+}(aq) + 3e^- \rightarrow \text{Au}(s) )</td>
<td>+1.50</td>
</tr>
<tr>
<td>( \text{Cl}_2(g) + 2e^- \rightarrow 2\text{Cl}^-(aq) )</td>
<td>+1.36</td>
</tr>
<tr>
<td>( \text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6e^- \rightarrow 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}(l) )</td>
<td>+1.33</td>
</tr>
<tr>
<td>( \text{MnO}_4^{2-}(aq) + 4\text{H}^+(aq) + 2e^- \rightarrow \text{Mn}^{2+}(aq) + 2\text{H}_2\text{O}(l) )</td>
<td>+1.23</td>
</tr>
<tr>
<td>( \text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O}(l) )</td>
<td>+1.23</td>
</tr>
<tr>
<td>( \text{Br}_2(l) + 2e^- \rightarrow 2\text{Br}^-(aq) )</td>
<td>+1.07</td>
</tr>
<tr>
<td>( \text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- \rightarrow \text{NO}(g) + 2\text{H}_2\text{O}(l) )</td>
<td>+0.96</td>
</tr>
<tr>
<td>( 2\text{Hg}^2+(aq) + 2e^- \rightarrow \text{Hg}_2^2+(aq) )</td>
<td>+0.92</td>
</tr>
<tr>
<td>( \text{Hg}_2^2+(aq) + 2e^- \rightarrow 2\text{Hg}(l) )</td>
<td>+0.85</td>
</tr>
<tr>
<td>( \text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s) )</td>
<td>+0.80</td>
</tr>
<tr>
<td>( \text{Fe}^{3+}(aq) + e^- \rightarrow \text{Fe}^{2+}(aq) )</td>
<td>+0.77</td>
</tr>
<tr>
<td>( \text{O}_2(g) + 2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2\text{O}_2(aq) )</td>
<td>+0.68</td>
</tr>
<tr>
<td>( \text{MnO}_4^{2-}(aq) + 2\text{H}_2\text{O}(l) + 3e^- \rightarrow \text{MnO}_4^{-}(aq) + 4\text{OH}^{-}(aq) )</td>
<td>+0.59</td>
</tr>
<tr>
<td>( \text{I}_2(s) + 2e^- \rightarrow 2\text{I}^-(aq) )</td>
<td>+0.53</td>
</tr>
<tr>
<td>( \text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- \rightarrow 4\text{OH}^{-}(aq) )</td>
<td>+0.40</td>
</tr>
<tr>
<td>( \text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s) )</td>
<td>+0.34</td>
</tr>
<tr>
<td>( \text{AgCl}(s) + e^- \rightarrow \text{Ag}(s) + \text{Cl}^-(aq) )</td>
<td>+0.22</td>
</tr>
<tr>
<td>( \text{SO}_4^{2-}(aq) + 4\text{H}^+(aq) + 2e^- \rightarrow \text{SO}_2(aq) + 2\text{H}_2\text{O}(l) )</td>
<td>+0.20</td>
</tr>
<tr>
<td>( \text{Cu}^{2+}(aq) + e^- \rightarrow \text{Cu}(aq) )</td>
<td>+0.15</td>
</tr>
<tr>
<td>( \text{Sn}^{4+}(aq) + 2e^- \rightarrow \text{Sn}^{2+}(aq) )</td>
<td>+0.13</td>
</tr>
<tr>
<td>( 2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g) )</td>
<td>0.00</td>
</tr>
<tr>
<td>( \text{Pb}^{2+}(aq) + 2e^- \rightarrow \text{Pb}(s) )</td>
<td>-0.13</td>
</tr>
<tr>
<td>( \text{Sn}^{4+}(aq) + 2e^- \rightarrow \text{Sn}(s) )</td>
<td>-0.14</td>
</tr>
<tr>
<td>( \text{Ni}^{2+}(aq) + 2e^- \rightarrow \text{Ni}(s) )</td>
<td>-0.25</td>
</tr>
<tr>
<td>( \text{Co}^{3+}(aq) + 2e^- \rightarrow \text{Co}(s) )</td>
<td>-0.28</td>
</tr>
<tr>
<td>( \text{PbSO}_4(s) + 2e^- \rightarrow \text{Pb}(s) + \text{SO}_4^{2-}(aq) )</td>
<td>-0.31</td>
</tr>
<tr>
<td>( \text{Cd}^{2+}(aq) + 2e^- \rightarrow \text{Cd}(s) )</td>
<td>-0.40</td>
</tr>
<tr>
<td>( \text{Fe}^{2+}(aq) + 2e^- \rightarrow \text{Fe}(s) )</td>
<td>-0.44</td>
</tr>
<tr>
<td>( \text{Cr}^{3+}(aq) + 3e^- \rightarrow \text{Cr}(s) )</td>
<td>-0.74</td>
</tr>
<tr>
<td>( \text{Zn}^{2+}(aq) + 2e^- \rightarrow \text{Zn}(s) )</td>
<td>-0.76</td>
</tr>
<tr>
<td>( 2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq) )</td>
<td>-0.83</td>
</tr>
<tr>
<td>( \text{Mn}^{2+}(aq) + 2e^- \rightarrow \text{Mn}(s) )</td>
<td>-1.18</td>
</tr>
<tr>
<td>( \text{Al}^{3+}(aq) + 3e^- \rightarrow \text{Al}(s) )</td>
<td>-1.66</td>
</tr>
<tr>
<td>( \text{Be}^{2+}(aq) + 2e^- \rightarrow \text{Be}(s) )</td>
<td>-1.85</td>
</tr>
<tr>
<td>( \text{Mg}^{2+}(aq) + 2e^- \rightarrow \text{Mg}(s) )</td>
<td>-2.37</td>
</tr>
<tr>
<td>( \text{Na}^{+}(aq) + e^- \rightarrow \text{Na}(s) )</td>
<td>-2.71</td>
</tr>
<tr>
<td>( \text{Ca}^{2+}(aq) + 2e^- \rightarrow \text{Ca}(s) )</td>
<td>-2.87</td>
</tr>
<tr>
<td>( \text{Sr}^{2+}(aq) + 2e^- \rightarrow \text{Sr}(s) )</td>
<td>-2.89</td>
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<tr>
<td>( \text{Ba}^{2+}(aq) + 2e^- \rightarrow \text{Ba}(s) )</td>
<td>-2.90</td>
</tr>
<tr>
<td>( \text{K}^+(aq) + e^- \rightarrow \text{K}(s) )</td>
<td>-2.93</td>
</tr>
<tr>
<td>( \text{Li}^+(aq) + e^- \rightarrow \text{Li}(s) )</td>
<td>-3.05</td>
</tr>
</tbody>
</table>